Pt Nanowires Made by Electrospinning and Their Application in PEM Fuel Cells

by

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Curriculum Vitae

Jianglan Shui was born in October, 1977 in Anhui province, China. He attended Tianjin University in China from 1996 to 2000, and earned his Bachelor of Engineering degree in 2000. His major was Chemical Engineering Machinery and Equipment. He also completed a minor in Foreign Trade of Industry to broaden his knowledge. After graduation, he worked as an assistant engineer in Huanqiu Contracting & Engineering Corp. China during 2000~2001. He continued his education at the University of Science & Technology of China after one year working in industry. His research area was electrode materials in Li-ion batteries. He continued his research work in the United States in the Materials Science program at the University of Rochester beginning in 2006, working on the fabrication of Pt nanowire catalysts by electrospinning and their application in PEM Fuel Cells.
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Abstract

Pt catalyst is the crucial component in Proton Exchange Membrane Fuel Cells (PEMFC). Short life and high cost of Pt are the main obstacles for the commercialization of proton exchange membrane fuel cells. In the conventional design, the agglomeration of Pt nanoparticles cannot be avoided; this is the main reason for electrochemical degradation. Furthermore, these nanoparticles cannot stand alone. They are usually supported by carbon nanoparticles, which are prone to oxidation and corrosion over time as well as detachment from the Pt particles.

This research aims at finding a new form of Pt-based catalyst. Pt nanowires were chosen because of their structure stability without the need of a support. The electrospinning method was used to make Pt and Pt alloy nanowires, which form a self-supporting net, avoiding the agglomeration problem of nanoparticles. This research began with producing Pt nanowires and studying the influences of various parameters on the composite fiber morphology. The major problems of avoiding the formation of beads along the nanowires and reducing the wire diameters to several nanometers were investigated. To our knowledge, 5~6 nm thick Pt nanowires are the thinnest that have been produced by electrospinning at present. They are still larger than the diameters of Pt nanoparticles in the commercial catalyst (~3 nm). In further research, a method was found to make long, continuous, and yet porous PtFe alloy nanowires with large surface area per unit mass. These wires can stand alone, without support. The overall wire
diameter is about 10~20 nm and since it is porous, the ligament size is only about 2 to 3 nm. Electrochemical tests indicated a surface area as high as 55 m²/g Pt. The large films (~1 μm thickness) composed of porous PtNiFe alloy nanowires were used in a membrane electrode assembly (MEA) as the cathode catalyst layer. This MEA offered large active surface area (>60 m²/mg Pt), high current level (>5 A/mg Pt), high power density (~2 W/mg Pt) and very good durability compared with commercial Pt/C nanoparticle catalysts.

To save more Pt, a new platinum alloy catalyst was designed—a PtNi nanowire covered with a platinum shell. The core-shell long nanowires had diameters approximately 10~20 nm. They were made by electrospinning followed by acid and heat treatment. The resultant Pt-shell nanowires can prevent nickel (>70 atom%) from dissolving in 1M hot sulfuric acid. At this point, very thin, very porous and even core-shell structure Pt alloy nanowires have been made using the electrospinning technique. Unfortunately, in electrochemical tests it was found that Pt alloy nanowires are not as stable as expected for use as cathode catalysts in fuel cells.

Despite its 1-D structure, the leaching of non-noble metals and the diffusion of Pt could not be avoided when Pt diameters were very small (3~4 nm). Therefore, it is believed that thick carbon nanofibers covered with a thin Pt shell may be the path to pursue the production of a stable and economical catalyst.
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Foreword

The second chapter of this thesis was mainly done by Jianglan Shui while academic advisor James C. M. Li did thermodynamic analysis. A paper has been published in Nano Letters and a patent has been applied by Jianglan Shui and James C.M. Li.

The third chapter of this thesis was mainly done by Jianglan Shui. Master student Chen Chen and undergraduate student Yuan Jia helped with partial experiments. Advisor James C. M. Li provided some suggestions. Two papers have been submitted with authors Jianglan Shui, Chen Chen, Yuan Jia and James C. M. Li. One patent has been arranged with authors Jianglan Shui, Chen Chen, and James C. M. Li.

The fourth chapter of this thesis was mainly done by Jianglan Shui. Master student Jingwen Zhang helped with partial experiments. Advisor James C. M. Li provided some theoretical suggestions. One paper has been organized by authors Jianglan Shui, Jingwen Zhang, and James C. M. Li.

Advisor James C. M. Li’s constant guidance and advice benefited me enormously throughout the whole project.
Chapter 1 Introduction

1.1 Background of fuel cell

A fuel cell is a clean power source. The chemical energy of fuels is converted directly into DC electricity in the cell, as a result of chemical reactions at both anode and cathode. In 1839, Sir William Grove discovered the fuel cell operation principle that gaseous fuels could generate electricity [1]. There are various kinds of fuel cells grouped by the type of electrolyte involved, such as alkaline fuel cells (AFC), proton exchange membrane (PEM) fuel cells, phosphoric acid fuel cells (PAFC) and solid oxide fuel cells (SOFC). This dissertation will discuss nanowire catalysts for PEM fuel cells.

The basic electrochemical reactions that occur in PEM fuel cells are [2]:

At the anode: \( \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \)

At the cathode: \( \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O} \)

Overall: \( \text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} \)

The theoretical fuel cell potential with hydrogen/oxygen fuels at 25°C can be calculated [2]:

\[
E = -\frac{\Delta G}{nF} = \frac{237340 \text{ J mol}^{-1}}{2 \cdot 96485 \text{ C mol}^{-1}} = 1.23 \text{ Volts}
\]

The fuel cell polarization curve may be found from the following equation [2]:

\[
E_{\text{cell}} = E_{r,T,p} - \frac{RT}{\alpha F} \ln\left(\frac{i}{i_0}\right) - \frac{RT}{nF} \ln\left(\frac{i_{L-i}}{i_L-i}\right) - iR_i
\]
where $E_{r,T,P}$ = equilibrium cell potential at temperature $T$ and pressure $P$.

$R = \text{gas constant, } 8.314 \text{ J mol}^{-1}\text{K}^{-1}$

$\alpha = \text{transfer coefficient}$

$F = \text{Faraday's constant, } 96485 \text{ C mol}^{-1}$

$n = \text{number of electrons involved, } 2$

$i_L = \text{limiting current density}$

$i_o = \text{effective exchange current density}$

$R_i = \text{internal resistance}$

### 1.1.1 Configuration of a PEM fuel cell

The structure of PEM fuel cells is simple. With many of them the power is sufficient to power a car. Therefore, much attention has been drawn to this type of fuel cell. A typical PEM fuel cell schematic diagram and working principles are illustrated in Scheme 1.1.

**Scheme 1.1** Schematic diagram of a polymer electrolyte membrane fuel cell.
PEM stands for “polymer electrolyte membrane” or “proton exchange membrane”. The polymer membrane in a PEM fuel cell is impermeable to gases but conductive to protons. This membrane is squeezed between two porous and electrically conductive catalyst layers, where the chemical reactions occur. The catalysts typically consist of platinum (or its alloys) nanoparticles, supported by carbon nanoparticles or carbon nanotubes. Carbon fiber paper or carbon cloth is typically used to conduct electrons, fuel gases and water on the outsides of catalyst layers. The carbon layers are called gas diffusion layers (GDL). In other words, the catalyst layer is at the interface between the electrode and the membrane. The membrane and electrodes are all squeezed between two collector plates. These plates are typically made of highly compacted graphite. They are called bipolar plates when they are used in a stack. The many channels on these plates are designed for gas and water flow.

1.1.2 Synthesis methods for typical catalyst - carbon supported Pt and its alloy nanoparticles

This section discusses the synthesis of the state-of-the-art Pt nanoparticle catalysts. Up to now, Pt based metals are still the best-performing catalysts for both anode and cathode. The first-generation Pt catalyst was Pt black. It was used in large quantities to supply considerable power output in a cell. To save noble metal Pt and improve operating efficiency, catalysts are now made of
nanoparticles supported on carbon black or carbon nanotubes. The following are some commonly used methods to prepare Pt (or Pt alloy)/C catalysts.

(1) Sol-gel method

Pt and other metal nanoparticle gels are formed by a reduction reaction in a solution containing salts of these metals. Carbon supports (carbon black with high surface area or carbon nanotubes) are dispersed into the gel and metal nanoparticles adsorb onto the carbon surface. After washing, drying and reducing in H₂ (depends on metal type), 3~4 nm particle catalysts can be obtained [3, 4].

(2) In-situ reducing (conventional impregnation) method

Carbon supports are first dispersed in salt solution, and then a reducing agent is dropped into this hot suspension little by little. Grigoriev et al. used ethylene glycol and formaldehyde as reductants to reduce H₂PtCl₆ in a suspension of Vulcan XC-72. The Pt nanoparticles were deposited onto carbon nanoparticles during reduction [5]. Rajalakshmi et al. made a Pt/MWCNTs catalyst by mixing carbon nanotubes into a H₂PtCl₆ precursor solution. After stirring for 12 hours, a mixture of 0.1 M NaBH₄ and 1 M NaOH was slowly added to reduce Pt from its metal salt. Finally, the mixtures were filtered, washed with excess DI water, and dried in a vacuum [6].

(3) Sputtering method

Plasma sputtering is a physical method to deposit a Pt layer onto a substrate. Caillard et al. [7] sputtered platinum onto carbon nanofibers (CNFs), which
resulted in the formation of nanoclusters (3~8 nm) on the periphery of the CNFs.

(4) Microwave method

A microwave heated polyol process can be employed to synthesize carbon-supported Pt catalysts for fuel cell catalysis. In a study by Chen et al. [8], a polyol (ethylene glycol) solution containing catalyst metal precursor salts H₂PtCl₆ and carbon support was irradiated in the center of a microwave for just 60 s. A Pt/C catalyst was synthesized with uniform Pt nanoparticles, 3.5~4 nm in diameter.

1.1.3 Degradation of Pt nanoparticles in the fuel cell

Pt/C and Pt alloy/C nanoparticles are the state-of-the-art catalysts due to their high surface area, low overpotential and high catalytic activity for hydrogen oxidation reactions (HOR) and oxygen reduction reactions (ORR). But their loadings are still high and degradation is too serious to satisfy practical requirements, e.g. 5000 hours for cars and 40,000 hours for stationary applications [9].

(1) Platinum degradation mechanisms

From studies of fuel cell durability, Pt/C catalyst degradation can generally be summarized as (1) Pt nanoparticle agglomeration and growth, (2) Pt loss and redistribution in the fuel cell. Both effects cause the loss of effective catalytic surface area and result in poor performance during long-term operation.
The agglomeration of Pt nanoparticles has been widely reported and may be the most serious amongst all degradation mechanisms. Very small Pt nanoparticles have high surface energy. Agglomeration helps to reduce surface area per unit mass, so Pt nanoparticles have an inherent tendency to agglomerate into larger particles to reduce their surface energy. Particle growth is enhanced when the membrane electrode assembly (MEA) is tested under accelerated stress conditions in a cell, such as potential cycling and high operation temperature [10, 11].

