Efficient Electrocatalyst Utilization: Electrochemical Deposition of Pt Nanoparticles Using Nafion Membrane as a Template

Ju Chou,[†,§] Shrisudersan Jayaraman,[†,||] Asanga D. Ranasinghe,[‡] Eric W. McFarland,[†] Steven K. Buratto,[‡] and Horia Metiu*[,‡]

Department of Chemical Engineering, and Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106

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We deposit Pt particles electrochemically on an electrode covered with a Nafion membrane. Platinum ions travel through the hydrophilic channels of the membrane, and platinum deposits are formed at the place where the channels make contact with the planar electrode. This procedure deposits the catalyst only at the end of the hydrophilic channels that cross the membrane; no catalyst is placed under the hydrophobic domains, where it would not be in contact with the electrolyte. By performing a series of cyclic voltammograms with this system, we show that deposition of the platinum through the membrane achieves better platinum utilization than deposition of platinum on the naked electrode followed by the placement of the membrane on top.

Introduction

Nafion membranes are used as electrolytes in methanol and hydrogen fuel cells. Under the operating conditions the membrane absorbs water and phase separates into hydrophobic (mainly the Teflon backbone) and hydrophilic (mainly water, protons, and the SO_3^- groups) domains. Proton transport from the anode to the cathode takes place through the hydrophilic channels.[1−3] To participate in electricity production these channels must satisfy two conditions: they must provide a continuous pathway from the anode to the cathode, and they must have a catalyst at both ends. Figure 1 shows a schematic description of a cell in which the catalytic particles painted red participate in electrochemistry; those shown in yellow do not and are wasted. Since the cost of Pt and Pt/Ru catalysts is high, it would be beneficial to place the catalyst only in the channels that traverse the membrane. In a previous paper, we have shown that this can be done, by depositing the Pt particles electrochemically, through the Nafion membrane.[4]

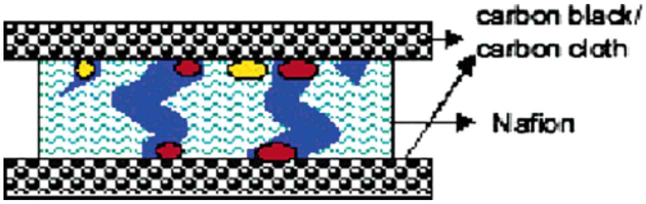

Figure 1. Schematic of ion-conducting channels in the Nafion membrane placed between two electrodes. The hydrophilic channels are shown in blue. The yellow and red spots are the catalyst particles. Only the catalytic particles in red contribute to the current in the cell; particles in yellow are wasted.

The concept described above assumes that a catalyst particle that is located under a hydrophobic domain is not in contact with water and therefore cannot produce protons (at the anode) or be reached by them (at the cathode). However, this assumption may fail for several reasons. It is possible that water penetrates between the electrode and the hydrophobic domains in the membrane and makes contact with all catalytic particles. There is also a remote possibility that when the membrane is deposited on the electrodes, the platinum catalyst interacts with the water in the membrane and favors the formation of a hydrophilic channel around itself. Finally, the network of hydrophilic channels may be three-dimensional and so highly branched that a proton in any hydrophilic channel will always find a path to travel from one end of the membrane to the other. While we believe that these possibilities are not very likely, we have been looking for an experiment that will show that catalytic particles that are not in a channel traversing the membrane are wasted. We describe here such an experiment.

