FLEXIBLE METAL OXIDE NANOWIRE ELECTROLYTES WITH METALLIC NANOSTRUCTURED PLATINUM AND NICKEL THREE PHASE BOUNDARIES FOR APPLICATION IN SOLID OXIDE FUEL CELLS (SOFCs).

by

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<td>1-D</td>
<td>One dimension</td>
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<tr>
<td>8YSZ</td>
<td>8% Y₂O₃ stabilized ZrO₂</td>
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<tr>
<td>AcOH</td>
<td>Acetic acid</td>
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<td>At%</td>
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<tr>
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<td>BSE</td>
<td>Back scattering electrons</td>
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<td>CPT</td>
<td>Co-precipitation</td>
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<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DP</td>
<td>Double perovskites</td>
</tr>
<tr>
<td>EC</td>
<td>Electronic conductor</td>
</tr>
<tr>
<td>ED</td>
<td>Electrode distance</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive x-ray</td>
</tr>
<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field emission scanning electron microscopy</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast Fourier Transform</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High resolution TEM</td>
</tr>
<tr>
<td>IC</td>
<td>Ionic conductor</td>
</tr>
<tr>
<td>i-PrOH</td>
<td>Isopropanol</td>
</tr>
<tr>
<td>LSM</td>
<td>Lanthanum strontium manganate</td>
</tr>
<tr>
<td>MIEC</td>
<td>Mixed ionic electrical conductor</td>
</tr>
<tr>
<td>MO</td>
<td>Metal oxide</td>
</tr>
<tr>
<td>MOE</td>
<td>Metal oxide electrolyte</td>
</tr>
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<td>MO-EC</td>
<td>Metal oxide electronic conductor</td>
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<td>MO-MIEC</td>
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<td>NW</td>
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<tr>
<td>Zr(OPr)_4, (i-PrOH)</td>
<td>Zirconium isopropoxide isopropanol complex</td>
</tr>
<tr>
<td>Zr(OBu)_4</td>
<td>Zirconium tert-butoxide</td>
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CHAPTER I

Literature Review
1.0 Introduction

1.1 Relevance of metal oxides nanomaterials as ionic conductors

“There is plenty of room at the bottom,” stated Richard P. Feynman at a talk given to the American Physical Society on December 1959, where he emphasized the possible advantages of miniaturization of materials. Today, we know them as nanomaterials. This concept involves creating new materials atom by atom, from the bottom up. Materials are considered “nano” when we are considering size dimensions less than 100 nm.\(^1,^2\) The invention of the integrated circuit is a prime example of the benefits of miniaturization. It allowed manufacturing of more components per chip, faster operation, lower cost, and less power requirements.\(^3\) It has also opened a way to explore new phenomena that are only associated with materials of nanoscale size, like size dependent excitation/emission and single electron tunneling (SET).\(^4-^6\)

Ionic solid conductors and solid electrolytes are materials that allow electrical current to pass through where the charged species are anions or cations instead of electrons.\(^7\) It is prudent that we understand that there is a difference between the terms ionic solid and solid electrolyte. The two types of conductors differ by (i) the mobile species and (ii) the mechanism of propagation. The properties of these two types of solids are summarized in Table 1.\(^8\)

Metal oxide-type solid electrolyte is the primary focus of topic in this dissertation. Metal oxide electrolytes (MOEs) are those species that have O\(^{2-}\) as the mobile phase and are responsible for carrying the charge. MOEs are further divided into their different types and are shown in Table 2. Some of the recent results of O\(^{2-}\) species conductivity analysis of ionic conductors and solid electrolytes are shown in Figure 1.
### Table 1. Ionic solid vs solid electrolyte\(^{9,10}\)

<table>
<thead>
<tr>
<th>Material type</th>
<th>Examples</th>
<th>Mobile species</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic solid</td>
<td>AgI, RbAg(_4)I(_5)</td>
<td>Ag(^+)</td>
<td>• Migration of cation and anion</td>
</tr>
<tr>
<td></td>
<td>NaAl(<em>{11})O(</em>{17}), Na(_3)Zr(_2)PSi(<em>2)O(</em>{12})</td>
<td>Na(^+)</td>
<td>• Formation of Schottky pair</td>
</tr>
<tr>
<td></td>
<td>Cubic stabilized ZrO(<em>2) (Y(<em>x)Zr(</em>{1-x})O(</em>{2-x/2})(\delta)-Bi(_2)O(_3))</td>
<td>O(^2-)</td>
<td>• Dissociation of vacancy pair</td>
</tr>
<tr>
<td></td>
<td>Defect Perovskites Ba(_2)In(_2)O(_5)</td>
<td></td>
<td>• Small number of mobile species</td>
</tr>
<tr>
<td></td>
<td>PbF(_2), AF(_2) (A = Ba, Sr, Ca)</td>
<td>F(^-)</td>
<td>• Only one species is mobile</td>
</tr>
<tr>
<td>Solid electrolyte</td>
<td></td>
<td></td>
<td>• Hopping mechanism with low activation energy (E(_a))</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Occurs mainly with F(^-) and O(^2-)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Large number of mobile species (so higher conductivity than ionic solid at high temperature)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Lattice structure can deform to facilitate the migration of the mobile phase.</td>
</tr>
</tbody>
</table>

### Table 2. Different types of oxide conductors.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Examples</th>
<th>Refs:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorite oxide</td>
<td>Zr(<em>{1-x})Y(<em>x)O(</em>{2-y}), Ce(</em>{1-x})Gd(<em>x)O(</em>{2-y})</td>
<td>11,12</td>
</tr>
<tr>
<td>Perovskite oxides</td>
<td>La(_{1-x})Sr(<em>x)Ga(</em>{1-y})Mg(_y)O(_3)</td>
<td>13</td>
</tr>
<tr>
<td>LAMOX family (LAMOX = lanthanum molybdate)</td>
<td>La(_2)Mo(_2)O(_3)</td>
<td>14</td>
</tr>
<tr>
<td>Apatite</td>
<td>La(_{10-x})Ge(<em>6)O(</em>{26+y})</td>
<td>15</td>
</tr>
<tr>
<td>BIMEVOX (BI= bismuth, ME= metal dopant, V=vanadium, OX= oxide)</td>
<td>Bi(<em>2)Mg(<em>x)V(</em>{1-x})O(</em>{5.5-3x/2})</td>
<td>16</td>
</tr>
<tr>
<td>Mixed conductors (ionic-electric conductors)</td>
<td>La(_{1-x})Sr(_x)CoO(_3)</td>
<td>17</td>
</tr>
<tr>
<td>K(_2)NiF(_4) type oxides</td>
<td>K(_2)NiF(_4)</td>
<td>18</td>
</tr>
</tbody>
</table>
Figure 1: Arrhenius plots of different types of ionic conductors and solid electrolytes. Data for concentrated H$_2$SO$_4$, a typical liquid electrolyte, are shown for comparison. The target for improved solid electrolytes is therefore, the top right-hand corner of this Figure.\textsuperscript{9}

1.1.1 Uses of metal oxide ionic conductors (MOIC)

Metal oxides have been widely used in the advancement of energy conversion and storage devices. One of the major contributions of modern electrochemical materials is commercialization of solid oxide fuel cell (SOFC) technology as a remote electrical energy generator. It is also used in the manufacturing of commercial lithium ion batteries and oxide gas sensors.\textsuperscript{9,19,20} MOICs have also been developed as individual components used in the production of fuel cells. These components include cathodes (LiCoO$_2$),\textsuperscript{21} anodes (Li$_{4.4}$Si),\textsuperscript{22,23} and solid electrolytes [(ZrO$_2$)$_{1-x}$ (Y$_2$O$_3$)$_x$].\textsuperscript{19}

1.1.2 Mechanism of ionic conduction

Ionic conductivity is a process in which ionic species move through vacant sites on the crystal lattice or through the interstitial space. This process is also known as ionic migration, hopping, or diffusion.
In an undoped crystal, there is no place for the ions to move through its lattice. However, this undoped crystal might have defects, like the absence of a cation or anion, that can form due to stacking faults during its synthesis. In that case, the adjacent ion can readily move to the vacant spot. This empty spot is called a vacancy site. In a situation where there is no defect in the crystal, there can still be ionic conduction. This type of conduction occurs by the cation or the anion occupying the space between the sites of closest packed lattice called interstitial sites. This process can only occur if the cation or anion size is small enough to fit in the interstitial space.

In MOEs-type conductors, the defect concentration increases with temperature, which allows the \( \text{O}^{2-} \) species to move more easily. This can be observed when materials such as \( \text{ZrO}_2 \) are heated to temperatures \( \sim 600^\circ\text{C} \). While heated at high temperature, the zirconia undergoes a phase transition from monoclinic to tetragonal to cubic polymorphs. Typically, conductivity values of yttria-stabilized zirconia (YSZ) are in the range of \( 10^{-1} - 10^{-2} \) (S cm\(^{-1}\)) at 800°C with an activation energy of the process ranging from 0.8 – 1.3 eV. It should be recognized that the solid electrolytes are sometime also known as “superionic” or “fast ion conductors”. Even though these terms are commonly used, they are actually misleading as they are neither “super” nor “fast”.

### 1.1.3 Charge migration through point defects

Point defects are imperfections in the crystal lattice during its formation. These defects occur differently during the crystallization process of pure samples from that of doped samples (samples with the deliberate addition of impurities). Both types of defects depend on the two basic forms, interstitial and vacancy defects. Interstitial defects, arise specially when a cation is placed (or removed) in the space between a cation and an anion. It is usually the cation, which is displaced because of its size being much smaller than its counter anion. The vacancy defects are usually
associated with anions, which forms when an ion is absent from its intended location, as shown in the Figure 2.

![Figure 2: (a) Types of point defects that can emerge in a crystal; (b) differences between Schottky and Frenkel defects.](image)

Defects usually occur in accordance with charge neutrality (both in the case of interstitial and vacancy defects) to minimize the chance of the crystal to have a resultant charge. This conservation of charge neutrality is known as an intrinsic defect and is further divided into two types, Schottky and Frenkel defects. Schottky defects arise when the cation is removed at the same time an anion is removed from a lattice. This kind of defect is usually found in materials where the size of the cation is similar to that of the anion. Frenkel defects occur when a cation moves to an interstitial space, as shown in Figure 2 (b), and are observed where the size of the cation is smaller relative to the anion. The cation occupying interstitial space and the vacancy it left behind are together known as the Frenkel pair defect. Extrinsic defects are also that arise from doping a
pure crystal with species that introduce vacancies to that of the host crystal (as shown in Figure 3). \(^9,^{10,24}\)

![Diagram of vacancy formation in a yttria doped zirconia lattice](image)

Figure 3: Vacancy formation in a yttria doped zirconia lattice (extrinsic defects). \(^9\)

1.2 Important concepts regarding metal oxide electrolytes

1.2.1 Ionic, electrical, and mixed metal oxide conductors

MOCs are classified according to their crystal structure, which ultimately dictates their conductive properties. Metals (M) are the simplest type of conductors and have been used most often for electrical conductivity, like metallic Cu in electrical wires. Fluorite (F) type MOCs have unit cells which resemble the crystal structure of CaF\(_2\), and are generally represented as AO\(_2\). Perovskite (P) structures resemble the crystal structure of the mineral CaTiO\(_3\). The unit cell has an ABO\(_3\) type structure, with small B cations within a tetrahedral oxygen frame and large A cations with 12 oxygen coordination, as shown in Figure 4. \(^{26,27}\) Double perovskites (DP) and Ruddlesden-
Popper (RP) type perovskites have complex crystal structures and will not be discussed as it is outside the scope of this dissertation. Unit cell structures of all the different types of conductors discussed so far are shown in Figure 4. Each of these conductors has their own unique mechanism of conduction and therefore is suitable for different applications. Figures 4 and 5 provide an overview of the relationships between the unit cells of these conductors and the type of conductivity exhibited.

<table>
<thead>
<tr>
<th>Material</th>
<th>Type of crystal structure</th>
<th>Examples</th>
<th>Type of conductor</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>Fluorite (AO₂)</td>
<td>(ZrO₂)₁₋ₓ (Y₂O₃)ₓ</td>
<td>IC</td>
<td>Solid electrolyte; good catalyst</td>
</tr>
<tr>
<td>P</td>
<td>Perovskite (ABO₃)</td>
<td>SrTiO₃</td>
<td>EC, IC</td>
<td>Good EC but moderate IC</td>
</tr>
<tr>
<td>DP</td>
<td>Double perovskites (AA’B₂O₅₋δ)</td>
<td>Sr₂FeMoO₆</td>
<td>MIEC</td>
<td>Oxygen deficient perovskites</td>
</tr>
<tr>
<td>RP</td>
<td>Ruddlesden-Popper type perovskite (A₂BO₄)</td>
<td>Sr₂RuO₄</td>
<td>MIEC</td>
<td>High interstitial diffusion rate</td>
</tr>
<tr>
<td>M</td>
<td>Metal (M)</td>
<td>Ni⁰, Cu⁰</td>
<td>EC</td>
<td>Good catalyst</td>
</tr>
</tbody>
</table>
Figure 4: Unit cell structures of MOCs.\textsuperscript{24}

Figure 5: MOC materials relationship to their conductivity pathways. The functionalities are ionic conductor (IC), electronic conductor (EC) and mixed ionic and electronic conductors (MIEC). Grey circles represent the type of MOC and their unit cell structures.\textsuperscript{24}

\textbf{M} = Metal  \\
\textbf{F} = Fluorite  \\
\textbf{P} = Perovskite  \\
\textbf{DP} = Double perovskite  \\
\textbf{RP} = Ruddlesden-Popper type perovskite
1.2.1.1 Metal oxide ionic conductors (MO-IC)

In Fluorite-type metal oxide conductors such as YSZ, the conductivity of the material increases with the increase in amount of dopant added to it (e.g. Y$_2$O$_3$ added to ZrO$_2$). This is due to the formation of vacancies near the site of the dopant cation (Y$^{3+}$). Zr$^{4+}$ has a coordination number of +4 and with the introduction of the dopant, the coordination number at that site becomes +3, thus creating a vacancy (dashed squares) as shown in Figure 3. However, over time these defects can come together in clusters where two vacancies form a pair, with a cation between them.$^{24,41}$ These defects eventually form aggregates at higher temperature causing net a loss in the vacancy sites for the O$^{2-}$ and therefore decreases the overall conductivity.

The conductivity increases when the dopant added is between 5-10 mole % (Y$_2$O$_3$), as more vacancies are introduced.$^{27}$ Beyond that, the conductivity starts decreasing. This is because with an increase in dopant concentration, more and more vacancy sites are created and that can lead to an increased amount of defect aggregation, called aging. It also acts like a trap for migrating vacancy sites by adding it to the defect and increases its overall size.

Goff and co-workers$^{28}$ have reported that regions with low dopant ions (when Y$_2$O$_3$ is less than 8%) can cause a partial phase transformation from cubic to tetragonal. This is a problem because it can change the unit cell type, which over time can cause fractures in the electrolyte. The volume can also undergo phase transformations if there is a phase separation between Y$_2$O$_3$ and ZrO$_2$.$^{29,30,105}$ The composition of doped electrolytes over time may change due to the phase separation which can change its conductive properties associated with a certain temperature. This temperature vs. phase relationship is shown in the phase diagram in Figure 6.
1.2.1.2 Metal oxide electronic conductors (MO-EC)

This type of metal oxide is known to be a good semiconductor of electrons. P-type semiconductors such as non-stoichiometric NiₓO have been shown to be good candidates for anode materials, as reported by Pizzini et al. The holes have been reported to propagate by changing the oxidation state of Ni from +2 to +3. Perovskites such as lanthanum strontium manganate (LSM), La₁₋ₓSrₓMnO₃, have also been extensively investigated as electronic conductors.

There have also been reports of BaTiO₃ and SrTiO₃ being used similarly as a cathode material (n-type semiconductor) when doped with Co³⁺ and anode material (p-type semiconductor) when doped with Ni²⁺. In the case of SrTiO₃ the conductivity is achieved by electrons moving from valence band of O-2p orbitals to the Ti-3d conduction band.

1.2.1.3 Metal oxide mixed ionic and electrical conductors (MO-MIEC)

MIEC are materials that can conduct both electronically and ionically. They are also called cermet materials. One example of such composites is the non-stoichiometric Ni-YSZ
system. Ni (in Ni/NiO electrode) acts as an electron acceptor and is reduced to Ni(0) by O$_2^-$, during reduction reaction. However, the problem with this system is that during the reduction process, nickel undergoes a change in volume, which in turn causes stress on the interfacial region with YSZ and can result in fracture/crack formation. This system is useful as it can extend the electrochemical interface to include the entire electrode/electrolyte contact area.\(^{33}\)

1.2.2 Three phase boundaries

A three phase boundary (TPB) is the intersecting point of the gas phase (oxygen), electrode (electronic conductor) and metal oxide electrolyte (ionic conductor) which defines catalytic sites for the redox reaction to take place. Figure 7 (a) shows the mechanism that occurs at the cathode (Pt) and (b) showing the reaction at the anode (Ni/NiO). The mechanism of this reaction varies based on the type of electrode-electrolyte interface (metal oxide-electrical conductor to electrolyte interface or metal oxide-mixed conductor to electrolyte interface).\(^{38}\)

![Figure 7](image_url)

Figure 7: (a) O$_2$ reduction reaction at Pt cathode, (b) O$_2^-$ oxidation reaction at Ni/NiO TPB anode.
Figure 7 demonstrates only the non-stoichiometric dissociation of O₂ and H₂ molecules to emphasize fundamental concept behind a fuel cell operation.

1.2.3 **Key concepts related to ion conductivity**

1.2.3.1 **Diffusion**

Isothermal movement of ions/electrons/holes through material relies on the concentration gradient of the mobile species, and related electrical fields. This is known as diffusion and for charged particles can be described according to Nernst-Planck equation (Eqn. 1), which states that the particle flux ($J_i$) is proportional to the concentration gradient ($\nabla C_i$) and electric potential gradient ($\nabla \Phi$).

$$J_i = -D_i \left[ \nabla C_i + \frac{z_i e}{k_B T} (C_i \nabla \Phi) \right]$$

(Eqn. 1)

Diffusivity ($D_i$) follows Fick’s Law electrical conductivity ($\sigma$) obeys Ohm’s Law. Therefore, in relation to charge transport, in the presence of external electrical potential gradient, the Ohm’s Law needs to be introduced (Eqn. 2), where $J_Q$ is the current density.

$$J_Q = -\sigma \nabla \Phi$$

(Eqn. 2)

Using Nernst-Einstein equation (Eqn. 3), it can be shown that the electrical conductivity of the material is directly proportional to the mobility of the particle ($\mu_i$) and the electrical charge they carry (Eqn. 4).

$$\mu_i = D_i \left[ \frac{z_i e}{k_B T} \right]$$

(Eqn. 3)

$$\sigma = D_i \left[ \frac{C_i (z_i e)^2}{k_B T} \right]$$

(Eqn. 4)
Where,

\[ k_B = \text{Boltzmann constant} \]
\[ T = \text{temperature (in kelvin)} \]
\[ z_i = \text{mobile ion} \]
\[ e = \text{elementary charge} \]
\[ C_i = \text{mobile ion concentration} \]

1.2.3.2 Arrhenius relationship to diffusion and conductivity

During diffusion, the mobile species needs energy to move from one site to another. The energy, which is required for the species to jump over to a neighboring vacancy defect site, is called the activation energy \( (E_a) \). So the probability of such a jump happening depends on the temperature of the system and the rate jump can be written according to the Arrhenius equation:

\[
D_i = D_0 e^\left(\frac{-E_a}{k_B T}\right) \quad \text{(Eqn. 5)}
\]

Where \( D_0 \) is the pre-exponential coefficient (which includes ion jump distance and jump frequency intrinsic to the material) and is assumed to remain constant with varying temperature.\(^1,7,19,37,39,40\)

This equation can be manipulated to get a linear form:

\[
\ln D_i = \left(\frac{-E_a}{k_B}\right) \frac{1}{T} + \ln D_0 \quad \text{(Eqn. 6)}
\]

The activation energy of the system can be experimentally determined from the slope of the Arrhenius plot. It is very important to remember where Eqn. 6 can be applied and where it cannot.\(^41\) It can only be used in case of (a) electron/hole conductivity, (b) an ionic conductor like Na\(^+\), Ag\(^+\) and F\(^-\), (as shown in Table 1), and (c) a metal oxide of (undoped) pure composition. For example, pure AgI ionic conductors are species that do not need dopants for conductivity and therefore considered as pure compounds.\(^39\)

Non-stoichiometric metal oxide ionic conductors are materials where impurities or dopants are added, in a controlled manner, to enhance conductivity. The dopants create a desired
concentration of vacancy sites that allows the migration of $O^{2-}$ species across the electrolyte. An example of such system is 8% $Y_2O_3$-stabilized $ZrO_2$ (8YSZ) where yttria is added to create vacancy sites as demonstrated in Figure 3.\textsuperscript{9} Here we need to use a modified equation to find the $E_a$ of 8YSZ type system using the Arrhenius plot. From Eqn. 4, we learned the following relationship:

$$\sigma \propto \frac{D_i}{T}$$  \hspace{1cm} (Eqn. 7)

Therefore, we can re-write Eqn. 6 as,

$$ln \ (\sigma T) = \left( -\frac{E_a}{k_B} \right) \frac{1}{T} + ln \ (\sigma_0)$$  \hspace{1cm} (Eqn. 8)

However, most publications report data calculated as shown in Eqn. 9 and therefore, the activation energy calculations (of this dissertation) will be performed using the same equation.

$$ln \ \sigma = \left( -\frac{E_a}{k_B} \right) \frac{1}{T} + ln \ \sigma_0$$  \hspace{1cm} (Eqn. 9)

1.3 Common morphologies and fabrication routes of 8YSZ electrolytes

1.3.1 Morphologies

The most widely investigated form of 8YSZ materials and other metal oxide electrolytes is thin film. Since Wagner realized the importance of anionic conductors in 1943,\textsuperscript{42} there has been significant development in the morphologies and fabrication processes of 8YSZ electrolyte technology.

The reason behind the use of this morphology is relative ease of deposition on electrodes or other supporting substrates. The thin film also forms a non-porous layer, which is necessary for applications, such as fuel cells. The thin film acts as a wall between gaseous fuel and oxygen.\textsuperscript{43,44} It also allows more control over the electrolyte layer thickness. The thickness of the material plays
an important role as the resistivity of the electrolyte increases with the increase in the distance between the anode and the cathode.\textsuperscript{45}

Numerous papers have been published encompassing 8YSZ thin films as an electrolyte material with micron sized thickness. Chang and co-workers\textsuperscript{46} prepared thin films of thickness ~600 µm to characterize the conductivity of micron-sized electrolyte materials. In another case, Vogt and co-workers\textsuperscript{47} were able to fabricate thinner films of ~300 µm thickness. In both cases, spray pyrolysis was used to prepare the thin films. Spray pyrolysis is a process where precursor solutions are aerosolized, followed by thermal decomposition and precipitation of the product.\textsuperscript{9}

Synthesis of submicron sized thickness thin films have also been reported by a few authors. Chen and co-workers\textsuperscript{48} fabricated ZrO\textsubscript{2} and 8YSZ thin film of thickness ~500 nm to investigate the effects of submicron thickness on the annealing parameters and O\textsuperscript{2-} conductivity across this electrolyte at elevated temperatures.

More recent focus has concerned the development of fabrication techniques to achieve nano-scale thickness films. Oh \textit{et al.}\textsuperscript{49} have developed a process to produce ultra-thin films of 8YSZ-GDC (GDC = gadolinia doped ceria) electrolytes of thickness ~100 nm. The electrolyte was prepared by spin coating the precursor solution over a MIEC cathode, which also acted as the support structure for the electrolyte film. This heterostructure was used to investigate the performance of intermediate operating temperatures (400°C to 600°C) of SOFCs. Fabrication of thinner films have been reported to be in the range of 30 nm to 300 nm.\textsuperscript{50}

One of the problems associated with nano-scale thin films is the increase in the leakage current, which is the loss of very small number of electrons across the O\textsuperscript{2-} electrolyte layer. Such problems can be prevented when the electrolyte is fabricated in a form of a film with MIEC-like GDC as demonstrated by Kleinlogel \textit{et al.}\textsuperscript{45} Perednis \textit{et al.} have produced similar structures when
the ultra-thin 8YSZ electrolyte layer formed a bilayer over 100 nm thick of 8YSZ-NiO MIEC anode material.\textsuperscript{51,52} Table 4 provides an overview of other reports of metal oxide thin film fabrication and the corresponding thickness of the films.

<table>
<thead>
<tr>
<th>Electrolyte composition</th>
<th>Electrolyte thickness</th>
<th>Process used for electrolyte fabrication</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>8YSZ</td>
<td>200 µm</td>
<td>Tape casting</td>
<td>53</td>
</tr>
<tr>
<td>8YSZ</td>
<td>600 µm</td>
<td>Plasma spray</td>
<td>46</td>
</tr>
<tr>
<td>8YSZ</td>
<td>300 µm</td>
<td>Spray pyrolysis</td>
<td>47</td>
</tr>
<tr>
<td>8YSZ</td>
<td>150 µm</td>
<td>Synthesized NWs scaffold adhesion on substrate</td>
<td>54</td>
</tr>
<tr>
<td>8YSZ</td>
<td>125 µm - 200 µm</td>
<td>Electron beam vapor deposition</td>
<td>55</td>
</tr>
<tr>
<td>8YSZ</td>
<td>20 µm</td>
<td>Screen printing</td>
<td>19</td>
</tr>
<tr>
<td>8YSZ</td>
<td>30 µm</td>
<td>Slurry + tape casting</td>
<td>56</td>
</tr>
<tr>
<td>8YSZ</td>
<td>1 µm - 4 µm</td>
<td>DC - Sputtering</td>
<td>45</td>
</tr>
<tr>
<td>8YSZ</td>
<td>40 µm</td>
<td>Plasma spray</td>
<td>57</td>
</tr>
<tr>
<td>8YSZ</td>
<td>100 µm – 300 µm</td>
<td>Screen printing</td>
<td>57</td>
</tr>
<tr>
<td>8YSZ</td>
<td>10 µm</td>
<td>Suspended particle</td>
<td>58</td>
</tr>
<tr>
<td>8YSZ</td>
<td>500 nm</td>
<td>Co-precipitation</td>
<td>48</td>
</tr>
<tr>
<td>8YSZ</td>
<td>526 nm</td>
<td>Pulsed laser deposition</td>
<td>59</td>
</tr>
<tr>
<td>8YSZ</td>
<td>100 nm</td>
<td>Chemical solution deposition + Spin coating</td>
<td>49</td>
</tr>
<tr>
<td>8YSZ</td>
<td>100 nm to 250 nm</td>
<td>Pulsed laser deposition</td>
<td>60</td>
</tr>
<tr>
<td>8YSZ</td>
<td>10 µm</td>
<td>CVD</td>
<td>61</td>
</tr>
<tr>
<td>8YSZ</td>
<td>225 nm</td>
<td>Pulsed laser deposition</td>
<td>62</td>
</tr>
<tr>
<td>8YSZ</td>
<td>30 nm – 300 nm</td>
<td>DC - sputtering</td>
<td>63</td>
</tr>
<tr>
<td>8YSZ</td>
<td>40 nm – 200 nm</td>
<td>DC - sputtering</td>
<td>64</td>
</tr>
<tr>
<td>8YSZ</td>
<td>100 nm</td>
<td>Electron beam evaporation</td>
<td>65</td>
</tr>
</tbody>
</table>
1.3.2 Thin film fabrication processes

The morphologies that have been discussed in the previous section have been fabricated using various methods shown in Table 4. The table shows various methods of fabrication but in this section only the processes that resulted in nano sized thin films will be highlighted.

8YSZ and other metal oxide thin film fabrication processes have mostly been successful using physical vapor deposition (PVD). PVD is an umbrella term that includes several processes, which involves techniques that deposited the products on a substrate. It includes processes like sputtering, ion plating, pulsed laser deposition, and electron beam vapor deposition. These processes have been the most successful to deposit 8YSZ thin films as it only requires physical means to form a thin film instead of utilizing chemical reactions to control the process. For example, sputtering uses a plasma to eject materials from the target in order to deposit the material on the surface. Spin coating has been shown to produce ultra-thin films (~100 nm thickness) as shown by Chen et al. The process is relatively simple, and provides more controlled deposition of materials in comparison to chemical vapor deposition (CVD). The film thickness can be easily controlled by changing the spin speed. However, there are few disadvantages associated with spin coating. It has been reported that during spin coating almost 95% reactant that is being applied is flung off the substrate, which results in waste of material.

Other systems such as CVD, spin coating and solution co-precipitation (CPT) have also been effective ways to prepare nano electrolytes. However, these processes are often difficult to control and therefore produce inconsistent results. Brinkman and co-workers developed a process where CVD was used to fabricate thin films of ~500 nm thickness using ZrCl₄ and YCl₃ as precursors. The film thickness could not be lowered to the sub-micron region because the fabrication process was difficult to control and therefore resulted in uneven film coverage on the
substrate. The regions with low coverage showed presence of pore, which acted as the sites for film to form fractures.

Co-precipitation and other wet methods like sol-gel reactions have also been proven to be a good process to prepare thin films. These are discussed in more detail in the next section. In general, alkoxide sol-gel synthesis is the process where metal alkoxides are hydrolyzed to form M-O-M (M = metals) bonds to form an oligomeric network, as shown in Figure 8. These networks for spherical colloids are called sols. This process has been used to fabricate both thick\textsuperscript{68,69,70} and thin\textsuperscript{71,72,73,74} films. Xia and coworkers performed a comparative study of gadolinium-doped ceria (GDC) thin films where they showed the enhancement of conductivity (in comparison to 8YSZ), at elevated temperatures, when the film was deposited using the sol-gel process.\textsuperscript{75}

1.3.3 Fabrication method pertaining to the current project

1.3.3.1 Sol-gel method

After initial hydrolysis of M-OR bond(s), sol-gel reactions involving metal oxide synthesis are normally subjected to post-deposition heat treatment to form strong -O-M-O-linkages (where M is the metal), as shown in Figure 8.

![Figure 8: Overall condensation polymerization reaction of zirconium alkoxide showing the formation of the metal oxide framework.](image-url)
1.3.3.2 Acid catalyzed sol-gel reaction mechanism

Acid catalyzed reaction proceeds by protonation on the alkoxide oxygen atom, which makes it a good leaving group. This is followed by a nucleophilic attack of the metal by the lone pair electrons on the water molecule through a $S_N^2$ mechanism. This further propagates to the condensation step where the –OH nucleophile attacks the metal alkoxide to form M-O-M bonds, as shown in Figure 9.

Step 1: Acid catalyzed hydrolysis reaction

Step 2: Acid catalyzed condensation reaction

Figure 9: Step 1: Sol-gel acid catalyzed hydrolysis and condensation reaction of zirconium alkoxides to form –O-M-O- framework.

The use of metal chelation is necessary to slow down the rate of reaction and subsequent gel formation in this kind of sol-gel reaction. Most commonly used chelating agents used are acetylacetone (acac) and carboxylic acids (AcOH). Courtin et al., demonstrated the ability of this process by mixing zirconium (IV) propoxide (70 wt % Zr(OPr)$_4$ in 1-propanol) and acac to form sols containing Zr-O-Zr bonds. Examples of the chelate complexes formed via this routes are
shown in Figure 10, where (a) is the structure of Ti alkoxides complex with AcOH bridging, and (b) acac chelated titanium (IV) isopropoxide complex.

Figure 10: Titanium alkoxide chelation with (a) carboxylic acid and (b) acac to reduce the reactivity of the air sensitive meal alkoxides.  

1.3.3.3 Electrospinning method

Electrospinning is a process in which electrostatic force is used to produce nanofibers from a solution. This process has received significant attention in last 20 years especially in the areas of nanofibers fabrication. Theoretically, electrospinning process is divided into three parts. It begins with the formation of the Taylor cone, followed by the thinning stage and finally the drying phase. A solution (containing the reactants and a polymer) is ejected from the tip of a needle, under the influence of a strong electric field, in form of a droplet. The polymer acts as a template for the nanowires and at the same time is used to control the viscosity of the solution. The buildup of electrostatic charge on the surface of the droplet induces the formation of a jet, which is stretched from the tip of the needle to the collector to form nanofibers (as shown in Figure 11).
When the electric field is large enough, the droplet is deformed into the Taylor cone. The formation of the cone is a result of several forces acting on the droplet. The electric field generates an electrical polarization stress on the droplet that starts pulling it against the viscosity and surface tension of the liquid, as shown in Figure 12.\textsuperscript{86} This causes a fine charged jet is to form that is typically 1/100 in diameter of the needle. After leaving the cone, this jet then moves toward the counter electrode. During this process the jet becomes unstable and undergoes bending of the fibers, as shown in Figure 11. It is during this bending process the solvent evaporates from the fibers.
This process is used in conjunction with the sol-gel process to produce metal oxide nanowires where a polymer is used as a template for the sol-gel reaction product and at the same time controls the viscosity of the solution. Together, this process allows fabrication of metal oxide nanowires film with controlled formation of M-O-M bonding, followed by annealing in air to remove the polymer template.

Li and coworkers\textsuperscript{84} have shown one such example of metal oxide nanowires synthesis, using a polymer as a template. In this work, Ti(OiPr)\textsubscript{4} and polyvinylpyrrolidone (PVP) was used to produce TiO\textsubscript{2} nanowire with an average nanowires diameter of 50 nm, by using sol-gel reaction in conjugation with the electrospinning technique. The study also showed the dependence of average nanowire diameter on the electrospinning parameters. It was reported that the average nanowire diameter increased with an increase in the PVP concentration and the flow rate of the pump. However, the diameter decreased with an increase in the electric field (kV/cm).\textsuperscript{85} This diameter reduced because the higher electric field generated a stronger attraction between the Taylor cone and the counter electrode which caused thinner diameter fibers.
1.3.3.4 Nanoparticle impregnation

The development of novel electrode materials with unique microstructures is one of the critical issues in the development of new generation SOFCs. One of the most critical parts of fuel cells is the TPB, where the actual electrochemical reactions take place. Porous electrodes with fine particle size are preferred in SOFCs to achieve a high surface area. This provides an increase in the overall active sites for the reaction(s). One of the approaches to achieve this is to decrease the thickness of the solid electrolyte from several hundred micrometers. Usually the thickness in conventional electrolyte-supported cells have been around ten micrometers. Therefore, advanced fabrication processes are needed in order to create dense porous electrode films with detailed microstructures, which ultimately can allow ionic conductivity at lower operating temperatures (400°C to 600°C). One such process is the impregnation of nanostructures on the surface of the electrolyte and construct hierarchical structures from the bottom up.

Nanoparticle impregnation on metal oxide substrates is achieved by applying the precursor solution (of the nanoparticles) over the solid substrate. This process requires thermal treatment after the deposition in order to decompose the precursors and form nanoparticles. The size and density of these particles are controlled by varying the concentration of the precursor solution and by applying multiple cycles of precursor coating and heating, as shown in Figure 13. One such process has been reported by Lenormand and co-workers where they demonstrated infiltration of lanthanum strontium manganate (LSM) which was directly deposited on YSZ by thermal decomposition of the precursors (as nitrate salts) at 800°C. Other reports of cathode deposition using the infiltration method have be reported where LSM has been impregnated on YSZ and SDC as well as copper manganese (Cu$_{1.25}$Mn$_{1.75}$O$_4$) spinel infiltration on YSZ.
1.4 Current status of MOEs applications

1.4.1 Solid oxide fuel cells (SOFCs)

Currently, most of the work regarding metal oxides has been focused on the development of the cathode and anode materials for solid oxide fuel cells (Figure 14) and electrolyzer (SOFCs that are used to generate H\(_2\) and O\(_2\) gas from H\(_2\)O). The most important advantage of using SOFC over the other types of fuel cells is its high efficiency and the flexibility when it comes to using the type of fuel. A SOFC requires high operating temperature, which allows running it directly on practical hydrocarbon fuels without the need for complex and expensive external fuel reformer and purification systems. It can also use a mixture of H\(_2\) and CO gas, (called Syngas) to produce CO\(_2\) and H\(_2\)O, which eliminates the production of pollutants such as NO\(_x\) and SO\(_x\) from hydrocarbon fuels.
Figure 14: Schematic showing the operation of a typical SOFC. 91

The efficiency of SOFCs are higher compared to the other types of fuel cells because the heat generated to initiate the electrochemical reaction can be harvested easily and reused, thus minimizing a constant use of energy to maintain operation temperature.24 In addition, it also reduces overpotential loss (lower reduction potential requirement of thermodynamic compared the observed experimental reduction potential) by high efficiency conversion through utilization of waste heat (from ohmic loss).92

Thin film MOEs are commonly used for the fabrication of solid oxide fuel cells (SOFCs). Two types of designs have been developed for the use of thin film MOE-SOFCs: (1) The transistor type and (2) tubular architecture, as shown in Figure 15.93 This tubular material is a more developed architecture than the transistor-type system, but it is also hard to fabricate due to its brittle nature. Both structures have been reported to have an electrolyte thickness (non-porous) in the 40-50 nm range.94
Even though thin film electrolytes are an improvement over bulk material (lower resistivity and are more flexible), they still have some fundamental flaws. One of the problems with the use of a thin film arises from the fundamental aspect of MOEs conductivity. Resistivity is proportional to the distance between electrodes. With increases in film thickness, the resistance increases because ions have to cover more ground to migrate from one electrode to another. However, there is a limit on how small the distance between electrodes. If the film is too thin, it will have diminished mechanical stability and will crack easily.

Figure 15: Two different designs of thin film based MOE-SOFCs where, (a) transistor type (side view), (b) tubular type (side view) and (c) tubular type open (side view). (Adapted from Reference 93).
1.4.2 Current Challenges

The performance of modern fuel cells depends on Faradaic (charge transfer) and non-Faradic processes (mass transport).\textsuperscript{95} Thermal degradation is one of the major drawbacks when it comes to the use of MOEs. Ceramic electrolytes and electrodes are extremely brittle and susceptible to cracks or fractures due to thermal shock. The formation of fractures can also develop over time due to aging. It can also form fractures at the interface of electrode and electrolyte if their thermal expansion coefficients are not similar. Such problems are observed in MO-MIEC systems like Ni-YSZ. During the redox reaction of Ni to NiO and back, it undergoes a significant change in its dimension. It has been reported that Ni based anodes also undergo a volume decrease of 40.9\% during reduction of NiO to Ni and an increase of 69.2\% during its oxidation.\textsuperscript{96} Other problems associated with this system include Ni being susceptible to sulfur poisoning which deactivates the TPB. It has also been reported that other impurities such as SiO\textsubscript{2} form a glassy phase on the surface of zirconia as it has lower surface energy compare to that of Ni-YSZ. This reduces the sites for oxygen adsorption.\textsuperscript{97,98}

Perovskites are the ideal type of material for the use of oxide conductivity in MO-MIECs because it allows the construction of single –phase metal oxide electrolyte system (LSM-YSZ system). There are some associated problems that need to be overcome. Perovskites are prone to phase separation and reorganization at high temperature. This is due to the different sizes of the cations that form the basic perovskite unit cell structures. The phase separated oxides aggregate on the perovskite surface which causes a barrier to form on the perovskite surface and therefore prevents gaseous O\textsubscript{2} from being adsorbed. In SrTiO\textsubscript{3}, SrO forms a “island” layer on the outer surface and inhibits the perovskite bulk to transfer electrons to the oxygen and limits the overall electrode reaction, as shown in Figure 16.\textsuperscript{24,99}
Fluorite-type electrolytes like doped CeO$_2$ (as in Ce$_{1-x}$Gd$_x$O$_{2-x/2}$), have much higher conductivity than stabilized zirconia, because of their lower activation energy. However, they are unstable and cannot maintain a +4 oxidation state and thus are easily reduced from Ce$^{4+}$ to Ce$^{3+}$. This reduction occurs when a small amount of O$^{2-}$ is converted to O$_2$ (g) in a process where the electrons are left with the vacancy defect site:

$$O^{2-} \leftrightarrow \frac{1}{2}O_2 (g) + V_o^{**} + 2e^- \quad (Rxn. \ 1)$$

Here $V_o^{**}$ is the Kroger–Vink notation for crystal defects representing the vacancy created by O$^{2-}$ removed from the lattice.

1.4.3 Recent advances in the fabrication process

One of recent developments in the fabrication of MOEs for application in fuel is the impregnation process. Impregnation process involves deposition of the catalytic materials like Pt and Ni on the electrolyte by application of a precursor solution, followed by thermal decomposition.
it to form nanoparticles. Out of all the different types of MOEs, the most promising have been the impregnation of perovskite materials like LSM on electrolyte materials like YSZ.\textsuperscript{24} However, these types of materials are prone to react with ZrO\textsubscript{2} at higher temperature and are more suited for intermediate temperature fuel cells.\textsuperscript{100}

It has been reported that the reduction of O\textsubscript{2} reaches its maximum when the impregnation loading is above 30\%.\textsuperscript{24} However, achieving this value requires multiple application of the impregnating solutions. One alternative solution for this process is using the layer-by-layer technique,\textsuperscript{101} which requires pretreating an electrode material prior to impregnation in order to increase maximum adhesion or use molten precursors instead of precursor solutions. The molten precursor route might require more processing time, but it is still considered as it provides an effective method for MOE impregnation. Standalone scaffolds with cathode and anode impregnated over it has been a route that has also been investigated.\textsuperscript{102}

Exsolution is a new process under investigation that has shown the most beneficial results when considering metal oxide conductivity.\textsuperscript{24} This process requires anchoring of the entire nanoparticle on the surface, which is done by heating until the sample interface is in a state between solid and liquid. At that point the nanoparticles are introduced and the sample is allowed to cool. The solidification of the molten part anchors the nanoparticles to the MOE surface. Analysis of such composites has been performed using TEM where it was shown that the lattices plans of both Ni and the perovskite have been aligned along the (110) plane, as shown in Figure 17.\textsuperscript{103,104} This infusion of the two lattices is very important as it eliminates the grain boundaries from restricting the mobility of the charge carrier species.
1.5 Overcoming the Challenges

As pointed out above, nanoscale MOEs are of great importance as they provide certain advantages and enhancements in the fabrication and performance in devices like SOFCs. With the decrease in size, the increase in surface area is achieved relatively to its value because there are more exposed regions for the TPB catalytic sites to be formed. In addition, there is also an increase in surface area for $O_2$ to be absorbed and undergo catalytic reduction.

A decrease in size also provides advantages to the fabrication methods, as MOEs are known to be intrinsically brittle and can form fractures easily during the fabrication process. These fractures prevent $O^{2-}$ ions to conduct across the electrolyte, as the ions cannot migrate across these voids, hence increasing the total migration pathways. It can also further expand during the heating / cooling cycles and result in a catastrophic failure of the MOEs heterostructure.
Taking these size-dependent phenomena into consideration, it is necessary to investigate the fabrication and characterization of new nano-sized MOEs systems. The most commonly used systems involve the use of thin films where the $\text{O}^2$ migrates from cathode to anode. Given the aforementioned issues with thin film MOEs, this dissertation will focus on the fabrication of MOEs nanowires using two separate synthetic routes: (1) a suspended particle route, and (2) a combined sol-gel/electrospinning method. Both these routes will have similar techniques involved for fiber production; however, these fibers will then be transformed to nanowires involving two different classes of starting materials: suspended particles and sol-gel reactions. In both cases, a final annealing step to remove original templating species is necessary.

In the case of the suspended particle route, the process is initiated with the use of commercially-available preformed metal oxide nanoparticles. These particles are used to form a suspension in an appropriate solvent, followed by the addition of a polymer that will act as a template and will control the suspension viscosity. The polymer/nanoparticles suspension is then mixed to obtain a homogenous distribution (ideally) of metal oxide nanoparticles. It is then used to produce nanofibers using the electrospinning technique. The collected fibers are slowly heated to 700°C so the polymer template is gradually removed. This leaves only the nanoparticle partially fused with each other to ideally form the morphology of its initial polymer template. The product is a MO nanowire film (NWF) in a network of fused nanoparticles in a distinct (ideally) 1-D geometric form.

The sol-gel method involves similar use of the electrospinning technique to form nanofibers and post-synthesis annealing at 700°C. However, this process begins by mixing appropriate reagents with alcohol to form a clear solution. These starting materials can be metal salts, metal carboxylates (like bismuth 2-ethylhexanoate) or metal alkoxides (like Zr(O'Bu)$_4$). For
the purpose of this dissertation, the alkoxide is the chosen sol-gel route precursor (instead of metal salts like ZrCl₄ or Zr(NO₃)₄). When metal salts are used as precursors, it is difficult to control the M-O-M bond formation chemistry in relation to alkoxides. The advantages of using the sol-gel transformation is that it provides more control over the O-M-O bond formation which results in the formation of metal oxide oligomeric networks. In selected cases, solid state conductivity measurement of these new nanoscale fabricated metal oxide materials will also be described later in this dissertation.
Chapter II

Fabrication and characterization of ZrO$_2$, YSZ and Bi$_2$O$_3$ nanowires using the suspended particle route
2.0 Introduction

Nanoscale metal oxide electrolytes (MOEs) have been the subject of interest in recent times. The most commonly used morphology for MOEs is thin films. These thin films are non-porous, 2-D layers fixed on a substrate.\textsuperscript{69,70,74,106} As described in Chapter I, the main advantage of using nanoscale materials in this regard is an increase in total surface area relative to its volume, in comparison to thin film form. As a result, there are more exposed regions on the electrolyte for the TPB formation and thus the reduction rate of gaseous O\textsubscript{2} is increased. In addition, the increase in surface area also means that the O\textsubscript{2} gas has more accessibility for adsorption onto the MOEs surface, which increases the chance for it to undergo catalytic reduction, as shown in the reaction below in Rxn. 2.\textsuperscript{84-86}

\[
\text{O}_2 (g) + 4e^- \rightarrow 2\text{O}^{2-} \quad \text{(Rxn. 2)}
\]

This dissertation will encompass nanowire synthesis using two separate routes: (a) suspended particles route (SPR) and (b) sol-gel route (SGR). The focus of this chapter is nanowire (NW) fabrication of Zirconia (ZrO\textsubscript{2}), 8\% yttria stabilized zirconia (YSZ), and bismuth (III) oxide (Bi\textsubscript{2}O\textsubscript{3}) by a suspended particles route. These three materials were chosen because they are some of the most thoroughly investigated MOEs materials for O\textsuperscript{2-} conductivity (in thin film form) to date.\textsuperscript{50,110,111}

YSZ was chosen in order to produce a doped (Y\textsubscript{2}O\textsubscript{3}) ZrO\textsubscript{2} NW structure by this route. Both doped (YSZ) and undoped (ZrO\textsubscript{2}) NWs were fabricated using the same recipe and electrospinning parameters. Similarly, Bi\textsubscript{2}O\textsubscript{3} is often doped with tungsten oxide (WO\textsubscript{3}) to stabilize the δ-phase (most conductive phase for O\textsuperscript{2-} species).\textsuperscript{97} However, WO\textsubscript{3} doped Bi\textsubscript{2}O\textsubscript{3} (WBO) NWs were not prepared by a suspended particle route as WBO nanoparticles are not yet commercially available.
In each case, NW fabrication required careful examination of the electrospinning parameters in order to determine the optimum conditions needed to fabricate 1-D structures. Therefore, each type of MOEs nanoparticle was used to perform multiple sets of experiments where only one variable was changed at a time. The four parameters, which affect the morphology of the nanofibers and their diameters, are: (1) suspension viscosity; (2) voltage; (3) electrode distance; and (4) flow rate.\textsuperscript{84,112,113}

In this dissertation, the terms nanofibers and nanowires are used often and it is important that their meanings are defined clearly. Nanofibers are those structures that are obtained from the electrospinning process and have not been annealed. When the nanofibers are annealed (using a two-step annealing process), the metal oxide nanostructures that are left behind are referred to as nanowires.

\section{Experimental procedures for ZrO\textsubscript{2}, 8YSZ, and Bi\textsubscript{2}O\textsubscript{3} fabrication by SPR}

Overall, the NWs fabricated using the SPR is carried out in three stages: (1) reactant mixing; (2) nanofiber fabrication using electrospinning; and (3) two stage annealing process to remove the polymer template and to form crystalline MOE structures. The three stages of nanowire fabrication are presented in detail for ZrO\textsubscript{2} NWs. As the 8YSZ NWs and Bi\textsubscript{2}O\textsubscript{3} NWs were prepared in a similar fashion by the SPR, their preparative procedures are not described with the same level of detail.

\subsection{ZrO\textsubscript{2} nanowires fabrication using a suspended particle route (SPR)}

\subsubsection{ZrO\textsubscript{2} nanoparticle suspension preparation}

Preformed ZrO\textsubscript{2} nanoparticles were purchased from Sigma-Aldrich with an average nanoparticle diameter of < 100 nm. In the first step, ZrO\textsubscript{2} (0.1 g, Aldrich) was mixed with absolute
ethanol (EtOH, 2.5 g, Pharmco-Aaper) to form a ZrO$_2$/EtOH suspension, which was allowed to sonicate for 30 minutes. The polymer polyvinylpyrrolidone (PVP, MW = 1.3 M, 0.4 g, Aldrich) was dissolved separately in EtOH to form a solution which was then added to the ZrO$_2$/EtOH suspension and mixed with a stir bar for 10 minutes. It was then loaded into a 5 ml syringe (Popper & Sons) with 2 cm long 21-gauge needle, for electrospinning.

### 2.1.1.2 Electrospinning of ZrO$_2$ suspended particles with PVP and EtOH

Electrospinning is a technique which uses an electric field generated by a power supply between two terminals. The reaction solution/suspension is initially loaded into a glass syringe with a metallic needle attached. This needle acts as one of the two terminals. The other terminal is attached to a cylindrical drum, which is wrapped with commercially available Al foil and together acts as the nanofibers collector. This technique includes the use of a piston pump to push the piston of the syringe at a controlled rate. The solution/suspension that is being pumped out of the needle (to create a droplet at the tip), is introduced in the electric field created due to the potential difference between the two terminals. As described in Chapter I, the droplet reacts to the field by forming a Taylor cone, which ultimately produces nanofibers. These fibers are drawn to the collecting drum due to the electrostatic attraction between the terminals.

The electrospinning setup (Figure 18) includes a DC power supply, which provided the necessary voltage to the syringe needle. The potential difference created between the needle and the custom built drum caused the nanofibers to be attracted to the rotating drum. This rotating drum, which is powered by an attached DC motor, collects them as a film of nanofibers, as shown in Figure 18 (b). In the synthesis of ZrO$_2$ NWs, a 20kV potential was applied across the two terminals separated by a distance of 21 cm. This high voltage was generated by using a power supply (Harrison 6206B DC Power Supply, Hewlett-Packard) which was coupled with a flyback...
transformer to boost the supplied potential to 20kV. The ZrO$_2$ / EtOH suspension was pumped at a flow rate of 3 ml/hr using a piston pump (Model no. NE-300, New Era Pump System, Inc.), resulting in the formation of the nanofibers. Table 5 shows the fabrication parameters used for each set of reactions, which will be discussed further in the upcoming section.

![Diagram of electrospinning setup](image)

**Figure 18:** Diagram of electrospinning setup used in the synthesis of both suspended particles NWs (adopted from Ref 70.b), where (a) syringe containing the precursor solution, (b) rotating drum for collecting nanofibers, and (c) voltage supply (d) arrow showing the force applied by the piston pump (not drawn) (e) arrow representing the DC motor for drum rotation.

Figure 19 shows some of the equipment, processes and products that are typical to the fabrication of NWs using the SPR. Figure 19 (a) shows a photograph of the actual DC power supply used in part to generate a 20kV potential difference during the electrospinning process (the flyback transistor is not shown in this figure). Figure 19 (b) shows the piston pump used to control the flow rate of the suspension precisely during the electrospinning process. During the fabrication process, one of the steps involves mixing together the precursor nanoparticles, PVP and ethanol. This process is demonstrated in Figure 19 (c). The same suspension when mixed adequately was then transferred to a glass Popper syringe as shown in Figure 19 (d). The suspension was finally electrospun to produce nanofibers, which were collected on the drum as shown in Figure 19 (e). Once the liquid suspension was depleted and the fabrication was completed, the drum was removed...
from the apparatus. The nanofiber films were removed from the drum (Figure 19 (f)) and stored in a desiccator.

Figure 19: Photos showing the equipment and stages of a typical electrospinning process: (a) the voltage supply unit, (b) piston pump for the syringe, (c) mixing of suspended particles in the presence of PVP and ethanol, (d) suspension loaded in a glass syringe with 21 gauge needle, (e) collection of nanofibers on the drum with some nanowires deposited over the attached power supply electrode, and (f) nanofibers collected from the drum placed in a petri dish for storage.

