

# Effects of Spin Coating Catalysts on Micro-Fuel Cells Efficiency

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## ABSTRACT

Micro-fuel cells are making breakthroughs with its usefulness for portable electronics. Proton exchange membrane (PEM) is the core of a fuel cell stack. DuPont's Nafion 117 is the current PEM commercially used in larger scale applications. Alternatively, porous silicon (PSi), with much study, displays physical resilience, which Nafion lacks, even though fuel crossover is a continued roadblock. The technique used to fabricate PSi is a repeatable process that is able to fabricate pores on the order of one micron or within the range of 1-10 nm.

Methods for applying catalysts onto the PEM are a central issue. The most common method for applying catalyst is the use of a small commercial paintbrush. This technique, however, produces uneven topography. Spin coating is another common technique, which provides even distribution of fluid onto a particular solid surface. Even catalyst distribution attempts to increase efficiency. Currently, spin coating is commonly used for other applications.

Catalyst topography is expected to have strong correlation to voltage outputs. Modeling and simulation work have been done previously examining efficiency with PSi and how competitive it is with Nafion. [4]

**Keywords:** spin coating, porous silicon (PSi), efficiency, proton exchange membrane (PEM).

## 1 INTRODUCTION

### 1.1 Current Results

In previous work, catalyst was applied with a small commercial paintbrush while this work led to important results. This method resulted in a non-uniform distribution of nanoparticles. The porosity of PSi prior to catalyst application measured as 60-80% porous. After catalyst was applied, the porosity decreased to 45-55%. [1][2] The pore spacing shown through scanning electron microscope (SEM) was measured to be ~2.5  $\mu\text{m}$  between pores. Previous research has also shown that PSi with isopropyl alcohol (IPA) solvent had the potential to reach a maximum output of 0.09-0.15 V. [1]

### 1.2 EDL Theory

The role of electrical double layer (EDL) is important to fuel cell applications owing to the small size of the membrane pores. Many surfaces that are commonly

used, such as glass or in this research, porous silicon, are highly charged. Two important variables regarding EDL are zeta potential and Debye length. Zeta potential is the charge along the surface. Debye length is the distance away from the wall for the zeta potential to decay to the bulk value.

Counterion concentrations are affected by the ratio between the capillary diameter and the Debye length. At any scale, concentration is higher along the walls than it is in the middle of the capillary, which is referred to as the bulk section. At micro-/nano-scale, the Debye length from opposite sides of the capillary wall overlap, thus increasing the counterion concentration. Debye length overlap minimizes the bulk section of the flow. There is no overlap in macro-scale fluidics. [1][3]

Figure 1 illustrates the increase in counterion concentration. [1]

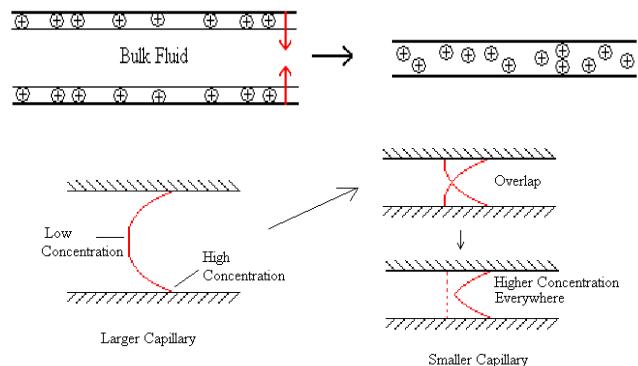


Figure 1: Counterion concentration change due to scale length

Change in counterion concentration affects the transport of the coions from the fuel. At higher counterion concentration, the coions have a higher density of attractive locations to which to attach. This allows coion transport to be less difficult and more efficient.

### 1.3 Spin coating

Spin coating produces even distribution across a surface allowing consistent topography. The most common application for this technique is photolithography on non-porous silicon wafers. In addition to the centrifugal force of the spinning as a key element, the viscosity of the fluid being distributed is also important. The distribution evenness using solvents of different viscosity for the catalyst ink is the main unsteady variable examined in this research.

PSi is distinctive by its rough surface and its hydrophobicity. Hydrophobicity makes it difficult to

distribute any solution that contains a significant percentage of water in the solution. The initial trade off of decreasing water percentage is to increase the percentage of another organic solvent. However, when the viscosity of the organic solvent is too thin, fast evaporation occurs leaving no pattern of the catalyst ink behind therefore the distribution of the nanoparticles cannot be observed with the naked eye.

## 2 METHODS

### 2.1 PEM Fabrication

Porous silicon wafers were fabricated through an anodization process using hydrofluoric acid (HF). Silicon wafers were submerged in a HF solution while a current was passed through an electrolyte. The variables including HF concentration, pH level, current density, potential, resistivity, temperature, duration, and stirring condition could affect the porosity of the resulting PSi. [2] Through the fabrication technique, PSi dimensions from SEMs showed that the pore size ranges 1-1.5  $\mu\text{m}$  with an average of 1.25  $\mu\text{m}$ . The thickness ranges from 100-150  $\mu\text{m}$ . The fabrication was conducted at University of Rochester. [1][2]

Nafion was used as the control PEM, which has a nominal thickness of 183  $\mu\text{m}$  (Nafion® 117CS Membrane by Fuel Cell Store).