Pt dissolution and wash-out is another degradation mechanism that occurs during cell operation. Luo et al. [12] measured significant Pt loss with a 10-cell stack after a 200 hour run. Bi et al. [13] found that Pt catalyst degradation was accelerated because Pt ion transportation was easier with increased relative humidity. Darling et al. [14] suggested a three-step dissolution model for Pt particles under stressed environments:

\[
(1) \quad Pt(s) \rightarrow Pt^{2+} + 2e^- ; \\
(2) \quad Pt + H_2O \rightarrow PtO + 2H^+ + 2e^- ; \\
(3) \quad PtO + 2H^+ \rightarrow Pt^{2+} + H_2O .
\]

The Pt\(^{2+}\) ions would move from the cathode to the anode, crossing the membrane, and redeposit anywhere when they were reduced by H\(_2\).
(2) Carbon support degradation

The most popular catalyst structure is 2~4 nm Pt nanoparticles distributed on carbon support materials to maximize the utilization of Pt. However, carbon is not stable under the PEM fuel cell operating conditions, which include high temperature, high humidity, low pH, high oxygen concentration, presence of Pt catalyst and high potential. Each of these can cause carbon oxidation and the subsequent detachment of Pt from the carbon surface, ultimately leading to motion and agglomeration of Pt nanoparticles [15, 16].

1.1.4 Other shapes of Pt catalysts

Due to the instability of nanoparticles, researchers have investigated other shapes of Pt, such as nanowires, nanotubes and nano-networks, in order to avoid the motion of Pt particles.

The template method is often used to make Pt wires. Zhang et al. [17] electrodeposited Pt-Cu alloy nanowires in nanochannel alumina templates and de-alloyed the Cu component, making porous Pt nanowire arrays. The Pt nanowires had diameters of about 40 nm and the ligament size was approximately 10 nm. This porous nanowire nanostructure enhanced both the electrocatalytic activity and stability of Pt electro-catalysts. Yan et al. [18] made orderly arrays of platinum nanowires with dimensions of 20 nm width, 5 nm height and 12 µm length on planar oxide thin films of silica, alumina, zirconia, and ceria by
nanoimprint lithography. The diameter and length of the Pt nanowires were uniform and controllable with nanometer precision. Song et al. [19] synthesized platinum nanowire networks by chemical reduction of a platinum complex in the presence of a soft template formed by cetyltrimethylammonium bromide in a two-phase water-chloroform system. The polycrystalline nanowires had diameters approximately 2.2 nm, and produced a very high surface area (53±1 m²/g) and electroactive surface area (32.4±3.6 m²/g). Zhao et al. [20] produced Pt and Pt-Ru nanowire array electrodes by electrodeposition of Pt and Ru into the pores of an anodic aluminium oxide (AAO) template on a Ti/Si substrate. The nanowires had a uniform diameter of about 30 nm. Choi et al. [21] synthesized platinum nanowires via a template method by electrodeposition of platinum within pores of a track-etched polycarbonate (PCTE) membrane. The unsupported Pt nanowires were 6 µm long and their diameters were approximately 60 nm. These wires showed better electrochemical mass activities in methanol oxidation than supported or unsupported Pt nanoparticles when the loading of Pt was very high. Lu et al. [22] sonochemically synthesized platinum nanowires on carbon nanotube templates with Pt nanowire diameters of 60–70 nm. The shortcoming of these wires was their large diameter, which causes poor Pt mass utilization.

Xie et al. [23] suggested a template-free synthetic route for production of porous Pt nanocrystals. The structure could be spheres, rod-shaped, knot shaped, and so on. The one-dimensional (1-D) rods usually had a length approximately
100 nm and a diameter of 15 nm. Lee et al. [24] prepared Pt- or W-supported Pt nanorods by direct growth along the <111> axis on the surface of Pt or W gauze. The rods had lengths between 50 and 100 nm, and diameters of 5 nm. Those Pt nanowires supported on Pt gauze showed the largest electrochemically active surface area with the greatest activity toward the methanol oxidation reaction. Chen et al. [25] discovered that the addition of a small amount of iron species (Fe$^{2+}$ or Fe$^{3+}$) to the polyol process could significantly alter the reduction kinetics of a Pt precursor and thus induce the formation of Pt nanorods. Their nanowires were as long as 100 nm with diameter ~5 nm.

Chen et al. [26] synthesized Pt nanotubes (PtNTs) and Pt-Pd nanotubes (PtPdNTs) by a galvanic replacement reaction of silver nanowires (AgNWs). The resultant PtNTs had 50 nm diameters, 5–20 µm lengths and 6 nm wall thicknesses. Electrochemical surface area (ECSA) of the PtNTs only decreased about 20% after 1000 cycles in the durability test, while the platinum-black and Pt/C catalysts lost about 51% and 90% of their platinum ECSA, respectively. The increase in platinum nanoparticle size from 2–5 nm to 10–20 nm was the primary cause of platinum ECSA loss in the Pt/C catalysts. Platinum black particle size also increased from 5–10 to 10–25 nm after CV cycling. In contrast, PtNTs did not change their morphologies after potential cycling. This indicates that the supportless one-dimensional structure of Pt wires made them substantially more durable than zero-dimensional Pt nanoparticles. Fenske et al. [27] made short Pt
nanowires by aggregation of quasi spherical particles. The nanowires obtained had a diameter approximately 2 nm and a length of 20~50 nm. The nanowires were found to be stable up to 140~160°C. Sun et al. [28] developed a wet chemical procedure to synthesize single-crystal Pt nanowires and their flower-like assemblies on carbon black via reduction of hexachloroplatinic acid by formic acid (HCOOH) at room temperature. These Pt nanowires had lengths from 10~30 nm and diameters from 4~5 nm. Their Pt nanowire catalysts showed a 50% higher mass activity than the commercial cathode. Teng et al. [29] synthesized Au48Pt52 and Au25Pt75 nanowires with average length of 100 nm and average diameter of 2.6 nm via a wet chemistry approach. Zhou et al. [30] synthesized crystalline one-dimensional metal nanowires using an ambient, surfactantless synthesis technique. Pt nanowires possessed a higher ORR specific surface area activity as compared with that of Pt nanoparticles.
1.2 Electrospinning technique: working mechanism and applications

1.2.1 Mechanism of electrospinning

The electrospinning technique was invented more than 70 years ago, and for years it was primarily used for producing ultrathin polymer fibers. In recent years, it has been developed to make ceramic and metal nanowires. An electrospinning setup generally consists of three major components (Scheme 1.2): a high-voltage power supply, a spinneret, and an electrically conductive collector [31]. The solution for spinning is loaded in a plastic syringe, which is fixed on a syringe pump and connected to a metallic needle.

The syringe pump pushes the solution into the needle so that a constant and adjustable feeding rate of the solution can be maintained. The solution droplet at the needle orifice sustains two kinds of forces when a high voltage is applied to the needle. One is the solution surface tension, which tends to contract the solution droplet. The other is the electrostatic repulsion force on the droplet, which tends to break one droplet into many in order to decrease the electrostatic repulsive force on the droplet’s surface by increasing the surface area. Combined with the electrostatic attraction from the oppositely charged collector, a conical jet is formed at the droplet when the voltage reaches a threshold value. A long, thin and uniform solution nanofiber is formed when the jet is elongated from the droplet. The solvent evaporates as the fiber flies from the orifice to the collector. The fiber length is elongated and its diameter is constantly reduced during flying.
Because of the high surface area of the fiber, solvents evaporate very quickly. Usually, all solvent has been eliminated when the fiber reaches the collector. The long, thin nanofibers weave a large network on the collector.

1.2.2 Application of electrospinning

Electrospinning was initially limited to the fabrication of polymer nanofibers. Many thin fibers made of functional polymers and their blends have been produced by electrospinning. For example, conductive polyaniline [32], piezoelectric poly(vinylidene fluoride) and photo- or electroluminescent poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-vinylene] have been prepared as fibers through electrospinning [33-34]. In addition to these organic polymers, natural biopolymers such as fibrinogens and viruses have been electrospun into fibers as well [35].

In the past decade, the electrospinning of ceramic nanofibers and nanotubes
has been extensively developed; electrospinning has produced materials such as nanostructured LiCoO$_2$, LiMn$_2$O$_4$ fibers [36], ultrafine alumina-borate oxide fibers [37], TiO$_2$-SiO$_2$ nanofibers [38], niobium oxide fibers [39], magnesium titanate nanofibers [40], zinc oxide nanofibers [41], and CeO$_2$ nanofibers [42].

Electrospinning can also be used to prepare nanofibers with core-sheath, hollow, or porous structures. Li et al. [43] prepared hollow fibers made of a PVP-TiO$_2$ composite and the hollow anatase nanofibers after calcination. McCann et al. [44] found that the immiscibility of solvents is critical to the production of well-defined core-sheath nanofibers. Meanwhile, miscible solvents (with immiscible polymers) were used to make highly porous fibers.

Only in the last 4 years, have metallic nanowires been fabricated with the electrospinning technique. Bognitzki et al. [45] made sub-micrometer copper wires via electrospinning in 2006. They prepared composite fibers of copper nitrate-polyvinylbutyral (PVB) followed by thermal treatment in air to decompose PVB and convert copper nitrate to copper oxide. Cu wires were obtained after reducing the CuO fibers in a hydrogen atmosphere. Wu et al. [46] prepared uniform nanowires of Fe, Co, and Ni with diameters approximately 25 nm and lengths longer than 100 µm. Their work showed that magnetic nanowires in aligned arrays have unique magnetic properties, with greatly enhanced coercivities compared to bulk materials. Pol et al. [47] prepared gold nanowires with diameters of 1~2 µm. Lee et al. [48] made platinum nanowires via electrospinning of Pt
precursor/polymer composite fibers followed by subsequent thermal annealing. Their work was similar to ours. However, their Pt nanowires were too thick, with diameters approximately 50 nm. Kim et al. [49] synthesized binary metallic nanowires (NWs) of PtRh and PtRu also with the electrospinning method. These NWs were highly alloyed, with diameters approximately 60 nm and lengths up to hundreds of micrometers. They found that the PtRh and PtRu NWs with 1:1 atomic ratio showed a higher catalytic mass activity in the methanol electrooxidation than those with different atomic ratios.
1.3 Our research work

Though Pt and Pt alloy nanowires have been made by electrospinning, their sizes are too large to be practical for fuel cells; the cost would be huge if 50 nm thick nanowire catalysts were used. In this work, ultrathin Pt and Pt alloy nanowires were fabricated using the electrospinning technique. The diameters can be made as small as 5~6 nm at the present stage. Wire length ranges from hundreds of nanometers to hundreds of microns. For porous nanowires, the overall wire diameter is about 10~20 nm and the ligament size is only about 2~3 nm. The wire network forms a uniformly thin black mattress with a controllable area, and is a possible replacement for the Pt/C nanoparticle catalyst. This design has the following advantages over the state-of-the-art Pt/C particle catalyst: (1) there is no need for support, so the carbon corrosion issue would not influence the catalyst layer much even if there is some carbon. (2) There is no agglomeration of Pt particles. The one-dimensional structure of Pt nanowires is mechanically more stable, so the problem of particles falling off and agglomerating to bigger ones does not exist. (3) The catalyst film composed of Pt wires has a much larger pore volume than conventional laminated catalyst layers. That means the transportation of fuel, gas, and water is much easier. This property is important in high current density operation.
References


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2.1 The influence of various electrospinning parameters on PVP/H₂PtCl₆ composite nanofiber morphologies

2.1.1 Introduction

Electrospinning is now a well-known technique for the production of submicron-sized fibers. Combined with a metal compound, it is possible to make metal nanowires. However, the formation of beads along the nanofibers is a nuisance which should be avoided before a uniform metal wire can be made. It is not yet known exactly how the beads form; but in general, it is due to the instability of a liquid jet which has a tendency to reduce its surface energy. For example, per unit length of a liquid jet of radius \( r \), the surface energy per unit volume is:

\[
\frac{2\pi r \gamma}{\pi r^2} = \frac{2}{r} \gamma
\]  

(1)

where \( \gamma \) is the surface energy per unit area.

