Title: ON DIRECT AND INDIRECT METHANOL FUEL CELLS FOR TRANSPORTATION APPLICATIONS
Author(s): XIAOMING REN, MAHLON S. WILSON, SHIMSHON GOTTESFELD

Submitted to: Proceedings of the 1st International Symposium on Proton Conducting Membrane Fuel Cells, Electrochemical Society, Chicago, IL

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

By acceptance of this article, the publisher recognizes that the U.S. government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
ON DIRECT AND INDIRECT METHANOL FUEL CELLS
FOR TRANSPORTATION APPLICATIONS

Xiaoming Ren, Mahlon S. Wilson and Shimshon Gottesfeld
Materials Science and Technology Division
Los Alamos National Laboratory, Los Alamos, NM 87545

Recently, we and others have achieved power densities in polymer electrolyte Direct Methanol Fuel Cells (DMFCs), which are only three times lower than those achieved with similar reformate/air fuel cells (RAFC). Comparisons of power densities, energy conversion efficiencies and projected costs reveal similar values for the DMFC and the methanol reformer + RAFC stack. We conclude that the DMFC could become the preferable methanol-fueled system due to its relative simplicity. However, important remaining DMFC issues are: improved anode catalyst activity, demonstrated long-term stable performance, and high fuel efficiencies.

INTRODUCTION

Polymer electrolyte fuel cell (PEFC) technology has advanced in the last few years to the point of being considered a viable option for primary power sources in electric vehicles. In the past, the systems considered in this context have been based on either hydrogen carried on board the vehicle, or the steam-reforming of methanol to generate a mixture of hydrogen and CO₂ as the fuel feed stream for the fuel cell stack. The latter system has been considered an attractive option because of the high energy density of the fuel (methanol), its availability and the relatively simple fuel distribution system required. However, the complexity and additional weight and volume associated with the reformer on board the vehicle have presented significant challenges in the implementation of this option. To date, the DMFC has not been considered a serious option for transportation applications due to its limited performance (low power density) in comparison to the RAFC.

Recent advancements in DMFC research and development have been quite dramatic, however, with the DMFC achieving power densities which are significant fractions of that provided by the RAFC. The more applied DMFC work, aimed primarily at the demonstration of enhanced stable performance of DMFC single cells or stacks, has been supported in the US by the DOE, Office of Transportation Technology, ARPA and the US Army. This type of work has taken place in several research institutes, including the Jet Propulsion Laboratory, Case Western Reserve University and Los Alamos National Laboratory, in collaboration with industries such as International Fuel Cells (IFC) and Giner, Inc. Similar efforts in Europe resulted in a demonstration at Siemens of a high-performance polymer electrolyte DMFC operating at temperatures above 120°C.

The recent strong advances in DMFC performance have been achieved without any breakthroughs in electrocatalysis, much the same way as in the previous cases of the hydrogen/air PEFC or the RAFC. The use of established Pt-Ru anode electrocatalysts and Pt cathode electrocatalysts in conjunction with polymer electrolyte DMFCs has resulted in very significant enhancements in DMFC performance when such cells are operated at
temperatures as high as 120-140°C, and particularly, as shown in this paper, when catalyst layer composition and structure have been optimized. Operation at elevated temperatures is facilitated in such polymer electrolyte fuel cells by the anode being continuously in contact with liquid methanol-water mixtures.

In the following section we describe recent experimental work at Los Alamos National Laboratory (LANL), which resulted in high performances of polymer electrolyte DMFCs. These recent results will be considered together with previously reported LANL results to comparatively evaluate (i) a polymer electrolyte DMFC stack and (ii) a system comprised of a methanol reformer and polymer electrolyte reformate/air fuel cell stack for transportation applications.