### 2.2 Catalyst Preparation

Two catalyst formulations were made. First, thirty-five milligrams of 10% Pt Black or 10% Pt/Ru (1:1) catalyst was mixed in with 8 ml of isopropyl alcohol (91% concentration), 1 ml of 10% Nafion solution (Fuel Cell Store), and 2 ml of deionized (DI) water. Mixing was conducted for 10 min in a Branson 1510 Sonicator.

Second, the same amount of each catalyst was mixed with 8 ml of Acetonitrile UV and 1 ml of 10% Nafion solution. This pair was also sonicated for 10 min.

All catalyst inks were mixed and used at room temperature. Stored catalyst inks were resonicated for 10 minutes before use.

### 2.3 Spin Coating Setup

Two types of PEM were used, which were Nafion and PSi. Nafion was taken directly from the fuel cell stack (car kit by Horizon Fuel Cell Technologies) without additional alterations. PSi, from University of Rochester, was treated with spin coating.

Each piece of PSi was spun while embedded in a Teflon cylinder. The Teflon cylinder has a square crevice with dimensions of 1 cm by 1 cm by 2 mm. Due to the drilling bit limitations; 2 mm was the smallest depth to be produced. Since the height of the seat is much deeper than the thickness of PSi, four layers of carbon paper (Toray Carbon Paper TGPH-120) was added as the “booster seat” in order to have the top surface of the PEM flush along the top

surface of the Teflon cylinder. A cover was clamped to the rotator and positioned over the Teflon cylinder during spinning in order to minimize dust and other airborne substances to settle onto the PEM.

PSi pieces were 0.75 cm by 0.75 cm +/- 0.25 cm. The discrepancy of size was due to cutting larger PSi pieces with an exacto knife in order to fit into the Teflon rotator seat. Figure 2 shows the setup with the Teflon cylinder attached to an analytical rotator (Modulated Speed Rotator by Pine Instruments).



Figure 2: Spin Coating Setup

### 2.4 Catalyst Application

Catalyst volume varied with the type of solvent. Fifteen to twenty  $\mu\text{l}$  of catalyst with IPA solvent was applied on a piece of PSi. Twenty to thirty  $\mu\text{l}$  of catalyst with Acetonitrile UV solvent was applied on another piece of PSi. Both sides of each PEM piece had the same amount of catalyst applied.

Difference in solvent led to difference in drying technique. First, the catalyst with IPA solvent was spun at for 1 min. The rotator was switched on with an initial rpm of 200 and every five seconds from then, 100 rpm was increased, until 600 rpm was reached. The distribution and drying statuses of the catalyst were checked after 1 min. One minute was sufficient for the catalyst to dry. If after one minute, the catalyst was not dried, an additional 30 sec was added to the spinning time.

Second, the catalyst with Acetonitrile UV solvent was only spun for 10 sec at 200 rpm and then dried in a vacuum.

### 2.5 Micro-Fuel Cell Assembly with PSi

A parafilm “M” replacement membrane sized to custom fit to each PSi piece replaced the original Nafion PEM in the fuel cell stack. The parafilm “M” has a thickness of 0.127 mm. A complete assembly is shown in Figure 3. Four screws, one at each corner, kept the entire system together. The membrane with the PEM was the section

subjected to effects of the compression. The tighter the screws were rotated; the more compression to which the membrane was subjected. This may lead to compression directly on top of the PEM. Therefore thickness of the membrane was to be taken into account.



Figure 3: Fuel Cell Stack with PSi

### 3 RESULTS

#### 3.1 Experimental Findings

Endurance test was conducted on spin coated PSi and compared to pre-catalyzed Nafion and paintbrushed PSi. Voltage readings of spin coated Psi was taken using a standard laboratory voltmeter. The readings were taken at 1 min intervals for the first five minutes, then at 5 min intervals for the next fifteen minutes. Two readings were taken at the 105 min and 120 min mark. Nafion and painbrushed PSi readings were taken using a computerized program.

Nafion's output readings had a maximum of 0.525 V even though ~0.50 V was the most consistent reading. [1][4] Figure 4 illustrates this trend. Spin coating on pre-catalyzed Nafion was not done. No adherence was observed when attempts were made to pipette the catalysts onto Nafion pieces.

