DIRECT METHANOL FUEL CELLS:
CATALYST IONOMER CONTENT AND ANODE PERFORMANCE

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ABSTRACT

In a study of DMFC anode catalyst layers, we have found that addition of recast ionomer does not improve anode performance when some unsupported PtRu catalysts are used. It seems that the protonic conductivity of a Ru oxide component in such catalysts is sufficient to allow effective utilization of catalyst sites. To examine possible interpenetration of catalyst and membrane material, ultramicrotomed thin sections of the MEA were examined by SEM. Images of such sections have not revealed significant catalyst/membrane interpenetration, supporting the interpretation that hydrous RuOx may provide sufficient protonic conductivity in some PtRu catalyst layers prepared with no added ionomer.

INTRODUCTION

Thin film catalyst layers for electrodes structures, a technology developed at Los Alamos National Laboratory (LANL) (1, 2) have been utilized in much of recent work involving both hydrogen and direct methanol polymer electrolyte fuel cells. Results obtained with such catalyst layers illustrate the importance of the thinness of the catalyst films with respect to proton and reactant accessibility to catalyst sites and, in the case of the direct methanol fuel cell (DMFC), CO2 removal. These thin catalyst layers are cast from dispersions of the catalyst particles in an aqueous, solubilized ionomer solution. Not only does the inclusion of the recast ionomer within the catalyst layer provide structural integrity to the catalyst layer; it has also been shown to be essential for sufficient ionic conductivity within the electrode structure. By varying the relative weight percentages (and hence volume percentages) of ionomer and catalyst in the catalyst layer, the relative ionic and electronic conductivities in the catalyst layer are varied, as is the average density of the layer. It has been recognized for some time that the optimal structure for high catalyst utilization is a catalyst layer that is as thin as possible, with an appropriate mixture of catalyst and ionomer (1, 3). However, past work has focused on carbon supported Pt catalysts utilized in the hydrogen PEFC, not on unsupported PtRu and Pt black catalysts used in the anode and cathode, respectively, of the DMFC. In the work reported in this paper, the wt. % of ionomer in thin film catalyst layers prepared for DMFC anodes was systematically varied to determine the effect, if any, on DMFC performance.
EXPERIMENTAL

Pretreatment of the proton form of the Nafion 117 membrane, preparation of membrane electrode assemblies (MEA) for a DMFC using a decal technique, and the single-cell fuel cell hardware have been previously described (2) as has the cell testing system used (4). Two unsupported PtRu blacks of nominal 1:1 atomic ratio were used, one supplied by E-TEK, Inc., Natick, MA, and the other by Johnson Matthey. Anode inks were made by dispersing appropriate amounts of the PtRu catalyst, deionized water and 5% Nafion solution (900 equivalent weight (EW), Solution Technology Inc.). The cathode inks contained unsupported Pt black (30 m²/g, Johnson-Matthey), deionized water and 5% Nafion solution (1100 EW Solution Technology Inc.). The geometric active area of all the MEAs prepared was 5 cm².

In all experiments, 1 mol/L methanol solution was pumped through the DMFC anode flow field at 1 – 2 mL/min. A back pressure, which varied with cell operating temperature, was imposed upon the anode outlet flow at temperatures above 80°C to ensure that the membrane would be in contact with a liquid solution of methanol. When operated in fuel cell mode, the cathode gas feed was air, at 60 psig pressure and a flow rate of 0.5 L/min. The air was sometimes pre-humidified at the same temperature as the operating temperature of the cell; occasionally no humidification of the air was used. When operated in driven cell mode to measure methanol anode polarization, the cathode gas was humidified hydrogen. The back pressures and humidification temperatures of the hydrogen gas varied with the operating temperature of the cell.

