DIRECT METHANOL FUEL CELLS:
CATHODE EVALUATION AND OPTIMIZATION

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ABSTRACT

Direct methanol fuel cell (DMFC) performance has been improved as a result of Pt cathode optimization based upon the process of robust design. Cathode performance has been evaluated using cathode polarization curves generated from DMFC data. The effects of variation of temperature and nature of cathode backings on DMFC cathode potential were investigated. Our results show that Pt rich DMFC cathodes, operating on ambient air at 60°C, can exhibit high performance of >0.85 V vs. RHE at 100 mA/cm².

INTRODUCTION

Demonstrated DMFC performance has improved significantly in recent years. Much attention has been devoted to evaluation of anode catalysts and optimization of anode structure, characterization of existing membranes and searching for alternatives (1, 2). Of equal importance is the contribution of the cathode to performance and performance stability, yet comparatively little effort has been devoted to this component of the DMFC (3 – 5). The work reported here describes some of the recent efforts undertaken in this laboratory to evaluate and optimize cathode performance in a DMFC, employing Pt black as the cathode catalyst. The results show that, in spite of the frequently mentioned lack of "methanol tolerance", Pt cathodes in optimized DMFCs can exhibit high performance which is only marginally lower than their methanol-free performance.

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EXPERIMENTAL

The cathode catalysts used in this series of experiments were unsupported Pt blacks. The anode catalyst was an unsupported PtRu alloy. Both catalysts were supplied by Johnson-Matthey. Inks were made by dispersing appropriate amounts of catalyst in deionized water and 5 % Nafion solution (Solution Technology Inc.). Inks were then applied to Nafion 117 membrane (DuPont) either directly or by a decal transfer process. The geometric active area of all membrane electrode assemblies (MEAs) prepared was 5 cm². Pretreatment of the proton form of the Nafion 117 membrane, preparation of MEAs for a DMFC using a decal technique, and the single-cell fuel cell hardware have been previously described (1) as has the cell testing system used (6).

For a given series of experiments, the anodes in all MEAs tested were identical, while parameters of the cathodes were varied. Cell, methanol anode and hydrogen anode performances were investigated at temperatures from 60°C to 100°C. When operated at 60°C, 0.5 mol/L methanol solution was used; 1 mol/L methanol solution was used at 80°C and 100°C. The methanol flow rate was held constant at 1 – 2 mL/min. A backpressure of 15 psig was imposed upon the anode outlet flow at 100°C to ensure that the membrane would be in contact with a liquid solution of methanol.

When operated in fuel cell mode, the anode feed was either hydrogen or methanol solution and the cathode feed was air. When operated in driven cell mode to measure methanol anode polarization, the cathode gas was humidified hydrogen. When operated in hydrogen pump mode, humidified hydrogen gas was supplied to both anode and cathode. The backpressures, flow rates and humidification temperatures of the cathode gases, air or hydrogen, varied with the operating temperature of the cell.

Programs written in Labview (National Instruments) and run from a Power Macintosh computer were used to control the experiments as well as generate cathode polarization and cathode loss curves.

RESULTS AND DISCUSSION

Optimization of Cathode Catalyst Layer Composition/Structure Using Robust Design

In this work, the process of robust design (7) was used to systematically investigate the effect of several variables on cathode performance. Robust design is a method, similar in concept to other techniques (8 – 10), of optimizing an experimental approach to effectively achieve a desired outcome. This method uses the mathematical tool of orthogonal arrays in which a large number of factors are investigated with a small number of experiments. In the matrix of experiments, an optimized set is performed in
which the levels of various factors are changed from one experiment to another. The data for all experiments in the matrix are analyzed together to determine the effect of each factor.

Three steps, each involving several components of the robust design process are typically followed. Only the main features are summarized in this paper.

(1) Planning the matrix of experiments. For the work reported in this paper, the desired outcome was identified as achieving the highest DMFC current density, \( J \), at 80°C, at a cell voltage of 0.5 V. Statistical treatment of the data was then based on a "larger-the-better" scenario in which a function, designated as \( \eta \), was defined as \( \eta = -10 \log \left( \frac{1}{n} \sum_{i} \frac{1}{I_i^2} \right) \) where \( n \) is the number of trials of each experiment number \( i \). The objective of maximizing the current density then became equivalent to maximizing \( \eta \).