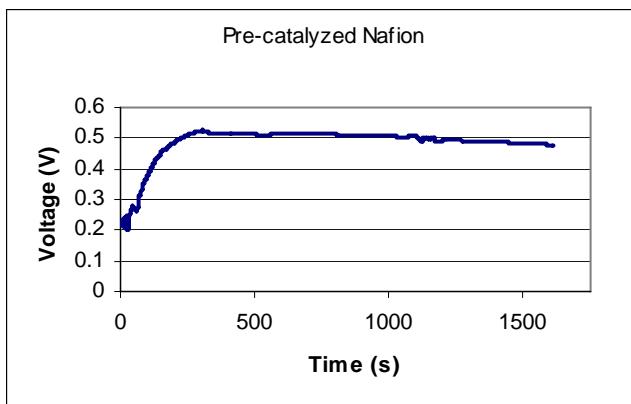


Figure 4: Endurance Test for Pre-Catalyzed Nafion

PSi with IPA solvent did not produce any output. Variables that contributed to the lack of reading include IPA concentration, ambient temperature, amount of applied

catalyst ink concentration, IPA viscosity, etc. The variables that caused the biggest effect were the amount of catalyst ink applied and IPA viscosity. Since IPA has low viscosity, the distribution of the catalyst ink produces a thinner layer on top of the PSi than that of Acetonitrile UV, a solvent with higher viscosity. There was only one layer of catalyst ink applied on each PEM piece. Even with thin layering, multiple layers of thin catalyst ink could assist with catalyst performance.

However, PSi with Acetonitrile UV solvent produced voltage ranged from 0.067 V to 0.002 V (time 0-120 min). The same fuel of 3% Methanol in DI water that was used in previous work was reformulated for this research. This output had the inverse trend that of Nafion. This showed that although Acetonitrile UV was a useful solvent for the catalyst ink, it did not assist with the endurance factor of PSi. Figure 5 shows result for PSi output.

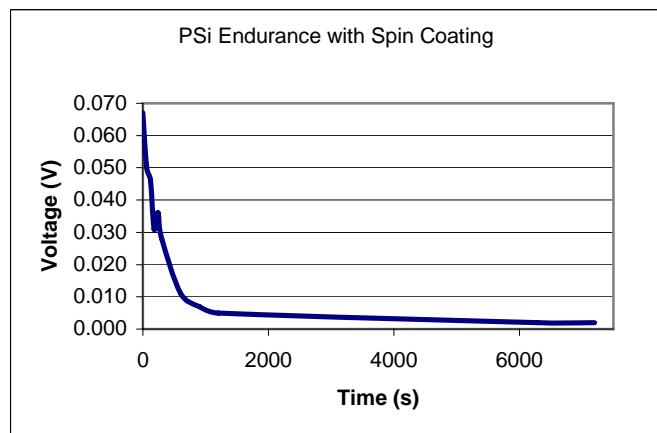


Figure 5: Endurance Test for PSi (spin coating)

Spin coating outputs did not reach comparable levels when compared to previous data. Previous results, illustrated in Figure 6, show that the PSi held a stable reading of ~0.9 V. [1] The catalyst for this particular test was applied with a commercial paintbrush.

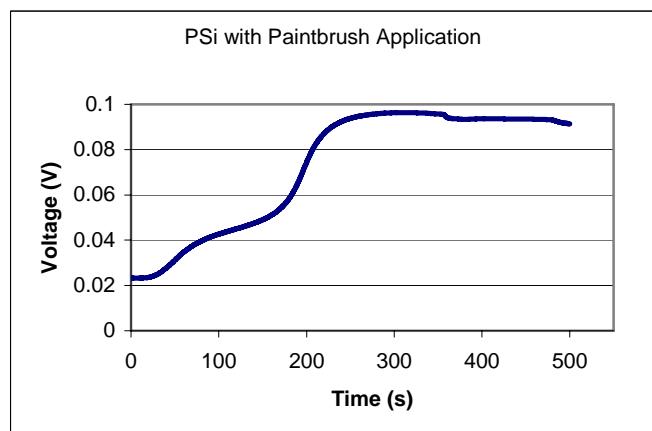


Figure 6: Endurance Test for PSi (paintbrush)

### **3.2 Discussion**

Paintbrush method is still the preferred method for catalyst application. Spin coating maximum output was much lower than that of paintbrush. Additionally, the paintbrush technique showed potential in carrying out even voltage output for an extended amount of time. Spin coating did not, considering the maximum voltage data was taken at the initial point.

The physical contact between the PEM and the paintbrush is hypothesized to be the one of the main reasoning that the catalyst adhered more successfully. Acetonitrile UV has a higher viscosity than other solvents used in the experiments such as 10% Nafion solution and IPA. Higher viscosity causes the solvent to adhere to the surface longer before flowing into the pores. The time frame in which the experiments were conducted potentially were not sufficient for Acetonitrile UV to settle into the initial layers of pores at ambient conditions. However, vacuum drying should assist with this issue. While air is pulled out of the pores, the catalyst solution would flow down in place. Potentially the replacement process created a thin film covering the negative PSi surface.

Neither Psi (paintbrush or spin coating) outputs were close to Nafion output. Many variables contributing to PSi performance includes, catalyst concentration, number of catalyst layers, fuel crossover, size of PEM, pore size, etc. Multiple additional tests need to be conducted in order to narrow down the main variable affecting PSi performance.

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