The idea of the experiment is simple. We place a Nafion membrane on top of a planar electrode and deposit Pt on the electrode, through the membrane. We perform cyclic voltammetry with this system and find results that are characteristic of the electrochemistry on platinum. Next, we dissolve the membrane and perform the same cyclic voltammetry on the platinum particles that are now directly exposed to the electrolyte solution. We find that the voltammogram produced by this system is very similar to that obtained when the membrane is present, except that the amount of current passed is larger. We expect this, since the mobility of the protons through the hydrophilic channels of the membrane is likely to be lower than in the solution. Next, we put the membrane back on the electrode and perform the cyclic voltammogram again. The current passing through the system is now substantially lower. We take this to mean that the hydrophobic domains of the membrane cover some of the platinum particles rendering them electrochemically inactive. Finally, to show that no platinum particles have been lost in the system during these manipulations, we remove the membrane again and determine the amount of Pt on the electrode by energy dispersion spectroscopy (EDS). We find that the amount of Pt is the same as that present after we

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* To whom all correspondence should be addressed. Phone: 805 893-2256. Fax: 805 893-4120. E-mail: metiu@chem.ucsb.edu.

[†] Department of Chemical Engineering.

[‡] Department of Chemistry and Biochemistry.

[§] Current address: Department of Chemistry and Physics, Southeastern Louisiana University, Hammond, LA 70402.

[||] Current address: Corning Incorporated, 1 Science Center Drive, Corning, NY 14831.

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first dissolved the membrane. In the remainder of this article, we describe in more detail how these experiments were performed.

Experimental Details

We use in these experiments a fluorine-doped tin oxide (FTO) planar electrode (Tec 8, 2.3 mm thick glass, Hartford Glass Co., Hartford City, IN) because it produces no background current in the cyclic voltammogram of Pt deposited on it. Prior to the deposition of the Nafion membrane, the electrode is sonicated in a 50:50 ethanol−water mixture for 15 min, then sonicated in DI water, then rinsed in DI water, and, finally, dried in air.

We used a Nafion solution (Nafion perfluorinated ion-exchange resin, 5 wt % solution in a mixture of lower aliphatic alcohols and 15−20% water) purchased from Aldrich. To prepare the membrane we dip the FTO electrode in the solution for 20 s, then slowly pull it out and let it dry for half an hour in air. This method has been described previously in the literature.[3,4] The thickness of Nafion membrane is about 2 to ~3 μm, as determined by scanning electron microscopy (SEM). After the membrane was dried, we deposited Pt by electrochemical pulse deposition[5] in a three-electrode system with a Pt mesh as the counter electrode and Ag/AgCl as the reference electrode. We use a symmetrical pulse sequence starting with a −0.5 V pulse, for 50 μs, followed by a +0.5 V pulse for 50 μs. Various samples were prepared by applying this sequence for 3, 10, or 15 min. These electrochemical experiments were performed using a potentiostat (EG&G 273A, Princeton Applied Research) controlled by the software written in Lab View. All potentials reported in this paper are versus the Ag/AgCl electrode.

The active surface area of the catalysts was determined from the cyclic voltammograms (CV) in 0.5 M H_2SO_4 solution purged, for at least 20 min, with high-purity nitrogen. Stable CVs of Pt are obtained after more than 20 cycles. The electrochemical surface area of a Pt catalyst is determined by the integrated currents of hydrogen adsorption and desorption. This method is based on the fact that each platinum surface atom adsorbs one hydrogen atom and the charge associated with adsorption−desorption reactions provides the number of active Pt sites and the surface area.

The platinum deposits were imaged by scanning electron microscopy (Philips XL-30 ESEM-FEG, ESEM stands for environmental scanning electron microscope and FEG for field emission gun, with which the ESEM is equipped).

Results and Discussion

Pt was deposited through Nafion, by using a variety of pulse times and total deposition times, in a 10 mM or a 1 mM H_2PtCl_6 solution. In some experiments we remove the Nafion membrane by dissolving the membrane into ethanol solution. After dissolving the membrane the Pt nanoparticles remain on the electrode surface as evidenced by energy dispersion spectroscopy (EDS) and scanning electron microscopy (SEM).

For comparison, the deposition of Pt was also performed on the FTO electrode without Nafion. Figure 2 shows representative SEM images of Pt nanoparticles deposited directly on the FTO support or through the Nafion membrane affixed to it. The SEM images were obtained after dissolving the Nafion and letting the surface dry for at least 30 min.