ZrO₂ nanowires prepared using a SPR route were divided into several sets. In each set, all variables (precursor masses and electrospinning parameters) were kept constant except one in order to investigate its effect on the morphology and the diameter of the ZrO₂ nanowires. The variables that were investigated were: (1) mass of ZrO₂ nanoparticles; (2) mass of PVP; (3) electrode distance during the electrospinning process; and (4) voltage used during the electrospinning process. The masses and the electrospinning parameters that were used in each set are shown in Table 5.
The annealing process is used to burn off the PVP template, leaving only ZrO$_2$ particles ideally in the morphology of the template. The electrospun samples were first cut to the desired dimension and placed on a Si wafer. The sample was then covered with another piece of Si wafer to prevent the nanowire film from curling during the annealing process. The sample was then annealed in a two-step process heating process (described below) to obtain the final product.

Before annealing, the tube furnace temperature distribution needed to be evaluated. A systematic approach was devised where the temperature inside the tube furnace (halfway between the two ends) was set at 600°C. Then a K-type thermocouple probe (Omega, probe length = 30.5 cm) was inserted all the way into the furnace (furnace length = 50 cm) through the opening on the

### Table 5. Typical experimental parameters used for the ZrO$_2$ fabrication nanofibers by SPR.

<table>
<thead>
<tr>
<th>Reaction Set.</th>
<th>Description</th>
<th>ZrO$_2$ nanoparticles mass (g)</th>
<th>PVP mass (g)</th>
<th>Electrode distance (cm)</th>
<th>Voltage (kV)</th>
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<td>~21.0</td>
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<td></td>
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<td>0.050</td>
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<td>4</td>
<td>Varying voltage</td>
<td>~0.2</td>
<td>~0.40</td>
<td>~21</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td>25</td>
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<td></td>
<td></td>
<td>28</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>30</td>
</tr>
</tbody>
</table>

#### 2.1.1.3 Annealing of ZrO$_2$/PVP nanofibers films

The annealing process is used to burn off the PVP template, leaving only ZrO$_2$ particles ideally in the morphology of the template. The electrospun samples were first cut to the desired dimension and placed on a Si wafer. The sample was then covered with another piece of Si wafer to prevent the nanowire film from curling during the annealing process. The sample was then annealed in a two-step process heating process (described below) to obtain the final product.
left side of the furnace. The probe was then taken out incrementally (Figure 20) and allowed to adjust to the temperature of the new position before recording the temperature. The same process was repeated with thermocouple insertion from the right side of the furnace. The distance of the thermocouple moved and their corresponding temperatures were used to position the nanofiber films in the furnace during the annealing process. This was done to identify the region inside the furnace where the temperature was relatively consistent. This region lies between the 19.5 cm and 34.7 cm marks when measured from the left of the furnace as indicated by two dashed lines in Figure 21.

Figure 20: (a) A prospective diagram of the tube furnace used to anneal electrospun samples. (b) Front view diagram of the tube furnace showing the initial position of the thermocouple at the and (c) the final position during the temperature distribution analysis as function of distance away from the center (600°C).
Figure 21: Distribution of temperature across the length of the tube furnace (measured from left to right). All the temperature measurements were done under the same furnace settings with the center of the furnace set at ~ 600˚C. The electrospun samples were annealed between 19.5 cm and 34.7 cm when measured from the left of the furnace.

2.1.1.4 Procedures of the two step annealing process of ZrO₂/PVP nanofiber films

In the first step, the ZrO₂/PVP nanofiber film is annealed from room temperature to 220˚C gradually over a period of 4 hours and held at temperature for 24 hours. This process is shown in Figure 22. The temperature was then lowered gradually to room temperature and the sample transferred to the tube furnace. The partially annealed samples were then covered with a second piece of Si wafer in order to maintain a flat morphology. The temperature was then increased up to about 800˚C over a period of 4-5 hours and held at that temperature for 24 hours. The second stage annealing process is shown in Figure 23.

Once the temperature was gradually cooled down to the room temperature, the flat ZrO₂ SPR-NWs film was collected. This two stage annealing process allows a gradual increase of the temperature during the initial annealing stage and thus prevents thermal shock from breaking apart the NW film. Photographs of samples (a) before and (b) after the second stage annealing process (annealed overnight at 800˚C) are shown in Figure 24.
Figure 22: The process of first stage of annealing of the nanofibers film fabricated using the electrospinning process. (a) Si wafer (commercially acquired) was used as the substrate for the annealing process. (b) An unannealed nanofiber film was cut into smaller pieces and placed on the Si wafer. (c) Diagrammatic representation of the pieces of the films as shown in the photograph (d).
Figure 23: Showing the stages of sample preparation for the second stage annealing of the nanofibers films at 800°C.

(a) Quartz plates were used for second stage annealing.

(b) Partially annealed nanofibers films were placed on the quartz plate.

(c) Arranged films were then placed in the oven for second stage annealing.
Figure 24: Photographs of (a) partially annealed nanofibers films before second stage annealing and (b) nanofibers films after annealing at 800˚C overnight.

There were significant decreases in the total area of the nanofiber films during both steps of the annealing processes. Figure 25 shows a comparison of nanofiber film area (a) before the first annealing step, (b) after the first annealing step, (c) before second annealing step and (d) after the second annealing step. The dashed lines in Figure 25 (b) represents the area of the film before the first annealing step and provides an idea of the extent of area reduction that is observed during the nanowires film calcination step. Sample in (b) and (c) are the same and the difference in color of the film is due to the substrate on which they were placed during the annealing process. Figure 25 shows that the first annealing step (a, b) was done on a Si wafer (grey) and the second step (b, c) on a quartz plate (white). The darker appearance of the film in Figure 25 (c) (in comparison to (d) is due to partial pyrolysis of the of the PVP template.
Figure 25: Reduction in the area of film during the both steps of the annealing process. (a) Film before the first annealing step, and (b) after the first annealing step. (c) the same sample as (b) but placed on a quartz plate before the second annealing step and (d) after second step annealing process. In (b) the dash line indicates the area of the nanowire film before the first annealing step.

Table 6. Reduction in nanowire film during the two annealing steps.

<table>
<thead>
<tr>
<th>Annealing step (initial and final temperatures)</th>
<th>Initial area of the film</th>
<th>Final area of the film</th>
<th>Percent reduction in area</th>
</tr>
</thead>
<tbody>
<tr>
<td>First step (24°C – 220°C)</td>
<td>36 cm²</td>
<td>12 cm²</td>
<td>67 %</td>
</tr>
<tr>
<td>Second step (24°C - 800°C)</td>
<td>16 cm²</td>
<td>5.1 cm²</td>
<td>68 %</td>
</tr>
</tbody>
</table>
The measurements for these calculations were done by taking each photograph against a calibrated ruler (not shown in the photographs) and measuring the dimensions of the films. These dimensions were then used to determine the percent area reduced due to the annealing steps. This investigation was necessary because it allowed control over the dimension of the post second step annealed films. For example, if the desired area of the film needed to be ~ 5 cm\(^2\) then a piece with 36 cm\(^2\) unannealed film would be used for the first annealing step.

### 2.1.2 8YSZ NWs fabrication using SPR in conjunction with electrospinning

YSZ suspended particle nanowires were prepared using the commercially-available 8% YSZ nanoparticles with an average particle size of ~ 700 nm (Sigma-Aldrich). The fabrication process consisted of three steps, similar to the ZrO\(_2\) suspended particle NW fabrication procedure, with the electrospinning and annealing parameters identical to those described above. In case of the YSZ NW fabrication, only three electrospinning parameters were evaluated: the mass of PVP; mass of YSZ nanoparticles; and the concentration of surfactant (Triton X-100). Only these three sets of reactions were performed because the results obtained from the ZrO\(_2\) NWs (reported in the Results and Discussion section) showed that the SPR method is insensitive to voltage, flow rate, and electrode distance. The results also revealed the formation of nanoparticle aggregates during electrospinning. In order to minimize aggregate formation, the influence of a surfactant was investigated (only for YSZ NWs). The protocols for each of these sets are reported in Table 7.
Table 7. Typical amounts of the reactants used for YSZ nanofiber fabrication by SPR.

<table>
<thead>
<tr>
<th>Reaction Set No.</th>
<th>Description</th>
<th>YSZ nanoparticles mass (g)</th>
<th>PVP mass (g)</th>
<th>Surfactant %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Varying YSZ suspended nanoparticle mass</td>
<td>0.05</td>
<td>0.40</td>
<td>No surfactant added</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.15</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>0.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Varying PVP mass</td>
<td>~0.30</td>
<td>0.30</td>
<td>No surfactant added</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Varying surfactant concentration</td>
<td>~0.30</td>
<td>0.40</td>
<td>0.2%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.3%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.4%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.5%</td>
</tr>
</tbody>
</table>

The mixing of 8YSZ nanoparticles, PVP and EtOH, the fabrication of the nanofibers using electrospinning, and finally the annealing performed in the same process as described in Section 2.1.1. Therefore, detailed descriptions of procedures are not repeated here for 8YSZ.

2.1.3 Bi₂O₃ NWs fabrication using SPR

Bi₂O₃ NWs fabrication by SPR was created by first making a suspension consisting of 0.1 g Bi₂O₃ (Aldrich) nanoparticles and 3.17 ml of absolute EtOH. The resulting suspension was shaken vigorously for 30 minutes. In a separate vial, 0.4 g of PVP was added to EtOH (3.17 ml) and shaken until the PVP dissolved into the solvent to form a clear colorless viscous liquid. The initial suspension and the PVP/EtOH solution were then mixed together to form a viscous bright yellow suspension. This suspension was shaken using a vortex mixer for 1 minute to ensure a
homogeneous mixture (amounts of all the precursors used are reported in Table 8). Mixing the sample did create some problems by trapping air bubbles in the viscous liquid. The sample had to be left in a homogenizer for 10 to 20 additional minutes to allow the bubbles to escape from the medium. If the bubbles remain, it would create voids in the nanofiber morphology.

The electrospinning parameters were kept the same as for the ZrO$_2$ SPR NW fabrication process described above. The maximum annealing temperature however, needed to be altered from 900˚C to 450˚C. Annealing Bi$_2$O$_3$ NWs at 900˚C (like the zirconia-based systems) resulted in the fusion of Bi$_2$O$_3$ NWs (m.p. = 830˚C at 1 atm).$^{114}$

It was also observed that the Bi$_2$O$_3$ NWs were more sensitive to the annealing temperature gradient compared to the zirconia species and produced vastly different morphologies (post annealing) even with small deviations in the temperature. These observations will be further discussed in the next section. The reaction sets were also confined to two parameters: mass of PVP and mass of Bi$_2$O$_3$ nanoparticles. The other parameters did not have any effect on the NW produced by the suspended particle route. The data for the two sets are reported in Table 8.

<table>
<thead>
<tr>
<th>Reaction Set No.</th>
<th>Experiment route</th>
<th>Description</th>
<th>Bi$_2$O$_3$ nanoparticles mass (g)</th>
<th>PVP mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bi$_2$O$_3$ suspended particles</td>
<td>Varying Bi$_2$O$_3$ nanoparticles mass</td>
<td>0.30</td>
<td>~0.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>Varying PVP mass</td>
<td>~0.50</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.40</td>
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<td></td>
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<td></td>
<td></td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.60</td>
</tr>
</tbody>
</table>
2.2 Instruments used for characterization

2.2.1 Scanning electron microscopy (SEM)

The structural and chemical characterization and analysis of the nanowires were performed using various types of instruments. Structural characterization was performed using a JEOL JSM-6100 scanning electron microscope (SEM). The samples were prepared by placing a small piece of NW film on a carbon adhesive tape (12 mm) that had been placed on an aluminum thimble (12.5 mm diameter). Both carbon tape and aluminum thimbles were purchased from Ted Pella.

2.2.2 Transmission electron microscopy (TEM)

A JEOL JEM-2100 transmission electron microscope was used to analyze finer morphologies associated with the nanowires that could not be seen with SEM. It was also used to obtain lattice images of selected crystalline materials. The samples for the TEM were prepared by taking a 2 mm by 2 mm annealed nanowire film and placing it in a vial. Acetone (3-4 ml) was added and the resulting suspension sonicated using a sonication horn (Branson Sonifier 450) for 30 seconds. Two or three drops of the suspension were placed on a TEM Cu grid (purchased from Electron Microscopy Sciences, EMS) and allowed to air dry between each drop. The grid was then loaded to a JEOL single tilt holder for analysis. Electron dispersive x-ray spectroscopy (EDS/EDX) analysis was performed to perform elemental characterization. The EDX spectrum obtained from the analysis was also used to perform atomic percent calculations of the desired samples.
2.2.3 X-ray diffraction (XRD)

The XRD analysis was performed on the suspended particle nanowires to investigate the phase composition of the annealed nanowires and is presented in the next section. This was necessary because at high temperature, the crystal lattices can rearrange to obtain its lowest energy polymorph.

ZrO$_2$ undergoes three different phase transitions during the annealing process, starting from monoclinic to tetragonal to cubic.$^{115}$ In YSZ materials, yttria is introduced to retain its cubic form at room temperature. Bi$_2$O$_3$ also undergoes a phase transition from monoclinic ($\alpha$-phase), then tetragonal ($\beta$-phase), body centered cubic ($\gamma$-phase) and finally face centered cubic ($\delta$-phase).$^{116}$ XRD analysis provides information regarding the phase purity of an annealed sample, which is very important as each phase has its own unit cell parameters and properties.

2.3 Results and Discussion

2.3.1 ZrO$_2$ NWs fabricated using the suspended particles route

High temperature was used in the second stage of annealing of ZrO$_2$ nanoparticles so that it leaves behind a fused array of nanocrystals without any polymer template. However, the annealing temperature was restricted to 800°C because this temperature can also result in the nanowire film fusing with Si wafer substrate and hence causes the film to break apart while being removed from the wafer. Therefore, making it was very difficult to obtain NW films that were stable enough to be handled easily.

Nanowire fabrication using the pre-synthesized ZrO$_2$ nanoparticles was done by dividing the process into four different categories or sets. In each set, only one variable was changed at a time in order to find out its effect on the resulting annealed nanowires diameters and overall morphologies. The four sets of experiments were: (1) varying ZrO$_2$ nanoparticle mass; (2) varying
PVP mass; (3) varying electrode distance; and (4) varying voltage. The values used for each of these sets are reported in Table 5.

2.3.1.1 Set 1: Varying ZrO\(_2\) nanoparticles mass

\[
\text{ZrO}_2 + \text{PVP} \xrightarrow{(a) \text{ EtOH}} \xrightarrow{(b) \text{ Electrospinning}} \text{ZrO}_2\text{-PVP nanofibers}
\]

ZrO\(_2\) nanoparticles masses:
1. 0.025 g
2. 0.050 g
3. 0.100 g
4. 0.200 g
(c) gradual annealing

This section is focused on varying the mass of ZrO\(_2\) nanoparticles used to fabricate the nanowires by the SPR. The procedures for this set of experiments have been discussed in detailed earlier in Section 2.1.1. The purpose of this set of experiments was to evaluate the effect of increasing the initial mass of the ZrO\(_2\) nanoparticles on the resulting annealed nanowire diameters. The ZrO\(_2\) mass was increased from 0.025 g to 0.200 g as shown in the scheme above. For each experiment in the set, SEM analysis and annealed nanowire diameters distribution histogram is presented and analyzed.

(i). ZrO\(_2\) nanowires fabricated using 0.025 g of nanoparticles

Figure 26 (a) shows a low magnification image of an unannealed sample with particles embedded within the nanofibers. A closer look demonstrates the particle distribution across the individual nanofibers. It is also clear that the particle sizes are not the same and they are not spread out evenly across the length of the individual nanofibers. Images (c) and (d) are nanowires obtained after the two-step annealing process. These annealed samples look more like a cluster of particles
of various sizes instead of well-defined one dimensional (1-D) structures. However, there are regions where the particles have been fused with one another to a form 1-D network, as shown in Figure 26 (d). The histogram of the nanowire diameter shown in Figure 27 was produced by measuring only clearly defined 1-D regions of the annealed products. It is recognized, however, that a significant portion of product appears in highly aggregated form.

Figure 26: SEM images showing (a, b) unannealed nanowires, (c,d) annealed nanowires prepared using 0.025 g ZrO₂. (In the figure above, the scale bars in (a), (b), (c) and (d) are 50, 10, 10 and 5 µm, respectively.)
Figure 27 also shows that the average nanowire diameter was 524 (± 154) nm. This means that the nanowire diameter varies widely and it is difficult to control using such a small mass of ZrO2 nanoparticles. Figure 27: Annealed nanowires diameter distribution when 0.025 g ZrO2 nanoparticles was used.

(1). ZrO2 nanowires fabricated using 0.050 g of nanoparticles

Nanowires fabricated using 0.050 g of ZrO2 nanoparticles was done in the same manner as the above process. SEM images (Figure 28) show different morphologies from the one observed in the previous sample. This sample showed the presence of more 1-D structures than nanoparticle clusters. A film composed of a network of nanowires and particles is shown in Figure 28 (c, d).

The nanowire diameter histogram, shown in Figure 29 demonstrates a slight increase in the average nanowire diameter from 524 (± 154) nm to 676 (± 197) nm in which the mass of ZrO2 nanoparticles was increased from 0.025 g to 0.050 g. However, this increase in diameter is obscured by the large standard deviation in the data.
Figure 28: SEM images showing (a, b) unannealed nanowires, (c, d) annealed nanowires prepared using 0.050 g ZrO$_2$. (In the figure above, the scale bars in (a), (b), (c) and (d) are 20, 10, 10 and 20 µm, respectively.)

Figure 29: Annealed nanowires diameter distribution when 0.050g ZrO$_2$ nanoparticles was used.

Average nanowire diameter: 676 ± 197 nm
(2) ZrO$_2$ nanowires fabricated using 0.100 g of nanoparticles

Nanowires prepared using 0.100 g resulted in a ZrO$_2$ suspended particle morphology similar to the one observed when prepared with 0.050 g ZrO$_2$. Figures 30 (a) and (b) shows unannealed networks of nanofibers with various size particles embedded within them. In Figures 30 (c) and (d), it can be easily seen that this sample contains more distinct 1-D structures in comparison to Figures 26 (c) and (d). When the histogram data is considered (Figure 31), it can be concluded that the increase in ZrO$_2$ nanoparticles mass to 0.100 g likely provided more material to form 1-D structures and slightly increased the average nanowire diameter. However, once again a large standard deviation associated with the data obscures a definite conclusion.

Figure 30: SEM images showing (a, b) unannealed nanowires, (c,d) annealed nanowires prepared using 0.100 g ZrO$_2$. (In the figure above, the scale bars in (a), (b), (c) and (d) are 20, 5, 50 and 10 µm, respectively.)
Figure 31: Annealed nanowires diameter distribution when 0.100 g ZrO2 nanoparticles was used.

(3). ZrO2 nanowires fabricated using 0.200 g of nanoparticles

Adding 0.200 g ZrO2 increased the concentration of the particles in the nanofibers significantly (Figure 32 (b)). An increase in the mass of nanoparticles resulted in no significant morphological changes in the fabricated nanowires (in comparison to the sample prepared with 0.100 g ZrO2). The histogram also shows a minimal increase in the average nanowire diameter.

Figure 32: SEM images showing (a, b) unannealed nanowires, (c, d) annealed nanowires prepared using 0.200 g ZrO2. (In the figure above, the scale bars in (a), (b), (c) and (d) are 50, 5, 50 and 10 µm, respectively.)
It can be concluded that ZrO$_2$ nanowire fabrication under these conditions has upper and lower limits for nanoparticle mass of 0.200 g and 0.050 g, respectively. Below 0.050 g there is not enough material present for the formation of nanowires as seen in the case of 0.025 g sample. The overall trend derived from this series of measurements (Figure 34) shows a slight increase in the annealed nanowire diameters with an increase in ZrO$_2$ nanoparticles mass. However, this increase is statistically insignificant due to large standard deviations associated with the average nanowire diameter. The big factor presumably associated with the observed standard deviation for NWs formation using SPR is the size dispersity of the ZrO$_2$ nanoparticles samples that were commercially obtained. Thus, minimal control over the nanowire diameter during the fabrication process of ZrO$_2$ NWs using SPR is possible.

Figure 34: Plot showing measured ZrO$_2$ nanowire diameters (annealed) vs mass of ZrO$_2$ used.
(4). Study of ZrO$_2$ nanoparticles mass versus nanowire diameter: TEM and EDX analysis

TEM analysis gives a more detailed picture of the nanoparticle morphology used for the ZrO$_2$ NWs fabrication using SPR. A typical TEM shows that pre-fabricated nanoparticles exist as a cluster of nano-sized crystallites (Figure 35 (a)) which aggregated further during the nanowire fabrication (using 0.025 g ZrO$_2$ nanoparticles) process to form the 1-D structures observed via SEM. The TEM was also used to do lattice imaging as shown in Figure 35 (b). The measured d-spacing confirms that the fabricated ZrO$_2$ nanoparticles are in their cubic form with a lattice spacing of $d_{111} = 0.306$ nm, and is similar to reported values.$^{47}$

![Figure 35: TEM analysis of ZrO$_2$ nanoparticles showing (a) cluster of nano-sized crystallites, and (b) lattice spacing ($d_{111} = 0.306$ nm) with FFT analysis as the inset.](image)

EDX analysis was used to confirm the presence of Zr and O species in the sample by evaluating their average atomic percentages and their intrinsic peaks at the specific energy values (shown in Figure 36 (a)). The inset in the same image shows the STEM image of the sample being analyzed using the EDX. The EDX map shows a homogenous distribution of the Zr and O specious across the samples that have been investigated (Figures 36 (b) and (c)). The average atomic
percentage obtained from the quantitative analysis of the ZrO$_2$ nanowires was 69.60% for Zr and 30.40% oxygen. This provides an atomic percent ratio for Zr:O as 2:1, in contrast to the formula ZrO$_2$, where Zr:O should be 1:2.

![EDX analysis showing (a) elemental composition (b,c) EDX map showing distribution of Zr (b) and O (c) of the sample shown in the inset.](image)

This observation can be explained in part if one evaluates the role of the electron interaction volume phenomenon associated with TEM and EDX analysis. The TEM electron beam forms a very specific region of space from which the matter emits x-rays. Figure 37 shows the electron interaction volume that is generated when the electron beam strikes the surface of the
material being analyzed in the TEM. Before the X-ray is produced from the incident beam, few other processes take place. The very first step involves production of the Auger electrons that are emitted from the material right below the outer surface of the material being analyzed. The layer right below it absorbs the energy and emits the secondary electrons. The third layer is responsible for the production of the back-scattering electrons (BSE). Finally, the incident beam reaches a point beyond the BSE and diffuses into a teardrop shape inside the material being analyzed. At this point, the sample produces the x-ray that is intercepted by the detector as an EDX signal.

This is where the inconsistent EDX result likely originates from for ZrO$_2$ suspended particles. It has been reported that elements with lower z values, like oxygen, undergoes Auger electron emission more often than atoms with high atomic numbers, as shown in Figure 38 (a).$^{119,120}$ Secondly, the TEM incident beam can penetrate up to 10 - 15 µm under 200kV. A study done using ZrO$_2$ with accelerating voltage ranging from 5 – 15 kV is shown in Figure 38 (b), where it is shown that even at 25kV the beam has a penetration power of more than 2000 nm.
Figure 38: (a) Qualitative comparison of penetration depth and various TEM accelerating voltages ($E_0$) and their effect on materials with varying atomic number ($Z$). (b) Electron beam penetration with $E_0$ 5-15kV on varying atomic numbered material.$^{120,121}$

Therefore, the ZrO$_2$ nanowires described in this chapter deal with nanowires that have a diameter with a maximum of about 1.1 µm. This means that the electron interaction volume generated on the nanowires mostly consists of the volume that is considered the pre-x-ray production region, which means that more Auger electrons are generated compared to the electrons being used to generate x-rays from the oxygen atoms. Hence, the majority of the electrons do no result in the x-ray emission and therefore provide a quantitative analysis that has a lower oxygen count then theoretically predicted.
(5). ZrO$_2$ mass vs nanowires diameters study - XRD analysis

The XRD analysis of the annealed ZrO$_2$ nanowires prepared by the SPR (0.025 g, 0.050 g, 0.100 g and 0.200 g ZrO$_2$ nanoparticles) is shown in Figure 39. The data shows characteristic peaks associated with ZrO$_2$ monoclinic phases.$^{121}$

The TEM, EDX and XRD analysis of the remaining sets of experimental data (involving ZrO$_2$ NWs fabricated using the SPR) are not presented here as these data are also very similar to those presented in the current set. As this investigation is mainly focused on the effect of the ZrO$_2$ mass on the nanowire diameter and their morphologies, only the SEM and NW diameter histogram analysis will be reported from this point forward.

![XRD peaks of ZrO$_2$ suspended particles NWs after annealing. The angles indicated in the figure correlate to the reference$^{107}$ peaks of the monoclinic phase (no tetragonal or cubic phases were observed).](image)

Figure 39: XRD peaks of ZrO$_2$ suspended particles NWs after annealing. The angles indicated in the figure correlate to the reference$^{107}$ peaks of the monoclinic phase (no tetragonal or cubic phases were observed).
2.3.1.2 Set 2: Varying PVP mass

\[ \text{ZrO}_2 + \text{PVP} \xrightarrow{\text{(a) EtOH}} \xrightarrow{\text{(b) Electrospinning}} \text{ZrO}_2 - \text{PVP nanofibers} \]

PVP mass:
1. 0.20 g
2. 0.30 g
3. 0.40 g
4. 0.50 g

(c) gradual annealing

In this series of experiments, only the mass of PVP was varied while keeping all other variables constant. This was done to investigate the effects of the suspension viscosity (viscosity depends on the PVP mass) on the annealed nanowire diameters and overall morphology. The PVP masses that have been used were 0.2 g, 0.3 g, 0.4 g, and 0.5 g. The experimental process has been presented earlier in this chapter. The results for this section will consist of the SEM analysis and the nanowire diameter histograms. The ZrO\(_2\) nanoparticles used in this set was the same batch that was used for the Set 1 (Section 2.3.1.1).

(1). ZrO\(_2\) nanowires fabricated using 0.200 g of PVP

Using 0.200 g of PVP did not result in the formation of nanofibers. The process electrospayed ZrO\(_2\) nanoparticles on the drum as shown in Figure 40 (c). The process also produced a small amount of very thin nanofibers with a lot of bead formation. The nanofiber diameter size distribution is shown in Figure 41 (with an average diameter of 238 ± 66 nm). This indicates that the suspension used for electrospinning did not have sufficient viscosity and the solution was ejected from the needle before a stable Taylor cone could be formed.
Figure 40: SEM images showing (a, b) unannealed nanofibers (with significant beading) and (c, d) annealed nanowire of samples fabricated using 0.200g PVP showing no nanowires after the annealing process. In the figure, the scale bars in (a), (b), (c) and (d) are 500, 20, 100 and 10 µm, respectively.

The process of bead formation during low viscosity has been studied extensively by Zhu et al.\textsuperscript{122} They explained that lower viscosity caused a lower surface tension of the suspension which was overcome easily by the accumulation of charge (at the tip of the syringe needle) during the formation of the Taylor cone. These beads formed clusters of particles after the annealing phase as shown in Figure 40 (d).
Figure 41: Unannealed nanofibers diameter distribution when 0.200 g PVP was used.

(2). ZrO<sub>2</sub> nanowires fabricated using 0.300 g of PVP

The use of 0.300 g of PVP in this type of process also showed a similar result as the previous sample where no discrete nanowires (post annealing) were observed under SEM. The electrospinning did produce nanofibers (Figures 42 (a) and (b)) but these nanofibers were not thick enough to load the suspended ZrO<sub>2</sub> particles in a significant amount. Therefore, the nanoparticles were not able to coalesce in the same morphology as its polymer template and resulted in clusters of particles as shown in Figure 42 (c). The nanofibers, however, did not produce any beads which were observed in the when 0.200 g PVP was used. This may suggest that the viscosity of the suspension was above the point necessary for the Taylor cone formation.
Figure 42: SEM images showing (a,b) unannealed nanofibers and (c,d) annealed nanowires of samples fabricated using 0.300 g PVP. In the figure, the scale bars in (a), (b), (c) and (d) are 50, 5, 10 and 10 µm, respectively.

Figure 43: Unannealed nanofibers diameter distribution when 0.300 g PVP was used.
(3). ZrO$_2$ nanowires fabricated using 0.400 g of PVP

In a similar way, the process using 0.400 g PVP did not produce any ZrO$_2$ nanowires after the two step annealing process. The analysis performed using the SEM showed similar cluster formation as seen in the previous two PVP masses (Figure 44 (d)). However, the unannealed nanofibers (Figures 44 (a) and (b)) did show an increase in the nanofibers diameters compared to the sample where 0.300 g PVP was used. It also did not show any signs of bead formation as the previous sample.

Figure 44: SEM images showing (a,b) unannealed nanofibers and (c,d) annealed nanowires of samples fabricated using 0.400 g PVP. In the figure, the scale bars in (a), (b), (c) and (d) are 20, 10, 20 and 5 µm, respectively.
The nanofibers produced using the 0.400 g PVP had an average diameter of 661 (± 137) nm. The nanofiber diameter increased when the PVP mass was increased from 0.300 g to 0.400 g. The nanofiber diameter distribution is shown in Figure 45.

Figure 45: Unannealed nanofibers diameter distribution when 0.400 g PVP was used.

(4). **ZrO\textsubscript{2} nanowires fabricated using 0.500 g of PVP**

Using 0.500 g PVP also did not form any nanowires upon annealing. It did form unannealed nanofibers (Figure 46 (b)) that were relatively more aligned compared to the sample prepared with 0.400 g PVP. After the annealing stages the nanofibers turned into a cluster of particles as shown in Figure 46 (d).
Figure 46: SEM images of (a,b) unannealed nanofibers and (c,d) annealed nanowires of samples fabricated using 0.500 g PVP. In the figure, the scale bars in (a), (b), (c) and (d) are 100, 10, 10 and 10 µm, respectively.

Figure 47: Unannealed nanofibers diameter distribution when 0.400 g PVP was used.

Average nanofiber diameter: \(1055 \pm 225\) nm
In this series of measurement of varying polymer template concentration, the different masses of PVP used did not result in the formation of nanowires when annealed. For that reason, histograms could not be generated. It was also observed that the unannealed nanofibers only produced beads at a very low PVP mass (0.300 g). The nanofibers did increase in diameter, and began forming more distinct 1-D structures, as the PVP mass was increased during the Set 2 investigations. Table 9 and Figure 48 shows the relationship between the PVP mass and unannealed nanofibers diameters.

<table>
<thead>
<tr>
<th>PVP mass (g)</th>
<th>Average unannealed nanofiber diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.200</td>
<td>238 ± 66</td>
</tr>
<tr>
<td>0.300</td>
<td>454 ± 104</td>
</tr>
<tr>
<td>0.400</td>
<td>661 ± 137</td>
</tr>
<tr>
<td>0.500</td>
<td>1055 ± 225</td>
</tr>
</tbody>
</table>

![Figure 48: Effect of increase in PVP mass on the unannealed nanofiber diameter.](image-url)
Even though this series of experiments did not provide useful details with respect to annealed nanowires thickness dependence on PVP mass, it still provided valuable information about the polymer nanofiber diameters and structures when used with prefabricated nanoparticles. There is a clear dependence of initial nanofiber widths on PVP concentration; however, the lack of any discrete NW formation upon annealing did not provide any useful information for the purpose of size control of ZrO$_2$ NWs.

### 2.3.1.3 Set 3: Varying electrode distance (ED)

\[
\text{ZrO}_2 + \text{PVP} \xrightarrow{(a) \text{EtOH}} \xrightarrow{(b) \text{Electrospinning}} \text{ZrO}_2 - \text{PVP nanofibers}
\]

Electrode distance (ED):
1. 15 cm
2. 18 cm
3. 21 cm
4. 25 cm
5. 27 cm

(c) gradual annealing to form ZrO$_2$ NWs

The scheme shown above gives an overview of Set 3 investigation where changes in ZrO$_2$ annealed nanowires diameter are evaluated when the electrode distance is varied. In the electrospinning process, the electrode distance is the distance between the tip of the syringe (containing the suspension) and the collecting drum. This series of experiments were done similarly to the previous two sets; in this case only the electrode distances were varied and all other variables kept constant.
(1). ZrO$_2$ nanowires fabricated with electrode distance of 15 cm

The first electrode distance (ED) was chosen to be 15 cm because in a trial run it was observed that the electrospinning process produces beads when ED < 15 cm.

Figure 49: SEM images of (a,b) unannealed nanofibers and (c,d) annealed nanowires of samples fabricated with electrode distance of 15 cm. In the figure above, the scale bars in (a), (b), (c) and (d) are 50, 10, 50 and 5 µm, respectively.

Figure 50: Annealed nanowire diameter histogram with an average diameter of 2308 (± 679) nm prepared with ED of 15 cm.
(2). ZrO$_2$ nanowires fabricated with electrode distance of 18 cm

The nanofibers collected at ED = 18 cm showed a very different morphology compared to the sample where an ED = 15 cm was used. The average diameter of the discrete ZrO$_2$ NW showed a decrease from 2308 (± 679) nm (for 15 cm ED) to 1039 (± 556) nm (for 18 cm ED).

![SEM images](image)

Figure 51: SEM images of (a,b) unannealed nanofibers and (c,d) annealed nanowires of samples fabricated with electrode distance of 18 cm. In the figure above, the scale bars in (a), (b), (c) and (d) are 100, 20, 200 and 50 µm, respectively.

In addition, the nanofibers on the top layer of the film (prepared using 18 cm ED) partially fused together to form a web-like network as shown in Figure 51 (a). There macro structures formed like an outer skin over the NW film and were more discretely visible after the annealing
processes (Figures 51 (c) and (d)). These macro structures were measured to have an average diameter of 5350 (± 1410) nm and were excluded from the histogram analysis (Figure 52).

Figure 52: Annealed nanowire diameter histogram with an average diameter of 1039 (± 556) nm prepared with ED of 18 cm.

(3). ZrO$_2$ nanowires fabricated with electrode distance of 21 cm

Use of an ED = 21 cm in this process showed samples lacking the presence of a web-like layer of ED = 18 cm, as seen in Figure 53 (a). It also showed the presence of very thin (~ 1 µm) nanofibers along with much thicker (~ 5µm) ones (Figure 53 (b)). After the two step annealing phase, only the thicker nanowires remained. These nanowires were mostly crooked and formed a fragile network (Figure 53 (c)). The average ZrO$_2$ NW diameter increased from 1039 (± 556) nm (ED = 18 cm) to 2075 (± 554) nm for the current sample. ZrO$_2$ NWs prepared using ED of 15 cm and 21 cm had diameters with values ~ 2 µm which is much larger compared to ~1 µm average diameter of the web-like sample prepared using ED of 18 cm.
Figure 53: SEM images of (a,b) unannealed nanofibers and (c,d) annealed nanowires of samples fabricated with electrode distance of 21 cm. In the figure above, the scale bars in (a), (b), (c) and (d) are 50, 20, 20 and 10 µm, respectively.

Figure 54: Annealed nanowire diameter histogram with an average diameter of 2075 (± 554) nm prepared with an ED of 21 cm.

(4). ZrO₂ nanowires fabricated with electrode distance of 24 cm

Samples prepared using an ED = 24 cm produced nanofibers that were straight and did not show the presence of the ultra-thin nanowires as seen in the previous section. However, the
annealed nanowires still appeared crooked similar to those of the ED = 21 cm samples (Figure 55 (d)). The nanowire diameter distribution is shown in Figure 56 with an average diameter of 1869 (± 468) nm.

![SEM images of (a,b) unannealed nanofibers and (c,d) annealed nanowires of samples fabricated with electrode distance of 24 cm. In the figure above, the scale bars in (a), (b), (c) and (d) are 50, 10, 50 and 10 µm, respectively.](image)

Figure 55: SEM images of (a,b) unannealed nanofibers and (c,d) annealed nanowires of samples fabricated with electrode distance of 24 cm. In the figure above, the scale bars in (a), (b), (c) and (d) are 50, 10, 50 and 10 µm, respectively.

![Annealed nanowire diameter histogram with an average diameter of 1869 (± 468) nm prepared with an ED of 24 cm.](image)

Figure 56: Annealed nanowire diameter histogram with an average diameter of 1869 (± 468) nm prepared with an ED of 24 cm.
(5). ZrO$_2$ nanowires fabricated with electrode distance of 27 cm

In this sample, most nanofibers on the very top of the film had relatively thicker diameters compared to those below them. Figure 57 (c) shows an overview of the annealed film with several NWs with one highlighted by the dash lined box.

Figure 57: SEM images of (a,b) unannealed nanofibers and (c,d) annealed nanowires of samples fabricated with electrode distance of 27 cm. In the figure above, the scale bars in (a), (b), (c) and (d) are 20, 10, 20 and 10 µm, respectively.
Figure 58: Annealed nanowire diameter histogram with an average diameter of 1323 (± 663) nm prepared with an ED of 27 cm.

In this section, the overall trend observed was that the annealed average nanowire diameter slightly decreases with an increase in the electrode distance as shown in Figure 59. This trend is obscured, however due to the large standard deviation associated with the diameter measurements.

Generally, with an increase in the distance between the capillary and the collector the diameter of electrospun nanofibers decreases.\textsuperscript{123} It has been explained that at smaller distances the solvent lacks significant time to evaporate completely and therefore results in nanofibers with flattened structures. These flattened structures when annealed, appear thicker. Therefore, with an increase in electrode distance the nanowires have more time for solvent evaporation and formation of a cylindrical form.\textsuperscript{124,125}

<table>
<thead>
<tr>
<th>Electrode dist. (cm)</th>
<th>Average diameter (nm)</th>
<th>Standard deviation (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>2308</td>
<td>679</td>
</tr>
<tr>
<td>18</td>
<td>1039</td>
<td>556</td>
</tr>
<tr>
<td>21</td>
<td>2075</td>
<td>554</td>
</tr>
<tr>
<td>24</td>
<td>1869</td>
<td>468</td>
</tr>
<tr>
<td>27</td>
<td>1323</td>
<td>663</td>
</tr>
</tbody>
</table>

Table 10: Overall trend of electrode distance vs. nanowire diameter
Figure 59: Overall trend of electrode distance vs. annealed ZrO$_2$ nanowire diameter shows slight decrease in the nanowires diameter with the increase in the electrode distance. However, the error bars associated with the data points obscure such a trend.

### 2.3.1.4 Set 4: Varying applied voltage

\[
\text{ZrO}_2 + \text{PVP} \xrightarrow{(a) \text{EtOH}} \xrightarrow{(b) \text{Electrospinning}} \text{ZrO}_2 - \text{PVP nanofibers}
\]

Voltage:
1. 16 kV
2. 20 kV
3. 25 kV
4. 28 kV
5. 30 kV

(c) Gradual annealing to form ZrO$_2$ NWs

In this Set 4, only the voltage was varied and all other parameters were kept constant. The scheme shown above summarizes the outline of the investigation conducted in this section. The voltage has a significant effect on the nanowires diameter because the electrostatic attraction between the syringe needle and the collecting drum can change the shape of the Taylor cone and in the process, can change the diameter of the nanofibers. As discussed earlier, higher the voltage, larger the electrostatic attraction and therefore, thinner the nanofibers.
(1). ZrO$_2$ nanowires fabricated with a 16 kV voltage

ZrO$_2$ NWs prepared using a 16 kV potential difference produced well-aligned nanofibers. The annealed nanowires were formed by nanoparticles fused together as seen before in other ZrO$_2$ nanowires prepared using the SPR (Figure 60).

![SEM images of (a,b) unannealed nanofibers and (c,d) annealed nanowires of samples fabricated with voltage of 16 kV. In the figure above, the scale bars in (a), (b), (c) and (d) are 50, 10, 20 and 10 µm, respectively.](image)

Figure 60: SEM images of (a,b) unannealed nanofibers and (c,d) annealed nanowires of samples fabricated with voltage of 16 kV. In the figure above, the scale bars in (a), (b), (c) and (d) are 50, 10, 20 and 10 µm, respectively.

![Annealed nanowire diameter histogram with an average diameter of 2128 ± 494 nm prepared with electrode potential of 16 kV.](image)

Figure 61: Annealed nanowire diameter histogram with an average diameter of 2128 ± 494 nm prepared with electrode potential of 16 kV.
(2). ZrO$_2$ nanowires fabricated with a 20 kV voltage

Use of a 20kV voltage produced nanofibers and nanowires of similar diameter to those produced in the 16 kV experiments.

Figure 62: SEM images of (a,b) unannealed nanofibers and (c,d) annealed nanowires of samples fabricated with voltage of 20 kV. In the figure above, the scale bars in (a), (b), (c) and (d) are 50, 20, 20 and 10 µm, respectively.

Figure 63: Annealed nanowire diameter histogram with an average diameter of 2152 ± 634 nm prepared with electrode potential of 20 kV.
(3). ZrO₂ nanowires fabricated with a 25 kV voltage

In Figure 64 (b), it appears that for the case of a 25 kV applied voltage the suspended particles were evenly embedded in the nanofibers with few large particles that are wider (~ 5µm) than the diameter of the nanofibers. The resultant annealed NWs produced a more distinct 1-D morphology compared to the previous samples (Figure 64 (d)).

![Figure 64: SEM images showing (a,b) unannealed nanofibers and (c,d) annealed nanowire of samples fabricated with voltage of 25 kV. In the figure above, the scale bars in (a), (b), (c) and (d) are 20, 20, 100 and 10 µm, respectively.](image-url)
Figure 65: Annealed nanowire diameter histogram with an average diameter of 1989 (± 547) nm prepared with electrode potential of 25 kV.

(4). ZrO\(_2\) nanowires fabricated a 28 kV voltage

Experiments using a 28 kV potential difference produced annealed nanowires that had an overall similar morphology as observed in the experiments conducted earlier in this series.

Figure 66: SEM images of (a,b) unannealed nanofibers and (c,d) annealed nanowire of samples fabricated with voltage of 28 kV. In the figure above, the scale bars in (a), (b), (c) and (d) are 20, 20, 10 and 50 µm, respectively.
However, the average NW diameter was significantly smaller in comparison to the samples fabricated using 16 kV, 20 kV and 25 kV voltages.

![Graph showing nanowire diameter distribution](image)

**Figure 67:** Annealed nanowire diameter histogram with an average diameter of $1028 \pm 346$ nm prepared with electrode potential of 28 kV.

**5. ZrO$_2$ nanowires fabricated with a 30 kV voltage**

Samples produced with 30 kV voltage also had similar morphology for both unannealed and annealed samples as the ones seen before in this set of experiments (16 kV, 20 kV, 25kV and 28kV). In this case, the average NW diameter was comparable to that of ZrO$_2$ NWs prepared with 28kV.
Figure 68: SEM images of (a,b) unannealed nanofibers and (c,d) annealed nanowires of samples fabricated with voltage of 30 kV. In the figure, the scale bars in (a), (b), (c) and (d) are 20, 20, 200 and 20 µm, respectively.

Figure 69: Annealed nanowire diameter histogram with an average diameter of 993 (± 399) nm prepared with electrode potential of 28 kV.
Theoretically, an increase in applied voltage causes a polymer drop to become unstable and become conical in shape until it reaches a critical point. Any further increase in voltage beyond the critical point generates something called “an inverse cone” where the primary Taylor cone is split into multiple jets.\textsuperscript{126} Each of these jets produce nanofibers that have small diameter compared to those produced from the primary jet.\textsuperscript{127} Reneker and coworkers\textsuperscript{128} have reported such a phenomenon where the average nanowire diameter decreased when the experiments were conducted at higher voltage using polyethylene oxide (PEO) dissolved in water/ethanol. In our system, this inverse cone apparently appeared slightly beyond the 25kV threshold.

<table>
<thead>
<tr>
<th>Applied voltage (kV)</th>
<th>Average nanofiber diameter (nm)</th>
<th>Standard deviation (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>2128</td>
<td>494</td>
</tr>
<tr>
<td>20</td>
<td>2152</td>
<td>634</td>
</tr>
<tr>
<td>25</td>
<td>1989</td>
<td>547</td>
</tr>
<tr>
<td>28</td>
<td>1028</td>
<td>346</td>
</tr>
<tr>
<td>30</td>
<td>993</td>
<td>399</td>
</tr>
</tbody>
</table>

Table 11: Overall trend of voltage vs. annealed nanowire diameter

![Graph](image)

Figure 70: Average annealed nanowire diameter (nm) vs. voltage (kV) of ZrO$_2$ nanowires at constant concentration and electrode distance.
2.3.2 Fabrication of 8% Y₂O₃ stabilized ZrO₂ (8YSZ) using the suspended particles route

The fabrication of 8YSZ nanowires was performed via the SPR by using prefabricated 8YSZ nanoparticles, which have been commercially purchased (Aldrich, with stating mean diameter of 700 nm). It was used to investigate the effect of electrospinning parameters on annealed 8YSZ nanowire diameter. The parameters that have been investigated are: (1) mass of 8YSZ; (2) mass of PVP; and (3) surfactant concentration. The electrospinning parameters, along with the amount of PVP and ethanol used are identical to those in Table 7. In this set of experiment only the mass of 8YSZ nanoparticles is varied.

2.3.2.1 Varying starting mass of 700 nm 8YSZ particles for fabrication of NWs

In this section the influence of an increase in the mass of 8YSZ nanoparticles on the nanowire diameters will be discussed. The scheme shown below provides an outline of the processes used in this system along with the six different 8YSZ nanoparticle masses that have been investigated to determine its effect on the annealed nanowire diameters.

\[
\begin{align*}
8\% \text{ Y}_2\text{O}_3 \text{ stabilized ZrO}_2 & \xrightarrow{\text{PVP}} (\text{8YSZ}) \ (700 \text{ nm}) \xrightarrow{(a) \ \text{EtOH}} \xrightarrow{(b) \ \text{Electrospinning}} 8\text{YSZ} - \text{PVP nanofibers} \\
\text{8YSZ nanoparticles mass:} & \\
1. \ 0.05 \ g & \ 2. \ 0.10 \ g & \ 3. \ 0.15 \ g & \ 4. \ 0.20 \ g & \ 5. \ 0.25 \ g & \ 6. \ 0.30 \ g \\
\text{(c) gradual annealing} & 
\end{align*}
\]

In each case, similar diameters and associated morphologies were obtained for the resultant YSZ nanowires upon annealing. Thus, the relevant SEM images and histograms are shown without additional commentary.
(1) 8YSZ NWs prepared using 0.05 g of 8YSZ nanoparticles

Figure 71: SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires and when 0.05 g 8YSZ nanoparticles were used. In the figure above, the scale bars in (a), (b), (c) and (d) are 5, 5, 10 and 10 µm, respectively.

Figure 72: Annealed nanowire diameter histogram with an average diameter of 779 ± 190 nm prepared with an 8YSZ mass of 0.05 g.
(2). 8YSZ NWs prepared using 0.10 g of 8YSZ nanoparticles

Figure 73: SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires and when 0.10 g 8YSZ nanoparticles used. In the figure above, the scale bars in (a), (b), (c) and (d) are 10, 5, 5 and 5 µm, respectively.

Figure 74: Annealed nanowire diameter histogram with an average diameter of 545 ± 114 nm prepared with a 8YSZ mass of 0.10 g.
(3). 8YSZ NWs prepared using 0.15 g of 8YSZ nanoparticles

![SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires and when 0.15 g 8YSZ nanoparticles used. In the figure above, the scale bars in (a), (b), (c) and (d) are 20, 5, 20 and 10 µm, respectively.](image)

Figure 75: SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires and when 0.15 g 8YSZ nanoparticles used. In the figure above, the scale bars in (a), (b), (c) and (d) are 20, 5, 20 and 10 µm, respectively.

![Average nanowire diameter: 770 ± 265 nm](image)

Figure 76: Annealed nanowire diameter histogram with an average diameter of 770 (± 265) nm prepared with a 8YSZ mass of 0.15 g.
(4). 8YSZ NWs prepared using 0.20 g of 8YSZ nanoparticles

Figure 77: SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires and when 0.20 g 8YSZ nanoparticles used. In the figure above, the scale bars in (a), (b), (c) and (d) are 20, 5, 50 and 5 µm, respectively.

Figure 78: Annealed nanowire diameter histogram with an average diameter of 669 (± 142) nm prepared with a 8YSZ mass of 0.20 g.
(5). 8YSZ NWs prepared using 0.25 g of 8YSZ nanoparticles

Figure 79: SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires and when 0.25 g 8YSZ nanoparticles used. In the figure above, the scale bars in (a), (b), (c) and (d) are 50, 5, 50 and 10 µm, respectively.

Figure 80: Annealed nanowire diameter histogram with an average diameter of $1015 \pm 237$ nm prepared with 8YSZ mass of 0.25 g.
(6). 8YSZ NWs prepared using 0.30 g of 8YSZ nanoparticles

Figure 81: SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires and when 0.30 g 8YSZ nanoparticles used. In the figure above, the scale bars in (a), (b), (c) and (d) are 20, 5, 10 and 10 µm, respectively.

Figure 82: Annealed nanowire diameter histogram with an average diameter of 825 (± 158) nm prepared with 8YSZ mass of 0.30 g.
(7). Overall trend of 8YSZ (700 nm) nanoparticles mass vs annealed NWs diameter

Figure 83 shows that there is no dependence of 8YSZ mass on the average nanowire diameter. As with the ZrO$_2$ structures, it is clear that the nanowire size depends on the starting nanoparticle size and morphology. A smaller pre-fabricated particles size needs to be used if smaller nanowire diameters are desired.

Table 12: Showing the 8YSZ mass used to fabricate NWs and the corresponding diameter of the annealed NWs.

<table>
<thead>
<tr>
<th>Mass of 8YSZ used (g)</th>
<th>Average nanowire diameter (nm)</th>
<th>Std. Dev. Of measured NW diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>779</td>
<td>190</td>
</tr>
<tr>
<td>0.10</td>
<td>545</td>
<td>114</td>
</tr>
<tr>
<td>0.15</td>
<td>770</td>
<td>265</td>
</tr>
<tr>
<td>0.20</td>
<td>669</td>
<td>142</td>
</tr>
<tr>
<td>0.25</td>
<td>1015</td>
<td>237</td>
</tr>
<tr>
<td>0.30</td>
<td>825</td>
<td>158</td>
</tr>
</tbody>
</table>

Figure 83: Nanowire diameter vs mass used plot for fabrication of 8YSZ (700 nm) NW using SPR. The diameters were measured from the SEM images.
(8). TEM and EDX analysis 8YSZ nanoparticles and fused nanowires

The TEM images shown in Figure 84 shows 8YSZ NWs formed by fused nanoparticles. Most of these segments separated as the annealed NWs were sonicated during the TEM sample preparation. The SEM images give a better idea of the overall morphology of the nanowire film obtained after the annealing phase.

Figure 84: TEM images of annealed NWs showing the irregular strands clumped together. These are nanoparticles interconnecting with each other to form 1-D structures and regions of aggregates (indicated with an arrow in Figure 84 (b)). The black bar at the bottom of Figure 84 (a) is a portion of the Cu grid on which the samples were placed for TEM analysis.

(9). EDX map of 8YSZ nanowires sample after annealing

The EDX analysis of 8YSZ nanowires showed the presence of O, Y and Zr species (Figure 85) and their distribution across the annealed sample. The map shows that Zr and O species remain homogenously distributed across the samples even after the two step annealing process (where maximum temperature was ~900°C).
Figure 85: (a) Shows the STEM image of the sample analyzed. EDX map analysis of O, Y and Zr atomic distribution over the sample, is shown in (b), (c) and (d) respectively.

<table>
<thead>
<tr>
<th>EDX quantitative analysis</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Average Atomic %</td>
</tr>
<tr>
<td>O</td>
<td>40.14</td>
</tr>
<tr>
<td>Y</td>
<td>6.09</td>
</tr>
<tr>
<td>Zr</td>
<td>53.78</td>
</tr>
</tbody>
</table>

Figure 86: EDX analysis of annealed 8YSZ NW fabricated using SPR with mass of 0.05g. The Cu Ka signal is from the grid used for the TEM analysis.
(10). XRD analysis of 8YSZ nanowires

The XRD of a typical YSZ annealed sample (in this case fabricated using 0.30 g 8YSZ) shows peaks that corresponds to the cubic phase 8YSZ when compared to the reported values.\textsuperscript{129,130}

The sharp peaks shown in Figure 87 correspond to the (111), (200), (220), (311) and (222) lattice planes of ZrO$_2$ at 2θ angles of 30.3°, 35.2°, 50.4°, 59.9°, 62.9°, respectively.

![XRD analysis of 8YSZ nanowires](image)

Figure 87: XRD analysis of YSZ nanoparticles post annealing showing the characteristic peaks of cubic phase 8YSZ.