To prepare samples of MEAs for microscopy examination, 1 mm wide strips were cut from the middle of a MEA, the performance of which had been previously evaluated in a fuel cell. A silicone embedding mold was slit to open when bent and the MEA strip was positioned in the slit to allow cross-sectioning. LR White epoxy in the “hard” formulation was used as the embedding resin. Sections of selected MEAs were prepared by ultramicrotomy using a Reichert Ultracut S ultramicrotome. All sections were cut using a diamond knife for materials science from SPI Supplies with a clearance angle of 4°. Sections were cut with the interfaces in the MEAs perpendicular to the knife edge. Best results were obtained using a cutting speed of 0.05 mm/s and section thickness of 2.5 μm. The sections were retrieved from the water bath contained in the diamond knife boat onto Formvar-coated copper grids. The sections were examined with a JEOL JSM-6300FXV scanning electron microscope (SEM) using 25 kV accelerating voltage and a working distance of ca. 15 mm.

X-ray diffraction (XRD) data for the anode catalyst powders were obtained using a Siemens diffractometer D5000. The operating conditions were 50 kV accelerating voltage and 40 mA of beam current using Cu Kα radiation with a Ge crystal monochromator.
RESULTS AND DISCUSSION

The anode catalyst used in this series of experiments was an unsupported alloy with a 1:1 PtRu atomic ratio, designated as RV3030, supplied by E-TEK, Inc. of Natick, MA. The loading of the PtRu alloy was kept at 2 ± 0.3 mg/cm². The wt. % of recast ionomer (900 EW) in the anode catalyst layers was varied from 0 % to 30 %. It was found that decreasing the amount of solubilized ionomer resulted in inks that were increasingly more difficult to paint on the Teflon blank (from which the catalyst film is transferred in a “decal” process to the membrane). With no recast ionomer in the anode ink, it became necessary to change the ink solvent from deionized water to isopropanol in order to obtain an ink that would wet the Teflon blank. All MEAs that were tested contained, in addition to the various anode catalyst layers, Nafion™ 117 membranes and cathode catalyst layers composed of 90 wt. % Pt black, loaded at 2.5 ± 0.5 mg/cm², and 10 wt. % recast ionomer (1100 EW).

The MEAs were first tested in a cell using a 1 mol/L aqueous methanol feed to the anode and humidified hydrogen gas to the cathode side of the cell. The cathode in this driven cell configuration acts as a counter/reference hydrogen electrode. To investigate anode catalyst layer performance in the oxidation of methanol, anode current dependence on potential vs. the H₂ electrode was measured. These anode polarization data provide a direct tool for comparing activities of anode catalyst layers. As shown in Figure 1, the current density achieved at an overpotential of 0.4 V (RHE) during a potential scan of the anode at 2 mV/s increased with decreasing wt. % of recast ionomer in the anode catalyst layer. This trend was observed at all temperatures tested. It was also repeated when the MEAs were operated in DMFC configuration, as shown in Figure 2, pointing to the dominant effect of the anode on overall DMFC performance. As the recast ionomer in the catalyst layer is an ionic conductor, and hence should enable mobility of hydrogen ions in the layer, the results shown in figures 1 and 2 were unexpected.

Several reasons can be hypothesized for this trend of increased current with decreased wt. % of recast ionomer in these PtRu anode catalyst layers. At given precious metal loading, decreasing the wt. % (and hence vol. %) of recast ionomer would decrease anode catalyst layer thickness with possible beneficial effects. For example, if hot pressing of the anode catalyst layer to the Nafion 117 membrane results in some embedding of catalyst into the membrane, a larger fraction of PtRu catalyst sites may establish sufficient protonic contact with the membrane when the catalyst layer is thinner. It can also be argued in the same context that less recast ionomer in the catalyst layer would result in a catalyst layer of greater hardness that would “bite” more deeply into the polymeric membrane. Thus, for the same loading of PtRu, the current achieved could increase if more significant catalyst/membrane interpenetration takes place during hot press. The finding presented in figure 1 could also mean that a possible limitation to catalyst utilization is poor electronic conductivity of the catalyst layer, since the electronic conductivity would decrease with increasing ionomer content in the composite layer.