For a sphere of radius \( r \), the surface energy per unit volume is

\[
\frac{4\pi r^2 \gamma}{(4/3)\pi r^3} = \frac{3}{r} \gamma
\]

(2)

So a liquid jet will not change into beads of the same radius, but it can change into beads of radius larger than 3/2 times the jet radius. The thinner the jet, the higher
the driving force that is available for bead formation. The conditions reported here minimize the formation of beads and can be used to successfully obtain Pt nanowires by electrospinning.

**Thermodynamics of Bead Formation**

When a bead forms during spinning, the liquid jet does not break up into drops of liquid. Beads form along the jets, which then solidify into nanofibers with beads on them. The formation process can be viewed as follows: for a bead to start to form along a jet of radius \( r \), a short length \( L \) of the jet may spread its volume around the jet in the form of a ring of a half circle cross section of radius \( R \) with the following volume balance:

\[
\pi r^2 L = 2\pi \left[ r + \frac{4R}{3\pi} \right] \left[ \frac{1}{2} \pi R^2 \right] \tag{3}
\]

which gives a relation between \( R \) and \( L \):

\[
\frac{L}{r} = \pi \left( \frac{R}{r} \right)^2 \left[ 1 + \frac{4R}{3\pi r} \right] \tag{4}
\]

The driving force for this process or the reduction of free energy is:

\[
\Delta G = 2\pi (r + R) \gamma - 2\pi r (L + 2R) \gamma = 2\pi r^2 \gamma \left[ (\pi - 2) \frac{R}{r} - \frac{4}{3} \left( \frac{R}{r} \right)^3 \right] \tag{5}
\]

which is plotted in Fig. 2.1. It is seen that there is a critical length of

\[
\frac{L}{r} = \frac{\pi (\pi - 2)}{4} \left[ 1 + \frac{2\sqrt{\pi - 2}}{3\pi} \right] = 1.10 \tag{6}
\]

corresponding to a radius of \( R/r = \sqrt{\pi - 2} / 2 = 0.534 \), below which the growth is
unstable. So the nucleation of a bead along the jet requires an activation energy of

$$\Delta G^* = \frac{16\pi}{3} \left( \frac{\pi - 2}{4} \right)^{3/2} r^2 \gamma = 2.55 r^2 \gamma$$

(7)

This activation energy increases with the radius of the jet and with the surface energy. Hence thinner jets with lower surface energy nucleate beads more easily even though higher surface energy provides a larger driving force for bead formation. The activation energy is too large to be overcome by thermal activation. So the nucleation of beads must depend on a macroscopic length fluctuation of more than

$$\frac{L}{r} = \frac{3\pi(\pi - 2)}{4} \left[ 1 + \frac{2\sqrt{3(\pi - 2)}}{3\pi} \right] = 3.746$$

(8)
corresponding to a radius of \( R/r = \sqrt{\frac{3(\pi - 2)}{2} / 0.925} \) above which stable bead can form and grow. Again, thinner jets require shorter length fluctuations, and hence beads can form easily on the thin jets. But the fluctuation counters the pulling force for extensional flow of the jet. Hence bead nucleation is difficult if the pulling force is high, the viscosity is high, the surface charge is high, the electric field is high or the feeding rate is low. On the other hand, high pulling forces, high surface charges and high electric fields all result in thinner jets, which favor bead formation.

Another consideration is that the equivalent pressure inside the liquid jet due to the surface energy is also \( 2\gamma/r \) and so the pressure, like the surface energy, increases the free energy of the system. Hence the vapor pressure of the liquid jet increases with decreasing radius. As a result, thinner jets may evaporate faster and hence solidify earlier. Once the jet has solidified into a nanofiber, the tendency for bead formation is eliminated. As a result, thinner jets may form fewer beads even though the driving force is higher, the activation energy is lower and the macroscopic fluctuation needed is smaller.

We see that bead formation is a complex process, as it competes with solidification. This gives us some room to play experimentally in attempts to avoid beads. For example, in the electrospinning of PEO (polyethylene oxide) in water, Fong et al. [1] found that by increasing the viscosity of the solution (higher polymer concentration), increasing the charge density (adding NaCl) or reducing
the surface tension (adding ethanol to water), all bead formation could be avoided. Lin et al. [2] eliminated bead formation on polystyrene nanofibers by adding a small amount of cationic surfactants during electrospinning. Um et al. [3] blew warm air at 57°C and 70 cuft/hr (about 550 ml/s) at the orifice and successfully made high quality hyaluronic acid nanofibers by increasing the rate of evaporation of the solvent. Tripatana suwan et al. [4] found that the rate of bead formation increased as the partial pressure of solvent approached saturation in the environment and thus the rate of evaporation reduced. Beads could be avoided by reducing the partial pressure of solvent in the environment to speed up evaporation. Eda et al. [5] used N,N-dimethylformamide (DMF) as a solvent and obtained continuous fibers without beads. They tried four other solvents, all of which resulted in beaded fibers.

In the experiments discussed in this chapter, several parameters were investigated for the experimental control of electrospinning of poly(vinyl pyrrolidone) (PVP) with the addition of H₂PtCl₆ to determine if they can produce thin nanofibers without beads. The ultimate goal of this work was to make nanowires of Pt for fuel cell catalysts.
2.1.2 Experiments

The setup for electrospinning is shown in Scheme 1.2. It consisted of a high voltage source (Dongwen, Tianjing, China), a syringe pump (Harvard Pump 11, USA) and a plastic syringe equipped with a 22\textsuperscript{g} gauge stainless steel needle. Carbon paper was used to collect the composite fibers. The polymer used was poly(vinyl Pyrrolidone) (PVP) of 1.3×10\textsuperscript{6} MW, obtained from Aldrich. The platinum salt was hexachloroplatinic acid (H\textsubscript{2}PtCl\textsubscript{6}·6H\textsubscript{2}O) from Aldrich. The solvent was a mixture of deionized water and ethanol with a typical volume ratio of H\textsubscript{2}O/C\textsubscript{2}H\textsubscript{5}OH = 0.12. The distance between the orifice and the carbon paper collector was 6 cm and the applied field was 1 kV/cm. The solution feeding speed was 0.25 ml/hr. The temperature was approximately 25°C in an ambient environment.

Field emission scanning electron microscope (FESEM, Zeiss-Leo DSM982 model) and scanning transmission electron microscope (FE(S)TEMFEI Tecnai F20) were used to characterize the morphologies of all fibers produced. X-ray diffraction (XRD) patterns were obtained with a Philips X’Pert high resolution materials research diffractometer with Cu K\textalpha1 radiation. The surface tension of the precursor solution was measured using a capillary method with glass capillary size of 0.8-1.1 mm purchased from Kimble Glass, Inc.
2.1.3 Results and Discussions

The effects of polymer concentration, concentration of H$_2$PtCl$_6$, the water content in the solvent, and the strength of the electric field and feeding rate on bead size, density and fiber diameter are reported here.

1. The effect of PVP concentration

Four PVP concentrations were chosen: 35, 24.5, 17.5 and 10.5 mg/ml. The H$_2$PtCl$_6$ concentration was fixed at 5.6 mg/ml for all four experiments. As shown in Fig. 2.2, at higher polymer concentration the fiber was smooth but thick with a diameter approximately 140 nm. Upon decreasing the polymer concentration, the fiber diameter decreased to 86, 46 and 26 nm, but was accompanied by increasing occurrence of beads. Such phenomena were also observed in pure polymers. For example, Li and Xia [6] found no beads when PVP was dissolved in 16:3 ethanol/water at a concentration of 7% by weight, but many beads at concentrations of 3 and 5% by weight. Shenoy et al. [7] found that a minimum PVP concentration of 9 wt.% in ethanol should be used to avoid beads altogether. Kim et al. [8] found beads when the concentration of poly(2-acrylamido-2-methul-1-propane sulfonic acid) in ethanol was 2 or 4 wt.% but no beads at 6 and 8 wt.%. Yu et al. [9] found beads when the concentration of polyaniline in 4% sulfuric acid was 10.6% and 11.5% but no beads at 14.0 and 17.9%. Zong, et al. [10] found a lot of beads for poly(D,L-lactic acid) in dimethyl formamide at a concentration of 20 wt.% but no beads when the concentration was
35 wt.%. The fibers were thicker at higher concentrations. They found a 50 fold increase in viscosity from 20 to 36 wt.%. They argued that at low polymer concentrations, more solvent must be evaporated and hence the fibers take longer to solidify. Of course, higher viscosity solutions required a larger force to spin and hence it was harder to nucleate a bead: thinner fibers had a higher driving force and beads nucleated more easily.

Gupta et al. [11] investigated the effect of chain entanglement on bead formation. They used the Berry number as an indicator of chain entanglement. The Berry number is the product of intrinsic viscosity and concentration. Intrinsic viscosity is the initial slope when specific viscosity is plotted against concentration. The specific viscosity is the relative viscosity (ratio of solution viscosity to solvent viscosity) minus one. For the electrospinning of poly(methyl methacrylate) (PMMA) from N, N-dimethyl formamide (DMF) solution without beads, they found that it was necessary to have a minimum Berry number of 7. According to Eda et al. [5], Megelski et al. [12] produced polystyrene fibers with beads from a tetrahydrofuran (THE) solution with a Berry number of 14 but no beads for a Berry number of 35. For the same system, Eda et al. [5] found a minimum Berry number of 9 to produce fibers without beads. Lee et al. [13] found no beads when the concentration of PS in a mixture of THF and DMF exceeded 15% by weight. According to Eda et al. [5], this solution had a Berry number of about 8. Tao and Shivkumar [14] produced stable fibers without beads when the Berry number was about 9, and the round fibers changed to ribbons at a Berry
number of about 12 in the electrospinning of polyvinyl alcohol (PVA) in water. They found that the fiber diameter in the stable region was a power function of the Berry number with an exponent of about 1.1. For the same system, Koski et al. [15] found for the same weight percent of PVA concentration, low molecular weight favored thin fibers with beads and high molecular weight favored thicker fibers without beads. For the same molecular weight, a larger weight fraction of PVA produced thicker fibers. For the same Berry number, high molecular weight produced thicker fibers with beads.

**Fig. 2.2** SEM morphologies of electrospun PVP/H$_2$PtCl$_6$ composite nanofibers at different PVP concentrations: (a) 35 mg/ml, (b) 24.5 mg/ml, (c) 17.5 mg/ml and (d) 10.5 mg/ml.
2. The effect of $\text{H}_2\text{PtCl}_6$ concentration

Next the $\text{H}_2\text{PtCl}_6$ concentration was varied from 16.8, 11.2, and 5.6 to 2.8 mg/ml. PVP concentration was fixed at 17.5 mg/ml for all four experiments. The feeding rate was 0.25 ml/hr except for Fig. 2.3(d), in which 0.15 ml/hr was used to stabilize the spinning. It was observed that $\text{H}_2\text{PtCl}_6$ concentration mainly influenced bead size, see Fig. 2.3. Beads were much larger but there were fewer per unit length when $\text{H}_2\text{PtCl}_6$ concentration was increased. Fiber diameter decreased a little with decreasing acid concentration. The charge density effect was reported by Fong et al. [1].