2.3.2.2 Varying starting mass of PVP for 8YSZ NWs fabrication

\[
\begin{align*}
8\% \text{ Y}_2\text{O}_3 \text{ stabilized ZrO}_2 & \quad + \quad \text{PVP} \quad \xrightarrow{(a) \text{ EtOH}} \quad \xrightarrow{(b) \text{ Electrospinning}} \\
(8\text{YSZ}) \ (700 \text{ nm}) & \quad \text{8YSZ - PVP nanofibers} \\
\end{align*}
\]

PVP masses:
1. 0.3 g
2. 0.4 g
3. 0.5 g
4. 0.6 g
5. 0.7 g

(c) gradual annealing

In this set of reactions, ZrO$_2$ NWs were fabricated by electrospinning via SPR with varying PVP mass (keeping all other variables constant). The purpose of this study is to evaluate
the dependence of the PVP masses on the average diameter of the annealed NWs. The TEM, EDX and XRD analysis of these pre-synthesized nanoparticles are the same as the ones used to investigate the NWs diameter dependence on the mass of nanoparticles used previously. Therefore, TEM, EDX and XRD data for the following experiments are not reported.

As with the case of the mass dependent synthesis of 8YSZ NW formation, similar NW diameters and morphologies are obtained in these experiments with varying PVP concentrations. Therefore, SEM and histogram data are shown collectively without detailed comments.

(1). 8YSZ NW fabrication using 0.3 g of PVP

![SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires and when 0.3 g PVP is used. In the figure above, the scale bars in (a), (b), (c) and (d) are 50, 10, 10 and 10 µm, respectively.](image)

Figure 88: SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires and when 0.3 g PVP is used. In the figure above, the scale bars in (a), (b), (c) and (d) are 50, 10, 10 and 10 µm, respectively.
Figure 89: Annealed nanowire diameter histogram with an average diameter of $1009 \pm 250$ nm prepared with 8YSZ mass of 0.30 g.

(2). 8YSZ NW fabrication using 0.4 g of PVP

Figure 90: SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires and when 0.4 g PVP is used. In the figure above, the scale bars in (a), (b), (c) and (d) are 10, 5, 50 and 10 µm, respectively.
Figure 91: Annealed nanowire diameter histogram with an average diameter of 825 (± 158) nm prepared with 8YSZ mass of 0.40 g.

(3), 8YSZ NW fabrication using 0.5 g of PVP

Figure 92: SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires and when 0.5 g PVP is used. In the figure above, the scale bars in (a), (b), (c) and (d) are 20, 10, 50 and 10 µm, respectively.
Figure 93: Annealed nanowire diameter histogram with an average diameter of 969 (± 223) nm prepared with 8YSZ mass of 0.50 g.

(4). 8YSZ NW fabrication using 0.6 g of PVP

Figure 94: SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires and when 0.6 g PVP is used. In the figure above, the scale bars in (a), (b), (c) and (d) are 20, 10, 10 and 10 µm, respectively.
Figure 95: Annealed nanowire diameter histogram with an average diameter of $816 \pm 188$ nm prepared with 8YSZ mass of 0.60 g.

\[(5)\] 8YSZ NW fabrication using 0.7 g of PVP

Figure 96: SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires and when 0.7 g PVP is used. In the figure above, the scale bars in (a), (b), (c) and (d) are 20, 10, 20 and 10 μm, respectively.
Figure 97: Annealed nanowire diameter histogram with an average diameter of 916 (± 143) nm prepared with 8YSZ mass of 0.70 g.

(6). Overall trends and conclusion of NWs fabrication using different PVP masses

The 8YSZ nanowires produced with 700 nm particles showed a relative insensitivity of nanowire diameter (summarized in Table 13) with changing the precursor PVP mass under the conditions used here (Figure 98). The observation reinforces the earlier conclusion that in order to achieve sensitive control of 8YSZ nanowires diameter, other nanoparticles sources and/or fabrication conditions must be used.

<table>
<thead>
<tr>
<th>Mass PVP used (g)</th>
<th>Average nanowires diameter (nm)</th>
<th>Std. Dev. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>1009</td>
<td>250</td>
</tr>
<tr>
<td>0.4</td>
<td>825</td>
<td>158</td>
</tr>
<tr>
<td>0.5</td>
<td>969</td>
<td>223</td>
</tr>
<tr>
<td>0.6</td>
<td>816</td>
<td>188</td>
</tr>
<tr>
<td>0.7</td>
<td>916</td>
<td>143</td>
</tr>
</tbody>
</table>
2.3.2.3 8YSZ (700 nm) NW fabrication with varying surfactant concentration

\[
8\% \text{Y}_2\text{O}_3 \text{stabilized ZrO}_2 + \text{PVP} \xrightarrow{(a) \text{EtOH}} \xrightarrow{(b) \text{Electrospinning}} \text{8YSZ - PVP nanofibers}
\]

Triton/Ethanol surfactant concentration (w/w %):
1. 0.10 %
2. 0.20 %
3. 0.30 %
4. 0.40 %
5. 0.50 %
(c) gradual annealing

The surfactant solution was prepared by using commercially obtained Triton-X100 (Aldrich) and 95% solvent grade ethanol. The YSZ precursor used for this set of experiment was also performed from the same batch of pre-fabricated 8YSZ nanoparticles (700 nm) that was used in the previous two sets. These experiments were conducted in order to evaluate the dependence of surfactant concentration on the annealed 8YSZ NWs diameters. The amounts used to prepare the different concentration of the surfactant solution are reported below in Table 14. The purpose of using surfactant was to investigate its possible influence on nanoparticles aggregation in the electrospun nanofibers and ultimately, in the nanowires product. The surfactant concentrations that
were used varied from 0.1% to 0.5%. Once again, SEM/histogram data for each experiment in this category are shown below without detailed comments.

<table>
<thead>
<tr>
<th>Table 14. Ethanol + Triton X-100 solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol (95%) mass (g)</td>
</tr>
<tr>
<td>------------------------</td>
</tr>
<tr>
<td>4.8020</td>
</tr>
<tr>
<td>4.8019</td>
</tr>
<tr>
<td>5.1142</td>
</tr>
<tr>
<td>4.9303</td>
</tr>
<tr>
<td>4.8930</td>
</tr>
</tbody>
</table>

(1) 8YSZ NWs produced using a 0.10% surfactant/ethanol solution

Figure 99: SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires when 0.10% Triton/ Ethanol solution is used. In the figure above, the scale bars in (a), (b), (c) and (d) are 20, 10, 10 and 5 µm, respectively.
Figure 100: Annealed nanowire diameter histogram with an average diameter of 618 (± 218) nm prepared using 0.1% surfactant solution (Triton-X in ethanol).

(2). **8YSZ NWs produced using a 0.20% surfactant/ethanol solution**

Figure 101: SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires and when 0.20% Triton/ Ethanol solution is used. In the figure above, the scale bars in (a), (b), (c) and (d) are 50, 10, 20 and 10 µm, respectively.
Figure 102: Annealed nanowire diameter histogram with an average diameter of 918 (± 256) nm prepared using 0.2% surfactant solution (Triton-X in ethanol).

(3). 8YSZ NWs produced using a 0.30% surfactant/ethanol solution

Figure 103: SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires and when 0.30% Triton/ Ethanol solution is used. In the figure above, the scale bars in (a), (b), (c) and (d) are 20, 10, 10 and 10 µm, respectively.
Figure 104: Annealed nanowire diameter histogram with an average diameter of 745 (± 207) nm prepared using 0.3% surfactant solution (Triton-X in ethanol).

(4). 8YSZ NWs produced using a 0.40% surfactant/ethanol solution

Figure 105: SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires and when 0.40% Triton/Ethanol solution is used. In the figure above, the scale bars in (a), (b), (c) and (d) are 10, 10, 10 and 10 µm, respectively.
Figure 106: Annealed nanowire diameter histogram with an average diameter of 689 (± 228) nm prepared using 0.4% surfactant solution (Triton-X in ethanol).

(5). 8YSZ NWs produced using a 0.50% surfactant/ethanol solution

Figure 107: SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires and when 0.50% Triton/ Ethanol solution is used. In the figure above, the scale bars in (a), (b), (c) and (d) are 10, 10, 20 and 10 µm, respectively.
Figure 108: Annealed nanowire diameter histogram with an average diameter of $788 \pm 217$ nm prepared using 0.5% surfactant solution (Triton-X in ethanol).

(6). Overall diameter trend of NWs prepared using different surfactant concentrations

From the data presented, it appears that the presence of a surfactant (Triton X-100) during the electrospinning event has no measurable effect on the average diameter of 8YSZ nanowires. The annealed nanowires diameter remains the same with the increase in the percent surfactant in the solution. Ideally, the surface tension of the solution should decrease with the increase in the amount of surfactant, but again such an effect is obscured by the relatively large particle size of 88YSZ used as starting material.

<table>
<thead>
<tr>
<th>Surfactant concentration (%)</th>
<th>Average nanowires diameter (nm)</th>
<th>Std. Dev. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>825</td>
<td>158</td>
</tr>
<tr>
<td>0.1</td>
<td>681</td>
<td>218</td>
</tr>
<tr>
<td>0.2</td>
<td>918</td>
<td>256</td>
</tr>
<tr>
<td>0.3</td>
<td>745</td>
<td>207</td>
</tr>
<tr>
<td>0.4</td>
<td>689</td>
<td>228</td>
</tr>
<tr>
<td>0.5</td>
<td>788</td>
<td>217</td>
</tr>
</tbody>
</table>
2.3.3 Bi$_2$O$_3$ NWs fabrication using SPR via electrospinning process

The fabrication of Bi$_2$O$_3$ NW fabrication electrospinning technique was done by using commercially purchased (Aldrich) prefabricated nanoparticles (of diameters ranging from 90 to 210 nm). This set of reactions was performed to investigate only two of the variables associated with electrospinning. The dependence of (i) mass of Bi$_2$O$_3$ nanoparticles mass on the NW diameter is investigated along with the dependence of (ii) PVP mass on resulting NWs diameter. All reactions were performed using the same batch of Bi$_2$O$_3$ nanoparticles so the TEM, EDX and XRD analysis of the nanowires will be presented once for the fabrication method where the mass of Bi$_2$O$_3$ is varied. The electrospinning parameters and the masses of other starting materials used for the synthesis of Bi$_2$O$_3$ NWs using the SPR is presented in Table 8, in the experimental section.
2.3.3.1 Varying starting mass of Bi$_2$O$_3$ particles for fabrication of NWs

\[ \text{Bi}_2\text{O}_3 \text{ + PVP} \xrightarrow{(a) \text{ EtOH}} \xrightarrow{(b) \text{ Electrospinning}} \text{Bi}_2\text{O}_3 \text{- PVP nanofibers} \]

Bi$_2$O$_3$ nanoparticles mass:
1. 0.30 g
2. 0.40 g
3. 0.50 g
4. 0.60 g

(c) gradual annealing

(1) Bi$_2$O$_3$ NW fabrication using 0.30 g of Bi$_2$O$_3$ nanoparticles

Bi$_2$O$_3$ nanowire film fabrication was carried out using 0.30 g Bi$_2$O$_3$ for the first sample of this set. After the two stage annealing process, it was observed that the nanofibers in the film transformed into a network of Bi$_2$O$_3$ nanowires (Figure 110 (d)). This nanowire film was measured to be ~25 µm in thickness and was very brittle. The average nanowire diameters were measured to be 814 nm (± 213 nm).

The nanoparticles that were embedded into the PVP nanofibers (Figure 110 (b)) during electrospinning gradually coalesced together as the PVP was pyrolyzed during the annealing processes. Once the template was removed, the nanoparticles were able to fuse with each other to form continues Bi$_2$O$_3$ NWs, as shown in Figure 110 (d). The nanowires intertwined to form networks and give rise to a two dimensional highly porous Bi$_2$O$_3$ thin film (Figure 110 (c)).
Figure 110: SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires when 0.30 g Bi$_2$O$_3$ is used. In the figure above, the scale bars in (a), (b), (c) and (d) are 100, 10, 50 and 20 µm, respectively.

Figure 111: Annealed nanowire diameter histogram with an average diameter of 814 ± 213 nm prepared using 0.3 g of Bi$_2$O$_3$ nanoparticle.
(2). Bi$_2$O$_3$ NWs fabrication using 0.40 g of Bi$_2$O$_3$ nanoparticles

Use of 0.40 g of Bi$_2$O$_3$ produced similar-sized NW diameters as that made from 0.3 g nanoparticles. Figure 112 (d) shows representative images of such structures consistent with a morphology best described as bundles of nanoparticles that are fused together to form braid like nanowires. This might have resulted from a coalescence of small (submicron) diameter adjacent NWs during the annealing process.

![Figure 112: SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires when 0.40 g Bi$_2$O$_3$ is used. In the figure, the scale bars in (a), (b), (c) and (d) are 50, 5, 20 and 5 µm, respectively.](image)
Figure 113: Annealed nanowire diameter histogram with an average diameter of $848 \pm 218$ nm prepared 0.4 g Bi$_2$O$_3$ nanoparticle.

(3). Bi$_2$O$_3$ NWs fabrication using 0.50 g of Bi$_2$O$_3$ nanoparticles

This sample produced nanowires with the similar morphology as mentioned for 0.4 g Bi$_2$O$_3$ sample but with a slightly thicker diameter (Figure 114 (d)). However, this increase is obscured by the large standard deviation associated with the measurement.

Figure 114: SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires when 0.50 g Bi$_2$O$_3$ is used. In the figure above, the scale bars in (a), (b), (c) and (d) are 20, 20, 10 and 5 µm, respectively.
Figure 115: Annealed nanowire diameter histogram with an average diameter of 888 (± 269) nm prepared 0.5 g Bi$_2$O$_3$ nanoparticle.

(4). Bi$_2$O$_3$ NWs fabrication using 0.60 g of Bi$_2$O$_3$ nanoparticles

NWs produced using 0.6 g Bi$_2$O$_3$ nanoparticles had reduced average diameter compared to samples prepared with 0.3 g, 0.4 g, and 0.5 g of Bi$_2$O$_3$ nanoparticles.

Figure 116: SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires when 0.60 g Bi$_2$O$_3$ is used. In the figure above, the scale bars in (a), (b), (c) and (d) are 100, 20, 5 and 10 µm, respectively.
Again, the standard deviation of the measure diameter prevents a definitive conclusion. The NW morphology remains unchanged, with a braided network of nanowires observed in Figure 116 (c).

![Graph showing nanowire diameter distribution](image)

Figure 117: Annealed nanowire diameter histogram with an average diameter of 666 ± 160 nm prepared 0.6 g Bi$_2$O$_3$ nanoparticle.

**(5). Overall trend of NWs fabrication using different masses of Bi$_2$O$_3$ nanoparticles**

Overall the nanowires diameter remained relatively unchanged with an increase in Bi$_2$O$_3$ nanoparticles mass as shown in Figure 118. The morphology of the annealed samples had nanowires-like characteristics, with average diameters reported in Table 16. This can be explained by looking at the annealing duration time. Even though the melting point of Bi$_2$O$_3$ is 817°C, presumably the relatively long annealing time, even at the greatly reduced temperature of 450°C promotes a coalescence of the individual Bi$_2$O$_3$ nanoparticles sufficiently to form large size wires.

<table>
<thead>
<tr>
<th>Bi$_2$O$_3$ nanoparticles mass (g)</th>
<th>Average nanowires diameter (nm)</th>
<th>Std. Dev. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>814</td>
<td>213</td>
</tr>
<tr>
<td>0.4</td>
<td>848</td>
<td>218</td>
</tr>
<tr>
<td>0.5</td>
<td>888</td>
<td>269</td>
</tr>
<tr>
<td>0.6</td>
<td>666</td>
<td>160</td>
</tr>
</tbody>
</table>
Figure 118: Plot showing Bi$_2$O$_3$ average NW diameter increases with an increase in Bi$_2$O$_3$ nanoparticle masses.

(6). TEM and EDX analysis of Bi$_2$O$_3$ NWs fabricated using the SPR

So far in this experimental set, only the SEM/histogram data of fabricated Bi$_2$O$_3$ NWs (produced by varying the Bi$_2$O$_3$ nanoparticles) have been presented. Figure 119 shown below represents TEM images of annealed Bi$_2$O$_3$ nanowires fabricated using the SPR via electrospinning method (Bi$_2$O$_3$ nanoparticles mass of 0.4 g). The TEM analysis of the NWs fabricated, using each of the Bi$_2$O$_3$ nanoparticles masses mentioned earlier, showed characteristic braid-like morphology interconnected (Figure 114 (c)) to form a network. Due to the average diameters and morphologies being consistent for the NWs obtained from the different Bi$_2$O$_3$ nanoparticles masses, only one TEM has been shown for this current set (Figure 119).

During the TEM analysis a higher resolution imaging of nanowires was not possible as the TEM electron beam (200 kV) caused localized heating of the nanowires which caused them to melt and disintegrate. Therefore, lattice imaging of these nanowires also could not be recorded.
Figure 119: TEM analysis showing Bi$_2$O$_3$ NWs after annealing. The nanowires shown in the SEM images are formed from these clusters of fused nanoparticles. The scale bars in both figures (a) and (b) are 2 µm.

Figure 120: EDX analysis showing average atomic % of Bi and O in the annealed Bi$_2$O$_3$ NWs. The insets show EDX maps of Bi (bottom) and O (top) and their distribution over a selected area on a Bi$_2$O$_3$ NW.
EDX analysis (Figure 120) shows Bi$_2$O$_3$ NWs after annealing shows lower atomic percent for oxygen species compared to bismuth. This is due to the oxygen atoms interact with the electron beam to release Auger electron instead of x-rays. This process was discussed in detail earlier in this chapter.

(7). XRD analysis of Bi$_2$O$_3$ nanoparticles

The XRD shows the presence of β phase Bi$_2$O$_3$ (Figure 121) and the corresponding angles and lattice reflection plains are presented in Table 17. A comparison of the observed values with the literature$^{[131]}$ finds that an assignment as the β phase is indeed reasonable.

![XRD Peaks of Bi$_2$O$_3$ Nanoparticles](image)

Figure 121: XRD peaks of Bi$_2$O$_3$ nanoparticles. The identity of the peaks is reported in Table 17.

<table>
<thead>
<tr>
<th>$2\theta$ (degree)</th>
<th>Crystal phase (lattice reflection)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.53</td>
<td>β(201)</td>
</tr>
<tr>
<td>30.36</td>
<td>β(002)</td>
</tr>
<tr>
<td>31.26</td>
<td>β(220)</td>
</tr>
<tr>
<td>44.79</td>
<td>β(222)</td>
</tr>
<tr>
<td>45.46</td>
<td>β(400)</td>
</tr>
<tr>
<td>52.85</td>
<td>β(203)</td>
</tr>
<tr>
<td>54.05</td>
<td>β(421)</td>
</tr>
<tr>
<td>56.32</td>
<td>β(402)</td>
</tr>
</tbody>
</table>
2.3.3.2 \( \text{Bi}_2\text{O}_3 \) NWs fabrication with varying PVP masses

\[
\begin{align*}
\text{Bi}_2\text{O}_3 & \quad + \quad \text{PVP} & \xrightarrow{(a) \text{ EtOH}} & \quad \text{Bi}_2\text{O}_3 - \text{PVP} \text{ nanofibers} \\
& \quad (b) \text{ Electrospinning} & & \\
\text{PVP mass:} & \\
1. & 0.30 \text{ g} & \\
2. & 0.40 \text{ g} & \\
3. & 0.50 \text{ g} & \\
4. & 0.60 \text{ g} & \\
(c) & \text{gradual annealing} & 
\end{align*}
\]

The scheme above shows the overview of this set of experiments where the mass of PVP was varied to investigate its effects on the annealed nanowires diameter. The \( \text{Bi}_2\text{O}_3 \) nanoparticles used were from the same batch that was used in the previous set where the \( \text{Bi}_2\text{O}_3 \) nanoparticles mass was varied.

\textbf{(1).Bi}_2\text{O}_3 \text{ NWs fabrication using 0.30 g of PVP}

In this set of experiments 0.30g PVP was used with 0.5 g of \( \text{Bi}_2\text{O}_3 \) to produce nanowires that are shown in Figure 122 (d). The nanofibers produced using 0.30 g PVP had smaller diameter than the clusters of nanoparticles embedded in the film as shown in Figure 122 (b). Overall the annealed nanoparticles clump together into a film composed of clusters of these aggregates. These aggregates when examined at a lower magnification (Figure 122 (c)) resemble the product of an electrospray event rather than an electrospinning one. After annealing, the nanofibers agglomerated together as shown in Figure 122 (c). Figure 123 shows the diameter distribution of \( \text{Bi}_2\text{O}_3 \) fused clusters as shown in (c). The histogram does not represent nanowire diameter as there was no distinct one dimensional structures seen during SEM analysis of the annealed product.
Figure 122: SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires and when 0.30g PVP is used. In the figure above, the scale bars in (a), (b), (c) and (d) are 20, 10, 5 and 20 µm, respectively.

Figure 123: Bi$_2$O$_3$ cluster formed after annealing with domains size of 1009 ± 250 nm.
For the remaining samples of this series, negligible variations in the NWs diameters as a function of PVP mass were observed, so the images and associated histograms are provided without additional comment.

(2). Bi₂O₃ NWs fabrication using 0.40 g of PVP

Figure 124: SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires and when 0.40g PVP is used. In the figure above, the scale bars in (a), (b), (c) and (d) are 50, 5, 20 and 10 µm, respectively.
Figure 125: Annealed nanowire diameter histogram with an average diameter of 825 ± 158 nm prepared 0.4 g PVP.

(3). Bi$_2$O$_3$ NWs fabrication using 0.50 g of PVP

Figure 126: SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires and when 0.50g PVP is used. In the figure above, the scale bars in (a), (b), (c) and (d) are 50, 5, 50 and 20 µm, respectively.
Figure 127: Annealed nanowire diameter histogram with an average diameter of 969 ± 223 nm prepared 0.5 g PVP.

(4). Bi$_2$O$_3$ NWs fabrication using 0.60 g of PVP

Figure 128: SEM analysis showing (a,b) unannealed nanowires, (c,d) annealed nanowires and when 0.60g PVP is used. In the figure above, the scale bars in (a), (b), (c) and (d) are 20, 10, 20 and 10 µm, respectively.
Figure 129: Annealed nanowire diameter histogram with an average diameter of 816 (± 188) nm prepared 0.6 g PVP.

(5). Diameter distribution overview of Bi$_2$O$_3$ NWs fabricated using varying PVP masses

Once again, a variation in the mass of PVP precursor had a negligible effect on the diameter of the annealed nanowires as shown in Figure 130. This may be because with the increase in the PVP mass, the viscosity increases which in turn increases the Bi$_2$O$_3$/PVP nanofibers diameter. At this low level of PVP, the viscosity of the solution was so low that it formed very thin fused nanofibers, which looked more like the product of an electrospraying process.

<table>
<thead>
<tr>
<th>Mass PVP used (g)</th>
<th>Average nanowires diameter (nm)</th>
<th>Std. Dev. Of measured NW diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>*0.3</td>
<td>*1009</td>
<td>*250</td>
</tr>
<tr>
<td>0.4</td>
<td>825</td>
<td>158</td>
</tr>
<tr>
<td>0.5</td>
<td>969</td>
<td>223</td>
</tr>
<tr>
<td>0.6</td>
<td>816</td>
<td>188</td>
</tr>
</tbody>
</table>

*Sample prepared with 0.3 g PVP did not produce NWs but instead produced fused clusters (Figure 122 (c)) with an average diameter of 1009 (± 250) nm.
2.4 Chapter II Conclusions

For ZrO$_2$, 8YSZ, and Bi$_2$O$_3$, a series of experimental conditions were developed to successfully prepare relatively large diameter NWs of these metal oxides via a combined suspended particle and electrospinning technique. For the case of Bi$_2$O$_3$, the relatively lower melting point results in a more fused network of nanowires when compared to ZrO$_2$ and 8YSZ.

In any event, it is clear that the SPR method heavily rely on the size, dispersity and quality of the prefabricated nanoparticles employed. Further investigations, involving different nanoparticles sizes, are necessary to provide a more broadly tunable range of nanowires widths for a given metal oxide.
Chapter III

Fabrication, characterization, and analysis of ZrO$_2$ and 8YSZ nanowire films produced using a sol-gel method in conjugation with electrospinning technique.
3.0 Introduction

Synthesis and characterization of nanoscale metal oxide electrolytes (MOEs) are the primary topics of this dissertation. This chapter focuses on the fabrication, characterization and properties of ZrO$_2$ and 8YSZ nanowire thin films that are produced using a sol-gel reaction in conjunction with an electrospinning process and post-fabrication annealing. The sol-gel process ideally provides control over the nanoparticle size and morphology by carefully controlling the reaction parameters (pH, rate of reaction, and types of precursor) associated with the reactions.

3.1 A brief overview of sol-gel reactions

A sol-gel reaction proceeds by the formation of a colloidal suspension called sols that occurs through the hydrolysis and the condensation of metal alkoxide precursors. These spherical colloids crosslink to form a network and result in gel formation (Figure 131). The post gelation treatments include the aging (to maximize crosslinking), drying (removal of the solvent) and calcination (metal oxide crystal lattice formation) processes.$^{132,133,134,140}$

The advantages of the sol-gel route for the fabrication of ZrO$_2$ and YSZ nanowires are that it ideally provides more local control over the formation of -Zr-O-Zr- and -Y-O-Zr- bonds during ZrO$_2$ and 8YSZ nanowire fabrication, respectively. In the case of 8YSZ nanowires, it also allows for a uniform distribution of Y$^{3+}$ and Zr$^{4+}$ species throughout a given nanowire film.
3.1.1 Use of Zr alkoxides as the preferred precursor for ZrO$_2$ and YSZ nanowires

Metal alkoxides by nature are very air-sensitive and expensive compared to the traditionally used metal citrates and nitrates as the sol-gel precursor. The Pechini method is one such sol-gel process that uses metal citrate precursors in the presence of chelating ligands and ethylene glycol in an aqueous medium. This process involves a transesterification reaction to form a polyesterified network with the metal ions trapped in it. The advantage of using the metal alkoxides as the precursor is that it allows synthesis of nano-sized sols whereas citrates and nitrates have shown to produce in particles in the micron range. Therefore, Zr(O$^\text{iPr}$)$_4$•(i-PrOH) and Zr(O$^\text{tBu}$)$_4$ are used here as precursors for ZrO$_2$ and YSZ nanowire fabrication using the sol-gel route.

3.1.2 Sol-gel reaction in non-aqueous solvent

The use of metal alkoxide precursors limit the sol-gel reactions to non-aqueous environments. In aqueous based sol-gel processes, the reaction proceeds by hydrolysis and

Figure 131: (a) A sol composed of metal-oxane oligomer where the dashed line represents repetition of -Zr-O-Zr- structures. (b) Network formed by crosslinking of the sol shown in (a). Figure is adapted from reference [135].
condensation of the metal alkoxide.\textsuperscript{142,143} This causes the precursors to immediately react in an uncontrolled manner and precipitate in form of aggregates.\textsuperscript{144} The reaction mechanism associated with an aqueous based sol-gel reaction has been demonstrated earlier in this dissertation (Section 1.3.3.1, Figure 9).

The sol-gel reactions pertaining to ZrO\textsubscript{2} and YSZ nanowire fabrication were conducted in absolute ethanol. In non-aqueous sol-gel reactions of alkoxides, the metal-oxane bond formation is achieved without using a hydrolysis step. Instead, the process has been reported to undergo via alcoholysis (only for bulky alkoxides) and condensation steps. During the alcoholysis, bulky alkoxide motifs are replaced by the less bulky solvent (ethanol) molecules which exist in a state of equilibrium when performed at room temperature\textsuperscript{145,146,158} (Figure 132 (a)). In non-hydrolytic sol-gel reactions the metal-oxane bonds are formed using the oxygen from the solvents or from the alkoxides themselves.\textsuperscript{147,148} The condensation reaction step between two alkoxide precursor results in an ether elimination, as shown by Pinna and coworkers (Figure 132 (b)).\textsuperscript{149,150,151}

![Non-hydrolytic sol-gel reaction mechanism](image.png)

Figure 132: Non-hydrolytic sol-gel reaction mechanism showing (a) acid catalyzed alcoholysis reaction between zirconium alkoxide and alcohol solvent and (b) metal-oxane bond formation via condensation reaction of zirconium alkoxides with ether as side product. (Mechanism adapted from references 145, 149, 150, 151, and 158).
Acid catalyzed reactions have been shown to favor branching and crosslinking between the oligomers during the sol-gel reaction. In contrast, base catalyzed reactions favor an increase in size of individual sols (Figure 133). The sol-gel reactions that will be presented in this chapter were performed under acidic to obtain the desired nanowire size (diameter < 300 nm) and morphology (maximum branching and crosslinking of nanowires).

![Diagram of pH effect on morphology](image)

**Figure 133**: Effect of pH on the morphology of particles in sol-gel reactions showing cross-linkage formation at lower pH (Image taken from reference 152).

### 3.2 Experimental Section

ZrO$_2$ and YSZ nanowire fabrication using the sol-gel route were carried out in three steps: (1) mixing the reactants; (2) fabricating nanofibers using the electrospinning process; and (3) annealing process (two stage) to remove the polymer template and promote crystallization of the metal oxide domains within the nanowires.
3.2.1 ZrO$_2$ nanowires fabrication using sol-gel method

Zr(O$i$Pr)$_4$•(i-PrOH) complex and Zr(O$^t$Bu)$_4$ are the two zirconium alkoxide precursors that were used to fabricate ZrO$_2$ nanowires. The experimental procedures for the use of these two precursors are presented next.

3.2.1.1 Zr(O$i$Pr)$_4$•(i-PrOH) as precursor for ZrO$_2$ NWs fabrication

(1) Zr(O$i$Pr)$_4$•(i-PrOH) solubility test

It was necessary to choose a proper solvent for Zr(O$i$Pr)$_4$•(i-PrOH) complex (99.9%, Aldrich) as a precursor for ZrO$_2$ nanowires fabrication using the sol-gel route. The following criteria were considered for the reaction solvent system: (1) a solvent that can dissolve Zr(O$i$Pr)$_4$•(i-PrOH) without causing it to hydrolyze; (2) a solvent that can dissolve PVP; and (3) a solvent that is suitable for the electrospinning process.

Isopropanol (i-PrOH, 99.8%, Pharmco), ethanol (EtOH, 99.5%, Pharmco), dimethylformamide (DMF, 99.8%, Aldrich), tetrahydrofuran (THF, 99.5%, Aldrich) and dichloromethane (CH$_2$Cl$_2$, 99.5%, Pharmco) were considered as potential solvents. The solvents were chosen based on different solvent classifications in order to diversify the selection. Some of the individual classification and some of their physical properties are shown in Table 19.

<p>| Table 19: List of solvents chosen to investigate Zr(O$i$Pr)$_4$•(i-PrOH) solubility and their physical properties. (Taken from Ref 153-155) |</p>
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Classification</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iso-propanol (i-PrOH)</td>
<td>Polar protic</td>
<td>82</td>
</tr>
<tr>
<td>Ethanol (EtOH)</td>
<td></td>
<td>79</td>
</tr>
<tr>
<td>Dimethylformamide (DMF)</td>
<td>Polar aprotic</td>
<td>153</td>
</tr>
<tr>
<td>Tetrahydrofuran (THF)</td>
<td></td>
<td>66</td>
</tr>
<tr>
<td>Dichloromethane (CH$_2$Cl$_2$)</td>
<td>Non-polar</td>
<td>40</td>
</tr>
</tbody>
</table>
The amount of each of these solvents used during the solubility test (along with PVP and Zr(O^iPr)_4•(i-PrOH) masses) is shown in Table 20.

<table>
<thead>
<tr>
<th>Solvent (mass used)</th>
<th>Zr(O^iPr)_4•(i-PrOH) complex mass (g)</th>
<th>Stir time (hours)</th>
<th>Mass of PVP added (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>i-PrOH (1.6354 g)</td>
<td>0.0434 g</td>
<td>5</td>
<td>Not added</td>
</tr>
<tr>
<td>EtOH (1.6388 g)</td>
<td>0.0491 g</td>
<td>5</td>
<td>Not added</td>
</tr>
<tr>
<td>DMF (1.6437 g)</td>
<td>0.0477 g</td>
<td>5</td>
<td>Not added</td>
</tr>
<tr>
<td>CH_2Cl_2 (1.4508 g)</td>
<td>0.0238 g</td>
<td>5</td>
<td>0.2115 g</td>
</tr>
<tr>
<td>THF (1.4697 g)</td>
<td>0.0382 g</td>
<td>5</td>
<td>0.203 0g</td>
</tr>
</tbody>
</table>

The solubility test was divided into several steps: (1) measured quantities of Zr(O^iPr)_4•(i-PrOH) were added to the solvents (masses shown in Table 20) in separate vials; (2) suspensions were stirred for 5 hours at room temperature; (3) measured amounts of PVP were added to solvents that were able to dissolve Zr(O^iPr)_4•(i-PrOH) complex; and (4) selected Zr(O^iPr)_4•(i-PrOH)-PVP solutions were electrospun to produce nanofibers.

Zr(O^iPr)_4•(i-PrOH) suspensions were prepared by mixing the alkoxide in separate vials containing premeasured i-PrOH, EtOH, DMF, CH_2Cl_2, and THF solvents (Table 20). The samples were then stirred at room temperature for 5 hours to allow dissolution of the alkoxide precursor. The results were the formation of clear solutions of Zr(O^iPr)_4•(i-PrOH) that used CH_2Cl_2 and THF as the initial solvents (as shown in Figure 134 (a)).
Figure 134: (a) Dissolution experiment of Zr(O\(^{i}\)Pr)\(_4\)•(i-PrOH) in i-PrOH, EtOH, DMF, CH\(_2\)Cl\(_2\) and THF showing the result after 5 hours of mixing. The zirconium alkoxide only dissolved in solvents CH\(_2\)Cl\(_2\) and THF. (b) A vial place upside down to show the gel formation when the PVP was added to Zr(O\(^{i}\)Pr)\(_4\)•(i-PrOH) solution prepared in CH\(_2\)Cl\(_2\).

PVP (0.2115 g and 0.2030 g, respectively) was only added to the CH\(_2\)Cl\(_2\) and THF containing solutions of the Zr alkoxide as i-PrOH, EtOH and DMF were unable to dissolve Zr(O\(^{i}\)Pr)\(_4\)•(i-PrOH). When PVP was added to the sample containing CH\(_2\)Cl\(_2\), it formed a clear colorless viscous solution which turned into a gel in ~ 2-3 minutes (Figure 134 (b)). PVP did not dissolve in Zr(O\(^{i}\)Pr)\(_4\)•(i-PrOH)/THF solution.

Due to the rapid gel formation, these samples dissolved in CH\(_2\)Cl\(_2\) could not be used to fabricate nanofibers using the electrospinning process. However, it was possible to re-dissolve the gel by (1) heating it at 100°C for 5 min to remove CH\(_2\)Cl\(_2\) and (2) mixing it with ~ 2.0 g of absolute ethanol at room temperature for 12 hours. Once re-dissolved in EtOH, it was possible to fabricate ZrO\(_2\)/PVP nanofibers using the electrospinning route.

(2). Investigation of Zr(O\(^{i}\)Pr)\(_4\)•(i-PrOH) mass dependence on ZrO\(_2\) NW diameter fabricated via sol-gel method

A new set of experiments were performed where ZrO\(_2\) nanowires were fabricated by sol-gel method in conjunction with the electrospinning technique. In this batch of experiments only
Zr(O\textsuperscript{i}Pr)\textsubscript{4}(i-PrOH) mass was varied while keeping all other masses and electrospinning parameters constant. The purpose of this set of experiments was to investigate the dependence of Zr(O\textsuperscript{i}Pr)\textsubscript{4}(i-PrOH) masses on the average NW diameters and is depicted in Figure 135. The sol-gel reactions were performed similarly to the method mentioned earlier in Section 1.3.3.1. Table 21 shows the masses of the reactants and solvents used in this set of experiments.

![Diagram of sol-gel reaction procedure for ZrO\textsubscript{2}/PVP nanofiber fabrication using Zr(O\textsuperscript{i}Pr)\textsubscript{4}(i-PrOH) as starting material.](image)

**Figure 135:** Sol-gel reaction procedure for ZrO\textsubscript{2}/PVP nanofiber fabrication using Zr(O\textsuperscript{i}Pr)\textsubscript{4}(i-PrOH) as starting material.
ZrO₂/PVP nanofibers were produced by the electrospinning method which had a setup similar to the one described in Section 2.1.1.2 (Figures 18 and 19). The two stage annealing process was performed to remove the polymer template and to obtain ZrO₂ NWs with crystalline domains. The annealing procedure was similar to the one discussed in Section 2.1.1.3, (Figure 20), in the previous chapter. The parameters that were used in the electrospinning and annealing processes are presented in Table 22. The results of this investigation (dependence of Zr(O^{i}Pr)₄•(i-PrOH) mass on average NW diameter of ZrO₂ prepared via sol-gel route) will be discussed later in this chapter (Section 3.4.1.1).

### Table 21: Typical experimental parameters used for the ZrO₂ fabrication nanofibers by sol-gel route from Zr(O^{i}Pr)₄•(i-PrOH) precursor.

<table>
<thead>
<tr>
<th>Description</th>
<th>Zr(O^{i}Pr)₄•(i-PrOH) mass (g)</th>
<th>PVP mass (g)</th>
<th>CH₂Cl₂ mass (g)</th>
<th>EtOH mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Varying Zr(O^{i}Pr)₄•(i-PrOH) precursor mass</td>
<td>0.100 g</td>
<td>~0.50 g</td>
<td>~6.0 g (~4.5 ml)</td>
<td>~2.0 g (~2.5 ml)</td>
</tr>
<tr>
<td></td>
<td>0.075 g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.050 g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.025 g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.010 g</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 22: Electrospinning and annealing parameters used for ZrO₂ NWs fabrication from Zr(O^{i}Pr)₄•(i-PrOH) precursor

<table>
<thead>
<tr>
<th>Electrode distance (cm)</th>
<th>Voltage (kV)</th>
<th>Annealing temperatures (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21 cm</td>
<td>16 kV</td>
<td>Step 1: 220°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Step 2: 900°C</td>
</tr>
</tbody>
</table>

The use of Zr(O^{i}Pr)₄•(i-PrOH) as the starting material for the ZrO₂ nanowires (using sol-gel method along with electrospinning technique) had proven to be challenging. Due to that reason, it was necessary to find a replacement precursor for ZrO₂ NWs fabrication process (using sol-gel...
coupled with the electrospinning process. Zr(O'Bu)₄ was chosen as the replacement Zr precursor. However, the reasons behind Zr(O'Pr)₄’s lack of solubility must be evaluated.

Out of the five solvents (i-PrOH, EtOH, DMF, THF and CH₂Cl₂) only THF and CH₂Cl₂ was successful at dissolving the alkoxide. This observation can be explained by data reported by Spijksma et al.¹⁵⁶, Bradley et al.¹⁵⁷,¹⁵⁸, and other investigators¹⁵⁹,¹⁶⁰,¹⁶¹, where they have shown Zr(O'iPr)₄•(i-PrOH) existing as a solvated dimer.

In general, metal alkoxides are capable of forming several different structures (depending on the central atom, alkoxide carbon chain length and other physical parameters): (a) [M₂(µ-OR)₂(OR)₄], (b) [M₂(µ-OR)₂(OR)₈], (c) [M₃(µ₃-OR)₂(µ-OR)₃(OR)₄(HOR)₂], (d) [M₃(µ-OR)₆(OR)₆], and (e) [M₄(µ-OR)₆(OR)₆]. Figure 136 shows the structure motifs of the alkoxides mentioned above.¹⁵⁸,¹⁶²,¹⁶³,¹⁶⁴

![Figure 136: Various metal alkoxide motifs.](image)

In case of Zr(O'iPr)₄•(i-PrOH), two O'iPr groups are believed to be bonded via a pair of µ-OR bridges to form a bi-octahedral dimer structure, [Zr₂(µ-O'iPr)₂(O'iPr)₆(i-PrOH)₂] (Figure 137 (a)). In addition to the µ-OR bridging motif, Bradley also reported the formation of a pair of H-bonds between the axial alkoxo (O'iPr) and iPrOH, as shown in Figure 137 (b).¹⁶⁵,¹⁶⁶
Figure 137: (a) Zr(O^{i}Pr)_{4}(i-PrOH) exists as a dimer (in solid state) where the monomers are bonded via a pair of $\mu$-OR bridges. (b) H-bonding between the axial alkoxo (O^{i}Pr) and i-PrOH. Structure (a) and (b) have been adopted from references [157] and [165], respectively, where R = O^{i}Pr.

Bradley and coworkers$^{157,158,167,168}$ have also shown a decrease in vapor pressure with the increase in oligomerization of Group 4 (Ti, Zr, Hf) alkoxide homologous series.$^{169,170}$ Table 23 (obtained from Reference [158]) shows the change in enthalpy ($\Delta H_{v}$) and entropy ($\Delta S_{15.0}$) of vaporization ($\Delta S_{15.0}$ indicates change in entropy at 15°C) of Zr(O^{i}Pr)_{4} and Zr(O^{t}Bu)_{4}. Bradley argued that a higher tendency of Zr(O^{i}Pr)_{4} to oligomerize is responsible for its larger $\Delta H_{v}$ (31.5 kcal/mol) compared to that of Zr(O^{t}Bu)_{4} ($\Delta H_{v} = 15.2$ kcal/mol), where the additional energy is required for depolymerization of the complex in Zr(O^{i}Pr)_{4}•(i-PrOH). The larger $\Delta S_{15.0}$ value of Zr(O^{i}Pr)_{4} compared to Zr(O^{t}Bu)_{4} has been associated with a polymeric to monomeric transition as shown in Rxn. (3). The molecular complexity ($C_{m}$) (also known as the degree of polymerization) is the ratio between oligomer and monomer molecular weight (M.W.) is shown in Eqn. (10).

$$C_{m} = \frac{M.W.\text{oligomer}}{M.W.\text{monomer}}$$  (Eqn. 10)
Bradley finally established the following trend for Zr alkoxides based on their ability to form oligomers (vapor pressure is proportional to the alkoxide branching): Zr(OEt)$_4$ $\gg$ Zr(O$i$Pr)$_4$ $>$ Zr(O$t$Bu)$_4$ $\sim$ Zr(O$^t$Am)$_4$.

3.2.1.2 Zr(O$^t$Bu)$_4$ as precursor for ZrO$_2$ NWs fabrication using the sol-gel route

(1). Zr(O$^t$Bu)$_4$ solubility tests

Zr(O$^t$Bu)$_4$ (99%, Alfa Aesar) was selected as a possible precursor for ZrO$_2$ NWs fabrication (using the sol-gel route) because of the intrinsic liquid state of the precursor at room temperature. The liquid state of Zr(O$^t$Bu)$_4$ is unique compared to the other Zr alkoxides in its homologous series which provided an advantage over the solid alkoxides by its ability to readily mix with solvents.

Acetonitrile (CH$_3$CN, 99.8%, Aldrich), diethyl ether ((CH$_3$CH$_2$)$_2$O, 99.0%, Aldrich) chloroform (CHCl$_3$, 99.5%, Pharmco), dichloromethane (CH$_2$Cl$_2$, 99.5%, Pharmco) and ethanol (EtOH, 99.5%, Pharmco) were evaluated to determine the best compatibility for Zr(O$^t$Bu)$_4$/PVP solution formation which could also be suitable for the electrospinning process. Table 24 shows

<table>
<thead>
<tr>
<th>Alkoxide</th>
<th>Boiling point (°C/mm)</th>
<th>Enthalpy of vaporization (ΔH$_v$) (kcal mol$^{-1}$)</th>
<th>Entropy of vaporization (ΔS$_{15.0}$) (cal deg$^{-1}$ mol$^{-1}$)</th>
<th>Degree of polymerization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr(OEt)$_4$</td>
<td>234.8/5.0</td>
<td>30.2</td>
<td>59.4</td>
<td>3.6</td>
</tr>
<tr>
<td>Zr(O$i$Pr)$_4$</td>
<td>203.8/5.0</td>
<td>31.5</td>
<td>66.1</td>
<td>3.0</td>
</tr>
<tr>
<td>Zr(O$t$Bu)$_4$</td>
<td>89.1/5.0</td>
<td>15.2</td>
<td>42.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Zr(O$^t$Am)$_4$</td>
<td>138.4/5.0</td>
<td>16.3</td>
<td>39.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

*O$^t$Am = tert-amyloxide = tert-pentaoxide

Table 23: Thermodynamic data and molecular complexities of Zr alkoxides. ($subscript V =$ vaporization, 15.0 = temperature of measurement (in 15.0°C)
the observations made during the investigation of mixing Zr(OtBu)₄ (~0.04 g) and PVP (~0.10 g) with the above solvents.

Zr(OtBu)₄ dissolved readily to form a clear solution when added to ether and EtOH, while forming slight turbidity in case of the other three solvents (Figure 138 (a)). Upon addition of PVP, only EtOH containing solution remained clear, as shown in Figure (b). Based on the solubility test, ZrO₂ NWs were fabricated using EtOH via sol-gel route (in combination with the electrospinning technique).

<table>
<thead>
<tr>
<th>Solvent Name</th>
<th>Solvent volume used (ml)</th>
<th>Observation after adding Zr(OtBu)₄ to the solvents</th>
<th>Observation after adding PVP to Zr(OtBu)₄ solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CN</td>
<td>~ 1 ml</td>
<td>Insoluble</td>
<td>Insoluble</td>
</tr>
<tr>
<td>(CH₃CH₂)₂O</td>
<td></td>
<td>Clear solution</td>
<td>Insoluble</td>
</tr>
<tr>
<td>CHCl₃</td>
<td></td>
<td>Turbid</td>
<td>Insoluble</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td></td>
<td>Turbid</td>
<td>Insoluble</td>
</tr>
<tr>
<td>EtOH</td>
<td></td>
<td>Clear solution</td>
<td>Soluble</td>
</tr>
</tbody>
</table>

Figure 138: Observations made (a) after adding Zr(OtBu)₄ to the solvents mentioned and (b) after adding PVP to the Zr(OtBu)₄ solutions from (a).
(2). Sol-gel reaction preparation for ZrO$_2$ NWs fabrication using Zr(O$^t$Bu)$_4$ as precursor

Three sets of experiments were performed to investigate the influence of parameters (Zr(O$^t$Bu)$_4$ mass, PVP mass and reaction time) on the ZrO$_2$ NWs diameter. The parameters used in each set are shown in Table 25.

<table>
<thead>
<tr>
<th>Description</th>
<th>Zirconium (IV) tert-butoxide mass (g)</th>
<th>PVP mass (g)</th>
<th>Reaction time (hour)</th>
<th>solvent system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Studying effects of NWs diameter and morphology by varying Zr(O$^t$Bu)$_4$ mass</td>
<td>0.050</td>
<td>~ 0.350</td>
<td>2</td>
<td>3.17 ml EtOH + 3 drops AcOH</td>
</tr>
<tr>
<td></td>
<td>0.100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.150</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.200 g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Studying effects of NWs diameter and morphology by varying PVP mass</td>
<td>~ 0.150</td>
<td>0.250</td>
<td>2</td>
<td>3.17 ml EtOH + 3 drops AcOH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.350</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.450</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Studying effects of NWs diameter and morphology by varying sol-gel reaction aging time</td>
<td>~ 0.150</td>
<td>~ 0.350</td>
<td>5 (min)</td>
<td>3.17 ml EtOH + 3 drops AcOH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The reaction procedures involved mixing the different reactants in a very specific sequence which had been developed by a trial and error process. Initially, when the reactants were mixed in the amounts mentioned in Table 25, the resulting Zr(O$^t$Bu)$_4$/PVP/EtOH solution gradually changed from a clear solution to a cloudy suspension. During this period, the viscosity of the solution also increased. It was assumed that the cloudiness was due to the formation of ZrO$_2$ particles. Together, these two factors resulted in an inconsistent solubility behavior in the sample to be electrospun. Therefore, it was necessary to determine a sequence of steps to prevent the formation
of any white precipitate and slow down the increase in viscosity (by presumably slowing down reaction rate). The sequence of mixing the reagents shown below in Figure 139 eliminated the precipitation and increased viscosity issues.

![Diagram of reagent mixing sequence]

Figure 139: Sequence of mixing reagents during the ZrO$_2$ NWs fabrication using the sol-gel route.

In Step (a) (Figure 139), the reaction procedure involved dividing the measured EtOH (~3.17 ml) in two vials; one containing ~ 2.5 ml of the total measured amount and the second containing ~ 0.67 ml. Liquid Zr(O'Bu)$_4$ precursor was measured by directly adding it to ~ 0.67 ml EtOH to prevent any hydrolysis due to the moisture in air. Care was taken to make sure that the
drops of liquid Zr(OtBu)$_4$ did not touch the glass vial and instead were added directly to EtOH. This was necessary as earlier attempts that resulted in Zr(OtBu)$_4$ being placed on the inner wall of glass vial resulted in formation of white insoluble particles (assumed to be ZrO$_2$ due to the hydrolysis by the adsorbed water on the vial walls). This process corresponds to step (a) demonstrated in Figure 139.

In Step (b), acetic acid is added to the Zr(OtBu)$_4$/EtOH solution that was prepared in the previous step. Five drops of glacial acetic acid (AcOH, 99.85%, ER) was added to the solution and mixed vigorously for 10 min. Acetic acid was added as a blocking agent in order to reduce the rate of sol-gel reaction. A similar use of AcOH to stabilize alkoxides has been reported$^{171}$, where AcOH was added to zirconium n-propoxide to form zirconium propoxide diacetate which gradually increased in viscosity over a period of few days.$^{172,173}$ In another report, in situ H$_2$O generation from esterification reactions between alcohol and acetic acid is proposed to facilitate M-O-M linkage formation via a condensation reaction.$^{171,174,175}$

In Step (c) ~ 2.5 ml EtOH was added directly to ~ 0.35 g PVP (M.W = 1.5 M g/mol, Aldrich) and stirred vigorously until a viscous to form a homogenous viscous solution. In Step (d) PVP/EtOH solution was added to Zr(OtBu)$_4$/EtOH/AcOH solution dropwise. Each drop was allowed to mix thoroughly before additional drops were added to the solution. When PVP/EtOH solution was added too quickly it caused the PVP/EtOH phase separate and therefore could not be electrospun.

The final viscous solution containing all the reactants were allowed to mix for 5-6 min before it was transferred to a 5 ml syringe (Popper & Sons) with a 2 cm long 21-gauge needle for electrospinning.
(3). Electrospinning and annealing of ZrO₂/PVP nanofibers produced via sol-gel route using Zr(O\textsuperscript{i}Bu)\textsubscript{4} as the precursor

The electrospinning process was carried out as described in the previous chapter (Section 2.1.1.2). Table 26 shows the typical electrospinning and annealing parameters used to fabricate ZrO₂ NWs using the Zr(O\textsuperscript{i}Bu)\textsubscript{4} derived sol-gel route. Other electrospinning parameters such as the electrode distance, voltage and flow rate were not varied for the sol-gel route system as they had previously (in Chapter 2). The reaction time was considered to be a factor in the electrospinning process as sol-gel reactions tend to increase the solution viscosity (during the gelation phase)\textsuperscript{132,176} which can have an effect on the nanofiber diameters during the electrospinning process.