Figure 3 shows a scanning electron micrograph of a cross section of a MEA. The MEA section is supported on a Cu grid covered with a thin Formvar polymer film. This particular MEA, with no recast ionomer in the anode catalyst layer, had been tested in a DMFC. The cross section displays carbon cloth electrode backings on either side of the anode and cathode catalyst layers. It can be seen that both the anode and cathode catalyst
layers are noncontinuous in this section and similar discontinuities were observed in other sections of this MEA, as well as other MEAs. It is unknown as to whether such cracking of the catalyst layers occurred during preparation of the MEA, operation of the fuel cell, embedding of the used MEA into resin, or sectioning of the embedded MEA.

Figures 4, 5 and 6 are micrographs of the anode catalyst layers containing no recast ionomer, 10.5 % recast ionomer, and 30.7 % recast ionomer in the anode catalyst layers, respectively. For the sections sampled, the anode catalyst layer with no recast ionomer had an average thickness of ca. 1 μm. The average thickness of the anode catalyst layer containing 10.5 wt. % recast ionomer was ca. 7 μm while that of the anode containing 30.7 wt. % recast ionomer was ca. 15 μm. All MEAs showed a distinct interface between the anode catalyst layer and the membrane, with no evidence of greater penetration of the membrane by the anode catalyst layer containing no recast ionomer.

It is interesting to compare the observed thicknesses of the anode catalyst layers with the calculated thicknesses based on zero porosity. If it is assumed that the catalyst was 1:1 metallic PtRu black, with an average density of 17.2 g/cm³, the calculated thickness of the anode catalyst layer containing no recast Nafion is 0.97 μm. If it is assumed that the catalyst was Pt/RuO₂, with an average density of 11.6 g/cm³, the calculated thickness of this same catalyst layer is 1.4 μm. The observed thickness of this anode catalyst layer was ca. 1 μm. For the anode catalyst layer containing 10.5 % recast ionomer, the average density of the anode catalyst layer, assuming a density of 1.8 g/cm³ for the ionomer, is 7.4 g/cm³ if the catalyst is assumed to be Pt/RuO₂ and 9.2 g/cm³ if the catalyst is assumed to be PtRu. These values provide calculated thicknesses of the anode catalyst layer of 2.8 μm and 2.2 μm, respectively. Contrast these values with the observed thickness of ca. 7 μm. Obviously, introduction of the recast ionomer into the anode catalyst layer introduces a degree of porosity that increases with increasing amounts of ionomer. This decrease in particle interconnectivity could explain a decrease in electronic conductivity within the anode catalyst with increased ionomeric content. Enhanced porosity in such catalyst layers would explain the relatively high permeabilities of gaseous reactants, as concluded before from modeling and diagnostics of PEFC air cathodes [3].

In the absence of evidence for significant embedding into the membrane of anode catalyst layers prepared with no recast ionomer, we must conclude that protonic conductivity in a PtRu anode catalyst layer with no recast ionomer might possibly arise from another source. If the RV3030 catalyst powder, nominally PtRu black with a 1:1 atomic ratio, contains some form of ruthenium oxide, RuOₓ, the RuOₓ in hydrous form could provide the necessary protonic conductivity (5, 6). Hence both the electronic and protonic conductivity necessary in the anode catalyst layer would be provided by the RV3030 itself and addition of recast ionomer would serve only to increase the thickness of the catalyst layer and thereby decrease access to catalyst sites. An additional beneficial effect of RuOₓ in the catalyst layer, replacing recast PFSA material, may be lowering the local acidity of the system, which would improve the interfacial kinetics of methanol electro-oxidation.

Figure 7 is the XRD spectrum of the as-received E-TEK catalyst, RV3030, that was used in this series of experiments. Figure 8 is the XRD spectrum of the same catalyst after reduction with H₂. The presence of amorphous RuOₓ in the as-received catalyst is inferred from the broad peaks (Figure 7) which are substantially lessened upon reduction.
of the RuO\(_x\) to alloyed PtRu (Figure 8). This suggests that the amount of RuO\(_x\) in the as-received catalyst is sufficient to provide protonic conductivity.

