Electrospinning of Polymeric and Ceramic Fibers: Understanding of the Morphological Control and Its Application

by
Qing Du

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Supervised by
Professor Hong Yang

Department of Chemical Engineering Arts, Science and Engineering
Edmund A. Hajim School of Engineering and Applied Sciences

University of Rochester
Rochester, New York

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Biographical Sketch

The author was born and grew up in her beloved hometown of Wuhan, Hubei Province, China. In the fall of 2001, she joined the Class of National Base of Chemistry, Wuhan University and earned her Bachelor of Science degree in Chemistry in 2005. In the same year, she joined Changchun Institute of Applied Chemistry, Chinese Academy of Sciences to study Polymer Chemistry and Physics and obtained her Master of Science degree in 2008. Immediately after that, she came to the United States and began her doctoral studies in the Department of Chemical Engineering at the University of Rochester. Following a period of study on copper indium gallium selenium solar cells, she started her research in the area of electrospinning of polymeric and ceramic fibers - understanding of the morphological control and its application, under the direction of Professor Hong Yang. She was awarded Horton Fellowships in 2010, 2011 and 2012. She received her second Master of Science degree in Chemical Engineering from the University of Rochester in 2012.

Part of Qing’s research work during doctoral study is reflected from the following publication list:

1. Qing Du, Hong Yang, David Harding, “Magnetic-Field-Assisted Electrospinning of Twisted Peanut-shaped Poly (Vinyl Pyrrolidone) Ribbons.” Polymer, under review.
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Abstract

In this dissertation, polymeric fibers, poly(vinyl pyrrolidone) (PVP), and two kinds of ceramic fibers, silicon carbide (SiC) and niobium-doped titania (Nb-TiO₂), were successfully fabricated by the electrospinning technique. The morphology of electrospun fibers was studied by adjusting the parameters during the electrospinning process, especially the humidity. The application of Nb-TiO₂ fibers was explored.

Firstly, helical peanut-shaped ribbons of poly(vinyl pyrrolidone) were prepared by a magnetic field-assisted electrospinning method. The formation mechanism of helical ribbons was attributed to the synergistic interaction of bending instability and rigidity of the polymers during the electrospinning process. The relative humidity was found to significantly influence the morphology of PVP fibers. When the relative humidity of the environment decreased, the morphology changed from straight rods to helical ribbons, and the percentage of helical ribbons increased dramatically. At the same time, the cross-section of electrospun fibers changed from circle, to ellipse, and to peanut shape. These fibers had different mechanical properties, and the helical ribbons were shown to have the largest ultimate elongation.

Secondly, SiC fibers were synthesized by electrospinning from preceramic polymer without the help of guiding polymer, UV Cure and pyrolysis processes. The morphology and diameter of the electrospun preceramic fibers is controlled by varying mixtures of solvents. UV cure was used to crosslink and strengthen the preceramic fibers. As a result, the morphology of SiC fibers remained intact during the pyrolysis process.
Lastly, a facile method to fabricate niobium-doped titania supported platinum (Pt@Nb-TiO$_2$) catalyst membrane for oxygen-reduction reaction (ORR) in polymer electrolyte membrane fuel cell (PEMFC) was developed by a new two-step approach, electrospinning and atomic layer deposition (ALD). The 30000-cycle accelerated-stability test on the Pt@Nb-TiO$_2$ catalyst membrane showed that it had high stability. The effect of fiber morphology, doping amount of niobium, number of ALD cycle, post-treatment temperature and crystal phase of Nb-TiO$_2$ support on the catalytic activity of Pt@Nb-TiO$_2$ membrane were discussed. The area-specific ORR activity of Pt@Nb-TiO$_2$ catalyst membrane was increased by about 20 folds over the Pt@TiO$_2$ fiber membrane, if 10 at% of Nb was incorporated into the ceramic fibers. The area-specific activity also increased with the number of ALD cycles. The ORR activity further increased to 0.28 mA/cm$^2_{\text{Pt}}$ at 0.9 V after post-treatment of the catalyst membrane at high temperature in H$_2$–containing atmosphere, due to conductivity improvement of Nb-TiO$_2$ fiber membrane and better crystalinity of Pt NPs. The area-specific activity of Pt@Nb-TiO$_2$ catalyst with rutile phase of support was higher than the one with anatase phase of support due to the improvement of support conductivity.
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Chapter 1 Introduction

One-dimensional (1D) nanostructures have gained tremendous attention in recent years because of their unique chemical and physical properties and wide applications. A number of methods have been demonstrated to fabricate 1D nanostructures, especially fibers. These methods include vapor-liquid-solid (VLS) growth, template synthesis, conventional fiber spinning (wet spinning, dry spinning, melt spinning and gel spinning), and electrospinning. Electrospinning has obvious advantages superior to other methods because it is a cost-effective, simple and direct method with universality. Compared to conventional spinning, it can generate fibers with much smaller diameter. Overall, electrospinning is a versatile method which can process almost any soluble or fusible polymers or preceramic polymers into polymeric or ceramic fibers with diameters ranging from nanometers to micrometers.

1.1 History of Electrospinning

Just as Newton discovered the laws of universal gravitation, the first observation of electrospinning, at that time it was called electrospraying, is full of occasionlity. In the late 1500s, William Gilbert found when a suitably charged piece of amber was brought near a droplet of water, it would form a cone shape and small droplets would be ejected from the tip of the cone. It is the beginning of the story of eletrospinning.
Later, the development of electrospinning went into a long quiet period. The process of electrospinning was patented by J.F. Cooley in May 1900\textsuperscript{36} and February 1902\textsuperscript{37} and by W.J. Morton in July 1902.\textsuperscript{38} In these patents, the conditions to form fibers rather than droplets by electrospinning are pointed out. (i) Solution must have sufficient viscosity. (ii) Solvent is volatile enough to allow generation of the solid polymer. (iii) The intensity of the electric field must be within a certain range.

After that, the development of electrospinning accelerated. In 1914 John Zeleny began the attempt to mathematically model the behavior of fluids under electrostatic forces.\textsuperscript{39-41} In 1934, the electrospinning of polymeric materials was first patented by Anton Formhals.\textsuperscript{42} Later, he filed several other patents to produce continuous fine fibers for use on standard textile machinery.\textsuperscript{43-46} In 1936, electrospinning from a melt rather than a solution was patented by C.L. Norton.\textsuperscript{47} In 1938 Nathalie D. Rozenblum and Igor V. Petryanov-Sokolov generated electrospun fibers, which were developed into filter materials known as "Petryanov filters".\textsuperscript{48} By 1939, this work had led to the establishment of a factory in Tver' for the manufacture of electrospun smoke filter elements for gas masks.

Between 1964 and 1969, Geoffrey I. Taylor worked on electrostatics and contributed to electrospinning by mathematically modeling the shape of the cone formed by the fluid droplet under the effect of an electric field.\textsuperscript{49-51} He concluded that the conical interface between air and the fluid was stable at the semi-angle conical angle of 49.3°, which is a universal value for conductive fluids. This characteristic droplet shape is now
known as the Taylor cone, which is important as it defines the onset of the electrospinning process.

In the early 1990s, Reneker and Rutledge popularized the name electrospinning for the process and demonstrated that many organic polymers could be electrospun into nanofibers. Since then, the number of publications about electrospinning has been increasing exponentially every year. Figure 1.1 shows the number of publications searched in Web of Science by the topic of “electrospinning” or “electrospraying”.

![Figure 1.1](image.png)

**Figure 1.1.** The number of publications searched in Web of Science by the topic of “electrospinning” or “electrospraying”.
The theoretical mechanism of the electrospinning process has also been developed since 1995. Yarin described the shape of the Taylor cone and the subsequent ejection of a fluid jet.\textsuperscript{52, 53} Reneker visualized the real jet trajectory with the help of a high speed camera resulting in a major breakthrough in the development of the electrospinning process.\textsuperscript{54, 55} It offered direct evidence of the mechanisms of electrospinning. Hohman described the most important instability to the electrospinning process, the bending (whipping) instability.\textsuperscript{56}

### 1.2 Theory of Electrospinning

#### 1.2.1 Apparatus of Electrospinning

The standard setup of electrospinning consists of a spinneret, a high-voltage DC power supply and a grounded collector. Two bar magnets are introduced at the collector region to obtain aligned fibers by an additional radial Lorenz force in our group, which is called Magnetic-Field-Assisted Electrospinning.\textsuperscript{57}

#### 1.2.2 Electrospinning Process

When the solution or the melt is injected by the syringe pump at a constant rate, sessile and pendant droplets would hang on the end of spinneret due to surface tension. If an electric field is added between the spinneret and the collector, the shape of droplet will be deformed according to the equilibrium of electric forces and surface tension. When the
intensity of electric field is increased, a conical shape, the so-called Taylor cone, will form at a critical potential. Then a charged fluid jet will be ejected from the tip of the Taylor cone towards the collector if the electric field continues to be increased. During the travel process in the air between the spinneret and the collector, the fluid jet is elongated by electrostatic forces and dried as the solvent is evaporated. Finally, solidified fibers are obtained at the collector.

1.2.3 Mechanism of Electrospinning

Electrospinning is basically a drawing process based on electrostatic interactions. The hardest part to understand electrospinning is why a droplet with size of millimeter could be transferred into a fiber with diameter of nanometer. When an electric field about is applied to the droplet, charges from the electrode flowed onto the surface of the liquid droplet and three kinds of forces are generated within the droplet. The first one is the electrical force from the external field, pulling the droplet toward the collector. The second one is the Coulomb repulsive forces between the charges, which try to decrease the density of charges by increasing the surface area per unit mass fluid. The last one is cohesive force (surface tension), the intermolecular attraction between molecules within the fluid, which prevents the deformation of droplet. When the intensity of the electric field increases, the balance of these forces is disturbed. The droplet is deformed into a conical shape which is called the Taylor cone by the new balance of three forces. And a fluid jet is ejected from the Taylor cone towards collect, which is formed by the
combination of the first and second forces. The surface area is increased and electrical charges are carried away from the droplet by the flowing jet. As long as there are enough fluid and charges supplied to the droplet, the fluid jet is maintained.

The real jet trajectory offered by a high speed camera shows that the fluid jet is a straight path at first, but after a short distance, around several millimeters, the straight path grows into a spiral coil.\textsuperscript{54,55} It is called bending instability. And after several turns, a new electrical bending instability (second bending instability) formed a smaller coil on the basis of the larger coil. The coils are formed due to the balance of these forces. As the intensity of charges on the surface of the fluid jet are so high that the coulomb repulsive force is very large. Take the charge on Scheme 1.1 as an example, the charge on the top will pull it downward ($F_d$) heavily and the charge on the bottom will push it upward ($F_u$) heavily. It is not a stable status. As a result, the fluid jet bends. Then the force from the above charge becomes downward and outward ($F_{do}$); and the force from the below charge becomes upward and outward ($F_{uo}$). The direction of result force ($F_{out}$) is outward. Cohesive force prevents the deformation due to the high viscosity of solution and generates an inward force ($F_{in}$). External electrical force pulls it downward, resulting a downward force ($F_{down}$). The combination of $F_{out}$, $F_{in}$ and $F_{down}$ generates a centrifugal force. So the bend part grows into a three-dimensional coil (Scheme 1.1). The shape occupied by the spiral path is an envelope cone. As diameter of fluid jet becomes smaller and smaller due to coulomb repulsive force. Cohesive force decreases and the centrifugal force increases. So the radius of coils grows larger. The size of the fluid jet shrinks
continuously from the spinneret to the collector until it solidifies. The fiber may be elongated by 10,000 times from the initial length of the fluid segment.

Scheme 1.1. Schematic illustration of formation of spiral coils.

1.2.4 Important Parameters of Electrospinning

Electrospinning appears to be straightforward, but it is a rather complicated process which depends on material, technical, and ambient parameters. Only a proper combination of these parameters would successfully result in uniform fibers.\textsuperscript{59, 60} Otherwise, a range of other morphologies such as dots,\textsuperscript{61, 62} break-up, beads\textsuperscript{63, 64} and branching\textsuperscript{65, 66} will show up.
Material parameters include physical properties of target polymer or preceramic polymer (molecular weight, melting point and glass transition temperature), physical properties of solvents (boiling point, vapor pressure, surface tension and dielectric constant), concentration of electrospun materials, surfactant usage and so on. At first, a target polymer or preceramic polymer with high molecular weight needs to be chosen to enable enough chain entanglements. If the material is electrospun in the form of melt, its melting temperature and glass transition temperature will be optimized to obtain uniform fibers.\(^{67,68}\) If it is electrospun in the form of solution, a good solvent, either single or mixed, should be carefully selected.\(^{69-71}\) The solvent should have suitable surface tension and dielectric constant so that enough ions could be generated on the surface of fluid jet. In addition, the volatility of solvent should be high to dry the fluid jet during the travel path, which means the solution should have a low boiling point and a high vapor pressure at room temperature. The concentration of solution is related to the viscosity of the fluid jet. The influences of these parameters on the morphology and diameter of electrospun fibers vary greatly according to the target material. However, some common rules exit. Usually, the diameter of electrospun fibers would increase if the molecular weight of target material is enlarged, or if the concentration of the electrospun solution increases. Adding surfactants or salts to the electrospun solution would eliminate beads and shrink the size of fibers.\(^{72}\)

Technical parameters are consisted of the intensity of the electric field, the distance between the spinneret and the collector, feeding rate and size of the spinneret. The most important factor is the intensity of the electric field. Only when it is larger than
the critical potential, fiber can be electrospun. Further increasing the intensity decreases the diameter of the fiber. In some case, the critical potential is so large that the conductivity of the electrospun melt or the solution needs to be increased by adding surfactants or using solvents with high dielectric constant.\textsuperscript{73, 74} The distance between the spinneret and the collector should be long enough to dry the fluid jet in the air. Otherwise wet fibers may fuse together on the collector. In a suitable range, increasing feeding rate will increase the diameter of the electrospun fiber but the influence is trivial. Excessively increasing the feeding rate may destroy the equilibrium of electrospinning, leading to beaded fibers.\textsuperscript{75-77} Increasing the size of spinneret slightly increase the diameter of fibers.\textsuperscript{78, 79}

Ambient parameters include temperature, humidity and air velocity. All these parameters can affect the drying rate of fluid jet, affecting the morphology and size of the electrospun fibers. Humidity is especially important when water is used as the solvent. But the influence of humidity is rarely studied. Besides drying rate, temperature may also affect the crystallinity of fibers.