![Fig. 2.3 SEM morphologies of electrospun PVP/$\text{H}_2\text{PtCl}_6$ composite nanofibers at different $\text{H}_2\text{PtCl}_6$ concentrations: (a) 16.8 mg/ml, (b) 11.2 mg/ml, (c) 5.6 mg/ml and (d) 2.8 mg/ml. Corresponding high magnification pictures are inset.](image-url)
Increasing charge density reduced the occurrence of beads without affecting bead size. Jun et al. [16] found that the addition of an organic salt, pyridinium formiat, to poly-L-lactide solution caused a significant reduction in the number of beads. Son et al. [17] found beads in an acid solution but not in an alkaline solution in the electrospinning of PVA in water, with the pH adjusted by adding HCl or NaOH. In their experiments, neither the viscosity nor the surface tension was affected by pH. Here an additional effect was seen: larger beads were observed with higher concentrations of acid. It is possible that the concentration of acid was so high that the vapor pressure of the solvent was lowered; slowing vaporization and allowing the beads time to grow to very large sizes.

Additional experiments with different concentrations of H$_2$PtCl$_6$ and PVP are shown in Fig. 2.4. The concentrations used in the two figures are listed in the following table:

<table>
<thead>
<tr>
<th>Figure</th>
<th>PVP, mg/ml</th>
<th>H$_2$PtCl$_6$, mg/ml</th>
<th>Figure</th>
<th>PVP, mg/ml</th>
<th>H$_2$PtCl$_6$, mg/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>4(a)</td>
<td>17.5</td>
<td>16.8</td>
<td>5(a)</td>
<td>33.1</td>
<td>10.6</td>
</tr>
<tr>
<td>4(b)</td>
<td>17.5</td>
<td>11.2</td>
<td>5(b)</td>
<td>33.1</td>
<td>2.6</td>
</tr>
<tr>
<td>4(c)</td>
<td>17.5</td>
<td>5.6</td>
<td>5(c)</td>
<td>9.9</td>
<td>10.6</td>
</tr>
<tr>
<td>4(d)</td>
<td>17.5</td>
<td>2.8</td>
<td>5(d)</td>
<td>9.9</td>
<td>2.6</td>
</tr>
</tbody>
</table>
By comparing Figs. 2.4(b), 2.3(d) and 2.4(d), the effect of polymer concentration at low acid concentration can be seen. High polymer concentration produced thicker fibers without beads, while low polymer concentration produced thinner fibers with beads. By comparing Figs. 2.4(a), 2.3(b) and 2.3(c), the effect of polymer concentration at high acid concentration can be seen. Again, high polymer concentration produced thicker fibers without beads and low polymer concentration produced thinner fibers with beads. When the polymer concentration was high, such as in Figs. 2.4(a) and (b), smooth fibers were produced despite the difference in acid concentration. On the other hand, when the polymer concentration was low, such as Figs. 2.4(c) and (d), beads were produced no matter what the acid concentration was.

Fig. 2.4 SEM morphologies of electrospun PVP/H\textsubscript{2}PtCl\textsubscript{6} composite nanofibers at different ratios of PVP/H\textsubscript{2}PtCl\textsubscript{6}: (a) 3.12/1, (b) 12.73/1, (c) 0.93/1 and (d) 3.81/1.
3. The effect of water content

Next, the effect of H₂O/C₂H₅OH ratio on the final composite fiber morphologies was evaluated. When the H₂PtCl₆ solution was dropped into the PVP solutions in ethanol, flocs were produced and needed a little water to be dissolved. It was also observed that by replacing ethanol with methanol, a clear solution could be obtained without water. So water was necessary for the ethanol/H₂PtCl₆ solution. Besides, mixing water in ethanol should increase surface tension since water has a surface tension of 72.75 mN/m vs. 22.32 mN/m for ethanol. Six volume ratios of H₂O/C₂H₅OH were chosen: 0.036, 0.075, 0.117, 0.163, 0.212, and 0.265. PVP and H₂PtCl₆ concentrations were 17.5 mg/ml and 5.6 mg/ml respectively in all of the experiments. The measured surface tension of the precursor solution as a function of H₂O concentration is plotted in Fig. 2.5, including limiting concentration of pure ethanol (20.1 mN/m) and pure deionized water (66.6 mN/m). It was observed that precursor solution surface tension increased gradually from 21.1 to 24.5 mN/m as water/ethanol ratio increased from 0.036 to 0.265.
In Fig. 2.6, it was observed that in the low water/ethanol ratio range, increasing the water content made fibers thinner. In the high water/ethanol ratio range, fiber diameter did not change much with increasing water content, but bead density increased. Surface tension is the driving force for bead formation. Fong et al. [1] also found that when the ethanol/water ratio was changed, the bead density along the poly(ethylene oxide) fiber increased with increasing water content.

Yang et al. [18] also found a solvent ratio effect for the electrospinning of PVP in an ethanol/N,N-dimethyl-formamide mixture 50/50 by weight. They obtained 20 nm fibers without beads and attributed the bead-free fibers to the combined effects of viscosity (0.014 Pa·s) and surface tension (35 mN/m). For the same 4 wt.% of PVP but dissolved in pure ethanol, the diameter of the fiber was 250 nm. Beads were observed if the weight ratio of the solvents was 35/65.
Fig. 2.6 SEM morphologies of electrospun PVP/H$_2$PtCl$_6$ composite nanofibers with H$_2$O/C$_2$H$_5$OH ratios: (a) 0.036, (b) 0.075, (c) 0.117, (d) 0.163, (e) 0.212 and (f) 0.265.
4. The effect of feeding rate

The influence of solution feeding rate on the morphologies of the final composite nanofibers was checked next. Four feeding rates were chosen: 0.1, 0.2, 0.3, and 0.4 ml/hr. The PVP concentration was 17.5 mg/ml, and the H$_2$PtCl$_6$ concentration was 5.6 mg/ml for each experiment. At 0.1 ml/hr, feeding was discontinuous, while at 0.4 ml/hr, big drops of liquid fell onto the collecting plate during spinning.

![Fig. 2.7 SEM morphologies of electrospun PVP/H$_2$PtCl$_6$ composite nanofibers at following feeding rates: (a) 0.1 ml/hr, (b) 0.2 ml/hr, (c) 0.3 ml/hr and (d) 0.4 ml/hr.](image-url)
Mejelski et al. [12] found no beads along polystyrene (PS) fibers in THF when the feeding rate was less than 0.1 ml/m. Zong et al. [10] observed relatively thicker fiber diameters and larger beads in fibers spun from a higher feeding rate (75 µl/min) and thinner fibers and smaller beads for a lower feeding rate (20 µl/min). But there was no obvious effect of feeding rate on fiber diameter, except that the beads were larger at higher feeding rates as shown in Fig. 2.8, in agreement with Zong et al. [10]. Zong et al. proposed that, at higher feeding rates, the size of the drop was larger and the liquid jet moved faster so there was not enough time for it to dry before it reached the collection plate. As a result, the beads grew larger.

5. The effect of electric field

Next the influence of the electric field on the morphologies of the composite nanofibers was checked. Four voltages were chosen: 5, 6, 7, and 8 kV across a distance of 6 cm from the orifice to the collecting plate. Different electric fields meant different drawing forces, which can cause different shapes of the suspending droplet and a different initiation position of the jet at the orifice [9, 11]. Different feeding rates were used for different electric fields in an attempt to make the stable jet initiation condition similar for all the samples. Thus the feeding rates used were 0.1, 0.15, 0.3, and 0.4 ml/hr corresponding to the above voltages. The PVP concentration was 16.5 mg/ml, and the H₂PtCl₆ concentration was 5.15 mg/ml for all of the experiments. As shown in Fig. 2.8, thinner fibers and larger
beads were observed at higher electric field strength. This can be understood [10] as follows: with increasing electric field, the jet speed is faster so the jet has less time to evaporate, allowing the bead to grow larger before solidification.

Deitzel et al. [19] found no beads along the PEO fiber when 5.5 kV was applied across a distance of 6.5 in or 16.5 cm, but found beads at 7 kV and the bead density increased 10 fold at 9 kV. However the size of the beads and diameters of the fibers remained similar. Zong et al. [10] also found more beads at higher electric fields. However, Helgeson et al. [20] found no beads at high electric fields, but observed beads at low strength fields when the polymer (polyethylene oxide in water) concentration exceeded 2 wt.%. Mejelski et al. [12] found beads when the distance between the needle and collecting plate was reduced from 35 cm to 30 cm for the same applied voltage.
Fig. 2.8 SEM morphologies of electrospun PVP/H$_2$PtCl$_6$ composite nanofibers at following electric field strengths: (a) 5 kV/6 cm, (b) 6 kV/6 cm, (c) 7 kV/6 cm and (d) 8 kV/6 cm. Corresponding high magnification pictures are inset.
Platinum nanowires

An example of the Pt nanowires obtained is shown in Fig. 2.9 and a diameter distribution is shown in Fig. 2.10. X-ray diffraction showed that the peak (111) was at 2θ=39.8 indicating the wires were pure Pt, see Fig. 2.12. The diameter distribution indicated a possible bimodal behavior. We hope that further optimization could allow us to make Pt nanowires with an average diameter of only a few nanometers, useful for fuel cell applications.

Fig. 2.9 An example of some Pt nanowires obtained under the following conditions: 17.5 mg/ml (PVP), 5.6 mg/ml H₂PtCl₆, ratio of H₂O/H₆C₂O = 0.12, feeding speed 0.25 ml/hr, spinning distance: 6 cm, applied voltage 1 kV/cm, RH: 30%, T: 20°C.
2.1.4 Conclusion

The effects of several operating parameters on the morphology of composite nanofibers made by electrospinning were investigated. A PVP/H₂PtCl₆ system was chosen to make Pt nanowires for fuel cell applications. It was found that, in order to obtain a uniform fiber structure without beads, a certain high polymer concentration was necessary such as 20 mg/ml, a low water/ethanol ratio such as 0.1, a low feeding rate such as 0.1 ml/hr and a low electric field strength such as 6 kV across a distance of 6 cm. These conditions must be further optimized together with heat treatment to make Pt nanowires.

Fig. 2.10 Diameter distribution of Pt nanowires showing a possible bimodal behavior.
2.2 Heat treatment of electrospun salt/polymer composite nanofibers to pure metal or alloy nanowires

2.2.1 Introduction

Ceramic nanofibers and metal nanowires have been made using the electrospinning technique in the last few years. A number of papers about the fabrication of nanofibers of various materials have been published. However, some basic understanding of process is still missing, such as the thermal decomposition process from spun polymer/salt composite fibers to final ceramic or metal nanowires. In this chapter, the thermal decomposition process will be presented with TEM images.

2.2.2 Experiments

The setup for electrospinning is illustrated in the previous section. The poly(vinyl pyrrolidone) (PVP) of $1.3 \times 10^6$ MW, $\text{H}_2\text{PtCl}_6\cdot6\text{H}_2\text{O}$ (99.9%), and $\text{CuCl}_2\cdot2\text{H}_2\text{O}$ (99%) were obtained from Aldrich. $\text{NiCl}_2$ (99%), $\text{ZrCl}_4$ (98%), and $\text{Al(NO}_3)_3\cdot5\text{H}_2\text{O}$ were from Alfa Aesar. The solvent used was a mixture of de-ionized water and ethanol. The exact composition of precursor solution was given in each individual part. The temperature was approximately 25°C in environmental atmosphere. Relative humidity was approximately 30%. Except where noted, the electrospinning conditions included a distance of 6 cm from
orifice to substrate and an applied voltage of 1 kV/cm. The solution feeding speed was 0.25 ml/hr.