**PROGRESS IN DIRECT METHANOL FUEL CELLS AT LANL**

**Membrane/Electrode Assemblies**

Over the course of the DMFC development effort at LANL, a number of different methods were investigated for forming the membrane/electrode assembly (MEA) in cells based on Nafion™ membranes (DuPont). These included conventional PTFE-treated wet-proofed electrodes, catalyst/ionomer inks applied to carbon cloth and thin-film catalysts formed by applying catalyst ink to transfer decals.1 The various types of catalyst structures were then bound to the Nafion membranes by hot-pressing. The thin film catalysts bonded to the membrane by the decal method1,2 provided the best results in terms of catalyst utilization and cell performance. Such decal-formed thin-film catalyst layer structures have been used previously for H2/air fuel cells in this laboratory and proved to provide the highest catalyst utilizations.

The protocol for forming the high performance DMFC assemblies described here is somewhat different than that for the H2/air cells. Nafion 112, 115 and 117 membranes were cleaned and converted into the acid form by successively boiling the membranes for at least one hour in each of the following solutions: 3% H2O2, deionized (DI) water, 0.5 M H2SO4, and then DI water again. Unsupported Pt-RuOx (Pt:Ru = 1:1, sample designated RV30-30 from E-TEK, Inc., Natick, MA) was used for the anode catalyst and Pt-black (20 m2/g, Johnson Matthey) was used for the cathode catalyst. Catalyst inks were prepared by adding 5% Nafion solution (900 EW, Solution Technology, Inc.) to the water-wetted metal catalysts. Suitable dry ink compositions were 85 wt % Pt-RuOx and 15 wt % Nafion for the anode ink, and 93 wt % Pt-black/ 7 wt % Nafion for the cathode ink. To prepare the MEAs, appropriate amounts of anode and cathode inks were uniformly applied to 5 cm2 Teflon decal blanks to give metal catalyst loadings of approximately 2.2 mg/cm2. The inked decals were then dried at 100°C, and the catalyst layers were transferred from the Teflon blank to the pre-dried Nafion membranes (45 min. on a 60°C heated vacuum table) by hot-pressing at 120°C and 105 atm for 120 s. After the decal blanks were removed, the MEAs were inserted into the fuel cell hardware, and sandwiched between two 5.5 cm2 uncatalyzed carbon-cloth gas-diffusion backings from E-TEK. The reasons for the use of such backings are discussed briefly elsewhere.4 The single-cell fuel cell hardware consists of nuclear-grade graphite blocks with machined serpentine flow channels, gold-plated copper current collectors, and stainless steel compression plates.3 The cell testing1 and high-frequency resistance measurement4 systems have been described previously.
Specific activities (i.e., activities per mg Pt) of unsupported Pt-Ru anode catalysts are not as high as those described by Watanabe\(^5\) for Pt-Ru/C, or those we have obtained ourselves with commercially available Johnson-Matthey Pt-Ru/C catalysts (e.g. their FCA-6X).\(^6\) However, an unsupported, highly active Pt-Ru catalyst (as described by Kosek et al.\(^7\)) provides a significantly higher overall anode performance. This is mainly due to the high catalyst utilization, enabled by effective simultaneous access of protons, electrons and methanol to a large number of active catalyst sites in thin layers of high site density. The overall loadings in such layers of unsupported Pt-Ru catalysts are indeed higher than those typically obtained for supported Pt alloy catalysts (1-4 mg/cm\(^2\) vs. 0.1-0.5 mg/cm\(^2\)). However, a key advantage that has permitted the relatively high performances of DMFC anodes with such unsupported catalysts is not just the higher loading, but the dense thin-film catalyst layer structure, which permits high methanol and proton transport rates to a large number of active sites. For example, DMFC performance enhancement cannot be achieved by increasing the loading of a supported anode catalyst well above 0.5 mg/cm\(^2\), because of an excessive catalyst layer thickness.

Our findings for DMFC cathode catalyst layers have been similar to those for the DMFC anode, in that catalyst/ionomer thin-films bonded to the membrane provided performances equal to or better than other (e.g., wet-proofed) electrode configurations. High loading, unsupported Pt-black thin-film catalyst layers were found superior to low-loading, supported Pt/C catalysts typically used in our H\(_2\) fueled PEM cells. In this case, the advantages of the high loading, unsupported catalyst appear to be enhanced methanol tolerance, in addition to the high volume density of catalyst sites.