### 1.3 Applications of Electrospinning

Electrospun fibers (also called nonwovens) have various applications, such as template, filler and textile, catalysis, nanofiber reinforcement and medical application. Electrospun polymeric fibers can be used as templates for the preparation of hollow fibers.\textsuperscript{80, 81} Pore structure of nonwovens controls its properties and functions in filter and
textile applications. Nonwovens composed of nanofibers can greatly enhance airflow resistance of textile. As electrospun fibers have high surface area, it is applied to load monometallic or bimetallic nanoparticles to increase catalyst activity. Electrospun glass fibers, carbon fibers, and poly(p-phenylene terephthalamide) fibers are used for the reinforcement of synthetic materials in many technical products. Electrospun fibers have also been extensively studied in the medical applications including tissue engineering, transport and release of drugs.

1.4 Objective and Overview of Thesis

The objective of this dissertation is to fabricate polymeric fiber (poly(vinyl pyrrolidone)) and ceramic fibers (silicon carbide and niobium-doped titania) by electrospinning technique. It will study the effect of parameters during electrospinning process, especially the humidity, on the morphology of electrospun fibers. Some applications of the electrospun polymeric and ceramic fibers are explored.

Chapter 2 is focused on the preparation of helical peanut-shaped ribbons of poly(vinyl pyrrolidone) (PVP) and understanding their formation mechanism. The influences of the relative humidity on the morphology, shape of cross-section and the ultimate elongation of the electrospun fibers are studied.

Chapter 3 is concentrated on the fabrication of silicon carbide (SiC) fibers by electrospinning from preceramic polymer without the help of guiding polymer. The importance of UV Cure on morphology preservation is pointed out.
Chapter 4 and 5 describe a facile method to fabricate niobium-doped titania supported platinum (Pt@Nb-TiO₂) catalyst membrane for oxygen reducing reaction by a new two-step approach, including electrospinning and atomic layer deposition. Chapter 4 is focused on electrospinning of anatase Nb-TiO₂ fiber support and discussing the effect of fiber morphology, doping amount of niobium, number of ALD cycle and the temperature of post-treatment on the catalyst activity of Pt@Nb-TiO₂. Chapter 5 is focused on the formation of rutile phase Nb-TiO₂ fibers by electrospinning.
1.5 References


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Chapter 2 Helical Peanut-Shaped Poly(Vinyl Pyrrolidone) Ribbons Generated by Electrospinning

2.1 Introduction

Electrospinning is a facile and versatile method to fabricate nanometer (nm)- and submicron-sized fibers for a range of applications.\(^1\)-\(^5\) Electrospun fibers have been shown to be useful for tissue engineering, especially in those areas where guided growth of cells is important.\(^6\)-\(^10\) The morphology may play important roles in determining the function of materials made of electrospun fibers.\(^11\)-\(^16\) Straight round-shaped fibers are the most commonly observed, with a few exception that helical fibers with different shapes in cross-section are made, although detailed studies on the factors that affect fiber morphologies have hardly been reported.

A rare example for the formation of fibers with non-circular cross-section is based on thin polymer skins.\(^17\) Circular tube made of thin polymer layers collapsed under atmospheric pressure to form elliptical or flat shape as the solvent evaporated. For helical ribbons, however, there are even fewer examples and no clear understanding on the mode of formation to date. It was observed that this morphology was the result of particular types of polymers and solvents;\(^18\)-\(^19\) or formed in a narrow range of polymer concentration.\(^20\) The spirals were attributed to the difference in the azimuthal angles of those planes of collapsing segments.\(^17\) Different solvent evaporation rates in the mixture were also important to the formation of spirals observed in poly(4-methyl-1-pentene).
fibers.\textsuperscript{21-23} The lack of a convincing mechanism for the formation of helical ribbons in part is due to the fact that there is no reliable method to control the degree of spirals in the spun fibers. In this article, we describe the preparation of helical peanut-shaped PVP ribbons by magnetic-field-assisted electrospinning (MFAE) method. We show that extent of the spiral and shape of the fiber cross-section can be well controlled through adjusting the relative humidity of the environments. We offer our understanding on the effect of relative humidity on the fiber morphology, which is an important but often overlooked factor in the electrospinning process.

\section{2.2 Experimental Section}

\textbf{Electrospinning of Poly(Vinyl Pyrrolidone) (PVP) Fibers.} The magnetic-field-assisted electrospinning (MFAE) method was used to prepare PVP fibers.\textsuperscript{24} Typically, PVP (molecular weight: 1300 kg mol\textsuperscript{-1}, Sigma-Aldrich) was dissolved in a mixture of anhydrous ethyl alcohol and de-ionized (DI) water to form a polymer solution at various concentration. Normally the concentration of 13\% (w/v) was used. The volumetric ratio of ethyl alcohol to water was kept at 4:1 unless indicated otherwise. The polymer solution was loaded into a plastic syringe with an 18-Gauge (inner diameter: 0.033 inch) stainless-steel needle if not indicated specifically. The sharp tip of the needle was cut and sanded into smooth circular, flat opening to ensure the proper direction of fluid jets. The needle was connected to a high-voltage power supply and the collector was grounded and 8 cm below the needle tip. The voltage between the needle and the collector was maintained at
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15 kV. The feeding rate was controlled by a syringe pump at a constant rate of 1 mL/h. The humidity of the environment was adjusted by a humidifier in an enclosed space and monitored by a digital hygrometer during the electrospinning process.

**Characterization.** The morphology of the fibers was studied by Field Emission Scanning Electron Microscopy (FE-SEM, Zeiss-Leo DSM982) and Field Emission Transmission Electron Microscopy (FE-TEM, FEI TECNAI F-20). Average diameter was measured by Image J (National Institutes of Health, USA). Thermal Mechanical Analyzer (TMA, Pyris Diamond, Perkin Elmer) was used to study the mechanical property of PVP fibers made under different relative humidity. A bundle of aligned PVP fibers were fixed by two small chucks and then loaded onto TMA. An extension force was exerted on the two chucks at a constant rate of 15 mN/min until the fibers were fractured. Load and fiber extension were recorded and used to calculate the ultimate elongation.

2.3 **Results and Discussion**

2.3.1 **Formation of Helical Ribbons**

Morphology of electrospun polymer fibers was observed to be depended heavily on humidity of the environment. When the relative humidity of the environment was ~16%, helical ribbons were obtained (Figure 2.1). These fibers were made of PVP from its ethyl alcohol and de-ionized (DI) water solution. The fibers were uniform; and their cross-section had a peanut shape with a typical width of 1.4 µm and a height of 430 nm.
(Figure 2.1B). Noticeably, such fiber had a thin skin layer of 30 - 100 nm in thickness. Because of this unique morphology, the fiber formed spirals along its longitude direction (Figure 2.1C). Overall, the surface of these helical ribbons was fairly smooth.

**Figure 2.1.** (A, B) SEM images and (C, D) TEM micrographs of PVP fibers made at a relative humidity of 16%.

The formation of helical ribbons should be closely related to the electrospinning process (Scheme 2.1). When an electric field is applied between a spinneret and a
collector, charges are generated on the surface of the polymer solution droplet, which hang on the tip of the spinneret due to surface tension. If the static force surpasses the surface tension, a Taylor cone forms and a fluid jet is ejected and travels to the collector. The longitudinal stress caused by the external electric field stabilizes the straight jet to a certain distance. Then the internal repulsive forces between the adjacent segments, which carry the same charges, generate the bending instability and turn the straight path into a spiral caused by the Coulomb repulsive forces.\textsuperscript{25-28} The subsequent bending instability generates new and size-reduced spirals on the existing ones until the fluid jet reaches the collector and dries.\textsuperscript{25, 29} Previously, buckled fibers were made based on this principle.\textsuperscript{30} Similar helical fibers were observed in this polymer system (Figure 2.2), suggesting small spirals were formed due to the second or third bending instability during the electrospinning process. With the MFAES method, aligned fibers could be formed and suspended over the gap between two magnets under Lorentz force.\textsuperscript{24, 31} This additional force could alter the direction of the fluid jet and pull the two ends of small spirals to align them over the gap. If the polymer has enough rigidity, the jet cannot fully relax but retain the spiral feature while being pulled by the Lorentz force, leading to the formation of helical ribbons (Scheme 2.1). In another word, the uniformity of helical ribbons is attributed to such interaction. In the followings, we further discuss the effect of humidity on the morphology of helical ribbons, which could not completely be explained based on the existing theory.\textsuperscript{17}
**Scheme 2.1.** Schematic illustration of formation process of helical ribbons.

**Figure 2.2.** SEM images of helical fibers collected on the top of magnets.
2.3.2 Effect of the Relative Humidity on the Fiber Morphology

The humidity played an important role in controlling the morphology of the electrospun PVP fibers. When the relative humidity of the environment changed from 32% to 16%, the morphology of spun PVP fibers changed from straight round fibers to helical ribbons, and the percentage of helical ribbons also increased (Figure 2.3). The electrospun jets of PVP solution formed straight round fibers or flat ribbons when the relative humidity of the environment was in the range between 26% and 32% (Figure 2.3.A-C). At the relative humidity of 23-24%, helical ribbons began to show up in the samples made using an 18-Gauge needle (inner diameter: 0.033 inch) (Figure 2.3.D). When relative humidity further decreased, percentage of helical ribbons increased (Figure 2.3.E-H). The observed changes of fiber morphology at different humidity and the size of fibers were summarized in Table 2.1. The same trend of morphological transformation was observed even when the inner diameter of the needle decreased from 0.033 to 0.024 inch (20-Gauge). However, the transition from one kind of morphology to another tended to be at lower relative humidity for 20-G needle (Table 2.1).
Figure 2.3. SEM images of PVP fibers made at different relative humidity of the environment: (A) 31-32%, (B) 28-29%, (C) 26-27%, (D) 23-24%, (E) 22%, (F) 21%, (G) 18%, and (H) 16%, respectively.

Table 2.1. Summary of morphology and diameter (nm) of electrospun PVP fibers made using 18-G and 20-G needles under different relative humidity.

<table>
<thead>
<tr>
<th>Humidity</th>
<th>Needle Size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>31-32%</td>
</tr>
<tr>
<td>18 Gauge</td>
<td>□/○</td>
</tr>
<tr>
<td></td>
<td>887</td>
</tr>
<tr>
<td>20 Gauge</td>
<td>□/○</td>
</tr>
<tr>
<td></td>
<td>768</td>
</tr>
</tbody>
</table>

※※※: strongly helical peanut-shaped ribbons, the percentage of helical ribbons > 90%
※※: mildly helical peanut-shaped ribbons, the percentage of helical ribbons ~60%
※: weakly helical peanut-shaped ribbons, the percentage of helical ribbons ~30%
※□: helical peanut-shaped ribbons and flat ribbons, the percentage of helical ribbons ~10%
□/○: flat ribbons or straight round fibers
□: flat ribbons
○: straight round fibers
There were two possible reasons for this observed trend. First, small spirals formed due to the existence of higher order bending instability, when the relative humidity decreased. When the relative humidity decreased, fibers dried relatively faster. The characteristic charge relaxation time, that is the period required for the excess charged toward to the equilibrium position on the surface of a fluid jet, increased because charges travelled at a reduced rate in solid than in liquid. If the characteristic charge relaxation time increased, there should be additional charges on the surface of a fluid jet. Therefore, the bending instability occurred readily. In the case where the distance between the spinneret and the collector was kept constant, characteristic charge relaxation time increased, resulting in a shortened straight path and increased subsequent bending instability. Hence, small spirals formed easily when the relative humidity was low. Second, a fluid jet became rigid if the relative humidity was lowered. Under fast drying rate of the fluid jet, fibers turned rigid and resisted to further relaxation. As a result, fibers tent to maintain the spiral morphology under the influence of Lorentz force. Collectively, these factors caused the ribbons to spiral when the relative humidity was low. Thus, the percentage of the helical ribbons increased from 0% to 99%, when the relative humidity decreased from 32% to 16% (Figure 2.4). When the size of spinneret decreased from 0.033 (18-G) to 0.024 inch (20-G), the size of the droplet hang on the tip of spinneret decreased, which was exposed to the environment, resulting in a slower drying rate of the
fluid jet. As a result, the transition from straight round fiber to helical ribbon became slower.

![Graph showing the percentage of helical ribbons on relative humidity](image)

**Figure 2.4.** Dependence of the percentage of helical ribbons on the relative humidity. The electrospinning was carried out with an 18-Gauge and 20-Gauge needle.

### 2.3.3 Effect of the Relative Humidity on the Cross-section Shape

The cross-section of the fibers changed continuously from circle, to ellipse, and to peanut shape when relative humidity of the environment decreased from 32% to 16% (Figure 2.5). At the relative humidity between 23% and 32%, the cross-section had a round or elliptical shape. When the relative humidity decreased to 22%, rectangular and
peanut-shaped cross-sections formed. PVP fibers obtained at a relative humidity of 28% had an elliptical cross-section with the transverse diameter of around 570 nm and the conjugate diameter of around 315 nm (Figure 2.5A). PVP fibers with a circular cross-section could still be observed at a relative humidity of 23%, but their diameters were relatively large and ~2 µm (Figure 2.5B). A rectangular cross-section appeared at a relative humidity of 22% as shown in the SEM image of the side view of a fiber (Figure 2.5C). The width of rectangle for this particular fiber was ~460 nm. Peanut-shaped cross-section could be observed for fibers made at a relative humidity of 16% (Figure 2.5D).
Figure 2.5. SEM images of the cross-section or side-view of PVP fibers generated at different relative humidity of the environment: (A) 28%, (B) 23%, (C) 22%, and (D) 16%, respectively.

