

Short communication

Methanol conditioning for improved performance of formic acid fuel cells

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Abstract

This paper considers the effect of methanol pretreatment on the performance of a direct formic acid fuel cell (DFAFC). We find that conditioning of the cell in methanol results in a substantial increase in current. The current at 60 °C increases from 95 to 320 mA/cm² at 0.3 V. The maximum power density increases from 33 to 119 mW/cm². The cell resistance decreases from 0.37 to 0.32 Ω cm². CO stripping experiments show that the catalyst is not being greatly affected by these changes. Our interpretation of the data is that the anode layer of membrane electrolyte assembly (MEA) undergoes some change during the methanol conditioning. The change improves the performance.

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1. Introduction

In a previous paper, our group [1,2] has demonstrated that formic acid is a viable fuel for direct fuel cell systems. Direct formic acid fuel cells (DFAFCs) using a Pt/Pd nanoparticle catalyst [3,4] have higher open circuit potentials and current densities than direct methanol fuel cells (DMFCs), lower crossover, and a wider range of operation [1].

In this paper, we investigate the influence of methanol and hydrogen conditioning on the behavior of the DFAFC. Recall, that the anodes of DMFCs are normally conditioned in hydrogen prior to use [5,6]. The conditioning process lowers the cell resistance and increases the current. In contrast, methanol conditioning (i.e. running the cell with methanol) has little irreversible effect on the steady state cell performance (CO builds up on the surface, but the CO is easy to remove). If anything, there is a slight loss of performance [7]. Interestingly, in many cases the loss of performance is reversed when the cell is recondition in hydrogen.

When we started these experiments, we expected a similar effect with a direct formic acid fuel cell, i.e. an increase in performance after hydrogen conditioning; little change or a

small decrease in performance after methanol conditioning. However, we were surprised to find just the opposite effect. If we ran the cell with methanol and then switched to formic acid the currents were much higher than before the methanol treatment. Hydrogen conditioning *decreased* the performance back to the former level. We also found a new conditioning procedure that allows us to freeze in the improvements. The purpose of this paper is to present the results and show the performance enhancements that are obtained.

2. Experiment

All of the measurements reported here were made on a UIUC fuel cell described elsewhere [1]. The fuel cell contained standard graphite flowfields, a Nafion 117-based MEA. The MEA was fabricated in house using a 'direct paint' technique to apply the catalyst layers to a Nafion 117 membrane as described by Rice et al. [1]. The catalyst was first dispersed in deionized, Millipore filtered water and 5 weight percent Nafion solution (1200 EW, Solution technology Inc.). The cathode contained approximately 7 mg/cm² of unsupported platinum black (Johnson Matthey fuel cell grade, HiSpec 6000), while the anode contained approximately 4 mg/cm² platinum black that had been

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coated with a fraction of a monolayer of palladium via spontaneous deposition [3]. Carbon cloth diffusion layers (E-Tek) and 35 durometer Si gasketing were placed between the graphite flow channels and the MEA as described in Rice et al. [1,4]. The catalyst had a geometric area of 5 cm^2 .

Two different conditioning procedures were used: a hydrogen conditioning and a methanol conditioning. During the hydrogen conditioning, 100 sccm of hydrogen humidified to 75°C was fed into the anode of the cell, 200 sccm of oxygen humidified to 70°C was fed into the cathode, and then the cell was run for 40 min with a load sufficient to hold the cell potential at 0.6 V. Then the flow of formic acid was begun.

In the methanol conditioning, 1 ml/min of 1 M methanol made from Fisher methanol was fed to the anode, and 100 sccm of O_2 humidified to 70°C was then fed to the cathode. A series of loads were applied to the cell so that the cell polarization was slowly ramped from 0.4 to 0.1 V. Then the methanol was flushed from the cell with deionized, Millipore filtered water, and the flow of formic acid was begun.