**Single Cell Testing**

A 1 M methanol solution was pumped through the DMFC anode flow-field at relatively high flow-rates.\(^8\) The outlet flow could be controlled such as to impose a desired amount of back-pressure to ensure saturated vapor conditions at the temperature of operation, such that the membrane would be in contact with a liquid solution of methanol on the anode side. The mild pressures required to ensure a two-phase, liquid/vapor system on the anode side of the DMFC also provide a well humidified membrane, and thus, good protonic conductivity at temperatures as high as 130°C. The oxygen or air feed to the cathode was humidified to provide water vapor saturated gas at temperatures 0°-10°C below the cell temperature. Cell performances were evaluated over the range of 30° to 130°C.

Figure 1 shows polarization and high frequency resistance curves of DMFCs operated at 130°C with 5 atm oxygen cathodes using Nafion 112, 115, and 117 membranes. The best performance (670 mA/cm\(^2\) at 0.5 V cell voltage) was obtained using the relatively thin (50 µm) Nafion 112 membranes. The high-frequency (8 kHz) cell resistances for the three cells are also depicted in Figure 1. As the membrane thickness increases, cell resistance increases and cell performance decreases correspondingly. As a matter of fact, the iR-corrected polarization curves for the three different Nafion MEAs virtually overlay one another. Since the methanol permeation rate through the membranes is expected to be greater in the thinner membranes, the cathode should be handling higher fluxes of methanol. The similarity of the iR corrected polarization curves suggests that the cathodes are highly tolerant to such variations in methanol flux. The relative insensitivity of the cathodes does not indicate, however, that the fuel efficiency is unaffected, as the methanol permeation rate is indeed higher with the thinner barriers.\(^9\) Additional strategies, such as methanol barrier membranes or lean-feed DMFCs,\(^9\) will need to be implemented to maximize the total efficiencies of DMFCs.
As shown in Figure 1, the high-frequency cell resistivities of the DMFCs operating at 130°C were as low, or lower than those typically seen for conventional, well-humidified H₂/air cells operating at 80°C. Clearly, the membranes were well hydrated even at these elevated temperatures. This is most probably a result of the maintenance (by pressurization) of a liquid in the anode compartment. If, as expected, the methanol in the liquid feed wets (hydrophilizes) the anode backing, liquid water would come in direct contact with the membrane. Since the membrane uptake of water from the liquid is greater than that from the vapor, particularly at such higher temperatures, a level of water content and hence, conductivity, is attained that could not have been possible if the membrane were equilibrated with water vapor alone. However, others have operated direct methanol polymer electrolyte fuel cells at 130°C on vaporized water/methanol feeds.

All of the cells described here demonstrated reasonable performance stability. The performance of the Nafion 112 based cell dropped from 670 mA/cm² to 600 mA/cm² at constant 0.5V cell voltage after one week of running 4 hours each day. Longer term performance stabilities warrant further investigation.

Although the use of the neat oxygen cathode minimizes the oxygen reduction reaction (ORR) losses, most terrestrial applications require the use of an air cathode, preferably under modest pressure conditions. In a similar vein, high temperatures are of some concern because of cell longevity and increased pressure requirements. Figure 2 shows polymer electrolyte DMFC performances under conditions that may be more amenable to transportation applications. Air cathodes at only 3 atm were used instead of higher pressure oxygen and the cell temperatures were also set somewhat lower, at 110°C. Still, Figure 2 shows that with the Nafion 112 membrane/electrode assembly, a current of 370 mA/cm² at 0.5 V cell voltage was obtained with a 1M methanol feed. As shown in Figure 3, the peak power output of this type of DMFC was almost 400 mW/cm² for the oxygen cathode at 130°C and about 250 mW/cm² for the air cathode at 110°C.