Fluid jet typically has a circular cross-section to minimize the surface tension. During its travel from a spinneret to a collector, the fluid jet however dries gradually and the cross-section changes accordingly because of the force associated with drying. This drying force is generally influenced by two factors. One is the decreasing rate of solvent mass due to evaporation. This rate is determined by the following equation:

\[
\frac{\partial M_s}{\partial t} = -\rho h_m [C_{s,eq}(T) - C_{s,\infty}] 2\pi a \lambda ds
\]

**Equation 2.1**

where \(\frac{\partial M_s}{\partial t}\) is the mass decreasing rate of solvent, \(C_{s,eq}(T)\) is the saturation vapor concentration of a solvent at temperature of \(T\), \(C_{s,\infty}\) is the vapor concentration in atmosphere far from the jet, \(\rho\) is the density of solvent, \(h_m\) is the mass transfer coefficient for evaporation, \(a\) is the cross-sectional radius, \(\lambda\) is the geometrical stretching ratio, and \(s\) is Lagrangian parameter.\(^{28,32}\)

The other factor is the diffusion rate of solvent from the core to surface region of the fluid jet due to the concentration gradient within the jet. The diffusion rate is calculated based on the relationship below:

\[
\frac{\partial \phi(r,t)}{\partial t} = D \nabla^2 \phi(r,t)
\]

**Equation 2.2**

where \(D\) is the diffusion coefficient and \(\phi(r,t)\) is the density of the diffusing material at location \(r\) and time \(t\).

The solvents used in this system were ethyl alcohol and DI water. During the electrospinning process, the solvents of fluid jet evaporated quickly because they had low boiling points and high vapor pressure at room temperature (Table A1). \(C_{s,eq}(T)\) of ethyl
alcohol and water remained unchanged because all the experiments were carried out at the same temperature. $C_{\infty}$ of water was proportional to the relative humidity of the environment. Its value decreased as relative humidity decreased. As a result, the mass decreasing rate of water $\frac{\partial M_s}{\partial t}$, increased according to the Equation 2.1 when the relative humidity decreased. Assuming the diffusion rates of the solvents were the same, the decreasing rate of solvent mass should be smaller than or almost the same as the diffusion rate when relative humidity was high, as illustrated in Scheme 2.2. Thus, solvent in the fluid jet evaporated in all directions to the environment evenly and the circular cross-section maintained upon the drying of the fluid jet (Scheme 2.2A). If the relative humidity was low, the decreasing rate of solvent mass was larger than the diffusion rate. The outer shell of the fluid jet was dried firstly to form a thin polymer skin (Scheme 2.2B). As the solvent continuously evaporated and diffused outwards, the inner pressure inside the polymer shell decreased and could not be balanced by the outward one. As a result, the pressure was imposed on the polymer skin in all directions. If the round fluid jet collapsed along any given direction, the charges were no longer distributed evenly but flowed to the surface regions with high curvature due to the point effect. The pressure from the environment continued to push the polymer skin until the fluid jet was completely dried. Under such situation, an elliptical or rectangular cross-section was obtained (Scheme 2.2B).
Scheme 2.2. Schematic illustration of the formation of electrospun polymeric fibers with different shapes in cross-section.
If the relative humidity dropped below 22%, the decreasing rate of solvent mass became fast, resulting in various pores in the wall of the semi-dried fluid jet due to rapid drying, which generated a capillary force. When a liquid is transported in a porous media, the cumulative volume $V$ of absorbed liquid after a time $t$ is $V = AS\sqrt{t}$, where $A$ is cross-sectional area of the pores and $S$ is the sorptivity of the medium. The transportation rate is related to the sorptivity of the porous media, which is a constant. When the humidity decreased, the density of pores increased due to the quick shrinking of polymers, which caused by the increase of the mass decreasing rate. Then the diffusion rate increased due to the capillary force, and it increased with the density of pores. As a consequence, the overall drying rate of the fluid jet greatly increased with the decrease of the relative humidity. Once the fluid jet was dried, the fibers became rigid and could no longer be deformed by the atmospheric pressure. Since the charges on the surface of fluid jet concentrated at the two side regions with high curvature, two circular shapes formed around those regions due to the charge repulsion. As a result, a peanut-shaped cross-section formed (Scheme 2.2C).

The diameter of the polymeric fibers or width of the ribbons could be controlled by changing the relative humidity. As the relative humidity decreased, the diameter or width increased (data are summarized in Table 2.1). Two main factors could attribute to this observed trend. Firstly, when the relative humidity was high (in the situation of Scheme 2.2A), the fluid jet dried uniformly and slowly. If the relative humidity increased,
fluid jet dried slower. Coulomb repulsive force could cause the elongation of the fibers during a relative longer period, thus reduced the size in fiber diameter. Secondly, when the relative humidity was low (in the situation of Scheme 2.2B), the size of fibers were controlled by the synergistic interaction between the mass decreasing rate and diffusion rate of the solvents. If the mass decreasing rate was slightly larger than the diffusion rate and the fluid jet collapsed slightly before it was dried completely, resulting in narrow width. If the humidity was further decreased, the decreasing rate was much larger than the diffusion rate. The fluid jet spread outwards further before it was totally dried. As a result, the width increased.

2.3.4 Effect of Solvents on the Fiber Morphology

To further explore this concept, the volumetric ratio of ethyl alcohol (EtOH) to DI water (H$_2$O) was varied from 3:1, 2:1, 1:1, to 1:2, while keeping the relative humidity at 16%. When EtOH/H$_2$O volumetric ratio was at 4:1 or 3:1, the morphology of electrospun PVP fibers was helical peanut-shaped ribbon (Figure 2.6A). Percentage of the helical ribbons decreased from 98% to 85% when EtOH/H$_2$O ratio changed from 4:1 (v/v) to 3:1 (v/v). At the volumetric ratio of 2:1 or 1:1, the morphology changed to flat ribbon or straight round fiber (Figure 2.6B and 2.6C). The width of flat ribbons or diameter of straight round fibers decreased from 1.2 µm to 770 nm when EtOH/H$_2$O ratio changed from 2:1 (v/v) to 1:1 (v/v). Thin round fibers with beads formed when the ratio reached 1:2 (v/v) (Figure 2.6D).
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As shown in Table A1, boiling point of DI water is higher than ethyl alcohol, while the vapor pressure is lower at room temperature. Thus the mass decreasing rate of water is smaller than that of ethyl alcohol under the experimental conditions. As volumetric percentage of water increases, decreasing rate of solvent mass should decrease. This effect should hold the same as relative humidity of the environment increases. As a result, the morphology of electrospun PVP fibers changed from helical peanut-shaped ribbons to flat ribbons and eventually to straight round fibers while the volumetric percentage of water increased. Meanwhile, percentage of helical ribbons and the width of flat ribbons decreased. In additional, the surface tension and dielectric constant of water are much higher than those of ethyl alcohol. Coulomb forces and the surface tension could not be balanced in the fluid jet if other conditions retain the same. The fluid jet became unstable and beads began to form (Figure 2.6C and D).
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Figure 2.6. SEM images of PVP fibers generated at the EtOH/H₂O volumetric ratio of (A) 3:1, (B) 2:1, (C) 1:1, and (D) 1:2, respectively. The relative humidity of the environment was 16%.

2.3.5 Effect of Concentration on the Fiber Morphology

When the concentration of electrospun solution was varied from 11%, 9% to 7% (w/v) while other conditions were maintained the same, the morphology of PVP fibers changed from helical peanut-shaped ribbon to flat ribbon or straight round fiber, and at last to thin fiber with beads (Figure 2.7). The percentage of helical ribbon decreased from 83% to 26% and at last to 0%. The width of flat ribbons or diameter of straight round
fibers decreased from 489 nm to 346 nm when the concentration of solution changed from 9% (w/v) to 7% (w/v). Thin round fibers with beads formed when the concentration decreased to 7% (w/v).

Figure 2.7. SEM images of PVP fibers generated at the concentration of electrospun solution of (A) 11%, (B) 9% and (C) 7% (w/v), respectively. The relative humidity of the environment was 16%.

Concentration of polymer solution affects on morphology of the electrospun fiber, the bead formation, bead density and diameter of the fiber. As the concentration of polymer solution decreased, the viscosity of fluid jet decreased accordingly, leading to a lower drying rate. So the same trend was observed just as the volume percentage of DI-water increased or as the humidity of environment increased. While the concentration was as low as 7%, the viscosity was so lower that cohesive force decreased. The surface tension was dominant which tended to form beads. Then the fluid jet became unstable and beads formed.

2.3.6  Ultimate Elongation of Fibers Electrospun at Different Relative Humidity
Thermal mechanical analyzer was used to characterize the elasticity of the electrospun fibers. Figure 2.8 shows the ultimate elongation of PVP fibers with different morphologies and percentage of helical ribbons electrospun at a range of relative humidity. The ultimate elongation decreased when the relative humidity increased.

![Graph showing the dependence of Ultimate Elongation and Helical Ribbons (%) on Relative Humidity (%).]

**Figure 2.8.** Dependence of ultimate elongation of PVP fibers and percentage of helical ribbons on the relative humidity.

It is because the ultimate elongation of helical ribbons is larger than that of straight round fibers. As illustrated in Scheme 2.3, if the extension force is applied on the two ends of helical ribbons, the degree of spiral decreases continuously until almost no spiral exists. Subsequently, the width of the ribbons decreases until the ribbons breaks.
However, if the extension force is exerted on the two ends of the straight round fibers, the diameter of the fibers decreases until the fibers are fractured. The percentage of helical ribbons decreased when the relative humidity increased as mentioned in Section 2.3.2. Therefore, if the relative humidity increases, the ultimate elongation decreases.

**Scheme 2.3.** Schematic illustration of the deformation of (A) a helical ribbon and (B) a straight round fiber under extension forces $F$. 
2.4 Conclusion

This chapter describes the preparation and understanding of helical peanut-shaped ribbons of poly(vinyl pyrrolidone) (PVP) by a magnetic field-assisted electrospinning method. The relative humidity was found to significantly influence the morphology of PVP fibers. When the relative humidity of the environment decreased from 32% to 16%, the morphology of the electrospun PVP fibers changed from straight fiber to helical ribbon, and the percentage of helical ribbons increased to 99%. The cross-section of electrospun fibers changed from circle, to ellipse, and to peanut shape. The ultimate elongation was 33% for straight round fibers made at relative humidity of 32% and 43% for helical ribbons made at relative humidity of 16%. The formation of helical ribbons was explained based on the synergistic interaction of bending instability of electrospun jet, and the rigidity of the polymer materials during the MFAE process, involving the mass decreasing rate and the diffusion rate of the solvents. This work provides insights on the effect of relative humidity on the extent of spirals and the shape of the cross-section of the electrospun polymer fibers. Additionally, the influence of solvent property and concentration on the morphology of electrospun fibers were also discussed. Controllable morphology of electrospun fibers may be applied to guide the growth of cells, thus the technique described in this work is potentially useful for making biomaterials in tissue engineering. This technique also offers a way to control the mechanical property of electrospun fiber scaffolds.
2.5 References


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Chapter 3 Fabrication of SiC Fibers by Electrospinning and UV Cure

3.1 Introduction

Silicon carbide (SiC) has various desirable properties including high tensile strength, high elastic modulus, excellent thermal stability, outstanding oxidation resistance and remarkable electronic properties.\(^1-^4\) As a result, it is a good reinforcement material and a good candidate for high-speed electronics.

Fabrication of one dimensional (1D) SiC catches a lot of attentions. Catalyst assisted pyrolysis method is cheap and fast.\(^5-^8\) But the low yield and the involvement of metallic elements limit the practical utilization of final 1D materials. Template modulated method necessitates the use of template and etchant, which increases the fabrication cost and increases the chance to impair the fibers.\(^9-^{10}\) Additionally, the length of 1D materials fabricated by catalyst assisted and template modulated methods is limited. Conventional spinning method, although good for producing SiC fibers with large aspect ratio, is only useful for making SiC with the diameter of larger than 10µm.\(^10-^{11}\) Compared to these methods, electrospinning is a much superior method, because it can fabricate 1D fibers with the size ranging from nanometer to micrometer facilely. For example, SiO\(_2\) fibers are fabricated by electrospinning from preceramic precursor tetraethoxysilane (TEOS) with the help of guiding polymer polyvinyl alcohol (PVA) or polyacrylonitrile (PAN) at first; then they are carbonized by graphite to obtain SiC fibers.\(^12-^{14}\) SiC fibers were also
obtained from preceramic polymer, polycarbosilane, with the help of guiding polymer by emulsion electrospinning\textsuperscript{15} and concentric electrospinning.\textsuperscript{16} In addition, to maintain the morphology of preceramic fibers when converting it to SiC fibers by pyrolysis, electron beam (e-beam) irradiation up to 10 MGy in an inert gas atmosphere was used.\textsuperscript{17-19}

In this chapter, preceramic fibers could be obtained directly by magnetic-field-assisted electrospinning (MFAE) method from the preceramic polymer without any guiding polymer. Later, SiC fibers were produced by UV Cure and post-pyrolysis treatment of the preceramic fibers. Compared to e-beam irradiation, the UV Cure method is a much energy-conserving technique and easy to handle.

### 3.2 Experimental Section

**Materials.** Allylhydridophenylpolycarbosilane (RD, $M_n=1340$, $M_w=10300$) was purchased from Starfire System. Toluene (anhydrous, 99.8%), dichloromethane (anhydrous, $\geq 99.8\%$), n-methyl-2-pyrrolidone (NMP, anhydrous, 99.5%) were purchased from Aldrich. All chemicals were used as received without further purification.

