Advances in direct oxidation methanol fuel cells

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Abstract

Fuel cells that can operate directly on fuels such as methanol are attractive for low to medium power applications in view of their low weight and volume relative to other power sources. A liquid feed direct methanol fuel cell has been developed based on a proton-exchange membrane electrolyte and Pt/Ru and Pt-catalyzed fuel and air/O_2 electrodes, respectively. The cell has been shown to deliver significant power outputs at temperatures of 60 to 90 °C. The cell voltage is near 0.5 V at 300 mA/cm^2 current density and an operating temperature of 90 °C. A deterrent to performance appears to be methanol crossover through the membrane to the oxygen electrode. Further improvements in performance appear possible by minimizing the methanol crossover rate.

Introduction

Direct oxidation methanol fuel cells are attractive for several defense and transportation applications in view of their lower weight and volume compared with indirect fuel cells [1, 2]. The weight and volume advantages of direct oxidation fuel cells are due to the fact that they do not require any fuel processing equipment. Elimination of the fuel processor also results in simpler design and operation, higher reliability, less maintenance, and lower capital and operating costs. Further, direct oxidation fuel cells are projected to have rapid and multiple start-up capabilities, and the ability to easily follow varying loads.

Under a task sponsored by the Defense Research Projects Agency (DARPA), Jet Propulsion Laboratory, University of Southern California, and Giner, Inc. are engaged in the development of direct methanol fuel cells for future defense applications. A near-term objective of the program is to identify advanced catalysts and electrolytes and demonstrate the technology of the direct oxidation methanol fuel cells at the cell level. This paper describes the progress made to date on this effort.

Assessment of catalysts for the oxidation of methanol

Anodic oxidation behavior of methanol was investigated in half-cells using both supported and unsupported catalysts at a loading of 0.5 mg/cm^2. In these experiments

0.5 M sulfuric acid was used as the electrolyte along with 0.001 M perfluorooctane-sulfonic acid, the fuel concentration was 1.0 M, and the temperature was 45 °C. Anodic oxidation characteristics of methanol at various unsupported (Pt–Sn and Pt–Ru) and supported catalysts (Pt, Pt–Sn and Pt–Ru) are given in Figs. 1 and 2. It can be seen from these results that Pt–Ru is the most promising among the state-of-the-art Pt-based catalysts for the oxidation of methanol. This observation is in agreement with the results reported in the literature [3, 4]. All further studies were carried out using Pt–Ru catalyst.

Improved kinetics of methanol oxidation on Pt–Ru catalyst were observed with an increase in temperature, catalyst loading, and methanol concentration. Figure 3 reveals a significant reduction of polarization as the temperature is raised from 25 to
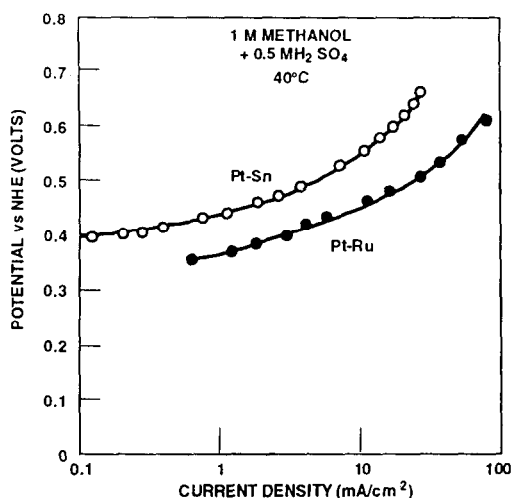

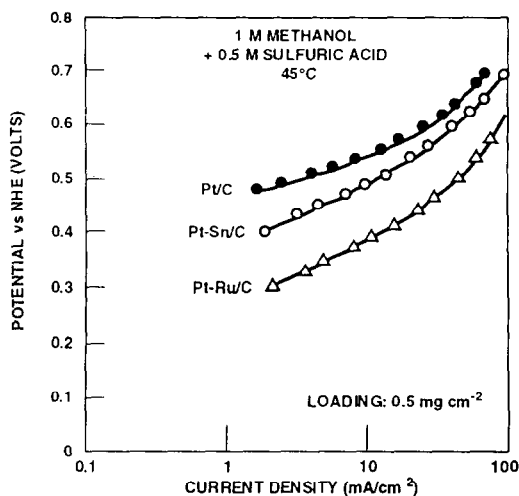Fig. 1. Evaluation of unsupported catalysts for methanol oxidation.