Figure 4 depicts DMFC performances for various Nafion membranes with thin-film catalyst layers as a function of cell temperature. Generally, the cells performed relatively poorly at cell temperatures below 80°C. As the cell temperatures were increased, significantly better cell performances were obtained, primarily due to the substantial improvement in anode kinetics. While even higher temperatures will further enhance the anode performance, 130°C is probably near the upper limit for the long-term stability of perfluorosulfonic acid membranes in contact with methanol/water mixtures.

To summarize this brief description of our newest DMFC results, we have shown that high polymer electrolyte DMFC performances can be obtained with MEAs prepared by the decal thin-film electrode fabrication method, using perfluorosulfonic acid membranes and unsupported Pt-Ru anode catalysts. Improvements over previously reported performances are attributable in part to cell temperatures well above 100°C, demonstrated to be feasible in slightly pressurized DMFCs, possibly due to the liquid (methanol/water) in contact with the anode side of the membrane. It is interesting to note that, because the anode feed can be kept in liquid state at such elevated temperatures, the polymer electrolyte DMFC is easier to operate than the hydrogen/air polymer electrolyte fuel cells at temperatures above 100°C. Another very important factor in achieving these high performances is the high catalystutilizations achieved with optimal catalyst layer structures, as attained with thin-film electrodes bonded to the membrane. Such MEAs have provided the highest DMFC performance in cells prepared by us based on Nafion membranes.
apparently high methanol tolerance of our cathodes at higher temperatures suggests that the present performance is primarily limited by anode catalyst activity. With improved anode catalysts and less methanol permeable membranes, it should be possible to obtain yet higher cell performances and fuel efficiencies, using the same general fuel cell package.

DMFC STACK VS. METHANOL REFORMER + RAFC STACK

The significant increase in demonstrated DMFC performance, as shown above and by other research groups, has brought the peak power density of the polymer electrolyte DMFC to a level which is only three times lower than that of the reformate/air fuel cell. Consequently, at this point, some simple calculations reveal that the two options, (i) a DMFC stack and, (ii) a methanol reformer + reformate/air fuel cell (RAFC) stack, start showing comparable overall system characteristics.

Table I. Calculation of Energy Conversion Efficiencies for DMFC and RAFC Systems

| Assumptions |
|-------------|
| • Methanol is either: |
| (case 1) Converted directly in DMFC, or |
| (case 2) Steam reformed to H2 and converted in RAFC |

**Efficiency calculation**

(case 1, DMFC)

Total Eff. = \((V_{cell})_1 \times \eta_{fuel,fc} \times \eta_{V} = \frac{\eta_{fuel,fc}}{\eta_{fuel,fc}}\)

(case 2, RAFC)

Total Eff. = \(\eta_{ref} \times \eta_{prox} \times \eta_{V} \times \eta_{fuel,fc} \times \eta_{fuel,fc} \times \eta_{ref} \times \eta_{prox}\) = \((\eta_{fuel,fc})_2 \times \eta_{V} \times \eta_{fuel,fc} \times \eta_{fuel,fc} \times \eta_{ref} \times \eta_{prox}\)

**Conclusion**

To achieve equal overall conversion efficiencies (MeOH to dc power):

\((V_{cell})_1 = (V_{cell})_2 \times \frac{\eta_{fuel,fc} \times \eta_{fuel,fc} \times \eta_{ref} \times \eta_{prox}}{\eta_{fuel,fc} \times \eta_{fuel,fc} \times \eta_{ref} \times \eta_{prox}}\)

Assuming \((\eta_{fuel,fc})_1 = 0.90, \eta_{ref} = 0.72\) and \(\eta_{prox} = 0.97\), then

\((V_{cell})_1 = 0.79 \times (V_{cell})_2\)

i.e., same overall energy conversion for DMFC operating at 0.55 V and RAFC at 0.70 V.