**Electrospinning of Preceramic Fibers.** Aligned preceramic fibers was fabricated by magnetic-field-assisted electrospinning method from preceramic polymer RD directly. RD was dissolved into various mixtures of solvents while the concentration of solution was kept at 50 wt\%. The polymer solution was loaded into a plastic syringe with a 22-Gauge (inner diameter: 0.028 inch) stainless-steel needle. The sharp tip of the needle was cut and sanded into smooth circular, flat opening to ensure the proper direction of fluid
jets. The needle was connected to a high-voltage power supply and a collector was grounded and 15 cm below the needle tip. The voltage between the spinneret and the collector was maintained at 23 kV. The collector was a U-type bracket wrapped by foil and placed on the top of the two magnets. The space between the two arms of the U-type bracket was the same as the distance between two magnets. So the electrospun preceramic fibers could hang on the arms of the bracket. The feeding rate was controlled by a syringe pump at a constant rate of 1.5 mL/h.

**Fabrication of SiC Fibers.** The as-spun preceramic fibers fixed by U-type bracket were cured by a UV lamp (254nm, PSD-UVT, Novascan Technologies Inc.) in Ar atmosphere at room temperature under various durations. After UV Cure, the fibers became robust and could be cut from the bracket integrally. Later, the fibers were pyrolyzed at 1100 °C in Ar atmosphere to form SiC fibers.

**Characterization.** The morphology of the preceramic fibers and SiC fibers were studied by Field Emission Scanning Electron Microscope (FE-SEM, Zeiss-Leo DSM982). Average diameter was measured by Image J (National Institutes of Health, USA). $^1$H NMR spectra were recorded in CDCl$_3$ on Brucker Avance 400-2 NMR Spectrometer at 400 MHz. Attenuated total reflectance infrared spectra (ATR-IR) were collected on a Shimadzu FTIR-8400S spectrophotometer with a MIRacle ATR accessory. Powder X-ray diffraction (PXRD) patterns were recorded using a Philips MPD diffractometer with a Cu $K_{α}$ X-ray source ($\lambda = 1.5405$ Å). The thermal gravimetric analysis (TGA) was conducted on an SDT-Q600 TA instrument. In a standard procedure, ~5 mg samples were transferred into a platinum pan, which was subsequently placed onto the dual beam
sample holder. The samples were heated from room temperature to 1000 °C with a heating rate of 2 °C/min. The flow rate of N₂ was set at 50 mL/min.

3.3 Results and Discussion

3.3.1 Morphology and Diameter Control of Preceramic Fibers

The morphology and diameter of the electrospun preceramic fibers can be adjusted by varying mixtures of solvents. When the mixture of toluene and dichloromethane was used as solvent, the morphology of preceramic fibers changed continuously from beaded fiber to straight fiber by varying the weight percentage of toluene \((\frac{w_{\text{toluene}}}{w_{\text{mixture}}} \times 100\%)\) from 30%, to 20%, to 10%, and to 0% (Figure 3.1). The density of beads dwindled and the diameter of fibers increased from 1.5µm with 30% of toluene in solvent mixture, to 2.1µm with 20%, to 2.3µm with 10%, and to 3.4µm with no toluene.
Figure 3.1. SEM images of preceramic fibers using mixture of toluene and dichloromethane as solvent. The weight percentage of toluene was (A) 30%, (B) 20%, (C) 10% and (D) 0%, respectively.

The diameter of preceramic fibers could be tuned by using mixture of n-methyl-2-pyrrolidone (NMP) and dichloromethane as solvent (Figure 3.2). The diameter was 600 nm when the weight percentage of NMP \( \left( \frac{W_{NMP}}{W_{mixture}} \times 100\% \right) \) in solvent was 20% and 1 \( \mu \)m when it was 10%. The morphology of the fibers was flat ribbon.
Figure 3.2. SEM images of preceramic fibers using mixture of NMP and dichloromethane as solvent. The weight percentage of NMP was (A) 20% and (B) 10%.

Physical properties of solvent are vital to the morphology of electrospun fibers, including boiling point, vapor pressure at room temperature, surface tension and dielectric constant.\textsuperscript{20-23} Boiling point and vapor pressure at room temperature determine the drying rate and viscosity of the fluid jet, which influence the viscoelastic stress. Dielectric constant determines the density of the charge generated in the fluid jet and therefore affect the Coulomb repulsive force.\textsuperscript{23} As a result, different mixtures of solvents lead to different balances of Coulomb force and surface tension, which would yield fibers with various morphologies and diameters.

The morphology and the size of electrospun fibers could be modified by changing the physical properties of solvent through mixing different solvents. Fluid jet with high surface tension and low charge density per unit area (low dielectric constant) tends to form beads. The dielectric constant of toluene is much lower than that of dichloromethane, though they have similar surface tension (Table A1). As a result, by
using mixture of toluene and dichloromethane as solvent, fiber with beads was obtained. By decreasing the weight percentage of toluene, the density of beads decreased until the straight fibers were obtained. Normally higher bead density would generate thinner fibers, and lower bead density would generate thicker fibers. So the diameter of fibers also increased.

Although the surface tension of NMP is higher than that of dichloromethane, its dielectric constant is much higher. As a result, Coulomb repulsive force became stronger by mixing NMP into dichloromethane. In addition, the boiling point of NMP is higher and vapor pressure at room temperature is lower than that of dichloromethane. The drying rate of fluid jet is much slower when NMP is used as the solvent. Therefore the fiber could be elongated further before it solidified. So by increasing the weight percentage of NMP, fiber diameter decreased. In the following sections, pure dichloromethane was chosen as the solvent.

3.3.2 Characterization of Preceramic Polymer

Silicon carbide (SiC) fibers could be obtained by pyrolysis of as-spun preceramic fibers in Ar atmosphere at elevated temperature. But RD materials melt above 100 °C. It is a great problem to maintain the morphology of fibers while pyrolyzing. To solve this problem, the properties of RD are characterized at first.

RD was characterized by $^1$H NMR and ATR-IR to determine its structural formula. In the $^1$H NMR spectrum (Figure 3.3), resonances corresponding to benzene,
\( \text{CH}_2=\text{CH}, \text{SiH}, \text{SiCH}_2 \text{ and SiCH}_3 \) are observed in the regions of 7.1-7.7 (peak a), 4.8-5.7 (peak b), 3.1-4.4 (peak c), 1.1.6 (peak d) and 0-0.6 (peak e) ppm respectively. Peak f is the resonances of solution CDCl\(_3\). Based on these data; the structural formula of RD is deducted and sketched on the top of \(^1\)H NMR spectrum. ATR-IR spectrum (Figure 3.4) further confirms its structure. Characteristic vibrations of SiH, C=C, Si-C (phenyl) and Si-C (alkyl) are observed at 2112, 1589, 1430 and 1110, and 1250 cm\(^{-1}\) respectively.

\[ \text{Figure 3.3.} \text{ } ^1\text{H NMR spectra of RD material. The structural formula of RD was sketched on the top.} \]
Figure 3.5 shows the TGA curve of RD material. From the TGA curve, it is noticed that the weight loss took place in three stages. A weight loss of 10% observed below 250 °C is due to the loss of low molecular weight oligomers. During this stage, RD melted and formed a gel. The major weight loss occurs in the region 250 – 550 °C (17 wt% loss), which can be attributed to the loss of phenyl and hydrogen from the polymeric chain resulting in onset of cross-linking. The third stage of weight loss (~6%) noticed in the region 550 – 700 °C is attributed to the loss of the CH₄. During the second and third stage, the color of RD materials darkened; the gel solidified gradually and finally formed a black solid. The weight loss of RD finishes at 750 °C, but higher temperature
treatment (larger than 1200 °C) is needed to transfer amorphous SiC to crystalline SiC. The net ceramic residue of the RD is found to be 65 wt% at 1350 °C in argon atmosphere.

![TGA curve of RD material](image)

**Figure 3.5.** TGA curve of RD material.

XRD pattern of RD pyrolyzed at 1350 °C is given in Figure 3.6. Diffraction lines corresponding to (111), (200), (220) and (311) planes of β-SiC are detected. It verifies that SiC could be obtained by pyrolysis of preceramic polymer RD.
Figure 3.6. XRD patterns of RD pyrolyzed in Ar atmosphere at 1350 °C. XRD patterns of β-SiC are shown by the red lines as a reference based on the JCPDS database (No. 74-2307).

3.3.3 Influence of UV Cure on Morphology of SiC Fibers

According to the result of TGA, RD material melted and formed a gel at first when the temperature of pyrolysis was elevated from room temperature due to its low molecular weight and glass transition point. Subsequently, cross-linking reaction happened at high temperature and the gel solidified gradually due to the growth of molecular weight. To solve the problem of morphology deformation of preceramic fibers during the pyrolysis process, as-spun fibers need to be pre-cured to improve its molecular weight and glass transition point. In this study, UV cure is chosen, whose wavelength is 254 nm.
SEM images of SiC fibers, which were cured by UV light at different durations followed by pyrolyzing in Ar atmosphere at 1100 °C, are shown in Figure 3.7. Fibers cured by UV light for only 15 min totally fused together after the pyrolysis treatment. Fibers cured for 30 min also fused together but the outline of the fibers could be seen. For the batches which were cured for 1 hr, only a few fibers fused together. For the batches which were cured for 2 hr, the morphology of as-spun fibers was integrally maintained.

Figure 3.7. SEM images of SiC fibers which were cured by UV light at different durations and then pyrolyzed in Ar atmosphere at 1100 °C. The periods of UV cure were (A) 15 min, (B) 30 min, (C) 1 hr, and (D) 2 hr, respectively.
UV light can break and reunite some bonds of polymer. \textsuperscript{19, 28} So UV cure crosslinks the precursor polymer RD, resulting in the increase of its molecular weight and glass transition point. Therefore, as-spun preceramic fibers after UV cure become stable enough for the post-pyrolysis treatment. ATR-IR spectra of as-spun preceramic fibers cured by UV light at different durations are shown in Figure 3.8. The progress of the crosslinking reaction is monitored by the absorbance of Si-H stretching vibration (2112 cm\(^{-1}\)), Si-Phenyl group (1430 and 1110 cm\(^{-1}\)) and Si-CH\(_3\) group (1250 cm\(^{-1}\)) in the IR spectra. Overall, all the intensity of these absorbance decreased as the period of UV Cure increased, indicating that the amount of these groups decreased with progress of crosslinking reaction. Particularly, in the region of characteristic absorbance of Si-H stretching vibration (red square in Figure 3.8), the intensity of the peak at 2112 cm\(^{-1}\) decreased while the ones at 2025 and 1974 cm\(^{-1}\) increased when the duration of UV cure was prolonged. It is due to the differences of the adjoining group to Si-H, such as R group in R-Si-H. According to the book of \textit{Aldrich Library of FT-IR}, the peak of Si-H shifts from 2120 to 2090 cm\(^{-1}\) if R group changes from methyl, ethyl, to isopropyl group; and it also shifts from 2120 to 2110 cm\(^{-1}\) if R group varies from phenyl group to hexane group. \textsuperscript{29} In the region of the characteristic absorbance of Si-phenyl group (green square in Figure 3.8), the intensity of peak at 1430 cm\(^{-1}\) decreased while the one at 1408 cm\(^{-1}\) increased when the duration was extended. Indeed the absorbance peak at 1430 cm\(^{-1}\) is C-H (in Si-phenyl) bending vibration peak, and the one at 1408 cm\(^{-1}\) is C-H (in Si-CH=CH\(_2\)) .
bending vibration peak.\textsuperscript{29} It indicates that the benzene ring of phenyl group in Si-phenyl was broken into ethylene group gradually by UV exposure.

![Figure 3.8. ATR-IR spectra of as-spun preceramic fibers which were cured by UV light at different durations.](image)

According to the results of ATR-IR spectra, crosslinking reactions are proposed (Scheme 3.1). When RD material is irradiated by UV light, double bonds break and free radicals are generated. The free radicals may attack CH\textsubscript{2} or Si-H group as illustrated in the proposed reaction. Then the amount of Si-H, Si-phenyl and Si-CH\textsubscript{3} group decrease
with progress of crosslinking reaction. R group in R-Si-H changes from methyl to isopropyl group, resulting in the variation of peaks of Si-H stretching vibration in ATR-IR spectra. Si-phenyl group is transferred to Si-vinyl group leading to the change of peaks of Si-phenyl group in ATR-IR spectra. All these are consistent with the results of IR spectra. It supports our proposition that UV cure can crosslink the precursor polymer RD and increase its molecular weight. Therefore, as-spun preceramic fibers after UV cure become stable and the morphology could be maintained during the post-pyrolysis treatment.
Scheme 3.1. Schematic illustration of crosslinking reactions of as-spun preceramic fibers during the treatment of UV cure.

Additional evidence of crosslinking reaction is that the solubility of RD material in dichloromethane decreases when the duration of UV cure is increased. As shown in Figure 3.9, RD material without UV cure could be dissolved completely in dichloromethane. A few part of the material could not be dissolved when it was cured by UV light for 1 hr. And the amount of insoluble part increased when the duration was extended to 2 hr.

Figure 3.9. Solution of RD in dichloromethane after RD was cured by UV light for different durations.
3.4 Conclusion

In this chapter, SiC fibers were synthesized by electrospinning from preceramic polymer, UV Cure and pyrolysis processes. The morphology and diameter of the electrospun preceramic fibers could be adjusted by using various mixtures of solvents. UV cure can crosslink and strengthen the preceramic fibers, leading to the preservation of morphology during pyrolysis process at high temperature. The morphology of preceramic fibers could be maintained if they were cured by UV light for duration of longer than 2 hr. The mechanism of UV cure was proposed. UV light could break double bonds of RD material and generate free radicals. The free radicals attacked CH₂ or Si-H group, leading to the crosslink reaction and stability of preceramic fibers.