In Pt nanowires fabrication, the following concentrations were used: 15.5 mg/ml (PVP), 5.2 mg/ml (H₂PtCl₆), and the ratio of H₂O/H₆C₂O = 0.14. In PtNi₃ nanowires: 38 mg/ml (PVP), 6 mg/ml (H₂PtCl₆), H₂O/H₆C₂O = 0.13. In Zr₅₀Ni₁₀Cu₃₀Al₁₀ nanowires: ZrCl₄, NiCl₂, CuCl₂·2H₂O, Al(NO₃)₃·5H₂O were dissolved in water and ethanol mixture according to composition Zr₅₀Ni₁₀Cu₃₀Al₁₀. The total concentration of salts was 12 mg/ml, 21 mg/ml (PVP), H₂O/H₆C₂O = 0.1.

Field emission scanning electron microscope (FESEM, Zeiss-Leo DSM982 model) and scanning transmission electron microscope (FE(S)TEM FEI Tecnai F20) were used to characterize the morphologies of all wires produced. X-ray diffraction (XRD) patterns were obtained with a Philips X’Pert high resolution materials research diffractometer with Cu Kα1 radiation.

2.2.3 Discussion

2.2.3.1 Thermal decomposition process

When PVP/H₂PtCl₆ composite fibers were thermally decomposed, Pt nanoparticles appeared on the fiber surface first; their diameters were too small to be measured until 15 minutes had elapsed. Then, the polymer burned off gradually and Pt particle size increased over the duration of the treatment. The particles
were 2~3 nm after 25 minutes. They increased to approximately 3~4 nm after 35 minutes. Pt particles contacted each other, forming a string of Pt grains after 50 minutes of heat treatment. The particle size was about 6 nm. The particles diffused into each other and formed bigger Pt grains along the wire after a further 10 minutes of sintering. The thermal decomposition process is shown in Fig. 2.11.

Fig. 2.11 TEM images of thermal decomposition process of PVP/H₂PtCl₆ composite nanofibers. Treatment durations are indicated in individual pictures.
XRD result of the final wires (Fig. 2.12) indicated that they were metallic Pt with FCC crystal structure.

![X-ray diffraction patterns of Pt nanowires.](image)

**Fig. 2.12** X-ray diffraction patterns of Pt nanowires.

2.2.3.2 Heat treatment design

The heat treatment process must be carefully designed. A slow heat treatment was necessary in the low temperatures to keep the wire structure. In Fig. 2.13(a), a dense film formed, and the wires appeared to have melted. Local temperatures on PVP/H$_2$PtCl$_6$ composite nanofibers were measure by wrapping a lot of composite fibers on a thermocouple tip with a lab view program monitoring during the heat treatment in air. An exothermic peak approximately 400°C was found when the sample was heated from 50°C to 600°C over 3 hours, as seen in Fig. 2.14(a). This exothermic phenomenon was believed to be the reason for the apparent melting of the wires. The wire structure was kept intact if the sample was heated slowly in the low temperature range, for example 220°C to 300°C in 15 hours, Fig. 2.13(b) and Fig. 2.14(b). In this case the exothermic peak was not seen.
Fig. 2.13 SEM morphologies of electrospun PVP/H$_2$PtCl$_6$ composite nanofibers after heat treatment in air: (a) from 50°C to 575°C in 3 hr, (b) from 220°C to 250°C in 10 hr and 250°C to 300°C in 5 hr and 300°C to 400°C in 2 hr and 400°C to 600°C in 2 hr and finally annealed at 600°C for 0.5 hr.

Fig. 2.14 Local temperature on PVP/H$_2$PtCl$_6$ composite nanofibers during heat treatment in air: (a) from 50°C to 575°C in 3 hr, (b) from 220°C to 250°C in 10 hr and 250°C to 300°C in 5 hr and 300°C to 400°C in 2 hr and 400°C to 600°C in 2 hr and finally annealed at 600°C for 0.5 hr.
2.2.3.3 Amorphous metal composition

Heat treatment process produced unexpected behavior in the Pt nanowires. To study this in more detail, a similar experiment was conducted on an amorphous metal composition. The Zr$_{50}$Ni$_{10}$Cu$_{30}$Al$_{10}$ is normally an amorphous metal after rapid cooling. However during fabrication of such glass metal wires, well-crystallized alloy wires were obtained instead. Firstly, salts/PVP composite fibers were made, and then they were heated in air at 350°C for one hour to decompose the polymer. After reduction in H$_2$ at 400°C, crystallized alloy wires were obtained, as shown by XRD, Fig. 2.15. Their morphology is shown in Fig. 2.16. A possible explanation for the easy formation of crystal alloy for Zr$_{50}$Ni$_{10}$Cu$_{30}$Al$_{10}$ was that the conventional amorphous alloy was made by cooling molten metals from a very high temperature to room temperature. It was difficult to nucleate individual metal crystals so the solid remained amorphous. Here the metal oxides formed during polymer burned off. After reduction, a single FCC structure appeared. More work has to be done.
Fig. 2.15 XRD of Zr$_{50}$Ni$_{10}$Cu$_{30}$Al$_{10}$ nanowires with FCC crystal structure.

Fig. 2.16 SEM morphology of electrospun Zr$_{50}$Ni$_{10}$Cu$_{30}$Al$_{10}$ nanowires.
2.2.4 Conclusion

Metal nanowires were produced through thermal decomposition of electrospun salt/polymer composite nanofibers. The thermal decomposition process of Pt/PVP nanofibers was investigated. PVP gradually decomposed and contracted, while the salt began to decompose into individual Pt nanoparticles. These nanoparticles appeared in the polymer fibers and grew larger as heating time increased. Finally, the polymer burned off and these particles contacted each other, forming a Pt nanowire. It was found that a slow heating process in the low temperature range was necessary to keep the wire structure intact. Attempts to create Zr$_{50}$Ni$_{10}$Cu$_{30}$Al$_{10}$ nanowires produced nanowires that were not amorphous as expected. Metal crystal structure appeared.
References


Chapter 3 Long and Porous Nanowires of Pt Alloy as Catalyst in Proton Exchange Membrane Fuel Cells and Other Applications

3.1 Introduction

Porous Pt nanowires supply more surface area than the corresponding dense wires. Porous Pt networks from the CO-induced self organization of monodisperse primary Pt nanoparticles offer good porosity with rod diameter of 15 nm, but the rod is very short, approximately 100 nm [1]. Zhang et al. reported the fabrication of Pt porous nanowire arrays (PNWAs) utilizing nanochannel alumina templates by electrodepositing Pt–Cu alloy nanowires and de-alloying the Cu component. This could be used as an effective electrocatalyst for ethanol oxidation in direct alcohol fuel cells [2], but its continuous porous network was formed with a characteristic ligament size as large as 10~20 nm, pore size as small as 2~5 nm and wire length less than 2 micrometers.

Smaller ligament, larger pore sizes and longer wires are preferable for a catalyst. Remita et al. [3] synthesized porous Pt nanoballs using soft templates made by a quaternary system as a nano reactor. Balls had typical sizes of 50~80 nm and the average diameter of the nanorods was about 2.8 nm. This type of ball had better porosity, but their network was too small for good mechanical stability in a fuel cell. Therefore, it is desirable to find an efficient process for producing interconnected porous nanowires (or network) of Pt that can be used as a catalyst.
in a PEM fuel cell and other applications without the above-noted deficiencies of carbon-supported nanoparticles, short or insufficiently porous wires, or large ball Pt catalysts.

This chapter describes a procedure for making a long and porous nanowires network of Pt. Long nanowires were interweaved forming a large thin film (thickness \( \sim 1 \mu m \)). Every nanowire had very good porosity and very thin ligaments. This kind of catalyst was self-supported, without carbon. Electrodes made with such porous nanowires offered high active surface area, high power density and very good durability.

### 3.2 Experiments

The setup for electrospinning is shown in a previous paper [4]. It consisted of a high voltage supply (Dongwen, Tianjing, China), a syringe pump (Harvard Pump11, U.S.A.), and a plastic syringe equipped with a 20x6" stainless steel needle. Carbon paper set on a motor was used to collect the composite fibers. The distance between the orifice and the carbon paper collector was 7 cm and the applied field was 1 kV/cm. The solution feeding speed was 0.15 ml/hr. Ambient temperature was approximately 25°C in the lab environment. The polymer used was PVP of \( 1.3 \times 10^6 \) MW, obtained from Aldrich. The hexachloroplatinic acid (H\(_2\)PtCl\(_6\)-6H\(_2\)O) was from Aldrich. Iron nitrate (Fe(NO\(_3\))\(_3\)) and nickel(II) nitrate hexahydrate (Ni(NO\(_3\))\(_2\)-6H\(_2\)O) were from Alfa Aesar. Surfactant tetrabutyl
ammonium chloride was obtained from Aldrich. The solvent was pure methanol. The film composed of nanowires with atom ratio of Pt:Fe = 1:5 was heated up to 575°C in air, then reduced in H₂ at 200°C for one hour. The PtFe₅ nanowires were treated in various concentrations of H₂SO₄ at different temperatures for different periods to dissolve Fe and make Pt nanowires or networks with various porosities.

Both field emission scanning electron microscope (FESEM, Zeiss-Leo DSM982 model) and scanning-transmission electron microscope (FE(S)TEM FEI Tecnai F20) were used to observe the morphologies and analyze the composition of nanowires. X-ray diffraction (XRD) patterns were obtained with a Philips X'Pert high resolution materials research diffractometer with Cu Kα1 radiation.

Electrochemical measurements were carried out in a conventional three-electrode electrochemical cell at 25°C, using a glassy carbon (GC) rotating disk electrode (RDE, 5 mm diameter, 0.198 cm²) setup (VMP, Princeton Applied Research) with CHI test station (model 600C) to collect data. The reference electrode was a saturated Ag/AgCl electrode and the counter electrode was a piece of Pt. The solution was 0.1 M HClO₄. All potentials in this study were given relative to the reversible hydrogen electrode (RHE). The commercial catalyst ink was prepared by making suspensions of 50 mg Pt/C (40%, BASF) in 1 ml H₂O and 4 ml isopropyl alcohol with 20 mg Nafion solution (1%) catalyst and ultrasonic mixing for about 60 min. 20 mg of such catalyst suspension was transferred onto the carbon substrate, leading to a metal loading of 9.5 µg Pt. For
Pt porous nanowires, a cake was made with many small pieces of catalyst films, composed of long porous nanowires with Nafion.