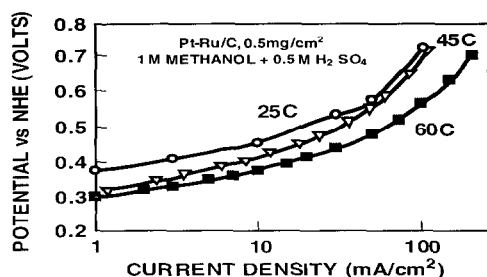Fig. 2. Evaluation of supported catalysts for methanol oxidation.

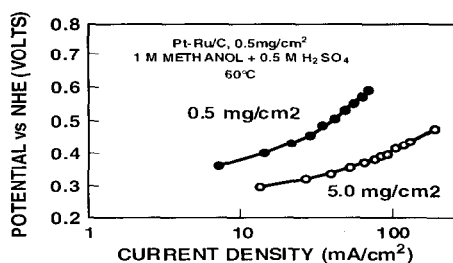Fig. 3. Effect of temperature on performance of Pt–Ru electrodes.

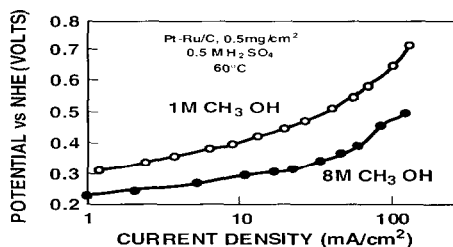Fig. 4. Effect of catalyst loading on performance of Pt–Ru electrodes.

Fig. 5. Effect of fuel concentration on performance of Pt–Ru electrodes.

60 °C. Throughout the current density range of 1 to 100 mA/cm^2 the polarization is reduced almost 100 mV by this temperature increase. Figure 4 gives the results of the catalyst loading studies. Results show that an increase in loading from 1 to 5 mg/cm^2 resulted in the reduction of almost 100 mV polarization throughout the current density range from 1 to 100 mA/cm^2. Increasing the methanol concentration also resulted in lower anodic polarization for the oxidation of methanol (Fig. 5).

Evaluation of electrolytes for the oxidation of methanol

Liquid electrolytes

Boron trifluoride dihydrate, triflic acid, perfluoroethane sulfonic acid and perfluorooctane sulfonic acid (C_8 acid) were evaluated as candidate electrolytes for the oxidation of methanol. Experiments were carried out in half-cells using activated Pt–Ru gas-diffusion electrodes obtained from commercial sources. Pt–Ru electrodes were
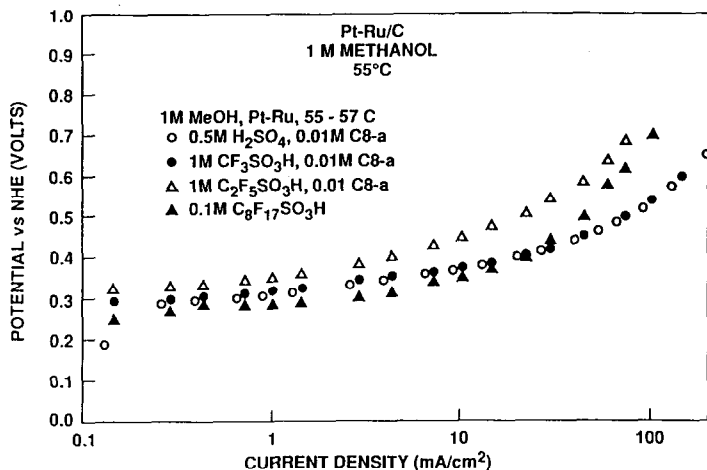
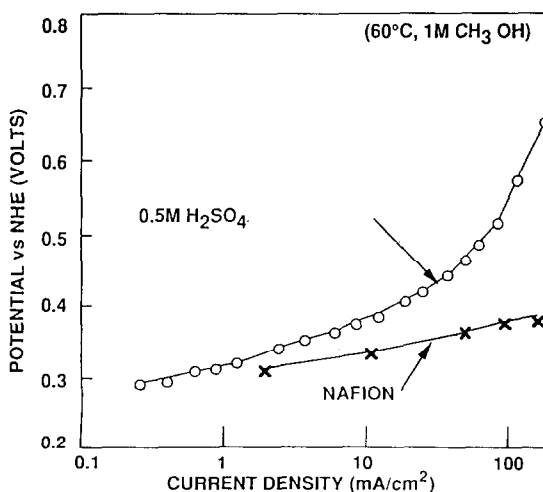Fig. 6. Anodic oxidation of methanol in various electrolytes; C_8 acid: perfluorooctane sulfonic acid.