<table>
<thead>
<tr>
<th>Description</th>
<th>Electrode distance (cm)</th>
<th>Voltage (kV)</th>
<th>Annealing temperatures (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Varying Zr(O\textsuperscript{i}Bu)\textsubscript{4} mass</td>
<td>21 cm</td>
<td>20 kV</td>
<td>Step 1: 220°C</td>
</tr>
<tr>
<td>Varying PVP mass</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Varying reaction time</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The nanofibers were annealed in accordance to the two stage annealing procedure discussed earlier in this chapter. The purpose of the annealing phase was to obtain ZrO₂ NWs in the morphology of the PVP template and allow crystallization of the amorphous zirconia domains in the nanofibers. The Figure 140 below shows the size comparison of the ZrO₂/PVP nanofiber films (fabricated using varying Zr(O\textsuperscript{i}Bu)\textsubscript{4} mass) before and after the annealing process.
3.2.2 YSZ NWs fabrication using sol-gel and electrospinning method

YSZ NWs were fabricated via a sol-gel method in combination with the electrospinning process using commercially available Zr(O\textsubscript{t}Bu)\textsubscript{4} and Yttrium (III) 2-ethylhexanoate (Y(EHx)\textsubscript{3}), 99.8%, Alfa Aesar) as precursors. Yttrium alkoxides were not used for the YSZ NWs fabrication as they primarily exist as oligomers due to likely alkoxo bridging, thus making them insoluble.\textsuperscript{158,177,178}

**Experimental procedures for YSZ NWs fabrication by sol-gel method**

YSZ NWs fabrication procedure (via a sol-gel route) was very similar to the route used to fabricate ZrO\textsubscript{2} NWs (also using a sol-gel route). In case of YSZ, pre-measured Zr(O\textsubscript{t}Bu)\textsubscript{4}, Y(EHx)\textsubscript{3}, and PVP (as shown in Table 27) were mixed with anhydrous EtOH as portrayed by Steps (a), (b) and (e), respectively, in Figure 141. One difference between YSZ and ZrO\textsubscript{2} NWs fabrication process is the addition of glacial AcOH. In this case, the AcOH was added to a given Y(EHx)\textsubscript{3}/EtOH suspension (Figure 141, Step (c)) instead of a Zr(O\textsubscript{t}Bu)\textsubscript{4}/EtOH solution (Figure
This was done to promote dissolution of solid clumps of Y(EHx)\textsubscript{3} which initially formed a suspension upon addition to EtOH. The insolubility of Y(EHx)\textsubscript{3} could be due to formation of polymetallic species as reported by Mishra and others.\textsuperscript{179-182}

<table>
<thead>
<tr>
<th>Description</th>
<th>Precursor mass</th>
<th>PVP mass</th>
<th>Aging time</th>
<th>solvent + AcOH</th>
<th>Electrospinning parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Studying effects of varying PVP mass on nanofiber morphology, keeping Zr and Y ratio fixed</td>
<td>~ 0.100 g (Zr) + ~ 0.023 g (Y)</td>
<td>~ 0.300 g</td>
<td>10 min</td>
<td>~ 3.17 ml EtOH + 2-3 drops AcOH</td>
<td>Voltage: 20 kV</td>
</tr>
<tr>
<td></td>
<td>~ 0.350 g</td>
<td></td>
<td></td>
<td></td>
<td>Electrode dist.: 21 cm</td>
</tr>
<tr>
<td></td>
<td>~ 0.400 g</td>
<td></td>
<td></td>
<td></td>
<td>Flow rate: 3 ml/hr</td>
</tr>
<tr>
<td></td>
<td>~ 0.450 g</td>
<td></td>
<td></td>
<td></td>
<td>Volume dispensed: 2 ml</td>
</tr>
<tr>
<td>Studying the effect of varying Y:Zr ratio on NWs diameter and morphology</td>
<td>~ 0.100 g (Zr) + ~ 0.011 g (Y)</td>
<td>~ 0.300 g</td>
<td>10 min</td>
<td>~ 3.17 ml EtOH + 2-3 drops AcOH</td>
<td>Voltage: 20 kV</td>
</tr>
<tr>
<td></td>
<td>~ 0.100 g (Zr) + ~ 0.023 g (Y)</td>
<td></td>
<td></td>
<td></td>
<td>Electrode dist.: 21 cm</td>
</tr>
<tr>
<td></td>
<td>~ 0.100 g (Zr) + ~ 0.037 g (Y)</td>
<td></td>
<td></td>
<td></td>
<td>Flow rate: 2 ml/hr</td>
</tr>
<tr>
<td></td>
<td>~ 0.350 g</td>
<td></td>
<td></td>
<td></td>
<td>Volume dispensed: 2 ml</td>
</tr>
<tr>
<td>Studying the effect of varying the aging time (after adding PVP) on the unannealed nanofibers diameter and morphology (to evaluate if the viscosity increases over time or not)</td>
<td>~ 0.100 g (Zr) + ~ 0.023 g (Y)</td>
<td>~ 0.250 g</td>
<td>1 hr</td>
<td>~ 3.17 ml EtOH + 2-3 drops AcOH</td>
<td>Voltage: 20 kV</td>
</tr>
<tr>
<td></td>
<td>~ 0.350 g</td>
<td></td>
<td>2 hr</td>
<td></td>
<td>Electrode dist.: 21 cm</td>
</tr>
<tr>
<td></td>
<td>~ 0.450 g</td>
<td></td>
<td>3 hr</td>
<td></td>
<td>Flow rate: 2 ml/hr</td>
</tr>
<tr>
<td>Study the effect of sol-gel solution volume dispensed vs nanofiber film thickness</td>
<td>~ 0.100 g (Zr) + ~ 0.023 g (Y)</td>
<td>~ 0.400 g</td>
<td>10 min</td>
<td>~ 3.17 ml EtOH + 2-3 drops AcOH</td>
<td>Voltage: 20 kV</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Electrode dist.: 21 cm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Flow rate: 3 ml/hr</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Volume dispensed: 2 ml</td>
</tr>
</tbody>
</table>

Table 27: Parameters of sol-gel reaction for YSZ nanofibers synthesis using electrospinning technique

148
In Step (c), when AcOH was added, Y(EHx)₃/EtOH suspension gradually formed a clear solution. This was added to Zr(O'Bu)₄/EtOH solution dropwise (Figure 141, Step (d)) and the resulting solution was allowed to mix for about 10 min. The PVP/EtOH solution prepared in Step (e) (Figure 141) was added to Zr(O'Bu)₄/Y(EHx)₃/EtOH/AcOH gradually dropwise (Step (f), Figure 141) to prevent phase separation of dissolved PVP from the rest of the solution. Once added,
the resulting solution stirred for another 5 min before being transferred to a syringe (volume of ~ 2 ml) for electrospinning. The reagent mixing time associated with each step of the YSZ solution preparation is summarized in Table 28. The electrospinning parameters used for nanofibers fabrication were similar to the ZrO$_2$ NWs fabrication process (Table 27).

<table>
<thead>
<tr>
<th>Step</th>
<th>Solution content</th>
<th>Solution mixing time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>Zr(O'Bu)$_4$/EtOH</td>
<td>~ 10</td>
</tr>
<tr>
<td>(b)</td>
<td>Y(EHx)$_3$/EtOH</td>
<td>~ 5</td>
</tr>
<tr>
<td>(c)</td>
<td>Y(EHx)$_3$/EtOH/AcOH</td>
<td>~ 5</td>
</tr>
<tr>
<td>(d)</td>
<td>Zr(O'Bu)$_4$/Y(EHx)$_3$/EtOH/AcOH</td>
<td>~ 10</td>
</tr>
<tr>
<td>(e)</td>
<td>PVP/EtOH</td>
<td>~ 10</td>
</tr>
<tr>
<td>(f)</td>
<td>Zr(O'Bu)$_4$/Y(EHx)$_3$/EtOH/AcOH/PVP</td>
<td>~ 5</td>
</tr>
</tbody>
</table>

3.3 Instruments used for characterization

The structural and chemical characterization and analysis of the nanowires were performed including scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Elemental characterizations were done using electron dispersive x-ray spectroscopy (EDS/EDX) along with x-ray diffraction (XRD) to analyze phase composition of the fabricated ZrO$_2$ and YSZ NWs. Details of these different characterization techniques, instruments and sample preparation processes have been discussed earlier in this dissertation (Section 2.2).
3.4 Results and Discussion

In this section, the results pertaining to ZrO$_2$ and YSZ NWs fabricated via the sol-gel method are presented. The ZrO$_2$ nanowires were fabricated using either Zr($i$Pr)$_4$•($i$-PrOH) or Zr($i$Bu)$_4$ as precursors, whereas YSZ NWs were fabricated using only Zr($i$Bu)$_4$ as the precursor. ZrO$_2$ and YSZ NWs were fabricated in several sets of experiments where a specific parameter was varied in order to investigate its effect on the fabricated NWs average diameter. In the case of ZrO$_2$, the following parameters were varied: (1) Zr precursor mass; (2) PVP mass; and (3) time of sol-gel reaction aging phase. The parameters that were varied in the YSZ NWs fabrication process were: (1) PVP mass; (2) Y(EHx)$_2$ mass; (3) time of sol-gel reaction aging phase; and (4) sol-gel solution volume dispensed during electrospinning of YSZ nanofibers. In this 4$^{th}$ set of YSZ NW fabrication, the investigation focused on the thickness of the overall NWs film instead of YSZ NW diameter.

3.4.1 ZrO$_2$ NWs fabrication using a sol-gel route in combination with electrospinning

Zr($i$Pr)$_4$•($i$-PrOH) was initially used as the precursor for the ZrO$_2$ NWs fabrication. This precursor was used to perform only one set of experiments where its mass was varied to evaluate its influence on the ZrO$_2$ NWs diameter. Experiments performed using Zr($i$Bu)$_4$ are discussed later in this section.

3.4.1.1 Dependence of Zr($i$Pr)$_4$•($i$-PrOH) precursor mass on ZrO$_2$ NW diameters

In this ZrO$_2$ NWs fabrication process, the initial mass of Zr($i$Pr)$_4$•($i$-PrOH) was varied while keeping all other parameters constants. The detailed procedure for the NWs fabrication process was discussed earlier in this chapter (Figure 135) and the corresponding reagent masses are shown in Table 21. The scheme below provides an overview of the fabrication process for the
synthesis of ZrO$_2$ NWs using the sol-gel route in combination with the electrospinning and annealing processes.

(a) CH$_2$Cl$_2$, EtOH

\[ \text{Zr(O}^\text{i} \text{Pr)}_4 \text{(i-PrOH) + PVP} \rightarrow \text{Zr(O}^\text{i} \text{Pr)}_4 \text{(i-PrOH)-PVP nanofibers} \]

(b) Electrospinning

\[ \text{Zr(O}^\text{i} \text{Pr)}_4 \text{(i-PrOH)} \]

masses used:
1. 0.010 g
2. 0.025 g
3. 0.050 g
4. 0.075 g
5. 0.100 g

(c) gradual annealing

(1). ZrO$_2$ NWs fabrication using 0.010 g of Zr(O$^i$Pr)$_4$•(i-PrOH)

The nanofibers produced from 0.01 g Zr(O$^i$Pr)$_4$•(i-PrOH) had an average diameter of 796 (± 224) nm whereas the nanowires had an average diameter of 79 (± 224) nm. The histogram for both the nanofibers and nanowires are shown in Figure 142.

![Histogram of nanofiber (left) and nanowire (right) diameters fabricated using 0.010 g Zr(O$^i$Pr)$_4$•(i-PrOH).](image)

Figure 142: Histogram of nanofiber (left) and nanowire (right) diameters fabricated using 0.010 g Zr(O$^i$Pr)$_4$•(i-PrOH).
NWs prepared with 0.010 g Zr(O\textsuperscript{i}Pr\textsubscript{4})(i-PrOH) were so small that they could not be properly imaged using the SEM available at that time and therefore TEM was used to evaluate its size and morphology. As shown in Figure 143 (d), the nanowires were composed of individual nanocrystallites fused together in the morphology of the PVP template to form the 1-D structures. The PVP template was removed during the annealing process of the nanofibers.

![Figure 143: Images showing ZrO\textsubscript{2} (a, b) nanofibers and (c, d) nanowires fabricated using 0.010 g of Zr(O\textsuperscript{i}Pr\textsubscript{4})(i-PrOH).](image)

(2). ZrO\textsubscript{2} NWs fabrication using 0.025 g of Zr(O\textsuperscript{i}Pr\textsubscript{4})(i-PrOH)

Nanofibers made using 0.025 g Zr(O\textsuperscript{i}Pr\textsubscript{4})(i-PrOH) produced a bimodal nanofiber diameter distribution with the maxima at ~ 450 nm and ~ 1250 nm (Figure 144 (left)). The average
nanofiber diameter (Figures 145 (a) and (b)) was 900 (± 357) nm and the large standard deviation can be attributed to the two distinct sized ranges of nanofibers produced in this experiment. However, the annealed NWs showed a single, Gaussian-like behavior in the histogram (Figure 144 (right)) and the average diameter was measured to be 137 (± 49) nm. It is quite possible that there existed a trace amount of Zr species in these small nanofibers that subsequently were removed during the annealing process. TEM was not used in the nanowire diameter analysis of this sample.

Figure 144: Histogram of nanofiber (left) and nanowire (right) diameters fabricated using 0.025 g Zr(OiPr)$_4$•(i-PrOH).
(3). ZrO$_2$ NWs fabrication using 0.050 g of Zr(O'Pr)$_4$•(i-PrOH)

Two distinct nanofiber diameter ranges were also observed when 0.050 g of the Zr precursor was used (Figure 147 (a)). The average nanofiber diameter was measured to be 847 (± 487) nm with approximately 600 nm and 1550 nm being the average values of the two different ranges produced during the electrospinning process (Figure 146 (left)). The annealed NWs were measured to have an average diameter of 159 (± 53) nm (Figure 146 (right)).

Figure 145: Images showing ZrO$_2$ (a, b) nanofibers and (c, d) nanowires fabricated using 0.025 g of Zr(O'Pr)$_4$•(i-PrOH).
Figure 146: Histogram of nanofiber (left) and nanowire (right) diameters fabricated using 0.050 g Zr(O'Pr)₄•(i-PrOH).

Figure 147: Images showing ZrO₂ (a, b) nanofibers and (c, d) nanowires fabricated using 0.050 g of Zr(O'Pr)₄•(i-PrOH).
(4). ZrO$_2$ NWs fabrication using 0.075 g of Zr(O$i^3$Pr)$_4$•(i-PrOH)

Nanofibers fabricated using 0.075 g Zr(O$i^3$Pr)$_4$•(i-PrOH) were unlike the bimodal size distribution of nanofibers produced using 0.025 g and 0.050 g Zr precursor, instead showing a single maximum (Figure 148 (left)). The average nanofiber diameter was measured to be 359 (± 161) nm which is smaller than others observed so far in this series of experiments. In addition, the electrospinning process also produced some bead formation, as shown in Figure 149 (a). The cause of bead formation is low viscosity of the solution that is being used in the electrospinning process.$^{183}$ The decrease in the nanofiber diameter along with the bead formation suggests that the increase of Zr(O$i^3$Pr)$_4$ mass to 0.075g caused the sol-gel solution to reach a critical viscosity where it resulted in the instability of the Taylor cone.$^{184}$ This produced multiple thinner jets originating from the primary Taylor cone and thus resulting in the decrease in the nanofiber diameter. The annealed nanowires had an average diameter of 210 (± 57) nm and the film showed heavy presence of debris (annealed beads) as shown in Figure 149 (c).

![Histogram of nanofiber (left) and nanowire (right) diameters fabricated using 0.075 g Zr(O$i^3$Pr)$_4$•(i-PrOH).](image)
Figure 149: Images showing ZrO$_2$ (a, b) nanofibers and (c, d) nanowires fabricated using 0.075 g of Zr(O$i$Pr)$_4$•(i-PrOH).

(5). ZrO$_2$ NWs fabrication using 0.100 g of Zr(O$i$Pr)$_4$•(i-PrOH)

In this sample, 0.100 g Zr(O$i$Pr)$_4$•(i-PrOH) was used to fabricate ZrO$_2$ NWs with average NW diameter of 266 (± 80) nm. Like the previous sample, this sample also produced beads/debris (Figure 150 (c)) that present throughout the NWs film. The nanofibers were measured to have an average diameter of 754 (± 257) nm. The nanofibers also had embedded particles, presumably ZrO$_2$, (Figure 151 (b)) that were not seen in the previous samples. The ZrO$_2$ presumably rapidly precipitated out of the solution before doing the electrospinning process and were trapped in the resulting nanofibers during electrospinning.
Figure 150: Histogram of nanofiber (left) and nanowire (right) diameters fabricated using 0.100 g Zr(OiPr)$_4$•(i-PrOH).

Figure 151: Images showing ZrO$_2$ (a, b) nanofibers and (c, d) nanowires fabricated using 0.100 g of Zr(OiPr)$_4$•(i-PrOH).
(6). Overview of the nanofibers and nanowires fabricated using Zr(O^iPr)_4•(i-PrOH).

The average nanofiber diameters of samples from this series of experiments are summarized below in Table 29 and the relationship between the Zr(O^iPr)_4 mass and nanofiber diameter is shown in Figure 152. From the graph is can be concluded that the nanofiber diameter is insensitive to the Zr precursor mass. The large standard deviation was due to the formation of bimodal size distributions of nanofibers discussed earlier. The sudden decrease in the nanofiber size (at 0.075 g of Zr(O^iPr)_4) could be due to the instability of a Taylor cone resulting from the increased sol-gel solution viscosity for this experiment.

<table>
<thead>
<tr>
<th>Zr(O^iPr)_4•(i-PrOH) mass used (g)</th>
<th>Ave. nanofiber diameter (nm)</th>
<th>Std. Dev. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.100</td>
<td>754</td>
<td>257</td>
</tr>
<tr>
<td>0.075</td>
<td>359</td>
<td>161</td>
</tr>
<tr>
<td>0.050</td>
<td>847</td>
<td>487</td>
</tr>
<tr>
<td>0.025</td>
<td>900</td>
<td>357</td>
</tr>
<tr>
<td>0.010</td>
<td>796</td>
<td>224</td>
</tr>
</tbody>
</table>

Figure 152: Plot showing the dependence of ZrO_2/PVP nanofiber diameters and Zr(O^iPr)_4•(i-PrOH) masses, fabricated using the sol-gel route.
The annealed NWs diameters for this series of samples are summarized in Table 30 and the Zr(O\textsuperscript{i}Pr\textsubscript{4}) mass vs nanowires diameter trend is shown in Figure 153. The NWs average diameter increased with increasing Zr(O\textsuperscript{i}Pr\textsubscript{4})\textbullet\(\text{PrOH}\) mass. There was also an increased amount of bead formation when the Zr(O\textsuperscript{i}Pr\textsubscript{4}) mass was 0.050 g (along with some ZrO\textsubscript{2} precipitates) as observed in the unannealed nanofibers prepared from 0.100 g of Zr(O\textsuperscript{i}Pr\textsubscript{4})\textbullet\(\text{PrOH}\).

<table>
<thead>
<tr>
<th>Zr(O\textsuperscript{i}Pr\textsubscript{4})\textbullet(\text{PrOH}) mass used (g)</th>
<th>Ave. nanowire diameter (nm)</th>
<th>Std. Dev. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0994</td>
<td>266</td>
<td>80</td>
</tr>
<tr>
<td>0.0747</td>
<td>210</td>
<td>56</td>
</tr>
<tr>
<td>0.0481</td>
<td>159</td>
<td>53</td>
</tr>
<tr>
<td>0.0252</td>
<td>137</td>
<td>49</td>
</tr>
<tr>
<td>0.0101</td>
<td>79</td>
<td>35</td>
</tr>
</tbody>
</table>

Figure 153: Plot showing the dependence of ZrO\textsubscript{2} nanowire diameters and Zr(O\textsuperscript{i}Pr\textsubscript{4})\textbullet\(\text{PrOH}\) masses, fabricated using the sol-gel route.
(7). Overview of the TEM, lattice spacing and EDX analysis of ZrO$_2$ NWs prepared using Zr(OPr)$_4$·(i-PrOH) via a sol-gel route.

Figure 154 shows the lattice analysis of the crystallites that fused together to form the ZrO$_2$ nanowires as shown earlier in Figures 143 (c) and (d). The crystallites shown in Figure 154 (b) had an average size of 19.7 ± 6.01 nm. The lattice spacings were measured to be 0.324 nm, 0.368 nm, and 0.284 nm, which corresponds to the reported\textsuperscript{185,186} (-111), (011) and (111) lattice planes of the monoclinic crystal phase of ZrO$_2$. The XRD shown in Figure 156 matches the reported\textsuperscript{187,188} values and confirms the monoclinic phase of the annealed ZrO$_2$ NWs.

The EDX analysis (Figure 155) shows Zr and O peaks which correspond to the reported\textsuperscript{189} transitions. The elemental analysis resulted with an atomic % ratio of 35:65 (~1:2) which is in agreement with the formula ZrO$_2$. The Cu signal in the EDX originates from the Cu grid used to prepare the TEM sample. The inset in Figure 155 shows the STEM image of the nanowire being analyzed.

Figure 154: TEM images of annealed NWs showing fused nano crystallites fused together to form 1-D nanostructures. showing HRTEM images of fused crystallites with predominantly ZrO$_2$ monoclinic phases. The inset are FFT analysis of the HRTEM images.
Figure 155: EDX spectrum and quantitative elemental analysis of ZrO$_2$ NWs fabricated using Zr(O'iPr)$_4$•(i-PrOH) via sol-gel route. The inset shows the STEM image of the NWs being analyzed. The table shows Zr:O At % of ~ 1:2 which is in agreement with its formula ZrO$_2$.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>24.6</td>
<td>65.0</td>
</tr>
<tr>
<td>Zr K</td>
<td>75.4</td>
<td>35.0</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 156: XRD spectrum of annealed ZrO$_2$ NWs prepared using Zr(O'iPr)$_4$ as precursor via sol-gel route. The peaks show the presence of only monoclinic ZrO$_2$. The original spectrum was processed through FFT filter (with Cutoff Frequency = 24 pt) using Origin (Version 9.0) to smoothen the noise. (The subscript “m” represents monoclinic phase).
3.4.2 ZrO$_2$ NWs fabrication using Zr(O$^t$Bu)$_4$ as the sol-gel precursor with electrospinning

In this section the results are presented for the experiments that were conducted using Zr(O$^t$Bu)$_4$ as the starting material. Three sets of experiments were conducted where the ZrO$_2$ NWs diameters were evaluated while changing one variable in each case. The variables that were changed were: (1) Zr(O$^t$Bu)$_4$ mass; (2) PVP mass; and (3) sol-gel reaction aging time.

3.4.2.1 Varying starting mass of Zr(O$^t$Bu)$_4$ for to investigate its dependence on ZrO$_2$ NWs

\[
\text{Zr(O}^t\text{Bu)}_4 + \text{PVP} \xrightarrow{(a) \text{EtOH, AcOH}} \xrightarrow{(b) \text{Electrospinning}} \text{Zr(O}^t\text{Bu)}_4 \text{ - PVP nanofibers}
\]

Zr(O$^t$Bu)$_4$ masses used:
1. 0.050 g
2. 0.100 g
3. 0.150 g
4. 0.200 g

(c) gradual annealing

The ZrO$_2$ NWs were fabricated using the process discussed earlier in the reaction scheme shown in Figure 139. The quantities of each reagent used in this set of experiments are reported in Table 25. The following sections will include nanowire diameter histograms, SEM, TEM, and EDX (spectrum, line scans and maps) analysis for the nanowires fabricated using Zr(O$^t$Bu)$_4$ masses mentioned in the scheme above. The XRD spectra are presented together at the end of the of this set of experiments for side by side comparison between them.

(1). ZrO$_2$ NW fabrication using 0.050 g Zr(O$^t$Bu)$_4$

The nanofibers fabricated using 0.050 g Zr(O$^t$Bu)$_4$ did not show any beads or other debris as seen in some of the sample fabricated using Zr(O$^i$Pr)$_4$ (Figure 157). The unannealed nanofibers
were measured to be 614 (± 127) nm and the annealed NWs had an average diameter of 103 (± 26) nm as shown in the histograms of Figure 158. Neither nanofiber or nanowire diameter histograms showed the presence of a bimodal size distribution as was observed for the samples prepared using Zr(O^iPr)_4 (Figure 144).

Figure 157: Images showing ZrO_2 (a, b) nanofiber and (c, d) nanowire fabricated using 0.050 g of Zr(O^iBu)_4.

![Images showing ZrO_2 (a, b) nanofiber and (c, d) nanowire fabricated using 0.050 g of Zr(O^iBu)_4.](image1)

Figure 158: ZrO_2/PVP nanofiber (left) and nanowire (right) diameter distribution prepared using 0.050g Zr(O^iBu)_4.

![ZrO_2/PVP nanofiber (left) and nanowire (right) diameter distribution prepared using 0.050g Zr(O^iBu)_4.](image2)
TEM analysis showed the NWs to be constructed of crystallites fused together to form the 1-D in the morphology of the polymer template nanofibers. These crystal domains when formed at the end of a nanowire present semi-spherical shapes (Figure 159 (b)). This suggests that the spherical domains were not in a solid form during the fusion process and must have been present in a gel state when two or more of these domains began to coalesce to take the final shape of its polymer template. The lattice spacings are consistent with the reported values.\textsuperscript{189}

![Figure 159](image)

Figure 159: TEM analysis of ZrO\textsubscript{2} fabricated using 0.050 g Zr(O\textsuperscript{t}Bu)\textsubscript{4} showing (a, b) nanowires composed of fused crystallites which forms the basis of the nanowire architecture, (c,d) monoclinic crystal phase with lattice spacing of (-111), (011) planes.

It can only be speculated that these structures came together during the initial annealing step when the nanofibers coalesce (due to loss of residual solvents trapped in the polymers) and
caused densification of the nanofibers by compacting these packets of gels together. The process continued until the domains could not be shrunk further. At that point the PVP polymer pyrolysis continued until only the fused crystalline domains (Figure 159 (c)) remained in the morphology of its host PVP template. Brinker and Scherer described this process as “viscous sintering” which resulted in the formation of “space filling fractal clusters”.

The EDX analysis confirmed the presence of Zr and O species in the NWs fabricated with Zr:O atomic% ratio of ~ 1:1 which had slightly lower O content in comparison to formula, ZrO₂. The Cu signal shown in the spectrum (Figure 160) originated from the TEM grid used to prepare the ZrO₂ sample for the TEM analysis.

![EDX spectrum of NWs fabricated using 0.050 g Zr(OtBu)₄ showing the characteristic peaks associated to ZrO₂.](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>15.0</td>
<td>50.1</td>
</tr>
<tr>
<td>Zr K</td>
<td>85.0</td>
<td>49.9</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

The NWs fabricated using 0.050 g of Zr(OtBu)₄ were also analyzed using EDX mapping and line scans as shown in Figure 161. The EDX mapping demonstrated a homogenous distribution of both Zr and O species across the NWs being analyzed. The line scan confirmed this observation when the analysis was performed by scanning the nanowire from the left to the right. The Zr and
O signals intensities mimicked the NW contour as shown in the STEM image shown in Figure 161 (d).

![Figure 161: EDX analysis of the nanowires showing (a) STEM image of the NW being analyzed, (b) EDX map of Zr, (c) EDX map of O and (d) line scan across a ZrO$_2$ nanowire fabricated using 0.050 g Zr(O'Bu)$_4$.](image)

(2). ZrO$_2$ NW fabrication using 0.100 g Zr(O'Bu)$_4$

ZrO$_2$ fabricated using 0.100 g Zr(O'Bu)$_4$ produced ZrO$_2$/PVP nanofibers with an average diameter of 563 (± 132) nm and the histogram showed a Gaussian type distribution (Figure 163 (left)). The presence of two different diameter nanowires was detected in the histogram shown in Figure 163 (right). Even through the average diameter was measured to be 148 (± 36) nm for the
annealed nanowires, it consists two groups of nanowires with an average diameters of ~ 90 nm and ~ 165 nm. TEM analysis supported this data showing NWs of average diameter of ~165 nm NWs in Figure 164 (a) and ~90 nm in Figure 164 (b).

![Figure 162: Images showing ZrO\textsubscript{2} (a, b) nanofiber and (c, d) nanowire fabricated using 0.100 g of Zr(OtBu\textsubscript{4}).](image)

![Figure 163: ZrO\textsubscript{2}/PVP nanofiber (left) and nanowire (right) diameter distribution prepared using 0.100g Zr(OtBu\textsubscript{4}).](image)
The TEM analysis also confirmed the ZrO₂ crystal phase is monoclinic with the lattice spacing of 0.318 nm and 0.370 nm which corresponds to the (-111) and (011) planes, respectively. The insets in Figures 164 (c) and (d) are the FFT analysis of the HRTEM lattice images shown.

![Figure 164](image)

Figure 164: TEM images showing (a,b) nanowires fabricated using 0.100g Zr(O^tBu)_4 and (b,c) its crystal lattice spacing confirming the presence of monoclinic phase.

The EDX analysis (Figure 165) provided a Zr:O At% of 1:2 which was consistent with the formula ZrO₂. The line scan (Figure 166 (a)) showed an asymmetric plot for O species which was not present in case of the Zr line. It could be possible that the oxygen species were shifted by
the 200 kV electron beam as it moved from the left to the right side of the nanowire (due to the intrinsic mobile nature of O species in MOEs like ZrO$_2$). This conclusion is supported by the EDX map (Figure 166 (b)) which showed a slightly reduced intensity for O in comparison to the Zr (Figure 166 (c)) at the region where the line scan was performed prior to the EDX mapping.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>22.2</td>
<td>61.9</td>
</tr>
<tr>
<td>Zr K</td>
<td>77.8</td>
<td>38.1</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 165: EDX spectrum of NWs fabricated using 0.100 g Zr(O'Bu)$_4$.

Figure 166: (a) Line scan of two nanowires showing an asymmetry in oxygen concentration when scanned from left to the right of the nanowires and EDX map showing (b) oxygen and (c) Zr distribution across the same NWs used for the line scan.
(3). ZrO$_2$ NW fabrication using 0.150 g Zr(O'Bu)$_4$

NWs fabricated using 0.150 g Zr(O'Bu)$_4$ produced nanofibers and nanowires with an average diameter of 671 (± 298) nm and 152 (± 72) nm, respectively.

![Images showing ZrO$_2$ (a, b) nanofiber and (c, d) nanowire fabricated using 0.150 g of Zr(O'Bu)$_4$. The scale bars in (a), (b), (c) and (d) corresponds to 100 µm, 10 µm, 20 µm and 5 µm, respectively.]

Figure 167: Images showing ZrO$_2$ (a, b) nanofiber and (c, d) nanowire fabricated using 0.150 g of Zr(O'Bu)$_4$. The scale bars in (a), (b), (c) and (d) corresponds to 100 µm, 10 µm, 20 µm and 5 µm, respectively.

![ZrO$_2$/PVP nanofiber (left) and nanowire (right) diameter distribution prepared using 0.150g Zr(O'Bu)$_4$.]

Figure 168: ZrO$_2$/PVP nanofiber (left) and nanowire (right) diameter distribution prepared using 0.150g Zr(O'Bu)$_4$. 
The TEM and EDX analysis were consistent with the samples prepared using 0.050 g and 0.100 g Zr(O\textsubscript{t}Bu\textsubscript{4}). The d-spacing (0.528 nm) shown in Figure 169 (c) corresponds to the ZrO\textsubscript{2} (010) plane of the monoclinic phase. The Zr:O At% ratio was measured to be ~1:1 which indicates a lower concentration of oxygen species in the NW analyzed.

![Figure 169](image)

Figure 169: (a,b) TEM analysis of the NWs fabricated with 0.150g Zr(O\textsubscript{t}Bu\textsubscript{4}) and (c) its lattice spacing indicating the presence of the monoclinic phase.

![Figure 170](image)

Figure 170: EDX spectrum of the NWs fabricated using 0.150g Zr(O\textsubscript{t}Bu\textsubscript{4}).

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>10.6</td>
<td>40.3</td>
</tr>
<tr>
<td>Zr K</td>
<td>89.4</td>
<td>59.7</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

(4). ZrO\textsubscript{2} NW fabrication using 0.200 g Zr(O\textsubscript{t}Bu\textsubscript{4})

Using 0.200 g Zr(O\textsubscript{t}Bu\textsubscript{4}), the nanofibers produced had an average diameter of 746 (± 311) nm. The annealed nanowires presented a bimodal distribution with approximate diameters of ~
120 nm and ~250 nm, and an overall average diameter of 200 (± 95) nm (Figure 172 (right)). This bimodal behavior is evident in the SEM images of the annealed nanowires (Figure 171 (d)).

Figure 171: Images showing ZrO$_2$ (a, b) nanofiber and (c, d) nanowire fabricated using 0.200 g of Zr(O'Bu)$_4$. The scale bars in (a), (b), (c) and (d) corresponds to 100 µm, 10 µm, 50 µm and 5 µm, respectively.

Figure 172: ZrO$_2$/PVP nanofiber (left) and nanowire (right) diameter distribution prepared using 0.200g Zr(O'Bu)$_4$. 

Average nanofiber diameter: 746 ± 311 nm

Average nanowire diameter: 200 ± 95 nm
The TEM analysis performed in the annealed NWs also showed two distinct average diameter NWs as shown in Figure 173 (a). These NWs were also formed by fusion of the individual crystalline domains and were more evident than those NWs which were composed of individual crystallites fused end to end to form 1-D structure (Figure 173 (c)). HRTEM analysis of one such crystallite was used to conduct lattice imaging and was identified to be ZrO$_2$ crystal in the monoclinic phase with a d-spacing (011) of 0.377 nm.

![Figure 173: (a,b,c) Showing TEM analysis of the NWs fabricated with 0.200g Zr(OtBu)$_4$ and (d) its lattice spacing indicating the presence of the monoclinic phase.](image)

The quantitative elemental analysis generated from the EDX spectrum (Figure 174) showed a lower oxygen content in the NWs. This could be due to the oxygen migration away from the high localized temperature of the 200 kV electron beam. The EDX line scan (Figure 175 (b))
showed Zr and O line profiles similar to the NWs STEM image as shown in Figure 175 (a). The EDX maps of Zr and O (Figure 176), indicate a homogenous distribution of the Zr species across the NWs being analyzed.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>10.4</td>
<td>39.9</td>
</tr>
<tr>
<td>Zr K</td>
<td>89.6</td>
<td>60.1</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 174: EDX spectrum of the NWs fabricated using 0.200 g Zr(O'Bu)$_4$.

Figure 175: EDX line scan of the NWs fabricated using 0.200 g Zr(O'Bu)$_4$. 
Figure 176: EDX map of the NWs fabricated using 0.200 g Zr(OtBu)_4 showing (a) STEM image, (b) oxygen signal and (c) Zr signal distributions.

The XRD analysis of NWs fabricated with 0.050 g, 0.100 g, 0.150 g and 0.200 g are shown in Figures 177 (a), (b), (c) and (d), respectively. In these figures the subsets m and t refers to monoclinic and tetragonal crystal phase.

All four XRD spectra showed the presence of ZrO_2 in the monoclinic crystal phase which supported the lattice spacing measurement shown earlier in Figures 159, 164, 169 and 173 for the samples with Zr(OtBu)_4 masses 0.050g, 0.100g, 0.150g and 0.200g, respectively. The reflections shown at 2θ = 24.2°, 28.2°, 31.4°, 34.3° and 49.5° corresponded to the ZrO_2 monoclinic phases (110), (-111), (111), (020) and (220), respectively and matches the literature values\textsuperscript{187,188}. The small peaks at 2θ = 40.5° and 44.7° are due to the (-112) and (211) ZrO_2 monoclinic plane reflections.

However, there was some evidence of the tetragonal phases in the XRD analysis of ZrO_2 NWs prepared using 0.100 g and 0.200 g of Zr(OtBu)_4. In these two cases, the characteristic ZrO_2 tetragonal (111) peak was observed at 30.2° (Figures 178 (b) and (d)).
Figure 177: XRD spectra of ZrO$_2$ NWs fabricated using (a) 0.050g, (b) 0.100g, (c) 0.150g and (d) 0.200g of Zr(O$^4$Bu)$_4$. The superscripts $m$ and $t$ corresponds to monoclinic and tetragonal phases. The initial spectra of the four samples were subjected to signal a smoothening process using the FFT filter (27 pts) on Origin (Version 9.0).
(5). Summary of nanofiber and nanowire diameter trends

Overall, the average ZrO$_2$/PVP nanofiber diameter showed an insensitive response with increasing Zr(O$^t$Bu)$_4$ mass (Figure 178). It is difficult to draw any definitive conclusion as the differences in the data is obscured by the standard deviations associated with the diameter measurements. As for the annealed nanowires, the average diameter showed an upward trend but not statistically significant (Figure 179).

<table>
<thead>
<tr>
<th>Zr(O$^t$Bu)$_4$ mass (g)</th>
<th>Nanofiber diameters (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.050</td>
<td>614 ± 127</td>
</tr>
<tr>
<td>0.100</td>
<td>563 ± 132</td>
</tr>
<tr>
<td>0.150</td>
<td>671 ± 298</td>
</tr>
<tr>
<td>0.200</td>
<td>746 ± 311</td>
</tr>
</tbody>
</table>

Figure 178: Zr(O$^t$Bu)$_4$ mass vs nanofiber diameter relationship.
<table>
<thead>
<tr>
<th>Zr(O\text{Bu})_4 mass (g)</th>
<th>Nanowire diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.050</td>
<td>104 ± 26</td>
</tr>
<tr>
<td>0.100</td>
<td>148 ± 36</td>
</tr>
<tr>
<td>0.150</td>
<td>152 ± 72</td>
</tr>
<tr>
<td>0.200</td>
<td>200 ± 95</td>
</tr>
</tbody>
</table>

Figure 179: Zr(O\text{Bu})_4 mass vs average nanowire diameters (at constant PVP mass).

3.4.2.2 Varying mass of PVP to investigate its dependence on ZrO\textsubscript{2} NWs diameter

In this section, results relating to ZrO\textsubscript{2} NWs diameter (by varying PVP mass) are presented. Three different PVP masses were used (as shown in the scheme below) to fabricate the NWs and evaluate their influence on the annealed NW diameters. The nanowires were fabricated via a sol-gel method in combination with the electrospinning and annealing processes discussed earlier in the chapter (Figure 139). The quantities of the reagent used for the following processes have been reported earlier in Table 25.
Nanofibers and nanowires fabricated using 0.250 g PVP have an average diameter of 530 (± 160) nm and 160 (± 40) nm, respectively, as demonstrated in the histograms shown in Figure 181. It indicates the presence of a very unstable Taylor cone during the electrospinning of the nanofibers which can result from the PVP concentration being too low. The nanofiber formation depends on a balance between the solution surface tension and the electrostatic attraction between the electrodes. Theoretically, when the viscosity is low (at lower PVP mass), surface tension of the solution at the tip of the needle can be easily influenced (by different factors) to produce a jet which can ultimately lead to formation of nanofibers with varying diameters as seen in this sample.

The TEM analysis also showed that the annealed NWs were composed of the fused crystallites (Figure 182 (c)). The measured lattice spacing indicated the presence of tetragonal ZrO$_2$ crystal phase with a 0.251 nm value corresponding to the (110) plane (Figure 182 (d)).
Figure 180: SEM images showing ZrO$_2$ (a, b) nanofiber and (c, d) nanowire of fabricated using 0.250 g PVP.

Figure 181: Nanofiber (left) and nanowire (right) diameter distribution prepared using 0.250g PVP.
Figure 182: (a,b,c) TEM analysis of the NWs fabricated with 0.250g PVP and (d) its lattice spacing indicating the presence of the tetragonal phase.

The EDX analysis showed the corresponding K shell transition for both Zr and O species which was used to determine the Zr:O At% ratio of ~ 1:2 (Figure 183). The line scan (Figure 184 (a)) generated a profile that was consistent with the STEM image of the NW that was being analyzed. The EDX map (Figures 184 (c) and (d)) supported the line scan results by showing a homogenous distribution of the Zr and O species throughout the cluster of NWs that was being analyzed.
Figure 183: EDX spectrum of the NWs fabricated using 0.250 g PVP.

Figure 184: EDX (a) line scan and (b,c,d) map of the NWs fabricated using 0.250 g PVP.

(2). ZrO$_2$ NW fabrication using 0.350 g PVP

NWs fabricated using 0.350 g PVP were the same sample that was fabricated using 0.150g Zr(O'Bu)$_4$ in the previous section. Therefore, the same data will not be repeated. However,
the nanofiber and nanowire average diameters reported for 0.150 g Zr(O'Bu)₄ sample will be added to the 0.250 g and 0.450 g PVP data later to draw the relationship between their masses and the corresponding diameters.

(3). ZrO₂ NW fabrication using 0.450 g PVP

The nanofiber sample produced using 0.450 g PVP showed two distinct diameter ranges as shown in Figure 186 (b). The relevant bimodal histogram supported this observation by showing highest counts at ~ 400 nm and ~ 1100 nm regions (Figure 185 (left)). The overall average diameter of the unannealed nanofibers were measured to be 860 (± 380) nm. The annealed nanowires histogram (Figure 185 (right)) also indicated a rather broad NW distribution with an overall average of 300 (± 100) nm. The SEM image confirmed this observation (Figure 186 (d)).

![Graphs showing nanofiber and nanowire diameter distributions](image)

Figure 185: Nanofiber (left) and nanowire (right) NW diameter distribution prepared using 0.450g PVP.
Figure 186: SEM images showing ZrO$_2$ (a, b) nanofiber and (c, d) nanowire of fabricated using 0.450 g PVP. The scale bars in (a), (b), (c) and (d) corresponds to 100 µm, 10 µm, 5 µm and 5 µm, respectively.

The TEM images, shown in Figure 187 (a) demonstrate this broad nanowire diameter distribution. The lattice spacing analysis suggested the presence of a ZrO$_2$ (111) monoclinic crystal phase with a value of 0.281 nm (Figure 188 (d)). The EDX map indicated a homogenous distribution of both Zr and O species across the analyzed NWs (Figure 188). During the line scan (Figure 189) the Zr line profile fit the NWs shown in the STEM mode but the oxygen signal diminished during the scan from the left to the right. Once again this could be due to either oxygen’s mobile nature in these kinds of ceramic materials or due to the electron beam induced erosion of the oxide species.
Figure 187: (a,b,c) TEM analysis of the NWs fabricated with 0.450g PVP and (d) its lattice spacing indicating the presence of the monoclinic phase.

Figure 188: EDX map of the NWs fabricated with 0.450g PVP showing homogeneous distribution of (a) STEM image (b) O and (c) Zr species.
Figure 189: EDX line scan of the NWs fabricated using 0.450 g PVP showing a decay of oxygen signal when performing the scan left to the right.

Analysis of XRD data showed that both samples prepared using 0.250 g and 0.450 g PVP were composed of a monoclinic crystalline phase. However, there was a slight presence of the tetragonal phase as indicated by (111), peak around $2\theta = 30.2^\circ$ (Figure 190).

Figure 190: XRD spectrum NWs fabricated with (a) 0.250 g and (b) 0.450 g PVP.
Overall the average nanofiber diameter increased very slightly with an increase in the PVP mass (Figure 191). The nanofiber data for all three sample diameters are summarized in Table 33. This increase in diameter is somewhat obscured by the larger standard deviation which is a result of the dual nanofiber diameter data combined in the calculation of the average diameter for 0.350g and 0.450g PVP masses.

<table>
<thead>
<tr>
<th>PVP mass (g)</th>
<th>Nanofiber diameter (nm)</th>
<th>Std. Dev. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2500</td>
<td>530</td>
<td>160</td>
</tr>
<tr>
<td>0.3500</td>
<td>690</td>
<td>300</td>
</tr>
<tr>
<td>0.4500</td>
<td>860</td>
<td>380</td>
</tr>
</tbody>
</table>

Table 33: PVP mass vs average nanofiber diameter.

The annealed nanowires showed an increase in the NWs diameter with the increase in the PVP mass (Figure 192). The average diameters with their standard deviations are summarized Table 34.
Table 34: PVP mass vs average nanowire diameter.

<table>
<thead>
<tr>
<th>PVP mass (g)</th>
<th>Annealed nanowire diameter (nm)</th>
<th>Std. Dev. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2500</td>
<td>160</td>
<td>40</td>
</tr>
<tr>
<td>0.3500</td>
<td>260</td>
<td>60</td>
</tr>
<tr>
<td>0.4500</td>
<td>300</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 192: Plot showing the nanowire diameter vs PVP mass relationship.

From the results obtained, it can be concluded that both nanofibers and nanowires diameter increases with an increase in the PVP mass. At higher PVP content, the nanofibers tend to form two distinct diameter nanofibers, which was evident in their histograms. The nanowires mostly possessed a monoclinic phase with some evidence of tetragonal form as seen in lattice spacing and XRD analysis.
3.4.2.3 Investigation of dependence on ZrO$_2$ NW diameters on varying reaction time (with PVP and Zr(OBu)$_4$ mass being constant)

\[
\text{Zr(OBu)}_4 + \text{PVP} \xrightarrow{(a) \text{EtOH, AcOH}} \text{Zr(OBu)}_4 - \text{PVP nanofibers} \xrightarrow{(b) \text{Electrospinning}} \text{Sol-gel solution aging time before electrospinning} \]

1) 5 min
2) 1 hour
3) 2 hours
4) 3 hours

(c) gradual annealing

In this set of investigations, the effect of sol-gel reaction aging phase time on the nanofibers (unannealed NWs) were investigated. As discussed in Chapter 1, one of the electrospinning parameters that influences the nanofiber diameter is the viscosity of the solution that is being electrospun. The sol-gel reaction propagates through several steps (discussed earlier in this chapter) with one being the aging phase where the interconnection between the oligomer chains are initiated. This networking results in the increase in the viscosity of the sol-gel solution.

In the current system such an increase in viscosity could change the diameter and the morphology of the ZrO$_2$ NWs being fabricated using the electrospinning system. Therefore, the ZrO$_2$ NWs fabrication via this route was conducted where the sol-gel reaction was allowed to age for periods of 5 min, 1, 2, and 3 hours (scheme shown above). It was followed by nanofiber diameter measurements to determine the diameter variation between each aging time.

In this case only the diameter histograms, SEM, TEM results are presented for each nanofiber sample, followed by a comparison of the XRD and EDX data at the end. The 2 hours aging time sample is one that was prepared using 0.150 g Zr(O'Bu)$_4$ and 0.350 g PVP (discussed in Section 3.4.2.1) and therefore will not be re-presented in detail in this section.

191
ZrO₂ NWs fabrication with solution aging time of 5 min

The nanofibers fabricated using 5 min of aging time produced a diameter of 1140 (± 480) nm which after annealing were measured to be 340 (± 140) nm (Figure 194). The SEM images of the nanofiber and nanowires are shown in Figures 193 (a,b) and (c,d), respectively. The TEM images (Figure 195 (b)) revealed smaller diameter nanowires branching off the larger diameter nanowires of a monoclinic phase (Figure 195 (d)).

![SEM images of nanofibers and nanowires](image-url)

**Figure 193:** (a,b) ZrO₂/PVP nanofibers and (c,d) ZrO₂ nanowires fabricated with a sol-gel aging time of 5 min before electrospinning.
Figure 194: Histogram of ZrO$_2$/PVP nanofibers (left) and ZrO$_2$ nanowires (right) fabricated with a sol-gel aging time of 5 min before electrospinning.

Figure 195: (a,b,c) TEM analysis of the ZrO$_2$ NWs fabricated with aging time of 5 min and (d) its lattice spacing indicating the presence of the monoclinic phase.
(2). **ZrO$_2$ NWs fabrication with solution aging time of 1 hour**

After one-hour aging, the nanofibers produced using the electrospinning process were measured to be 700 (± 340) nm and annealed to obtain NWs with an average diameter of 380 (± 80) nm (Figure 197). The SEM images shown in Figure 196 (b) indicated that there were two sets of diameters present in the nanofiber sample. This observation was confirmed by the two relative maxima (~ 300 nm and ~ 950 nm) in the corresponding histogram shown in Figure 197 (left).

![Figure 196](image)

Figure 196: (a,b) ZrO$_2$/PVP nanofibers and (c,d) ZrO$_2$ nanowires fabricated with a sol-gel aging time of 1 hour before electrospinning. The scale bars in (a), (b), (c) and (d) corresponds to 50 µm, 10 µm, 20 µm and 5 µm, respectively.
Figure 197: Histogram of ZrO$_2$/PVP nanofibers (left) and ZrO$_2$ nanowires (right) fabricated with a sol-gel aging time of 1 hour before electrospinning.

The TEM analysis showed a nanowire network composed of fused domains (Figure 198 (c)) of ZrO$_2$ crystallites with a $d_{200}$ spacing of 0.197 nm corresponding to the monoclinic phase (Figure 198 (d)).

Figure 198: (a,b,c) TEM analysis of the ZrO$_2$ NWs fabricated with aging time of 1 hour and (d) its lattice spacing indicating the presence of the monoclinic phase.
(3). ZrO$_2$ NWs fabrication with solution aging time of 2 hours

The 2 hours aging time sample data is taken from the series (Section 3.4.2.1) where the Zr(O'Bu)$_4$ mass was varied while keeping all other parameters constant. The histogram shown below (Figure 199) corresponds to the Zr(O'Bu)$_4$ mass of 0.150 g. This sample was also aged for 2 hours (along with the others in the Zr(O'Bu)$_4$ mass varying series) and was measured to have average nanofiber and nanowire diameters of 690 (± 300) nm and 260 (± 60) nm respectively. TEM, and SEM data for the 2 hours aging sample can be found in Section 3.4.2.1.

![Figure 199: Histogram of ZrO$_2$/PVP nanofibers (left) and ZrO$_2$ nanowires (right) fabricated with a sol-gel aging time of 2 hours before electrospinning.](image)

(4). ZrO$_2$ NWs fabrication with solution aging time of 3 hours

In this sample, the nanofibers had a bimodal size distribution observed in the SEM image (Figure 200 (b)) which was confirmed in its histogram distribution as shown in Figure 201 (left). The average nanofiber and nanowire diameters were measured to be 760 (± 340) nm and 350 (± 110) nm, respectively.

The TEM images (Figure 202 (a)) showed mostly larger diameters NWs (~ 350 nm to ~450 nm) which were constructed from smaller crystallite domains (Figure 202 (c)). The crystallite domains were identified to have a monoclinic crystal phase, with a (220) d-spacing of 0.172 nm.
Figure 200: (a,b) ZrO$_2$/PVP nanofiber and (c,d) ZrO$_2$ nanowires fabricated with a sol-gel aging time of 3 hours before electrospinning. The scale bars in (a), (b), (c) and (d) corresponds to 50 µm, 10 µm, 20 µm and 5 µm, respectively.

Figure 201: Histogram of ZrO$_2$/PVP nanofibers (left) and ZrO$_2$ nanowires (right) fabricated with a sol-gel aging time of 3 hours before electrospinning.

Average nanofiber diameter: 
760 ± 340 nm

Average nanowire diameter: 
350 ± 110 nm
Figure 202: (a,b,c) TEM analysis of the ZrO$_2$ NWs fabricated with aging time of 3 hours and (d) its lattice spacing indicating the presence of the monoclinic phase.

The overall EDX analysis of the nanowires fabricated in this set of experiments resulted in the spectra similar to the one shown in Figure 203 with a quantitative elemental analysis resulting with a Zr:O At% of $\sim 1:1$. The XRD spectra shown in Figure 204 corresponds to samples with aging times of: (a) 5 min, (b) 1 hour, (c) 2 hours and (d) 3 hours. The XRD samples showed mostly the monoclinic phase and the relevant peaks are highlighted using (*) in the figure. However, the 1 hour and 3 hours again time samples showed peaks (▲) that were identified to be reflections associated with the tetragonal phase of ZrO$_2$. 

$\text{d}_{220} = 0.172 \text{ nm}$

ZrO$_2$ (monoclinic)
Figure 203: Typical EDX spectrum and quantitative analysis result observed in ZrO$_2$ NWs sample where the sol-gel aging time was varied.

Figure 204: XRD spectrum of ZrO$_2$ NW samples with aging times (a) 5 min, (b) 1 hour, (c) 2 hours and (d) 3 hours showing the presence of mostly monoclinic phases (*). Tetragonal phased ZrO$_2$ peaks are observed in (b) and (d) and are indicated by (▲). All XRD patterns shown here were generated by processing it through the FFT filter in Origin (Version 9.0) in order to reduce the signal noise.
An analysis of the overall changes in diameter in relation to the reaction aging time is presented in Table 35. The trend showed no observable change in nanofibers diameter with the increase in the aging time (Figure 205). The sample with an aging time of 5 min had slightly higher diameters but its large standard deviation obscured a conclusive indication of such increase. The annealed nanowires showed a similar trend where the nanowires diameters remained unchanged with the increase in the aging time (Table 36) as demonstrated in Figure 206.

<table>
<thead>
<tr>
<th>Zr(O\text{Bu})_4 mass (g)</th>
<th>PVP mass (g)</th>
<th>Rxn aging time (hr)</th>
<th>Nanofiber diameter (nm)</th>
<th>Std. Dev. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1546</td>
<td>0.3501</td>
<td>5 min</td>
<td>1140</td>
<td>480</td>
</tr>
<tr>
<td>0.1538</td>
<td>0.3501</td>
<td>1</td>
<td>700</td>
<td>340</td>
</tr>
<tr>
<td>0.1577</td>
<td>0.3500</td>
<td>2</td>
<td>690</td>
<td>300</td>
</tr>
<tr>
<td>0.1516</td>
<td>0.3503</td>
<td>3</td>
<td>760</td>
<td>340</td>
</tr>
</tbody>
</table>

Figure 205: Nanofiber diameter vs reaction aging time.
Table 36: Nanowire diameters vs reaction aging time.

<table>
<thead>
<tr>
<th>Zr(O\textsuperscript{t}Bu)\textsubscript{4} mass (g)</th>
<th>PVP mass (g)</th>
<th>Rxn aging time (hr)</th>
<th>Nanowire diameter (nm)</th>
<th>Std. Dev. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1546</td>
<td>0.3501</td>
<td>5 min</td>
<td>340</td>
<td>140</td>
</tr>
<tr>
<td>0.1538</td>
<td>0.3501</td>
<td>1</td>
<td>310</td>
<td>80</td>
</tr>
<tr>
<td>0.1577</td>
<td>0.3500</td>
<td>2</td>
<td>260</td>
<td>60</td>
</tr>
<tr>
<td>0.1516</td>
<td>0.3503</td>
<td>3</td>
<td>350</td>
<td>110</td>
</tr>
</tbody>
</table>

3.4.3 YSZ NWs fabrication via sol-gel route (in combination with electrospinning)

The fabrication process for YSZ nanowires was presented earlier in the chapter (Figure 141) and the quantities associated with all the reagents used in the process were reported in Table 27. The ZrO\textsubscript{2} NWs were fabricated using a combination of Zr(O\textsuperscript{t}Bu)\textsubscript{4} and Y(EHx)\textsubscript{3} resulting in a product consisting of a Y\textsubscript{2}O\textsubscript{3}:ZrO\textsubscript{2} molar ratio of 8:92 (8% Y\textsubscript{2}O\textsubscript{3} stabilized ZrO\textsubscript{2} or 8YSZ). In the following sections, the results of annealed NW diameter dependence on different parameters are presented. The parameters that varied during these investigations were: (1) PVP mass; (2) Y:Zr ratio and (3) sol-gel reaction aging time. In addition, an analysis of the solution volume that
produced nanowire films with increased flexibility are also discussed. In this case, several annealed nanowire film thicknesses were analyzed using SEM, which were compared to the sol-gel solution volumes dispensed to fabricate those specific films.