3.5 References

6. Vakifahmetoglu, C.; Colombo, P.; Carturan, S. M.; Pippel, E.; Woltersdorf, J. Growth of One-Dimensional Nanostructures in Porous Polymer-Derived Ceramics by
Chapter 3


Chapter 3

Chapter 4 Catalyst Membrane of Pt@Nb-TiO$_2$ Fabricated by Electrospinning and Atomic Layer Deposition

4.1 Introduction

Polymer electrolyte membrane fuel cell (PEMFC) is considered to be a green energy conversion technology for the future.$^{1-5}$ Among the PEMFCs, supported Pt and Pt alloys have been extensively explored as electrocatalysts in oxygen-reduction reaction (ORR), which is the major challenge in the system.$^{6-9}$ Carbon black is the typical support material for catalysts because of its large surface area, high electrical conductivity, and well-developed pore structure.$^{10}$ However, during the ORR cycles, carbon tends to be corroded under the harsh electrochemical reaction conditions.$^{11-14}$ The corrosion of carbon support causes the agglomeration and sintering of Pt catalyst particles, resulting in a decreased electrochemical surface area (ECSA) and activity of the catalysts. Carbon corrosion also leads isolated Pt particles to detach from the support. Moreover, it has been found that Pt can accelerate the corrosion rate of carbon support.$^{15-16}$ These effects strongly affect the durability of PEMFCs. Therefore, non-carbon supports increasingly attract a great deal of attention.$^{17-23}$ TiO$_2$ becomes an alternative candidate for the support material, because it has excellent stability in both acidic and oxidative environments.$^{24}$

To use TiO$_2$ as the electrocatalyst support, one has to develop novel approach to the deposition of highly active catalysts on TiO$_2$. The support also has to be conductive,
because the conductivity of TiO₂ is several orders of magnitude lower than that of carbon black (Vulcan XC-72). In this context, electrospinning and atomic layer deposition (ALD) are both simple and controllable techniques and the combination of these two may be suitable for production of TiO₂-supported Pt catalysts. Mats consisted of one-dimensional TiO₂ fibers with high surface area are made before by electrospinning. ALD technique is able to deposit uniform nanoparticles (NPs) without capping ligands on granular and porous materials, thus avoiding surface contaminations by organic capping molecules. In addition, high degree of control over size of NPs is possible using ALD technique due to its ability to precisely control the delivery of chemical reagents and to the self-limiting nature of the surface-saturated reactions mechanism. Compared with normal Pt/C catalysts, Pt NPs are anchored on the surface of supports by ALD technique instead of simple mixing, which hinders the agglomeration and surface diffusision of NPs and increases the stability of catalysts.

A typical method for improving the conductivity of TiO₂ is through the incorporation of n-type dopants, such as vanadium (V), niobium (Nb), and tantalum (Ta). Another approach is heat treatment at high temperatures under reducing atmosphere in order to create oxygen vacancies in TiO₂. When dopant method is used, Nb is often preferred, because Nb⁵⁺ (r = 0.70 Å) has similar ionic radii as Ti⁴⁺ (r = 0.68 Å), there exists negligible lattice mismatch between TiO₂ and Nb₂O₅. Thus, Nb₂O₅ forms a complete range of solid solutions with TiO₂.

In this work, we present an innovative approach for making catalyst membranes of Pt NPs on Nb-doped titania (Pt@Nb-TiO₂) fiber membranes. This approach is
developed based upon the recent success in two independent areas, namely, the fabrication of TiO$_2$ fibers by electrospinning$^{25-28}$ and the deposition of Pt NPs on supports, such as WC,$^{30}$ Al$_2$O$_3,$$^{41}$ SrTiO$_3$,$^{31, 42}$ and carbon nanotube by ALD.$^{43-44}$ These catalyst membranes could potentially be directly integrated in membrane electrode assembly (MEA) as the catalyst layer, avoiding complicated process of making catalyst inks and then spaying or painting them onto a gas diffusion layer, because the catalyst layer is already in a membrane form. The effects of Nb amount, conditions for ALD and post-treatment on electrocatalytic activity and stability of the membranes are studied.

### 4.2 Experimental Section

**Materials.** Polyvinyl acetate (PVAc, Mw 500,000), titanium (IV) isopropoxide (Ti(O$i$Pr)$_4$, 99.999%) and niobium ethoxide (Nb(OEt)$_5$, 99.95%) were purchased from Sigma Aldrich. N,N-dimethyl formamide (DMF, anhydrous) was obtained from Honeywell Burdick and Jackson. Acetic acid (glacial, 99.7%) was from Alfa Aesar. Nafion 117 solution was from Fluka. All chemicals were used as received without further purification.

**Synthesis of Membrane Supports Made of Nb-TiO$_2$ Support.** Typically, 0.123 g PVAc was dissolved in 1 mL of DMF in glove box.$^{35}$ After complete dissolution, Ti(O$i$Pr)$_4$, Nb(OEt)$_5$ and 0.119 g acetic acid were added into the solution in glove box. The atomic ratio of Ti(O$i$Pr)$_4$ and Nb(OEt)$_5$ was varied according to the predetermined Nb percentage, while the total amount of Ti and Nb was kept at 1.67 mmol. The resulting
solution was mixed well and electrospun at an accelerating voltage of 20 kV and at a flow rate of 1 mL/h. The membrane of polymeric fibers was collected on a grounded aluminum foil placed 15 cm below the spinneret. The relative humidity of environment was kept at above 40% if not mentioned particularly. The membrane was then peeled off from foil using tweezers and left in the air for ~10 h to let the hydrolysis reaction go to completion. Then the membrane was sintered in air at 500 °C for 24 h to remove PVAc and allow nucleation and growth of niobium-doped titania (Nb-TiO₂) particles in the fiber structure.

**Synthesis of Membrane of Pt@Nb-TiO₂ Catalysts.** Atomic layer deposition (ALD) is utilized to deposit Pt NPs onto the membrane of Nb-TiO₂ fibers. The membrane of Nb-TiO₂ fibers was fixed in a chuck and hung in the air inside the chamber of ALD system (Savannah 100 & 200, Cambridge Nano Tech Inc.) to ensure both side of the membrane to be exposed to the reactants. The chamber was kept at 270 °C. Platinum precursor, Trimethyl(methylcyclopentadienyl) platinum(IV) ((MeCp)Pt(CH₃)₃), was kept at 70 °C and gas lines were held at 150 °C to avoid precursor condensation. High-purity O₂ was used as the co-reactant, and high-purity N₂ was used as both the carrier and purge gas. The flow rate of N₂ was maintained at 5 sccm. A typical ALD cycle was as follows: 2 s of Pt precursor pulse, 5 s of N₂ purge, 2 s of O₂ pulse and 28 s of N₂ purge. Pt NPs with different sizes were obtained by changing the total number of ALD growth cycle. For electrochemical measurement, catalyst membrane of Pt@Nb-TiO₂ was treated at either 200 °C or 500 °C in 5% H₂ in Ar atmosphere for 2 h.
**Electrochemical Measurement.** A three-electrode cell was used to perform the electrochemical measurements. The working electrode was a glassy-carbon rotating-disk electrode (RDE; area: 0.196 cm$^2$). Pt foil (1 cm × 1 cm) was used as the counter electrode. A reversible hydrogen electrode (RHE) was used as the reference electrode, which was placed in a separate compartment. The electrolyte for all of the measurements was 0.1 M perchloric acid, which was diluted with de-ionized water from a 70% doubly distilled stock solution (GFS Chemicals, USA). To prepare the working electrode, the Pt@Nb-TiO$_2$ catalyst was first dispersed in ethanol and the mixture was sonicated for 30 min. 5 µL of suspension was added onto RDE by a pipette and dried under air. It was repeated until the surface of RDE was covered by a thin-uniform layer of the catalysts. Then 10 µL of 0.0125% (wt%) Nafion-ethanol solution was dropped on the surface of the thin film to prevent the catalysts from detaching by the flow of testing solution. The measurements of the total electrochemically active surface area (ECSA) were performed by integrating the hydrogen adsorption from the cyclic voltammetry (CV) data, which was recorded at room temperature in argon saturated solution of 0.1 M HClO$_4$. The potential scan rate was 50 mVs$^{-1}$ for the CV measurements. The ORR measurements were conducted at a rotation rate of 1600 rpm in 0.1 M HClO$_4$, which was purged with oxygen for 30 min prior to and during the measurements. The scan rate for the ORR measurements was 10 mVs$^{-1}$ in the positive direction. The accelerated-stability test was conducted at ambient temperature in an Ar-protected 0.1 M solution of aqueous HClO$_4$. The potential was cycled 30000 times between 0.6 and 1.0 V (versus RHE) at a scan rate of 100 mVs$^{-1}$ and the polarization curves were recorded after every 10000 cycles. The
area-specific activity was obtained by normalizing the kinetic current density against the ECSA values, and the kinetic current density was obtained from the Koutecky-Levich plot.

**Characterization.** The morphology of the fibers and Pt@Nb-TiO₂ catalyst membrane were studied by field emission scanning electron microscope (FE-SEM, Zeiss-Leo DSM982) and field emission transmission electron microscopy (FE-TEM, FEI TECNAI F-20). Scanning transmission electron microscopy (STEM) and elemental maps were carried out using the high-angle annular dark field (HAADF) mode on FE-TEM. Energy dispersive X-ray (EDX) analysis of catalysts was carried out on FE-SEM equipped with an EDAX detector. Average diameter was measured by Image J (National Institutes of Health, USA). Powder X-ray diffraction (PXRD) patterns were recorded on a Philips MPD diffractometer with a Cu Kα X-ray source (λ = 1.5405 Å).

### 4.3 Results and Discussion

#### 4.3.1 Experimental Process

Scheme 1 illustrates the two-step process for the fabrication of catalyst membrane by combining the electrospinning and ALD techniques. In the first step, support membrane of Nb-TiO₂ was produced by electrospinning technique and sintering. At first, membrane of polymeric fibers was obtained by electrospinning from ceramic precursors (Ti(O\text{Pr})₄ and Nb(OEt)₃) and guiding polymer PVAc. The Nb-doped percentage was varied by controlling the atomic ratio between Ti(O\text{Pr})₄ and Nb(OEt)₃. Then the
membrane of Nb-TiO$_2$ was obtained by hydrolysis and sintering of the as-spun membrane in the air. In the second step, Pt NPs were deposited onto the support membrane by ALD technique to form catalyst membrane of Pt@Nb-TiO$_2$. Typically, an ALD cycle began with a organometallic precursor ((MeCp)Pt(CH$_3$)$_3$) pulse. (MeCp)Pt(CH$_3$)$_3$ reacted with oxygen atoms on the surface of Nb-TiO$_2$ membranes, generating PtC$_x$H$_y$-containing compounds and byproducts of CH$_4$, CO$_2$ and H$_2$O. The excess (MeCp)Pt(CH$_3$)$_3$ and byproducts were cleared by N$_2$ purging gas, followed by the O$_2$ pulse. O$_2$ reacted with PtC$_x$H$_y$ segment to form Pt–O and byproduct, CO$_2$ and H$_2$O. The O atom generated could be used to react with (MeCp)Pt(CH$_3$)$_3$ in the subsequent ALD cycle. The ALD cycle was finished by another N$_2$ purge to eliminate excess O$_2$ and byproducts. By repeating the ALD growth cycle, different size of Pt NPs could be deposited onto the Nb-TiO$_2$ membrane. Because the reaction streams of (MeCp)Pt(CH$_3$)$_3$ and O$_2$ were separated by a purge gas of N$_2$. During each reactant pulse, only one reactant reacted with substrate surface, through a self-limiting process that was capable of precisely controlling the growth of Pt NPs.
Scheme 4.1. Schematic illustration of the process for the production of Pt@Nb-TiO$_2$ catalyst membrane. (A) Step 1: preparation of Nb-TiO$_2$ support membrane by electrospinning technique and sintering. (B) Step 2: preparation of catalyst membrane of Pt@Nb-TiO$_2$ by the ALD technique. The SEM image shows a final membrane made of Pt@Nb-TiO$_2$ fibers.

Figure 4.1 shows the TEM, STEM and HAADF-STEM micrographs of Pt NPs dispersed on a Nb-TiO$_2$ fiber made after 40 ALD cycles. The patchy, uneven contrast shown in the TEM micrograph indicates the surface of Nb-TiO$_2$ fiber was not smooth. Both TEM and STEM micrographs show that the Pt NPs were uniformly dispersed on the
ceramic fibers with an average diameter of 14 nm. Several studies previously show the dispersion of Pt particles increased with increasing the number of oxygen-containing surface species in the support.\textsuperscript{45-47} In this system, Nb-TiO\textsubscript{2} fibers contained abundant oxygen surface groups. As a result, the deposition of Pt NPs was uniform. The HAADF-STEM micrograph indicates that Pt, Ti and Nb elements were distributed homogeneously throughout the Nb-TiO\textsubscript{2} fiber. These results indicate metal nanoparticles with high uniformity in size could be deposited onto metal oxide fiber membranes by electrospinning and ALD techniques. This two-step process is easy to operate and scalable, because the size of the membrane generated by electrospinning and ALD could be very large depending on the scale of the equipment. In our experiment, the size of a typical membrane was 1.5 cm × 2.2 cm and limited by the operating area of the ALD system and the tube furnace (inserted photo in Scheme 4.1B).