Figure 9 is the XRD spectrum of an as-received, unsupported PtRu sample provided by Johnson Matthey. The spectrum shows more complete alloying of the Pt and Ru, with far less of the Ru being present as RuO\(_x\). Anode layers for MEAs with identical loading of the JM catalyst were prepared using 0 wt. % and 15 wt. % recast ionomer. The results summarized in Table I indicate that the addition of recast ionomer to this PtRu catalyst, of less RuO\(_x\) content, increases anode (and DMFC) performance. With this latter anode catalyst composition, the increased thickness of the anode catalyst layer caused by the inclusion of recast ionomer is apparently more than compensated for by increased ionic conductivity within the anode. Without addition of recast ionomer to the anode catalyst layer, the relatively small amount of RuO\(_x\) present in the Johnson Matthey catalyst does not provide sufficient protonic conductivity.

| Ionomer content (wt. %) | \(i\) (mA/cm\(^2\)) at anode overpotential of 0.35 V (RHE) | \(i\) (mA/cm\(^2\)) at cell potential of 0.5 V |
|-------------------------|------------------------------------------------------|-------------------|
| 0                       | 130                                                  | 150               |
| 15                      | 200                                                  | 170               |

It is important to stress here that the presence of Ru oxide in PtRu anode catalysts is not necessarily the key for maximizing DMFC anodic activity. Whereas the results presented here indicate that RuO\(_x\), probably in its hydrous version, can provide protonic conductivity within the catalyst layer, the overall electrocatalytic process of anodic methanol oxidation involves much more than proton transport. In fact, some other PtRu catalysts of stronger metallic character (lower RuO\(_x\) content) as received seem to exhibit the highest electrocatalytic activity in polymer electrolyte DMFC anodes. As expected, such catalysts would require the addition of recast ionomer to the formulation to achieve the maximum activity of the anode catalyst layer.

CONCLUSION

When a component of the catalyst itself provides sufficient protonic conductivity, for example, RuO\(_x\) in PtRu catalysts, maximum DMFC anode performance can be achieved by reducing, or even eliminating, the recast ionomer in the catalyst layer. The optimal ionomer content in the PtRu anode catalyst layer will thus be a function of the RuO\(_x\) content of the catalyst and hence may vary with catalyst supplier and catalyst batch.
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Figure 1 Effect of wt. % recast ionomer in the anode catalyst on iR corrected current density as a function of cell temperature. Anode: 1 mol/L methanol at 2 mL/min. with 0, 0, 20, and 40 psig back pressures at cell temperatures of 60°C, 80°C, 100°C and 120°C, respectively. Cathode: Humidified H₂ at 0.3 L/min. and back pressure of 15 psig.

Figure 2 Effect of wt. % recast ionomer in the anode catalyst on non iR corrected DMFC current density at cell voltage of 0.5 V as a function of cell temperature. Anode: 1 mol/L methanol at 2 mL/min. with 0, 20, and 40 psig back pressures at cell temperatures of 80°C, 100°C and 120°C, respectively. Cathode: Air at 0.5 L/min. and 60 psig, humidified at 80°C at 80°C cell temperature and bypassed at cell temperatures of 100°C and 120°C.
Figure 3 Scanning electron micrograph of a cross section of a membrane electrode assembly that has been previously used in a fuel cell with portions of backing on each side of the catalyst layers.
Figure 4 Scanning electron micrograph of PtRu anode catalyst layer containing no recast ionomer in the anode catalyst layer
Figure 5  Scanning electron micrograph of PtRu anode catalyst layer containing 10.5 % recast ionomer in the anode catalyst layer
Figure 6 Scanning electron micrograph of PtRu anode catalyst layer containing 30.7% recast ionomer in the anode catalyst layer.
Figure 7 XRD spectrum of as-received E-TEK unsupported PtRu anode catalyst, RV3030

Figure 8 XRD spectrum of E-TEK unsupported PtRu anode catalyst, RV3030, after reduction with H₂.
Figure 9  XRD spectrum of as-received Johnson Matthey unsupported PtRu anode catalyst