OPTIMIZING THE OVERALL CONVERSION EFFICIENCY
OF A DIRECT-METHANOL FUEL CELL

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ABSTRACT

It is important to be able to maximize the conversion efficiency of a PEM direct-methanol fuel cell (DMFC) over the broadest possible range of cell power density. The research presented here provides conceptual framework for a control strategy that provides such an optimization. This framework leads into a system level optimization of efficiency *vs.* power, and an operational strategy for controlling a direct-methanol fuel cell for maximum efficiency from minimum to maximum power density. Contrary to the conventional wisdom regarding DMFCs, the research reported here shows that, if such operational strategy could be implemented, DMFCs can be considered for highly dynamic applications – including automotive use – without resorting to "hybrid" power systems.

INTRODUCTION

The potential range of application for the direct-methanol fuel cell (DMFC) depends on its conversion efficiency across a broad spectrum of power density levels. Certainly there are potential niche applications for DMFC power systems that can only be operated efficiently at relatively fixed power, or in "hybrid" power systems. However, if the potential use of the DMFC is limited to such niches, this greatly restricts the eventual markets for the DMFC.

The objective of the research reported here is to critically examine the limitations on the efficiency of the DMFC – when operated over a broad power range. The conventional wisdom was that the DMFC could not efficiently operate across the range of

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power levels demanded in applications such as automotive power systems. It is shown here that this conclusion may be incorrect.

This paper is organized into four sections, followed by a summary of the results. First, there is an explanation of the experimental conditions used to obtain the DMFC data reported and analyzed here. Next, unique features of the DMFC are discussed – focusing on the methanol crossover phenomenon. This is followed by the presentation of the conceptual framework for the optimization of conversion efficiency, which introduces the idea of the Maximum Conversion Efficiency Curve. Finally there is a discussion of the optimized conversion efficiency in terms of the familiar concepts of voltage efficiency and fuel utilization.

EXPERIMENTAL

Pretreatment of the Nafion™ 117 in the H^+ form, preparation of membrane electrode assemblies (MEAs) for a DMFC using a decal technique, and the single-cell fuel cell hardware have been previously described[1,2] as has the cell testing system used.[3] Two unsupported dispersed Pt-Ru catalysts of nominal 1:1 atomic ratio were used for anode preparation, both supplied by Johnson Matthey. Anode inks were made by dispersing appropriate amounts of the Pt-Ru catalyst in deionized/distilled water and adding 5% Nafion™ solution (1200 in equivalent weight, Solution Technology Inc.). The cathode inks contained unsupported Pt black (30 $m^2 g^{-1}$, Johnson-Matthey), deionized/distilled water and 5% Nafion™ solution (1100 equivalent weight, Solution Technology Inc.). In some cases, the catalyst layers involved direct application of the catalyst inks to PTFE-treated carbon cloths. The geometric active area of all the MEAs prepared was 5 cm^2.

Methanol solutions, between 0.25 and 2.0 M in concentration, were pumped through the DMFC anode flow field at precisely controlled rates (0.5-3.0 ml min^{-1}) using a Shimadzu LC-10AS HPLC pump. A back pressure of about 15 psig was imposed upon the anode outlet flow to ensure that the membrane would be in contact with a liquid solution of methanol at the cell operating temperature of 100°C. The cathode gas feed was air at a pressure of 30 psig and flow rate of 0.5 l min^{-1}. The air was usually pre-humidified at the same or similar temperature as that of the operating cell.

The crossover of methanol as a function of cell current density was recorded together with the corresponding cell polarization (V-I_C) chracteristic. The determination of crossover was based upon the amount of carbon dioxide in the cathode exhaust, as measured using a GMM12 Carbon Dioxide IR Sensor (Vaisala Oy, Finland). The IR detector was earlier pre-calibrated with a gaseous mixture of 4% CO_2 and 96% N_2. The CO_2 content in the cathode exhaust was converted into the corresponding amount of

methanol that had crossed through the membrane, expressed as current density of MeOH oxidation on the cathode, I_X (see below).