### 3.4.3.1 Investigation of dependence of PVP mass on 8YSZ NW diameters

\[
\text{Zr(O\text{Bu})}_4 + Y(\text{EHx})_3 + \text{PVP} \xrightarrow{\text{(a) EtOH, AcOH}} \text{Zr(O\text{Bu})}_4 - Y(\text{EHx})_3 - \text{PVP nanofibers}
\]

(b) Electrospinning

PVP masses used:
1) 0.300 g (12%)
2) 0.350 g (14%)
3) 0.400 g (16%)
4) 0.450 g (18%)

(c) gradual annealing

In this investigation, the PVP mass used to fabricate 8YSZ NWs was varied. The masses used are shown in the scheme above along with the associated percent PVP solution. The results presented for this investigation include the annealed diameter distribution, SEM, TEM, EDX and XRD analysis. The nanofiber diameter analysis is not presented for this set of experiments, as the earlier nanofiber diameter analysis with Zr(O\text{Bu})_4 (for ZrO_2) was insensitive to the change in the PVP mass.

1. **8YSZ NWs fabrication using 0.300 g (12%) PVP**

   The average nanowire diameter was measured to be 101 (± 72) nm with a very broad size distribution (Figure 207). As with other experiments, the 8YSZ nanowires were also constructed by fusion of individual crystallites that morphed into a 1-D structure by the PVP template during the annealing process (Figure 209 (b)). The lattice spacing analysis indicated the presence of cubic phase ZrO2 in the 8YSZ sample with a d-spacing (0.306 nm) corresponding to the (111) plane (Figure 209 (d)).
Figure 207: Histogram of annealed 8YSZ nanowire diameters fabricated using 0.300 g PVP.

Average nanowire diameter: 101 ± 72 nm

Figure 208: SEM images showing 8YSZ (a,b) nanofibers and (c,d) nanowires fabricated using 0.300 g PVP. The scale bars in (a), (b), (c) and (d) corresponds to 20 µm, 10 µm, 5 µm and 20 µm, respectively.
Figure 209: (a,b,c) TEM analysis of the 8YSZ NWs fabricated using 12% (0.300g) PVP and (d) its lattice spacing indicating the presence of the cubic phase ZrO$_2$.

The EDX quantitative elemental analysis was performed using the K-shell signal intensities of Y and Zr to determine the relative atomic % (At %). The Y:Zr At % ratio was determined to be ~ 17:83, which corresponds to ~ 8:92.
(2). 8YSZ NWs fabrication using 0.350 g (14%) PVP

YSZ NWs prepared using 0.350 g PVP (14%) showed similar bimodal nanowires diameter distribution as observed in the previous samples. The two different groups of nanowire diameters presented in this system had approximate diameters of 60 nm and 180 nm (Figure 211) which was in the same range as the dual nanowires diameters observed for the sample prepared with 0.300 g PVP. The SEM images showed that the nanowires and nanofibers were devoid of any beads or debris (Figure 212).

![Figure 210: EDX spectrum of annealed 8YSZ nanowires fabricated using 0.300 g PVP.]

![Figure 211: Histogram of annealed 8YSZ nanowire diameters fabricated using 0.350 g PVP.]

**Average nanowire diameter:**

\[87 \pm 54 \text{ nm}\]
Figure 212: SEM images showing 8YSZ (a,b) nanofibers and (c,d) nanowires fabricated using 0.350 g PVP. The scale bars in (a), (b), (c) and (d) corresponds to 200 µm, 20 µm, 20 µm and 5 µm, respectively.

The TEM analysis (Figure 213) showed NWs constructed of fused nanocrystal domains that took the morphology of its parent polymer template to form a 1-D polycrystalline structure consisting of cubic phase ZrO\(_2\) stabilized by ~8% Y\(_2\)O\(_3\) as indicated by the EDX quantitative analysis (Figure 214). The EDX quantitative analysis was performed using only the K-shells of Zr and Y to maintain consistency in the data. The inset in the EDX analysis shows the STEM image of the NWs associated with the EDX measurements.
Figure 213: (a,b,c) TEM analysis of the NWs fabricated using 14% (0.350g) PVP and (d) its lattice spacing indicating the presence of the cubic phase.

Figure 214: EDX spectrum of annealed 8YSZ nanowires fabricated using 0.350 g PVP.
(3). 8YSZ NWs fabrication using 0.400 g (16%) PVP

NWs fabricated using 16% PVP solution also produced a bimodal size distribution where the histogram showed two maxima with approximate diameters of 90 nm and 210 nm as shown in Figure 215.

Figure 215: Histogram of annealed 8YSZ nanowire diameters fabricated using 0.400 g PVP.

These diameters were larger than those measured in the 12% and 14% 8YSZ samples. The TEM images (Figure 217) once again demonstrated the architecture of the 8YSZ nanowires arising from fusion of individual crystallites (Figure 217 (c)) with a characteristic cubic ZrO₂ lattice spacing (Figure 217 (d)).
Figure 216: SEM images showing 8YSZ (a,b) nanofibers and (c,d) nanowires fabricated using 0.400 g PVP.

Figure 217: (a,b,c) TEM analysis of the NWs fabricated using 16% (0.400g) PVP and (d) its lattice spacing indicating the presence of the cubic phase.
Figure 218: EDX spectrum of annealed 8YSZ nanowires fabricated using 0.400 g PVP.

(4) 8YSZ NWs fabrication using 0.450 g (18%) PVP

The 8YSZ nanowires fabricated from a solution containing 18% PVP showed a broad histogram with tail as shown in Figure 219 and were measured to have an average nanowire diameter of $103 \pm 73$ nm. The TEM and EDX analysis were very similar to the sample prepared with 16% PVP solution as shown in Figures 217 and 218, respectively.

Figure 219: Histogram of annealed 8YSZ nanowire diameters fabricated using 0.450 g PVP.
Figure 220: SEM images showing 8YSZ (a,b) nanofibers and (c,d) nanowires fabricated using 0.450 g PVP.

Figure 221: (a,b,c) TEM analysis of the NWs fabricated using 18% (0.450g) PVP and (d) its lattice spacing indicating the presence of the cubic phase.
The EDX analysis showed the characteristic peaks relevant to Zr and Y with an quantitative analysis resulting in a Y:Zr At % of 16:84 (Figure 222).

![Figure 222: EDX spectrum of annealed 8YSZ nanowires fabricated using 0.450 g PVP.](image)

Overall, the YSZ nanowire diameter showed no sensitivity to an increase in the PVP mass as shown in Figure 223. The average diameters and the standard deviations are summarized below in Table 37. The EDX maps of the 8YSZ nanowires showed homogeneous distribution of all the species as shown in Figure 224.

<table>
<thead>
<tr>
<th>PVP mass % (mass/g)</th>
<th>Average nanowire diameters (nm)</th>
<th>Standard deviation (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12% (0.300 g)</td>
<td>101</td>
<td>72</td>
</tr>
<tr>
<td>14% (0.350 g)</td>
<td>87</td>
<td>54</td>
</tr>
<tr>
<td>16% (0.400 g)</td>
<td>112</td>
<td>69</td>
</tr>
<tr>
<td>18% (0.450 g)</td>
<td>103</td>
<td>76</td>
</tr>
</tbody>
</table>
Figure 223: Dependence of 8YSZ nanowire diameters on PVP mass \%.

Figure 224: Typical EDX map of 8YSZ NWs produced in this set of experiment where the PVP mass was varied. This figure shows the (a) STEM image of the NWs being analyzed, EDX map of (b) O, (c) Y and (d) Zr species.

### 3.4.3.2 8YSZ NWs fabrication with varying Zr:Y ratio

In this set of experiments only the Y precursor was increased in relation to the Zr(O\(^t\)Bu\(_4\)) mass to evaluate its effect on the resulting nanowire diameters. Once again, case the results include only the annealed NWs histograms and the SEM image of the nanofibers and nanowires. For the purpose of this set of experiments, the analysis and discussion for all the different Y:Zr ratios will be presented after the histograms and SEM images are shown. In this section ZrO\(_2\):Y\(_2\)O\(_3\) ratios of 96:4, 92:8, and 88:12 are abbreviated as 4YSZ, 8YSZ, and 12YSZ, respectively.
(1) 8YSZ NWs fabrication using ZrO_2:Y_2O_3 = 96:4

Average nanowire diameter: 316 ± 70 nm

Figure 225: Histogram of annealed 4YSZ nanowire diameters.

Figure 226: SEM images showing (a,b) nanofibers and (c,d) nanowires composed of 4YSZ.
Figure 227: EDX quantitative analysis of 4YSZ nanowires.

(2). 8YSZ NWs fabrication using ZrO$_2$:Y$_2$O$_3$ = 92:8

Figure 228: Histogram of annealed 8YSZ nanowire diameters.
Figure 229: SEM images showing (a,b) nanofibers and (c,d) nanowires composed of 8YSZ.

(3). 8YSZ NWs fabrication using ZrO$_2$:Y$_2$O$_3$ = 88:12

![Histogram of annealed 12YSZ nanowire diameters.](image)

Average nanowire diameter:
297 ± 60 nm

Figure 230: Histogram of annealed 12YSZ nanowire diameters.
Figure 231: SEM images showing (a,b) nanofibers and (c,d) nanowires composed of 12YSZ.

Figure 232: EDX quantitative analysis of 12YSZ.
Table 38: Dependence of 8YSZ NW diameters on Y$_2$O$_3$% in YSZ

<table>
<thead>
<tr>
<th>Y:Zr composition</th>
<th>Y% in YSZ</th>
<th>Nanowire diameter (nm)</th>
<th>Std. Dev. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4Y96Zr</td>
<td>4</td>
<td>316</td>
<td>70</td>
</tr>
<tr>
<td>8Y92Zr</td>
<td>8</td>
<td>203</td>
<td>43</td>
</tr>
<tr>
<td>12Y8Zr</td>
<td>12</td>
<td>297</td>
<td>60</td>
</tr>
</tbody>
</table>

Figure 233: Annealed nanowire diameter dependence on changes in the Y$_2$O$_3$ mol%.

Figure 234: Typical XRD spectrum observed during the nanowires fabrication process in this set of experiments where the Y$_2$O$_3$ mol% was varied. The superscript $c$ represents cubic phase of ZrO$_2$. XRD spectrum shown here is has Y$_2$O$_3$:ZrO$_2$ ratio of 8:92.
Figure 235: TEM images of annealed 12YSZ nanowires.

The annealed nanowire diameters showed an initial decrease followed by an increase while increasing in the relative Y content in the 8YSZ nanowires (Figure 233). The average nanowire diameters and standard deviations are presented in Table 38. The histogram analysis did not show the presence of a dual nanowire diameter system as observed in other systems previously. However, the SEM image (Figure 231) demonstrated that the nanofibers form significant beading when the Y content was increase to 12%. This could be due to a phase separation of $Y(EHx)_3$
during the sol-gel reaction process. Further investigation is necessary to evaluate this outcome. The TEM analysis (Figure 235) showed the presence of cubic ZrO\textsubscript{2} crystallites fused together to result in the formation of the annealed nanowires. This result is confirmed by the XRD analysis (Figure 234) which showed the presence of only the cubic phase in the resulting nanowires associated with all the Y:Zr ratios addressed in this set of experiments.

3.4.3.3 Investigation of sol-gel solution aging time on 8YSZ nanofiber diameters

![Diagram showing sol-gel solution aging time analysis](image)

Figure 236: Scheme showing the outline of the YSZ sol-gel reaction time analysis for different sets of PVP masses.

In this investigation, the sol-gel reaction aging time was evaluated as shown in the scheme above. The nanofibers were fabricated using three different PVP masses followed by a variation in aging for the mentioned periods of time. The solutions were then electrospun and the nanofiber
diameters measured to determine any variation in the resulting nanofibers in relation to the aging time. For this section the results are presented first followed by an analysis of the overall trend and discussion.

**PVP mass = 0.25 g**

Aging time = 1 hour  
Aging time = 2 hours  
Aging time = 3 hours

![SEM images](a)(b)(c)

Figure 237: SEM image of the nanofibers fabricated with 0.25 g PVP along with the histogram with the corresponding aging times of 1, 2, and 3 hours.
Figure 238: SEM image of the nanofibers fabricated with 0.30 g PVP along with the histogram with the corresponding aging times of 1, 2, and 3 hours.
Overall, the samples containing 0.25 g, 0.30 g and 0.35 g PVP demonstrated insensitivity with regard to the nanofiber diameters with increasing PVP masses investigated in this series. Figure 240 shows the relative changes in the measured nanofiber diameters for this series.
Figure 240: Overall relationship between the nanofibers diameters and sol-gel aging times of three different PVP masses indicated.
3.4.3.4 8YSZ NWs film flexibility and thickness evaluation based on the sol-gel solution volume dispensed during electrospinning process.

This investigation resulted from an observation made during the nanowires fabrication process. It was observed that when a nanowire film of 8YSZ had a thickness between ~10 µm to 15 µm it was highly flexible and could be bent easily. This was a significant discovery, as ceramic materials like ZrO₂ have been known to be extremely brittle. For this purpose, a sample was mounted against a protractor (Figure 241) and annealed nanowire film of thickness ~ 15 µm bent using the tip of a stick (Figure 242). The images presented shows bending of an annealed 8YSZ NW film at angles: (a) 45°, (b) 90°, (c) 135° and (d) 180° against a protractor placed in the background.

Following this, previously fabricated annealed NWs film thickness were also measured and plotted against the volume of sol-gel solution dispensed to fabricate the films. The SEM images of the annealed nanowires thickness are shown in Figure 243 and the relationship between the thickness and volume dispensed during electrospinning is displayed in Figure 244.

Figure 241: (a) Protractor and (b) annealed nanowire sample attached to a glass slide that was placed in front of the protractor for the bending experiment.
Figure 242: Images showing the bending of an annealed nanowire film with thickness ~ 15 µm prepared from a sol-gel solution volume of 0.7 ml solution being bent at (a) 45°, (b) 90°, (c) 135° and (d) 180° against a protractor placed in the background.

Figure 243: SEM images of the nanowire film thickness prepared using (a) 0.25 ml, (b) 0.50 ml, (c) 0.75 ml, (d) 1.00 ml and (e) 1.25 ml.
Other samples prepared using sol-gel solution volume more than 2.0 ml resulted in nanowire films greater than 50 µm which were extremely brittle (Figure 245).

Figure 245: Other films with sol-gel solution volume dispensed above 2.0 ml showed film thickness to be greater than 50 µm.

3.5 Chapter III Conclusions

In this chapter ZrO₂ and 8YSZ NWs were fabricated using the sol-gel route in combination with an electrospinning technique and annealing. It was observed that the Zr(O'Bu)₄
was a better starting material than Zr(O^tBu)_4 for the fabrication of ZrO_2 and 8YSZ NWs in terms of the number of steps required for the fabrication process.

The nanowires fabricated were composed of smaller domains that fused together in the morphology of the PVP template to form 1-D structures. Using the sol-gel route, ZrO_2 nanowires showed a sensitivity towards the changes in Zr(O^tBu)_4 and PVP mass. Zr(O^tBu)_4 precursor mass was varied from 0.050 g to 0.200 g to obtain nanowires with an average diameter of 104 (± 26) nm to 200 (± 95) nm, respectively. ZrO_2 nanowires fabricated with 0.250 g to 0.400 g PVP resulted in diameters ranging from 160 (± 40) nm to 300 (± 100) nm, respectively. The sol-gel reaction aging time showed an insensitivity towards the resulting nanowire diameters for ZrO_2. Unlike ZrO_2 NWs, YSZ nanowire diameters were insensitive toward the changes in PVP mass, Y content in YSZ and reaction aging time. YSZ NWs produced by varying PVP mass and Y:Zr ratio resulted in nanowire diameters ~ 100 nm and ~ 300 nm, respectively.

For the ZrO_2 nanowires samples prepared here, the TEM lattice spacing analysis and the XRD together confirmed the presence of mostly monoclinic ZrO_2. Samples containing Y_2O_3 resulted in purely cubic phase ZrO_2. In contrast, YSZ NW materials consistently produced structures that are of a cubic phase. Finally, the thickness of the nanowires films has shown to have an impact on the film flexibility. The ideal volume needed to be dispensed to obtain nanowires films was identified to be ~ 0.75 ml which resulted in film thickness (~15 µm) that allowed most flexibility.
Chapter IV

Fabrication, characterization, and analysis of bismuth oxide (Bi$_2$O$_3$) and tungsten (V) oxide doped Bi$_2$O$_3$ (WBO) nanowire films produced using a sol-gel method in conjugation with electrospinning technique.
4.0 Introduction

This chapter focuses on the fabrication, characterization, and properties of bismuth oxide (Bi$_2$O$_3$) and tungsten (V) oxide doped Bi$_2$O$_3$ (WBO) NW thin films that are produced using a sol-gel reaction in conjunction with an electrospinning process and post-fabrication annealing. The sol-gel process ideally provides control over the nanoparticle size and morphology by carefully controlling the reaction parameters (pH, rate of reaction, and types of precursor) associated with the reactions in a manner similar to the ZrO$_2$ and YSZ nanowire fabrication (via sol-gel route) presented in the previous chapter.

4.1 Brief overview on Bi$_2$O$_3$ and WBO as oxide ionic conductors

Bi$_2$O$_3$ has been the focus of interest for applications as solid state electrolyte in solid oxide fuel cells and oxide gas sensors.$^{190,191}$ δ-Bi$_2$O$_3$ has been reported to have twice the amount of oxygen ion conductivity compared to YSZ in solid oxide fuel cells (SOFCs).$^{192}$ The low operating temperature for δ-Bi$_2$O$_3$ (compared to YSZ) makes it an ideal candidate for the intermediate temperature (IT) range (700°C to 800°C) electrolyte for SOFCs.$^{193-195}$

Methods like electrodeposition$^{196}$, metalorganic chemical vapor deposition (MOCVD)$^{197}$, a template assisted route$^{198}$, vapor-liquid-solid (VLS) methods$^{199,200}$, a carbothermal reaction$^{201}$, a sol-gel reaction$^{202}$, a solvothermal method$^{203}$, a microwave-assisted method$^{204}$, an electrospinning (using Bi(NO$_3$)$_3$ as precursor) technique$^{205}$ have been used to fabricate Bi$_2$O$_3$ nanomaterials.

Several polymorphs of Bi$_2$O$_3$ have been reported: α-Bi$_2$O$_3$, β-Bi$_2$O$_3$, γ-Bi$_2$O$_3$, δ-Bi$_2$O$_3$, and ε-Bi$_2$O$_3$, which correspond to the monoclinic, tetragonal, body centered cubic (bcc), cubic and triclinic crystal phases, respectively.$^{206-209}$ Out of all these phases, β, γ, and δ are the only phases that exhibit ionic conductivity. α-Bi$_2$O$_3$ is an electrical conductor and ε has shown to be an insulator.$^{210-213}$
Takahashi and coworkers were the first to demonstrate that only the δ-phase Bi$_2$O$_3$ had the highest O$^{2-}$ conductivity when doped with other metal oxides.$^{214}$ Harwig carried out an extensive investigation on the conductivity of the different Bi$_2$O$_3$ phases as a function of temperature (Figure 246) where he demonstrated a decrease in Bi$_2$O$_3$ conductivity with a decrease in the operating temperature.$^{211,212}$

![Figure 246: Conductivity of the different Bi$_2$O$_3$ phases as a function of temperature [adopted from Ref 210].](image)

Undoped δ-Bi$_2$O$_3$ exists only between 728°C and 823°C (Bi$_2$O$_3$ m.p.) which transforms to α-Bi$_2$O$_3$ below 728°C. The two metastable phases β-Bi$_2$O$_3$ and γ-Bi$_2$O$_3$ have been reported to form (while cooling from molten Bi$_2$O$_3$) at 650°C and 628°C, respectively, and are often facilitated by the presence of impurities.$^{211,212,215}$ Mairesse briefly explained the cause for high ionic conductivity in δ-Bi$_2$O$_3$ as due to the following factors: (1) a vacancy of one oxygen atom at every fourth site in the fluorite-type δ-Bi$_2$O$_3$ crystal structures allows O$^{2-}$ effectively to jump during migration; (2) lone pair electrons in the relatively large valence shell of Bi$^{3+}$ are easily polarized to facilitate the O$^{2-}$ migration across the lattice; and (3) the ability of oxygen atoms (in δ-Bi$_2$O$_3$) to align in a specific orientation which facilitates in the mobility of the O$^{2-}$ species.$^{111,213,216}$
The use of dopants to stabilize the $\delta$-$\text{Bi}_2\text{O}_3$ to room temperature has been extensively investigated. Takahashi and coworkers have reported several dopants with their stoichiometric ratios that resulted in the stabilization of $\delta$-$\text{Bi}_2\text{O}_3$ at room temperature (Table 39).\textsuperscript{217} Watanabe and coworkers also have shown a high $\text{O}^2^-$ conductivity (with reduced activation energy) when 22 mol\% $\text{WO}_3$ was used to stabilize $\delta$-$\text{Bi}_2\text{O}_3$.\textsuperscript{213,218} For the purpose of this dissertation, only $\text{WO}_3$ has been used as a dopant for the stabilization of the $\delta$-$\text{Bi}_2\text{O}_3$.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Stoichiometric quantities (x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{Bi}_2\text{O}<em>3)</em>{1-x}(\text{Y}_2\text{O}_3)_x$</td>
<td>0.25-0.43</td>
</tr>
<tr>
<td>$(\text{Bi}_2\text{O}<em>3)</em>{1-x}(\text{Gd}_2\text{O}_3)_x$</td>
<td>0.35-0.50</td>
</tr>
<tr>
<td>$(\text{Bi}_2\text{O}<em>3)</em>{1-x}(\text{Nb}_2\text{O}_3)_x$</td>
<td>0.15-0.26</td>
</tr>
<tr>
<td>$(\text{Bi}_2\text{O}<em>3)</em>{1-x}(\text{Ta}_2\text{O}_3)_x$</td>
<td>0.20-0.25</td>
</tr>
<tr>
<td>$(\text{Bi}_2\text{O}<em>3)</em>{1-x}(\text{WO}_3)_x$</td>
<td>0.22-0.27</td>
</tr>
</tbody>
</table>

4.2 Instruments used for characterization

The structural and chemical characterization and analysis of the nanowires were performed using field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). Elemental characterization was done using electron dispersive x-ray spectroscopy (EDS/EDX) along with XRD to analyze phase composition of the fabricated $\text{Bi}_2\text{O}_3$ and WBO NWs. Details of these different characterization techniques, instruments, and sample preparation processes have been discussed earlier in this dissertation (Section 2.2).

4.3 Experimental section

As with $\text{ZrO}_2$ and YSZ, $\text{Bi}_2\text{O}_3$ and WBO nanowire fabrication using the sol-gel route was carried out in three steps: (1) mixing the reactants; (2) fabricating nanofibers using the
electrospinning process; and (3) annealing process (two stage) to remove the polymer template and promote crystallization of the metal oxide domains within the nanowires. Bismuth 2-ethylhexanoate (Bi(O$_2$C$_8$H$_{16}$)$_3$), 90+%, Alfa Aesar) and tungsten (V) ethoxide (W(OCH$_3$)$_5$, 95%, Gelest) were used to fabricate Bi$_2$O$_3$ and WBO NWs, respectively. In this chapter, Bi(O$_2$C$_8$H$_{16}$)$_3$ and W(OCH$_3$)$_5$ are abbreviated as Bi(2EHx)$_3$ and W(OEt)$_5$, respectively.

4.1.1 Bi$_2$O$_3$ NWs fabrication using a sol-gel method

Bismuth alkoxides, such as bismuth iso-propoxide (Bi(OCH$_3$)$_3$, 99%, Alfa Aesar) and bismuth tert-pentoxide (Bi(OCH$_{11}$)$_3$, 97+%, Alfa Aesar) were initially used as the Bi$_2$O$_3$ NWs precursor. However, due to the lack of precursor solubility in anhydrous solvents, Bi(2EHx)$_3$ was ultimately chosen for Bi$_2$O$_3$ NWs fabrication. The reduced solubility of the Bi-alkoxides might be due to their existence as polymeric chains.$^{219}$

The Bi$_2$O$_3$ NWs were fabricated by adding a given quantity of Bi(2EHx)$_3$ to a vial containing 0.80 ml EtOH and mixed vigorously with a magnetic stir bar for ~ 5 min. Measured amounts of PVP were placed in a separate vial followed by addition of ~ 2.37 ml EtOH. The resulting mixture was vigorously mixed until a clear viscous solution was obtained. This clear solution was then added dropwise to the Bi(2EHx)$_3$/EtOH solution over a period of 10-15 min. Once added, the Bi(2EHx)$_3$/PVP/EtOH clear solution was allowed to mix for an additional 10 min before transferring to a 5 ml Popper brand syringe for electrospinning. The measured amounts of Bi(2EHx)$_3$, PVP and EtOH used are shown in Table 40. The electrospinning and annealing procedure used was similar to the one described in the previous chapter (Section 2.2.1). Table 41 shows the typical electrospinning and annealing parameters used for the Bi$_2$O$_3$ NWs fabrication process.
Table 40: Bi₂O₃ nanofibers produced by sol-gel route

<table>
<thead>
<tr>
<th>Reaction Set No.</th>
<th>Description</th>
<th>Bi(2EHx)₃ mass (g)</th>
<th>PVP mass (g)</th>
<th>Solvent vol. (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Studying the effect of varying Bi precursor mass on nanowire diameter and morphology</td>
<td>~ 0.100 g</td>
<td>~ 0.350 g</td>
<td>~ 3.17 ml EtOH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>~ 0.200 g</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>~ 0.300 g</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>~ 0.400 g</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>~ 0.500 g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Studying the effect of varying PVP mass on nanowire diameter and morphology</td>
<td>~ 0.100 g</td>
<td>~ 0.150 g</td>
<td>~ 3.17 ml EtOH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>~ 0.250 g</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>~ 0.350 g</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>~ 0.450 g</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>~ 0.550 g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Studying the effect of annealing temperature on nanowire diameters and morphologies.</td>
<td>~ 0.200 g</td>
<td>~ 0.350 g</td>
<td>~ 3.17 ml EtOH</td>
</tr>
</tbody>
</table>

Annealing temperature and duration of heating:
- 350°C for 10 hours
- 400°C for 1.5 hours
- 450°C for 1.5 hours
- 500°C for 1.5 hours
- 550°C for 1.5 hours
- 600°C for 1.5 hours
- 650°C for 1.5 hours

Table 41: Electrospinning and annealing parameters used for Bi₂O₃ NWs fabrication.

<table>
<thead>
<tr>
<th>Electrode distance (cm)</th>
<th>Voltage (kV)</th>
<th>Annealing temperatures (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21 cm</td>
<td>20 kV</td>
<td>Step 1: 220°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Step 2: 550°C</td>
</tr>
</tbody>
</table>

In this chapter the three separate sets of experiments involving the fabrication of Bi₂O₃ NWs were carried out: (1) studying the effect of varying Bi(2EHx)₃ mass on Bi₂O₃ NW diameters and morphologies; (2) studying the effect of varying PVP mass on Bi₂O₃ NW diameters and
morphologies; and (3) studying the effect of annealing temperature on NW diameters and morphologies. It was necessary to evaluate the effect of annealing temperature on the NWs morphology because of Bi$_2$O$_3$ crystal phases are sensitive to the changes in the temperature.

4.3.1 WBO NWs fabrication using sol-gel method

Fabrication of WBO NWs were done in a similar manner to that described for Bi$_2$O$_3$ NWs. In this case, Bi(2EHx)$_3$ was measured into a vial containing 0.8 ml EtOH and mixed thoroughly. In a separate vial containing 0.5 ml EtOH, measured amounts of W(OEt)$_5$ were added and mixed thoroughly. After ~ 5 min of stirring the W(OEt)$_5$/EtOH solution were added dropwise to the clear yellow solution of Bi(2EHx)$_3$/EtOH and was allowed to mix for ~ 10 min. During that time, PVP was measured and added to a separate vial containing 1.97 ml EtOH to form a clear viscous solution. Finally, this PVP/EtOH solution was added dropwise to the vial containing the Bi(2EHx)$_3$/W(OEt)$_5$/EtOH solution. The resulting clear viscous solution was allowed to mix for an additional ~10 min before transferring to a syringe for electrospinning. The electrospinning and annealing parameters used for the WBO NWs fabrication were similar to ones used for the Bi$_2$O$_3$ NWs fabrication using the sol-gel route.

Two sets of experiments involving WBO NWs fabrication were carried out. These include: (1) studying the effects of varying PVP mass on nanofiber morphology, keeping Bi and W ratio fixed; and (2) studying the effect of varying W:Bi ratio on nanofiber morphology. The relevant masses used in these experiments are reported in Table 42. The results pertaining to both Bi$_2$O$_3$ and WBO NWs are presented and discussed in the next section.
### Table 42: WBO nanofibers produced by sol-gel route

<table>
<thead>
<tr>
<th>Reaction Set No.</th>
<th>Description</th>
<th>W(OEt)$_3$ mass (g)</th>
<th>Bi(2EHx)$_3$ mass (g)</th>
<th>W(OEt)$_3$:Bi(2EHx)$_3$ mol % ratios</th>
<th>PVP mass (g)</th>
<th>Solvent vol. (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Studying effects of varying PVP mass on nanofiber morphology, keeping Bi and W ratio fixed</td>
<td>~ 0.020 g</td>
<td>~ 0.150 g</td>
<td>25%W:75%Bi</td>
<td>~ 0.25 g</td>
<td>~3.17 ml EtOH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>~ 0.020 g</td>
<td>~ 0.200 g</td>
<td>8%W:92%Bi</td>
<td>~ 0.35 g</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>~ 0.030 g</td>
<td>~ 0.170 g</td>
<td>15%W:85%Bi</td>
<td>~ 0.35 g</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>~ 0.050 g</td>
<td>~ 0.150 g</td>
<td>25%W:75%Bi</td>
<td>~ 0.35 g</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>~ 0.070 g</td>
<td>~ 0.130 g</td>
<td>35%W:65%Bi</td>
<td>~ 0.35 g</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>~ 0.090 g</td>
<td>~ 0.110 g</td>
<td>45%W:55%Bi</td>
<td>~ 0.35 g</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Studying the effect of varying W:Bi ratio on nanofiber morphology</td>
<td>~ 0.020 g</td>
<td>~ 0.200 g</td>
<td>8%W:92%Bi</td>
<td>~ 0.35 g</td>
<td>~3.17 ml EtOH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>~ 0.030 g</td>
<td>~ 0.170 g</td>
<td>15%W:85%Bi</td>
<td>~ 0.35 g</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>~ 0.050 g</td>
<td>~ 0.150 g</td>
<td>25%W:75%Bi</td>
<td>~ 0.35 g</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>~ 0.070 g</td>
<td>~ 0.130 g</td>
<td>35%W:65%Bi</td>
<td>~ 0.35 g</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>~ 0.090 g</td>
<td>~ 0.110 g</td>
<td>45%W:55%Bi</td>
<td>~ 0.35 g</td>
<td></td>
</tr>
</tbody>
</table>

### 4.4 Results and Discussion

#### 4.4.1 Bi$_2$O$_3$ NWs fabrication using a sol-gel method

In this section, the results obtained from the three sets of Bi$_2$O$_3$ NWs fabrication experiments are presented. Three sets of experiments were conducted where the Bi$_2$O$_3$ NWs diameters were evaluated while changing one variable in each case. The variables that were varied were: (1) Bi(2EHx)$_3$ mass; (2) PVP mass; and (3) annealing temperature. In each case SEM, nanofiber and nanowire diameter histogram, EDX and XRD data analysis are presented.
4.4.1.1 Effect of changes in Bi(2EHx)$_3$ mass on Bi$_2$O$_3$ NW diameters

In this set of experiments, Bi(2EHx)$_3$ precursor mass was varied from 0.10 g to 0.50 g as shown in the reaction scheme below. All other reactant masses, electrospinning and annealing parameters were kept constant during the NWs fabrication process.

\[
\text{Bi(2EHx)$_3$ + PVP} \quad \xrightarrow{\text{(a) EtOH}} \quad \text{Bi(2EHx)$_3$ - PVP nanofibers} \\
\quad \xrightarrow{\text{(b) Electrospinning}} \\
\text{Bi(2EHx)$_3$ masses used:} \\
1. 0.10 g \\
2. 0.20 g \\
3. 0.30 g \\
4. 0.40 g \\
5. 0.50 g \\
\quad \xrightarrow{\text{(c) gradual annealing}}
\]

(1). Bi$_2$O$_3$ NWs fabrication using 0.10 g Bi(2EHx)$_3$

Structures fabricated using 0.10 g Bi(2EHx)$_3$ produced Bi$_2$O$_3$/PVP nanofibers without the presence of any debris or beads (Figure 247 (b)) and were measured to have an average diameter of 428 (± 96) nm. The diameter distribution for both the nanofibers (before annealing) and nanowires (after annealing) are shown in Figure 248 (a). The nanowires were measured to have an average diameter of 138 (± 44) nm and the distribution is shown in Figure 248 (b). The SEM images of the NWs showed (Figure 247 (d)) fused interlinked 1-D Bi$_2$O$_3$ nanowires.

The quantitative EDX analysis (Figure 249) showed a Bi:O At\% ratio of ~ 2:3 which is consistent with the Bi$_2$O$_3$ formula. The characteristic EDX peaks of O and Bi are consistent with the values previously reported.$^{220}$
Figure 247: SEM images of Bi$_2$O$_3$ NWs fabricated using 0.10 g Bi(2EHx)$_3$. In this figure, the scale bars associated with the images (a), (b), (c) and (d), all correspond to 1 µm.

Figure 248: Bi$_2$O$_3$ (a) nanofiber and (b) nanowire diameter histograms fabricated using 0.10 g Bi(2EHx)$_3$. 

Average nanofiber diameter: 428 ± 96 nm
Average nanowire diameter: 138 ± 44 nm
Figure 249: EDX analysis of Bi$_2$O$_3$ NWs fabricated using 0.10 g Bi(2EHx)$_3$. The inset shows the region of nanowires that was analyzed.

(2). Bi$_2$O$_3$ NWs fabrication using 0.20 g Bi(2EHx)$_3$

SEM images of the nanofibers and nanowires prepared with 0.20 g Bi(2EHx)$_3$ are shown in Figure 250. The average nanofiber diameter was measured to be 422 (± 119) nm and the distribution is shown in Figure 251 (a). The nanowires had an average diameter of 198 (± 52) nm (Figure 251 (b)) which is slightly higher than the nanowires fabricated using 0.10 g Bi(2EHx)$_3$.

The EDX analysis (Figure 252) indicated a Bi:O At% ratio of ~ 1:1. It can be speculated that the slightly lower concentration of oxygen atoms is due to oxygen migration as a consequence to the 200 kV TEM electron beam.
Figure 250: SEM images of Bi$_2$O$_3$ NWs fabricated using 0.20 g Bi(2EHx)$_3$. In this figure, the scale bars associated with the images (a), (b), (c) and (d) correspond to 10 µm, 1 µm, 1 µm and 1 µm, respectively.

Figure 251: Bi$_2$O$_3$ (a) nanofiber and (b) nanowire diameter histograms fabricated using 0.20 g Bi(2EHx)$_3$. 

Average nanofiber diameter: $422 \pm 119$ nm

Average nanowire diameter: $198 \pm 52$ nm
Figure 252: EDX analysis of Bi$_2$O$_3$ NWs fabricated using 0.20 g Bi(2EHx)$_3$. The inset shows the region of nanowires that was analyzed.

(3). Bi$_2$O$_3$ NWs fabrication using 0.30 g Bi(2EHx)$_3$

Bi$_2$O$_3$ nanofibers fabricated using 0.30 g Bi(2EHx)$_3$ showed similar morphologies (Figure 253 (a)) as observed in samples prepared with 0.10 g and 0.20 g Bi(2EHx)$_3$. However, after annealing, the nanowires did not retain the morphology of its polymer template (Figure 253 (d)). The nanofibers and nanowires were measured to have an average diameter of 384 (± 78) nm (Figure 254 (a)) and 183 (± 46) nm (Figure 254 (b)), respectively.

The quantitative EDX analysis of Bi$_2$O$_3$ (Figure 255) revealed a Bi:O At% ratio of ~3:1 which is not consistent from the stoichiometric ratio in the formula Bi$_2$O$_3$. This can also be due to the high O$^2-$ mobility observed under electron irradiation.
Figure 253: SEM images of Bi$_2$O$_3$ NWs fabricated using 0.30 g Bi(2EHx)$_3$. In this figure, the scale bars associated with the images (a), (b), (c) and (d) correspond to 10 µm, 1 µm, 1 µm and 1 µm, respectively.

Figure 254: Bi$_2$O$_3$ (a) nanofiber and (b) nanowire diameter histograms fabricated using 0.30 g Bi(2EHx)$_3$.
Figure 255: EDX analysis of Bi$_2$O$_3$ NWs fabricated using 0.30 g Bi(2EHx)$_3$. The inset shows the region of nanowires that was analyzed.

(4). Bi$_2$O$_3$ NWs fabrication using 0.40 g Bi(2EHx)$_3$

Nanofibers produced using 0.40 g Bi(2EHx)$_3$ showed the presence of particles infused within the nanofibers as shown in Figure 257 (b). This could be due to the formation of Bi$_2$O$_3$ precipitates before the electrospinning was performed to produce the nanofibers. The nanofibers were measured to have an average diameter of 419 (± 183) nm (Figure 258 (a)). The SEM images of the nanowires showed a higher degree of dislocation of atoms positioned at the nanowire surface (Figure 257 (d)). This resulted in the coalescence of the NWs and an increase in the nanowire diameters. These nanowires were measured to have an average diameter of 231 (± 67) nm (Figure 258 (b)).

The fusion of the Bi$_2$O$_3$ nanowires at elevated temperature likely occurs via several mechanisms as proposed by Jonghe and Rahaman (Figure 256). The authors indicated that
during the ceramic sintering process, when the particles are heated above the softening temperature, they are driven to coalesce together to minimize the surface free energy.\textsuperscript{222}

**Mechanisms:**
1. Surface diffusion
2. Lattice diffusion (from surface)
3. Vapor transport
4. Grain boundary diffusion
5. Lattice diffusion (from the grain boundary)
6. Plastic flow (stress and strain induced)

Figure 256: Solid state sintering mechanism of two particles. Image adapted from pg 191 of Ref 221.

EDX analysis (Figure 259) was performed on the particulates observed on the nanofibers. The EDX quantitative analysis of the particles and the surrounding regions on the NWs were conducted and were measured to have a similar Bi:O At% ratio of \~1:3 compared to the other samples fabricated in this series of experiments. Therefore, the cause of the particle formation was not determined. The average Bi:O At% ratio of the annealed nanowires were determined to be 60.14:39.86 (\~3:2).
Figure 257: SEM images of Bi$_2$O$_3$ NWs fabricated using 0.40 g Bi(2EHx)$_3$. In this figure, the scale bars associated with the images (a), (b), (c) and (d), all correspond to 1 µm.

![SEM images of Bi$_2$O$_3$ NWs](image)

Figure 258: Bi$_2$O$_3$ (a) nanofiber and (b) nanowire diameter histograms fabricated using 0.40 g Bi(2EHx)$_3$.

![Diameter histograms](image)
Figure 259: EDX analysis of particulates incorporated with Bi$_2$O$_3$ nanofibers fabricated using 0.40g Bi(2EHx)$_3$.

(5). Bi$_2$O$_3$ NWs fabrication using 0.50 g Bi(2EHx)$_3$

SEM images of the nanofibers and nanowires fabricated using 0.50 g of Bi(2EHx)$_3$ are shown in Figures 260 (a, b) and Figures 260 (c, d), respectively. The nanofibers and nanowires were measured to have an average diameter of 290 ($\pm$ 121) nm (Figure 261 (a)) and 203 ($\pm$ 66) nm (Figure 261 (b)). The annealed nanowires showed similar fusion of particles (Figure 260 (d)) as observed in the previous Bi(2EHx)$_3$ masses (0.10 g, 0.20 g, 0.30 g, 0.40 g) used in this series of experiments.

EDX analysis showed a Bi:O At% ratio of $\sim$1:3 which is slightly deviated from the 2:3 as represented in the formula, Bi$_2$O$_3$. This fluctuation in the ratio can once again be associated with the high mobility of oxygen species induced by the localized heating by the TEM electron beam.
Figure 260: SEM images of Bi$_2$O$_3$ NWs fabricated using 0.50 g Bi(2EHx)$_3$. In this figure, the scale bars associated with the images (a), (b), (c) and (d) correspond to 10 µm, 1 µm, 10 µm and 1 µm, respectively.

Figure 261: Bi$_2$O$_3$ (a) nanofiber and (b) nanowire diameter histograms fabricated using 0.50 g Bi(2EHx)$_3$. 

(a) Average nanofiber diameter: $290 \pm 121$ nm

(b) Average nanowire diameter: $203 \pm 66$ nm
Figure 262: EDX analysis of Bi$_2$O$_3$ NWs fabricated using 0.50 g Bi(2EHx)$_3$. The inset shows the region of nanowires that was analyzed.

(6). Overall nanofiber and nanowire diameter analysis

The average Bi$_2$O$_3$ nanofiber diameters (fabricated by varying the Bi(2EHx)$_3$ mass) are summarized in Table 43. The correlation between the average nanofiber diameters of nanofibers and Bi(2EHx)$_3$ masses used to fabricate the nanofibers is shown in Figure 263. The average nanofiber diameter was found to be insensitive to the changes in Bi(2EHx)$_3$ masses. There was a slight decrease in the diameters observed for the sample prepared using 0.50 g Bi(2EHx)$_3$, but due to the large standard deviation no definitive conclusion could be drawn.
Table 43: Average $\text{Bi}_2\text{O}_3$ nanofiber diameters fabricated using variable $\text{Bi}(2\text{EHx})_3$ masses.

<table>
<thead>
<tr>
<th>$\text{Bi}(2\text{HEx})_3$ mass (g)</th>
<th>Average nanofiber diameters (nm)</th>
<th>Standard deviation of average nanofiber diameters (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>428</td>
<td>96</td>
</tr>
<tr>
<td>0.20</td>
<td>422</td>
<td>119</td>
</tr>
<tr>
<td>0.30</td>
<td>384</td>
<td>78</td>
</tr>
<tr>
<td>0.40</td>
<td>419</td>
<td>183</td>
</tr>
<tr>
<td>0.50</td>
<td>290</td>
<td>121</td>
</tr>
</tbody>
</table>

Figure 263: Plot showing dependence of nanofiber diameter on $\text{Bi}(2\text{EHx})_3$ mass.

The average $\text{Bi}_2\text{O}_3$ nanowire diameters are summarized in Table 44. The overall trend showed a gradual increase in the diameter with an increase in $\text{Bi}(2\text{EHx})_3$ mass (Figure 264). This is consistent with the theoretical trend, as the increase in mass supplies additional reactant material which results in an increase of the average nanowire diameters.
Table 44: Average Bi$_2$O$_3$ nanowire diameters fabricated using variable Bi(2EHx)$_3$ masses.

<table>
<thead>
<tr>
<th>Bi(2HE$_3$) mass (g)</th>
<th>Average nanowire diameters (nm)</th>
<th>Standard deviation of average nanowire diameters (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>138</td>
<td>44</td>
</tr>
<tr>
<td>0.20</td>
<td>193</td>
<td>52</td>
</tr>
<tr>
<td>0.30</td>
<td>183</td>
<td>46</td>
</tr>
<tr>
<td>0.40</td>
<td>231</td>
<td>67</td>
</tr>
<tr>
<td>0.50</td>
<td>203</td>
<td>66</td>
</tr>
</tbody>
</table>

Figure 264: Bi$_2$O$_3$ average nanowire diameter dependence on Bi(2EHx)$_3$ mass.

(7). Overall EDX analysis

Overall the Bi$_2$O$_3$ NWs presented in this series of experiments showed widely varied Bi:O ratios (Table 45) which is likely due to the high O$^2-$ mobility induced by the electron beam during the analysis.

Table 45: Summary of Bi$_2$O$_3$ EDX At% prepared with varying Bi(2EHx)$_3$ mass.

<table>
<thead>
<tr>
<th>Bi(2EHx)$_3$ mass (g)</th>
<th>Bi At%</th>
<th>O At%</th>
<th>Bi:O</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10 g</td>
<td>42.34</td>
<td>57.22</td>
<td>~2:3</td>
</tr>
<tr>
<td>0.20 g</td>
<td>48.25</td>
<td>51.75</td>
<td>~1:1</td>
</tr>
<tr>
<td>0.30 g</td>
<td>61.67</td>
<td>38.33</td>
<td>~3:1</td>
</tr>
<tr>
<td>0.40 g</td>
<td>60.14</td>
<td>39.86</td>
<td>~3:2</td>
</tr>
<tr>
<td>0.50 g</td>
<td>30.92</td>
<td>69.08</td>
<td>~1:3</td>
</tr>
</tbody>
</table>
(8). Overall XRD analysis

A typical XRD spectrum observed for this set of experiments (Figure 265) shows the corresponding lattice plane reflections of α-Bi₂O₃ and β-Bi₂O₃ that are in agreement with the reported values²²³ for these phases.

![Graph showing XRD reflections of α-Bi₂O₃ and β-Bi₂O₃](image)

Figure 265: Typical XRD spectrum observed in Bi₂O₃ NWs fabricated by varying Bi(2EHx)₃ mass. This is a spectrum associated with Bi₂O₃ NWs fabricated using 0.50 g Bi(2EHx)₃.

(9). Other observations made during this series of experiments

During the electrospinning process, it was also observed that that the nanofiber films adhered to Al foil (used to cover the collecting drum for easy sample removal) more strongly as the Bi(2EHx)₃ mass was increased in this series of experiments. This created some difficulty in removing the nanofibers, thus reducing the amount of the product after the two step annealing process. Figure 266 shows the relative comparison of the quantity and shape/size of the nanofiber films (prepared with 0.50 g, 0.40 g, 0.30 g, 0.20 g and 0.10 g Bi(2EHx)₃ from left to right) after being removed from the Al foil.
Figure 266: Image showing the shape/size of the Bi$_2$O$_3$ nanofibers film fabricated using 0.50 g, 0.40 g, 0.30 g, 0.20 g and 0.10 g Bi(2EHx)$_3$ (left to the right)

4.4.1.2 Effect of changes in PVP mass on Bi$_2$O$_3$ NW diameters

In this section, the results of Bi$_2$O$_3$ NWs (fabricated by varying the PVP mass) are presented. The scheme below provides an overview of the procedure used for Bi$_2$O$_3$ nanofiber fabrication. The detailed quantities of the reagents and parameters used for this fabrication of these nanofibers are presented in Table 40.

\[
\text{Bi(2EHx)$_3$ + PVP} \xrightarrow{(a) \text{EtOH}} \text{Bi(2EHx)$_3$ - PVP nanofibers} \xrightarrow{(b) \text{Electrospinning}} \]

PVP masses used:
1. 0.250 g
2. 0.350 g
3. 0.450 g
4. 0.550 g

(c) gradual annealing

(1). Bi$_2$O$_3$ NWs fabrication using 0.250 g PVP

SEM images of the nanofibers prepared using 0.250 g PVP showed extensive bead formation (Figure 267 (a)) during the electrospinning process. This suggests that the viscosity of the Bi(2EHx)$_3$/PVP/EtOH solution was relatively low for fiber formation. Overall the nanofibers were measured to have an average diameter of 292 (± 87) nm (Figure 268 (a)). SEM images of the
post annealing Bi₂O₃ nanowires (Figure 267 (c)) showed a close network of nanowires with a wide range of diameters. The larger nanowires could have been formed due to fusion of two or more nanowires during the annealing process and resulted in an average nanowire diameter of 222 (± 67) nm (Figure 268 (b)). The EDX analysis of the NWs resulted a Bi:O At% ratio of ~1:1 (Figure 269). This deficiency in oxygen observed in the EDX analysis is likely due to the higher mobility of the O²⁻ under the electron beam irradiation.

Figure 267: SEM images of Bi₂O₃ NWs fabricated using 0.250 g PVP. In this figure, the scale bars associated with the images (a), (b), (c) and (d) correspond to 10 µm, 1 µm, 1 µm and 1 µm, respectively.
Figure 268: Bi$_2$O$_3$ (a) nanofiber and (b) nanowire diameter histograms fabricated using 0.250 g PVP.

Figure 269: EDX analysis of Bi$_2$O$_3$ NWs fabricated using 0.250 g PVP. The inset shows the region of nanowires that was analyzed.

(2). Bi$_2$O$_3$ NWs fabrication using 0.350 g PVP

Bi$_2$O$_3$ nanofibers produced by using 0.350 g PVP showed similar bead formation (Figure 270 (a)) as observed in the previous sample (0.250 g PVP). The nanofibers without the beads were measured to obtain an average nanofiber diameter of 127 (± 44) nm with a histogram containing a
leading tail (Figure 271 (a)). SEM images of the Bi$_2$O$_3$ nanowire film (Figure 270 (d)) clearly showed fusion of adjacent nanofibers during the annealing process (max temperature ~ 550°C). These nanowires were measured to have an average nanowire diameter of 86 (± 21) nm with a bell-shaped size distribution as shown in Figure 271 (b).

The EDX quantitative analysis resulted in a Bi:O ratio of ~ 3:2 which is inconsistent with the formula Bi$_2$O$_3$. It is possible that the e$^-$ beam induced O$^2$- migration which resulted in the formation of Bi$_2$O$_3$/Bi$_2$O$_4$-$x$ type nanostructures, given the earlier reports of Hameed and co-workers where they observed a similar analysis with Bi$_2$O$_3$ nanoparticles.$^{224}$

![Figure 270: SEM images of Bi$_2$O$_3$ NWs fabricated using 0.350 g PVP. In this figure, the scale bars associated with the images (a), (b), (c) and (d) correspond to 10 µm, 1 µm, 1 µm and 100 nm, respectively.](image)
Figure 271: Bi$_2$O$_3$ (a) nanofiber and (b) nanowire diameter histograms fabricated using 0.350 g PVP.

![Bi$_2$O$_3$ Diameter Histograms](image)

Average nanofiber diameter: 127 ± 44 nm

Average nanowire diameter: 86 ± 21 nm

Figure 272: EDX analysis of Bi$_2$O$_3$ NWs fabricated using 0.350 g PVP. The inset shows the region of nanowires that was analyzed.

![EDX Analysis](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>(keV)</th>
<th>Mass%</th>
<th>Sigma</th>
<th>Atom%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>0.525</td>
<td>3.36</td>
<td>0.02</td>
<td>31.21</td>
</tr>
<tr>
<td>Bi M</td>
<td>2.419</td>
<td>96.64</td>
<td>0.08</td>
<td>68.79</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.00</td>
<td></td>
<td>100.00</td>
</tr>
</tbody>
</table>

(3). Bi$_2$O$_3$ NWs fabrication using 0.450 g PVP

Nanofibers prepared using 0.450 g PVP did not produce any beads, as shown in the SEM images in Figure 273 (a). However, it did show the presence of particulates that were trapped inside the nanofibers (Figure 273 (b)) which could be due to Bi$_2$O$_3$ precipitation prior to the
electrospinning process. The nanofibers had an average diameter of 525 (± 193) nm with a wide size distribution (Figure 274 (a)). The nanowires showed retention of its polymer template morphology and were measured to have an average diameter of 149 (± 34) nm (Figure 274 (b)). EDX analysis showed similar ~3:2 ratio of Bi:O, as observed before in NWs prepared with 0.350 g PVP.

Figure 273: SEM images of Bi$_2$O$_3$ NWs fabricated using 0.450 g PVP. In this figure, the scale bars associated with the images (a), (b), (c) and (d) correspond to 1 µm, 1 µm, 1 µm and 100 nm, respectively.
Figure 274: Bi$_2$O$_3$ (a) nanofiber and (b) nanowire diameter histograms fabricated using 0.450 g PVP.

Figure 275: EDX analysis of Bi$_2$O$_3$ NWs fabricated using 0.450 g PVP. The inset shows the region of nanowires that was analyzed.

(4). Bi$_2$O$_3$ NWs fabrication using 0.550 g PVP

The nanofibers obtained using 0.550 g PVP also showed the presence of particles that were incorporated into the nanofibers (Figure 276 (a)). The nanofibers had an average diameter of 714 (± 43) nm with a tailing histogram (Figure 277 (a)). The annealed nanowires showed an
asymmetric distribution of nanowire diameters (Figure 277 (b)) with an average of 171 (± 43) nm. The nanowires were composed of fused domains that were packed together to form the 1-D morphologies (Figure 276 (d)). The EDX analysis provided with a Bi:O At% ratio of ~1:1 (Figure 278).

