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AN OPTION FOR TRANSPORTATION APPLICATIONS

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OCT 11 1996
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Submitted to: Fuel Cell Seminar, Kissimmee, FL, November 1996

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**POLYMER ELECTROLYTE DIRECT METHANOL FUEL CELLS:
AN OPTION FOR TRANSPORTATION APPLICATIONS**

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Introduction

In the last few years polymer electrolyte fuel cell (PEFC) technology has advanced to the point of being considered a viable option for primary power sources in electric vehicles. The systems most frequently considered in this context have been based on either hydrogen carried on board the vehicle, or steam-reforming of methanol on board to generate a mixture of hydrogen and CO₂. Direct methanol fuel cells (DMFCs), which use a liquid methanol fuel feed, completely avoid the complexity and weight penalties of the reformer. Yet until recently DMFCs have not been considered a serious option for transportation applications, primarily because of the much lower power densities achieved compared with operation on hydrogen rich gaseous feeds. Recent advancements in DMFC research and development have been quite dramatic, however, with the DMFC reaching power densities which are significant fractions of those provided by the reformate/air fuel cell (RAFC). The use of established Pt-Ru anode electrocatalysts and Pt cathode electrocatalysts in polymer electrolyte DMFCs has resulted in very significant enhancements in DMFC performance particularly when such cells are operated at temperatures above 100°C and when catalyst layer composition and structure are optimized. The higher DMFC power densities recently achieved provide a new basis for consideration of DMFCs for transportation applications.

DMFC fabrication and testing at LANL

Thin film catalysts bonded to the membrane by the decal method [1,2] provided our best results in terms of catalyst utilization and DMFC performance. Unsupported Pt-RuO_x (Pt:Ru = 1:1) or supported PtRu/C catalysts were used for the anode catalyst and Pt-black or Pt/C was used for the cathode catalyst. Unsupported Pt-Ru anode catalysts yielded the highest overall anode performances. Catalyst inks were prepared by adding 5% Nafion solution to the water-wetted metal catalysts. To prepare the membrane/electrode assemblies (MEAs), appropriate amounts of anode and cathode inks were uniformly applied to Teflon decal blanks to give metal catalyst loadings of approximately 2 mg/cm². The single-cell fuel cell hardware, cell testing and high-frequency resistance measurement [3] systems have been described previously.

Figure 1 shows polymer electrolyte DMFC performances under conditions that take advantage of the significant increase in DMFC performance with temperature but may still be amenable to transportation applications. Air cathodes at 3 atm were used and the cell temperatures were set at 110°C. Figure 1 shows that, with the Nafion 112 MEA, a current of 370 mA/cm² at 0.5 V cell voltage was obtained with a 1M methanol feed. The low cell resistances measured at 110°C (Figure 1) are apparently brought about by the liquid anode feed in contact with the membrane. The polymer electrolyte DMFC may thus be easier to operate at temperatures above 100°C than the hydrogen/air PEFC. Figure 2 summarizes DMFC power outputs we obtained with oxygen and with air cathodes at 130°C and 110°C, respectively, and shows peak power outputs for this type of DMFC at almost 400 mW/cm² for the case of an oxygen cathode at 130°C and about 250 mW/cm² for the air cathode at 110°C.

DMFC vs. Reformer + RAFC: A Comparative Evaluation:

The significant increase in demonstrated DMFC performance, as shown above and by other research groups [4,5], has brought the peak power density of the polymer electrolyte DMFC to a

level which is only 2-3 times lower than that of a reformat/air fuel cell (RAFC). Consequently, at this point, some simple calculations reveal that the two options, (i) a DMFC stack and, (ii) a methanol reformer + RAFC stack, show comparable overall system characteristics.