During the fuel cell testing, the cell was conditioned either in hydrogen or in methanol. Then 1 ml/min of 9 M formic acid made from Aldrich, 96% A.C.S. grade formic acid was fed into the anode, 100 sccm of O_2 humidified to 70°C was fed to the cathode. Then cell polarization measurements were performed. The cell was started at the open cell potential. Then the potential was varied in 50 mV steps down to 0.1 V. At each step, we waited 30 s for the voltages to settle. Then the potential was averaged over a 30 s period. We also did life tests, where the cell was held at a fixed potential for up to 10 h and the current was measured as a function of time. All the flow rates, the backpressures, temperatures, and the load of the cell were controlled by using a fuel cell testing station (Fuel Cell Technologies Inc.). No backpressure was used in any of the experiments. The cell temperature was set at 60°C during all of the experiments reported here.

CO stripping cyclic voltammogram (CV) was acquired in situ by saturating the surface of the anode with CO, purging the cell with argon and then acquiring the CV using a Solartron SI 1287 potentiostat and a dynamic hydrogen reference electrode (DHE). The DHE was created by feeding 100 sccm of humidified H_2 to the cathode with a backpressure of 10 psig. During the adsorption of CO, the cell potential was applied at 0.1 V versus DHE the anode was exposed to 460 sccm of a 1% CO in argon gas mixture humidified at 75°C for 60 min with backpressure of 10 psig. The anode flow channel was then purged for 20 min by flowing 460 sccm of humidified argon with the backpressure of 10 psig. The cell potential was maintained at 0.1 V versus DHE during the purging. The adsorbed carbon monoxide was stripped from the anode catalyst layer by applying cyclic potential sweep between 0.1 and 0.72 V versus DHE at the scan rate of 5 mV/min. The first positive going scan is reported in Fig. 3.

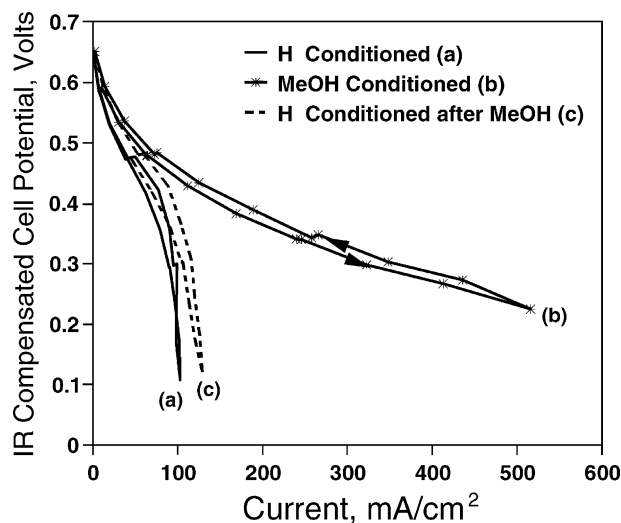


Fig. 1. The influence of various conditioning processes on the V/I characteristics of the direct formic acid fuel cell at 60°C , and 9 M formic acid: (a) after hydrogen conditioning, (b) after subsequent methanol conditioning, and (c) after subsequent hydrogen conditioning.

3. Results

Fig. 1 shows the results of a series of experiments where we conditioned the cell in hydrogen, measured a cell polarization curve, reconditioned the cell in methanol and measured a cell polarization curve, then reconditioned in hydrogen and measured a third cell polarization curve. All of the cell polarization curves were measured at 60°C .

The first cell polarization curve is similar to those we reported previously [1]. The potential of the cell falls from 0.65 to 0.3 V as the current rises from 0 to 95 mA/cm^2 . Then there is a rapid drop off in potential. The cell produces a maximum of 113 mA/cm^2 .

When the cell is conditioned in methanol, the V/I curve changes greatly. In this case, the cell produces 320 mA/cm^2 at a potential of 0.3 V. We also find that the current is slightly higher on the reverse scan. Interestingly, the potential curves are very similar in the high potential region suggesting that something is changing once the current exceeds about 50 mA/cm^2 .

Surprisingly, the improved cell performance disappears when the cell is reconditioned in hydrogen. In this case, the currents are only slightly higher than those found in the initial experiments.

Fig. 2 shows the same experimental data from the Fig. 1 in terms of the power density. For the hydrogen-conditioned cell, the power density increases initially until it reaches a maximum value of 33 mW/cm^2 , followed by a sharp decrease. For the methanol-conditioned cell, the power density increased up to 119 mW/cm^2 and then it leveled off without a sharp decrease.

