NOVEL PROCESS FOR IMPROVED LONG-TERM STABILITY OF DMFC MEMBRANE-ELECTRODE ASSEMBLIES

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ABSTRACT

In this work, we introduce a new process for fabrication of Nafion®-based membrane-electrode assemblies for direct methanol fuel cell (DMFC). The process relies on modified formulation of catalyst inks and high-temperature treatment of the MEA, both leading to improved long-term performance stability relative to standard MEAs used in DMFC testing at LANL. Unrecoverable performance loss of the novel MEA after 3000-hour life test at a cell voltage of 0.50 V has been estimated to be ~10 mV (at 100 mA cm\(^{-2}\)). This number compares favorably with the performance loss of a standard MEA, measured at ~60 mV under the same conditions. Most of the gains are due to improved properties of the Pt-Ru anode. In particular, better stability of the anode helps to reduce loss in the catalyst surface area over time, providing net performance gain of 25-30 mV over the standard anode. Improved anode stability also reflects on long-term performance of the cathode thanks to reduced methanol crossover at long operating times of the cell (~15 mV gain).

INTRODUCTION

Thanks to liquid form fuel and ensuing high system specific energy, the direct methanol fuel cell (DMFC) is viewed as a promising power source for portable electronics and other low-power applications. In order to become fully commercially viable, DMFCs not only need to deliver high initial performance but also maintain that performance over long operating times, perhaps as long as thousands of hours.

Several routes of DMFC performance degradation over time have been identified to date, including: (i) Pt cathode catalyst oxidation,\(^1\) (ii) gradual loss of the electrochemical surface area of electrodes,\(^2\) (iii) ruthenium crossover from the anode to the cathode side of the cell,\(^3\) (iv) loss of hydrophobic properties of the cathode, and (v) membrane degradation. In spite of, generally agreed upon, importance of performance durability for commercialization of direct methanol fuel cells, relatively little data has been reported to date on long-term DMFC performance and on methods of reducing the impact of various cell/MEA degradation routes. The objective of this work has been to minimize unrecoverable performance loss of the Nafion®-based DMFC by introducing a high-temperature processing step into the membrane-electrode assembly (MEA) fabrication process. Long-term performance of the MEA obtained by using this new approach is compared to that of the standard LANL MEA fabricated without the high-temperature step.
The approach used in this study was based upon expectation that electrode stability should improve once anode and cathode “inks” are subjected to a temperature higher than the Tg of Nafion®, thus allowing the polymer to create a more robust electrode.

The high-temperature MEA fabrication process employed requires subsequent re-protonation of the membrane in an acid bath. It was expected that exposure of the anode catalyst to acid could diminish ruthenium crossover from the anode to the cathode side of the cell further helping cell performance by lowering cathode contamination with ruthenium.

**EXPERIMENTAL**

**Standard MEA Preparation**

The MEA was prepared using HiSPEC 6000 Pt-Ru black anode catalyst and HiSPEC 1000 Pt black cathode catalyst, both commercially available from Johnson Matthey. The catalyst loading was 6 mg cm⁻² and 8 mg cm⁻² for the cathode and the anode catalyst, respectively. Both catalyst inks were obtained by dispersing the blacks in the Millipore® water and adding recast Nafion® (1100 equivalent weight) suspended in a mixture of alcohols (Solution Technology). Catalyst inks were applied to Nafion® 117 H⁺-membrane at 75°C. Such-prepared MEA was placed in a 22-cm² test fuel cell without further treatment.

**Novel MEA Preparation**

Anode and cathode catalysts used and catalyst loadings were the same as for the standard MEA. Catalyst inks were obtained by dispersing catalysts in the Millipore® water mixed with a proprietary Nafion® solution. Catalyst inks were applied to the Nafion® 117 membrane (Na⁺-form) at 75°C, then hot-pressed at a high temperature between two Teflon decal blanks. The form of Nafion® used in the electrodes did not degrade at pressing temperatures.

**Fuel Cell Testing**

Prior to testing, MEAs were humidified for two hours at 80°C using water-saturated, high-purity nitrogen, flowing to the anode and the cathode side of the cell at a 20-psig backpressure. After the initial CO stripping experiments described below, the MEAs were conditioned in hydrogen-air fuel cell mode at a cell voltage of 0.7 V and temperature of 80°C for another two hours. The flow of anode hydrogen and cathode air was 300 sccm (standard cubic centimeters per minute) and 466 sccm, respectively. 20-psig backpressure was used on both sides of the cell. Without changing the cell...
operating conditions, H₂/air polarization plots were then recorded to determine cathode performance.