Typically 4 to 8 factors are optimized in one matrix of experiments. In this work, ionomer equivalent weight (EW) and ionomer content in the cathode catalyst layer, cathode catalyst loading and hot pressing temperature during the decal transfer process of the catalyst layers to the membrane were the factors investigated. Levels of each of these 4 factors were chosen. Typically three levels sufficiently far apart, the level currently in use and a level on either side of it, are employed. Although construction of an orthogonal array specific to the project under consideration is possible, a standard array of 9 experiments (7), shown in Table I, was adopted to study the effect of the 4 factors, in contrast to the 81 experiments required for a full factorial analysis.

| Expt. # | Factor A | Factor B | Factor C | Factor D |
|---------|----------|----------|----------|----------|
| 1       | 1        | 1        | 1        | 1        |
| 2       | 1        | 2        | 2        | 2        |
| 3       | 1        | 3        | 3        | 3        |
| 4       | 2        | 1        | 2        | 3        |
| 5       | 2        | 2        | 3        | 1        |
| 6       | 2        | 3        | 1        | 2        |
| 7       | 3        | 1        | 3        | 2        |
| 8       | 3        | 2        | 1        | 3        |
| 9       | 3        | 3        | 2        | 1        |
(2) Performing the experiments. After the orthogonal array was chosen, the matrix of experiments could be performed, as shown in Table II. It is important to stress that control of all variables, other than the factors being tested, should be as stringent as possible. For example, the same batch of Pt black catalyst as well as a standard anode formulation were used for all experiments. Importantly, all experiments in a matrix of experiments must be completed. If data are missing, orthogonality is lost and analysis of such experiments is complicated.

Table II
Experimental Log Sheet

| Exp. # | Ionomer | Ionomer Content (wt. %) | Cathode Loading (mg/cm²) | Hot Press Temp (°C) |
|--------|---------|-------------------------|--------------------------|--------------------|
| 1      | 900     | 4                       | 3.5                      | 80                 |
| 2      | 900     | 10                      | 6.0                      | 125                |
| 3      | 900     | 16                      | 8.5                      | 140                |
| 4      | 1100    | 4                       | 6.0                      | 140                |
| 5      | 1100    | 10                      | 8.5                      | 80                 |
| 6      | 1100    | 16                      | 3.5                      | 125                |
| 7      | 1200    | 4                       | 8.5                      | 125                |
| 8      | 1200    | 10                      | 3.5                      | 140                |
| 9      | 1200    | 16                      | 6.0                      | 80                 |

In this work, only one MEA was prepared for each of the 9 experiments. The average, from three consecutive trials, of the current densities achieved with each MEA at 0.5 V and 80°C, was used for analysis of the data. Table III summarizes these average DMFC current densities and the value of the $\eta$ function for each of the 9 experiments.

Table III
DMFC Current Densities @ 0.5 V @ 80°C and $\eta$ Values for the Matrix of Experiments

| Expt. # | 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8     | 9     |
|---------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Current density (mA/cm²) | 210   | 285   | 125   | 190   | 250   | 235   | 255   | 255   | 285   |
| Value of $\eta$ function | 46.4  | 49.1  | 41.9  | 45.6  | 48.0  | 47.5  | 48.1  | 48.1  | 49.2  |
Analyzing and verifying the experimental results. The effect of each factor is estimated by a statistical treatment of the data during which average values of the η function are calculated for each level of each factor. For example, the effect of an ionomer content of 4 wt. % is determined from averaging the η values from experiments 1, 4 and 7. The optimum level of each factor is determined as that level of the factor that gives the largest average value of η. This matrix of experiments indicated that the highest DMFC performance at 0.5 V at 80°C should be obtained with a cathode fabricated with an ink made with Nafion of EW = 1200, at 10 % recast ionomer by weight, loaded at 6 mg of Pt/cm² of electrode area, and hot pressed to the decal at 125°C.