DMFC CHARACTERISTICS

A unique feature of the direct-methanol PEM fuel cell – when compared to a direct-hydrogen or reformate fuel cell – is the significant crossover of methanol from the anode through the membrane into the cathode. For the purposes of this study, the critical result of the crossover is an efficiency loss due to an unproductive fuel consumption mechanism.

It is possible to treat methanol crossover analytically within the concept of "fuel utilization", while dealing with the cell polarization curve (voltage *vs.* cell current) separately in terms of "voltage efficiency". This is commonly done for reformate PEM fuel cells. However, this disguises the physical interaction between the cell current and crossover current (methanol crossover expressed as equivalent current density of MeOH oxidation to carbon dioxide at the cathode), and obscures the possibilities for optimizing cell current and power density *vs.* crossover losses.

In this paper, we introduce a concept of viewing the crossover current density, together with the cell current density, and voltage – in terms of a "composite" polarization curve. An example of this type of composite polarization curve is shown in **Figure 1**, for a particular set of experimental conditions. The conceptual value of this composite polarization curve is that it explicitly illustrates the interaction between the cell and crossover current densities.

The cell current density (I_C) and crossover current density (I_X) curves in Figure 1 allow to predict the behavior of a direct-methanol cell under variable cell current, illustrating the characteristic impact of increasing the cell current on crossover current losses. When the cell current increases the crossover current decreases and the fuel utilization increases, in this example to almost 90% at about 0.3 V, 0.31 A cm^{-2}. In contrast, where the I_C and I_X curves cross (about 0.6 V in this case) the fuel utilization is 50% and, for the lowest cell current density shown, fuel utilization falls to about 10%.

It is obvious that we would choose to operate a cell with the polarization curve shown in Figure 1 at the highest possible cell current (maximum cell power density), in order to reduce crossover losses. This has led to an argument that direct-methanol cell may have to be a part of a "hybrid" power system – *i.e.*, where the fuel cell is only operated at its highest power density and another electrical energy storage device is used to provide lower power levels.

However, as we will try to show below, there is no fundamental reason to limit the operation of a DMFC power system to a "hybrid" power system configuration. High fuel utilization can be achieved over a complete range of power densities without resorting to additional energy storage devices and without creating the need to control and manage the output from two separate power sources.

The key cognitive step is to realize that the example shown in Figure 1 is for a particular set of anode (and cathode) conditions. However, for a different set of anode conditions, *i.e.*, a different methanol concentration and solution flow rate, the crossover current, cell current, voltage and power density will all change, in a given cell, in a predictable and controllable way. Thus, we will show that it is possible to minimize the crossover losses for a wide range of power densities by manipulating the anode feed conditions. This is illustrated in the next section using data for some direct-methanol fuel cells fabricated and tested at LANL.

EFFICIENCY OPTIMIZATION *vs.* POWER

As shown in the last section, by expressing the methanol crossover flux as a crossover current density, the DMFC performance characteristic can be represented by a set of I_C and I_X curves *vs.* cell voltage. Figure 1 illustrates this for a particular choice of anode and cathode conditions. For a different choice of anode methanol concentration and solution flow rate, there will be a different pair of I_X and I_C curves that characterize the cell.

A set of such curves is shown in **Figure 2** – for the case of a fixed methanol concentration and a variable solution flow rate to the anode. This particular methanol concentration was chosen to illustrate significant impact of anode flow conditions on the crossover current, combined with a fairly minor impact on cell current. Such beneficial effects of anode operation conditions are achieved by appropriate DMFC anode design. It is obvious that, with this set of composite polarization curves, one would choose to operate the cell at the lowest solution flow rate (curve labeled **a**) for this methanol concentration level.

This is further illustrated in **Figure 3**, where the cell power density is plotted *vs.* the cell fuel consumption density (cell plus equivalent crossover current density). In this presentation of the composite data for variable anode solution flow rate at constant anode feed concentration, it becomes even more obvious that one would choose to operate at the lowest solution flow rate (curve **a** for this particular methanol concentration). Curve **a** generates the highest power for every value of fuel consumption density (or fuel rate density).