Fig. 7. Evaluation of electrolytes for anodic oxidation of methanol; improved fuel oxidation characteristics with Nafion.

found to be unstable and dissolve in boron trifluoride dihydrate electrolyte. Hence no further experiments were carried out with this electrolyte. Anodic oxidation characteristics of methanol in the other three electrolytes are given in Fig. 6. Some of the important findings of this study are: (i) anodic oxidation of methanol in triflic acid is comparable with its oxidation is sulfuric acid; (ii) perfluoroethanesulfonic acid was found to be unattractive for the oxidation of methanol, and (iii) marginally improved oxidation behavior was observed with perfluorooctanesulfonic acid electrolyte.

Solid polymer electrolytes

Nafion, a proton-exchange membrane (PEM), is an attractive alternate to the liquid electrolytes for liquid feed methanol cells for several reasons including:

(i) simplified design; (ii) simplified assembly and operation; (iii) lower corrosion, and (iv) minimization or elimination of shunt currents. The material has been used quite successfully in gas feed hydrogen/oxygen fuel cells.

For these reasons, Nafion was evaluated as an electrolyte in a liquid feed half-cell. A methanol–water mixture only (without acid) was introduced to the fuel compartment with Nafion 117 (Du Pont) as electrolyte and the anode catalyst was a supported Pt–Ru type that was bonded directly to the Nafion. Figure 7 shows the improved performance of this cell with the Nafion electrolyte compared with the performance of the previously employed cell with sulfuric acid electrolyte. Hence, Nafion was selected as the candidate electrolyte in all further studies.

Cell design

Design optimization

Two cell design options were considered for direct oxidation methanol fuel cells including: (i) gas or vapor design, and (ii) liquid feed design. Initial considerations indicated that the gas feed design is preferable in that it could employ existing fuel cell type gas-diffusion electrodes. Furthermore, the gas feed design could operate at the higher temperatures that were anticipated to be necessary for high performance. Subsequent deliberations however considered the fact that the liquid feed design would not require a vaporizer and would therefore be much simpler in design and operation. Other potential advantages of liquid feed design are: (i) elimination of complex water and thermal management systems; (ii) multiple use capability of the methanol–water as the fuel, for humidification purposes and as an efficient stack coolant, and (iii) significantly lower system size and weight. Furthermore, this cell design does not suffer from the disadvantages of prior liquid feed cell designs, the problem of troublesome shunt currents and also corrosion of cell components. Tests have shown that the PEM does not degrade with operation and is suitable for continuous operation. In addition, fuel catalysts were found to exhibit improved performance with the solid electrolyte membrane. On this basis Jet Propulsion Laboratory began development of liquid feed type direct methanol fuel cells.

Schematic diagram of liquid feed direct methanol fuel cells

Figure 7 give a schematic diagram of the complete laboratory-type liquid feed methanol system employing the membrane electrolyte. The MEA (membrane-electrode assembly) consists of a layer of Nafion electrolyte (7 mil thick) with fuel and air/O_2 electrodes bonded to either side. Electrode dimensions are 2 in $\times$ 2 in by approximately 10 mil thick. The MEA is positioned between the machined portion of two graphite blocks. The machined area on each block is a rectangular pattern with open channels (designated as the low field) to allow flow of liquid or gas across the electrode surfaces. Inlet and outlet ports communicate with the flow fields via holes drilled into the carbon blocks and are equipped with threaded fittings at the sides of the blocks. Stainless-steel support plates, with the same overall length and width as the carbon plates, are located on the back surface of the plates. The stainless-steel plates as well as the carbon blocks are drilled in their outer perimeter to accommodate bolts that are used to compress the assembly for sealing and to provide electrical contact between the electrode and unrecessed area of the flow field.

