ABSTRACT

A feasibility analysis of a mixed-reactant, strip-cell direct methanol fuel cell concept is presented. In this type of cell, selective electrodes are mounted in an alternating fashion on the same side of a membrane electrolyte, which minimizes the need for ancillary equipment, and maximizes power density. At low current density, the fuel efficiency of the direct-methanol strip cell is shown to be higher than that of a bipolar cell with typical cathodes. The effect of geometric parameters on the performance of strip cells is discussed, and design recommendations are given for a simple geometry.

INTRODUCTION

High power density, small-scale direct methanol fuel cell stacks require minimization of weight and volume due to ancillary system components. One way to accomplish this is to use a “strip cell” arrangement, in which strips of anode and cathode material are alternated over strips of membrane electrolyte on the same side of a non-conducting support film. A diagram of this scheme is shown in Fig. 1. Selective electrodes that are active only to one reactant are employed to prevent parasitic chemical reactions. This approach reduces weight and volume by eliminating seals, separator plates, and load-bearing structures.

Previous reports have considered the merits of conventional strip cells, in which the cells are arranged in-plane, but the reactants are separated on opposite sides of the cell (1,2). Such designs provide high stack voltage in a small volume, but require complicated sealing to prevent leaks between reactant streams. Selective electrode fuel cells with mixed reactant feed have been considered for solid oxide (3) and proton-exchange membrane fuel cells (4,5). In none of these studies were the electrodes in a strip-cell arrangement.

Two selective cathode catalysts of current interest are iron tetramethoxyphenyl porphyrin (FeTMPP), and a transition metal cluster catalyst (Ru-Se-Mo). Both catalysts have been shown to be methanol tolerant (6,7). The main motivation for development of these selective cathode catalysts has been to reduce the effect of methanol crossover. As will be demonstrated, an important advantage of the selective electrode
approach for direct methanol fuel cells is that methanol crossover is eliminated as an issue.

The strip cell geometry places a premium on electrolyte and electrode conductivity, because current flows perpendicular to the thickness of these components. Proper electrolyte-membrane thickness, electrode widths, and electrode spacing must be chosen to minimize ohmic losses and maximize electrode utilization. This paper will conclude with a discussion of these issues.

FUEL EFFICIENCY

As previously stated, an important advantage of selective electrodes for direct methanol fuel cells is the elimination of the issue of methanol crossover. This can be demonstrated in Fig. 2. Here the polarization performance and the fuel efficiency of a selective-electrode cell with FeTMPP cathode catalyst and mixed feeds are compared with a more "traditional" DMFC with platinum catalysts and pure feeds. For these cells a constant rate of methanol crossover, \( N_{\text{ XO}} = 0.35 \ \mu\text{mol}/\text{cm}^2/\text{s} \), was assumed, equivalent to a crossover current of 200 mA/cm\(^2\) (8). The fuel efficiency is defined by

\[
\eta = \frac{IV}{\Delta H (N_a + N_{\text{ XO}})}
\]

where \(\Delta H\) is the heat of combustion of the fuel, which for pure methanol at 20°C and 1 atmosphere is 0.78 MJ/mol.

Both cells use a Nafion 117 membrane, which is highly permeable to methanol. The temperature of the cell is 80°C and at ambient pressure. Air is supplied to the cathode and 1 molar methanol to the anode. Although the performance of the "traditional" cell is better, its fuel efficiency is lowest at low current densities. The cell with mixed reactants and selective electrodes has an efficiency that is proportional to the cell potential. This highlights the key advantage of the selective electrodes. High fuel efficiency can be achieved if the selective-electrode cell is limited to low current density.

CELL GEOMETRIC DESIGN

The strip-cell configuration introduces an additional issue of possibly high ohmic losses. As shown in Fig. 3a, current passes in the plane of a strip cell, normal to the thickness and along the width of the electrodes and the membrane electrolyte. An appropriate strip-cell geometry must be chosen to minimize ohmic losses compared to those associated with electrode kinetics. In the following, the appropriate cell geometry will be discussed for a simple configuration.
Cell Conditions

The strip-cell assembly of Fig. 3a was simplified to a two-dimensional model, as shown in Fig. 3b. The important parameters in this geometry are the electrode widths, $w_c$ and $w_a$, the electrode spacing, $s$, and the thickness, $t$, of the membrane electrolyte. It is assumed here that the length, $L$, of the electrodes is much greater than their width or thickness. The width of each electrode is defined by the amount of overlap between the electrode and membrane. Base-case values for these parameters are specified in Table I. For simplicity, a constant cell current density of 20 mA/cm$^2$ was assumed, although other design constraints may alternatively be chosen.