\textbf{Figure 4.1.} (A) TEM and (B) STEM micrographs of Pt@Nb-TiO\textsubscript{2} catalyst. (C) HAADF-STEM study showing the distribution of Pt (blue), Ti (red) and Nb (green) elements. The area for HAADF-STEM study is the marked region in (B).
4.3.2 Effect of Fiber Morphology on Electrocatalytic Activity

Two kinds of morphology of Nb-TiO$_2$ fibers can be produced by electrospinning. Figure 4.2 shows SEM images of as-spun polymeric fibers (left column), ceramic fibers of Nb-TiO$_2$ with 10 at% of Nb (middle column) and catalysts of Pt@Nb-TiO$_2$ with 10 at% of Nb (right column) with these two kinds of morphology. One was straight fiber which could be obtained when the relative humidity was lower than 40% during electrospinning process (Figure 4.2A). The diameters of as-spun polymeric fibers and Nb-TiO$_2$ fibers after hydrolysis and sintering with morphology of straight fiber were 181 nm and 164 nm, respectively. The other was beaded fiber which could be obtained when the relative humidity was kept higher than 40% (Figure 4.2B). The diameters of fibers before and after sintering were 183 nm and 170 nm, respectively. The sizes of the beads were 368 nm and 343 nm, respectively.
Figure 4.2. SEM images of (A1 and B1) as-spun polymeric fibers, (A2 and B2) ceramic fibers of Nb-TiO$_2$ with 10 at% of Nb after hydrolysis and (A3 and B3) sintering and catalysts of Pt@Nb-TiO$_2$ with 10 at% of Nb after 40-cycle ALD of Pt NPs. The morphologies of the fibers were: (A) straight fiber and (B) beaded fiber.

During the electrospinning process, ceramic precursors contacted with the moisture in the air and were hydrolyzed partially. Meanwhile, the condensation reaction happened.$^{48}$-$^{49}$ The rate of hydrolysis and condensation reactions increased when the relative humidity of the environment increased. The molecular weight of ceramic precursors grew as the hydrolysis and condensation reactions continued, leading the increase of the viscosity of electrospun solution. In summary, the viscosity increased with the relative humidity. Then the balance of the Coulomb repulsive force and the surface
tension, which had close relationship with viscosity, was destroyed. As a result, electrospun jet became unstable and beads began to form when the relative humidity was higher than 40%.\textsuperscript{50}

In the following, Pt NPs were deposited onto the support membrane of Nb-TiO\textsubscript{2} with 10 at\% of Nb with these two kinds of morphology by 40-cycle ALD respectively. Although the morphology and size of the Nb-TiO\textsubscript{2} supports were different, the diameter of Pt NPs were all around 14 nm (Figure 4.2.A3 and B3). Thus, the size of Pt NPs apparently depended only on the operating temperatures of the Pt precursors and ALD chamber, and the number of ALD growth cycles.\textsuperscript{51-52} Then electrochemical measurement was carried out to study the area-specific ORR activity (\(i_{\text{s}}\)) of the catalyst membranes with these morphologies. The area-specific activity of catalyst membrane with morphology of straight fiber was 0.079 ± 0.008 mA/cm\textsuperscript{2}\textsubscript{Pt} at 0.9 V (versus RHE), and the one with beaded fiber was 0.16 ± 0.059 mA/cm\textsuperscript{2}\textsubscript{Pt}. The activity of the catalyst membrane with the morphology of straight fiber was much lower than the one with beaded fiber due to the difference of porosity. The porosity of the support membrane with morphology of beaded fiber was supposed to be higher due to the existence of beads, leading facilely deposition of Pt NPs into the inner holes of membrane during ALD process. So the activity of catalyst membrane with morphology of straight fibers was lower.
4.3.3 Effect of Nb-doped Percentage on Electrocatalytic Activity

Different amount of niobium (5 at%, 10 at% and 25 at%) were doped into TiO₂ to form Nb-TiO₂ support membranes by varying the Nb(OEt)₅/Ti(ÔPr)₄ atomic ratio from 5:95, to 10:90 and to 25:75 in the electrospun solution to improve the conductivity of the supports while other parameters were maintained the same. Pt NPs were loaded onto these membranes by 40-cycle ALD. Figure 4.3 shows SEM images of as-spun polymeric fibers (left column), Nb-TiO₂ fibers (middle column) and Pt@Nb-TiO₂ catalysts (right column). Table 4.1 summarizes the diameter of the fibers and size of the beads of as-spun polymeric and ceramic Nb-TiO₂ fibers with different doping amount of Nb. The diameter of Nb-TiO₂ fibers did not change much, when compared with the as-spun polymeric fibers. Void spaces were generated after the pyrolysis in air due to the removal of PVAc and to the homogeneous nature of the preceramic mixture of PVAc and metal alkoxide precursors (Figure 4.3, middle column). The ceramic fibers were continuous and made of small, crystal domains without preferred orientation (Figure 4.4). Although the morphology of fibers were different at the different compositions of Nb-TiO₂ ceramic, the diameter of Pt NPs deposited by 40-cycle ALD were all around 14 nm as mentioned in Section 4.3.2.
Figure 4.3. SEM images of (A1, B1, C1 and D1) as-spun polymeric fibers, (A2, B2, C2 and D2) Nb-TiO$_2$ fibers after hydrolysis and sintering and (A3, B3, C3 and D3) Pt@Nb-TiO$_2$ catalysts after 40-cycle ALD of Pt NPs. The amount of Nb was (A) 0 at%, (B) 5 at%, (C) 10 at%, and (D) 25 at%, respectively.

Table 4.1. Summary of the diameter of fibers and size of beads of as-spun polymeric and Nb-TiO$_2$ fibers at different Nb-doped amount (at%).

<table>
<thead>
<tr>
<th>Nb amount (at%)</th>
<th>as-spun polymeric fiber</th>
<th>Nb-TiO$_2$ fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>fiber (nm)</td>
<td>bead (nm)</td>
</tr>
<tr>
<td>0</td>
<td>193</td>
<td>405</td>
</tr>
<tr>
<td>5</td>
<td>212</td>
<td>426</td>
</tr>
<tr>
<td>10</td>
<td>183</td>
<td>368</td>
</tr>
<tr>
<td>25</td>
<td>270</td>
<td>-</td>
</tr>
</tbody>
</table>
XRD patterns of the support membranes only show the diffraction peaks, which could be assigned to anatase phase of TiO$_2$ (Figure 4.5). No diffraction peaks from niobium oxide were observed, which indicates that Nb was incorporated into the TiO$_2$ crystal structure. The formation of mixed oxide ceramic could be attributed to the similar ionic radii between the two metal ions. Increased Nb amount in the ceramic resulted in large lattice strain and the shift in the lattice parameters.$^{53-54}$ The XRD peaks of Nb-TiO$_2$ shifted to the low 2θ angles gradually when the amount of Nb increased, primarily because of relative large radius of Nb.
Figure 4.5. XRD patterns of Nb-TiO$_2$ fibers with different amount of Nb. XRD patterns of anatase TiO$_2$ are shown by the black lines as a reference based on the JCPDS database (No. 84-1286).

Figure 4.6 shows the dependence of area-specific ORR activities ($i_a$) of Pt@Nb-TiO$_2$ catalyst membranes on the amount of Nb. The area-specific activity changed from 0.0084 mA/cm$^2_{Pt}$ for Pt@TiO$_2$, to 0.086 mA/cm$^2_{Pt}$ for Pt@Nb-TiO$_2$ with 5 at% of Nb, and to 0.16 mA/cm$^2_{Pt}$ for Pt@Nb-TiO$_2$ with 10 at% of Nb at 0.9 V (versus RHE). The catalyst membrane of Pt@Nb-TiO$_2$ with 10 at% of Nb showed a ~20-fold enhancement in ORR activity over the Pt@TiO$_2$ membrane. Increasing the Nb amount further to 25% did not result in further increase in ORR activity. Since there was no major difference in size and shape of the Pt NPs, the change in catalytic activity could largely attributed to
the Nb-TiO$_2$ fiber membranes. It is known that the conductivity of Nb-doped TiO$_2$ increases with the relative amount of Nb in thin film$^{55}$ and powders.$^{56-57}$ Wang et al. reported that the conductivity of Nb-doped titania powders changed from $4.9 \times 10^{-8}$ S·cm$^{-1}$, to $9.6 \times 10^{-7}$ S·cm$^{-1}$, to $7.9 \times 10^{-5}$ S·cm$^{-1}$ and to $1.2 \times 10^{-3}$ S·cm$^{-1}$ when the amount of Nb increased from 0 at%, to 5 at%, to 10 at% and to 20 at%.$^{57}$ Thus, the area-specific ORR activities of Pt@Nb-TiO$_2$ catalyst membrane increased when the percentage of Nb increased from 0 at% to 10 at% due to improvement of conductivity of the ceramic support. However, when the Nb-doped amount increased to 25 at%, the morphology of support was straight fiber while others were beaded fiber (Figure 4.3). According to Section 4.3.2, the area-specific activity of Pt@Nb-TiO$_2$ catalysts would be higher if the morphology of support was beaded fiber. This kind of morphology could be obtained if the relative humidity of environment was maintained higher than 40% when Nb-doped percentage was between 0 at% and 10 at%. If the Nb amount increased to 25 at%, only straight fibers were obtained. Due to the differences of morphology, the activity of Pt@Pt@Nb-TiO$_2$ with 25 at% of Nb decreased.
Figure 4.6. Plot showing the dependence of area-specific ORR activities of Pt@Nb-TiO$_2$ catalyst membrane at 0.9 V (versus RHE) on Nb-doped percentage in the ceramic fibers.

4.3.4 Effect of ALD Cycles and Post-treatment on Electrocatalytic Activity

ALD is typically used to deposit thin films of oxides on flat substrate through a self-limiting process. When ALD was used to grow Pt on substrates, however, discrete Pt NPs formed and dispersed uniformly over the supports (Figure 4.7). As the number of ALD cycles increased, the size of Pt NPs grew up and the distance between isolated Pt NPs decreased (Figure 4.7A-C) until the Pt nanocrystals became to connect with each other (Figure 4.7D). Normally the reactivity difference between substrate and Pt active sites led to a preference for Pt NPs to grow up rather than to nucleate new particles on the substrate. But sometimes, new particles also nucleated with the growth of large Pt NPs showing obvious small particles (Figure 4.7C). The average size of Pt NPs on Nb-TiO$_2$
with 10 at% of Nb was 4.5 nm after the growth of 10 ALD cycles, 9.2 nm after 20 cycles and 14 nm after 40 cycles at the post-treatment temperature of 200 °C. If the number of ALD cycles increased to 80, Pt particles became to connect with each other.

As the ALD process of Pt ended with an oxygen pulse, the outer layer of Pt NPs was covered with PtO (Scheme 4.1B). Thus the catalyst membranes of Pt@Nb-TiO$_2$ were post-treated at 200 °C in 5% H$_2$ w/ Ar atmosphere to reduce PtO to Pt. This procedure did not affect the size and morphology of Pt NPs. To check the effect of temperature on ORR activity, the membranes were treated at 500 °C in 5% H$_2$ w/ Ar. At this temperature, the size and morphology of Pt NPs changed. Pt NPs would migrate and coalesce on the surface of support at high temperature according to Smoluchowski model; and atoms from small Pt NPs can evaporate and condense on larger ones in a process similar to the Ostwald ripening of dispersed precipitates in solution. So Pt NPs grew up when post-treated at 500 °C. The sizes of Pt NPs increased to 7.5 nm for sample made after 10 ALD cycles, 12.6 nm after 20 cycles, and 18.7 nm after 40 cycles (Figure 4.7 E-G). The Pt particles also became connected if the number of ALD cycle increased to 80 (Figure 4.7H). In addition, the surface of Pt NPs was not smooth; edges and faces were noticed obviously because of the crystallite growth of Pt NPs at high temperature (Figure 4.7G and H).
Figure 4.7. SEM images of Pt@Nb-TiO$_2$ catalysts with 10 at\% of Nb obtained by different numbers of ALD cycle and different temperature of post-treatment in 5\% H$_2$ w/ Ar atmosphere. (A-D) were treated at 200 °C. (E-H) were treated at 500 °C. The numbers of ALD cycle were as following: (A, E) 10, (B, F) 20, (C, G) 40, and (D, H) 80.

The area-specific ORR activities of catalyst membrane of Pt@Nb-TiO$_2$ with 10 at\% of Nb increased with the number of ALD cycle (Figure 4.8). Weight percentage of Pt in the catalyst increased from 49\% for catalyst membrane with 10 ALD cycles, to 65\% with 20 cycles, to 80\% with 40 cycles, and to 87\% with 80 cycles, based on the energy dispersive X-ray analysis. The increase in weight percentage of Pt NPs could also help to improve the conductivity of catalyst membrane.
Figure 4.8. Plot showing the dependence of area-specific ORR activities of Pt@Nb-TiO$_2$ with 10 at% of Nb at 0.9 V (versus RHE) on the number of ALD cycle for making Pt NPs, and the temperature of post-treatment in 5% H$_2$ w/ Ar atmosphere.

Comparing area-specific activities of the Pt@Nb-TiO$_2$ catalyst membranes with the Pt NPs deposited by the same number of ALD cycle, the one post-treated at 500 °C had higher activities. One reason was the increase of crystallinity of Pt NPs, which was improved after the post-treatment at high temperature. In addition, hydrogen treatment at high temperature could result in hydrogen doping into Nb-TiO$_2$ support.$^{38}$ The n-type TiO$_2$ formed by introducing hydrogen interstitial or substitution sites.$^{61}$ Thus the conductivity of the support was further increased. As a result, the area-specific activity of catalyst membrane treated at 500 °C in H$_2$ atmosphere was higher than those treated at 200 °C.
4.3.5 Accelerated-stability Test

Accelerated-stability test was conducted to examine the electrochemical stability of the Pt@Nb-TiO$_2$ catalyst with 10 at% of Nb. The sample was pretreated by 40 cycles of cyclic voltammetry (CV) measurement between 0.05 and 1.0 V (versus RHE) before the test to active the catalyst. Subsequently, the first ($1^{st}$) cycle of ORR and CV measurements were tested. For the stability test, the potential was cycled 30000 times between 0.6 and 1.0 V (versus RHE), while the ORR and CV measurements were performed every 10000 cycles (Figure 4.9). Table 4.2 summarizes the electrochemically active surface area (ECSA), kinetic-current density ($i_k$) and area-specific activity ($i_a$) at 0.9 V (versus RHE). The ORR polarization curves barely changed after the 30000-cycle accelerated-stability test, indicating that the catalyst membranes were very stable. Kinetic current density decreased only within 10% after 30000 cycle accelerated-stability test although area-specific activity decreased 25% (Table 4.2). The big differences between kinetic current density and area-specific activity were due to the problem of ECSA measurement.
Figure 4.9. Accelerated-stability test of Pt@Nb-TiO$_2$ catalyst with 10 at% Nb: (A) CV curves and (B) ORR polarization curves measured at 1600 rpm.
Table 4.2. Electrochemically active surface area (ECSA), kinetic current density \( (i_k) \) and area-specific current density \( (i_s) \) at 0.9 V (versus RHE) of Pt@Nb-TiO\(_2\) catalyst membranes with 10 at% of Nb after a given number of potential cycles during accelerated-stability test; relative percentages are given in parentheses.