The methanol solution is introduced into the fuel compartment of the cell via a pump and then returned to a fuel storage reservoir as shown in Fig. 8. The end
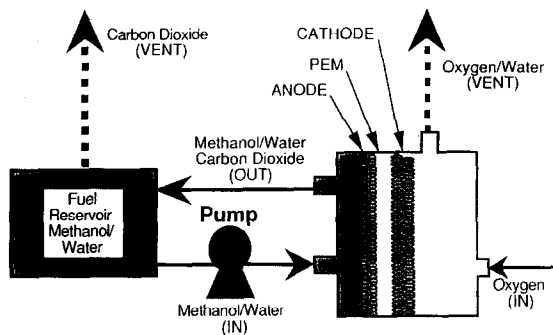
Fig. 8. Diagram of liquid feed direct methanol fuel cell developed in the Jet Propulsion Laboratory.
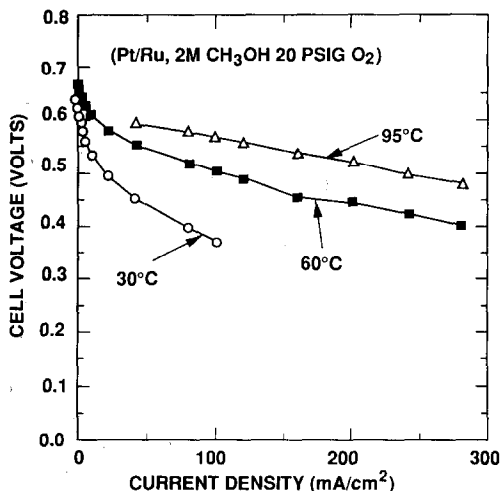

Fig. 9. Effect of temperature on cell performance.

product, carbon dioxide, entrapped in the exit fuel line, is released in the storage reservoir. Pressurized air or O_2 is introduced to the air compartment of the cell and vented without circulation. Heaters are located on the outside surface of the cell to control cell temperature. Finally, the cell is equipped with a small closed end hole to accommodate an internal thermocouple.

Performance of liquid feed direct methanol fuel cells

Effect of temperature

Voltage–current characteristics of the liquid feed direct methanol fuel cell were measured over a range of temperatures with 2 M methanol as fuel and pure O_2 as oxidant. Results are given in Fig. 9 in terms of operating cell potential versus current density. Each point represents an essentially steady-state voltage that was achieved after about 5 min of continuous operation at the indicated current density. Inspection of Fig. 9 reveals a marked increase in performance with increase in temperature over

the range of 30 to 90 °C. For example, at a potential of 0.55 V, the current density outputs are 10, 45, and 140 mA/cm^2 at temperatures of 30, 60, and 95 °C, respectively. Similarly, at a potential of 0.50 V, the current density outputs are 20, 110, and 260 mA/cm^2 at 30, 60 and 95 °C. The trend of increased output with increase in temperature is in accord with that exhibited by other fuel cells. The increased output at higher temperatures is attributed to a combination of factors consisting of a reduction of cell ohmic resistance, activation polarization, and concentration polarization.