The analysis method used in the robust design process allows estimation of the η value that would be obtained under optimized conditions. Once the "optimized" η value is determined, the current density resulting from the optimized factors can be calculated. Based on the analysis of the η values determined from the 9 experiments, DMFC cell performance at 0.5 V at 80°C under the optimized conditions was predicted to be 300 mA/cm². A verification experiment was conducted with one MEA fabricated using the optimized levels of each factor. The actual average performance achieved, based on three consecutive trials, indeed was 300 mA/cm². Robust design is an iterative method; additional matrix experiments could next be designed to further optimize the formulation and conditions.

The following work, in which other factors were studied to determine their effect on cathode performance, used MEAs fabricated at the levels of ionomer EW, ionomer content, Pt loading and hot press temperature determined to be optimum from the preceding robust design process.

Cathode Potential vs. Current Density Curves

To evaluate a DMFC air cathode performance, it would obviously be desirable to know the potential of the cathode under DMFC operation conditions. The use of a reference electrode to obtain the cathode potential in an operating DMFC frequently poses problems of instability. We preferred here to evaluate the DMFC cathode potential from ordinary, two electrode cell polarization measurements. Using a two electrode configuration within the operating cell, current density vs. potential curves for a DMFC air cathode were derived from three iR corrected voltage/current density V* (J) measurements for (i) a methanol/air cell, (ii) a driven cell with the same methanol anode and a hydrogen evolving cathode, and (iii) a driven "hydrogen pump" cell with a hydrogen oxidation anode and a hydrogen evolving cathode.

The iR corrected potential differences measured in these three cells at given J, can be written as:

\[ V^*_{\text{MeOH/air}} (J) = E^\text{MeOH}_\text{air} (J) - E^\text{MeOH} (J) \] \[[1a]\]

\[ V^*_{\text{MeOHH2}} (J) = E^\text{MeOH} (J) - E^\text{HER} (J) \] \[[1b]\]

\[ V^*_{\text{H2/H2}} (J) = E^\text{HER} (J) - E^\text{HER} (J) \] \[[1c]\]
where the asterisk designates “iR corrected” and the potential differences are written to yield positive voltage values in each case. The E’s are electrode potentials (vs. some arbitrary fixed reference potential) at current density J for a methanol anode at the relevant DMFC anode conditions, E_{MeOH} (J), a DMFC air cathode at relevant DMFC cathode conditions, E_{air}^{MeOH} (J), and (well humidified) hydrogen oxidation electrode, E_{HOR} (J), and hydrogen evolution electrode, E_{HER} (J), in contact with the ionomeric membrane. The superscript (MeOH) in the symbol for the DMFC air cathode potential, E_{air}^{MeOH} (J), indicates that this cathode suffers the effects of methanol penetration. Each value of E is, obviously, a function of the concentration of reactants, pressure of gases and activity of protons and water, but all of those are maintained identical in the three cell measurements [la] - [lc]. Summing [la] and [lb], and subtracting [lc], one obtains:

\[ E_{air}^{MeOH} (J) - E_{HOR} (J) = V_{MeOH/air}^{*} + V_{MeOH/H2}^{*} - V_{H2/air}^{*} \]  

Equation 2 explains the derivation of DMFC cathode potential at given J vs. the potential of a hydrogen oxidation anode operating at the same J. Figure 1a displays the results of the process for such a cathode operating at 60°C.

Unlike an ideal reference electrode, the HOR electrode potential varies somewhat with J. However, one can readily compare measured E_{air}^{MeOH} (J) vs. E_{HOR} (J) to measured air cathode potential vs. E_{HOR} (J) in a hydrogen/air fuel cell - the latter value is simply the iR corrected voltage of the hydrogen/air fuel cell:

\[ E_{air} (J) - E_{HOR} (J) = V_{H2/air}^{*} \]  

The cathode loss specifically caused by methanol penetration to the DMFC air cathode can thus be evaluated directly from the difference between E_{air} (J) and E_{air}^{MeOH} (J), as derived from equations [3] and [2], respectively, demonstrated in Figure 1b.