By following the procedure illustrated above in Figures 2 and 3 for a range of inlet methanol solution concentrations, it is possible to select an optimum flow rate for each concentration value. The result of this optimization procedure is shown in **Figure 4** for three values of methanol concentration: 0.25, 0.5 and 1.0 M (curves **a, b,** and **c,** respectively). A 100% conversion efficiency curve is also shown in Figure 4 as reference.

It is obvious from Figure 4 that, assuming one were limited to only these three values of concentration, there is a control strategy that will optimize the power output for a given fuel flow rate or power level. The correct control strategy is: begin with curve **a** for low power levels, transition to curve **b** for moderate power levels, and finally transition to curve **c** for the highest power levels. This control strategy would insure both the highest power density and highest efficiency for every fuel consumption (fuel rate) density.

This result is illustrated in **Figure 5**, where the cell overall conversion efficiency is plotted *vs.* the flow rate for the three sets of conditions in Figure 4, together with an envelope of the discrete curves depicting the limiting case of continuously variable methanol concentration and flow rate. This envelope is referred to as the Maximum Conversion Efficiency Curve. We also refer to it as the "Op Curve" (short for Operating Curve) that maximizes DMFC efficiency for variable methanol feed concentration and flow conditions in the anode.

This Op Curve is displayed in **Figure 6** in a somewhat different format – conversion efficiency *vs.* power density. This format is particularly useful for power system analysis and modeling applications.

DISCUSSION OF RESULTS

It is instructive to translate the results illustrated in Figures 5 and 6, and particularly the resulting Op Curve, into more familiar settings – specifically into the equivalent power density, composite polarization, and fuel utilization curves that correspond to the Op Curve. These composite equivalent curves obtained for the Op Curve control strategy can then be compared with the corresponding curves for fixed anode conditions. This helps us to understand the physical basis for the improved efficiency achieved with the Op Curve control strategy.

Figure 7 shows the Op Curve as cell power density *vs.* cell fuel consumption density. In this representation, it is, of course, simply the envelope of the three discrete curves in Figure 4 – obtained under the condition of continuously variable methanol concentration and solution flow rate.

Figure 8 presents a comparison of both I_C and I_X for (i) the Op Curve control strategy, and (ii) a fixed methanol concentration and solution flow rate case. (The fixed anode condition curves chosen corresponds to the concentration and flow rate for maximum cell power density.) This figure illustrates quite clearly that, while the Op Curve produces somewhat higher voltage at a given cell current density (compared to the cell under fixed anode conditions), the major improvement is a significant reduction in I_X at low current density (power density) values. Thus the primary effect of the Op Curve control strategy is to reduce the crossover losses by up to 50% at low power levels – while also achieving marginally higher voltage efficiency.

Finally, **Figure 9** explicitly shows the impact of the Op Curve control strategy on the crossover losses – using the "fuel utilization" factor (the ratio of the cell current density to the cell plus crossover current density) to evaluate the performance of the DMFC with the Op Curve control strategy. The fuel utilization is plotted *vs.* cell current density (a surrogate for cell power density). This illustrates quite clearly that the primary effect of the Op Curve control strategy is to significantly increase the fuel utilization at low current (power) levels. It is this effect that maintains a relatively high level of cell conversion efficiency across a broad range of power levels, *i.e.*, the result illustrated in Figure 6. There is, of course, also a contribution from the improved voltage efficiency – again primarily at low cell current (power) density.

SUMMARY OF RESULTS

The conceptual framework presented in this paper has established the following:

(i)   At a given DMFC fuel consumption density, the DMFC power density is maximized by simultaneously controlling the methanol concentration and solution flow rate to the anode. This is illustrated in Figure 4, where cell power density is plotted *vs.* the sum of the cell and crossover current densities for three particular choices of anode conditions at fixed cathode conditions.

(ii) The envelope of all such points of maximum power density – each for a given fuel consumption – provides the maximum conversion efficiency for the complete range of fuel consumption. This is illustrated in Figure 5, displayed as conversion efficiency versus the fuel rate density.