Effect of methanol concentration

The effect of methanol concentration on the cell performance was also determined in three separate runs carried out at 60 °C each with a different fuel concentration of 0.5 M, 2.0 M, and 4.0 M methanol. The effect of fuel concentration on overall cell performance is given in Fig. 10 in terms of voltage–current characteristics. Inspection of these results shows that at high operating current densities, the highest cell voltage is obtained with 2 M methanol while somewhat lower voltages are obtained with both the higher concentration, 4 M methanol, and the lower concentration, 0.5 M methanol. On this basis there appears to be an optimum concentration that may be between 0.5 and 2 M methanol. The lower performance of the cell at fuel concentrations less than 0.5 M is probably due to the concentration polarization effects. The poor performance of the cell at higher methanol concentrations is attributed to the fuel crossover phenomenon. Support for the proposed impact of crossover at high concentrations was shown in half-cell studies on the oxygen electrode. Therein, it was found that the O$_2$ electrode performance is significantly lowered at higher methanol concentrations [5]. For example, the O$_2$ electrode potential dropped more than 100 mV at 100 mA/cm^2 as methanol concentration was increased from 2 to 4 M methanol. This finding emphasizes the need to minimize the crossover rate to improve performance of the O$_2$ electrode and hence the overall cell performance.
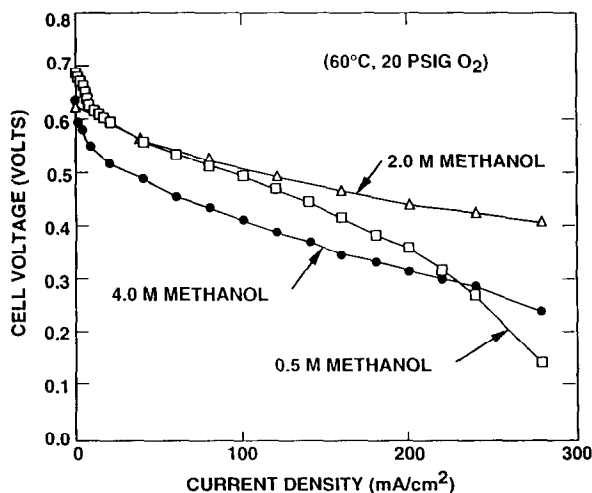

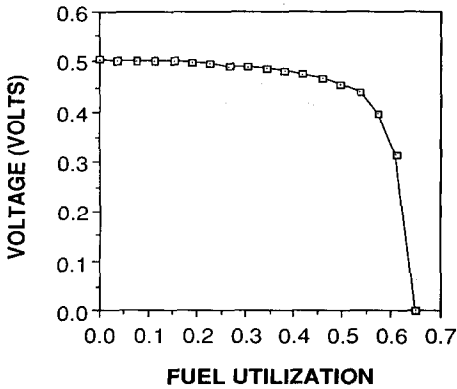Fig. 10. Effect of fuel concentration on cell performance.

FIG. 11. Voltage vs. fuel utilization curve; 1 M methanol initial concentration, 75 mA/cm^2 current density, 62 °C, and 20 psig oxygen.

Fuel utilization studies

In order to examine fuel utilization, a cell was set up and run continuously at constant current with a finite amount, 200 ml of 1.0 M methanol solution in the circulation tank, without replenishment of the methanol. Initially the current was set at 1.875 A (75 mA/cm^2). Results are given in Fig. 11 in terms of cell voltage versus percent utilization of the fuel. The utilization was taken as output Ah/theoretical Ah (from the amount of methanol and its electrochemical equivalent). Inspection of Fig. 11 reveals that voltage drops sharply at 75 mA/cm^2 when utilization approaches 60%. The sharp drop in voltage at this point is believed to be associated with concentration polarization of the fuel electrode that is, in turn, due to an inadequate supply of methanol to the electrode. The methanol supply is, in turn, limited by the low methanol concentration at this point (near 0.2 M or less). The phenomenon is consistent with prior half-cell studies that revealed the onset of high polarization when methanol concentration declines below this level.

Problems and issues

Performance of the liquid feed methanol fuel cells is already attractive for some applications and is approaching the levels required for electric vehicle propulsion. With some improvements in electrical performance, efficiency and cost, this system can indeed be considered a serious candidate for electric vehicle applications. These improvements can be achieved by developing high performance anode catalysts, new membranes with reduced methanol permeability, methanol insensitive cathode catalysts, and low cost materials (non Pt-based catalysts, membranes, bipolar plate materials, etc.).

Conclusions

Some of the major findings of the study are:

1. Pt–Ru-catalyzed electrodes are well suited for oxidation of methanol.

2. Performance of Pt–Ru-catalyzed carbon electrodes increases with increased temperatures (25 to 60 °C), increased fuel concentration, (0.5 to 2 M methanol) and increased catalyst loading (0.5 to 5 mg/cm^2).

3. A new liquid feed direct oxidation methanol fuel cell has been developed based on a proton-exchange membrane electrolyte, Pt–Ru-catalyzed fuel electrode, and Pt-catalyzed air/O_2 electrodes.

4. The new cell can deliver significant outputs in excess of 250 mA/cm^2 at potentials near 0.5 V at moderate temperatures (less than 88 °C).

Acknowledgement

References

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