The effect of the methanol conditioning on the high frequency cell resistance has also been measured. The cell

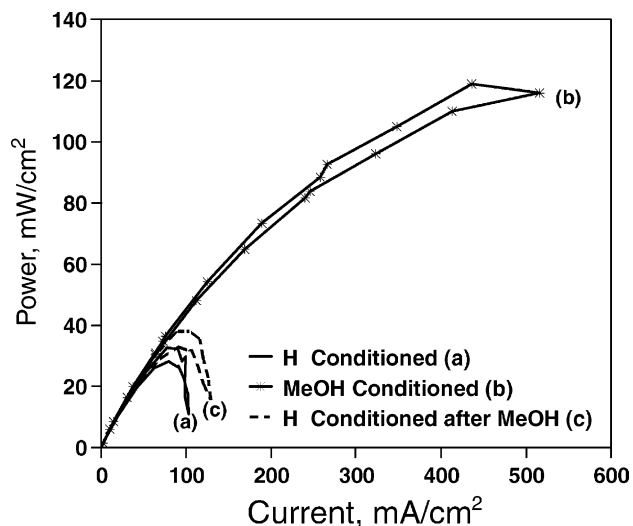


Fig. 2. The influence of various conditioning processes on the power output from the direct formic acid fuel cell at 60 °C, and 9 M formic acid: (a) after hydrogen conditioning, and (b) after subsequent methanol conditioning (c) after subsequent hydrogen conditioning.

showed an average resistance of $0.36 \Omega \text{ cm}^2$ after hydrogen conditioning and $0.31 \Omega \text{ cm}^2$ after the methanol conditioning.

Fig. 3 shows the CO stripping CV after hydrogen conditioning and after the methanol conditioning. After hydrogen conditioning, the CV shows a single sharp peak at 618 mV versus DHE. The peak shifts to 612 mV versus DHE after methanol conditioning and the peak broadens significantly. Interesting, the integrated area under the peak did not change within the experimental error during the methanol conditioning process. The electrochemical

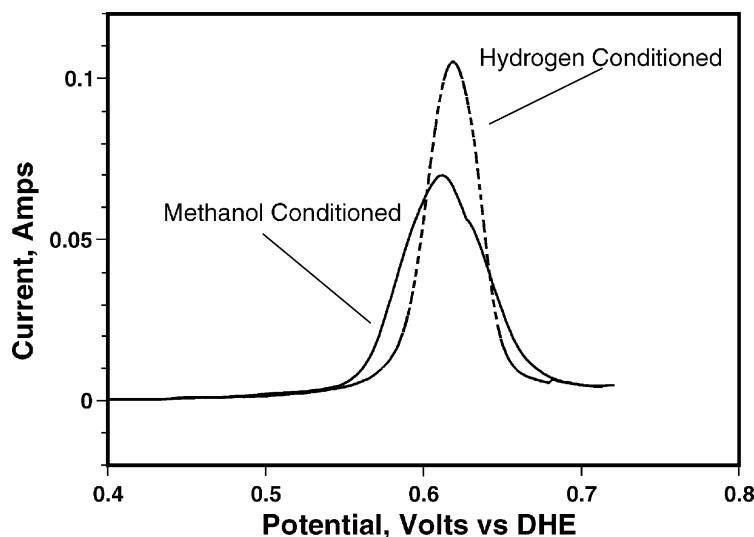


Fig. 3. The influence of various conditioning processes on the CO stripping at 60 °C; (a) after hydrogen conditioning, and (b) after subsequent methanol conditioning. In each case, the sample was exposed to 0.1% CO in argon, the CO was purged from the cell and then the CO stripping peaks were measured. The electrochemical surface area of the sample was 4540 cm^2 after hydrogen conditioning and 4640 cm^2 after methanol conditioning.

surface area, measured via the area under the hydrogen evolution peak showed a slight increase in the electrochemical surface area, from 4540 to 4640 cm^2 during the methanol conditioning process. However, this change is insufficient to account for the changes in behavior in Fig. 1.