As Figure 1a reveals, the potential of this, heavily Pt loaded air cathode, operating in a DMFC at 60°C on ambient air, is rather high: 0.85 V vs. the HOR electrode potential at 100 mA/cm². That this is very close to the full activity of this air cathode is seen in Figure 1b, which confirms that the presence of methanol has only marginal effect on the air cathode potential at 100 mA/cm².

Effect of temperature on cathode potential. Computer generated cathode polarization curves based on three, iR corrected cell polarization curves, as described by equations [1] and [2], were used to assess the effect of methanol crossover on cathode potential at different temperatures. As shown in Figure 2a, the increase in DMFC performance is not nearly as significant when the temperature change is from 80°C to 100°C as it is when the cell temperature is increased from 60°C to 80°C. Polarization of the anode against a hydrogen evolving electrode (cell [1b]) indicates that anode performance increases monotonously with increase in temperature, as shown in Figure 2b. The cathode
polarization curves (Figure 2c) show that the cathode potential increases (cathode activity increases) with temperature between 60°C and 80°C but the potential of the cathode at 100°C is, in fact, below that at 80°C. This deviation from the behavior expected based on monotonous oxygen reduction rate enhancement with temperature must be explained by more substantial effects of methanol crossover on cathode performance at the elevated temperature of 100°C (11). Under the simplest circumstances, methanol entering the cathode from the membrane would cause a shift of air cathode potential, given by

$$\Delta E_{\text{air}} = b \log \left( \frac{J_{\text{orr}} - J_{\text{crossover}}}{J_{\text{orr}}} \right) = b \log \left[ 1 - \left( \frac{J_{\text{crossover}}}{J_{\text{orr}}} \right) \right]$$  \hspace{1cm} \text{(4)}$$

where b is the Tafel slope for the ORR, $J_{\text{orr}}$ is the oxygen reduction current density at the relevant cathode potential E and $J_{\text{crossover}}$ is the methanol crossover current density. Equation [4] describes the shift of the DMFC air cathode potential under the conditions described in (12) as "no apparent interaction". As the temperature increases, $J_{\text{orr}}$, an interfacial process with activation energy of ca. 15 kcal/mol (13), should increase proportionately more than $J_{\text{crossover}}$, which is determined by methanol diffusivity through the ionomeric membrane, associated with an activation energy of the order of only 5 - 6 kcal/mole (11). Hence, the drop of cathode potential with temperature between 80 and 100°C must be the result of additional effects of methanol penetration on cathode potential, possibly excessive flooding.

**Cathode catalyst evaluation using cathode polarization curves.** Different batches of Pt black were tested to determine their effectiveness as cathode catalysts. Figure 3a shows the performance of three MEAs in DMFC configuration at 80°C, each of the MEAs using a different batch of Pt black. Figure 3b provides the cathode polarization curves for the same three Pt black cathode preparations. The relative performance of the three Pt black cathodes, as indicated by their polarization curves (Figure 3b), matches well the relative DMFC performance (Figure 3a). This result demonstrates the good repeatability of DMFC anode performance in repeated MEA fabrication and clearly points to possible gains, particularly at higher cell currents, derived from further optimization of cathode catalysts and catalyst layer preparation.

**Effect of cathode backing on cathode potential.** Evaluation of DMFC cathode polarization has also allowed us to isolate the effect of the nature of the air electrode backing on DMFC performance. The effect of applying the carbon powder-PTFE mixture to different substrates is indicated in Figure 4a. Under comparable conditions of carbon powder-PTFE mixture composition and loading, our DMFC cathode (and cell) performances were consistently better when a carbon cloth substrate was used for preparation of the cathode backing. A cell with cathode backing based on a carbon cloth substrate was operated continuously for a period approaching 400 hours. This cell showed stable performance at different temperatures and there was no visible deterioration of the cathode backing material after such testing.

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With a carbon cloth based cathode backing selected, several types of such backing layers with somewhat different structures were evaluated for their effect on DMFC performance. Figure 4b shows the results, in terms of cathode polarization plots, for three such cathode backing layers. The commercial E-TEK backing consisted of carbon-Teflon® mixture applied to both sides of a carbon cloth, the experimental E-TEK backing had the same carbon-Teflon® mixture applied to one side of the cloth only and the “LANL backing” was also a construction based on the application of a carbon-PTFE mixture to carbon cloth. Clearly, the mode and extent of application of the carbon powder-PTFE mixture to the carbon backing affects performance, particularly at higher current densities. These advantages in cathode performance were also reflected in the performance of the corresponding methanol/air cells.