To compare electrochemical performance in a real fuel cell between Pt porous nanowires and conventional Pt/C particles, two kinds of MEA were prepared. The catalysts used in this work were Pt/C (40%, BASF) and homemade porous Pt alloy nanowires. The MEA was a seven-layer structure. The gas diffusion layer (GDL) for the anode and cathode catalyst layers was water-proofed carbon paper coated with a hydrophobic diffusion layer. The BASF catalyst powder (40 wt.% Pt) and Nafion ionomer solutions (15 wt.%) were ultrasonically mixed in isopropyl alcohol to form a homogeneous catalyst ink. The Nafion content in both the anode and the cathode catalyst layers was 25 wt.%. For MEA1, the catalyst ink was sprayed onto ethyl tetrafluorethylen (ETFE) film, and then transferred onto Nafion N212 membrane. The Pt metal loading was 0.17 mg Pt on anode and 0.33 mg Pt on cathode. For MEA2, the anode part was the same as MEA1. The cathode was made by laying a piece of catalyst film composed of PtNi_{0.5}Fe_{6.5} nanowires on an ETFE film, and dropping a little PTFE and nafion ionomer diluted solution on it. After drying, the cathode and anode were hot pressed on either side of a piece of a Nafion membrane (DuPont 112) with a pressure of 110 lb/cm² at 140°C for 120 s. The MEA was treated in 2 M H₂SO₄ at 80°C for 50 min to transfer PtNi_{0.5}Fe_{6.5} nanowires into Pt rich porous naowires, then washed in 80°C de-ionized water for 30 min. In the MEA, Nafion and PTFE
were mixed together with catalyst wires. A stronger corrosion condition was chosen in order to make an effective porosity treatment. Electrochemical performance was tested in a PEM fuel cell fixture. The cathode fuel was 70°C humidified air and anode fuel was 80°C humidified hydrogen. H₂ flowed at 150 sccm + 100 sccm/A, air flowed at 150 sccm + 200 sccm/A. They were transferred into the cell at ambient pressure. The cell temperature was 80°C and the electrode area was 5 cm². An accelerated degradation test was conducted by voltage cycling of the cell between 0.6~0.95 V at the scanning speed of 50 mV per 10 s. MEAs were tested in a 5 cm² cell interfaced with the fuel cell test station (model 850e) from Scribner Associates, Inc.

3.3 Discussion

The original PtFe₅ wires had a diameter approximately 20~30 nm, see Fig. 3.1(a). SEM pictures show that the wires were dense and uniform. After de-alloying in 0.005 M H₂SO₄ at 80°C for 3 min. the diameter was still approximately 15 nm. These nanowires now had become porous, see Fig. 3.1(b). The composition of these porous nanowires was approximately Pt:Fe=70:30 (atom ratio) based on EDAX results. The leftover Fe was covered in the inner part in every ligament, but the amount of Fe could be further reduced in a higher corrosive environment. The ligament around the pores had a size of only 2~3 nm. Because of the small ligament size, the physical surface area per unit mass was
sufficiently high comparable to commercial Pt/C nanoparticles of 3~4 nm. A clearer nanostructure can be seen in the TEM image, Fig. 3.2(c).

![Fig. 3.1](image1.png)

**Fig. 3.1** Images of PtFe\textsubscript{5} nanowires (a) before and (b) after treatment in 0.005 M H\textsubscript{2}SO\textsubscript{4} at 80°C for 3 min.

X-ray diffraction of nanowires before H\textsubscript{2}SO\textsubscript{4} treatment indicates that the wire had Pt and PtFe alloys, Fig. 3.2(a). After H\textsubscript{2}SO\textsubscript{4} treatment, the Fe rich PtFe alloy peak moved to a lower angle close to pure Pt because most Fe had been dissolved from the PtFe alloy, Fig. 3.2(b).

![Fig. 3.2](image2.png)

**Fig. 3.2** X-ray diffractions of PtFe\textsubscript{5} nanowires (a) before and (b) after acid treatment.
The formation of porosity appeared as follows based on TEM images (Fig. 3.3) and XRD results. As illustrated in Scheme 3.1, after reducing in hydrogen the wire was composed of Pt and Pt rich PtFe alloy nanoparticles (black particles) embedded in the Fe rich PtFe alloy (low contrast part) as shown in Scheme 3.1(a) and Fig. 3.3(a). When Fe was dissolved from the Fe rich PtFe alloy little by little into the hot acid solution, the ratio of Pt/Fe gradually increased and some Pt atoms would join nearby black particles as shown in Scheme 3.1(b) and Fig. 3.3(b). Then with further de-alloying the shrunken PtFe alloy would form bridges connecting the Pt particles. Wire diameters shrank and pores became larger. Pt rich porous nanowires were formed, as shown in Scheme 3.1(c) and Fig. 3.3(c). The nonuniform distribution of Pt and Fe in the nanowire seems to be the cause of porosity formation. De-alloying process occurred in the Fe rich part of the alloy wire. The inset image in Fig. 3.3(c) is the lattice fringes on a ligament surface. Lattice distance 2.26 Å corresponds to (111) atomic plane of almost pure metallic platinum. In general, the porosity increases with acid concentration, treatment time and temperature.

Scheme 3.1. Porosity formation in PtFe₅ alloy nanowires.
Fig. 3.3 TEM images of PtFe$_5$ nanowires: (a) after treatment in 0.0025 M H$_2$SO$_4$ for 70 s, (b) after treatment in 0.0025 M H$_2$SO$_4$ for 180 s and (c) after treatment in 0.005 M H$_2$SO$_4$ for 60 s.

It was observed that wire composition was not uniform; many 2 nm black particles appeared in the wire after heat treatment in air and before reduction in H$_2$, see Fig. 3.3(a). During reduction, the whole nanowire would become more uniform with increasing temperature. To confirm the above porous nanowire formation process, we made a sample with uniform composition by reducing it at higher temperature. The outmost edge was a layer of iron oxides. The inner part was uniform without black particles, Fig. 3.4(a, b). After acid treatment, the
nanowires were still dense and without porous structure, no matter whether high or low concentration of H₂SO₄ was used, see Fig. 3.4(c, d). The only change was the decreased diameter.

![TEM and SEM images of PtFe₅ nanowires](image)

**Fig. 3.4** (a) TEM and (b) SEM images of PtFe₅ nanowires reduced in H₂ at 300°C for 1 hr, (c) PtFe₅ nanowires after treatment in 0.1 M H₂SO₄ for 1 hr at 80°C, (d) PtFe₅ nanowires after treatment in 0.001 M H₂SO₄ for 1 hr at 80°C.

Pt atoms refilled the holes of nearby Fe atoms when Fe atoms were dissolved from the alloy. The Pt atom concentration became higher and higher on the surface as the Fe dissolved and the wire diameter shrank. Finally, a Pt rich layer was formed on the surface, and the nanowires stopped shrinking.
The electrochemically active surface area and its degradation were tested by cyclic voltametry by an electrochemical station (CHI600C). Accelerated degradation was carried out by scanning the porous PtFe₅ nanowires and commercial Pt/C (40%) in 0.1 M HClO₄ at room temperature and an air environment. PtFe₅ nanowires were treated by 2 M H₂SO₄ for 1 hour after treatment in 0.005 M H₂SO₄ at 80°C for 3 minutes in order to get rid of more iron. Its porosity was much higher than those treated in dilute acid, Fig. 3.8(a). Its composition was Pt:Fe = 91:9 based on EDAX measurement. Voltage was cycled between 0.4 and 0.9 V vs Ag/(Ag/Cl) at 40 mV/s. The electrochemically active surface area of commercial Pt/C particles was 82 m²/g Pt, but these particles were not stable. The active area decreased quickly to only 16% of the original value after 3000 scanning cycles, see Fig. 3.5. Many have reported such fast degradation [5].

Porous Pt nanowires showed very good stability compared with Pt nanoparticles. They retained 76% of their original area after 9000 scanning cycles, see Fig. 3.6. The comparison of these two kinds of catalysts was shown in Fig. 3.7. The electrochemically active surface area of porous Pt nanowires was approximately 55 m²/g Pt. This value is consistent with a wire of 3 nm diameter whose geometrical area is 62.3 m²/g Pt. It should be mentioned that porous structure was not necessarily stable. After CV cycles, porous wires gradually changed into dense nanowires, with composition Pt:Fe = 93:7 (atom), Fig. 3.8(b).
During this period, Fe was further dissolved. Pt diffused a lot to decrease surface area. Karl J. J. Mayrhofer et al. [6] have qualitatively demonstrated that Co atoms could segregate to the surface of Pt₃Co nanoparticles during cycling in typical fuel cell cathode application ranges. This work showed that a similar phenomenon occurred in an acid environment. One dimensional Pt wires still coarsen, even without the particle agglomeration problem. So obtaining a stable Pt structure at 2~3 nm is still a challenge blocking the fuel cell vehicle from commercialization.

**Fig. 3.5** Degradation of commercial Pt/C nanoparticle catalysts in 0.1 M HClO₄ by cyclic voltametry by an electrochemical station (CHI600C).
Fig. 3.6 Degradation of porous Pt alloy nanowire catalysts in 0.1 M HClO₄ by cyclic voltametry by an electrochemical station (CHI600C).

Fig. 3.7 Degradation comparison between porous Pt nanowire catalysts and commercial Pt/C nanoparticle catalysts in 0.1 M HClO₄ by cyclic voltametry method.
Fig. 3.8 Degradation of porous Pt nanowires: (a) fresh PtFe$_5$ alloy porous nanowires, (b) PtFe alloy nanowires after 9000 cyclic voltametry.

PtFe porous nanowires were too brittle to perform well in a real fuel cell. We found that a small amount of Ni added to the wire helped to improve the mechanical stability of the wire. Nanowire catalysts with a starting composition PtNi$_{0.5}$Fe$_{6.5}$ became porous after a series of treatments in H$_2$SO$_4$ at 80°C. The PtNi$_{0.5}$Fe$_{6.5}$ nanowires were 15~30 nm thick with shallow holes on surface after a series of heat treatments on electrospun nanowires, Fig. 3.9(b). These wires were fairly long. We could not trace one single wire from one end to the other end, even in zoomed out SEM pictures. The length of the wires was estimated to be several micrometers. They were also interwoven like a net. So we could say they were interwoven long nanowires. After acid treatment the whole film shrank a lot and every wire became porous. For a single wire the diameter was approximately 10~15 nm. The ligament surrounding pores had a size of only 2~4 nm, Fig. 3.9(b).
The atom compositions (Pt/Ni/Fe) were 13/6/81 for raw PtNi$_{0.5}$Fe$_{6.5}$ nanowires and 82/5/13 for porous nanowires based on EDAX measurement. This indicated that most non-noble metals were dissolved and the porous wires were Pt rich. The Pt should have concentrated on the surface, based on the results on acid treated PtNi$_5$ nanowires discussed in Chapter 4.

**Fig. 3.9** SEM images of PtNi$_{0.5}$Fe$_{6.5}$ nanowires (a) and porous nanowires (b) after treatment in 0.0025 M H$_2$SO$_4$ for 10 min, then in 0.05 M H$_2$SO$_4$ for 10 min, then in 1 M H$_2$SO$_4$ for 10 min at 80°C.
The porous nanostructure could be seen clearly in TEM pictures, Fig. 3.10. Pores were 4–6 nm large and the ligament around the pores had a size of only 2–4 nm, so its physical surface area per unit mass was sufficiently high, comparable to commercial catalyst Pt/C nanoparticles of 2–3 nm. In the high resolution picture, the lattice distance of 2.27 Å corresponds to (111) atomic plane of pure metallic platinum. So most platinum was distributed on surface, which was a platinum rich alloy layer. On the outmost surface, it might be pure platinum which could protect Fe and Ni from being corroded.

![TEM images of PtNi0.5Fe6.5 nanowire after treatment in 0.0025 M H2SO4 for 10 min, then in 0.05 M H2SO4 for 10 min, then in 1 M H2SO4 for 10 min at 80°C. (a) The image of a single wire, (b) a zoomed-in image of (a).](image)

X-ray diffraction of nanowires before H2SO4 treatment indicated that the nanowire was composed Pt, PtNiFe alloy and Fe3O4. After H2SO4 treatment, only PtNiFe alloy and Pt were left. Fe3O4 disappeared and the PtNiFe alloy peak
moved to a lower angle, close to the Pt (111) peak, Fig. 3.11. Because most small metallic atoms such as Fe (atom radius 0.124 nm) and Ni (atom radius 0.125 nm) had been dissolved from the PtNiFe alloy, the new alloy was composed of more Pt. Pt atoms are larger (atom radius 0.139 nm) than Fe and Ni atoms, so the lattice distance has been enlarged.