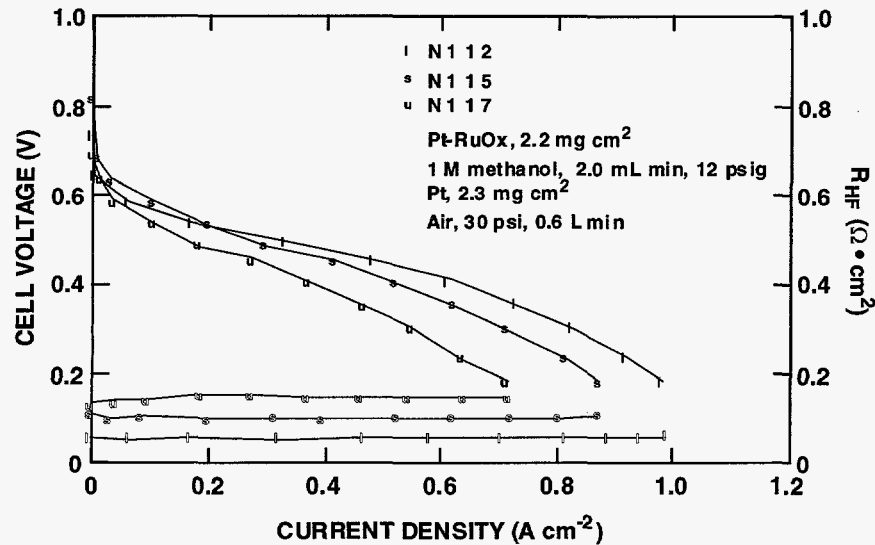


Figure 1. Polarization and high frequency resistance curves for a 110°C, 3 atm air cathode DMFC based on thin-film catalyzed membranes. Anodes: 2.2 mg/cm² Pt-RuO_x, 1 M methanol at 2 ml/min and 1.8 atm. Cathodes: 2.3 mg/cm² Pt-black.

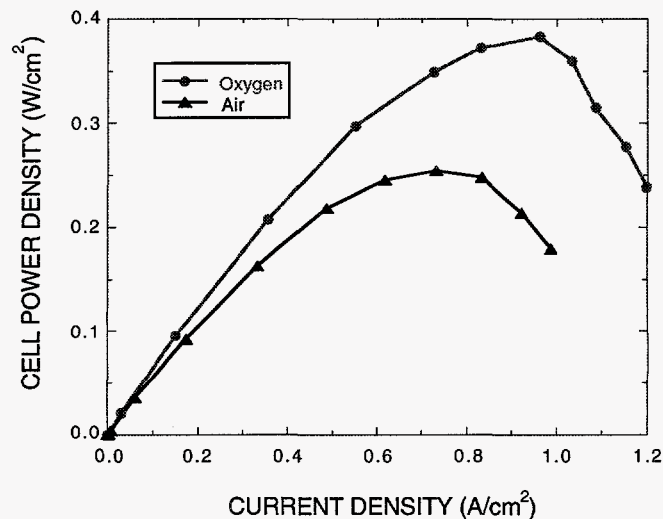


Figure 2. Power density curves for the thin-film catalyzed Nafion 112 assembly, operating at 130°C on oxygen and at 110°C on air.

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

<p><u>Assumptions</u></p> <ul style="list-style-type: none"> • Methanol is either: <ul style="list-style-type: none"> (case 1) Converted directly in DMFC, or (case 2) Steam reformed to H₂ and converted in RAFC <p><u>Efficiency calculation</u></p> <p>(case 1, DMFC) $\text{Total Eff.} = \eta_v \cdot (\eta_{\text{fuel,fc}})_1 = [(V_{\text{cell}})_1 / V^\circ \text{MeOH/CO}_2] \cdot (\eta_{\text{fuel,fc}})_1$</p> <p>(case 2, RAFC) $\begin{aligned} \text{Total Eff.} &= \eta_{\text{ref}} \cdot \eta_{\text{prox}} \cdot \eta_v \cdot (\eta_{\text{fuel,fc}})_2 \\ &= [(V_{\text{cell}})_2 / V^\circ \text{MeOH/CO}_2] \cdot (\eta_{\text{fuel,fc}})_2 \cdot \eta_{\text{ref}} \cdot \eta_{\text{prox}} \end{aligned}$</p> <p><u>Conclusion</u></p> <p>To achieve equal overall conversion efficiencies (MeOH to dc power):</p> $(V_{\text{cell}})_1 = (V_{\text{cell}})_2 \cdot [(\eta_{\text{fuel,fc}})_2 / (\eta_{\text{fuel,fc}})_1] \cdot \eta_{\text{ref}} \cdot \eta_{\text{prox}}$ <p>Assuming $(\eta_{\text{fuel,fc}})_1 = 0.90$, $\eta_{\text{ref}} = 0.72$ and $\eta_{\text{prox}} = 0.97$, then</p> $(V_{\text{cell}})_1 = 0.79 (V_{\text{cell}})_2$ <p>i.e., same overall energy conversion for DMFC operating at 0.55 V and RAFC at 0.70 V.</p>
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Subscripts: v = voltage, fuel.fc = fuel use in the fuel cell, ref = reforming + shift reactors, prox = preferential oxidation reformer.