Several variations of the conditioning procedures were also tested. One conditioning process that was tried was to feed methanol into the cell, without applying a load and experiments were done to see if the performance of the cell changed. Experimentally, there appeared to be a small enhancement in the current after conditioning, but the effect is much smaller than when load is applied during the conditioning process. Thus, it seems that loading of the cell is a critical part of the enhancement process. The methanol concentration during the conditioning process was also varied. The best performance came with a 3 M methanol solution.

The one weakness of the methods used to condition the membranes in Fig. 1 is that the conditioning process is reversible. The current goes up after methanol conditioning and down again after subsequent treatment in hydrogen. We have also found another procedure that produces a permanent enhancement in the fuel cell performance. The procedure is to start with a freshly painted membrane, condition in 3 M methanol at 30 °C, heat the membrane to 60 °C under load, then repeat the conditioning process with 1 M methanol. MEAs conditioned in this way maintained their enhanced activity in 10 h life tests and the MEAs can be removed and reinserted several days later without degradation in performance. The activity dropped slightly after hydrogen conditioning, but the activity was restored once the cell ran for a 30 min in formic acid.

4. Discussion

The results here did not come out as expected. Figs. 1 and 2 show that methanol conditioning increases the maximum current produced by the fuel cell while hydrogen conditioning reduces the maximum current. Yet, the open cell potential and the behavior below 50 mA/cm^2 are very similar with the two conditioning processes. There are also small changes in cell resistance, but those changes are not large enough to account for the change in behavior. Also, the conditioning process is most effective when load is applied to the cell during the conditioning process. The application of load is critical to the success of the conditioning process.

The experiments show that the changes in the catalyst itself is insufficient to account for the changes in performance. Fig. 3 shows that the CO CV peak is broadened during methanol conditioning, but the peak position and the area of the peak remains constant. If the methanol was substantially changing the catalytic activity of the nanoparticles, one would expect substantial changes in the position of the CO stripping peak. Yet, only a 6 mV peak shift is observed. The area of the CO stripping peak is constant before and after the methanol conditioning. If the methanol were removing impurities from the nanoparticles, the area of the CO stripping peak should change. We do see peak broadening as expected if the distribution of planes in the nanoparticles changed [8–10], but the effects do not appear to be large enough to produce the changes in the current observed in Fig. 1.

We also believe that the methanol conditioning process is not changing the flow fields or the carbon cloth. Recall, that the conditioning process works best if load is applied during the conditioning process. It is hard to see how the application of load during conditioning would affect characteristics of the flow fields or the carbon cloth since the most of the voltage drop in the cell occurs at the membrane. On the other hand, treatment of the membrane under load is known to affect the structure of the anode layer [5–7]. Therefore, there is reason to suspect that the conditioning process is changing the anode layer.

Changes in the structure of the anode layer could account for the results observed here. Recall, that the anode layer is formed from an ink containing Pt/Pd nanoparticles and Nafion in a solvent base. When the ink dries, the pores in the Nafion are initially unoriented, but the pores become oriented when load is applied. We find that methanol conditioning under load substantially improves cell performance, while simply doing the same process without loading the cell has a much smaller effect. Therefore, it seems that loading the membrane is an important part of the conditioning process. Loading is also known to result in pore alignment [6]. Thus, pore alignment could be part of the reason that methanol conditioning is effective.

Another issue is that CO_2 bubbles form when the cell is loaded. The CO_2 bubbles can induce porosity in the cast Nafion film provided the film has not fully dried when the conditioning is started.

At this point, we do not know exactly what the methanol is doing. However, we observe reproducible enhancements in fuel cell performance that are only seen when a load is applied to the cell during the conditioning process.

5. Conclusions

In summary then, in this paper we have demonstrated that methanol conditioning is more effective than hydrogen conditioning for the activation of fuel cells for formic acid. The cell polarization curves in Fig. 1 clearly show that the methanol conditioning increases the performance of the direct formic acid fuel cell. Methanol conditioning increases the current and power densities, and decreases the cell resistances but does not change the open circuit potential. We attribute the changes to changes in the anode layer that occur during the conditioning process.

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