Figure 276: SEM images of Bi$_2$O$_3$ NWs fabricated using 0.550 g PVP. In this figure, the scale bars associated with the images (a), (b), (c) and (d) correspond to 10 µm, 1 µm, 1 µm and 100 nm, respectively.
Figure 277: Bi₂O₃ (a) nanofiber and (b) nanowire diameter histograms fabricated using 0.550 g PVP.

Figure 278: EDX analysis of Bi₂O₃ NWs fabricated using 0.550 g PVP. The inset shows the region of nanowires that was analyzed.

The average nanofiber and nanowire diameters are summarized in Tables 46 and 47, respectively. The average nanofiber diameter showed an increase with the increase in PVP mass (Figure 279). A similar trend was observed for the nanowires as shown in Figure 280. In both cases, there was an initial decrease in the diameter when PVP mass was increased from 0.250 g to 0.350 g. It could be that the Bi(2EHx)_3/PVP nanofibers fabricated were very small and unstable which caused them to fuse together during the annealing process. A nano-scale size dependent melting point depression in a variety of materials has been reported previously.²²⁵,²²⁶,²²⁷
Table 46: Average Bi$_2$O$_3$ nanofiber diameters fabricated using variable PVP masses.

<table>
<thead>
<tr>
<th>PVP mass (g)</th>
<th>Average Bi$_2$O$_3$ nanofiber diameters (nm)</th>
<th>Diameter Std. Dev. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.250</td>
<td>292</td>
<td>87</td>
</tr>
<tr>
<td>0.350</td>
<td>127</td>
<td>44</td>
</tr>
<tr>
<td>0.450</td>
<td>525</td>
<td>103</td>
</tr>
<tr>
<td>0.550</td>
<td>714</td>
<td>109</td>
</tr>
</tbody>
</table>

Figure 279: Average Bi$_2$O$_3$ nanofiber diameters fabricated using varied PVP masses.

Table 47: Average Bi$_2$O$_3$ nanowire diameters fabricated using variable PVP masses.

<table>
<thead>
<tr>
<th>PVP mass (g)</th>
<th>Average Bi$_2$O$_3$ nanowire diameters (nm)</th>
<th>Std. Dev. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.250</td>
<td>222</td>
<td>67</td>
</tr>
<tr>
<td>0.350</td>
<td>86</td>
<td>21</td>
</tr>
<tr>
<td>0.450</td>
<td>149</td>
<td>34</td>
</tr>
<tr>
<td>0.550</td>
<td>174</td>
<td>43</td>
</tr>
</tbody>
</table>

Figure 280: Average Bi$_2$O$_3$ NW diameters fabricated using varied PVP masses.
Figure 281 shows the XRD spectra obtained for the nanowire films fabricated with 0.250 g and 0.550 g PVP mass only, as there was not enough Bi$_2$O$_3$ materials from the 0.350 g and 0.450 g samples available for XRD analysis. Both Figures 281 (a) and (b) show the presence of α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$ phases in the annealed nanowires.

![XRD spectra](image)

**Figure 281**: Showing only the XRD spectra of Bi$_2$O$_3$ NWs fabricated by using (a) 0.250 g and (b) 0.550 g PVP. The peaks associated with the α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$ correlates to the literature values$^{228,229}$.
High resolution FE-SEM images of the annealed nanowires are shown in Figure 282, where the images (a), (b), (c), and (d) correspond to the samples fabricated using 0.250 g, 0.350 g, 0.450 g, and 0.550 g PVP. Figure 282 showed a progressive transformation of the NWs where the surface morphology changed from: (a,b) smooth; to (c) fused semi-spherical particles; to (d) stacked lamellar domains. This evolution of nanowire morphology is due to the formation of bismuth oxide sub-carbonate ((BiO)$_2$CO$_3$) which has been reported to form hierarchical nano-sheets with photo catalytic and antibacterial properties.$^{230,231}$ The characteristic XRD peaks$^{232}$ associated with (BiO)$_2$CO$_3$, coincides with the major peaks of $\alpha$-Bi$_2$O$_3$ and $\beta$-Bi$_2$O$_3$ and therefore could not been identified on the spectra shown in Figure 281.

![Figure 282: High resolution SEM images of Bi$_2$O$_3$ NWs fabricated using (a) 0.250 g (b) 0.350 g (c) 0.450 g and (d) 0.550 g PVP showing the evolution of NWs morphology with the increase in PVP mass. In this figure, the scale bars associated with the images (a), (b), (c) and (d) correspond to 100 nm, 100 nm, 100 nm and 100 nm, respectively.](image-url)
4.4.2 Investigation of changes in Bi$_2$O$_3$ NW diameters and morphologies with the increase in the annealing temperature.

During the annealing of the nanowires in the previous sets of experiments, it was observed that there was a size dependent melting point depression which caused fusion of adjacent NWs during the process. Therefore, it was necessary to perform a systematic evaluation of the annealing process and its effect on the nanowire diameter and morphology. In this case, nanofiber films were annealed from room temperature to 220°C and held for 12 hours. The film was transferred to a high temperature furnace where the partially pyrolyzed nanofibers were heated to 350°C for an additional 10 hours. The temperature was then increased by 50°C every 1.5 hours until the final temperature of 650°C was achieved. The SEM images and nanowire diameter histograms (following each temperature increment) are presented in the section below.

The unannealed nanofibers were measured to have an average diameter of 479 (± 234) nm with a bimodal distribution profile (Figure 283 (b)) which is shown in Figure 283 (a). The nanofibers were observed to have a brownish color during the annealing steps from 350°C to 450°C (Figures 284 to 286) indicating incomplete pyrolysis of the PVP template. The color of the nanofibers/nanowires changed from brown to yellow after annealing for 1.5 hours at 500°C and remained unchanged. The lamellar-type nanosheet associated with Bi$_2$O$_3$CO$_3$ was only observed after annealing at 450°C and 500°C (Figures 286 and 287). Above 550°C, the nanowire diameter gradually increased and the morphology changed from NWs to a sub-micron size fused Bi$_2$O$_3$ network (as shown in Figures 289 and 290). The average diameter of NWs measured after each annealing step is summarized in Table 48. The average diameter versus the annealing temperature plot is shown in Figure 291, showing that a minimum diameter was achieved between 500°C and 550°C.
Figure 283: (a) SEM image and (b) diameter distribution of unannealed Bi$_2$O$_3$ nanofibers fabricated via the sol-gel route.

Figure 284: (a, b) SEM images and (c) diameter distribution of Bi$_2$O$_3$ nanofibers/nanowires annealed at 350°C for 10 hr.

Figure 285: (a, b) SEM images and (c) diameter distribution of Bi$_2$O$_3$ nanofibers/nanowires annealed at 400°C for 1.5 hr.
Figure 286: (a, b) SEM images and (c) diameter distribution of Bi$_2$O$_3$ nanowires annealed at 450°C for 1.5 hr.

Figure 287: (a, b) SEM images and (c) diameter distribution of Bi$_2$O$_3$ nanowires annealed at 500°C for 1.5 hr.

Figure 288: (a, b) SEM images and (c) diameter distribution of Bi$_2$O$_3$ nanowires annealed at 550°C for 1.5 hr.
Figure 289: (a, b) SEM images and (c) diameter distribution of Bi$_2$O$_3$ nanowires annealed at 600°C for 1.5 hr.

Figure 290: (a, b) SEM images and (c) diameter distribution of Bi$_2$O$_3$ nanowires annealed at 650°C for 1.5 hr.

<table>
<thead>
<tr>
<th>Annealing temperature (°C)</th>
<th>Nanofiber/nanowire color observed</th>
<th>Average nanofiber/nanowire diameter (nm)</th>
<th>Std. Dev. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 (unannealed)</td>
<td>white</td>
<td>479</td>
<td>234</td>
</tr>
<tr>
<td>350</td>
<td>light brown</td>
<td>244</td>
<td>105</td>
</tr>
<tr>
<td>400</td>
<td>dark brown</td>
<td>140</td>
<td>51</td>
</tr>
<tr>
<td>450</td>
<td>dark brown</td>
<td>145</td>
<td>69</td>
</tr>
<tr>
<td>500</td>
<td>yellow</td>
<td>146</td>
<td>46</td>
</tr>
<tr>
<td>550</td>
<td>yellow</td>
<td>213</td>
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<tr>
<td>600</td>
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<td>226</td>
<td>52</td>
</tr>
<tr>
<td>650</td>
<td>yellow</td>
<td>580</td>
<td>361</td>
</tr>
</tbody>
</table>

Table 48: Plot showing the changes in Bi$_2$O$_3$ nanofiber/nanowire diameters with the increase in annealing temperature.
Figure 291: Plot showing the changes in Bi$_2$O$_3$ nanofiber/nanowire diameters with the increase in annealing temperature.

EDX quantitative analysis performed on the sample that was annealed to 550°C showed a Bi:O At% ratio of 3:2 (Figure 292).

Figure 292: Typical EDX analysis of Bi$_2$O$_3$ NWs used to evaluate its NWs diameters and morphology dependence on the annealing temperature. The inset shows the region of nanowires that was analyzed. This particular EDX analysis was performed using Bi$_2$O$_3$ NWs after annealing to 600°C.
4.4.3 WBO NW fabrication using a sol-gel, electrospinning and annealing method

In this section results pertaining to the fabrication of WBO NWs are presented. Two sets of experiments were performed where: (1) W(OEt)$_5$:Bi(2EHx)$_3$ precursor molar ratios and (2) PVP masses were varied while keeping all other parameters constant. For each set of experiments, SEM, diameter histogram, EDX and XRD results are presented in the following section.

4.4.3.1 Investigation of the effect of the change in W(OEt)$_5$:Bi(2EHx)$_3$ mole ratios on WBO NW diameters

WBO NWs were fabricated using the precursor molar ratios shown in the scheme below. The detailed masses of the reagents and parameters used for the WBO nanofibers fabricated was presented previously in Table 42.

\[
\text{Bi(2EHx)$_3 + W(OEt)$_3 + PVP} \xrightarrow{(a) \text{EtOH}} \text{Bi(2EHx)$_3 - W(OEt)$_3 - PVP nanofibers} \xrightarrow{(b) \text{Electrospinning}} \text{Bi(2EHx)$_3 - W(OEt)$_3 - PVP nanofibers}
\]

W(OEt)$_5$:Bi(2EHx)$_3$ molar ratios used:
1. 9:91
2. 15:85
3. 25:75
4. 35:65
5. 45:55

(c) gradual annealing

In this section, the SEM data and diameter analysis (of nanofibers and nanowires) for each WBO composition are shown first which is followed by the XRD, high resolution SEM (HR-SEM) images of NWs surface morphology, and EDX quantitative and area map analysis.

(1). WBO NWs fabrication using a W:Bi ratio of 9:91

SEM images of nanofibers and nanowires prepared using a W:Bi precursor ratio of 9:91 are shown in Figure 293 and had average diameters of 311 (± 147) nm and 135 (± 30) nm, respectively. A bimodal diameter distribution was only observed for the nanofiber sample (Figure
294 (a)) with maxima of ~ 150 nm and ~ 400 nm. The resultant nanowires showed a Gaussian-type size distribution (Figure 294 (b)).

Figure 293: SEM images of WBO NWs fabricated using a W:Bi precursor molar ratio of 9:91. In these figures, the scale bars associated with the images (a), (b), (c) and (d) correspond to 1 µm, 1 µm, 1 µm and 100 nm, respectively.

Figure 294: WBO (a) nanofiber and (b) nanowire diameter histograms fabricated using a W:Bi precursor molar ratio of 9:91.
(2). WBO NWs fabrication using a W:Bi ratio of 15:85

The nanofibers and nanowires fabricated using a W:Bi precursor ratio of 15:85 are shown in Figure 295. The SEM images of the nanofibers (Figure 295 (b)) showed the presence of particles that were infused in the nanofibers.

Figure 295: SEM images of WBO NWs fabricated using a W:Bi precursor molar ratio of 15:85. In this figure, the scale bars associated with the images (a), (b), (c) and (d) correspond to 10 μm, 1 μm, 1 μm and 100 nm, respectively.

The SEM images of the nanowires (Figure 295 (a)) showed a mostly homogenous nanowire morphology except for few areas where nanowires formed a granulated texture (Figure 296) on their surfaces (compared to the smoother nature as observed in Figure 295 (b)). The nanofibers and nanowires had an average diameter of 508 (± 119) nm and 133 (± 40) nm, respectively. Only the nanofibers showed a bimodal diameter distribution (Figure 297 (a)) with local maxima ~ 410 nm and ~ 560 nm.
Figure 296: Clusters of WBO (W:Bi = 15:85) nanowires with rough surface texture were observed in some areas on the annealed film.

Figure 297: WBO (a) nanofiber and (b) nanowire diameter histograms fabricated using a W:Bi precursor molar ratio of 15:85.

(3). WBO NWs fabrication using a W:Bi ratio of 25:75

The SEM images of samples prepared with a W:Bi precursor ratio of 25:75 showed trapped particulates in the WBO nanofibers as shown in Figure 298. The nanofiber and nanowire...
showed Gaussian type distributions (Figure 299) with average diameters of 411 (± 115) nm and 141 (± 37) nm, respectively.

Figure 298: SEM images of WBO NWs fabricated using a W:Bi precursor molar ratio of 25:75. In this figure, the scale bars associated with the images (a), (b), (c) and (d) correspond to 10 µm, 1 µm, 1 µm and 1 µm, respectively.

Figure 299: WBO (a) nanofiber and (b) nanowire diameter histograms fabricated using a W:Bi precursor molar ratio of 25:75.
(4). WBO NWs fabrication using a W:Bi ratio of 35:65

SEM images of nanofibers and nanowires fabricated using a W:Bi ratio of 35:65 are shown in Figure 300. The nanofibers were measured to have an average diameter of 482 (± 226) nm and had a bimodal distribution with approximate maxima at 250 nm and 650 nm (Figure 301 (a)). The nanowires were measured to have an average diameter of 178 (± 59) nm.

![SEM images of WBO NWs fabricated using a W:Bi precursor molar ratio of 35:65.](image)

Figure 300: SEM images of WBO NWs fabricated using a W:Bi precursor molar ratio of 35:65. In this figure, the scale bars associated with the images (a), (b), (c) and (d) correspond to 10 µm, 1 µm, 1 µm and 1 µm, respectively.

![Average nanofiber diameter: 482 ± 226 nm](image)

Figure 301: WBO (a) nanofiber and (b) nanowire diameter histograms fabricated using a W:Bi precursor molar ratio of 35:65.
(5). WBO NWs fabrication using a W:Bi ratio of 45:55

The nanofibers fabricated using a W:Bi precursor ratio of 45:55 showed some precipitates that were infused in the nanofibers. Both WBO nanofibers and nanowires showed Gaussian type diameter distributions (Figure 303) and were measured to have average diameters of 460 (± 131) nm and 222 (± 62) nm, respectively.

Figure 302: SEM images of WBO NWs fabricated using a W:Bi precursor molar ratio of 45:55. In this figure, the scale bars associated with the images (a), (b), (c) and (d) correspond to 10 µm, 1 µm, 1 µm and 100 nm, respectively.

Figure 303: WBO (a) nanofiber and (b) nanowire diameter histograms fabricated using a W:Bi precursor molar ratio of 45:55.
(6). Summary of nanofiber and nanowire diameter trends

This investigation was performed assuming that the changes in W:Bi ratios would not significantly affect the nanowire diameters. The goal was to evaluate any changes in the morphology resulting from the phase separation of the two oxides.

The WBO nanofibers and nanowire average diameters are summarized in Table 49 and Table 50, respectively. The increase in W(OEt)$_5$ mol % compared to Bi(2EHx)$_3$ (where the total mass of the was kept constant) did not have any measured effect on the nanofiber diameters as shown in Figure 304. However, there is a slight increase in the average nanowire diameters when the W(OEt)$_5$ mol % was increased above 35% (Figure 305).

<table>
<thead>
<tr>
<th>W(OEt)$_5$ mol%</th>
<th>Nanofiber diameter (nm)</th>
<th>Diameter Std. Dev. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>311</td>
<td>147</td>
</tr>
<tr>
<td>15</td>
<td>508</td>
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<tr>
<td>25</td>
<td>411</td>
<td>115</td>
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<tr>
<td>35</td>
<td>482</td>
<td>226</td>
</tr>
<tr>
<td>45</td>
<td>460</td>
<td>131</td>
</tr>
</tbody>
</table>

Figure 304: Average WBO nanofiber diameter change with the increase in W(OEt)$_5$ mol%.
Table 50: Average WBO nanowire diameter dependence on increase in W(OEt)$_5$ mol% 

<table>
<thead>
<tr>
<th>W(OEt)$_5$ mol%</th>
<th>Nanowire diameter (nm)</th>
<th>Diameter Std. Dev. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>135</td>
<td>30</td>
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<tr>
<td>15</td>
<td>133</td>
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<td>25</td>
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<td>49</td>
</tr>
<tr>
<td>45</td>
<td>222</td>
<td>62</td>
</tr>
</tbody>
</table>

Figure 305: Average WBO nanowire diameter change with the increase in W(OEt)$_5$ mol%.

(7). XRD analysis of WBO NWs fabricated by varying W(OEt)$_5$:Bi(2EHx)$_3$ ratios

The XRD analysis of the WBO NWs fabricated using W(OEt)$_5$:Bi(2EHx)$_3$ mol ratios of 9:91, 15:85, 25:75, 35:65 and 45:55 are shown in Figures 306 (a), (b), (c), (d) and (e), respectively. From the XRD peak analysis its was concluded that that the precursor mol% ratio of 9:91 produced WBO NWs with mixed β and δ-Bi$_2$O$_3$ phases (Figure 306 (a)). W:Bi precursor ratios of 15:85 and 25:75 resulted in pure δ-Bi$_2$O$_3$ NWs (Figures 306 (b) and (c), respectively). When the mol% ratio was increased to 34:65, the NWs began to phase separate (Figure 306 (d)) and resulted in a mixed product consisting of β and δ-Bi$_2$O$_3$ where the β-Bi$_2$O$_3$ peaks were mostly overshadowed by the δ-Bi$_2$O$_3$ (except for the (400) and (421) reflections of β-Bi$_2$O$_3$). The W:Bi ratio of 45:55 resulted in WBO NWs with multi-phase Bi$_2$O$_3$ including phase separated WO$_3$ crystals (Figure 306 (e)). Therefore, it can be concluded that single phase δ-Bi$_2$O$_3$ WBO NWs can be fabricated using...
W(OEt)$_5$:Bi(2EHx)$_3$ mol% ratios of 15:85 and 25:75. In the XRD peaks all Bi$_2$O$_3$ phases were consistent with the reported values.$^{229,230,235-240}$

Figure 306: XRD analysis of WBO NWs with W(OEt)$_5$:Bi(2EHx)$_3$ precursor mol% ratios of (a) 9:91, (b) 15:85, (c) 25:75, (d) 35:65 and (e) 45:55.
(8). Changes in WBO NWs surface morphology with an increase in W(OEt)$_5$ mol%

The WBO nanowire surface texture was evaluated using FE-SEM where the images of NWs prepared with W(OEt)$_5$:Bi(2EHx)$_3$ (W:Bi) ratios of 9:91, 15:85, 25:75, 35:65 and 45:55 are shown in Figures 307 (a), (b), (c), (d) and (e), respectively.

Figure 307: HR-SEM showing the changes in WBO NWs morphologies with W:Bi precursor molar ratios of (a) 8:92, (b) 15:85, (c) 25:75, (d) 35:65 and (e) 45:55.
Initially the WBO NWs surface had a bumpy texture which appeared to have resulted from fusion of individual domains of Bi$_2$O$_3$ nanoparticles (Figure 307 (a)). The WBO NWs surface showed an smooth morphology (Figure 307 (b)) relative to the NWs prepared with W:Bi ratio of 9:91. When the W(OEt)$_5$ mol% was increased above 25%, WBO NWs showed increasing roughness on the NWs surface (Figure 307 (c)). WBO NWs that were fabricated with 35% and 45% W(OEt)$_5$ showed distinct coarsening as shown in Figures 62 (d) and (e), respectively. The increase in the roughness was most likely due to WO$_3$ phase separation from Bi$_2$O$_3$ during the annealing process.

(9). EDX analysis of the WBO NWs fabricated with varying W(OEt)$_5$:Bi(2EHx)$_3$ ratios

In this section the precursor mol% refers to the percent of W(OEt)$_5$ in the precursor solution consisting W(OEt)$_5$ and Bi(2EHx)$_3$. The EDX At% ratio refers to the ratio of W and Bi At% resulting from the EDX quantitative analysis.

The EDX analysis in Figure 309 demonstrates quantitative analysis of two types of NWs (fabricated using a W:Bi precursor ratio of 15:85) as shown earlier in Figure 296. The EDX analysis of WBO nanowires showed a W:Bi At% 10:90 which corresponds to the NWs fabricated using a W:Bi precursor ratio of 9:91 (Figure 308). The smoother surface NWs (top of the image) were measured to have a W:Bi At% ratio of ~20:80, whereas the rougher NWs had a W:Bi At% ratio of ~24:76. The average ratio over a larger area was measured to be ~ 18:88.
Figure 308: EDX analysis of WBO NWs fabricated with a W(OEt)$_5$:Bi(2EH)$_3$ ratio of 9:91. The inset shows the region of nanowires that was analyzed.

Figure 309: EDX analysis of WBO NWs fabricated with a W(OEt)$_5$:Bi(2EH)$_3$ ratio of 15:85. The inset shows the region of nanowires that was analyzed. The average At% of 17.63% (W) and 82.37% (Bi).
Earlier in Section 4.3.3.1 it was shown that during the fabrication of WBO/PVP nanofibers, there were precipitates present in the nanofibers (as shown in Figure 298). These nanofibers were prepared using WBO precursor ratio of 25:75. EDX analysis of such particles (Figure 310) showed W:Bi At% ratio ~ 19:81. The analysis of a region on that same nanofiber where there was no precipitate present showed W:Bi At% ratio of ~ 30:70. This indicated a higher concentration of Bi species was present in the particle compared to the surrounding regions which showed Bi(2EHx)₃ oxidation prior to the electrospinning process. The annealed NWs of the same composition had W:Bi ratio of ~ 30:70.

![EDX spectra](image)

Figure 310: EDX analysis of WBO nanofibers fabricated with a W(OEt)₅:Bi(2EHx)₃ ratio of 25:75. The inset shows the region of nanofiber that was analyzed. Nanowires showed an average At% of 30.36% (W) and 69.64% (Bi).

NWs fabricated with W:Bi precursor mol% ratio of 35:65 and 45:55 resulted in a EDX W:Bi At% ratio of 39:61 (Figure 311) and 41:59 (Figure 312), respectively.
Figure 311: EDX analysis of WBO NWs fabricated with a $\text{W(OEt)}_5:\text{Bi(2EHx)}_3$ ratio of 35:65. The inset shows the region of nanowires that was analyzed.

Figure 312: EDX analysis of WBO NWs fabricated with a $\text{W(OEt)}_5:\text{Bi(2EHx)}_3$ ratio of 45:55. The inset shows the region of nanowires that was analyzed.
The W(OEt)$_5$:Bi(2EHx)$_3$ mol% and EDX W:Bi At% are summarized in Table 51. In this case the W(OEt)$_5$ mol% is calculated using the formula (to determine the theoretical At%):

$$W(OEt)_5 \text{ mol}\% = \left[ \frac{W(OEt)_5 \text{ mol}}{W(OEt)_5 \text{ mol} + (Bi(2EHx)_3 \text{ mol})} \right] \times 100\%$$

<table>
<thead>
<tr>
<th>W(OEt)$_3$ mass (g)</th>
<th>Bi(2EHx)$_3$ mass (g)</th>
<th>W(OEt)$_3$ mol</th>
<th>Bi(2EHx)$_3$ mol</th>
<th>W(OEt)$_5$ mol%</th>
<th>W(OEt)$_5$:Bi(2EHx)$_3$ mol% ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.84E-02</td>
<td>1.98E-01</td>
<td>4.50E-05</td>
<td>3.11E-04</td>
<td>13%</td>
<td>13:87</td>
</tr>
<tr>
<td>3.08E-02</td>
<td>1.71E-01</td>
<td>7.53E-05</td>
<td>2.68E-04</td>
<td>22%</td>
<td>22:78</td>
</tr>
<tr>
<td>5.26E-02</td>
<td>1.52E-01</td>
<td>1.29E-04</td>
<td>2.37E-04</td>
<td>35%</td>
<td>35:65</td>
</tr>
<tr>
<td>7.00E-02</td>
<td>1.31E-01</td>
<td>1.71E-04</td>
<td>2.05E-04</td>
<td>46%</td>
<td>46:54</td>
</tr>
<tr>
<td>8.90E-02</td>
<td>1.11E-01</td>
<td>2.18E-04</td>
<td>1.73E-04</td>
<td>56%</td>
<td>56:44</td>
</tr>
</tbody>
</table>

The WO$_3$:Bi$_2$O$_3$ is also calculated from the EDX At% obtained from quantitative analysis and are presented in Table 52. The oxide ratio is calculated using the formula (where Bi(2EHx)$_3$:Bi$_2$O$_3$ molar ratio is 1:2). The reason for using these formula was to compare the theoretical and measured W:Bi At% ratios.

$$WO_3 \text{ mol}\% (\text{calc. from EDX At%}) = \left[ \frac{W \text{ At}\%}{W \text{ At}\% + \left( \frac{Bi \text{ At}\%}{2} \right)} \right] \times 100\%$$

<table>
<thead>
<tr>
<th>W At% in (W(OEt)$_5$)</th>
<th>Bi At% in Bi(2EHx)$_3$</th>
<th>Bi At% in Bi$_2$O$_3$</th>
<th>W% in W(OEt)$_5$:Bi(2EHx)$_3$</th>
<th>WO$_3$:Bi$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.3</td>
<td>89.7</td>
<td>44.8</td>
<td>19%</td>
<td>19:81</td>
</tr>
<tr>
<td>17.6</td>
<td>82.4</td>
<td>41.2</td>
<td>30%</td>
<td>30:70</td>
</tr>
<tr>
<td>30.4</td>
<td>69.6</td>
<td>34.8</td>
<td>47%</td>
<td>47:53</td>
</tr>
<tr>
<td>38.6</td>
<td>61.4</td>
<td>30.7</td>
<td>56%</td>
<td>56:44</td>
</tr>
<tr>
<td>51.2</td>
<td>48.8</td>
<td>24.4</td>
<td>68%</td>
<td>68:32</td>
</tr>
</tbody>
</table>
The summary of the theoretical and measured At% is presented in Table 53 which showed similar ratios between them.

<table>
<thead>
<tr>
<th>Table 53: Summary of theoretical and measured W:Bi At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical W:Bi ratio</td>
</tr>
<tr>
<td>13:87</td>
</tr>
<tr>
<td>22:78</td>
</tr>
<tr>
<td>35:65</td>
</tr>
<tr>
<td>46:54</td>
</tr>
<tr>
<td>56:44</td>
</tr>
</tbody>
</table>

4.4.3.2 Effect of changes in PVP mass on WBO NW diameter

The NWs in this case are fabricated by varying the PVP mass from 0.250 g to 0.450 g as indicated in the scheme below.

\[
\text{Bi(2EHx)₃ + W(OEt)₃ + PVP} \xrightarrow{(a) \text{EtOH}} \xrightarrow{(b) \text{Electrospinning}} \text{Bi(2EHx)₃ - W(OEt)₃ - PVP nanofibers}
\]

PVP masses used:
1. 0.250 g
2. 0.350 g
3. 0.450 g

(c) gradual annealing

(1). WBO NWs fabrication using 0.250 g PVP

The nanofibers and nanowires fabricated using 0.250 g are shown in Figure 313 and were measured to have an average diameter (Figure 314) of 235 (± 78) nm and 70 (± 20) nm, respectively.
Figure 313: SEM images of WBO NWs fabricated using 0.250 g PVP. In this figure, the scale bars associated with the images (a), (b), (c) and (d) correspond to 1 µm, 1 µm, 1 µm and 100 nm, respectively.

Figure 314: WBO (a) nanofiber and (b) nanowire diameter histograms fabricated using 0.250 g PVP.

(2). WBO NWs fabrication using 0.350 g PVP

WBO nanofibers and nanowires fabricated using 0.350 g PVP are shown in Figure 315 and were measured to have average diameters of 370 (± 107) nm and 111 (± 24) nm (Figure 316).
Figure 315: SEM images of WBO NWs fabricated using 0.350 g PVP. In this figure, the scale bars associated with the images (a), (b), (c) and (d) correspond to 10 µm, 1 µm, 1 µm and 100 nm, respectively.

Figure 316: WBO (a) nanofiber and (b) nanowire diameter histograms fabricated using 0.350 g PVP.

Average nanofiber diameter: 370 ± 107 nm

Average nanowire diameter: 111 ± 24 nm
(3). WBO NWs fabrication using 0.450 g PVP

Nanofibers and nanowires fabricated with 0.450 g PVP are shown in Figure 317 and were measured to have average diameters of 516 (± 200) nm (Figure 323 (a)) and 516 (± 200) nm (Figure 323 (b)), respectively.

![Figure 317: SEM images of WBO NWs fabricated using 0.450 g PVP. In this figure, the scale bars associated with the images (a), (b), (c) and (d) correspond to 10 µm, 1 µm, 1 µm and 100 nm, respectively.](image)

![Figure 318: WBO (a) nanofiber and (b) nanowire diameter histograms fabricated using 0.450 g PVP.](image)
The WBO nanofiber and nanowire diameters are summarized in Tables 54 and 55 respectively. The nanofiber diameter showed an increase with an increase in PVP mass as shown in Figure 319. The WBO nanowires also showed an increase in nanowire diameter with the increase the PVP mass as indicated in Figure 320.

<table>
<thead>
<tr>
<th>PVP mass (g)</th>
<th>Nanofiber diameter (g)</th>
<th>Std. Dev. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.250</td>
<td>235</td>
<td>78</td>
</tr>
<tr>
<td>0.350</td>
<td>370</td>
<td>107</td>
</tr>
<tr>
<td>0.450</td>
<td>516</td>
<td>200</td>
</tr>
</tbody>
</table>

Table 54: WBO nanofiber diameter dependence on the PVP mass

<table>
<thead>
<tr>
<th>PVP mass (g)</th>
<th>Nanowire diameter (g)</th>
<th>Std. Dev. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.250</td>
<td>70</td>
<td>20</td>
</tr>
<tr>
<td>0.350</td>
<td>111</td>
<td>24</td>
</tr>
<tr>
<td>0.450</td>
<td>144</td>
<td>36</td>
</tr>
</tbody>
</table>

Table 55: WBO nanowire diameter dependence on the increase in PVP mass

Figure 319: WBO Nanofiber diameter dependence on changes in PVP masses.
The EDX analysis shows ~12:88 W:Bi At% ratios for all three samples fabricated using 0.250 g, 0.350 g and 0.450 g which was as expected.

Figure 320: WBO nanowire diameter dependence on the changes in PVP mass

Figure 321: EDX analysis of WBO NWs fabricated with 0.250 g PVP. The inset shows the region of nanowires that was analyzed.
Figure 322: EDX analysis of WBO NWs fabricated with 0.350 g PVP. The inset shows the region of nanowires that was analyzed.

Figure 323: EDX analysis of WBO NWs fabricated with 0.450 g PVP. The inset shows the region of nanowires that was analyzed.
4.5 Conclusions

In this chapter the fabrication of Bi$_2$O$_3$ and WBO nanofibers and nanowires (via sol-gel route in conjunction with electrospinning and annealing) was described with a variation of precursor mass and amount of PVP template. Bi$_2$O$_3$ nanofiber and nanowire diameters showed no dependence on increases in bismuth precursor mass.

However, it is shown that this system could be used to fabricate Bi$_2$O$_3$ nanowires with an average diameter of ~ 350 nm and ~ 250 nm, respectively. The nanowires possess a mix of α and β phases of Bi$_2$O$_3$ which was verified with XRD analysis. With an increase in PVP mass, Bi$_2$O$_3$ NWs diameters increased as well. Bi$_2$O$_3$ nanowires showed complete loss of all organics at 550°C where the nanowire diameter was also measured to be at a minimum. This complete pyrolysis temperature is important because Bi$_2$O$_3$ starts fusing extensively above that temperature.

As expected, nanofibers and WBO nanowires showed no diameter sensitivity to the increase in the W(OEt)$_5$ mol%. However, the nanowires did show a slight upward trend in diameters above 35% W(OEt)$_5$ mol%. The XRD analysis showed the δ-Bi$_2$O$_3$ to be phase pure only at a precursor concentration between 15% and 25% W(OEt)$_5$. It was also determined that with increasing PVP content, the average diameter of WBO NWs also increased. The average WO$_3$ content (Atomic %) of these WBO samples was ~ 12% (EDX).

WBO NWs fabricated by varying W(OEt)$_3$ mass showed an increase in surface roughness with an increase in the amount of W(OEt)$_5$. This evolution of the surface morphology is likely due to WO$_3$ and Bi$_2$O$_3$ phase separation during the annealing phase. The presence of the characteristic WO$_3$ XRD peaks (in the samples containing higher mass of W(OEt)$_5$) supported the phase separation hypothesis.
Chapter V

Fabrication, characterization, and analysis of barium titanate (BaTiO$_3$) (BTO) and barium strontium titanate (Ba,Sr)TiO$_3$ (BST) nanowire films produced using a sol-gel method in conjunction with an electrospinning technique.
5.0 Introduction

5.1 \( \text{BaTiO}_3 \) and \((\text{Ba,Sr})\text{TiO}_3\) as piezoelectric material

Barium titanate (BTO) and barium strontium titanate (BST) belong to a group of perovskite materials (\(\text{ABO}_3\)) that are piezoelectric, which means that these materials produce a charge when mechanical stress is applied to them.\(^{239,240}\) \(\text{BaTiO}_3\) undergoes phase transformations from (1) tetragonal to cubic, (2) cubic to orthorhombic, and (3) orthorhombic to rhombohedral (hexagonal) at temperatures of 120°C, 0°C and -90°C, respectively (Figure 324). Dopants such as \(\text{SrO}_3\) are used to stabilize the BTO tetragonal phase where the central \(\text{Ti}^{3+}\) atom moves slightly when stress or electric field is applied. This loss is symmetry results in spontaneous polarization of the material (Figure 325).\(^{241}\)

**Figure 324:** \(\text{BaTiO}_3\) phase changes with temperature.

**Figure 325:** \(\text{BaTiO}_3\) polarization due to the phase transformation below 120°C.
This work was performed in collaboration with Dr. Till Fromling (Ceramics group of Prof. Dr. Jürgen Rödel) from Technische Universität Darmstadt, Germany. The goal of this project was to fabricate flexible BaTiO$_3$ and (Ba,Sr)TiO$_3$ NW films for investigating their piezoelectric properties. Fabrication methods like mechanochemical$^{242}$, co-precipitation$^{243}$, sol-gel$^{244}$ and hydrothermal$^{245}$ routes have been previously reported for the synthesis of BTO and BST nanowires and films.

5.2 Experimental Section

The nanowires presented in this chapter were fabricated using a modified sol-gel process (in combination with electrospinning and annealing steps) reported by Maensiri and co-workers.$^{246}$ The differences between the reported procedure and the procedure used here to fabricate BTO and BST nanowires are presented below in Tables 56 and 57.

<table>
<thead>
<tr>
<th>Table 56: Precursors used for the fabrication of BTO and BST NWs.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Precursors</strong></td>
</tr>
<tr>
<td>Ti precursor</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Ba precursor</td>
</tr>
<tr>
<td>Sr precursor</td>
</tr>
<tr>
<td>Solvents</td>
</tr>
<tr>
<td>Polymer template</td>
</tr>
<tr>
<td>Acid catalyst</td>
</tr>
</tbody>
</table>
### Table 57: Electrospinning parameters differences between the reported and one used for the fabrication of BTO and BST NWs in this chapter.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Reported by Maensiri et al.(^{247})</th>
<th>Used for this dissertation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrospinning voltage</td>
<td>12.5 kV</td>
<td>16 kV</td>
</tr>
<tr>
<td>Electrode distance</td>
<td>12 cm</td>
<td>12 cm</td>
</tr>
<tr>
<td>Flow rate</td>
<td>0.5 ml/hr</td>
<td>1 ml/hr</td>
</tr>
<tr>
<td>Needle size</td>
<td>23 gauge</td>
<td>21 gauge</td>
</tr>
<tr>
<td>Max annealing temperature</td>
<td>800°C</td>
<td>1000°C</td>
</tr>
</tbody>
</table>

### 5.2.1 BaTiO\(_3\) NWs fabrication via a sol-gel route

In this series of experiments, five separate samples of BTO NW films were fabricated where only the sol-gel solution volume dispensed for electrospinning (containing the precursors) was varied. The dependence of BTO NW diameter on the reaction parameters was not evaluated in this case as this was a preliminary investigation of the piezoelectric behavior of the NW films and we did not evaluate any NW diameter size dependence. The sol-gel reagents masses and electrospinning parameters used for the fabrication of BTO NWs are presented in Table 58. The reagents were measured and mixed separately as outlined in Figure 326. All five BTO NWs samples were prepared from the same stock sol-gel reaction solution.

### Table 58: Reagent masses used for the fabrication of BaTiO\(_3\) nanofibers

<table>
<thead>
<tr>
<th>(\text{Ba(OAc)}_2)</th>
<th>(\text{Ti(OiPr)}_4)</th>
<th>PVP (40K MW)</th>
<th>EtOH</th>
<th>AcOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.330 g</td>
<td>0.388 g</td>
<td>1.000 g</td>
<td>1.70 ml</td>
<td>1.054 g</td>
</tr>
</tbody>
</table>
Table 59: Electrospinning and annealing parameters used for BTO NWs fabrication

<table>
<thead>
<tr>
<th>Voltage</th>
<th>Electrode distance</th>
<th>Flow rate</th>
<th>Annealing</th>
<th>Sol-gel solution volume dispensed during electrospinning</th>
</tr>
</thead>
<tbody>
<tr>
<td>16 kV</td>
<td>12 cm</td>
<td>1 ml/hr</td>
<td>220°C for 12 hours 1000°C for 3 hrs</td>
<td>BTO Sample 01 0.500 ml</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>BTO Sample 02 0.500 ml</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>BTO Sample 03 0.517 ml</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>BTO Sample 04 0.716 ml</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>BTO Sample 05 0.891 ml</td>
</tr>
</tbody>
</table>

Ba(OAc)$_2$ + Ti(OiPr)$_4$ + AcOH

PVP + EtOH

Ba(OAc)$_2$ / Ti(OiPr)$_4$ / AcOH / PVP / EtOH

Mixed for 2 hrs followed by electrospinning

Figure 326: Sequence of mixing reagents for the fabrication of BTO/PVP nanofibers.

All the BTO and BST samples presented in this chapter were annealed using the same annealing conditions. The rates of temperature increase for the step 1 and step 2 of the annealing process are shown in Figure 327 and were calculated to be ~ 1°C/min and ~3°C/min, respectively.
Figure 327: Plot showing the rate of temperature increase during the (a) step 1 and (b) step 2 in the nanofiber annealing process.

5.2.2 (Ba_{1-x}Sr_x)TiO_3, (x=0.4) NWs fabrication via sol-gel route

In this experiment four separate samples of BST NW films were fabricated where only the sol-gel reaction solution volume (containing the precursors) was varied. Again, the focus here is on a preliminary evaluation of the piezoelectric properties of these films, the dependence of the BST NW diameter on the reaction parameters was not evaluated. The masses of the reagents used for the BST NWs fabrication are shown in Table 60. BST NWs with composition (Ba_{1-x}Sr_x)TiO_3 where x = 0.4 was fabricated in this case. The reagents were mixed separately according to the sequence shown in Figure 328. The electrospinning and annealing parameters used to fabricate the BST nanowires are shown in Table 61.

<table>
<thead>
<tr>
<th>Table 60: Masses of reagents used for BST NWs fabrication with the composition (Ba_{1-x}Sr_x)TiO_3 where x = 0.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba(OAc)_2</td>
</tr>
<tr>
<td>------------</td>
</tr>
<tr>
<td>0.205 g</td>
</tr>
</tbody>
</table>
Table 61: Electrospinning and annealing parameters used for BST NWs fabrication

<table>
<thead>
<tr>
<th>Voltage</th>
<th>Electrode distance</th>
<th>Flow rate</th>
<th>Annealing</th>
<th>Sol-gel solution volume dispensed during electrospinning</th>
</tr>
</thead>
<tbody>
<tr>
<td>16 kV</td>
<td>12 cm</td>
<td>1 ml/hr</td>
<td>220°C for 12 hours, then 1000°C for 3 hours</td>
<td>BST Sample 01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>BST Sample 02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>BST Sample 03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>BST Sample 04</td>
</tr>
</tbody>
</table>

\[
\text{Ba(OAc)}_2 + \text{Sr(OAc)}_2 + \text{AcOH} + \text{Ti(OiPr)}_4 \\
\downarrow \\
\text{PVP + EtOH} \\
\downarrow \\
\text{Ba(OAc)}_2 / \text{Ti(OiPr)}_4 / \text{AcOH} / \text{PVP} / \text{EtOH} \\
\downarrow \\
\text{Mixed for 2 hrs followed by electrospinning}
\]

Figure 328: Sequence of mixing reagents for the fabrication of BST/PVP nanofibers.

5.3 Instrumentation

The structural and chemical characterization and analysis of the nanowires were performed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Elemental characterizations were done using electron dispersive x-ray spectroscopy
(EDS/EDX) along with x-ray to analyze phase composition of the fabricated BTO and BST NWs. Raman spectroscopy was also used in addition to the techniques mentioned. Details of these characterization techniques, instruments and sample preparation processes have been discussed earlier in this dissertation (Section 2.2).

5.4 Results and Discussion

5.4.1 BaTiO$_3$ NWs fabrication via sol-gel processing, electrospinning and annealing

Barium titanate (BaTiO$_3$) nanowires were prepared by using a sol-gel reaction with a molar precursor composition of 1:1 ratio of barium to titanium atoms. In this section the results pertaining to the five BTO NW film samples prepared (from the same stock sol-gel solution) are presented starting with the SEM images of the nanofibers and nanowires, followed by an overview of the NW film thickness, TEM, EDX, XRD and Raman analysis. The nanowire diameters were measured using the TEM images only and therefore the histograms are presented with the TEM images. The only variation between the five samples was the volume of sol-gel solution that was used to prepare the nanofiber films during the electrospinning process.

The SEM images of the five BTO samples showed similar nanofiber and nanowire morphologies and was devoid of any beads or debris. The SEM images of the five BTO samples 01, 02, 03, 04, and 05 are shown in Figures 329, 330, 331, 332, and 333.

5.4.1.1 SEM images of BTO nanofiber and nanowires

(1). SEM images of BTO Sample 01

The nanowires are prepared by using 0.500 ml of the sol-gel solution with a morphology as shown in Figure 329 below.
Figure 329: BTO (a) nanofibers and (b) nanowires fabricated using 0.500 ml of sol-gel reaction solution.

(2). SEM images of BTO Sample 02

The nanowires are prepared by using 0.500 ml of the sol-gel solution with a morphology as shown in Figure 330 below.

Figure 330: BTO (a) nanofibers and (b) nanowires fabricated using 0.500 ml of sol-gel reaction solution.
(3). SEM images of BTO Sample 03

The nanowires are prepared by using 0.517 ml of the sol-gel solution with a morphology as shown in Figure 331 below.

![SEM images of BTO Sample 03](image)

Figure 331: BTO (a) nanofibers and (b) nanowires fabricated using 0.517 ml of sol-gel reaction solution.

(4). SEM images of BTO Sample 04

The nanowires are prepared by using 0.716 ml of the sol-gel solution with a morphology as shown in Figure 332 below.

![SEM images of BTO Sample 04](image)

Figure 332: BTO (a) nanofibers and (b) nanowires fabricated using 0.716 ml of sol-gel reaction solution.
(5). SEM images of BTO Sample 05

The nanowires are prepared by using 0.891 ml of the sol-gel solution with a morphology as shown in Figure 333 below.

![SEM images of BTO Sample 05](image)

Figure 333: BTO (a) nanofibers and (b) nanowires fabricated using 0.891 ml of sol-gel reaction solution.

5.4.1.2 BTO nanowire film thickness comparison

The BTO NW film thickness was evaluated using SEM (Figure 334) and the results are summarized in Table 62. The results showed no direct correlation between the dispensed sol-gel solution volume and the resulting BTO NW film thickness. This was somewhat puzzling as previously (in Chapter 3) a dependence of nanowire film thickness was observed during the fabrication of YSZ nanowires (via sol-gel and electrospinning route).

Such a result could be explained by looking at the differences in electrode distances used (during electrospinning) between the YSZ NWs and BTO NWs. YSZ NWs were fabricated using an electrode distance of 21 cm (with 20 kV voltage) where as BTO was fabricated using and electrode distance of 13 cm (with 16 kV voltage). This means that BTO NWs were fabricated
under a stronger electric field (voltage/cm) of 1.2 kV/cm vs the YSZ system (1.0 kV/cm). Therefore, it resulted in maximum BTO nanofiber collection along the middle region of the collector (where it was the shortest distance between the electrodes) and where the film thickness was higher relative to the sides of the collecting drum (Figure 335). The SEM images used to evaluate the BTO NW film thickness (Figure 334) were chosen randomly after the two-step annealing process, and the above data presumably reflect this.

<table>
<thead>
<tr>
<th>BTO Sample</th>
<th>Volume dispensed (mL)</th>
<th>Nanowire film thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>0.500</td>
<td>~ 40</td>
</tr>
<tr>
<td>02</td>
<td>0.500</td>
<td>~ 45</td>
</tr>
<tr>
<td>03</td>
<td>0.517</td>
<td>~ 10</td>
</tr>
<tr>
<td>04</td>
<td>0.716</td>
<td>~ 70</td>
</tr>
<tr>
<td>05</td>
<td>0.891</td>
<td>~ 35</td>
</tr>
</tbody>
</table>
Figure 334: SEM images of BTO nanowire film thickness which were fabricated using (a) 0.500 ml, (b) 0.500 ml, (c) 0.517 ml, (d) 0.716 ml and (e) 0.891 ml reaction solution.

Figure 335: Diagrammatic representation of the nanofiber deposition process (during electrospinning) which shows the maximum fiber are being deposited along the path of the needle when electrode distance of 13 cm was used. The needle is represented here by the arrow.
5.4.1.3 TEM images and nanowire diameter distribution of BTO NWs

The TEM images of the BTO samples 01, 02, 03, 04 and 05 (fabricated via the sol-gel route) shown in Figures 336, 337, 338, 339 and 340, respectively. In each of these Figures (a), (b), (c) and (d) corresponds respectively to: low magnification TEM image; high magnification TEM image; high resolution lattice image and nanowire diameter distribution, respectively.

Overall the BTO NWs morphology and average NW diameters (observed using TEM) remained unchanged between the different samples. The average BTO NW diameters are summarized in Table 63. The lattice spacings shown in the TEM images correspond to the (100) and (110) planes of tetragonal BTO phase with distances of ~ 0.40 nm and ~ 0.28 nm, respectively. These values were consistent with the reported values, for tetragonal phased BaTiO$_3$.

(1). TEM images and NW diameter distribution of BTO Sample 01

Figure 336: TEM images showing (a) low magnification, (b) high magnification, (c) lattice images and (d) nanowire diameter distribution of BTO NWs (Sample 01) prepared using 0.500 ml precursor solution.
(2). TEM images and NW diameter distribution of BTO Sample 02

Figure 337: TEM images showing (a) low magnification, (b) high magnification, (c) lattice images and (d) nanowire diameter distribution of BTO NWs (Sample 02) prepared using 0.500 ml precursor solution.
Figure 338: TEM images showing (a) low magnification, (b) high magnification, (c) lattice images and (d) nanowire diameter distribution of BTO NWs (Sample 03) prepared using 0.517 ml precursor solution.
(4). TEM images and NW diameter distribution of BTO Sample 04

Figure 339: TEM images showing (a) low magnification, (b) high magnification, (c) lattice images and (d) nanowire diameter distribution of BTO NWs (Sample 04) prepared using 0.716 ml precursor solution.
Figure 340: TEM images showing (a) low magnification, (b) high magnification, (c) lattice images and (d) nanowire diameter distribution of BTO NWs (Sample 05) prepared using 0.819 ml precursor solution.

Average nanowire diameter: 129 ± 26 nm
Table 63: Average NW diameters of the five BTO NW films fabricated via sol-gel route.

<table>
<thead>
<tr>
<th>BTO sample</th>
<th>Average NW diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>124 (± 28) nm</td>
</tr>
<tr>
<td>02</td>
<td>153 (± 32) nm</td>
</tr>
<tr>
<td>03</td>
<td>167 (± 27) nm</td>
</tr>
<tr>
<td>04</td>
<td>127 (± 20) nm</td>
</tr>
<tr>
<td>05</td>
<td>127 (± 26) nm</td>
</tr>
</tbody>
</table>

EDX spectroscopy analysis of BTO nanofibers and nanowires

BTO NWs were fabricated using a Ba(OAc)$_2$ and Ti(O$i$Pr)$_4$ molar ratio of ~ 1:1. All five BTO NWs samples were prepared from the same stock sol-gel reaction solution. The EDX quantitative analysis performed on the five BTO NW films showed similar Ba:Ti At% ratios. The results (in terms of At%) are summarized in Table 64. Figure 342 (EDX maps) indicate a relative uniform distribution of Ba and Ti in these samples.

Figure 341: EDX analysis shown here is of a BTO nanowire film fabricated using 0.891 ml solution which represents a typical spectrum observed for BTO NW films fabricated via sol-gel method.
Table 64: At % of Ba$^{2+}$ and Ti$^{4+}$ measured using EDX of the five BTO samples prepared.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ba At%</th>
<th>Ti At%</th>
<th>Ba:Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>58.48</td>
<td>41.52</td>
<td>~ 1:1.4</td>
</tr>
<tr>
<td>02</td>
<td>52.11</td>
<td>47.89</td>
<td>~ 1:1.1</td>
</tr>
<tr>
<td>03</td>
<td>56.46</td>
<td>43.54</td>
<td>~ 1:1.3</td>
</tr>
<tr>
<td>04</td>
<td>52.01</td>
<td>47.89</td>
<td>~ 1:1.1</td>
</tr>
<tr>
<td>05</td>
<td>51.74</td>
<td>41.52</td>
<td>~ 1:1.2</td>
</tr>
<tr>
<td>Average</td>
<td>54.16 (± 3.11)</td>
<td>44.47 (± 3.23)</td>
<td>~1:1.2</td>
</tr>
</tbody>
</table>

Figure 342: EDX map shown here is of a BTO nanowire film (Sample 05) fabricated using 0.891 ml solution.

5.4.1.4 XRD spectroscopy analysis of BTO nanofibers and nanowires

The XRD analysis performed on the five BTO NW film samples is shown in Figure 343. The spectra showed the presence of the characteristic peaks of a BaTiO$_3$ tetragonal phase: (110), (111), (200), (210), (211), (220), (300), (310) and (311) and were consistent with the reported $2\theta$ values (shown in Table 65).$^{250-254}$
5.4.1.5 Raman spectroscopic analysis of BTO nanofibers and nanowires

The Raman peaks at ~ 300 cm$^{-1}$ and 520 cm$^{-1}$ correspond to vibrations of $A_1$(TO$_2$) and $A_1$(TO$_3$) symmetry of the BaTiO$_3$ tetragonal phase. In this case, $A_1$ corresponds to the symmetrical vibrational mode and TO$_3$ corresponds to a transverse optical phonon.$^{252}$ Both peaks were observed in the spectra for each sample, with some variation in intensity between them. Variation in the
intensities might be due to the differences in the NW film thickness and/or in the At% ratios between Ba$^{2+}$ and Ti$^{4+}$ oxide species.

Figure 344: Raman analysis of the four BTO samples showing the characteristic BaTiO$_3$ spectrum. The spectra were processed through FFT filter (18 unit) using Origin 9.0. The peaks have been verified with the reported values.$^{252,253}$

5.4.2 (Ba$_{1-x}$Sr$_x$)TiO$_3$, (x=0.4) (BST) NWs fabrication via a sol-gel route, electrospinning, and annealing

Barium strontium titanate, (Ba$_{1-x}$Sr$_x$)TiO$_3$, x=0.4, nanowires were prepared by using a sol-gel reaction with molar composition of 0.6:0.4:1.0 ratio of Ba: Sr: Ti. The BST NWs were fabricated by only varying the volume of sol-gel solution that was used to prepare the nanofiber films. The precursor masses and the electrospinning/annealing parameters used to fabricate the BST NWs were reported previously in Tables 60 and 61, respectively. The fabrication process was summarized in Figure 328. The NW film thickness did not show any dependence on the sol-gel volume dispensed (Table 65) during electrospinning (due to the same reason as discussed in Section 5.2.1.2).
5.4.2.1 SEM images of BST nanofibers and nanowires

(1). SEM images of BST Sample 01

The nanowires are prepared by using 0.500 ml of the sol-gel solution with a morphology as shown in Figure 345.