Table I. Base Case Cell Parameters

| Parameter                        | Value |
|----------------------------------|-------|
| Conductivity, $\kappa$ (mS/cm)   | 100   |
| Anode width, $w_a$ (cm)          | $2 \times 10^{-2}$ |
| Relative cathode width, $w_c/w_a$| 1     |
| Relative electrode spacing, $s/w_a$ | 0.1   |
| Relative membrane thickness, $t/w_a$ | 2     |
| Cell current density, $I$ (mA/cm$^2$) | 20    |

Each electrode is considered planar and infinitely conductive. Although electrode porosity is necessary for gas access, it was not considered here. High electrode conductivity may be practically achieved by addition of a conductive filler such as graphite. Tafel kinetics were assumed. Tafel parameters, which are representative of the anode and two cathode materials discussed above, are given in Table II. The assumption of Tafel kinetics is limited to current densities less than 100 mA/cm$^2$, such that mass-transfer effects may be neglected. Ohmic cell resistance was calculated using the Schwarz-Christoffel method (9,10), and the overall cell polarization was calculated using a boundary element method.

Table II. Kinetic Parameters for Selective Electrodes

| Parameter                        | Anode | FeTMPP Cathode | Ru-Se-Mo Cathode |
|----------------------------------|-------|----------------|------------------|
| Open Circuit Half-cell Potential, (V) | 0.0   | 1.23           | 1.23             |
| Exchange Current Density, (mA/cm$^2$) | $6.88 \times 10^{-4}$ | $4.95 \times 10^{-6}$ | $4.75 \times 10^{-4}$ |
| Tafel slope, (V)                  | $2.25 \times 10^{-2}$ | $3.74 \times 10^{-2}$ | $6.58 \times 10^{-2}$ |
Ohmic Cell Resistance

The ohmic resistance, i.e. the cell resistance for infinitely fast electrode kinetics, provides a preliminary understanding of the effects of geometry on true cell resistance. Such information indicates the ranges of geometric parameters for which ohmic losses may be minimized in the actual cell. Fig. 4 shows the variation of the dimensionless ohmic resistance of the cell, $LkR$, with electrode spacing, $s$, plotted with membrane thickness, $t$, as a parameter. In this plot, spacing and thickness are normalized by electrode width, $w$. As expected, the ohmic resistance decreases uniformly with decreasing electrode spacing. In contrast, as thickness decreases, the ohmic resistance is seen to increase. For $t/w > 2$ at small spacing, the resistance becomes essentially independent of thickness. For $s/w \leq 0.1$, this independence may be extended to $t/w = 1$. One may thus conclude that a practical design target is to set the electrode width to less than half the membrane thickness.

Overall Cell Polarization

Effect of electrode width. The kinetics of the chosen selective cathode materials, as given in Table II, are slow compared to supported noble metals. Such slow kinetics control the polarization behavior of the cell in cases where ohmic losses are low, such as when the membrane thickness is large and the electrode spacing is small.

For example, Fig. 5 is a plot of cell power density as a function of electrode width, $w = w_a = w_c$, for two cathode materials. The values of all fixed parameters are given in Table 1. The power density is defined as

$$P = \frac{IV}{L(w_a + w_c + s)} \quad [2]$$

where the quantity $(w_a + w_c + s)$ is an estimate of total cell width. For both cathode materials, cell power density increases as electrode width decreases and ohmic losses are reduced. The sensitivity of the power density to electrode width decreases with decreasing electrode width, however, as the cell polarization falls under the control of electrode kinetics. For both cell types, the power density begins to plateau as the electrode width decreases below 0.1 cm, and is insensitive to electrode width for $w < 0.01$ cm. For these electrode materials, therefore, an electrode size on the order of 0.1 cm may be appropriate.

Effect of membrane thickness. Fig. 6 shows the variation of cell power density with membrane thickness, with all fixed-parameter values given in Table 1. Power density appears to be only weakly dependent on membrane thickness over the range shown. As indicated by the primary cell resistance, the cell power density is independent of
membrane thickness for \( t/w > 1 \). A relative membrane thickness of \( t/w = 1.0 \) is sufficient to minimize ohmic losses under these conditions.

**Effect of electrode spacing.** In Fig. 7, the cell power density for a fixed cell current density is plotted as a function of electrode spacing for two cathode materials. Cell power density is shown to be only weakly dependent on electrode spacing for small spacing, such that \( s/w < 0.1 \). Under such conditions, cell polarization falls under mainly kinetic control. Under purely kinetic control, the electrode current density is uniform, and the electrode width, \( w \), becomes an important length scale for current flow. As electrode spacing decreases to much less than this width, the potential drop across this width becomes small compared to the total ohmic potential drop. One may conclude from these results that a normalized electrode spacing of \( s/w = 0.1 \) is the minimum from which practical benefit may be derived in this case.

**Effect of relative electrode width.** In a strip cell, electrodes of unequal macroscopic area can be employed in the same cell. Whether this added dimension can be exploited for performance gains depends on cell design criteria, e.g., whether cell potential or cell current is held fixed.

For example, Fig. 8 is a plot of cell power density as a function of cathode-anode width ratio, \( w_c/w_a \), for two cathode materials. The values of all fixed parameters are given in Table 1, with the exception that cell potential, not current density, is held fixed at 0.4 V. For fixed potential, a weak maximum appears for electrode width ratio \( w_c/w_a > 1 \). For the Ru-Mo-Se catalyst, a 13% increase in power density can be achieved by setting the cathode width to be about three times that of the anode. This maximum occurs at a width ratio such that decreased cathode losses, due to lower cathode current density, are matched by anode losses that increase with increasing anode current density. In this case, the value of \( w_c/w_a \) at maximum power density is greater than unity because the cathode kinetics are slower than are those of the anode. It should be noted that such performance gains may also be obtained by increasing the cathode catalyst loading.