Finally, the optimized conversion efficiency curve (Op Curve) provides a conceptual basis for an optimum DMFC system control strategy. Figure 6 illustrates the conversion efficiency resulting from this Op Curve control strategy.

A key feature of this optimized curve is its relative flatness versus power density (*e.g.*, greater than 30% efficiency over a range from about 70 to 230 mW cm^{-2}). This is a desirable shape for applications where power demand has a broad dynamic range – such as automotive applications.

The major operational conclusion from the analysis presented in this paper – and particularly illustrated by Figures 5 and 6 – is that it could be possible to optimize the conversion efficiency of a DMFC power system by manipulating the anode feed stream as a function of the system power demand. Such optimum control strategy for direct-methanol fuel cell power systems would be based on following a Maximum Conversion Efficiency Curve (Op Curve) as described in this paper. Needless to say, application of such strategy would depend on defining the system engineering requirements for implementation of a variable concentration, variable flow methanol feed stream.

Comment on cathode optimization

All of the analysis and optimization presented in this paper was illustrated for the case of constant cathode conditions – constant cathode air pressure and flow. This was done for the purpose of clarity in examining the impact of anode conditions. However, for an optimum overall DMFC power system it is necessary to further optimize the operation of the cell by controlling the cathode conditions. The general technique for such an optimization on the cathode side of the DMFC is illustrated in another paper presented in this Symposium (D. J. Friedman and R. M. Moore, *This Symposium*). This optimization for the DMFC is beyond the scope of the current paper, and is highly specific to the particular behavior of the DMFC cathode under the conditions of methanol crossover.

ACKNOWLEDGMENTS

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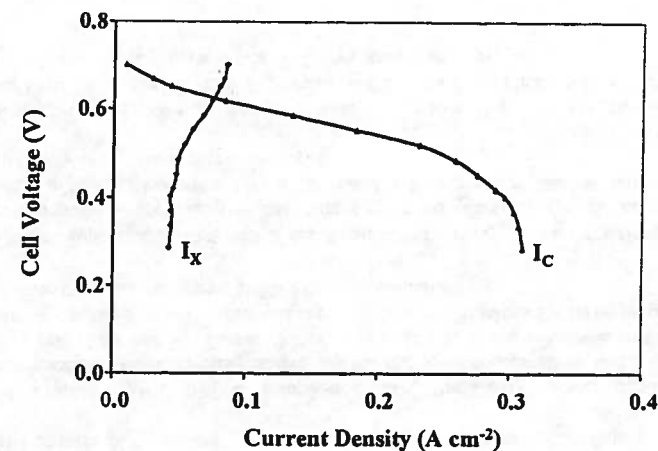
FIGURES

Figure 1. Current density curves for a DMFC, where I_X is methanol crossover current density and I_C is the cell current density (c=0.25 M, f=4 ml min^{-1}, T=100 °C).
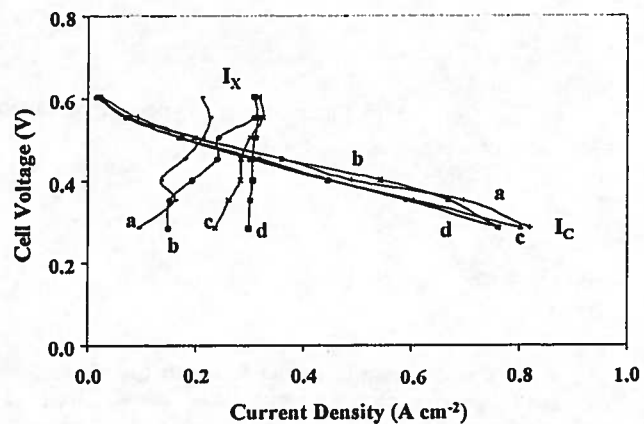
Figure 2. Crossover and cell current density curves for a DMFC; I_X is methanol crossover current density and I_C is the cell current density (c=2.0 M, f= variable; T=100 °C).
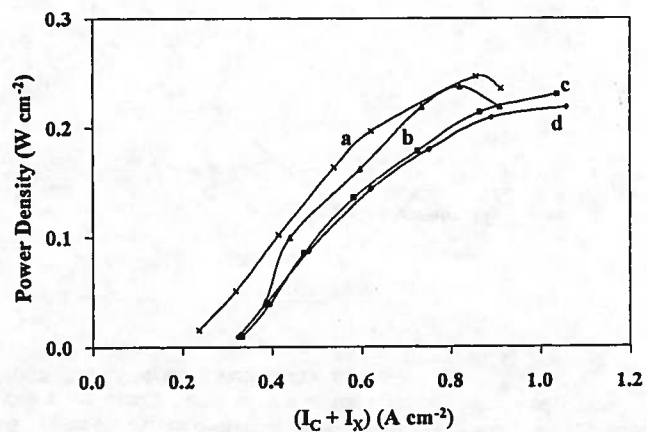