Following hydrogen-air testing, the cells were switched to DMFC mode and DMFC polarization plots were recorded at 75°C using 0.3 M methanol feed to the anode. Cathode conditions were 100 sccm airflow and 0-psig backpressure.

Anode catalyst activity was directly determined from anode polarization plots. In the anode testing, the fuel cell operated in externally driven mode, with pre-heated and pre-humidified H₂ flown to the fuel cell cathode at 100 sccm and against a 10-psig backpressure. As during DMFC operation, 0.3 M methanol was flown to the anode. After the initial diagnostics, both MEAs underwent long-term durability testing at a constant cell voltage of 0.5 V and temperature of 75°C. Life tests were stopped several times for fuel cell diagnostics to determine changes to the MEAs occurring during operation.

An unusual increase in the high-frequency resistance (HFR) of the cell with the standard MEA was observed after 1500 hours of the life test. This increase was found to occur at the interface between the metal endplate and graphite plate inside the cell, and was unrelated to the MEA itself. In order to prevent the increase in the hardware resistance from impacting cell performance comparison, all data presented in this work are iR-corrected.

The same testing protocol was used for both MEAs to ensure validity of the performance comparison.

![Figure 1. Life tests of novel and standard MEAs at 0.50 V. Cell operating temperature 75°C; ambient cathode pressure (0.76 atm).](image-url)
CO Stripping Voltammetry

Carbon monoxide stripping was carried out to determine electrochemical surface area (ESA) of catalysts and follow changes to the state of electrodes. CO chemisorption was performed under well-humidified conditions using 1% ultra high-purity CO in N₂ (carrier gas). At the end of the chemisorption process, excess CO was removed from the cell by flowing pure N₂ for approximately 30 min. During CO testing, cell temperature was reduced to 25°C and gas humidification bottles were maintained at 30°C. Voltammograms of CO stripping from the cathode were recorded in the potential range 0.1-1.3 V at a scan rate of 2 mV s⁻¹. In order to minimize ruthenium dissolution from the anode catalyst, CO stripping from the anode was performed between 0.1 V and 0.8 V, using 5 mV s⁻¹ scan rate.

RESULTS AND DISCUSSION

Long-Term Cell Performance

![Figure 2](image)

**Figure 2.** iR-corrected DMFC polarization plots for (a) standard MEA and (b) novel MEA. Cell operating temperature 75°C; 100 sccm airflow, ambient cathode pressure.

Life tests were carried out for a total of three thousands hours each (Figure 1). Recoverable performance loss was caused by Pt cathode oxidation and water accumulation at the cathode. Given the fact that the same membrane (Nafion® 117), gas diffusion-layers, and cell operation conditions were used in the two tests, similar recoverable performance losses can be assumed for both MEAs. If so, life test data in Figure 1 can be viewed as indicative of a faster unrecoverable performance loss of the standard MEA than the novel MEA. Quantitatively, the unrecoverable performance loss can be determined from DMFC polarization plots, recorded for both MEAs at after different times of cell operation (Figure 2). The standard MEA suffers from a continuous
(unrecoverable) loss in performance, which appears to be the fastest during the last 1000 hours of the life test (Figure 2a). In turn, the novel MEA incurs the largest unrecoverable performance loss in the first 2000 hours of the life test and very little, if any, loss during the last 1000 hours of testing (Figure 2b). The total unrecoverable performance loss over the 3000-hour life test is very different for both cells. At a cell current density of 100 mA cm$^{-2}$ that loss is 60 mV and 10 mV for the standard and novel MEA, respectively.

Above data confirm that the new MEA fabrication process helps long-term stability of the MEA. At the same time, because of better initial performance of the standard MEA (by ~40 mA cm$^{-2}$ at the life test voltage of 0.50 V), the performance difference observed at the end of 3000-hour test is not as significant as the performance loss numbers would suggest (no more than 15 mA cm$^{-2}$ at 0.50 V, Figure 2). Thus, the novel MEA processing method has a positive impact on the long-term MEA stability, but does not help the initial performance. This may be related to reduced initial porosity and lowered reactant permeability within the catalyst structure (cathode in particular, see below).

Anode Performance

Anode activity was measured directly from anode polarization plots (Figure 3). The results demonstrate that the two anodes performed similarly at the beginning of life tests. Initially, both MEAs achieved the reference current density of 100 mA cm$^{-2}$ at the anode potential of 0.28 V. However, over the time, the standard MEA anode lost approximately 30 mV at 100 mA cm$^{-2}$, whereas the novel MEA lost no more than 5 mV at the same current density.