Table I shows a comparison of overall system efficiencies. The calculation shows that the overall energy conversion efficiencies (methanol chemical energy to DC power) of the two systems are comparable (close to 40%) when the DMFC is operating at 0.55V and the RAFC is operating at 0.70V. This is true assuming:

- fuel efficiencies of 90% can be reached in the DMFC (100% fuel efficiency assumed for the RAFC),
- the methanol reformer efficiency (hydrogen energy out/methanol energy in), is 72%, and
- the overall energy efficiency of the preferential oxidation reactor (PROX) is 97%.

The main DMFC parameter that needs significant improvement to reach the DMFC performance level assumed in Table I is the fuel efficiency, which has been significantly smaller (around 50% at 80°C) in DMFCs employing Nafion[®] 1100 membranes. However, recent efforts to fabricate and evaluate DMFC membranes of significantly lower methanol "cross-over" rates (yet good protonic conductivity) have provided some promising results. The probability of reaching high DMFC fuel efficiencies following further similar efforts seems significant.

The conclusion of a comparable overall energy conversion efficiency for the two systems at the typical operation voltage per cell in each case (DMFC at 0.55V and RAFC at 0.70V) is significant yet obviously depends on the trade-off between the lower DMFC voltage efficiency and the efficiency losses of methanol reforming. Thus, the typically lower DMFC operation voltage is not to be taken as an immediate indication of an inferior overall system energy efficiency.

Table II. Projected DMFC and RAFC Stack And Systems Characteristics

	DMFC ^a	RAFC ^b
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)	750	750

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 PFSA membrane cost by order of magnitude. d) Assuming, in each case, a 50 kW; 300 kWh system of overall weight 400 kg and overall energy conv. efficiency 40%.

Table II uses some very rough estimates to compare three other key parameters for the two systems (DMFC and reformer + RAFC): the power densities, stack materials costs and system energy densities. The stack power density for the reformat/air fuel cell may be a factor of 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 to be four times higher for the DMFC, mainly due to the lower power density, however, the DMFC stack cost is a much larger percentage of the total systems cost. The total system energy density for a 50 kW vehicle with a range of 300 miles assuming average speed of 50 mph (80 kph) is estimated to be similar for both options, around 750 Wh/kg. These estimates are very rough, but it seems that the DMFC could become a serious candidate for transportation applications, provided the following requirements are met:

- (1) Catalyst loadings are further reduced,
- (2) Long term stable performances 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, "Thin-film Catalyst Layers for Polymer Electrolyte Fuel Cell Electrodes," *J. Appl. Electrochem.*, Vol. 22, pp. 1-7, 1992.
2. M. S. Wilson, J. Valerio and S. Gottesfeld, "Low Platinum Loading Electrodes for Polymer Electrolyte Fuel Cells Fabricated Using Thermoplastic Ionomers," *Electrochim. Acta*, Vol. 40, p. 355, 1995.
3. T. E. Springer, M. S. Wilson and S. Gottesfeld, "Modelling and Experimental Diagnostics in Polymer Electrolyte Fuel Cells," *J. Electrochem. Soc.*, Vol. 140, No. 12, pp. 3513-3526, Dec. 1993.
4. S. Surampudi, S. R. Narayanan, E. Vamos, H. Frank, G. Halpert, A. LaConti, J. Kosek, G. K. Surya Prakash and G. A. Olah, "Advances in Direct Oxidation Methanol Fuel Cells," *J. Power Sources*, Vol. 47, p. 377, 1994.
5. H. Grüne, G. Luft, K. Mund and M. Waidhas, "Research and Development of Low Temperature Fuel Cells at Siemens," Program and Abstracts, Fuel Cell Seminar, p. 474, San Diego, CA, Nov. 28 - Dec. 1, 1994.