![X-ray diffraction pattern of PtNi0.5Fe6.5 nanowires before and after acid treatment.](image)

**Fig. 3.11** X-ray diffraction of PtNi0.5Fe6.5 nanowires before (a) and after (b) acid treatment.

Electrochemically active surface area was measured in a 5 cm² testing cell. The surface area was 71.8 m²/g Pt before voltage scans, Fig. 3.12. After 2000 and 4000 voltage cycles between 0.6–0.95 V at the scanning speed of 50 mV per 10 s, active surface areas were 66.6 and 60.0 m²/g Pt, which are 93% and 84% of their previous values, respectively.
Fig. 3.12 Cyclic voltammograms test of porous nanowire catalysts operated in a cell. Scan rate 40 mV/s, Scan range 0~1.2 V, Cathode: 70°C N₂, Anode: 80°C H₂, Cell: 80°C. Humidified gases. Calculation: 0.06 V~0.35 V H⁺ adsorption process.

Electrochemical properties were compared between porous nanowire catalysts with commercial Pt/C nanoparticle catalysts in a real cell testing. Commercial catalysts degraded quickly, as shown in Fig. 3.13. Porous nanowire electrode was much more stable and did not change much after 4000 voltage cycles, Fig. 3.14. Its current density could be as large as 5 A/mg Pt, and the highest possible power density was 2 W/mg Pt. Since the composition of porous nanowires and the MEA fabrication process have not yet been optimized, even better performance can be expected after optimization.
Fig. 3.13 Polarization and power curves of MEA made with commercial Pt/C catalysts. (a) Current density based on unit cell area, (b) current and power density based on unit Pt mass on cathode and cathode Pt loading was 0.33 mg/cm². (□) before voltage cycles, (○) after 2500 voltage cycles, (△) after 5000 voltage cycles.
Fig. 3.14 Polarization and power curves of MEA with porous Pt alloy nanowires as the cathode catalyst. The anode is the commercial catalyst. (a) Current density based on unit cell area, (b) current and power density based on unit Pt mass on cathode and cathode Pt loading was 0.1 mg/cm². (□) before voltage cycles, (○) after 2000 voltage cycles, (△) after 4000 voltage cycles.
3.4 Conclusion

In summary, a network of long, porous Pt alloy nanowires was made by electrospinning and acid corrosion. The porous nanowires had diameters of 10–15 nm, 2–4 nm thick ligaments and 2–6 nm pore sizes. Platinum occupied more than 70 atom% in the whole wire and the wires were almost pure Pt on every ligament surface. This catalyst presented very good electrochemical performance in fuel cell testing. Its durability was much better than commercial nanoparticle catalysts, and its current density per gram Pt was also comparable to that of nanoparticle catalysts.
References


Chapter 4 Pt-Shell Pt-Ni Nanowires Made by Electrospinning

with Subsequent Acid and Heat Treatment

4.1 Introduction

The high cost is the primary concern for Pt catalysts, so it is usually made into nanoparticles. But these particles move, get lost or agglomerate. Alloying platinum with other noble (Au, Ru and Pd etc.) or non-noble (Fe, Ni, Pb and Cu etc.) metals were reported to help reduce cost and improve catalytic property at the same time [1-3]. But alloying platinum with other noble metals doesn’t decrease cost much and alloying with non-noble metals has to face the dissolution of these non-noble metals in corrosive environment when the concentration of non-noble metals is high. The bimetallic core–shell nanoparticles have attracted much attention because this structure not only saves Pt with Pt shell on surface but also enhances catalytic activity. The presence of other noble metals or transition metals located within the core causes the structure and electronic effects by the partial alloying and vacant d-orbital [4, 5]. The dissolution of the transition metal is expected to be reduced due to the protective effects of the Pt shell, but no stability tests were reported in acids. Furthermore the shell layer is suspected to be simply a deposited structure [5-7] which may not be stable after long time or high temperature exposure. Also, the problem of particle agglomeration is still not resolved.
The present catalyst design is going to overcome these shortages. Long nanowires form a self-supporting net which avoids platinum particle agglomeration. A core-shell structure was used to save noble metal. But the present core-shell structure is different from the usual ones formed by just depositing Pt on a core metal at low temperature. Core-shell structure is formed by a long time heat treatment in a reducing atmosphere after an acid treatment to produce a Pt rich rough surface. This heat treatment process was based on the understanding that Pt would like to stay on the surface to lower the energy of the shell rather than to form an alloy over the surface.

4.2 Experiments

The platinum-nickel alloy nanowires were fabricated using electrospinning which has been described elsewhere [11]. The polymer used was poly(vinyl pyrrolidone) (PVP) of $1.3 \times 10^6$ MW. The platinum salt was hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6\cdot\text{6H}_2\text{O}$). The nickel salt was nickel nitrate ($\text{Ni(NO}_3)_2\cdot\text{6H}_2\text{O}$). The surfactant was tetrabutyl ammonium chloride (TBAC). Solvent was methanol. All chemicals were from Aldrich. The distance between the orifice and the carbon paper collector was 7 cm and the applied field was 7 kV. Solution feeding speed was 0.2 ml/hr. Temperature was approximately 25°C in a laboratory environment. Relative humidity was approximately 45%. $\text{H}_2\text{PtCl}_6\cdot\text{6H}_2\text{O}$ concentration was 2.3 mM/ml. The molar ratio of $\text{H}_2\text{PtCl}_6\cdot\text{6H}_2\text{O}$ to $\text{Ni(NO}_3)_2$ was 1:5. PVP concentration
was approximately 22 mg/ml. TBAC concentration was 2.0 mM/ml.

Electrospun H$_2$PtCl$_6$-Ni(NO$_3$)$_2$-PVP composite nanofibers formed a large film and were heated in air from 220°C up to 575°C in 20 hours to decompose the salts and polymer. The resulting Pt-Ni-O nanofibers were reduced into PtNi$_5$ alloy nanowires in the mixture of H$_2$(5%)+Ar(95%) at 250°C for one hour. PtNi$_5$ nanowires were put into 0.001 M H$_2$SO$_4$ for 8 minutes then this diluted acid was heated up to 60°C in 4 minutes. After being washed in diluted acid, the film was washed in deionized water and ethanol several times. This step was designed to get rid of NiO on wire surface and some metallic nickel from surface alloy. Then the film received a heat treatment in a mixture of H$_2$(5%)+Ar(95%) at 300°C for 15 hours. This step was designed to rearrange the surface atoms.

Field emission scanning electron microscope (FESEM, Zeiss Supra 40VP) and scanning transmission electron microscope (FE(S)TEM FEI Tecnai F20) were used to observe the morphologies. Both microscopes were equipped with an EDAX x-ray spectrometer for compositional analysis. X-ray diffraction (XRD) patterns were obtained on a Philips X’Pert high resolution materials research diffractometer with Cu Kα1 radiation. The XPS spectra were recorded using a VG ESCA Lab system equipped with a He I (21.2 eV) gas discharge lamp and a Mg Kα X-ray source (1253.6 eV) of resolution ~1.4 eV.
4.3 Discussion

1. Model

The formation process of core-shell structure is illustrated in Scheme 4.1. Platinum and nickel are alloyed in raw PtNi5 nanowires after reducing in H₂ at 250°C. Because the wire is exposed to air after reducing and the nickel on surface will be oxidized by oxygen, the wire surface is covered by a layer of nickel oxide. First, treat the wire in a diluted H₂SO₄ solution to dissolve nickel oxide and a small number of metallic nickel atoms from the surface alloy lattice. This makes the wire surface platinum rich, but there should be a lot of holes and defects as a result of the nickel being etched off the surface. Second, heat treat the wire in a mixture of Ar and H₂ to smooth the surface. Because of the lower surface energy of Pt (2.35 J/m²) compared to that of Ni (2.69 J/m²), Pt would like to stay on the
surface [12]. A dense platinum rich surface is formed. Both steps are necessary to make this dense platinum protection layer.

2. Corrosion resistance

The corrosion resistances of the nanowires were tested by measuring the nickel content in atomic percent after 2 or 6 hours in 1 M H₂SO₄ solution at 60°C. The results are shown in Fig. 4.1. For Pt-shell structured wires, the nickel content did not change much. After acid and heat treatment there was 80% nickel left in the wire. After 6 hours there was still more than 70% nickel in the wires. Only less than 10% Ni was lost and this happened at the beginning within about 30 minutes. For untreated PtNi₅ nanowires the Ni content changed from 83% to less than 30% in 6 hours. To see whether the acid treatment was needed, a sample was made with only heat treatment in the mixture of Ar and H₂. Its nickel content decreased to approximately 30% after only 2 hours in 1 M H₂SO₄, at 60°C similar to the untreated PtNi₅ nanowires. The sample with only acid treatment also had a nickel loss of 44% in 5 hours.
2. Morphology

To see the microstructure of PtNi$_5$ nanowires after each treatment step, a series of SEM pictures were shown in Fig. 4.2. The untreated PtNi$_5$ nanowires were about 25 nm, the thickest among all the nanowires and they contained beads. Its surface was rough, Fig. 4.2(a). After dilute acid treatment, the wire became thinner, but still rough on the surface, Fig. 4.2(b). When heat treated 15 hours more at 300°C in a weak reducing atmosphere, the wire became smooth on surface Fig. 4.2(c). After being tested in 1 M H$_2$SO$_4$ at 60°C for 6 hours the Pt-shell nanowires seemed to maintain the morphology, Fig. 4.2(d).

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\text{Fig. 4.1} \quad \text{Corrosion tests of nanowires in 1 M H}_2\text{SO}_4 \text{ at 60°C, (▲) diluted acid and heat treated PtNi} _5; (●) only diluted acid treated PtNi} _5; (■) only heat treated (300°C for 15 hr in Ar, H}_2\text{) PtNi} _5; (▼) untreated PtNi} _5.
\]
Fig. 4.3(a) shows the HRTEM images and intensity profiles for untreated PtNi₅ nanowires. A layer of nickel oxide appeared on the surface based on its lower image contrast. The nickel signal was wider than platinum and its top was flat which meant nickel distribution was not even in the cross section. There was much more nickel on the wire surface. Platinum was in the inner part of the wire and its distribution was more uniform. Fig. 4.3(b) shows acid and heat treated PtNi₅ nanowires after 6 hours corrosion test in 1 M H₂SO₄ at 60°C. There is no more nickel oxide layer on the surface.