Figure 3. Power density curves for a DMFC vs. sum of I_X (methanol crossover current density) and I_C (cell current density); c=2.0 M; T=100 °C; f is (a) 0.5 ml min^{-1}, (b) 1.0 ml min^{-1}, (c) 2.0 ml min^{-1}, and (d) 3.0 ml min^{-1}.
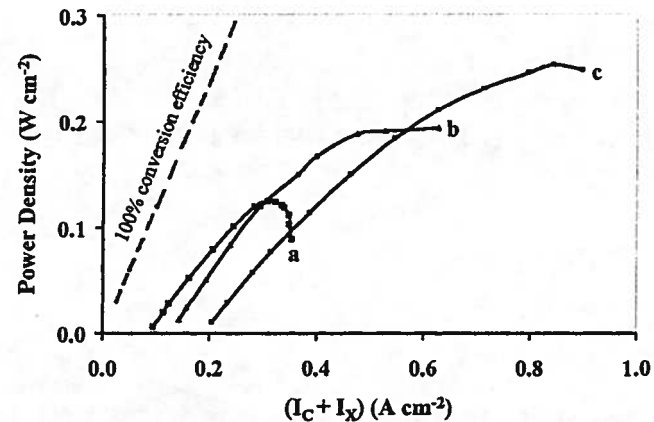

Figure 4. Power density of a DMFC for variable methanol concentration: (a) 0.25 M, (b) 0.5, (c) 1.0 M, as function of overall DMFC fuel consumption density. The reference 100% conversion efficiency plot corresponds to generation of electric power from MeOH at 100% fuel utilization, at the thermodynamically expected cell voltage of 1.21 V.
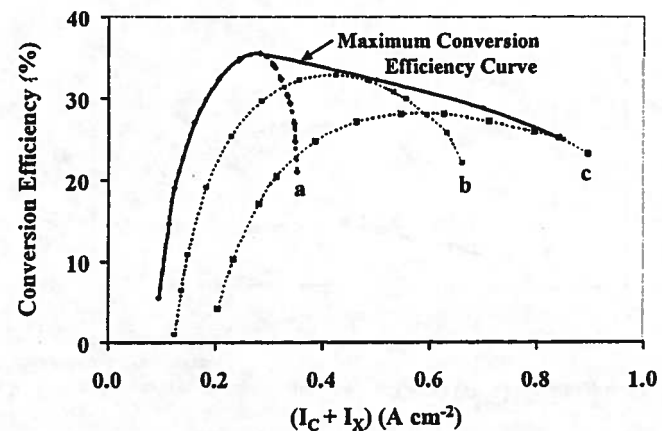