![Anode Performance Plot](image)

**Figure 3.** $iR$-corrected anode polarization plots for (a) standard MEA and (b) novel MEA. Cell temperature 75°C; 100 sccm H$_2$ flown through the fuel cell cathode against at a 10 psig backpressure (cathode serving as a counter/quasi-reference electrode).

Carbon monoxide stripping data in Figure 4 show very different patterns of changes in the surface properties of both anodes. Integration of charges under CO stripping peaks reveals much faster drop in the ESA of the standard MEA than the novel MEA.
As a result of possible agglomeration of the catalyst particles, partial dissolution of the anode catalysts and/or loss of electronic/ionic connectivity between particles, the surface area of the standard anode decreased by ~58% over 3000 hours. At the same time, the ESA loss of the novel MEA was much less, ~32%. At the very high anode catalyst loadings used in this work the activity of Pt-Ru catalyst in methanol oxidation is not directly proportional to the number of active catalyst sites surface, therefore even a significant loss in the catalyst ESA may have relatively little impact on the anode performance. Still, the difference in rates of surface area loss for anodes in this work appears to be sufficient to account for the ~25-mV performance gap between the two anodes at the end of 3000-hour life tests (Figure 3).

Figure 4. Carbon monoxide stripping plots from (a) standard MEA anode and (b) novel MEA anode. Cell temperature 30°C; scan rate 2 mV s⁻¹.

Figure 5. Relative change in the electrochemical surface area of the anodes.
Cathode Performance

Usually, hydrogen-air polarization plots provide a reasonably good insight into the DMFC cathode performance. Unfortunately, this approach to determining cathode activity cannot be used for cells with potentially significant crossover of methanol. This is often the case in experiments involving methanol-permeable Nafion® membranes and fixed methanol concentration of methanol, regardless of the current density, i.e. under conditions used in this work (cf. DMFC polarization plots in Figure 2). In order to account for possible differences in the way standard and novel MEA cathodes handle methanol crossover, the cathode performance at various stages of the life test was determined from DMFC polarization data rather than H₂-air polarization plots. Furthermore, to make cathode performance data independent of variations in the anode performance over time (Figure 3 above), the voltage values for every DMFC polarization plot were corrected for anode losses, as determined from the corresponding anode polarization plot (AP). Thus obtained \((V_{DMFC} + AP)\) polarization plots are shown in Figures 6a and 6b for the standard and the novel MEA, respectively. It is worth noting that these plots differ from the \(iR\)-corrected H₂-air polarization plots by the performance penalty suffered by the cathode as a result of methanol crossover.

As demonstrated in the Figure 6, initial cathode performance of the standard MEA at the reference current density of 100 mA cm⁻² is by ~25 mV better than that of the novel MEA. As already suggested above, the good initial performance of the standard MEA cathode may be caused by better accessibility of catalyst Pt sites to oxygen. Over the first 2000 hours, both cathodes suffer from a performance loss, which is more pronounced in the case of the standard MEA cathode than the novel MEA. At longer times, i.e. between 2000 and 3000 hours, there is further drop in the performance of the standard MEA cathode and but no change in the performance of the novel MEA cathode. In spite of the
faster performance degradation rate of the standard MEA cathode, final performance of that cathode remains better thanks to significantly higher initial activity of that electrode. The total cathode performance drop over the time of the live test is 25 mV and 10 mV for the standard and novel MEA cathode, respectively (Figure 6).

![Figure 7](image_url)

**Figure 7.** Relative change in CO-stripping charge (cathode ESA) as function of cell operating time.

The drop in carbon monoxide stripping charge for the two cathodes as a function of the cell operating time is shown **Figure 7**. The data indicate that a 20-25\% drop in the ESA is very similar for both tested cathodes. One may thus conclude that, unlike the standard MEA anode, faster performance drop of the standard MEA cathode must be for a different reason than accelerated loss in the ESA.