<table>
<thead>
<tr>
<th># of Cycle</th>
<th>ECA (cm(^2))</th>
<th>( i_k ) (mA/cm(^2))</th>
<th>( i_s ) (mA/cm(^2) Pt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^{st})</td>
<td>14.74 (100%)</td>
<td>15.87 (100%)</td>
<td>0.21 (100%)</td>
</tr>
<tr>
<td>10000(^{th})</td>
<td>15.80 (107%)</td>
<td>16.25 (102%)</td>
<td>0.20 (96%)</td>
</tr>
<tr>
<td>20000(^{th})</td>
<td>16.61 (113%)</td>
<td>15.13 (95%)</td>
<td>0.18 (85%)</td>
</tr>
<tr>
<td>30000(^{th})</td>
<td>17.44 (118%)</td>
<td>14.15 (89%)</td>
<td>0.16 (75%)</td>
</tr>
</tbody>
</table>

The total ECSA increased slightly after the stability study. This result is uncommon, because the ECSA value of the catalysts typically decreased after the accelerated-stability test because of the corrosion of catalyst support, agglomeration and sintering of Pt particles, and the detachment of Pt particles from the supports.\(^{11-12, 14}\) It indicated that the catalyst membranes were very stable. The increase was attributed to activation of the tiny holes in the fibers, which might only allow small H\(_2\) molecules to get in and adsorb on the surface but not O\(_2\). So these types of H\(_2\) adsorbed sites could not contribute the ORR. TEM micrographs of Pt@Nb-TiO\(_2\) catalyst with 10 at% of Nb before and after 30000-cycle accelerated-stability test shows that the catalysts were kept largely intact and the size of the Pt NPs did not have obvious change (Figure 4.10).
Figure 4.10. TEM micrographs of Pt@Nb-TiO$_2$ catalyst with 10 at% of Nb (A) before and (B) after the accelerated-stability test.
4.4 Conclusion

A facile method to fabricate niobium-doped titania supported platinum (Pt@Nb-TiO₂) catalyst membrane for oxygen-reduction reaction in polymer electrolyte membrane fuel cell was developed by a new two-step approach, electrospinning and atomic layer deposition. The process started with making niobium-doped titania fiber membrane by electrospinning, followed by the deposition of Pt NPs using atomic layer deposition technique. The area-specific activity of the catalyst membrane with support morphology of beaded fiber was higher than the one with morphology of straight fiber. The area-specific ORR activity of Pt@Nb-TiO₂ catalyst membrane was increased by about 20 folds over the Pt@TiO₂ fiber membrane, if 10 at% of Nb was incorporated into the ceramic fibers. The area-specific activity also increased with the number of ALD cycles. The ORR activity further increased to 0.28 mA/cm²Pt at 0.9 V after post-treatment of the catalyst membrane at high temperature in H₂–containing atmosphere, due to conductivity improvement of Nb-TiO₂ fiber membrane and better crystalinity of Pt NPs. The results of accelerated-stability test showed that the Pt@Nb-TiO₂ catalyst membrane was highly stable and lost only 10% of its initial activity after 30000 potential cycles (0.6 to 1.0 V vs. RHE) under a strong acidic condition. This method has the advantages of simplicity in making uniform ORR catalysts on new types of oxide supports with tunable conductivity and without the need for surface organic ligand through a controllable two-step approach.
4.5 References


Chapter 5 Synthesis of Rutile TiO$_2$ by Electrospinning and Its Supported Pt Electrocatalysts for the Oxygen Reduction Reaction

5.1 Introduction

Titanium dioxide (TiO$_2$) is a good candidate as catalyst support because of its large surface area, high mechanical resistance and excellent stability in acidic and oxidative environments.$^{1-2}$ However, the low conductivity of TiO$_2$, which is only eight orders of magnitude lower than that of carbon black (Vulcan XC-72), is a great deficit to its application. Normally, there exist two crystal structures of TiO$_2$: one is the anatase phase, and the other is the rutile phase. At room temperature, the rutile TiO$_2$ has a band gap of 3.0 eV while the anatase has a band gap of 3.2 eV. Due to this difference in their band gaps, the conductivity of the rutile TiO$_2$ is higher than that of the anatase phase.$^{3-4}$ It was found that the conductivity of the rutile phase (610 $\mu$S·cm$^{-1}$) was almost three orders of magnitude higher than that of the anatase phase (0.12 $\mu$S·cm$^{-1}$).$^5$ The highest reported conductivity of the rutile phase was 1.11 S·cm$^{-1}$ by Brank et al., which was comparable with carbon black.$^6$

TiO$_2$ nanomaterials can be prepared by many techniques including sol-gel process$^{7-8}$, pyrolysis$^9$, reactive sputtering$^{10-11}$, electron beam evaporation$^{12-13}$, plasma-enhanced chemical vapor deposition$^{14-16}$, atomic-layer deposition$^{17-18}$, molecular beam epitaxy$^{19-21}$ and hydrothermal technique$^{22}$. All these methods only generated titanium
dioxide powders or films. In contrast, electrospinning as a novel and direct technique is able to make fibers with size ranging from nanometer to micrometer. TiO$_2$ nanofibers with high surface area could be obtained by electrospinning.$^{23-27}$

In this work, rutile TiO$_2$ fibers were successfully prepared by electrospinning and pyrolysis. The morphology and crystal structure were discussed. Pt nanoparticles (NPs) were deposited on these rutile TiO$_2$ fibers by atomic layer deposition (ALD) technique. The electrocatalytic activity of rutile-titania supported platinum (Pt@r-TiO$_2$) for oxygen-reduction reaction was studied.

### 5.2 Experimental Section

**Materials.** Polyvinyl acetate (PVAc, Mw 500,000), titanium (IV) isopropoxide (Ti(O$i^i$Pr)$_4$, 99.999%) and niobium ethoxide (Nb(OEt)$_5$, 99.95%) were purchased from Sigma Aldrich. N,N-dimethyl formamide (DMF, anhydrous) was obtained from Honeywell Burdick and Jackson. Acetic acid (glacial, 99.7%) was from Alfa Aesar. Nafion 117 solution was from Fluka. All chemicals were used as received without further purification.

**Synthesis of Rutile TiO$_2$ Fibers.** Typically, 0.123 g PVAc was dissolved in 1 mL DMF in glove box.$^{28}$ After complete dissolution, 0.475 g Ti(O$i^i$Pr)$_4$ and 0.119 g acetic acid were added into the solution in glove box. The resulting solution was mixed well and electrospun at an accelerating voltage of 20 kV and at a flow rate of 1 mL/h. The membrane of polymeric fibers was collected on a grounded aluminum foil placed 15 cm below the spinneret. The membrane of polymeric fibers was then peeled off from foil
using tweezers and left in the air for ~10 h to let the hydrolysis reaction go to completion. Then the membrane was sintered in the air at 900 °C for 24 h to remove PVAc and allow nucleation and growth of titania (TiO$_2$) particles in the fiber structure. Titania doped with 10 at% niobium (Nb) fibers (Nb-TiO$_2$) were fabricated with similar method as TiO$_2$. In particular, the mixture of Ti(O'Pr)$_4$ and Nb(OEt)$_5$ was used instead of solo Ti(O'Pr)$_4$. The atomic ratio of Ti(O'Pr)$_4$ and Nb(OEt)$_5$ was 9 : 1 and the total amount of Ti and Nb was kept at 1.67 mmol.

**Synthesis of Pt@r-Nb-TiO$_2$ Catalysts.** Atomic layer deposition (ALD) is utilized to deposit Pt NPs onto the membrane of rutile Nb-TiO$_2$ (r-Nb-TiO$_2$) fibers. The membrane of r-Nb-TiO$_2$ fibers was fixed in a chuck and hung in the air inside the chamber of ALD system (Savannah 100 & 200, Cambridge Nano Tech Inc.) to ensure both side of the membrane to be exposed to the reactants. The chamber was kept at 270 °C. Platinum precursor, Trimethyl(methylcyclopentadienyl) platinum(IV) ((MeCp)Pt(CH$_3$)$_3$), was kept at 70 °C and gas lines were held at 150 °C to avoid precursor condensation. High-purity O$_2$ was used as the co-reactant, and high-purity N$_2$ was used as both the carrier and purge gas. The flow rate of N$_2$ was maintained at 5 sccm. A typical ALD cycle was as follows: 2 s of Pt precursor pulse, 5 s of N$_2$ purge, 2 s of O$_2$ pulse and 28 s of N$_2$ purge. Pt NPs were deposited by 40 ALD cycles. Before electrochemical measurement, catalyst membrane of Pt loaded r-Nb-TiO$_2$ (Pt@r-Nb-TiO$_2$) was treated at 200 °C in 5% H$_2$ w/ Ar atmosphere for 2 hr.

**Electrochemical Measurement.** A three-electrode cell was used to perform the electrochemical measurements. The working electrode was a glassy-carbon rotating-disk
electrode (RDE; area: 0.196 cm²). Pt foil (1 cm × 1 cm) was used as the counter electrode. A reversible hydrogen electrode (RHE) was used as the reference electrode, which was placed in a separate compartment. The electrolyte for all of the measurements was 0.1 M perchloric acid, which was diluted with de-ionized water from a 70% doubly distilled stock solution (GFS Chemicals, USA). To prepare the working electrode, the Pt@Nb-TiO₂ catalyst was first dispersed in ethanol and the mixture was sonicated for 30 min. 5 µL of suspension was added onto RDE by a pipette and dried under air. It was repeated until the surface of RDE was covered by a thin-uniform layer of the catalysts. Then 10 µL of 0.0125% (wt%) Nafion-ethanol solution was dropped on the surface of the thin film to prevent the catalysts from detaching by the flow of testing solution. The measurements of the total electrochemically active surface area (ECSA) were performed by integrating the hydrogen adsorption from the cyclic voltammetry (CV) data, which was recorded at room temperature in argon saturated solution of 0.1 M HClO₄. The potential scan rate was 50 mVs⁻¹ for the CV measurements. The ORR measurements were conducted at a rotation rate of 1600 rpm in 0.1 M HClO₄, which was purged with oxygen for 30 min prior to and during the measurements. The scan rate for the ORR measurements was 10 mVs⁻¹ in the positive direction. The area-specific activity was obtained by normalizing the kinetic-current density against the ECSA values, and the kinetic-current density was obtained from the Koutecky-Levich plot.

**Characterization.** The morphology of the fibers and Pt@r-Nb-TiO₂ catalyst membrane were studied by field emission scanning electron microscope (FE-SEM, Zeiss-Leo DSM982) and field emission transmission electron microscopy (FE-TEM, FEI...
Chapter 5

TECNAI F-20). Average diameter was measured by Image J (National Institutes of Health, USA). Powder X-ray diffraction (PXRD) patterns were recorded on a Philips MPD diffractometer with a Cu $K_\alpha$ X-ray source ($\lambda = 1.5405$ Å).

5.3 Results and Discussion

5.3.1 Synthesis and Characterization of r-TiO$_2$ Fibers

Figure 5.1 shows the SEM images of as-spun preceramic fibers and TiO$_2$ fibers after pyrolysis and sintering. The morphology of preceramic fibers was straight fiber with a diameter of 263 nm. After pyrolysis and sintering at 900 °C, the morphology of TiO$_2$ changed to chains which consisted of pearl-like grains with a smooth grain surface. The average diameter of the fibers was 191 nm. The size of the grains was not uniform, ranging from 157 nm to 609 nm.
TEM micrograph shows that the chains of TiO$_2$ fibers sintered at 900 °C were consisted of grains which linked together loosely (Figure 5.2). Most grains only contacted with two other grains. In other words, the end of one grain connected with the head of the second grain; and the end of the second grain connected with the head of the third one, and so on. Some adjacent grains just had edges contacted, and some had a small area overlapped together. As a result, the chains of TiO$_2$ were very fragile. Compared with Figure 4.4, TiO$_2$ fibers sintered at 500 °C were consisted with small crystal domains without preferred orientation. It proved that it was polycrystalline structure. However, TiO$_2$ fibers sintered at 900 °C were consisted of directive grains, indicating that its crystallinity was greatly increased. The morphology transformation was related to a dramatic change in crystalline structure. When titania fibers were calcined at 900 °C, the crystallite structure of titania changed into rutile phase. During crystallization, the crystal domains aggregated together, which favored the round shape to minimize the surface area.$^{29-31}$
Figure 5.2. TEM micrograph of TiO$_2$ fibers sintered at 900 °C.

XRD pattern of TiO$_2$ fibers sintered at 900 °C is shown in Figure 5.3. Strong diffraction peaks were appeared, suggesting the formation of well crystalline phases after the high temperature sintering. The diffraction peaks at 2$\theta$ of 27.4°, 36.1°, 39.2°, 41.2°, 44°, 54.3°, 56.6°, 62.8°, 64°, 69.0° and 69.8° could be indexed well to lattice planes of rutile TiO$_2$ (JCPDS, No.: 86-0147), suggesting rutile TiO$_2$ was successfully formed.
Figure 5.3. XRD patterns of TiO₂ fibers sintered at 900 °C. XRD patterns of bulk rutile TiO₂ are shown by the red lines as a reference based on the JCPDS database (No. 86-0147).