When the electrode is not covered by Nafion, the morphology of Pt varies with deposition parameters (Figure 2a−c). The size and the density of the Pt clusters become larger as the deposition time increases.

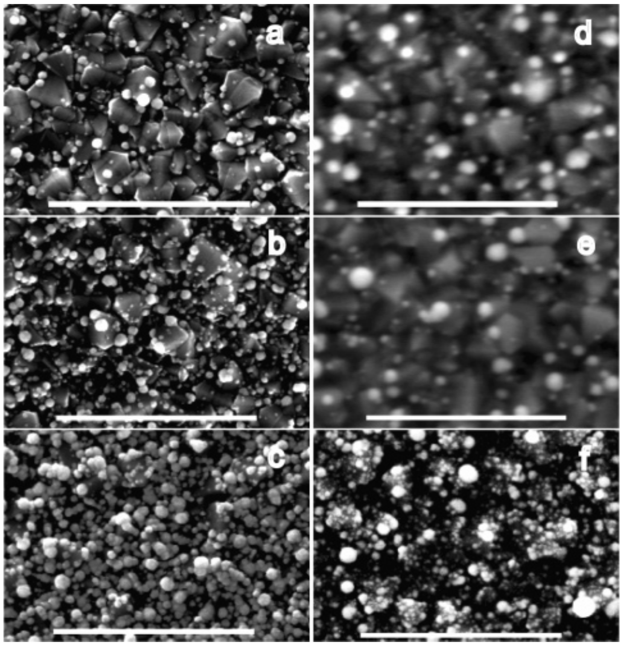

Figure 2. SEM images of Pt nanoparticles on FTO obtained by pulse deposition without Nafion (a−c) and with Nafion (d−f). Pulse potential from −0.5 to +0.5 V, pulse time 50 μs/50 μs, total deposition time is 3 min for (a) and (d), 5 min for (b) and (e), and 10 min for (c) and (f). All depositions were performed in 1 mM H_2PtCl_6. All the scale bars are 2 μm.

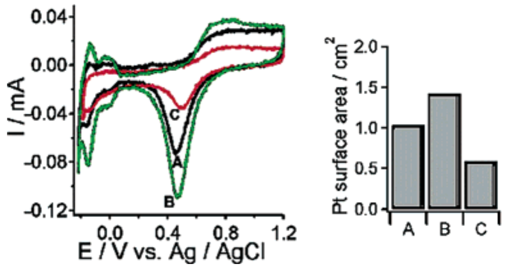

Figure 3. CVs (left) of Pt nanoparticles on the FTO electrode in 0.5 M H_2SO_4 solution purged with nitrogen for 30 min. Scan rate: 0.1 V/s. Histogram (right) of the surface areas of Pt. (A) Nafion-coated Pt electrode, (B) Nafion-removed Pt electrode, and (C) Nafion-recast Pt electrode.

The morphology of the particles deposited through Nafion is shown in Figure 2d−f. Because Nafion can be destroyed by a high-energy electron beam, we use initially a low-energy beam to image the electrode surface with the Nafion membrane on it. No Pt particles are observed on the top of the membrane (data not shown here). Therefore, the Pt nanoparticles seen after removing the membrane were located at the Nafion−electrode interface. We expect this, since one can hardly imagine that electrochemical reduction of the Pt ions can take place away from the electrode. When Pt is deposited through the membrane, the number of clusters formed per unit area is independent of the deposition time. This behavior, which is unlike that observed when the membrane is absent, suggests that the nucleation and the growth of the cluster takes place only in the hydrophilic channels that cross the membrane. In a previous paper we have shown that metal wires can be grown inside the membrane, in the hydrophilic channels.[4]

We used cyclic voltammetry to study the electrochemical properties of the Pt clusters produced by different preparation methods. The results and the conditions under which the CVs were obtained are described in the caption to Figure 3. Curve A in Figure 3 shows the CV obtained when the Pt clusters were