Figure 345: BST (a) nanofibers and (b) nanowires fabricated using 0.500 ml of sol-gel solution.

(2). SEM images of BST Sample 02

The nanowires are prepared by using 0.500 ml of the sol-gel solution with a morphology as shown in Figure 346.

Figure 346: BST (a) nanofibers and (b) nanowires fabricated using 0.500 ml of sol-gel solution.
(3). SEM images of BST Sample 03

The nanowires are prepared by using 0.700 ml of the sol-gel solution with a morphology as shown in Figure 347.

Figure 347: BST (a) nanofibers and (b) nanowires fabricated using 0.700 ml of sol-gel solution.

(4). SEM images of BST Sample 04

The nanowires are prepared by using 0.900 ml of the sol-gel solution with a morphology as shown in Figure 348.

Figure 348: BST (a) nanofibers and (b) nanowires fabricated using 0.900 ml of sol-gel solution.
5.4.2.2 SEM images SEM images of BST nanowire film thickness

Figure 349: SEM images of BST nanowire film thickness of BST NW film (a) sample 01, (b) sample 02, (c) sample 03, and (d) sample 04.

<table>
<thead>
<tr>
<th>BST Sample #</th>
<th>Volume dispensed (ml)</th>
<th>Nanowires film thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>0.500 ml</td>
<td>~ 30 µm</td>
</tr>
<tr>
<td>02</td>
<td>0.500 ml</td>
<td>~ 30 µm</td>
</tr>
<tr>
<td>03</td>
<td>0.700 ml</td>
<td>~ 10 µm</td>
</tr>
<tr>
<td>04</td>
<td>0.900 ml</td>
<td>~ 20 µm</td>
</tr>
</tbody>
</table>
5.4.2.3 TEM images and NW diameter distribution of BST NW films

TEM images and NW diameter distributions of BST NW sample 01, sample 02, sample 03 and sample 04 are shown in Figures 350, 351, 352 and 353. BST lattice spacing measurements shown in the TEM images were 0.233 nm, 0.298 nm and 0.396 nm corresponding to (111), (110) and (100) planes, respectively, and were consistent with the reported values\textsuperscript{254}. The average BST NW diameters (measured using TEM images) had relatively similar values for all the BST NW films (~107 to 125 nm with a standard deviation of ~ 25 nm) (Table 66). The darker regions in the NWs shown in Figure 350 (b) corresponds to high crystallinity of the overlapping crystallites.

(1). TEM images and NW diameter distribution of BST Sample 01

![Figure 350: TEM images showing (a) low magnification, (b) high magnification, (c) lattice images and (d) nanowire diameter distribution of BST NWs (Sample 01) prepared using 0.500 ml precursor solution.](image)
TEM images and NW diameter distribution of BST Sample 02

Figure 351: TEM images showing (a) low magnification, (b) high magnification, (c) lattice images and (d) nanowire diameter distribution of BST NWs (Sample 02) prepared using 0.500 ml precursor solution.
(3). TEM images and NW diameter distribution of BST Sample 03

Figure 352: TEM images showing (a) low magnification, (b) high magnification, (c) lattice images and (d) nanowire diameter distribution of BST NWs (Sample 03) prepared using 0.700 ml precursor solution.
Figure 353: TEM images showing (a) low magnification, (b) high magnification, (c) lattice images and (d) nanowire diameter distribution of BST NWs (Sample 04) prepared using 0.900 ml precursor solution.
Table 67: Average NW diameters of the five BST NW films fabricated via sol-gel route.

<table>
<thead>
<tr>
<th>BST sample</th>
<th>Average NW diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>01 (0.500 ml)</td>
<td>106 (± 23) nm</td>
</tr>
<tr>
<td>02 (0.500 ml)</td>
<td>121 (± 31) nm</td>
</tr>
<tr>
<td>03 (0.700 ml)</td>
<td>107 (± 22) nm</td>
</tr>
<tr>
<td>04 (0.900 ml)</td>
<td>125 (± 27) nm</td>
</tr>
</tbody>
</table>

5.4.2.4 EDX analysis of BST NWs films

Figure 354 shows the typical EDX spectrum observed for the BST NW films. (Ba$_{1-x}$Sr$_x$)TiO$_3$, $x=0.4$, nanowires were prepared by using a sol-gel reaction (in addition to electrospinning and annealing) with a precursor molar composition of 0.6:0.4:1.0 ratio of barium to strontium to titanium atoms. (Ba:Sr):Ti At% were evaluated using EDX quantitative analysis and were measured to have Ba:Sr ~ 1.7:1 and (Ba+Sr):Ti ~ 1.2:1 (Table 67).

Figure 354: EDX spectrum of BST NWs film (Sample 04) fabricated using 0.500 ml sol-gel solution. This spectrum represents the typical BST spectra observed in this series of experiments.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Ba At%</th>
<th>Sr At%</th>
<th>Ti At%</th>
<th>Ba:Sr</th>
<th>(Ba+Sr):Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>34.67</td>
<td>20.48</td>
<td>44.85</td>
<td>~ 1.7:1</td>
<td>~ 12:1</td>
</tr>
<tr>
<td>2</td>
<td>31.76</td>
<td>24.53</td>
<td>48.75</td>
<td>~ 1.3:1</td>
<td>~ 1.2:1</td>
</tr>
<tr>
<td>3</td>
<td>32.30</td>
<td>18.90</td>
<td>48.80</td>
<td>~ 1.7:1</td>
<td>~ 1.0:1</td>
</tr>
<tr>
<td>4</td>
<td>36.00</td>
<td>17.59</td>
<td>46.41</td>
<td>~ 2.0:1</td>
<td>~ 1.2:1</td>
</tr>
<tr>
<td>Average</td>
<td>33.68 (± 2.00)</td>
<td>20.38 (± 3.01)</td>
<td>47.20 (± 1.92)</td>
<td>~1.7:1</td>
<td>~ 1.2:1</td>
</tr>
</tbody>
</table>

The EDX map of the BST nanowire film is shown in Figure 32 which demonstrates a homogeneous distribution of O, Ba, Sr and Ti species across the nanowires that were investigated.

Figure 355: EDX map of BST NWs film (Sample 04) fabricated using 0.500 ml sol-gel solution.
5.4.2.5 XRD spectra of BST NWs films

The XRD peaks associated with BST showed characteristics peaks that are consistent with the tetragonal phase. The peaks have been verified with the reported values\textsuperscript{255,256,257}.

Figure 356: XRD analysis of the four BST samples showing the characteristic \((\text{Ba,Sr})\text{TiO}_3\) reflections of tetragonal phase.

5.4.2.6 Raman spectra analysis of BST NW films

The three peaks observed in the Raman spectra (Figure 357) corresponds to the BST bands \(A_{1}(\text{TO}_2)\), \(A_{1}(\text{TO}_3)\) and \(E(\text{TO}_4)\) at \(\sim 280 \text{ cm}^{-1}, 490 \text{ cm}^{-1}\) and \(517 \text{ cm}^{-1}\), respectively. The peaks have been verified with the reported values.\textsuperscript{258} Again, some variation in peak intensity is observed between samples.
5.5 Conclusion

In this chapter BTO and BST NWs fabrication via a sol-gel route in conjunction with electrospinning and annealing was presented. This investigation did not show any direct correlation between the sol-gel volume used for electrospinning and the resulting NWs film thickness. The BTO NWs were measured to have a diameter of ~ 125 nm to ~ 167 nm whereas the BST NWs were measured to be in ~ 106 nm to ~ 125 nm range. The EDX, Raman, EDX showed supported the presence of the tetragonal phase associated with the BTO and BST NWs prepared
via sol-gel and electrospinning route. The significance of these NW films is that they are very flexible (can be bent \( \sim 180^\circ \) and when released, it returns to original form) and such a configuration has not yet been reported previously. This new NW film morphology made it possible for our collaborator to subsequently evaluate the piezoelectric properties of BTO and BST NWs.
Chapter VI

Conductivity measurements of YSZ nanowires under N$_2$ and O$_2$ atmospheres.
6.0 Introduction

In this chapter the conductivity data of YSZ NW films, fabricated via a combined sol-gel, electrospinning, and annealing method, are presented. Yttria stabilized zirconia (YSZ) has been one of the most widely studied solid electrolyte ionic conductors to date and have been used in applications including oxide gas sensors and solid oxide fuel cells (SOFCs). However, the widespread use of such metal oxide electrolyte (MOE) materials for fuel cell application is restricted primarily by its high operating temperature (800°C to 1000°C). Reduction of its operation temperature to intermediate (700°C to 800°C) and low (600°C to 700°C) range have been the focus of recent research. The reduction in the charge transfer path through the electrolyte and increase in the catalyst surface area through nanostructuring, are two ways to lower the operating temperature for MOE based applications.

Currently the goal has been the development of porous cathode and anode materials to allow an increase in the surface area of the three phase boundary (TPB). Recall that a TPB is the active site where the electrode, electrolyte and O₂ coexists for the redox reaction to take place (Figure 358).

Figure 358: Diagrammatic representation of oxygen reduction at a TPB.
At the TPBs cathodes, supply electrons (e\(^-\)) to the oxygen molecules (O\(_2\)) which are adsorbed to its surface (Rxn. 2).\(^{268}\) The reduced oxygen (O\(^2-\)) is then transferred to the electrolyte phase (YSZ) where it is transported to the anode and oxidized (Rxn. 3).

\[
O_2 (g) + 4e^- \rightarrow 2O^{2-} \quad \text{(Rxn. 2)}
\]

\[
2O^{2-} \rightarrow 4e^- + O_2 (g) \quad \text{(Rxn. 3)}
\]

6.1 Reported MOE conductivity and activation energy (chart)

So far in this dissertation, fabrication of YSZ and Bi\(_2\)O\(_3\) 1D MOE materials have been presented. Other MOE materials have also been extensively studied and some of their conductivity data at elevated temperatures are summarized in Table 68.

<table>
<thead>
<tr>
<th>Metal oxide electrolytes</th>
<th>Conductivity ((\sigma/\text{S cm}^{-1}))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>800°C</td>
<td>1000°C</td>
</tr>
<tr>
<td>(ZrO(<em>2))</em>{0.98}(Y_2O_3)_{0.02}</td>
<td>0.0135</td>
<td>0.048</td>
</tr>
<tr>
<td>(ZrO(<em>2))</em>{0.97}(Y_2O_3)_{0.03} - 10 wt% Al(_2)O(_3)</td>
<td>0.012</td>
<td>0.040</td>
</tr>
<tr>
<td>(ZrO(<em>2))</em>{0.93}(Sc_2O_3)_{0.07}</td>
<td>0.086</td>
<td>0.274</td>
</tr>
<tr>
<td>(ZrO(<em>2))</em>{0.92}(Yb_2O_3)_{0.08}</td>
<td>0.050</td>
<td>0.158</td>
</tr>
<tr>
<td>(ZrO(<em>2))</em>{0.92}(Y_2O_3)<em>{0.04}(Yb_2O_3)</em>{0.04}</td>
<td>0.044</td>
<td>0.15</td>
</tr>
<tr>
<td>(ZrO(<em>2))</em>{0.92}(Y_2O_3)<em>{0.04}(Sc_2O_3)</em>{0.04}</td>
<td>0.062</td>
<td>0.221</td>
</tr>
<tr>
<td>(CeO(<em>2))</em>{0.70}(GdO_1.5)_{0.30}</td>
<td>0.093</td>
<td>0.25</td>
</tr>
<tr>
<td>(CeO(<em>2))</em>{0.80}(SmO_1.5)_{0.20}</td>
<td>0.096</td>
<td>0.25</td>
</tr>
<tr>
<td>(Bi(<em>2)O(<em>3))</em>{0.80}(Er_2O_3)</em>{0.20}</td>
<td>0.37 (700°C)</td>
<td>-</td>
</tr>
<tr>
<td>(Bi(<em>2)O(<em>3))</em>{0.85}(Nb_2O_5)</em>{0.15}</td>
<td>0.50 (880°C)</td>
<td>-</td>
</tr>
<tr>
<td>(Bi(<em>2)O(<em>3))</em>{0.75}(Dy_2O_3)</em>{0.25}</td>
<td>0.46 (880°C)</td>
<td>-</td>
</tr>
<tr>
<td>(La(<em>{0.9})Sr(</em>{0.1}))(Ga(<em>{0.8})Mg(</em>{0.2}))(<em>3)(</em>\alpha)</td>
<td>0.121</td>
<td>0.316</td>
</tr>
<tr>
<td>(HfO(<em>2))</em>{0.92}(Y_2O_3)_{0.08}</td>
<td>-</td>
<td>0.025</td>
</tr>
</tbody>
</table>
Jiang and coworkers\textsuperscript{261} demonstrated an increase in YSZ conductivity with a decrease in thin film thickness (Figure 359 (a)). In this system, the thickness of the film was defined as the distance between the working and counter electrodes and these were prepared using an electrodeposition method. Laurent and coworkers\textsuperscript{281} have demonstrated similar conductivity data for Bi$_2$O$_3$ thin films where the Bi$_2$O$_3$ thin film conductivity was shown to be higher than YSZ (Figure 359 (b)).

Figure 359: Arrhenius plots of (a) YSZ and (b) Bi$_2$O$_3$ based on film thickness which have been taken from reported publications. In this Figure, plots (a) and (b) are taken from Ref. 261 and Ref. 281, respectively.

The topics that are covered in this chapter include: (1) an impregnation process of platinum (Pt\textsuperscript{0}) and nickel (Ni\textsuperscript{0}) nanoparticle (NP) on YSZ NWs and their characterization; (2) construction procedures of the heterostructure and gas flow system used for the conductivity measurements; (3) calculations performed to generate the Arrhenius plots for conductivity

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>0.0075</th>
<th>279</th>
</tr>
</thead>
<tbody>
<tr>
<td>(ThO$<em>2$)$</em>{0.92}$(Y$_2$O$<em>3$)$</em>{0.08}$</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ThO$<em>2$)$</em>{0.93}$(CaO)$_{0.07}$</td>
<td>-</td>
<td>0.002</td>
<td>280</td>
</tr>
</tbody>
</table>
experiments performed in O\textsubscript{2} and N\textsubscript{2} atmosphere; and (4) determination of O\textsuperscript{2-} ion migration activation energy from the Arrhenius plots.

6.2 Experimental section

In this section the electrode deposition process, the YSZ NWs film heterostructure fabrication and equipment setup for the conductivity measurements are presented. However, before doing so a brief description of a typical transistor type fuel cell (Figure 360) is presented as electrode deposition process and YSZ NW electrolyte setup is derived from its design.

In a typical SOFC, the MOE is placed between two chambers containing O\textsubscript{2} and H\textsubscript{2} separately. The electrolyte is encompassed with a gas impermeable barrier that prevents the mixing of these two gases. The electrodes contain the TPB where the redox reaction takes place and are also wired to an external load. Based on this model, a heterostructure was assembled to evaluate the ionic conductivity of the 8YSZ NW films.
The heterostructure constructed for the conductivity measurements had a transistor type architecture where a rectangular shaped flat YSZ NWs film was impregnated with Pt NP electrodes. The dimensions of the YSZ NW film are characterized as shown in Figure 361 (a).

Figure 361: (a) Diagrammatic representation of the YSZ NW film placed between the cathode and anode and (b) side view of the transistor type heterostructure.
### 6.2.1 Impregnation of NPs on YSZ NW electrolyte

In this section, the impregnation of Pt and Ni NPs on 8YSZ NWs are presented. It is carried out according to the modified procedures previously reported.\textsuperscript{282,283} The fabrication process and characterization of the YSZ NW films were discussed earlier in Chapter 3 and have 8% Y\textsubscript{2}O\textsubscript{3} content in all YSZ nanowire films. All these 8YSZ NWs used for the conductivity measurements were fabricated using the sol-gel route in combination with electrospinning and annealing processes. The anode-electrolyte-cathode type layout was prepared using two different configurations: (1) Pt/8YSZ/Pt; and (2) Ni/8YSZ/Pt. These two types of configurations have been reported previously but not for a 8YSZ electrolyte with a NW film morphology (which is the primary focus of this dissertation).\textsuperscript{284-292}

This investigation involving the impregnation of Pt and Ni NP electrodes on 8YSZ NWs was divided into two sections: (1) variation of the volume of NP precursor solution; and (2) variation of the number of layers applied on the NWs film. The metallic Pt (Pt\textsuperscript{0}) NPs were fabricated using a H\textsubscript{2}PtCl\textsubscript{6} (Aldrich) solution prepared in 95% isopropanol (\textsuperscript{i}PrOH, Aldrich) in resulting 5.88 mM and 7.90 mM H\textsubscript{2}PtCl\textsubscript{6}/\textsuperscript{i}PrOH concentrations. Metallic Ni (Ni\textsuperscript{0}) NPs were deposited using 0.198 M tris(2,2'-bipyridine)nickel (II) chloride [Ni(bpy)\textsubscript{3}Cl\textsubscript{2}.5H\textsubscript{2}O] in ethanol. In this chapter, Ni(bpy)\textsubscript{3}Cl\textsubscript{2}.5H\textsubscript{2}O solution prepared in ethanol will be abbreviated as Ni(bpy)\textsubscript{3}Cl\textsubscript{2}/EtOH.
6.2.1.1 Investigation of Pt NP deposition on YSZ nanowires based on volume of the H₂PtCl₆/PrOH solution (5.88 mM)

The purpose of this investigation is to evaluate the effect of Pt NP deposition on 8YSZ-based on the amount of H₂PtCl₆/PrOH solution applied to the 8YSZ NWs film. The thermal decomposition mechanism of H₂PtCl₆ have been reported previously²⁹³ and is shown in Rxns. 4, 5 and 6. For this experiment, a 5.88 mM H₂PtCl₆/PrOH solution was used.

\[
\begin{align*}
\text{H}_2\text{PtCl}_6 (s) & \xrightarrow{(220^\circ C)} \text{PtCl}_4 (s) + 2\text{HCl} (g) \\
\text{PtCl}_4 (s) & \xrightarrow{(350^\circ C-415^\circ C)} \text{PtCl}_2 (s) + \text{Cl}_2 (g) \\
\text{PtCl}_2 (s) & \xrightarrow{(510^\circ C)} \text{Pt}^0 (s) + \text{Cl}_2 (g)
\end{align*}
\]

(Rxn.4)  
(Rxn.5)  
(Rxn.6)

In this set of experiments, the volume of H₂PtCl₆/PrOH (5.88mM) added to a set of 8YSZ NW films was varied. Four 8YSZ NWs films were prepared on which a H₂PtCl₆/PrOH solution was applied. In this case, 1 drop of solution is considered to be ~ 0.05 ml.²⁹⁴ The 1st 8YSZ NWs films were treated with 1 drop of H₂PtCl₆/PrOH solution and allowed to air dry. The 2nd, 3rd and 4th 8YSZ NWs films were coated with 2 drops (~0.10 ml), 4 drops (~0.20 ml) and 8 drops (~0.40 ml) of H₂PtCl₆/PrOH (5.88mM), respectively. In these cases, all drops were applied without any air drying step between them. A 5th sample was prepared where 8 drops of H₂PtCl₆/PrOH was applied with an additional air drying step between each drop. This was done to evaluate the differences between the 8-drop samples prepared with and without an air drying step between the application of the precursor solution. After the application of H₂PtCl₆/PrOH solution, all 8YSZ samples were placed in a furnace under a He atmosphere and heated to 550°C for 30 min. The Pt NPs impregnated 8YSZ NW films were then evaluated using TEM, EDX and Pt NPs diameter histogram analysis. The parameters used for this set of experiments are summarized in Table 69.
Table 70: Varying H$_2$PtCl$_6$/iPrOH (5.88mM) deposition volume

<table>
<thead>
<tr>
<th>Initial sample</th>
<th>Volume of solution added (ml)</th>
<th>Annealing temperature (°C)</th>
<th>Time of annealing (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8YSZ (uncoated)</td>
<td>~ 0.05 ml (1 drop)</td>
<td>550°C</td>
<td>30 min</td>
</tr>
<tr>
<td></td>
<td>~ 0.10 ml (2 drops)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>~ 0.20 ml (4 drops)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>~ 0.40 ml (8 drops)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>~ 0.40 ml (8 drops) (with air drying between each drop)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6.2.1.2 Investigation of Pt NP deposition on YSZ nanowires based on the number of layers of 7.90 mM H$_2$PtCl$_6$/PrOH solution was applied

A layered deposition of Pt NPs on 8YSZ NW film was also investigated using a 7.90 mM H$_2$PtCl$_6$/PrOH solution. The 1st layer of Pt NPs were deposited by applying ~ 0.10 ml (2 drops) of H$_2$PtCl$_6$/PrOH solution on a 8YSZ NWs film (placed on a Si wafer). Once the sample was air dried it was carefully covered with another Si wafer and annealed at 550°C for 30 min under a He atmosphere. This sample was labeled as 8YSZ+1XPt indicating the deposition of 1 layer of Pt NPs. After annealing, 8YSZ+1XPt was treated with 2 more drops of the H$_2$PtCl$_6$/PrOH solution and annealed (in a similar process used for 8YSZ+1XPt) at 550°C for 30 min under a He atmosphere and was labeled 8YSZ+2XPt. This process was repeated three more times to obtain samples 8YSZ+3XPt, 8YSZ+4XPt, and 8YSZ+5XPt which were coated with 3, 4, and 5 layers of Pt NPs, respectively. The parameters used for this set of experiments is shown in Table 70. After each annealing step, the Pt NP coated 8YSZ NW films easily detached from the Si wafer without the film breaking or cracking. This is important as the conductivity measurement requires a continuous electrolyte film between the electrodes for the O$_2^-$ migration.
### Table 71: Layered deposition of H$_2$PtCl$_6$/PrOH solution (7.90 mM) on 8YSZ NWs film

<table>
<thead>
<tr>
<th>Pt NPs layer</th>
<th>Sample name</th>
<th>Volume of H$_2$PtCl$_6$/PrOH solution applied</th>
<th>Annealing temperature (°C)</th>
<th>Annealing time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8YSZ + 1XPt</td>
<td>~ 0.10 ml (2 drops)</td>
<td>556°C</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>8YSZ + 2XPt</td>
<td>~ 0.10 ml (2 drops)</td>
<td>558°C</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>8YSZ + 3XPt</td>
<td>~ 0.10 ml (2 drops)</td>
<td>547°C</td>
<td>~ 30 min</td>
</tr>
<tr>
<td>4</td>
<td>8YSZ + 4XPt</td>
<td>~ 0.10 ml (2 drops)</td>
<td>552°C</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>8YSZ + 5XPt</td>
<td>~ 0.10 ml (2 drops)</td>
<td>540°C</td>
<td></td>
</tr>
</tbody>
</table>

#### 6.2.2 Ni$^0$ NPs impregnation of 8YSZ NWs film

It was necessary to evaluate deposition of Ni$^0$ NPs on 8YSZ NWs in order to fabricate Ni/8YSZ/Pt (anode/electrolyte/cathode) type NW films for conductivity measurements. Ni$^{2+}$ precursors that were evaluated for Ni$^0$ NP deposition process is shown in Table 71.

### Table 72: Ni$^{2+}$ precursors investigated for the deposition of Ni$^0$ NPs on 8YSZ NWs

<table>
<thead>
<tr>
<th>Ni$^{2+}$ precursor name</th>
<th>Name abbreviation used</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel (II) acetylacetonate [Ni(CH$_3$COCHCOCH$_3$)$_2$]</td>
<td>Ni(acac)$_2$</td>
<td>2-methoxyethanol [CH$_3$OCH$_2$CH$_2$OH]</td>
<td>295, 296, 297, 298</td>
</tr>
<tr>
<td>Tris(2,2'-bipyridine)nickel(II) chloride [Ni(2,2'-bipyridine)$_3$Cl$_2$.5H$_2$O]</td>
<td>Ni(bpy)$_3$Cl$_2$</td>
<td>95% Ethanol [CH$_3$CH$_2$OH]</td>
<td>299</td>
</tr>
<tr>
<td>Nickel (II) nitrate [Ni(NO$_3$)$_3$]</td>
<td>Ni(NO$_3$)$_3$</td>
<td>Methanol [CH$_3$OH]</td>
<td>300</td>
</tr>
</tbody>
</table>

Out of these, Ni(bpy)$_3$Cl$_2$.5H$_2$O was the only precursor that resulted in Ni$^0$ nanoparticles and at the same time did not break the 8YSZ NW film. Ni(acac)$_2$ and NiCl$_2$ both resulted in the fragmentation of the 8YSZ NW films during the annealing process. For this reason, only the method involving Ni(bpy)$_3$Cl$_2$.5H$_2$O precursor is presented in this chapter.
6.2.2.1 Ni$^0$ NPs deposition on 8YSZ NW films

(1). Synthesis of Ni(bpy)$_3$Cl$_2$.5H$_2$O

Ni(bpy)$_3$Cl$_2$ was synthesized according to a reported procedure$^{299,301}$ using NiCl$_2$.6H$_2$O, 2,2’-bipyridine and H$_2$O/EtOH (1:1 ratio) as solvent. The precursors and their quantities used for the fabrication of Ni(bpy)$_3$Cl$_2$ are presented in Table 72. The fabrication procedure is outlined in Figure 362. The reactants were mixed together and allowed to mix for 30 min at room temperature during which the solution color changed from green to dark blue to red. This red solution was placed in a vacuum chamber to increase the concentration. It was then placed in a refrigerator (2-3°C) overnight to induce crystallization. Once formed, the crystals are isolated by a decantation process and air dried before re-dissolving in 95% ethanol to form a 0.198 M Ni(bpy)$_3$Cl$_2$/EtOH solution.

| Table 73: Precursor quantities used for the synthesis of Ni(bpy)$_3$Cl$_2$.5H$_2$O |
|---------------------------------|---------------------------------|------------------|
| Reagent                        | Amount used | Source                                      |
| NiCl$_2$.6H$_2$O                | 0.2426 g   | Aldrich                                     |
| 2,2’bipyridine                 | 0.4686 g   | Matheson Coleman and Bell                   |
| 95% ethanol                    | 20.00 ml   | Pharmco-Aaper                               |
| D.I. H$_2$O                    | 20.00 ml   | Lab distiller                               |
Figure 362: Outline of the procedure used for the synthesis of Ni(bpy)$_3$Cl$_2$.5H$_2$O crystals.

(2). Ni$^0$ NPs impregnation on 8YSZ NWs

Impregnation of Ni$^0$ NPs on 8YSZ NWs takes place by deposition of a Ni(bpy)$_3$Cl$_2$/EtOH solution (0.198 M) in a layer by layer process with thermal decomposition$^{302}$ at 600°C (He atmosphere, 30 min) between the deposition of each layer. The He flow rate was set to 100 sccm (standard cubic centimeter per minute). The decomposition mechanism of Ni(bpy)$_3$Cl$_2$ has been reported$^{299}$ and is shown in Figure 363. The 1$^{st}$ layer of Ni$^0$ NPs was deposited by placing a 8YSZ NW film (fabrication process discussed in Chapter 3) on a Si wafer. Approximately 0.10 ml (2 drops) of Ni(bpy)$_3$Cl$_2$/EtOH (0.198 M) solution was placed on the 8YSZ film which was then placed in an oven (95°C) for 5 min to expedite the drying process. Once dried, the Ni(bpy)$_3$Cl$_2$ coated 8YSZ NWs film was covered with a second Si wafer and placed in the furnace (with He atmosphere, 100 sccm). The sample was heated at a rate of ~ 20°C/min to 600°C and held at that temperature for 30 minutes before cooling to room temperature. This sample was labeled as 8YSZ+1XNi which indicated the application of the first layer of Ni$^0$ NPs on 8YSZ NWs. The process was repeated twice more to obtain samples labeled 8YSZ+2XNi and 8YSZ+3XNi which corresponded to 8YSZ NWs films with 2 and 3 layers of the Ni$^0$ NPs, respectively.
6.2.3 Fabrication of Pt NPs on 8YSZ NWs film with anode/electrolyte/cathode configuration of Pt/8YSZ/Pt

For the conductivity measurements, the 8YSZ NW film needed to be impregnated with nanoparticle electrodes on the two ends of a 8YSZ NW film (Figure 364) to obtain an anode/electrolyte/cathode type configuration. The two types of anode/electrolyte/cathode configurations fabricated (on a single 8YSZ NW film) for conductivity measurements were: (1) Pt/8YSZ/Pt using 5.88 mM H₂PtCl₆/iPrOH solution; and (2) Ni/8YSZ/Pt. The Pt and Ni electrodes were deposited according to the process discussed in the previous section using the precursors H₂PtCl₆/iPrOH (7.90 mM) and Ni(bpy)₃Cl₂/EtOH (0.198 M), respectively.
6.2.3.1 Application of Pt\textsuperscript{0} NPs on 8YSZ NW films using the Parafilm mask method

The NP electrodes were deposited on a 8YSZ NW film using a masking method so that the impregnated NPs were confined only to the two ends of the 8YSZ NW film (to prevent an electrical short). In this case, Parafilm\textsuperscript{®} plastic film was used as the masking material due to its low melting point (68°C)\textsuperscript{303} and was observed to vaporize above 350°C. This allowed control over the deposition and removal of the mask.

The NP deposition process on 8YSZ NW film is carried out in 4 steps: (1) application of parafilm mask on one side of 8YSZ NW film; (2) deposition and thermal degradation of NP (Pt or Ni) precursor solution; (3) reapplication of the parafilm mask on the 8YSZ NW film; and (4) deposition and thermal decomposition of NP precursors on 8YSZ NW film (Figure 365).

Figure 364: Diagram showing (a) top view and (b) side view of a 8YSZ NW film with impregnated NPs as anode and cathode on the two ends of the 8YSZ NW film.
Figure 365: Process of NP deposition on 8YSZ NW film using the Parafilm method.
(1). Deposition of Parafilm® mask on one side of 8YSZ NW film

In step (1), a 8YSZ NW film (~ 4 mm X 3 mm) is placed on a dry Si wafer (Figure 366 (a)). A small rectangular piece of Parafilm (~ 1.5 mm X 3 mm) was cut and placed on one end of the 8YSZ NW film (Figure 366 (b)). The Si wafer substrate containing the 8YSZ NW film and parafilm was then placed on a pre-heated hot plate to melt the parafilm. Once melted (Figure 366 (c)), the liquid parafilm propagated towards the other side of the 8YSZ film (via a capillary effect) at which point the Si wafer was removed from the hot plate and placed on an ice cube to solidify the parafilm (Figure 366 (d)). The parafilm was solidified only when the liquid covered approximate 2/3 of the 8YSZ NW film. Figure 367 shows the images of the molten parafilm on a 8YSZ NW film.

Figure 366: Deposition process of the parafilm mask on the 8YSZ NW film.
(2). Application of 5.88 mM Pt NP precursor (H$_2$PtCl$_6$/isopropanol) on the unmasked side of the 8YSZ NW film and the thermal decomposition of the precursor

In this step, ~ 0.10 ml (2 drops) of H$_2$PtCl$_6$/PrOH (5.88 mM) was applied on the side of the 8YSZ NW film that was not coated with Parafilm (Figure 368 (a)). The H$_2$PtCl$_6$/PrOH solution was air dried (Figure 368 (b)) before it was covered with a second Si wafer and placed in a furnace. H$_2$PtCl$_6$/PrOH was thermally decomposed to Pt$^0$ (Figure 368 (c)) by heating a 8YSZ NW film at 600°C for 30 min (under a He atmosphere; 100 sccm). During this annealing process the Parafilm was also removed, leaving a 8YSZ NW film with impregnated Pt NPs on one side of the film.

Figure 368: Deposition of Pt NPs on 8YSZ NW film (partially covered with a Parafilm mask).
(3). Re-application of Parafilm mask on the side of 8YSZ NW film containing Pt NPs

This was done as described in step (1) where the parafilm was melted at 60°C (Figure 369 (a)), allowed to penetrate the 8YSZ NW film (Figure 369 (b)) and re-solidified by placing the substrate on an ice cube (Figure 369 (c)).

![Figure 369: Deposition of Parafilm mask over Pt NPs impregnated 8YSZ NWs film.](image)

(4). Application of H₂PtCl₆/iPrOH on 8YSZ and its thermal decomposition to form Pt⁰

This process was performed similarly as described in step (2) where ~ 0.10 ml (2 drops) of H₂PtCl₆/iPrOH (5.88 mM) was placed on the unmasked side of the 8YSZ NW film ((Figure 370 (a)). The solution was air dried (Figure 370 (b)) before it was covered with a 2nd piece of Si wafer and annealed at 600°C for 30 min (under a He atmosphere; 100 sccm). The process decomposed H₂PtCl₆ to Pt⁰ and removed the Parafilm mask (Figure 370 (c)). An image of the final 8YSZ NW film with 1 layer of spatially controlled Pt NPs impregnation is shown in Figure 371. TEM and EDX analysis of the three regions on 8YSZ NW film (Pt/8YSZ/Pt) are presented later in this chapter.
6.2.3.2 Application of Ni\(^0\) NPs and Pt\(^0\) NPs electrodes on 8YSZ NW films using the Parafilm mask method

This process was performed to fabricate an electrolyte material with the electrode configuration Ni/8YSZ/Pt (anode/electrolyte/cathode) for the conductivity measurements. A rectangular piece of 8YSZ NW film (~ 6 mm X 3 mm) was impregnated with Pt\(^0\) NPs on one side (using 7.90 mM H\(_2\)PtCl\(_6\)/PrOH) and Ni\(^0\) NPs on the other side with a region of unimpregnated
8YSZ NWs film between them. This was done using the Parafilm method described in the previous section where Ni(bpy)$_3$Cl$_2$/EtOH (0.198 mM) was used instead if H$_2$PtCl$_6$/iPrOH in step (3) of the process. An image of the final 8YSZ NW film with 1 layer of spatially controlled Pt NPs and Ni NP impregnation is shown in Figure 372. TEM and EDX analysis of these three regions on 8YSZ NW film (Ni/8YSZ/Pt) are presented later in this chapter.

![Image of 8YSZ NW film with Ni and Pt impregnation](image.png)

Figure 372: Image of a 8YSZ NW film with 1 layer of spatially separated Ni$^0$ and Pt$^0$ impregnated NP electrodes.

6.2.4 Conductivity measurement setup constructions and procedures

In this section the conductivity setup fabrication and measurement procedures are presented. It is divided into the followed sections: (a) fabrication of the heterostructure on which 8YSZ NW film is fixed upon; (b) thermocouple, electrode wiring and gas chamber setup; and (c) conductivity measurement procedures under O$_2$ or N$_2$ atmosphere at an elevated temperature.

6.2.4.1 Fabrication of the heterostructure on which 8YSZ NW film is fixed upon

For the conductivity measurements, 8YSZ NW film was fixed to a quartz plate (substrate). The quartz plate was cut into small rectangular shape on which a narrow trench was
made. This was done to restrict potential electrons from flowing through the quartz substrate instead of the 8YSZ NW film. The dimensions of a typical quartz substrate are shown in Figure 373.

The quartz substrates were then drilled with a diamond tipped drill bit (diameter 0.015 in., Harvey tools) to make two holes on the two sides of the trench (Figure 374 (a)). A piece of 10% Rh-Pt wire was then passed through each hole and wrapped around the side of the quartz substrate (Figure 374 (a)). The 10% Rh-Pt wiring connects the 8YSZ film electrodes to a Keithley 2420 SourceMeter. A piece of 8YSZ NW film (~ 4 mm X 3 mm) was placed on a quartz substrate (over the trench) between the two holes made for the wiring (Figure 374 (a)). Ag paint (60%, M. E. Taylor Engineering, Inc.) was used to anchor the 8YSZ NW film to the quartz substrate and to make an electrical contact between the 8YSZ NW film and the 10% Rh-Pt wire connected to the SourceMeter measure unit (Figure 374 (a)).

![Figure 373: Dimension of the quartz plate (substrate) on which 8YSZ NW film is placed for conductivity measurements.](image-url)
Figure 374: Process of constructing the heterostructure used for the 8YSZ NW film conductivity measurements. (Note: Figures not drawn to scale).

6.2.4.2 Thermocouple, electrode wiring and gas chamber setup

During a given conductivity measurement, O\textsubscript{2} or N\textsubscript{2} flow rate was controlled using an Omega rotameter (FL-3613ST). The temperature of the heated gas inside the quartz tube chamber was monitored using K-type thermocouples from Omega (FS-110-20-K-12). The gas lines supplying O\textsubscript{2}/N\textsubscript{2} to the reaction chamber was built from stainless 6.4 X 5.3 mm steel tubing (VWR) and Swagelok tube fittings. These were assembled together according to the diagram in Figure 375 (a) and was then attached to the gas chamber (Figure 375 (b)) for the conductivity measurements.
Figure 375: Diagram of the setup used to perform conductivity measurements.
The wiring and thermocouples were passed through a rubber cork attached to the top of the quartz tube to direct the outgoing gas through the side nozzle of the bottom glassware. This outgoing nozzle was connected to a bubbler which was used to monitor a continuous gas flow through the chamber. In situations where there was a leak at the joints between the top and bottom part of the gas chamber, the bubbler would stop, indicating the presence of a leak. To obtain a tight seal between the two pieces (Figure 375), hot glue (from a melted glue gun) was used to seal the joints. This glue was removed from the glassware after the experiments were completed using a butane torch.

6.2.4.3 Conductivity measurement procedures

Once the 8YSZ NW film fixed to a quartz substrate is assembled, wired and placed in the gas chamber inside the furnace, the conductivity measurements are performed. The wires connected to the anode and cathode (of 8YSZ NW film) are attached to a Keithley source measure unit which supplied the voltage and measured the current conducted 8YSZ film as a function of the operating temperature.

The temperatures at which the conductivity measurements were performed is shown in Table 73. When each of these temperature set points were reached, four consecutive electrical measurements were performed which and were later averaged. The temperature, voltage and current measurements were used to generate the Arrhenius plots.

<p>| Table 74: Temperature set points at which conductivity measurements were performed. |
|---------------------------------------------------|---------------------------------------------------|</p>
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>297</td>
</tr>
<tr>
<td>56</td>
<td>329</td>
</tr>
<tr>
<td>137</td>
<td>410</td>
</tr>
<tr>
<td>286</td>
<td>559</td>
</tr>
<tr>
<td>464</td>
<td>737</td>
</tr>
<tr>
<td>615</td>
<td>888</td>
</tr>
</tbody>
</table>
6.2.5 Calculation of activation energy using conductivity data

The classical Arrhenius relationship (Eqn. 9) is used to evaluate conductivity as a function of temperature. The activation energy ($E_a$) associated with the $O^2-$ migration is calculated from the Arrhenius plot using Eqn. 10 (where $k_B$ is the Boltzmann’s constant).

\[
\left( -\frac{E_a}{k_B} \right) = \text{slope of straight line in Arrhenius plot} \quad \text{(Eqn. 10)}
\]

However, to generate the Arrhenius plot, the conductivity ($\sigma_i$) (Eqn. 9) needed to be calculated starting from the voltage ($V$) and current ($I$) values obtained using a Keithley 2420 SourceMeter. Ohm’s Law (Eqn. 11) is used to calculate the resistance ($R$). The NW film cross sectional area ($A_F$) and the NW film length ($l_F$) (distance between the electrodes) were used in conjunction with the calculated $R$ values to determine the electrical (ionic) resistivity ($\rho_E$) (Eqn. 12). The $A_F$ is the product of the NW film width ($w_F$) and its thickness ($t_F$) (as shown in Figure 361 (a)). $\sigma_i$ is then derived from $\rho_E$ using Eqn. 13.

\[
R = \frac{V}{I} \quad \text{(Eqn. 11)}
\]

\[
\rho_E = \frac{R \times A_F}{l_F} \quad \text{(Eqn. 12)}
\]

\[
\sigma_i = \frac{1}{\rho_E} \quad \text{(Eqn. 13)}
\]

Due to the presence of void between adjacent NWs (in the film), the NW film cross-sectional area (positioned perpendicular to $l_F$) was calculated using: (1) the average YSZ NW radius ($r$), and (2) the average number of YSZ NWs ($n_F$) across the $A_F$ plane (perpendicular to $l_F$). The average $r$ was calculated from SEM images (by measuring NW diameters ($d_{NW}$)) which was used to determine the cross-sectional area of 1 YSZ NW ($A_{NW}$) using Eqns. 14.
The average NWs linear density ($\rho_L$) was determined from FE-SEM images by using ImageJ (Version 1.50i). During this process, the image was first adjusted by reducing its threshold to isolate the NWs on the outer most layer of the film (Figure 376 (a)). A line ($L_d$) was drawn on the edited image (Figure 376 (b)) and the number of NWs ($n_{NW}$) crossing $L_d$ was counted. The $\rho_L$ (NWs/µm) was obtained by dividing $n_{NW}$ by $L_d$ (Eqn. 15). This process was repeated using several different SEM images to obtain a $\rho_L$ of YSZ NWs for each batch of NW films fabricated.

![Figure 376: (a) the original YSZ SEM image and (b) processed image used to determine the NWs density in YSZ NW films. This sample was measured to have ~ 2.5 NWs/µm.](image)

$$A_{NW} = \pi r^2 = \pi \left(\frac{d_{NW}}{2}\right)^2 \quad \text{(Eqn. 14)}$$

$$\rho_L = \frac{n_{NW}}{L_d} \quad \text{(Eqn. 15)}$$

The total $n_{NW}$ across $A_F$ was calculated using NW linear density along the film width ($\rho_{L,w}$) and thickness ($\rho_{L,t}$) by using Eqn. 16. The film thickness ($t_F$) was measured using a SEM.
The film length ($l_F$) and width ($w_F$) was measured using a ruler (Figure 377 (b)). Finally, the $A_F$ calculated (Eqn. 17) was used to calculate $\sigma$ using Eqn. 12 and 13.

$$n_{NW} = \left( \rho_{LW} \times w_F \right) \times \left( \rho_{LW} \times t_F \right)$$  \hspace{1cm} (Eqn. 16)

$$A_F = (A_{NW}) \times (n_{NW})$$  \hspace{1cm} (Eqn. 17)

There were a few assumptions made during the conductivity calculations: (1) a given average YSZ NW diameter measured is the diameter of all the NWs in the film; (2) NW films had well defined edges; and (3) a given NWs density measured is uniform across the NWs film. These assumptions can result in certain errors in the conductivity calculation and assumed to be within an acceptable range for this approach. The results pertaining to the electrode NPs (Pt and Ni/NiO) deposition will be discussed in the next section.
6.2.6 Ag electromigration related problems encountered during conductivity measurements.

During the conductivity measurements, it was observed that the 8YSZ NW film changes its color from white to dark grey after operation at high voltages (above 25V) and high temperatures (above >800°C). The NW films also showed formation of cracks and fractures next to the Ag-YSZ film interface which caused the termination of selected conductivity measurements. The problem was Ag migration (from the Ag paint) used to anchor 8YSZ NW film. Ag migration in ZrO$_2$ (under bias) has been reported in resistive switching memory materials.\textsuperscript{304} It has also been reported that high voltage and temperature facilitates the migration process of high mobility cations like Ag$^+$ and Cu$^+$ along grain boundaries.\textsuperscript{305,306,307} In a recent publication it was reported that Ag deposited on YSZ undergoes oxidation at high temperature by reacting with the adsorbed oxygen ion species available on the YSZ surface.\textsuperscript{308}

Ag$^+$ electromigration occurred extensively at high temperature (T$>800$°C) when a potential $>$25V was used for the conductivity measurements (Figure 378). Therefore, the operating voltage was decreased to 10V. The YSZ NW film length was also restricted to a minimum of $\sim$ 4 mm to increase the migration distance and therefore hinder further transport of Ag species across the YSZ NW electrolyte film. However, one down side to the increase in film width is that it also adds to the O$^2-$ migration resistivity. FE-SEM and EDX analysis of the Ag disposition on the 8YSZ NWs are shown in Figure 379. The conductivity measurements upper limit temperature was also kept below 800°C to minimize melting of Ag (Ag sintering temperature = 150°C and sublimation temperature = 960°C).\textsuperscript{309}
Figure 378: (a) Photograph of a 8YSZ NW film post conductivity measurements (performed using 25V at a maximum temperature of 758°C under O₂ atm). (b) SEM image of the region marked with a dashed box in (a) showing the presence of Ag particles on 8YSZ NWs. (c) SEM image of Ag particles (~ 1 um in diameter) on 8YSZ NWs near the region of Ag paint application.

Figure 379: (a) EDX spectra of 8YSZ NW film near the region of Ag Paint application shown in Figure 21 (a). (b, c) EDX map of the same region showing the distribution of the Ag particles on 8YSZ NWs.

In addition, YSZ NWs close to the Ag-YSZ interface were sputtered with Au/Pd (10 nm thick) prior to the application of Ag paint to impede Ag⁺ migration from the paint to 8YSZ NWs. The idea was to deposit a barrier layer between the 8YSZ NWs and Ag to prevent Ag oxidation by the oxide species on the YSZ NW surface. The Au/Pd sputtering was done by placing the 8YSZ
NW film (with and without Pt NPs impregnation) on a Si wafer with a piece of Parafilm placed across the width of the NW film (Figure 380 (a)). The ends of the Parafilm were pressed on the wafer to anchor the NW film (in this case Parafilm was not melted). The sample was then sputtered coated the two ends of the film with 10 nm thick Au/Pd layer (Figure 380 (b)). An SEM image of the sputtered region is shown in Figure 381. The central region was not coated as the Parafilm acted as a mask over the film which was removed (without damaging the NW film) after sputtering was completed.

Figure 380: Au/Pd coating process (a) before and (b) after the application on 8YSZ NW film.

Figure 381: SEM image of 8YSZ NWs with sputtered Au/Pd (10 nm).
6.3 Instrumentation

The conductivity measurements were performed using a Keithley 2420 SourceMeter (GPIB enabled) connected to a PC via a KUSB-488B interface adapter. It was operated using a LabTracer SourceMeter Integration Software (Version 2.9). The parameters used for the conductivity measurements are shown in Table 7.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sweep starting voltage (V)</td>
<td>-10.00 V</td>
</tr>
<tr>
<td>Sweep stopping voltage (V)</td>
<td>+10.00 V</td>
</tr>
<tr>
<td>Voltage sweep steps</td>
<td>300</td>
</tr>
<tr>
<td>Step size (V/step)</td>
<td>~ 0.067 V/step</td>
</tr>
<tr>
<td>Sweep type</td>
<td>Linear</td>
</tr>
</tbody>
</table>

The structural and chemical characterization and analysis of the nanowires were performed using field emission scanning electron microscopy (FE-SEM, JSM-7100F) and transmission electron microscopy (TEM, JEM-2100). Elemental characterization was done using electron dispersive x-ray spectroscopy (EDS/EDX) along with x-ray diffraction (XRD; Philips XRG 3100) to analyze phase composition of the fabricated Bi$_2$O$_3$ and WBO NWs. Details of these different characterization techniques, instruments and sample preparation processes have been discussed earlier in this dissertation (Section 2.2).

6.4 Results and Discussion

6.4.1 Investigation of Pt NP deposition on YSZ by varying the deposition volume of H$_2$PtCl$_6$/isopropanol solution (5.88 mM)

TEM images and average particle diameter analysis of Pt NP deposited 8YSZ NW film using 5.88 mM H2PtCl6 in isopropanol is presented in this section. The TEM images were used to generate a Pt NP diameter distribution resulting from 1, 2, 4 and 8 drops which had average
diameters of 2.07 (± 0.67) nm, 2.34 (± 0.51) nm, 2.67 (± 0.72) nm, and 2.93 (± 0.92) nm, respectively.

Figure 382: TEM images and size distribution analysis of Pt NPs obtained after the application and thermal decomposition of ~ 0.05 ml (1 drops) of 5.88 mM H₂PtCl₆/isopropanol solution.

Figure 383: TEM images and size distribution analysis of Pt NPs obtained after the application and thermal decomposition of ~ 0.10 ml (2 drops) of 5.88 mM H₂PtCl₆/isopropanol solution.

Figure 384: TEM images and size distribution analysis of Pt NPs obtained after the application and thermal decomposition of ~ 0.20 ml (4 drops) of 5.88 mM H₂PtCl₆/isopropanol solution.
Figure 385: (a, b) TEM images and (c) size distribution analysis of Pt NPs obtained after the application and thermal decomposition of ~ 0.40 ml (8 drops) of 5.88 mM H$_2$PtCl$_6$/isopropanol solution.

A comparison experiment was performed between the Pt NP deposition by this 8-drop sample (with no air drying step between each drop applied) and another sample that was prepared by application of the H$_2$PtCl$_6$/iPrOH (5.88 mM) where the solution was allowed to air dry between the application of each drop. The TEM, lattice images NP diameter analysis are shown in Figure 386. The measured lattice images were consistent with the reported values.$^{310}$ The Pt NP impregnation with and without intermediate air drying steps resulted in average Pt NP diameters of 6.12 (± 1.67) nm and 2.93 (± 0.92) nm, respectively. This indicates that an air drying step between the drops increases the size of the Pt NP deposited using 5.88 mM H$_2$PtCl$_6$/PrOH.
Figure 386: Figure showing (a-c) TEM images of oPt NP on 8YSZ NWs, (d-e) lattice spacing analysis of the impregnated particles 8YSZ NWs and (f) size distribution of Pt NPs obtained after the application of ~ 0.40 ml (8-Drops) (with air drying step) and thermal decomposition.
Summary

The average Pt NP diameters and the densities deposited on 8YSZ NW film are summarized in Tables 75 and 76, respectively. The average Pt NP diameters had similar values with a slight upward trend. In comparison, the 8 drops sample prepared with an air drying step between the drops showed significantly larger diameters compared to the non-air drying samples (Figure 387). This was expected as the air drying step allowed cumulative deposition of the precursor on the YSZ NWs which was not the case when 8 drops were applied all at once.

<table>
<thead>
<tr>
<th>No. of H$_2$PtCl$_6$ solution (5.88 mM) applied</th>
<th>Pt NP average diameter (nm)</th>
<th>Std. Dev. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>~ 0.05 ml (1-Drop)</td>
<td>2.07</td>
<td>0.67</td>
</tr>
<tr>
<td>~ 0.10 ml (2-Drops)</td>
<td>2.34</td>
<td>0.51</td>
</tr>
<tr>
<td>~ 0.20 ml (3-Drops)</td>
<td>2.67</td>
<td>0.72</td>
</tr>
<tr>
<td>~ 0.40 ml (8-Drops)</td>
<td>2.93</td>
<td>0.92</td>
</tr>
<tr>
<td>~ 0.40 ml (8-Drops) (with air drying)</td>
<td>6.12</td>
<td>1.67</td>
</tr>
</tbody>
</table>

Figure 387: Pt NP diameter based on the number of H$_2$PtCl$_6$/PrOH (5.88 mM) drops applied.
The increase in the number of drops of precursor did show a slight increase in the density of the Pt NPs with a significantly larger density observed in the sample prepared by air drying step.

<table>
<thead>
<tr>
<th>Volume of H₂PtCl₆ solution applied</th>
<th>Pt nanoparticles count on YSZ</th>
<th>Area (nm²)</th>
<th>Area (µm²)</th>
<th>Density (count/ µm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>~ 0.05 ml (1-Drop)</td>
<td>67</td>
<td>3.1E+03</td>
<td>3.1E-03</td>
<td>2.1E+04</td>
</tr>
<tr>
<td>~ 0.10 ml (2-Drops)</td>
<td>81</td>
<td>3.1E+03</td>
<td>3.1E-03</td>
<td>2.6E+04</td>
</tr>
<tr>
<td>~ 0.20 ml (3-Drops)</td>
<td>112</td>
<td>3.9E+03</td>
<td>3.9E-03</td>
<td>2.9E+04</td>
</tr>
<tr>
<td>~ 0.40 ml (8-Drops)</td>
<td>109</td>
<td>3.8E+03</td>
<td>3.8E-03</td>
<td>2.9E+04</td>
</tr>
<tr>
<td>~ 0.40 ml (8-Drops) (with air drying)</td>
<td>112</td>
<td>2.7E+03</td>
<td>2.7E-03</td>
<td>4.1E+04</td>
</tr>
</tbody>
</table>

Figure 388: Pt NP density based on the number of H₂PtCl₆/iPrOH (5.88 mM) drops applied.

6.4.2 Investigation of Pt NP deposition on 8YSZ NW film by a multi-layer process using 7.90 mM H₂PtCl₆/iPrOH solution

In this section the results pertaining to the Pt NP deposition (by a multi-layer method) on 8YSZ NW film are presented. In this method, a relatively more concentrated H₂PtCl₆/iPrOH (7.90 mM) solution was applied to the 8YSZ NWs which was allowed to air dry and annealed at 550°C.
before applying additional precursors. A total of six samples were prepared with 1, 2, 3, 4, 5 and 6 layers of the precursor solution was applied which were labeled as 1XPt, 2XPt, 3XPt, 4XPt, 5XPt, and 6XPt, respectively. The analysis includes TEM images, Pt NP diameter distribution and NP coverage density on 8YSZ NWs. The TEM images and diameter distribution of these six samples are shown first, followed by the overall discussion.