Table I shows a comparison of overall system efficiencies. The overall efficiency of the DMFC is calculated as the voltage efficiency times fuel efficiency of the DMFC stack. The overall efficiency of the reformer+RAFC stack is calculated as a product of the energy conversion efficiency of the reformer, the efficiency of a preferential oxidation (prox) stage, the voltage efficiency of the RAFC stack and the fuel efficiency of the RAFC stack. The calculation shows that the overall energy conversion efficiencies: methanol chemical
energy to DC power of the two systems are comparable (43%) when a DMFC is operating at 0.55V and a RAFC is operating at 0.70V. This is true assuming:
(a) fuel efficiencies of 90% can be reached in the DMFC,
(b) the methanol reformer efficiency (hydrogen energy out/methanol energy in), is 72% (data from reformer manufacturer), and
(c) the overall efficiency of the PROX (hydrogen energy out/hydrogen energy in) is 97%. The fuel efficiency in the RAFC is assumed here 100%.

The main DMFC parameter that needs significant improvement to reach the level assumed above is the fuel efficiency, which to date is significantly smaller in polymer membrane DMFCs because of methanol cross-over. There are, however, some encouraging new results which show that the cross-over flux may possibly be decreased significantly (particularly at higher temperatures) by the use of lean methanol feeds to the anode, without sacrificing cell performance significantly. Adding this approach to possible membrane modifications aimed at lowering methanol permeability, the fuel efficiency of the DMFC could conceivably reach at higher temperatures the level of 90% assumed above.

This calculation, therefore, shows comparable overall energy conversion efficiencies for the two options, DMFC and reformer + RAFC, achieved at what may be described as typical operating voltages for each of the two types of fuel cells.

Table II. Projected DMFC and RAFC Stack And Systems Characteristics

|                              | DMFC | RAFC |
|------------------------------|------|------|
| Stack Power Density (kW/kg)  | 0.25 | 1.0  |
| Stack Materials Cost ($/kW)  |      |      |
| • Projected^c                | 200  | 45   |
| • Today                      | 2500 | 1500 |
| System Energy Density\(^d\) (Wh/kg) | 450  | 450  |

a). Advanced fuel cell stack is 50 - 75% of total weight. b). Advanced fuel cell stack is 10 - 30% of total weight. c). Assuming drop in membrane cost by an order of magnitude. d). Assuming (1) Similar overall conv. efficiency of 40%, and (2) Range of 240 mile @ 20 kW, 40 mph. Results of (1) and (2) are: DMFC system: 55 kg MeOH, 100 kg stack, 100 kg BOP; RAFC system: 55 kg MeOH, 20 kg stack, 180 kg BOP

Table II uses some very rough estimates to compare three other key parameters for the two systems: DMFC and the reformer+RAFC stack, i.e., the power density, stack materials costs and system's energy density. Table II shows that the stack power density for the reformate/air fuel cell may be a factor three higher, but the stack is only 10-30% of the total weight of the system vs. 50-75% of the weight expected in the case of the DMFC. The stack materials costs per kW are projected four times higher for the DMFC, mainly because of the lower power density. However, it should be remembered that the DMFC stack cost is a much more major component of the total systems cost. The total system energy density for a 20 kW vehicle with a range of 240 miles is estimated to be similar for both options, around 450 Wh/kg. It should be realized that all of these estimates are very rough indeed, but they do seem to lend support to the following general conclusions:
Having obtained roughly one-third the maximum power densities of reformate/air fuel cells, the methanol/air cell shows promise in becoming a serious competitor to the onboard methanol reforming system for methanol-fueled transportation applications. For these two different systems for conversion of methanol to DC power, we have shown that:

1. The mass or volume power density are quite similar for:
   (i) a DMFC stack operating at 0.25 W/cm², and
   (ii) a system comprising a methanol reformer+RAFC generating 1.0 W/cm².
2. The overall energy conversion efficiency for the complete process of methanol chemical energy to DC electric energy, will be similar (43%) for a system with a RAFC operating at 0.70V and a DMFC operating at 0.55V, provided the fuel efficiency in the DMFC is raised to 90%.
3. The cost per kW predicted for the DMFC is significantly higher, as long as the areal power density remains lower by a factor of about 3-4 and the catalyst loadings are not reduced significantly. However, the cost of the balance of plant is much higher in the case of the reformer-based system, lowering the cost differential between the two options significantly.