5.3.2 Synthesis and Characterization of r-Nb-TiO₂ Fibers

10 at% of Nb(OEt)₅ was mixed with Ti(OiPr)₄ in the ceramic precursors to obtain fibers of Nb-doped titania. Figure 5.4 shows the SEM images of as-spun preceramic fibers and Nb-TiO₂ fibers after pyrolysis and sintering at 900 °C. The morphology of preceramic fibers was straight fiber with a diameter of 207 nm. After pyrolysis and sintering, the morphology of Nb-TiO₂ was chains consisted of stone-like grains with sharp edge and smooth surface. The average diameter of the fibers was 183 nm.
Figure 5.4. SEM images of (A) as-spun polymeric fibers and (B) Nb-TiO$_2$ fibers after hydrolysis and sintering at 900 °C.

TEM micrograph of Nb-TiO$_2$ fibers sintered at 900 °C shows that the chains were consisted of grains which linked tightly (Figure 5.5). Compared with Figure 5.2, the size of grains was much smaller, and several grains connected with each other compactly. The contact area between grains was much larger. As a result, the chains of Nb-TiO$_2$ were robust.
Figure 5.5. TEM micrograph of Nb-TiO$_2$ fibers sintered at 900 °C.

Figure 5.6 shows XRD pattern of Nb$_{0.1}$Ti$_{0.9}$O$_2$ fibers sintered at 900 °C, which indicated a mixture of several different phases. The main diffraction peaks at 2θ of 27.4°, 36.1°, 39.2°, 41.2°, 44°, 54.3°, 56.6°, 62.8°, 64°, 69.0°, and 69.8° were indexed to lattice planes of rutile TiO$_2$ (JCPDS, No. 86-0147), suggesting rutile TiO$_2$ was formed. The diffraction peaks at 2θ of 25.3°, 37.8°, 48.1°, 54°, 55.1°, 62.8° and 75.1° were consisted with the lattice planes of anatase TiO$_2$ (JCPDS, No. 84-1286), indicating the existence of anatase phase. In addition, the weak diffraction peaks at 2θ of 23.9°, 26°, 26.3°, 32.8°, 44.1°, 47.8°, 51.2°, 55.2° and 62.8° could be indexed to the lattice planes of TiNb$_2$O$_7$ (JCPDS, No. 77-1374), showing that a small amount of TiNb$_2$O$_7$ existed. In conclusion,
the crystal structure of Nb-TiO$_2$ was a mixture of three phases: the majority was rutile phase of TiO$_2$; minority was anatase phase of TiO$_2$ and a little amount of TiNb$_2$O$_7$ phase.

Figure 5.6. XRD patterns of Nb-TiO$_2$ fibers sintered at 900 °C. XRD patterns of rutile TiO$_2$ are shown by the red lines (No. 86-0147), anatase TiO$_2$ by the blue lines (No. 84-1286), and TiNb$_2$O$_7$ by the green lines (No. 77-1374) as references based on the JCPDS database.

As mentioned in Chapter 4, Nb$_2$O$_5$ and TiO$_2$ can form a complete range of solid solutions Nb$_x$Ti$_{(1-x)}$O$_{2+y}$ due to the similar ionic radii of Nb$^{5+}$ and Ti$^{4+}$. The solubility limit of Nb into titania is greater than 0.1 for the anatase phase ($x > 0.1$) and 0.06 for the rutile phase ($x = 0.06$). If the preceramic fibers were calcinated at 500 °C, only anantase phase of TiO$_2$ formed as shown in Chapter 4. When they were sintered at 900 °C, once the solubility limit of Nb atoms was surpassed, a ternary phase ascribed to
TiNb$_2$O$_7$ showed up. In addition, high concentration of Nb helps to stabilize the anatase phase, which prevents grain coarsening and phase transformation.$^{34-35}$ As a result, mixed phases of rutile and anatase TiO$_2$ and TiNb$_2$O$_7$ formed. In addition, the size of grains was smaller than the one of pure rutile phase.

5.3.3 ORR Activity of Pt@r-Nb-TiO$_2$ Catalysts

Because r-TiO$_2$ fibers were very fragile, the membrane of r-TiO$_2$ always broke when Pt nanoparticles were deposited on it by ALD technique. Then Pt NPs were only deposited onto the surface of r-Nb-TiO$_2$ fibers by 40-cycle of ALD. Figure 5.7 shows SEM image of Pt@r-Nb-TiO$_2$ catalysts. The size of Pt NPs was 14 nm.
Figure 5.7. SEM image of Pt@ r-Nb-TiO$_2$ catalysts.

Electrochemical measurement was conducted to examine the electrocatalytic property of the Pt@r-Nb-TiO$_2$ catalyst (Figure 5.8). The total electrochemically active surface area (ECSA) was calculated by integrating the hydrogen adsorption from the cyclic voltammetry data, which was 8.72 cm$^2$. The area-specific activity ($i_s$) at 0.9 V (versus RHE) was 0.25 ± 0.03 mA/cm$^2_{Pt}$, which was much higher than the one of Pt@anatase-Nb-TiO$_2$ catalyst ($i_s = 0.16 ± 0.06$ mA/cm$^2_{Pt}$) characterized in Chapter 4.3.3 due to the higher conductivity of rutile phase.
Figure 5.8. Electrocatalytic property of Pt@r-Nb-TiO$_2$ catalyst: (A) CV curves and (B) ORR polarization curves measured at 1600 rpm.
5.4 Conclusion

Rutile phase titania were successfully fabricated by electrospinning, hydrolysis and sintering at 900 °C. The morphology of r-TiO$_2$ was chains consisted of pearl-like grains with a smooth grain surface. Rutile phase titania doped with 10 at% niobium was also synthesized under the same process. XRD pattern showed that the crystal structure of r-Nb-TiO$_2$ was actually a mixed phase of rutile and anatase TiO$_2$ and TiNb$_2$O$_7$, although rutile phase occupied the major part. The morphology of r-Nb$_{0.1}$Ti$_{0.9}$O$_2$ was chains consisted of stone-like grains with sharp edge and smooth surface. The area-specific activity of Pt@r-Nb-TiO$_2$ catalyst at 0.9 V (versus RHE) increased to 0.25 ± 0.03 mA/cm$^2_{Pt}$ due to the improvement of the conductivity of the support, compared with the one of anatase r-Nb-TiO$_2$ support.

5.5 References

Chapter 5


Chapter 6 Conclusions and Future Research

6.1 Conclusions

The objective of this dissertation is to fabricate polymeric and ceramic fibers by electrospinning technique, to control the morphology of fibers by adjusting the parameters during electrospinning process, especially the humidity, and to explore the application of the electrospun polymeric and ceramic fibers.

Chapter 2 is focused on preparation of polymeric fibers, poly(vinyl pyrrolidone) (PVP) and understanding the influence of the relative humidity on the morphology, shape of cross-section and the ultimate elongation of the electrospun fibers. In this chapter, PVP fibers were successfully fabricated by a magnetic field-assisted electrospinning method; especially helical peanut-shaped PVP ribbons were obtained at a particular condition. The morphology of the electrospun fibers was significantly influenced by the relative humidity. When the relative humidity of the environment decreased from 32% to 16%, the morphology of the electrospun PVP fibers changed from straight fiber to helical ribbon, and the percentage of helical ribbons increased to 99%. At the same time, the cross-section of electrospun fibers changed from circle, to ellipse, and to peanut shape. In addition, the ultimate elongation of electrospun PVP fibers was also affected by the relative humidity. It was 33% for straight round fibers made at a relative humidity of 32% and 43% for helical ribbons made at a relative humidity of 16%. The formation mechanism of helical ribbons was discussed. It was explained based on the synergistic interaction of bending instability of electrospun jet, and the rigidity of the polymer
Chapter 6

materials during the MFAE process, involving the mass decreasing rate and the diffusion rate of the solvents. In addition, the effect of solvent property and concentration on the morphology of electrospun PVP fibers were also discussed in this chapter.

Chapter 3-5 is concentrated on the fabrication of ceramic fibers by electrospinning technique. Normally, this process is divided into two steps. At first, preceramic fibers are electrospun from ceramic precursor with the help of guiding polymer. Secondly, the preceramic fibers are transformed into ceramic fibers by the pyrolysis process at high temperature.

In Chapter 3, silicon carbide (SiC) fibers were synthesized by electrospinning from preceramic polymer without the help of guiding polymer, UV cure and pyrolysis processes. The morphology and diameter of the electrospun preceramic fibers could be controlled by varying mixtures of solvents. The importance of UV cure on morphology preservation of SiC fibers was discussed. UV light could break double bonds of RD material and generate free radicals. The free radicals attacked CH₂ or Si-H group, leading to the crosslink reaction and stability of preceramic fibers. As a result, the morphology was preserved when transferring preceramic fiber into SiC fibers during pyrolysis process at high temperature.

Chapter 4 and 5 describe a facile method to fabricate niobium-doped titania supported platinum (Pt@Nb-TiO₂) catalyst membrane by a new two-step approach, electrospinning and atomic layer deposition, and explore the application of Pt@Nb-TiO₂ catalyst in oxygen reducing reaction (ORR) for polymer electrolyte membrane fuel cell. Chapter 4 is focus on electrospinning of anatase Nb-TiO₂ fiber support and discussing the
effect of fiber morphology, doping amount of niobium, number of ALD cycle and post-treatment temperature on the catalyst activity of Pt@Nb-TiO₂ membrane. The area-specific activities of the catalysts membrane of Pt@Nb-TiO₂ increased from 0.0084 mA/cm² Pt, to 0.086 mA/cm² Pt and to 0.16 mA/cm² Pt at 0.9 V (versus RHE) when the niobium atomic percentage increased from 0%, to 5% and to 10% due to the improvement of conductivity. The area-specific activity also increased with the number of atomic layer deposition cycles due to the increase of Pt weight percentage in the catalysts. The activity could further increased to 0.28 mA/cm² Pt at 0.9 V (versus RHE) by post-treatment of the catalyst membrane at high temperature in H₂ atmosphere, which resulted in conductivity improvement of Nb-TiO₂ fiber membrane and significant crystallite growth of Pt. The 30000-cycle accelerated-stability test on the Pt@Nb-TiO₂ catalyst membrane showed that it had high stability.

Chapter 5 is focused on the formation of rutile phase Nb-TiO₂ (r-Nb-TiO₂) fibers by electrospinning. Rutile phase of titania (r-TiO₂) fibers were successfully fabricated by electrospinning, hydrolysis and sintering at 900 °C. The morphology of r-TiO₂ was chains consisted of pearl-like grains with a smooth grain surface. Rutile phase titania doped with 10 at% niobium (r-Nb-TiO₂) fibers was also synthesized under the same process. But the crystal structure was a mixed phase of rutile and anatase TiO₂ and TiNb₂O₇, while rutile phase TiO₂ occupied the major part. The morphology of r-Nb-TiO₂ was chains consisted of stone-like grains with sharp edge and smooth surface. The area-specific activity of Pt@Nb-TiO₂ catalyst at 0.9 V (versus RHE) increased to 0.25 ± 0.03
mA/cm$^2_{Pt}$ due to the improvement of the conductivity of the support, compared with the one of anatase Nb-TiO$_2$ support.

### 6.2 Future Research

#### 6.2.1 Future Research of Helical Ribbons

Controllable morphology of electrospun fibers has been applied to guide the growth of cells.\textsuperscript{1-5} As mentioned in Chapter 2, helical PVP ribbons could be obtained by controlling the relative humidity of environment. This technique described in this work is potentially useful for making biomaterials in tissue engineering. In addition, because the ultimate elongation of helical ribbons is larger, this technique also offers a way to control the mechanical property of electrospun fiber scaffolds.

#### 6.2.2 Future Research of Electrospun Nb-TiO$_2$ Fibers

(1) Cell-Polarization Studies

Chapter 4 and 5 mentioned the catalyst membranes of Pt@Nb-TiO$_2$ can be applied in polymer electrolyte membrane fuel cell (PEMFC). Normally, membrane electrode assembly (MEA) in PEMFC is composed of a backing layer, a gas diffusion layer and a catalyst layer.\textsuperscript{6-8} Our catalyst membrane could be used as the catalyst layer directly to avoid complicated process of making catalyst inks and then spraying or painting them onto a gas diffusion layer, because the catalyst layer is already in a membrane form. But in these chapters, we only tested the oxygen-reduction reaction
(ORR) activity of the catalyst membranes. It is just half-cell characterization. In the future, full-cell characterization will be studied.

(2) Photoluminescence Studies

Reports show that rutile and anatase TiO$_2$ have very different photoluminescence spectrum.$^{9-10}$ We have fabricated many different kinds of Nb-TiO$_2$ fibers; for example, Nb-TiO$_2$ with different morphologies, niobium contents and crystal structures (pure anatase phase, pure rutile phase and a mixed phase of rutile, anatase TiO$_2$ and TiNb$_2$O$_7$). The photoluminescence of these fibers will be tested in the future.

(3) Application to Water Gas Shift Reaction

A number of metal catalysts such as Pt,$^{11-13}$ Au,$^{14-15}$ Ru,$^{16-17}$ and Re$^{12,18}$ loaded on oxide and mixed oxide supports have been reported for the application to water gas shift (WGS) reaction. As mentioned in Chapter 4 and 5, we have developed a facile method to fabricate niobium-doped titania supported platinum catalyst membrane by a new two-step approach, electrospinning and atomic layer deposition. These catalyst membranes have high stability. In the future, we will try to apply it to WGS reaction.

6.3 References


### Appendices

**Table A1.** Physical properties of solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Boiling Point (°C)</th>
<th>Vapor Pressure @ 20 °C (mmHg)</th>
<th>Surface Tension @ 25 °C (Dynes/cm)</th>
<th>Dielectric Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>78</td>
<td>44.6</td>
<td>21.97</td>
<td>25.3</td>
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<tr>
<td>Water</td>
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<td>17.5</td>
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<td>Toluene</td>
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<td>Dichloromethane</td>
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<td>353</td>
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<td>8.93</td>
</tr>
</tbody>
</table>