In the intensity profile, the Ni signal was round on top indicating uniform distribution in the cross section. Over the edge, the signals of Ni and Pt overlapped (without considering the noise at lower intensity level), but the Pt signal on surface was obviously stronger than that in the inner part. The atom ratio of platinum to nickel was ~ 5.3:1 on the outer edge according to the XPS results. The lattice distance 2.24 Å corresponded to (111) atomic plane of pure metallic platinum. So most platinum was distributed on the surface, which was a platinum rich alloy layer. On the outer most surface it might be pure platinum which could protect the Ni from being corroded. Fig. 4.3(c) shows untreated PtNi₅ nanowires corrosion tested for 6 hours in 1 M H₂SO₄. The surface was also smooth without any nickel oxide layer. The intensity profile shows much stronger signal of Pt than Ni since a lot of Ni had been dissolved.
Fig. 4.2 SEM images of PtNi$_5$ nanowires after different treatment steps: (a) untreated PtNi$_5$ nanowires, (b) PtNi$_5$ nanowires soaked in 0.001 M H$_2$SO$_4$ for 8 minutes at room temperature then heated up to 60°C for 4 minutes in the same acid, (c) the above treated nanowires heated to 300°C for 15 hr in the mixture of Ar(95%)+H$_2$(5%), (d) the above treated nanowires tested in 1 M H$_2$SO$_4$ at 60°C for 6 hr.
Fig. 4.3 High resolution TEM images and corresponding intensity profiles of (a) untreated PtNi₅ nanowires, (b) acid and heat treated PtNi₅ nanowires after being tested in 1 M H₂SO₄ at 60°C for 6 hr, the inset shows the crystal lattice, (c) untreated PtNi₅ nanowires after being tested in 1 M H₂SO₄ at 60°C for 6 hr.
The corresponding mapping image of 1 M H$_2$SO$_4$ tested wire is shown in Fig. 4.4. The mapping images of Pt and Ni are overlapped. We observed clearly a platinum rich layer in the surface.

![Image](a) ![Image](b)

**Fig. 4.4** PtNi$_5$ after coating treatment and acid test. (a) In overlapped mapping, the red points are Ni, green points are Pt. (b) The accompanying image shows the wire where mapping was executed.

![Image](a) ![Image](b)

**Fig. 4.5** (a) SEM images of PtNi$_5$ nanowires reduced at 300°C for 20 hr in the mixture of Ar(95%)+H$_2$(5%); (b) sample (a) after being tested in 2 M H$_2$SO$_4$ at 60°C for 1 hr.
The situation was different if the acid treatment was skipped. Fig. 4.5(a) reveals totally different morphology for heat treated nanowires without prior acid treatment. The microstructure looked similar to untreated nanowires of Fig. 4.2(a) with rough surfaces. After corrosion testing in 1 M H₂SO₄ at 60°C for one hour, the nickel content decreased from 84% to 40% with the appearance shown in Fig. 4.5(b). Apparently, there was no Pt shell to protect the Ni from dissolving in the acid.

3. Atomic spectra:

Fig. 4.6(a) is a Ni 2p spectrum of acid and heat treated PtNi₅ nanowires after being tested in 1 M H₂SO₄ for one hour at 60°C. Fig. 4.6(b) shows Ni 2p spectra of untreated PtNi₅ nanowires (i), acid and heat treated nanowires (ii) and after corrosion tested (iii). The corresponding Pt 4f spectra are shown in Fig. 4.6(c) and (d). The separation between metallic Ni 2p3/2 and 2p1/2 is 17.4, which agree with the handbook value [13]. The oxidized component had a complicated composition, so they were not resolved in the spectra and only one broad peak was used in the fitting. Both oxidized and metallic components could be observed in Ni 2p spectra in the untreated PtNi₅ nanowires (i). The oxidized Ni component was greatly reduced after the acid and heat treatment process (ii). With further testing in 1 M H₂SO₄ the oxidized feature was almost nonexistent. The disappearance of this oxide feature from sample (ii) to sample (iii) agrees well with the little nickel loss
for the acid and heat treated wires in Fig. 4.1. The metallic component of Ni 2p3/2 remained almost intact.

The energy separation between Pt 4f7/2 and 4f5/2 is 3.3 eV, which agrees very well with the handbook value 3.3 eV [12]. The general shape of the spectra remained the same for all samples. The intensity of the peaks increased significantly from sample (i) to (iii). The peak positions shifted continuously towards low binding energy from sample (i) to (iii). Quantitative analysis of final wires after 1 M H\textsubscript{2}SO\textsubscript{4} testing indicated that the atom ratio of platinum to nickel was 5.3:1 on the wire surface confirming that the surface was a platinum rich layer. The outer most surface could be pure Pt.
Fig. 4.6 (a), (c) X-ray photoelectron emission spectra of Ni2p and Pt4f of acid and heat treated PtNi$_5$ nanowires after being tested in 1 M H$_2$SO$_4$ at 60°C for 1 hr; (b), (d) the evolution of the core levels of Ni2p and Pt4f for (i) untreated PtNi$_5$ nanowires, (ii) acid and heat treated PtNi$_5$ nanowires and (iii) acid and heat treated PtNi$_5$ nanowires after being tested in 1 M H$_2$SO$_4$ at 60°C for 6 hr.
4. X-ray diffraction

XRD results of PtNi\textsubscript{5} nanowires before and after treatment are presented in Fig. 4.7. After reducing from the oxidation of the electrospun fibers with polymers, PtNi\textsubscript{5} nanowires were mainly alloyed, but there was still some NiO, see Fig. 4.7(a), which might be caused by the oxidation of nickel on the wire surface. The existence of NiO was also confirmed by the above HRTEM image and XPS results. After acid and heat treatment it was observed that the alloy peaks moved toward a lower angle meaning a reduction of nickel in the alloy wires. At the same time, there was still a trace amount of NiO after the acid and heat treatment.

![X-ray diffraction results of PtNi\textsubscript{5} nanowires (a) before and (b) after acid and heat treatment.](image)

**Fig. 4.7** X-ray diffraction results of PtNi\textsubscript{5} nanowires (a) before and (b) after acid and heat treatment.
The platinum and nickel were alloyed at a composition of PtNi$_5$ during the electrospinning process after being reduced in H$_2$ at 250°C. Since the wire was exposed to air after reduction and some nickel on the surface might be oxidized, the H$_2$SO$_4$ treatment should have dissolved most of the nickel oxide and also some metallic nickel from the surface. The surface should be platinum rich but might be rough after the nickel was etched off. The subsequent heat treatment in the mixture of Ar and H$_2$ should allow the surface atoms to rearrange. Here the Pt atoms inside the alloy wire might diffuse out to the surface since it preferred to stay on the surface. Both the acid treatment and the subsequent heat treatment appeared necessary to form this platinum shell as shown in the corrosion test described earlier.

4.4 Conclusion

It had been shown that an electrospun nanowire of PtNi$_5$ (atomic ratio) after proper acid and heat treatment formed a core-shell structure with a Pt rich shell sufficient to protect Ni from oxidation and dissolution in strong acid. The resultant Pt-shell nanowires had diameters approximately 10–20 nm and could prevent nickel (>70atom\%) from dissolving in 1 M hot sulfuric acid. This discovery enabled us to develop a strong and stable free-standing catalyst without support.
References


Summary and Further Research Suggestions

This research originated from the idea that a Pt nano network could be used as the catalyst in PEM fuel cells. Electrospinning was a good way to make very thin long fibers. An electrospinning technique was developed to make Pt nanowires in this work.

At first some thick Pt nanowires (20~100 nm) were fabricated, which looked like strings of beads. Their diameters were too large to be competitive with commercial Pt/C nanoparticle catalyst. To make thin wires, it was necessary to check the effects of several spinning parameters on the morphology of composite fibers composed of polymer (PVP) and salt (H₂PtCl₆) after electrospinning. High polymer concentration helped in eliminating beads, but it made the fiber thick as well. High salt concentrations would produce more beads and thinner fibers, while high water/ethanol ratio in solvent also resulted in more beads and thinner fibers.

Meanwhile, it was difficult to spin fibers during the summer. The high humidity in summer prevented fast drying of the spun fibers before reaching the substrate. This problem was solved by controlling environmental humidity and replacing the solvent (ethanol and water mixture) with methanol, which evaporated faster. A drier was also used to blow the jet during spinning to help the evaporation of solvent. A high polymer concentration such as 20 mg/ml, pure methanol solvent, a low feeding rate such as 0.15 ml/hr and a low electric field
strength such as 6 kV across a distance of 6 cm were the best parameters. Pt and Pt alloy nanowires had diameters of 6~20 nm. They were the finest Pt (or even pure metallic) nanowires made by electrospinning, but smaller nanowire diameter was still necessary to save Pt.

Heat treatment of composite nanofibers had been studied. The temperature of 300~400°C was not high enough to eliminate PVP, when the ratio of H₂PtCl₆ in the fiber was low. For pure Pt or Pt rich alloy nanowires, a very slow heat treatment (>10 hours) in the low temperature range (200~300°C) was necessary to keep the wire structure. The wires could appear partially melted during heat treatment when the sample was heated quickly from 200 to 600°C in 3 hours. Adding non-noble metal such as Ni or Fe helped when alloy wires were heated in air, the oxides of Ni and Fe were stable at high temperatures to support the wire structure during heat treatment. Spun fibers were placed between two pieces of sheet glass during heat treatment to make the film flat. As a result, flat catalyst films composed of 6 nm thick Pt alloy nanowires were made almost without beads, and they were large enough to make a 5 cm² MEA.

With the above innovations, especially the heat treatment, most Pt₃Ni wire diameters were as small as 6 nm. This size could be further decreased to 3~4 nm if the wire was treated in acid, dissolving most non-noble metals and therefore the wire would shrink.

In the meantime, Pt alloy nanowires could become porous after H₂SO₄
treatment. The formation process of the porous structure was investigated. The non-uniform composition in a single wire was the prerequisite. Long and porous PtFe nanowires were made, with wire diameters of 15–20 nm, ligaments diameters ~3 nm, and pores sizes 2–6 nm. These Pt alloy porous nanowires had more than 80 atom% Pt, with non-noble metal concentrated in the inner part. This nano size porosity was comparable with commercial Pt/C nanoparticle catalysts in terms of active surface area per unit Pt mass.

When evaluating the electrochemical properties of nanowires, a rotating disk electrode was used and MEAs were made to test these wire catalysts. In acid solution the electrochemically active surface area of nanowire catalysts were measured by cyclic voltametry method. Nanowire catalysts presented much better stability than commercial Pt/C catalysts. Conventional MEA techniques could not be used with the above film catalysts. A new method was developed and the optimal parameters were found. The MEA technique was based on a transfer printing method, and after transfer MEAs were treated in 0.5 M H2SO4 solution at 80°C for 1 hour. The MEA with nanowire catalysts presented very good stability and considerable power density.

While these wires presented much better stability than commercial Pt/C particles in electrochemical tests, this structure was not absolutely stable during extended tests. Pt atoms could diffuse in the cell operation condition when Pt particles or wires were of very tiny size. Core-shell nanowires with thin Pt shells
on thick Ni wires were made, but this kind of wire was still unstable in electrochemical tests because of the dissolution of non-noble metals. Though core-shell PtNi alloy nanowires were not stable in the fuel cell test condition, the Pt shell could protect Ni in the inner core from dissolution in 1 M H₂SO₄ at 60°C. This might be a good catalyst design for other applications.
Suggestions for future research for improving catalysts

Several kinds of nanowires composed of Pt and Pt alloy have been made in this dissertation. Porous Pt alloy nanowires were not absolutely stable in test condition. Pt alloys with a core-shell structure were expected to be more stable because of the lower curvature of Pt shell on the relatively thick Ni alloy core wires, but non-noble metal would separate out and be dissolved during extended periods of operation. Replacing a non-noble metal with carbon as the core material may supply a more stable catalyst for fuel cells because carbon is much more stable than alloyed Ni, and it is less expensive than metal. But making a uniform thin layer on carbon nanofibers is difficult. For future research, a network should be formed on the surface of carbon nanofibers; then further work should be focused on making the network thinner. The method can be electrospinning or other deposition techniques, such as CVD.
Closure

This work has explored the use of wire-like geometries of catalysts that offer self-support. A numerous creative approaches were employed to examine electrospun Pt and Pt alloys, including porous wires and core shell wires. Results look promising and further work will build in these ideas to form the catalysts of tomorrow.