(i). **Deposition of 1st layer of Pt NPs (1XPt)**

![TEM images and Pt NP diameter distribution after 1 layer of H$_2$PtCl$_6$\textsuperscript{i}PrOH (7.90Mm).](image)

**Figure 389:** TEM images and Pt NP diameter distribution after 1 layer of H$_2$PtCl$_6$\textsuperscript{i}PrOH (7.90Mm).
(ii). Deposition of 2nd layer of Pt NPs (2XPt)

Figure 390: TEM images and Pt NP diameter distribution after 2 layers of H$_2$PtCl$_6$/PrOH (7.90mM).
(iii). Deposition of 3rd layer of Pt NPs (3XPt)

Figure 391: TEM images and Pt NP diameter distribution after 3 layers of $\text{H}_2\text{PtCl}_6/^\text{PrOH}$ (7.90mM).
(iv). Deposition of 4th layer of Pt NPs (4XPt)

Figure 392: TEM images and Pt NP diameter distribution after 4 layers of H₂PtCl₆/iPrOH (7.90mM).

4XPt
Average Pt NP diameter (nm)
= 5.9 ± 1.9 nm

Pt NP density
= 1.5X10⁴ particle/µm²
(v). Deposition of 5th layer of Pt NPs (5XPt)

Figure 393: TEM images and Pt NP diameter distribution after 5 layers of H₂PtCl₆/PrOH (7.90mM).

- Average Pt NP diameter (nm) = 10.4 ± 4.1 nm
- Pt NP density = 4.2X10³ particle/µm²
(vi). Deposition of 6th layer of Pt NPs (6XPt)

Figure 394: TEM images and Pt NP diameter distribution after 6 layers of H$_2$PtCl$_6$/PrOH (7.90mM).
The average Pt NP diameters impregnated by multi-layer process is summarized in Table 77. The average NP diameters remained relatively unchanged for the first three layers of the precursor application. However, an increase in the diameter was observed after the application of the 4\textsuperscript{th} layer (Figure 395), reaching maximum diameter (10.4 ± 4.1 nm) after the 5\textsuperscript{th} layer and finally decreasing after 6\textsuperscript{th} layer.

<table>
<thead>
<tr>
<th>No. of layers applied</th>
<th>Average Pt NP diameter (nm)</th>
<th>Std. dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.8</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>3.4</td>
<td>1.1</td>
</tr>
<tr>
<td>3</td>
<td>3.17</td>
<td>0.73</td>
</tr>
<tr>
<td>4</td>
<td>5.91</td>
<td>1.93</td>
</tr>
<tr>
<td>5</td>
<td>10.4</td>
<td>4.1</td>
</tr>
<tr>
<td>6</td>
<td>7.62</td>
<td>2.83</td>
</tr>
</tbody>
</table>

Figure 395: Average Pt NP diameter changes with the increase in the layers of H\textsubscript{2}PtCl\textsubscript{6}/PrOH (7.90mM) deposition

The application of the first 3 layers acted as the nucleation step where the nanoparticles (~ 3 nm diameter) were impregnated on the 8YSZ NW film surface. The increase in the NP size after layer 3 might have resulted due to the end of the nucleation phase and the beginning the
growth phase.\textsuperscript{311} The growth phase may have been driven by either the coalescence or the Ostwald ripening process.\textsuperscript{312,313} This speculation can be supported by the data (Table 78) which shows a decrease in the NP density with the increase in the number of layers applied (Figure 396).

<table>
<thead>
<tr>
<th>No. of layers applied</th>
<th>Pt nanoparticles count on YSZ</th>
<th>Area (nm(^2))</th>
<th>Area (µm(^2))</th>
<th>Density (particles/µm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>37</td>
<td>1.04E+03</td>
<td>1.04E-03</td>
<td>3.56E+04</td>
</tr>
<tr>
<td>2</td>
<td>68</td>
<td>1.68E+04</td>
<td>1.68E-02</td>
<td>4.05E+03</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>1.88E+03</td>
<td>1.88E-03</td>
<td>8.00E+03</td>
</tr>
<tr>
<td>4</td>
<td>94</td>
<td>6.12E+03</td>
<td>6.12E-03</td>
<td>1.53E+04</td>
</tr>
<tr>
<td>5</td>
<td>36</td>
<td>8.66E+03</td>
<td>8.66E-03</td>
<td>4.16E+03</td>
</tr>
<tr>
<td>6</td>
<td>81</td>
<td>1.02E+04</td>
<td>1.02E-02</td>
<td>7.94E+03</td>
</tr>
</tbody>
</table>

Table 79: Approximate density of Pt NP deposited on YSZ by multi-layer step method using H\(_2\)PtCl\(_6\)/PrOH (7.90 mM)

Figure 396: Pt NP coverage density decreased with the increase in the layers of H\(_2\)PtCl\(_6\)/PrOH (7.90mM) deposition.

EDX analysis of 8YSZ NWs impregnated with Pt NP

A typical EDX map of 8YSZ NWs with impregnated 6 layers of Pt NP is shown in Figure 397 demonstrates the relative distributions of Zr, Y, O and Pt species in the analyzed sample. The EDX analysis of the 8YSZ NWs with 6 layers of Pt NPs showed a Zr:Y:Pt At\% ratio of 11:4:24
(Figure 398). In comparison, a 8YSZ sample that was coated with 1 layer of Pt NPs showed a ratio of 7:3:20 (spectrum analysis not shown).

Figure 397: EDX map of 8YSZ NWs impregnated with 6 layers of Pt NPs.

Figure 398: EDX spectra of 8YSZ NWs impregnated with 6 layers of Pt NPs.
6.4.3 Analysis of Ni NPs deposited on 8YSZ nanowires by varying the layers of Ni(bpy)$_3$Cl$_2$ solution applied

In this section the results of Ni NP impregnation on 8YSZ NW film using Ni(bpy)$_3$Cl$_2$/EtOH (0.198 M) solution are presented. The SEM, TEM and Ni NP diameter distribution data are shown first, followed by overall analysis of the three samples prepared by varying the number of deposition layers. The EDX and XRD analysis are also presented.

6.4.3.1 Microstructural analysis of NP diameter deposited on 8YSZ NWs

(i). 8YSZ NWs with 1 layer of Ni$^0$ NPs deposition

Figure 399: (a) SEM image of 8YSZ NW film with Ni NPs after the application and annealing of the 1$^{st}$ layer of Ni(bpy)$_3$Cl$_2$/EtOH. (b) Histogram of Ni$^0$ NP diameters generated from (a).
Figure 400: TEM images of Ni NPs deposited on 8YSZ NWs after the 1st layer application and annealing of Ni(bpy)$_3$Cl$_2$/EtOH

(ii). 8YSZ NWs with 2 layers of Ni$^0$ NPs deposition

Figure 401: (a) SEM image of 8YSZ NW film with Ni NPs after the application and annealing of the 2nd layer of Ni(bpy)$_3$Cl$_2$/EtOH. (b) Histogram of Ni$^0$ NP diameters generated from (a).
The NPs in the TEM images (Figure 402 (a)) had smaller diameters \((13.6 \pm 7.6 \text{ nm})\) compared to the NPs diameters measured \((257 \pm 48 \text{ nm})\) using the SEM image (Figure 401 (a)). This difference in the particle size can be explained by the process that was used to prepare the TEM samples. During the TEM sample preparation process, an ultra-sonication horn was used to break apart the NW from the film. During this process, loosely bound Ni NP might have been dislodged from the NWs surface and were not observed in the TEM images.

(iii). **YSZ NWs with 3 layers of Ni\(^0\) NPs deposition**

![Figure 403](image)

Figure 403: (a) SEM image of 8YSZ NW film with Ni NPs after the application and annealing of the 3\(^{rd}\) layer of Ni(bpy)\(_3\)Cl\(_2\)/EtOH. (b) Histogram of Ni0 NP diameters generated from (a).
Figure 404: TEM images of Ni NPs deposited on 8YSZ NWs after the 3\textsuperscript{rd} layers application and annealing of Ni(bpy)$_3$Cl$_2$/EtOH

The SEM images of 8YSZ NWs coated with 3 layers of Ni NP (Figure 403 (a)) showed a difference in the NP distribution compared to the TEM images (Figure 404 (b)). The difference in the particle density can be explained by TEM sample preparation method used (using a horn sonicator) as described earlier. Overall the Ni Pt diameter showed only a slight increase with the increase in the number of Ni(bpy)$_3$Cl$_2$/EtOH solution layers applied (Figure 405).

<table>
<thead>
<tr>
<th>Table 80: Average Ni NP diameter deposited using Ni(bpy)$_3$Cl$_2$/EtOH</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>No. of layers</strong></td>
</tr>
<tr>
<td>-------------------</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
</tbody>
</table>
Figure 405: Ni NP diameter changes with the number of layers of Ni(bpy)$_3$Cl$_2$/EtOH applied.

6.4.3.2 XRD analysis of Ni NPs deposited using Ni(bpy)$_3$Cl$_2$/EtOH

The XRD analysis performed on the 8YSZ NWs impregnated with Ni NPs showed the presence of peaks associated with cubic 8YSZ. In addition, peaks associated with the Fcc phase of Ni$^0$ was also present. The characteristics peaks representing the (111) and (200) reflections are shown in Figure 406. XRD analysis of Ni(bpy)$_3$Cl$_2$$\cdot$5H$_2$O (synthesized), cubic NiO (commercially purchased), Fcc Ni$^0$ NPs (commercially purchased), and cubic 8YSZ NWs (fabricated via sol-gel route) are shown in Figures 407 (a), (b), (c) and (d). All the XRD measurements performed are consistent with the reported peaks.  

Figure 406: XRD spectra of 8YSZ nanowires with impregnated Ni nanoparticles after 3 times Ni(bpy)$_3$Cl$_2$ solution application and annealing.
Figure 407: XRD analysis of (a) synthesized Ni(bpy)$_3$Cl$_2$•5H$_2$O crystals, (b) commercially purchased NiO NPs, (c) commercially purchased Ni$^{0}$ NPs and (d) fabricated 8YSZ NW film, were performed to compare the XRD obtained from Ni$^{0}$ NPs impregnation on 8YSZ NW film (Figure 406).
6.4.3.3 Typical EDX analysis of 8YSZ NW film coated with Ni\textsuperscript{0} NPs using Ni(bpy)\textsubscript{3}Cl\textsubscript{2}/EtOH

A typical EDX map and quantitative analysis of 8YSZ NW film impregnated with Ni NPs after the application of 3-layers of Ni(bpy)\textsubscript{3}Cl\textsubscript{2}/EtOH (0.198 mM) solution (Figure 408). The EDX map showed the presence of the Ni NPs within the 8YSZ NWs with Zr:Y:Ni At\% ratios of ~ 6:1:3. The EDX spectra shows the characteristic peaks associated with 8YSZ sample coated with Ni NPs (Figure 409).

![EDX map and spectra](image)

Figure 408: Typical EDX map of 8YSZ NWs coated with Ni\textsuperscript{0} NPs. This sample was prepared using 3-layer application Ni(bpy)\textsubscript{3}Cl\textsubscript{2}/EtOH solution.
Figure 409: EDX spectrum of 8YSZ NWs with 3 layers of Ni NPs.

6.4.4 TEM analysis of the 8YSZ NW films with Pt/8YSZ/Pt and Ni/8YSZ/Pt configurations fabricated using the Parafilm mask method

The NP impregnated 8YSZ films with the anode/electrolyte/cathode configurations of Pt/8YSZ/Pt and Ni/8YSZ/Pt were evaluated using SEM, TEM and EDX. The Pt/8YSZ/Pt sample was divided into three regions: (1) 8YSZ+1XPt, (2) 8YSZ and (3) 8YSZ+1XPt which corresponds to (1) an area with 1 layer Pt NP on the 8YSZ NW film, (2) an area on the 8YSZ NW film without NP impregnation and (3) an area of 1 layer Pt NP on the 8YSZ NW film, respectively (Figure 410).
6.4.4.1 8YSZ NW film with Pt/8YSZ/Pt configuration

The SEM and TEM images of 8YSZ+1XPt located on the left (Figure 411) and right (Figure 413) sides of the film showed homogeneous coverage of the 8YSZ NWs with Pt NPs. The middle regions did not have measurable Pt NP deposition (Figure 412) which indicates that the parafilm mask was able to isolate the middle region effectively during the application of \( \text{H}_2\text{PtCl}_6/\text{PrOH} \) (5.88 mM) solution during the Pt NP impregnation process.

Figure 411: (a) SEM and (b) TEM images showing Pt NPs on 8YSZ NWs from the left side of the film shown in Figure 410.
Figure 412: (a) SEM and (b) TEM images showing the absence of Pt NPs on 8YSZ NWs located on the middle region of the film shown in Figure 410.

Figure 413: (a) SEM and (b) TEM images showing Pt NPs on 8YSZ NWs from the right side of the film shown in Figure 410.
6.4.4.2 8YSZ NW film with Ni/8YSZ/Pt configuration

In the 8YSZ film with Ni/8YSZ/Pt configuration (Figure 414), the TEM analysis showed only the presence of Ni NPs impregnation on the left side of the 8YSZ film (Figure 415) which was coated with 1 layer of Ni NP (8YSZ+1XNi). The middle region (8YSZ) showed the presence of both Pt and Ni NPs impregnated on 8YSZ NWs (Figure 416). This indicates that the parafilm mask did not cover this region sufficiently and the Pt and Ni precursor solutions were able to reach the 8YSZ NWs. The right side of the film showed only the presence of Pt NPs (Figure 417) that was coated with 1 layer of 7.90 mM H$_2$PtCl$_6$/iPrOH solution (8YSZ+1XPt).

Figure 414: Photo of 8YSZ NW film with impregnated Ni and Pt NPs in Pt/8YSZ/Pt configuration.

Figure 415: HR-TEM images of Ni NP deposited using the Parafilm method did not show any presence of Pt NP impregnation on the left side of 8YSZ NW film (Figure 414). Lattice spacing are consistent with the reported values.\textsuperscript{317}
Figure 416: The middle region of the 8YSZ film (Figure 414) did show the presence of both Ni and Pt NPs species which can due improper Parafilm masking of the region.

Figure 417: The TEM images of the Pt NPs impregnated on the right side of the 8YSZ film (Figure 414) did not show any presence of the Ni species.
(1). EDX quantitative analysis of the two sides on 8YSZ NW film which was coated with Ni and Pt NPs.

Two additional NP impregnated 8YSZ NW films (with the configuration Ni/8YSZ/Pt) were prepared to evaluate the relative Ni:Pt At% ratios on the side of Ni NP deposition (left) and Pt NP deposition (right) on 8YSZ NW films. This was done to investigate the amount of Ni and Pt NPs migration across the Parafilm mask (over 8YSZ NW film) during the deposition of their corresponding precursors (Ni(bpy)$_3$Cl$_2$/EtOH and H$_2$PtCl$_6$/iPrOH). The average Ni:Pt At % ratio on the anode side (left) was ~ 27:1 and cathode side (right) ~1:8. This suggests that Ni species migrated towards the cathode much more than Pt species migrated towards the anode end. The higher Ni At% on the cathode side may be due the higher concentration of the Ni precursor (0.198M Ni(bpy)$_3$Cl$_2$/EtOH) compared to the Pt precursor (7.90 mM H$_2$PtCl$_6$/iPrOH).

| Table 81: EDX analysis of Ni:Pt At% ratios on the left (Ni NPs impregnated) and the right (Pt NPs impregnated) side of 8YSZ NW films with a Ni/8YSZ/Pt configuration |
|--------------------------------------------------|--------------------------------------------------|
| Left side                                        | Right side                                       |
| Ni                                               | Pt                                               | Ni/8YSZ/Pt Sample images | Ni       | Pt       |
| At%                                              | At%                                              | Sample 01                  | At%      | At%      |
| 96.02                                            | 3.99                                             | Sample 02                  | 13.55    | 86.45    |
| 24                                               | 1                                                | 1                           | 1        | 6.3      |
| At% ratio                                        | At% ratio                                        | Sample 03                  | At%      | At%      |
| 96.38                                            | 3.62                                             | Sample 03                  | 10.87    | 89.13    |
| 27                                               | 1                                                | 1                           | 1        | 8.2      |
| At%                                              | At%                                              | Sample 03                  | At%      | At%      |
| 93.05                                            | 6.95                                             | Sample 03                  | 9.53     | 90.47    |
| 13                                               | 1                                                | 1                           | 1        | 9.4      |
| Average                                          | Average                                          |                              | Average  | Average  |
| Ave. At%                                         | Ave. At%                                         | Ni side                     | 95.15    | 11.32    |
| (± 1.83)                                         | (± 2.05)                                         | Pt side                     | 4.85     | 88.68    |
| Ave. At% ratios                                   | Ave. At% ratios                                  | Ni side                     | 21       | 1        |
|                                                  |                                                  | Pt side                     | 1        | 8        |
6.4.5 Conductivity (σ) measurement results

The three sets of conductivity measurements performed under N₂ and O₂ atmospheres (atm) were: (1) quartz substrate (control); (2) 8YSZ NW film (with no NP impregnation); and (3) 8YSZ NW film with impregnated Pt NP electrodes in the configuration of Pt/8YSZ/Pt (labeled as 1XPt/8YSZ/1XPt)). The I-V data collected using a SourceMeter (Keithley 2420) was used to generate the Arrhenius plot of these three samples (described in Section 6.2.5). The activation energy associated with 8YSZ and 1XPt/8YSZ/1XPt conductivity under N₂ and O₂ environment.

6.4.5.1 Conductivity of Quartz Plate (control)

The conductivity (σ) of the quartz substrate was measured under both N₂ and O₂ atm. The average σ values for the quartz substrates (under N₂ and O₂ atm) are shown in Tables 81 and 82, respectively. Analysis of σ data measured under N₂ and O₂ showed an increase with the temperature (Figures 418 (a) and (b)). At 758°C, the conductivity of quartz plate showed a slightly higher value under an O₂ atm (2.22E-7 ± 5.71E-9 S cm⁻¹) compared to N₂ (1.79E-7 ± 2.77E-8 S cm⁻¹), respectively. The quartz conductivity was expected to increase with the increase in temperature.

The conductivity of quartz measured under an O₂ atmosphere (2.79E-10 S cm⁻¹ at ~500°C) was lower than the reported value (~10E⁻7 S cm⁻¹ at 500°C). This could be due to two reasons: (1) the trench on the quartz plate that was placed to separate the electrodes (Figure 373); and (2) the use of quartz plates without any impurities (impurities like Na⁺ and Mg⁺ are known to be the charge carriers which propagate via Frenkel defects in quartz). References of quartz conductivity values at temperatures > 500°C (and under a N₂ atmosphere) could not be found. However, it can be assumed that they will have a similar decrease in conductivity as observed for the sample under O₂ atmosphere (~500°C) due to the two reasons mentioned above.
Table 82: Quartz substrate conductivity under N\textsubscript{2} atmosphere

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Average σ (S cm\textsuperscript{-1})</th>
<th>Std. Dev. (S cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>464</td>
<td>2.79E-10</td>
<td>1.93E-10</td>
</tr>
<tr>
<td>615</td>
<td>1.92E-07</td>
<td>7.97E-08</td>
</tr>
<tr>
<td>758</td>
<td>2.22E-07</td>
<td>5.71E-09</td>
</tr>
</tbody>
</table>

Table 83: Quartz substrate conductivity under O\textsubscript{2} atmosphere

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Average σ (S cm\textsuperscript{-1})</th>
<th>Std. Dev. (S cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>464</td>
<td>1.75E-09</td>
<td>1.02E-09</td>
</tr>
<tr>
<td>615</td>
<td>2.20E-07</td>
<td>7.72E-08</td>
</tr>
<tr>
<td>758</td>
<td>1.79E-07</td>
<td>2.77E-08</td>
</tr>
</tbody>
</table>

Figure 418: Quartz substrate conductivity under (a) N\textsubscript{2} and (b) O\textsubscript{2} atmosphere.

6.4.5.2 Conductivity of 8YSZ (no Pt)

The conductivity measurements performed between 24°C and 758°C (under N\textsubscript{2} and O\textsubscript{2}) are reported in Tables 83 and 84, respectively. The conductivity of 8YSZ NW film (with no Pt
NPs impregnation) under N$_2$ and O$_2$ had similar values (~ 4E-3 S cm$^{-1}$) at 758°C. However, the values at this temperature showed a higher deviation (Figures 419 (a) and (b)).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Average $\sigma$ (S cm$^{-1}$)</th>
<th>Std. Dev. (S cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>1.27E-07</td>
<td>4.50E-08</td>
</tr>
<tr>
<td>56</td>
<td>1.72E-07</td>
<td>1.42E-07</td>
</tr>
<tr>
<td>137</td>
<td>1.54E-07</td>
<td>5.90E-08</td>
</tr>
<tr>
<td>286</td>
<td>1.29E-07</td>
<td>3.17E-08</td>
</tr>
<tr>
<td>464</td>
<td>3.74E-04</td>
<td>8.47E-04</td>
</tr>
<tr>
<td>615</td>
<td>3.91E-03</td>
<td>1.02E-03</td>
</tr>
<tr>
<td>758</td>
<td>4.67E-03</td>
<td>3.07E-03</td>
</tr>
</tbody>
</table>

Table 84: Conductivity of 8YSZ (no Pt) under N$_2$ atmosphere

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Average $\sigma$ (S cm$^{-1}$)</th>
<th>Std. Dev. (S cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>6.67E-08</td>
<td>4.66E-08</td>
</tr>
<tr>
<td>56</td>
<td>5.58E-08</td>
<td>2.71E-08</td>
</tr>
<tr>
<td>137</td>
<td>5.45E-08</td>
<td>1.59E-08</td>
</tr>
<tr>
<td>286</td>
<td>5.86E-08</td>
<td>6.15E-08</td>
</tr>
<tr>
<td>464</td>
<td>2.13E-04</td>
<td>4.20E-04</td>
</tr>
<tr>
<td>615</td>
<td>1.22E-03</td>
<td>5.66E-04</td>
</tr>
<tr>
<td>758</td>
<td>3.79E-03</td>
<td>2.19E-03</td>
</tr>
</tbody>
</table>

Table 85: Conductivity of 8YSZ (no Pt) under O$_2$ atmosphere
Figure 419: 8YSZ (no Pt impregnated) NW film conductivity under (a) N$_2$ and (b) O$_2$ atmosphere

The Arrhenius plots of 8YSZ NW film (without Pt) under N$_2$ and O$_2$ are shown in Figures 420 and 421 and the activation energy was calculated to be 1.21 eV and 1.22 eV for conductivity measured under N$_2$ and O$_2$, respectively. The data used to generate the Arrhenius plots under these N$_2$ and O$_2$ are summarized in Tables 85 and 86, respectively.

<table>
<thead>
<tr>
<th>Table 86: 8YSZ (No Pt) – Arrhenius plot under N$_2$ atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>24</td>
</tr>
<tr>
<td>56</td>
</tr>
<tr>
<td>137</td>
</tr>
<tr>
<td>286</td>
</tr>
<tr>
<td>464</td>
</tr>
<tr>
<td>615</td>
</tr>
<tr>
<td>758</td>
</tr>
</tbody>
</table>
Table 87: 8YSZ (No PT) - Arrhenius plot under O₂ atmosphere

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>1000/T (1000 K⁻¹)</th>
<th>Average ln (σ/S cm⁻¹)</th>
<th>Std. Dev. ln (σ/S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>3.37</td>
<td>-16.03</td>
<td>1.27</td>
</tr>
<tr>
<td>56</td>
<td>3.04</td>
<td>-16.75</td>
<td>0.46</td>
</tr>
<tr>
<td>137</td>
<td>2.44</td>
<td>-16.81</td>
<td>0.48</td>
</tr>
<tr>
<td>286</td>
<td>1.79</td>
<td>-16.89</td>
<td>0.78</td>
</tr>
<tr>
<td>464</td>
<td>1.36</td>
<td>-9.59</td>
<td>2.57</td>
</tr>
<tr>
<td>615</td>
<td>1.13</td>
<td>-6.36</td>
<td>0.92</td>
</tr>
<tr>
<td>758</td>
<td>0.97</td>
<td>-5.71</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Figure 420: Arrhenius plot (under N₂) of 8YSZ film without Pt deposition. The inset shows the linear regression analysis of this Arrhenius plot (between 286°C - 758°C) for Ea calculation.

\[ y = -14.05x + 9.07 \]

\[ Ea = 1.21 \pm 0.17 \text{ eV} \]
Figure 421: (a) Arrhenius plot of 8YSZ film without Pt deposition (O₂ atm) and (b) its linear regression analysis (between 286°C - 758°C) for $E_a$ calculation.

### 6.4.5.3 Conductivity of 8YSZ+1XPt

The conductivity measurements of 8YSZ NW film impregnated with 1 layer of Pt NPs was performed under N₂ and O₂ atms and the measurements are summarized in Tables 87 and 88, respectively. The conductivity of the 8YSZ under an O₂ atm (2.38E-03 (± 1.03E-3) S cm⁻¹) was higher than the measurement performed under N₂ atm (1.00E-04 (± 5.41E-5) S cm⁻¹) at 758°C. The comparison of these data is shown in Figures 422 (a).
### Table 88: Conductivity of 8YSZ+1XPt under N₂ atm

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>1000/T (1000 K⁻¹)</th>
<th>Average σ (S cm⁻¹)</th>
<th>Std. Dev. (S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>3.37</td>
<td>1.45E-08</td>
<td>5.07E-09</td>
</tr>
<tr>
<td>56</td>
<td>3.04</td>
<td>4.09E-08</td>
<td>4.25E-08</td>
</tr>
<tr>
<td>137</td>
<td>2.44</td>
<td>2.25E-07</td>
<td>2.52E-07</td>
</tr>
<tr>
<td>286</td>
<td>1.79</td>
<td>4.42E-08</td>
<td>2.37E-08</td>
</tr>
<tr>
<td>464</td>
<td>1.36</td>
<td>6.90E-06</td>
<td>2.70E-07</td>
</tr>
<tr>
<td>615</td>
<td>1.13</td>
<td>8.94E-05</td>
<td>2.13E-05</td>
</tr>
<tr>
<td>758</td>
<td>0.97</td>
<td>1.00E-04</td>
<td>5.41E-05</td>
</tr>
</tbody>
</table>

### Table 89: Conductivity of 8YSZ+1XPt under O₂ atm

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>1000/T (1000 K⁻¹)</th>
<th>Average σ (S cm⁻¹)</th>
<th>Std. Dev. (S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>3.37</td>
<td>4.03E-08</td>
<td>2.38E-08</td>
</tr>
<tr>
<td>56</td>
<td>3.04</td>
<td>3.59E-08</td>
<td>1.90E-08</td>
</tr>
<tr>
<td>137</td>
<td>2.44</td>
<td>4.20E-08</td>
<td>2.33E-08</td>
</tr>
<tr>
<td>286</td>
<td>1.79</td>
<td>6.20E-08</td>
<td>4.18E-08</td>
</tr>
<tr>
<td>464</td>
<td>1.36</td>
<td>1.50E-05</td>
<td>1.58E-05</td>
</tr>
<tr>
<td>615</td>
<td>1.13</td>
<td>8.41E-04</td>
<td>3.30E-04</td>
</tr>
<tr>
<td>758</td>
<td>0.97</td>
<td>2.38E-03</td>
<td>1.03E-03</td>
</tr>
</tbody>
</table>
Figure 422: 8YSZ+1XPt NW film conductivity under (a) N₂ and (b) O₂ atm. (The error bars on Figure (a) are small and are over showed by the data points.)

Using these conductivity data, the Arrhenius plots of 8YSZ+1XPt samples under N₂ and O₂ atmosphere were constructed (Figures 423 and 424, respectively). The data is summarized in Tables 89 and 90, respectively. 8YSZ+1XPt samples under N₂ and O₂ atms produced activation energies of 0.86 eV and 1.21 eV, respectively.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>1000/T (1000 K⁻¹)</th>
<th>Average ln (σ/S cm⁻¹)</th>
<th>Std. Dev. ln (σ/S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>3.37</td>
<td>-17.35</td>
<td>1.01</td>
</tr>
<tr>
<td>56</td>
<td>3.04</td>
<td>-17.10</td>
<td>0.89</td>
</tr>
<tr>
<td>137</td>
<td>2.44</td>
<td>-16.16</td>
<td>1.04</td>
</tr>
<tr>
<td>286</td>
<td>1.79</td>
<td>-17.01</td>
<td>0.56</td>
</tr>
<tr>
<td>464</td>
<td>1.36</td>
<td>-13.05</td>
<td>2.38</td>
</tr>
<tr>
<td>615</td>
<td>1.13</td>
<td>-9.67</td>
<td>1.00</td>
</tr>
<tr>
<td>758</td>
<td>0.97</td>
<td>-9.30</td>
<td>0.52</td>
</tr>
</tbody>
</table>
Table 91: YSZ+1XPt – Arrhenius plot under O₂ atm

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>1000/T (1000 K⁻¹)</th>
<th>Average ln (σ/S cm⁻¹)</th>
<th>Std. Dev. ln (σ/S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>3.37</td>
<td>-17.19</td>
<td>0.58</td>
</tr>
<tr>
<td>56</td>
<td>3.04</td>
<td>-17.30</td>
<td>0.48</td>
</tr>
<tr>
<td>137</td>
<td>2.44</td>
<td>-17.08</td>
<td>0.41</td>
</tr>
<tr>
<td>286</td>
<td>1.79</td>
<td>-17.17</td>
<td>0.84</td>
</tr>
<tr>
<td>464</td>
<td>1.36</td>
<td>-12.52</td>
<td>2.02</td>
</tr>
<tr>
<td>615</td>
<td>1.13</td>
<td>-7.47</td>
<td>1.00</td>
</tr>
<tr>
<td>758</td>
<td>0.97</td>
<td>-6.11</td>
<td>0.47</td>
</tr>
</tbody>
</table>

![Arrhenius plot](image.png)

Figure 423: Arrhenius plot (under N₂) of 8YSZ film with 1 layer of Pt NP (8YSZ+1XPt) deposition. The inset shows the linear regression analysis of this Arrhenius plot (between 286°C - 758°C) for $E_a$ calculation.

$E_a = 0.86 \pm 0.09$ eV
Figure 424: Arrhenius plot (under O₂) of 8YSZ film with 1 layer of Pt NP (8YSZ+1XPt) deposition. The inset shows the linear regression analysis of this Arrhenius plot (between 286°C - 758°C) for \( E_a \) calculation.

In this dissertation, the conductivity of the following four separate groups of 8YSZ samples were investigated: (1) 8YSZ (no Pt) NW film in N₂ atm; (2) 8YSZ (no Pt) NW film in O₂ atm; (3) 8YSZ+1XPt in N₂ atm; and (4) 8YSZ+1XPt in O₂ atm. These samples are represented as 8YSZ (no Pt)/N₂, 8YSZ (no Pt)/O₂, 8YSZ+1XPt/N₂ and 8YSZ+1XPt/O₂, respectively. The conductivity values (measured at 758°C) of all four samples were shown in showed similar values (~3E-3 Scm⁻¹) except for the 8YSZ+1XPt/N₂ which was approximately a factor of 10 lower (~1E-
4 Scm⁻¹) than the rest. These values are summarized in Table 91 (the quartz substrate conductivity results (under N₂ and O₂ atms) were shown previously in Tables 91 and 92, respectively).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atmosphere</th>
<th>Σ (S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8YSZ (no Pt)</td>
<td>N₂</td>
<td>4.67E-03 (±3.07E-03)</td>
</tr>
<tr>
<td>8YSZ NW film without Pt NPs</td>
<td>O₂</td>
<td>3.79E-03 (±2.19E-03)</td>
</tr>
<tr>
<td>8YSZ+1XPt</td>
<td>N₂</td>
<td>1.00E-04 (±5.41E-05)</td>
</tr>
<tr>
<td>8YSZ NW film with 1 layer of Pt NPs</td>
<td>O₂</td>
<td>2.38E-03 (±1.03E-03)</td>
</tr>
</tbody>
</table>

In addition, the average Eₐ value obtained for 8YSZ+1XPt (N₂ atm) was lower (8.86 ± 0.09 eV) than the other Eₐ values obtained for 8YSZ (no Pt) (O₂ atm), 8YSZ (no Pt) (N₂ atm) and 8YSZ+1XPt (O₂) samples. The values of these samples are summarized in Table 92. The standard error analysis of these Eₐ values were done using the LINEST function in Microsoft Excel 2016 365 ProPlus (Version 1610).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atmosphere</th>
<th>Activation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8YSZ (no Pt NPs)</td>
<td>N₂</td>
<td>1.21 ± 0.17 eV</td>
</tr>
<tr>
<td></td>
<td>O₂</td>
<td>1.22 ± 0.14 eV</td>
</tr>
<tr>
<td>8YSZ+1XPt</td>
<td>N₂</td>
<td>0.86 ± 0.09 eV</td>
</tr>
<tr>
<td></td>
<td>O₂</td>
<td>1.21 ± 0.13 eV</td>
</tr>
</tbody>
</table>

Some of these observations will be evaluated next based on comparisons for other 8YSZ systems described in the literature.
6.4.5.4 8YSZ conductivity and activation energy comparisons

Conductivity in (doped) polycrystalline electrolyte nanomaterials can be restricted due to: (1) a heterogeneous distribution of dopant in the host electrolyte; (2) the presence of non-crystalline domains; (3) lattice plane mismatches (stacking faults, grain boundaries, etc.) and oxygen vacancy site depletion due to space charge.\textsuperscript{321} It has been reported that in YSZ electrolytes, O\textsuperscript{2-} propagates through three possible separate routes: (a) grain volume (B), (b) grain boundary (GB); and (c) inter grain (IG).\textsuperscript{320,321,322} A diagrammatic representation of these migration processes (in a nanoscale polycrystalline 8YSZ electrolyte) are shown in Figure 425. \textit{E}_a values associated with different forms of 8YSZ electrolyte are summarized in Table 93.

![Diagram of 8YSZ electrolyte showing different O\textsuperscript{2-} migration pathways.](image)

**Figure 425:** Diagram of a polycrystalline YSZ electrolyte showing the different types of O\textsuperscript{2-} migration pathways: (a) grain volume, (b) grain boundary and (c) inter-grain boundary. (Figure adopted from reference [323]).
Several studies have suggested that the grain size significantly influences oxide conductivities in nano-scale YSZ crystallites.\textsuperscript{332} However, the exact mechanism of $O^{2-}$ migration in polycrystalline nanomaterials is still unclear. Several studies have demonstrated that YSZ (3%-10% $Y_2O_3$ dopant) electrolytes with micron-sized crystallites have lower grain boundary conductivity ($\sigma_{GB}$) values compared to the grain volume conductivity ($\sigma_V$).\textsuperscript{333,334,335} The nano-sized grains (diameter $\sim$ 20 nm) has been reported to have $E_{a,GB}$ and $E_{a,GV}$ values in the range of 1.0-1.2 eV and 0.84-0.93 eV, respectively.\textsuperscript{336} Others have shown increased $O^{2-}$ self-diffusion (D) in 8YSZ GB (diffusion $E_{a,GB} \sim 0.9$ eV) compared to the GV (diffusion $E_{a,GV} \sim 1.1$ eV) when the grain size was decreased to the nano-scale.\textsuperscript{337} Reported size dependent values for the GB and GV activation energies\textsuperscript{282} are summarized in Table 94.

<table>
<thead>
<tr>
<th>Grain size (nm)</th>
<th>Grain volume $E_a$ (eV)</th>
<th>Grain boundary $E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>0.93 ± 0.04</td>
<td>1.03 ± 0.02</td>
</tr>
<tr>
<td>50</td>
<td>1.13 ± 0.02</td>
<td>1.26 ± 0.02</td>
</tr>
<tr>
<td>100</td>
<td>1.13 ± 0.02</td>
<td>1.18 ± 0.02</td>
</tr>
<tr>
<td>900</td>
<td>1.12 ± 0.02</td>
<td>1.19 ± 0.02</td>
</tr>
</tbody>
</table>
When compared, $\sigma_{\text{GB}}$ has always been lower than the $\sigma_{\text{GV}}$ irrespective of the crystallite size. $\sigma_{\text{GV}}$ has been the dominant mode of vacancy defect ($V''$) migration in 8YSZ type electrolytes. However, several studies have shown a diminished conductivity of YSZ (with $Y_2O_3$ ranging from 2% - 8%) across the GB results due to the formation of a positive space charge region.$^{334,336,338}$

Formation of this thin layer results from a segregation of $Y^{3+}$ species at the grain boundary (via the Herring-Nabarro Creep method$^{339}$) at elevated temperatures during annealing (to promote crystal formation) or a conductivity measurement process.$^{322,340,341}$ The resulting negative space charge is induced that extends from the GB into the GV to a distance referred as the Debye length.$^{342}$ This negative space charge repels $O^{2-}$ ions from approaching the GB and in the process reduces the vacancy defect concentration close to it, resulting in the decrease in inter grain conductivity ($\sigma_{\text{IG}}$). Even in the absence of $Y^{3+}$, the GB is known to have an intrinsically higher $V''$ concentration relative to the GV in polycrystalline 8YSZ nanomaterials due to the inherent lattice mismatch.$^{343}$

YSZ conductivity under an inert atmosphere has shown to have lower conductivity values compared to an oxygen rich atmosphere. Surprisingly, the $E_{a,\text{GB}}$ values under a low $O_2$ environment (2% $H_2/Ar$ mix atmosphere (P(O$_2$)= 10E-18 atm, Temperature = 1000°C), was reported to be lower ($\sim 0.73$ eV) than the $E_{a,\text{GB}}$ ($\sim 1.1$ eV) evaluated under an O$_2$ atmosphere.$^{334}$ It was proposed that the lower $E_a$ under an inert atmosphere is due to a mixed electronic-ionic conduction mechanism occurring in polycrystalline 8YSZ (grain size of $\sim 1.6$ µm). The ionic conduction (dominant process) is said to propagate in $V''$ sites in grain volume whereas electrons conduct via accumulated $Y^{3+}$ and $V''$ sites along the grain boundary.
Evaluation of the conductivity and $E_a$ data presented in this chapter.

Based on the literature review, it can be speculated that $O^{2-}$ in 8YSZ (no Pt)/N$_2$ and 8YSZ (no Pt)/O$_2$ samples propagate via $V''$ defects along the NW surface grain boundary. This is indicated by the associated $E_a$ values observed under N$_2$ (1.21 ± 0.17 eV) and O$_2$ (1.22 ± 0.14 eV) atmospheres. The source of mobile oxide species under a N$_2$ atmosphere could have been supplied from the NWs interior to its surface. These conductivity experiments were conducted within a short time span and the 8YSZ NW films were only exposed to temperatures above 500°C for ~ 1 hour. Under this mild condition, it is unlikely that Y$^{3+}$ underwent extensive segregation to the GB. However, the intrinsic $V''$ present along the NW crystallite interface could have been sufficient to hinder the inter grain migration of $O^{2-}$ (due to space charge) and thus allowing the GB migration to dominate.

When 8YSZ+1XPt samples were evaluated under N$_2$ and O$_2$ atmospheres, oxide migration through the GB encountered similar resistance due to the space charge. However, in this set of samples, the surface GB sites were obstructed by Pt NPs which further hindered $O^{2-}$ migration, thus resulting in a several-fold decrease in 8YSZ+1XPt/N$_2$ conductivity (1.00E-04 ± 5.41E-05 S cm$^{-1}$) compared to 8YSZ (no Pt)/N$_2$ (4.67E-04 ± 3.07E-05 S cm$^{-1}$) at 758°C. This inhibition of GB migration of oxide species might have resulted in the electronic conduction (along the GB) to be the dominant route of charge transfer and is evident in the $E_{a,GB}$ value (0.86 ± 0.09 eV) that resulted from the conductivity measurement of 8YSZ+1XPt under a N$_2$ atmosphere.

On the other hand, the increased conductivity of 8YSZ+1XPt under O$_2$ atmosphere (2.38E-03 ± 1.03E-03 S cm$^{-1}$) can be explained by catalytic injection of $O^{2-}$ from the gas phase (O$_2$ (g)) at the TPB. It can be speculated that the increased mobile species compensated for the loss of a surface migration pathway due to the presence of Pt NPs. The $E_{a,GB}$ (1.21 ± 0.13 eV) observed
for this sample is consistent with the reported $E_{a,\text{GB}}$ values (Table 94). Future experiments need to be conducted to have a clearer understanding of the atomistic oxide migration mechanism involved in this 8YSZ NWs electrolyte system.

6.5 Conclusion

In this chapter the fabrication of heterostructures used for 8YSZ NW film conductivity measurements are presented. In addition, the deposition procedures of nanoparticle electrodes (Pt and Ni) on a single 8YSZ structure were also discussed. The conductivity measurements of 8YSZ (without Pt NP) and 8YSZ (with 1 layer of Pt NP impregnation) under N$_2$ and O$_2$ are also presented. It showed a similar conductivity of 8YSZ NW films under O$_2$ compared to a N$_2$ atmosphere. For 8YSZ+1XPt films, a higher conductivity was observed under O$_2$ compared to N$_2$ atmosphere which was speculated to be a result of the increased supply of Pt NP catalyst at the TPBs. It also showed an activation energies of 1.21 eV and 0.86 eV for these samples under O$_2$ and N$_2$ atmospheres, respectively. Based on literature comparisons, the lower $E_a$ observed under a N$_2$ atmosphere for these NWs can be speculated as due to the charge migration that occurred because of the surface GB migration pathways for prevalent oxide species in such materials.
CHAPTER VII

Concluding Remarks

The work presented in this dissertation focused on the fabrication of one dimensional metal oxide solid electrolyte nanowire films composed of either ZrO$_2$, 8YSZ, Bi$_2$O$_3$, or WBO NWs, using either (a) suspended particle/electrospinning/annealing route or (b) a sol-gel method in combination with electrospinning and annealing. These nanowire films were characterized using a combination of SEM, HRTEM, XRD, EDX, and in some cases, Raman spectroscopy. Oxide conductivity as a function of temperature and its associated activation energies under N$_2$ and O$_2$ atmospheres were also evaluated for 8YSZ NWs which were impregnated with nanostructured Pt nanoparticles. In addition, flexible metal oxide perovskite NWs films of BaTiO$_3$ and (Ba,Sr)TiO$_3$ were also fabricated in order to evaluate their one dimensional piezoelectric properties.

In Chapter II, a simple fabrication strategy for PVP template-assisted one dimensional ZrO$_2$, 8YSZ and Bi$_2$O$_3$ NW films was presented using prefabricated nanoparticles with preformed metal oxide nanoparticles as precursors. A series of experimental conditions were developed to successfully prepare relatively large diameter (~ 1-2 µm) one dimensional wires of these metal oxides via a combined suspended particle and electrospinning technique. In all three cases of oxide nanoparticle systems, it is clear that the suspended particle route method heavily relies on the size, dispersity and quality of the prefabricated nanoparticles employed. Further investigations, involving different nanoparticles sizes, are necessary to provide a more broadly tunable range of nanowires widths for a given metal oxide. For the case of Bi$_2$O$_3$, the relatively lower melting point of this material results in a more fused network of nanowires when compared to ZrO$_2$ and 8YSZ.

Chapter III focused on the development of a true bottom-up fabrication method for nanoscale one dimensional ZrO$_2$ and 8YSZ NWs network flexible films using a finely tuned non-
aqueous sol-gel reaction procedure in conjunction with electrospinning and annealing methods. In the sol gel reactions employed the alkoxide precursor hydrolysis and condensation reaction kinetics were carefully controlled (using bulky precursors and acetic acid mediated chelation) to facilitate metal oxane bond formation and \textit{in-situ} sol and final NW crystallite size.

The nanowires fabricated by the above route were composed of smaller domains that fused together in the morphology of the PVP template to form one dimensional structures. Using the sol-gel route, ZrO$_2$ nanowires showed a sensitivity towards the changes in Zr(O$^t$Bu)$_4$ and PVP mass and insensitivity towards reaction time. Zr(O$^t$Bu)$_4$ precursor mass was varied from 0.050 g to 0.200 g to obtain nanowires with an average diameter of 104 ($\pm$ 26) nm to 200 ($\pm$ 95) nm, respectively. ZrO$_2$ nanowires fabricated with 0.250 g to 0.400 g PVP resulted in diameters ranging from 160 ($\pm$ 40) nm to 300 ($\pm$ 100) nm, respectively. Unlike ZrO$_2$ NWs, YSZ nanowire diameters were insensitive toward the changes in PVP mass, Y content in YSZ, and reaction aging time. YSZ NWs produced by varying PVP mass and Y:Zr ratio resulted in nanowire diameters ~ 100 nm and ~ 300 nm, respectively. Both ZrO$_2$ and 8YSZ NW films expressed its unique flexibility between 10-20 $\mu$m film thickness.

The focus of Chapter IV was regarding Bi$_2$O$_3$ and WBO NWs fabrication using a similar bottom up approach via a sol-gel, electrospinning and annealing route with a variation of precursor mass and amount of PVP template. Bi$_2$O$_3$ nanofiber and nanowire diameters showed no dependence on increases in bismuth precursor mass but the process can be used to fabricate NWs with diameters between ~250 nm to ~350 nm. The nanowires possess a mix of $\alpha$ and $\beta$ phases of Bi$_2$O$_3$ which was verified with XRD analysis. With an increase in PVP mass, Bi$_2$O$_3$ NW diameters increased as well. Such nanowires showed complete loss of all organics at 550°C where the nanowire diameter was also measured to be at a minimum. This complete pyrolysis temperature is
important because Bi$_2$O$_3$ starts fusing extensively above that temperature. As expected, nanofibers and WBO nanowires showed no diameter sensitivity to the increase in the W(OEt)$_5$ mol%. The XRD analysis showed the δ-Bi$_2$O$_3$ to be phase pure only at a precursor concentration between 15% and 25% W(OEt)$_5$, and separation of WO$_3$ domains is observed when samples containing 35% and 45% W(OEt)$_5$ are annealed.

In Chapter V, flexible BST and BTO NW film fabrication and characterization was presented via the sol-gel, electrospinning and annealing system described in earlier Chapters. This was done to expand the scope of possible one dimensional nanowire oxide conductors to include perovskite ceramic electrode materials of this composition. However, due to time limitations, we restricted our focus to that of NW film morphology and relative flexibility, with possible piezoelectric property evaluation by our collaborator. The BTO NWs were measured to have a diameter of in the range of 125 - 167 nm, whereas the BST NWs were measured to be in the 106 - 125 nm range. BTO and BST NW film flexibility was only observed for film thicknesses between 10-20 µm.

Chapter VI described in detail processes for the incorporation of Pt and Ni NPs on 8YSZ NWs, and an evaluation of the conductivity of these NWs films using a configuration of (no Pt)/8YSZ/(no Pt) and 1XPt/8YSZ/1XPt under N$_2$ and O$_2$ atmospheres. At maximum operating temperature (758°C) the conductivity was $\sim$ 3E-3 S cm$^{-1}$ for all samples except for 1XPt/8YSZ/1XPt under N$_2$ atmosphere ($\sigma \sim$ 1E-4 S cm$^{-1}$). The oxide migration activation energies associated to these samples (under N$_2$ and O$_2$ atm) were consistent with a grain boundary migration process ($E_{a,GB} \sim 1.2$ eV). However, the evaluation of 1XPt/8YSZ/1XPt heterostructure under N$_2$ atmosphere showed a slightly depressed activation energy ($E_a \sim 0.8$ eV) compared to the other samples. It is speculated that under such conditions, the lower $\sigma$ and $E_a$ values correlate to an
electronic conduction process propagating along a $Y^{3+}$ rich grain boundary in the absence of mobile oxide species and impeded migration pathways.

The study presented in this dissertation is aimed toward the development of new highly flexible self-standing one dimensional metal oxide NW films for ultimate application in solid oxide fuel cells. These versatile flexible-metal oxide NW networks have the potential to further push the boundaries of size miniaturization in the field of alternative energy sources.
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VITA

EDUCATION

• **Texas Christian University**, Fort Worth, TX  
  Bachelor of Science in Chemistry  
  August 2005 - August 2008

• **Texas Christian University**, Fort Worth, TX  
  Doctoral candidate, Inorganic Materials Chemistry  
  January 2010 - Current

  Flexible metal oxide nanowire electrolytes with metallic nanostructured platinum  
  and nickel three phase boundaries for application in solid oxide fuel cell (SOFC).

RELEVANT EXPERIENCES

TCU Department of Chemistry  
May 2008 – August 2008

• Research Assistant (Air Sensitive Organometallic Synthesis)  
  Synthesis of Molybdenum Aryloxide compounds and analysis of these compounds  
  using NMR, IR, UV and Mass Spectrometer. X-Ray Diffraction is also to characterize  
  the crystal structure of the compounds.

TCU Department of Chemistry  
May 2006 – August 2006

• Research Assistant (Organic Chemistry, Synthesis)  
  Research focused on development of new synthetic methodology for preparation of  
  organophosphorus compounds particularly in the application involving synthesis of  
  key synthon for preparation of medicinally relevant GABA analogs.

TCU Department of Physics  
May 2005 – May 2008

• Research Assistant (Nanomaterial Synthesis)  
  Study the reaction kinetic, thermodynamics, chemistry of nanostructure silicon-  
  carbide. It included synthesis procedure of silicon-carbide grass from multiwalled  
  carbon nanotube and nano silicon in presence of high temperature and low pressure.

Los Alamos National Laboratory,  
Los Alamos Lujan Neutron Scattering Center, NM  
May 2007 – August 2007

• Research Assistant  
  The job required analysis of polymers under shear using Low-Q Diffractometer  
  (LQD). The job required literature searches on polymer synthesis, identify and  
  procure the required equipment, assist in assembling and testing the shear cell, and  
  help run the measurements.

ACTIVITIES

Oral & Poster presentation

• Texas Society of Microscopy – 2012
• American Society of Metallurgy – 2013
• American Chemical Society National Meeting, Topic: “Chemistry and Materials for  
  Energy” – 2014
• Gordon Research Conference, “Electrochemistry” – 2014
• Gordon Research Conference, “Nanomaterials for Applications in Energy  
  Technology” - 2015

HONORS

• Best Oral Presentation in Material Science – Texas Society of Microscopy – 2012
- American Chemical Society Certification – 2008
- Undergraduate Research Program Grant recipient, TCU Science and Engineering Research Center, 2007
- Undergraduate Research Program Grant recipient, TCU Science and Engineering Research Center, 2006
- TCU Dean’s Scholarship recipient – 2005

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ABSTRACT

FLEXIBLE METAL OXIDE NANOWIRE ELECTROLYTES WITH METALLIC NANOSTRUCTURED PLATINUM AND NICKEL THREE PHASE BOUNDARIES FOR APPLICATION IN SOLID OXIDE FUEL CELL (SOFC).

by

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Professor of Chemistry

Metal oxide electrolytes have been used extensively in applications such as solid oxide fuel cells due to their ability to permit oxide ion (O$_{2}^-$) conductance as a solid electrolyte at elevated temperatures. Yttrium oxide (Y$_2$O$_3$)-stabilized zirconium oxide (ZrO$_2$) (YSZ) and tungsten (VI) oxide (WO$_3$)-stabilized bismuth oxide (Bi$_2$O$_3$) (WBO) are among the most widely used materials for these applications.

The goal of this dissertation is to synthesize a network of one dimensional ZrO$_2$, YSZ, Bi$_2$O$_3$ and WBO nanowires that are coated with elemental platinum (Pt$^0$) nanoparticles (as the cathode) and nanostructures of metallic nickel (Ni$^0$) (as the anode). Reduction in the size of the electrolyte, cathode, and anode materials increases the reactive surface area for the reduction and oxidation of oxygen and hydrogen respectively, thus ideally increasing the efficiency of the SOFC.

In this research, the synthesis of nanostructured solid electrolytes was accomplished using either (a) suspended particle/electrospinning/annealing route or (b) a sol-gel method in
combination with electrospinning and annealing. The metal oxide nanowire films maintained its flexibility post-annealing only when its thickness was within a range of 10μm to 15μm.

The necessary three phase boundaries (TPB), where the reduction of oxygen and oxidation of hydrogen takes place in a catalytic fuel cell application, was prepared by thermal reduction of hexachloroplatinic acid (H₂PtCl₆) and tris(2,2’-bipyridine)nickel (II) chloride (Ni(2,2’-bipyridine)₃Cl₂.5H₂O) to elemental platinum and nickel nanocrystal form, respectively.

The characterization of these materials was achieved primarily by Field Emission Scanning Electron Microscopy (FE-SEM) (JEOL JSM-7100F), Transmission Electron Microscopy (TEM) (JEOL JEM-2100), energy-dispersive X-ray (EDX) spectroscopy, and X-ray diffraction (XRD). Temperature dependent ionic conductivity measurements were performed to investigate the current carrier mobility and activation energy associated with the solid electrolyte under nitrogen and oxygen atmospheres, separately.

The data obtained from these investigations was used to evaluate the conductivity of the electrolyte under various conditions in order to construct a nano-sized SOFC.