**Role of Ruthenium Crossover**

Recently,\(^3\) crossover (migration) of ruthenium species from the anode to the cathode side of the DMFC, followed by Ru deposition at the cathode catalyst surface, has been shown to lower cathode activity in the oxygen reduction reaction (ORR) and a cathode’s methanol tolerance. A convenient and sensitive method of determining quantities of Ru on the cathode catalyst surface consists of measuring the shift in potential of the carbon monoxide stripping peak from the Ru-contaminated cathode, relative to the potential of CO stripping on pure Pt surface.\(^5,3\) Voltammetric plots of carbon monoxide stripping from the standard MEA cathode and novel MEA cathode are shown in **Figures 8a** and **8b**, respectively. Also shown in these figures are reference voltammograms for CO stripping from the surface of Ru-free Pt black cathode (no surface Ru → the highest peak potential) and from Pt-Ru black anode (the highest Ru coverage → the lowest peak potential). Comparison of voltammograms recorded after 3000 hours of DMFC operation reveals a much bigger negative shift of the CO stripping peak from the standard MEA cathode than the novel MEA cathode. The total shift in the CO stripping peak potential is
~ 100 mV for the standard cathode and only ~20 mV for the novel MEA. These potential shift numbers indicate that, during long life test, the standard MEA cathode becomes much more contaminated with ruthenium than the novel MEA cathode.

![Figure 8. Carbon monoxide stripping plots for (a) standard MEA cathode and (b) novel MEA cathode. Cell temperature 30°C; scan rate 5 mV s⁻¹.](image)

As demonstrated by the peak potential versus time data in Figure 9, the novel MEA cathode might have been partially contaminated with traces of ruthenium during the membrane-electrode fabrication process, e.g. in the membrane re-protonation step (see Experimental section above). As a consequence, at the beginning of the life test, CO stripping from the novel MEA cathode takes place at a potential of ~40 mV more negative than from the standard MEA cathode. For the first 2000 hours of life test, the potential of CO stripping from both cathodes changes only very slightly thus indicating little change in the amount of Ru deposited on the catalyst surface in either case. A very significant negative shift (70-80 mV) in the peak potential of CO stripping from the standard MEA cathode occurs in the last 1000 hours of life test, attesting to a major increase in the amount of Ru at the Pt catalyst surface. Such potential shift is not observed with the novel MEA cathode.

In the absence of significant differences in the ESA of the two cathodes, the effect of ruthenium crossover appears to be mostly responsible for the faster performance loss of the standard MEA cathode at longer operating times. Significant increase in ruthenium contamination of the standard MEA cathode in the last 1000 hours of life test may be caused by an accelerated loss of anode integrity leading to increased flux of ruthenium species across the membrane. Such a change in the anode integrity could be caused by insufficient MEA “curing” (no high-temperature treatment has been used during the standard MEA fabrication). It correlates well with a substantial drop in the electrochemical surface area of the standard MEA anode at long cell operating times (Figure 5) and significant decrease in the standard MEA anode activity towards the end of the life test (Figure 3).
CONCLUSIONS

We demonstrate in this study that performance durability of Nafion®-based DMFC MEAs can be improved via modifications to the ink formulation and incorporation of high-temperature treatment step into the MEA fabrication process. An enhancement in long-term performance of such-prepared MEA is especially apparent at cell operating times longer than 2000 hours. The improvement is likely caused by better flow of the ionomer at high temperatures used for MEA curing and improved distribution of Nation® within the catalyst layer, both leading to more robust electrodes.

Most of the gains resulting from the new approach are due to improved properties of the Pt-Ru anode. In particular, better stability of the anode catalyst helps reduce losses in the electrochemical surface area – a net gain of 25-30 mV in the anode (cell) performance relative to the standard anode.

Improved stability of the anode also reflects on long-term performance of the cathode. Cathode performance gain due to reduced ruthenium crossover can be estimated at approximately 15 mV at 100 mA cm\(^2\). Thus, the combined anode and cathode performance advantage of the novel MEA over the standard LANL MEA is 40-45 mV at 100 mA cm\(^2\). This number is close to the 50-mV difference in DMFC voltage recorded at the end of both life tests (Figure 2).

One apparent drawback of the new approach to MEA fabrication is related to somewhat lower performance of the novel MEA at the beginning of life test. Further
optimization of catalyst ink formulation (that for the cathode in particular) and thermal treatment conditions should help resolve this problem, resulting in better DMFC performance of the novel MEA, not only at long, but also short cell operating times.

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REFERENCES

1 F. A. Uribe and T.A. Zawodzinski, Jr., Electrochim. Acta, 47, 3799 (2002).
2 E. Antolini, J. Mat. Sci., 38, 2995 (2003).
3 P. Piela, C. Eickes, E. Brosa, F. Garzon and P. Zelenay, J. Electrochem. Soc., 151 A2053 (2004).
4 S.C. Thomas, X. Ren, S. Gottesfeld and P. Zelenay, Electrochim. Acta, 47, 3741 (2002).
5 H.A. Gasteiger, N. Marković, P.N. Ross and E.J. Cairns, Jr., J. Phys. Chem., 98, 617 (1994).