Figure 5. Overall conversion efficiency of a DMFC for variable methanol concentration: (a) 0.25 M, (b) 0.5 M, (c) 1.0 M.
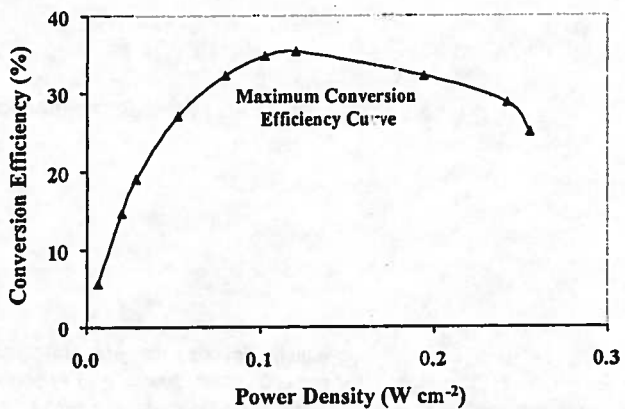
Figure 6. Optimum overall conversion efficiency *vs.* cell power density, plotted against fuel consumption density based on results for the same three feed concentrations of MeOH (0.25, 0.5, 1.0 M) and a variable flow option.
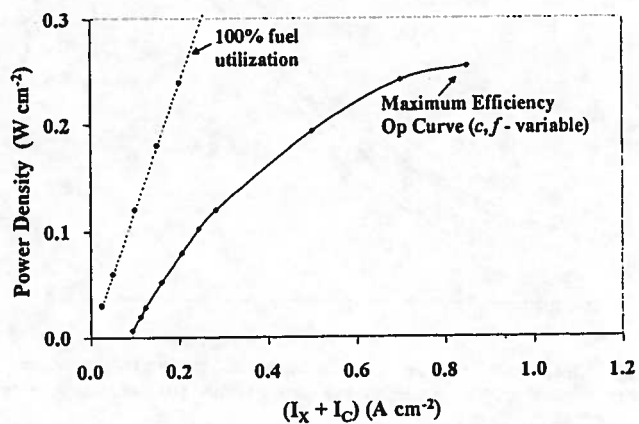

Figure 8. Cell and crossover current density for Op Curve (variable *c* and *f*) and for fixed *c* and *f* (maximum power curve).

Figure 7. DMFC power density achievable under Maximum Conversion Efficiency conditions ("Op Curve") employing variable methanol concentration and solution flow rate.
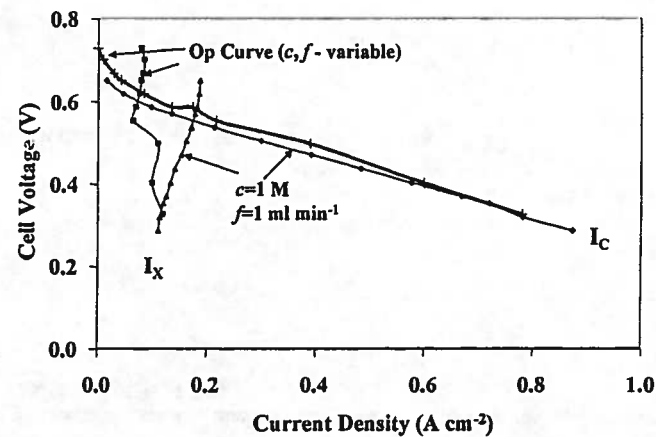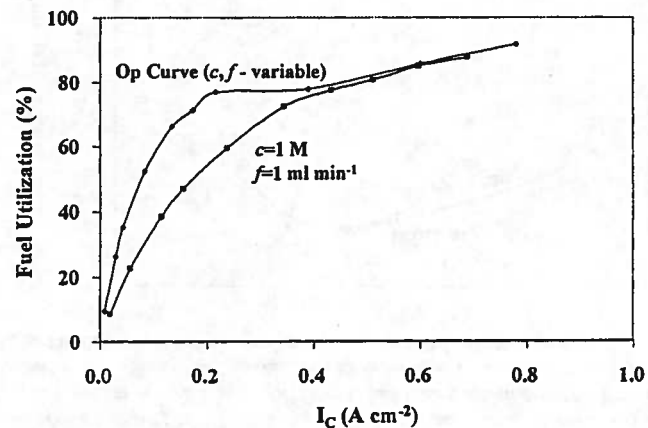

Figure 9. Fuel utilization *vs.* cell current density for Op Curve (*c* and *f* variable) and for fixed *c* and *f* (maximum power curve).