From the points made above, it seems that the DMFC could become a serious candidate for transportation applications, provided the following requirements are also met:

1. Catalyst loadings are further reduced (or alternative anode catalysts developed).
2. Long term stable performances (1000 hours time scale) are demonstrated, and
3. Fuel efficiencies are actually increased to the 90% level.

ACKNOWLEDGMENT

This work was supported by the U. S. Dept. of Energy, Office of Transportation Technology.

REFERENCES

1. M. S. Wilson and S. Gottesfeld, J. Appl. Electrochem., 22, 1 (1992).
2. M. S. Wilson, J. A. Valerio and S. Gottesfeld, Electrochimica Acta, 40, 355 (1995).
3. S. Srinivasan, E. A. Ticianelli, C. R. Derouin and A. Redondo, J. Power Sources, 22, 359 (1988).
4. T.E. Springer, M.S. Wilson and S. Gottesfeld, J. Electrochem. Soc. 140, 3515 (1993)
5. M. Watanabe, M. Uchida and S. Motoo, J. Electroanal. Chem., 229, 395 (1987).
6. M. S. Wilson, F. Uribe, S. Gottesfeld, and J. A. S. Bett, Manuscript in preparation.
7. J. A. Kosek, C. C. Crompton, G. Wilson, A. B. LaConti, S. Narayan, E. Vamos, S. Surampudi, and H. Frank, Proceedings of the 28th Intersociety Energy Conversion Engineering Conference (IECEC), Vol. 1, pp. 1209, Atlanta, Georgia (1993).
8. S. Surampudi, S. R. Narayanan, E. Vamos, H. Frank, G. Halpert, A. LaConti, J. Kosek, G. K. Surya Prakash and G. A. Olah, J. Power Sources, 47, 377 (1994).
9. X. Ren, T. A. Zawadowski, H. Dai and S. Gottesfeld, This Proceedings.
10. T. A. Zawadowski, T. E. Springer, J. Davey, R. Jestel, C. Lopez, J. Valerio, and S. Gottesfeld, J. Electrochem. Soc., 140, 1981 (1993).
11. H. Grüné, G. Luft, K. Mund and M. Waidhas, Program and Abstracts, Fuel Cell Seminar, p. 474, San Diego, CA, Nov. 28 - Dec. 1, 1994.
12. S. Gottesfeld, TOPTEC of the Society of Automotive Engineers (SAE), Santa Fe, New Mexico, March 29, 1995.
Figure 1. Polarization curves for 130°C, oxygen cathode DMFC based on thin-film catalyzed Nafion 112, 115 and 117 membranes. Anodes: 2.2 mg/cm² Pt-RuOₓ, 1 M methanol at 2 ml/min and 3 atm. Cathodes: 2.3 mg/cm² Pt-black, 5 atm O₂ at 0.6 L/min.

Figure 2. Polarization curves for 110°C, air cathode DMFC based on thin-film catalyzed Nafion 112, 115 and 117 membranes. Anodes: 2.2 mg/cm² Pt-RuOₓ, 1 M methanol at 2 ml/min and 1.8 atm. Cathodes: 2.3 mg/cm² Pt-black, 3 atm air at 0.6 L/min.
Figure 3. Power density curves for the thin-film catalyzed Nafion 112 assembly operating at 130°C on oxygen and at 110°C on air as depicted in Figs. 1 and 2.

Figure 4. The increase in DMFC current density at 0.5 V with temperature for the thin-film catalyzed Nafion 112, 115, and 117 assemblies. Other conditions noted in Figure 1.