No such maximum occurs for fixed cell current. Under electrode kinetic control, cell potential displays a weak, logarithmic dependence on cathode width; under resistance control, cell potential decreases with increasing cathode width. The linear increase in cell width therefore causes the fixed-current power density, as defined by Eq. 2, to decrease monotonically with increasing cathode width.

A strip cell with the FeTMPP cathode, in the base-case configuration, gives an ohmic potential loss of only 4 mV at 20 mA/cm\(^2\) current density. Such losses are small compared to the combined kinetic overpotential of about 800 mV. In terms of performance, therefore, the strip cell may be a practical configuration for the implementation of selective electrodes in a mixed-reactant, direct methanol fuel cell. The manufacturability of such strip cells with small electrode thickness and spacing is a separate, important issue that will not be discussed here.
Overall system power density. The power densities presented herein should not be mistaken for overall system values; they only reflect the power density of the electrochemical cell itself. An estimate of overall system power density, the minimization of which is a primary motivation for pursuit of mixed-reactant designs, requires detailed knowledge of a complete system, and will not be attempted here. Clearly, the power densities presented in Figures 5 to 8 are quite low compared to conventional DMFC systems with noble metal catalysts. This is particularly true for the Ru-Se-Mo cathode, which gives only 1.2 mW/cm² at 20 mA/cm², compared to ~11 mW/cm² at the same current density for the platinum-cathode cell of Fig. 2. For the present strip-cell system to be practical, such deficiencies must be redressed by elimination of ancillary structures.

CONCLUSIONS

This paper has discussed aspects of a direct methanol fuel cell in a strip-cell configuration, with selective electrodes and a mixed-reactant feed. The fuel efficiency of the strip cell configuration was demonstrated to be higher than that of a bipolar cell with noble-metal electrodes at low current density.

A design analysis of a simple strip-cell DMFC with selective electrodes was discussed. For the electrode materials considered, the following geometry is appropriate:

1. An anode width of about 0.1 cm.
2. A membrane thickness 1 to 2 times the average electrode width.
3. An electrode spacing one tenth the average electrode width.

Additionally, the cathode width ratio may be chosen to be different from that of the anode to take advantage of mismatched electrode kinetics. For an electrode width of 0.02 cm, using FeTMPP cathode material, these dimensions lead to an ohmic overpotential of just 4 mV at 20 mA/cm² cell current density. This demonstrates the viability of the strip cell configuration for the mixed-reactant feed DMFC. A complete strip-cell system is required to demonstrate that overall power-density improvements are achievable using such a configuration.

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LIST OF SYMBOLS

\[ I \] ..........Cell current (mA)
\[ L \] ..........Electrode length (cm).
\[ N_a \] ..........Rate of methanol consumption at the anode (mol/s).
\[ N_{XO} \] ..........Methanol crossover rate (mol/s).
\[ P \] ..........Cell power density, defined by Eq. 2 (W/cm\(^2\)).
\[ R \] ..........Cell resistance (\(\Omega\)).
\[ s \] ..........Electrode spacing (cm).
\[ t \] ..........Membrane thickness (cm).
\[ V \] ..........Cell potential (V).
\[ w \] ..........Anode and cathode width (cm).
\[ w_a \] ..........Anode width (cm).
\[ w_c \] ..........Cathode width (cm).

Greek

\[ \Delta H \] ..........Heat of combustion of methanol (J/mol).
\[ \kappa \] ..........Electrolyte conductivity (mS/cm).

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Support
Air
Water
MeOH
Flow
Anode
Cathode
Electrolyte
Power
Take-off
Buss

Figure 1. Strip Cell Concept.

Figure 2. Performance and fuel efficiency of a traditional DMFC compared to one with selective electrodes. The efficiency of the selective-electrode cell is highest at low current density, whereas that of traditional cell increases with current density.
Figure 3. Simplified Strip Cell Model.

Figure 4. Dimensionless resistance of strip cell, as calculated by Schwarz-Christoffel transformation. Resistance increases with increasing electrode spacing and with decreasing membrane thickness, and is independent of membrane thickness at high thickness and low spacing.
Figure 5. Effect of electrode width on cell performance. Both cells are sensitive to electrode width for $w > 0.1$ cm.

Figure 6. Effect of membrane thickness on cell performance. The performance of both cells is weakly dependent on membrane thickness, and is independent of thickness for $t/w > 1$. 
Figure 7. Effect of electrode spacing on cell performance. Thickness dependence becomes weak for $s/w < 0.1$.

Figure 8. Effect of cathode width on cell power density, at 0.4 V cell potential. The cell with Ru-Se-Mo cathode displays a strong maximum at $w_c/w_a = 3$. The maximum in the FeTMPP cell is weak.