SUMMARY AND CONCLUSIONS

This work indicates that investigation and optimization of variables related to DMFC Pt cathode construction can result in better DMFC cathode performance. It points to robust design techniques as means for minimizing the number of experiments required in such optimization efforts. DMFC cathode polarization curves, generated from polarization data for three, two-electrode polymer electrolyte cells, enable evaluation of air cathode performance in presence of the methanol “leaking” through the membrane. The results show clearly that, when the Pt air cathode in a DMFC is of sufficient loading and cell operation conditions are optimized, cathode loss in the DMFC caused by methanol is marginal (<20 mV at 100 mA/cm²). It is thus important to realize that the net performance of a Pt cathode in a DMFC could be really high (>0.85 V vs. RHE at 100 mA/cm²) in spite of the activity of Pt as a methanol electrooxidation catalyst. This is the result of the intrinsically superior activity of Pt as an ORR catalyst and the possibility to minimize, under some conditions, the penalty of the methanol in the cathode to only mixed potential effects (12).

Higher DMFC air cathode performance loss around temperatures of 100°C, as revealed in this work for DMFC cathodes of high Pt loading, remains a challenging target for further improvements.

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Figure 1a Derivation of DMFC cathode potential (6 mg Pt/cm²) vs. a hydrogen oxidation anode at 60°C. CH₃OH, 0.5 mol/L and 0 psig. Air at 0 psig and 50 sccm. H₂ at 10 psig, 0.3 L/min and 100°C humidification. Active area of cell is 5 cm².

Figure 1b Evaluation of cathode loss caused by methanol penetration to the DMFC air cathode with 6 mg Pt/cm² at 60°C. CH₃OH, 0.5 mol/L and 0 psig. Air at 0 psig and 50 sccm. H₂ at 10 psig, 0.3 L/min and 100°C humidification. Active area of cell is 5 cm².
Figure 2a Effect of temperature on DMFC polarization curves. CH₃OH, 0.5 mol/L and 0 psig at 60°C; 1 mol/L and 0 psig at 80°C; 1 mol/L and 15 psig at 100°C. Air at 0 psig with no humidification at 60°C; 30 psig and 110°C humidification at 80°C and 100°C.
Figure 2b  Effect of temperature on polarization curves in a CH₃OH/H₂ (driven) cell. CH₃OH, 0.5 mol/L and 0 psig at 60°C; 1 mol/L and 0 psig at 80°C; 1 mol/L and 15 psig at 100°C. H₂ at 10 psig and 100°C humidification at 60°C; 30 psig and 105°C humidification at 80°C and 100°C.

Figure 2c  Effect of temperature on DMFC cathode potential (vs. potential of a hydrogen oxidation electrode operating at the same current density). CH₃OH, 0.5 mol/L and 0 psig at 60°C; 1 mol/L and 0 psig at 80°C; 1 mol/L and 15 psig at 100°C. Air at 0 psig and no humidification at 60°C; 30 psig and 110°C humidification at 80°C and 100°C.
Figure 3a  Polarization curves for three CH$_3$OH/air cells at 80°C with MEAs containing three different Pt black cathode catalysts. Pt black loading in each case: 1.6 ± 0.1 mg/cm$^2$. 1 mol/L CH$_3$OH; air at 30 psig and 0.45 L/min.

Figure 3b  Cathode polarization curves at 80°C of three different Pt black cathode catalysts. Pt black loading 1.6 ± 0.1 mg/cm$^2$. 1 mol/L CH$_3$OH; air at 30 psig and 0.45 L/min.
Figure 4a Effect of cathode backing substrate material on cathode polarization (potential vs. HOR) in DMFC at 60°C. 0.5 mol/L CH₃OH; air at 0 psig and 50 sccm.

Figure 4b Effect of fine structure of the treated cathode backing layer on DMFC cathode polarization at 80°C, shown for three such layers based on the same carbon cloth substrate.