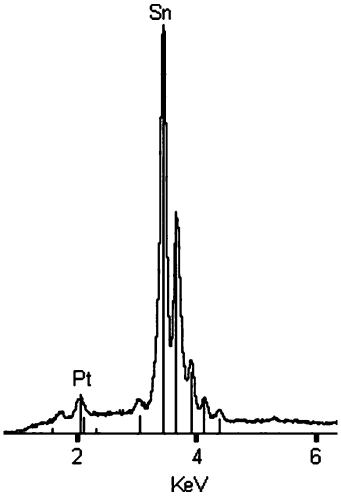

Figure 4. ED spectrum of Pt deposition after first removal of Nafion. The spectrum after the second removal is identical.

covered by the Nafion membrane. The shape of the CV is typical of Pt in a sulfuric acid solution. Curve B was obtained after the Nafion membrane was dissolved. The removal of the membrane caused a slight increase of the current. A larger current for a Pt electrode without Nafion was observed by other groups.[6,7] We assume that the increased current is due to the fact that ion transport is more facile in solution than through the membrane. Curve C shows the CV obtained after Nafion was redeposited on the electrode prepared by step B (FTO with Pt on it). The current in voltammogram C is substantially decreased as compared to that of voltammogram B. We attribute this to the fact that when the membrane is placed on the electrode with Pt on it, some of the Pt clusters are covered by the hydrophobic domains in the Nafion and are not accessible to the protons. Finally, to make sure that no Pt clusters have been removed from the electrode during the above manipulations, we removed the Nafion again and analyzed the surface composition by EDS. The EDS spectrum of this sample is the same as that obtained when we first dissolved the membrane (Figure 4). After the first removal of the membrane, the area under the Pt peak is 4.28% of the area under the Sn peak; after the second removal, it is 4.34%. This means that no Pt was removed from the surface during these manipulations.

Though all electrodes contain the same Pt particles, the currents generated in the three experiments are different. Based on the integrated current under the peak for the desorption/adsorption of hydrogen, we have estimated that the area of the accessible Pt surface is 1.04 cm^2, 1.41 cm^2, and 0.59 cm^2 for Nafion-coated, Nafion-removed, and Nafion-recast electrodes, respectively (see the histogram in Figure 3, right side). The difference in accessible Pt surface area between the Nafion-coated Pt electrode and the recast Nafion electrode represents the amount of current blocked by the hydrophobic domains in Nafion, when the membrane is deposited on the Pt/FTO electrode. Almost 43% of current is blocked by recasting the membrane. The same trend is observed when we use the platinum oxide reduction peaks to calculate the area of the Pt particles accessible to the electrolyte.

Discussion

In evaluating these results, one must keep in mind that polymeric membranes are not in thermodynamic equilibrium and their properties depend on the method of preparation. For this reason, it is not prudent to assume that the same results will be obtained on the membrane of a commercial fuel cell. In addition, our membrane is in contact with an electrolyte and has therefore the highest hydration possible. It is likely that this is why the size of the hydrophilic domains, as imaged by the size of Pt deposits, is larger than that generally accepted.

Nevertheless, our results indicate that, for the membranes used here, the utilization of electrochemically deposited Pt, by using Nafion as a template, is higher than that obtained when Pt is deposited first and then the membrane. Our measurements suggest that an electrochemical deposition of the catalyst, through the membrane, may achieve a 43% reduction in Pt loading. This method has the additional advantage that it can control accurately, through Faraday's law, the size of the catalytic particles (the number of particles per unit area is determined by the morphology of the channels in the membrane). If the catalytic activity is size dependent one can use this method to find and use the optimum size. Finally, we note that the method can be applied to deposit any catalyst, including multicomponent ones.

The deposition of Pt through the Nafion may be an effective way to place the catalyst in the fuel cell and make all catalyst accessible to the electrochemical process. We are currently pursuing this line of work.

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