

SOME ASPECTS OF THE DESIGN AND OPERATION  
OF DISSOLVED METHANOL FUEL CELLS

by

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INTRODUCTION

It has long been recognized<sup>1</sup> that a soluble fuel such as methanol may conveniently be used in low temperature fuel cells. However most early attempts to realize this type of fuel cell involved the use of an alkaline electrolyte, which would have been rapidly converted to carbonate. Thus potassium or sodium hydroxide solutions do not meet the requirements of invariance implicit in the definition of a fuel cell. At low temperatures, that is at ambient temperature and slightly above, carbonate electrolytes are unsuitable; not only is the performance of the oxygen electrode poor and the anode subject to concentration polarization, but formation of the bicarbonates, which are of low solubility, makes it difficult to conceive of a reasonably invariant system when such an electrolyte is used. If operation at around 120°C is acceptable, then Cairns and his co-workers<sup>2,3</sup> have shown that caesium and rubidium carbonates can be used as invariant electrolytes for methanol fuel cells. However, the performance of present oxygen electrodes in this electrolyte falls short of that obtained in strong acids and bases. Furthermore, as Williams and Gregory<sup>4</sup> have shown only strong acids and bases can be used as electrolytes for low temperature fuel cells if high current densities are required.

These considerations suggest that a strong acid is likely to be the most satisfactory electrolyte for a direct methanol fuel cell. Of the strong acids, sulphuric seems the best choice if operation at temperatures between ambient temperature and 60 or 70°C is required. This acid has a high specific conductivity, is non-volatile and, although it is

corrosive, the problems attendant upon its use are not insurmountable. In our experience the performance of oxygen electrodes in sulphuric acid is marginally better than in phosphoric acid, the major alternative; also the electrical conductivity of sulphuric acid is higher than that of phosphoric acid at low temperature. Perchloric acid offers no significant advantage over sulphuric acid with our electrodes and as there is a possible fire hazard with perchloric acid and methanol we preferred sulphuric acid.

Another advantage of acid electrolytes is that water removal is easier than with an alkaline electrolyte. This is because, with an acid electrolyte, hydrogen ions discharge on the air electrode to form water which is readily removed. On the other hand in alkaline systems, water has to be transported from the fuel electrode through the electrolyte to the air electrode. This process takes place against the concentration gradient as the concentration of electrolyte is highest, and hence vapour pressure of water lowest, at the region from which water is evaporated.

There are various reasons for accepting an upper limit of operating temperature of 70°C for the dissolved methanol cell. In the first place methanol, even in solution, is sufficiently volatile at temperatures above 60°C as to necessitate stringent precautions against loss by evaporation. Secondly, an upper temperature limit of about 70°C means that a wide range of cheap, commercially available plastics offers sufficient temperature and corrosion resistance to be useful for fuel cell construction. Additionally, corrosion problems, particularly in the vicinity of the air electrode, are aggravated by increased temperatures and offer a further incentive to relatively low temperature operation. Finally, if a cell is designed to run at about 60°C, it will have a reasonable output at room temperature and will start easily from cold.

The ability to operate an invariant acid electrolyte system at a relatively low temperature may be of importance where extreme longevity is required. In our experience the rate of electrode deterioration increases with increasing operating temperatures but even at the present state of the art, lives of the order of years appear possible if temperatures can be kept fairly close to 30°C.

#### EXPERIMENTAL

For our air electrodes we have developed a structure in which microporous polyvinyl chloride (P.V.C.) is used as the substrate<sup>5</sup>. This substrate is made conducting by being coated with an evaporated metal layer, which may be thickened by electrodeposition of more metal. Finally, a catalyst is applied to the electrode surface. In acid electrolytes we have used gold as the conducting metal layer. Since quite thin layers of gold are acceptable, the intrinsic value of the substrate (microporous polyvinyl chloride together with the gold film) is only about \$1.50 per sq.ft.

The performance of oxygen and air electrodes of this type in acid and in acid to which methanol has been added is shown in Figure 1 in which the scale of the ordinate is exaggerated in order to emphasize the differences in electrode performance. It can be seen that the voltage of the air electrode throughout the current range is within 50 mV of that of the electrode using pure oxygen. This is characteristic of electrodes of this type provided that the catalytic activity is high. Whilst the presence of methanol in the electrolyte has a substantial effect on the open circuit voltage of the air electrode, at useful current densities 1M methanol depresses the potential of the air electrode by only 20-50 mV.

We have found that the microporous plastic also makes an ideal substrate for methanol electrodes. This quite naturally led to our using both sides of the material to make a complete cell. One side of the substrate is used for the air electrode and the other side for the methanol electrode, the cell thickness being the thickness of the porous plastic itself. Thus it is now a relatively simple matter to make complete cells with an inter-electrode distance of 0.030 inch and having a very low internal resistance.

The performance of both methanol and air electrodes in a complete cell at 25°C and 60°C is shown in Figure 2. Over this temperature range, the air electrode is relatively unaffected by the temperature of operation whereas the voltage of the methanol electrode at reasonable current densities decreases by about 100 mV as the temperature is raised. The internal resistance of the fuel cells is, of course, varied by electrode separation. A typical voltage loss due to internal resistance at a current density of 100 mA/sq.cm would be 45 mV per cell.

Methanol-air batteries with sulphuric acid electrolyte have been built from cells of this type. The alternative design in which a separate piece of porous plastic is used for each electrode, with a relatively thick electrolyte layer between the electrodes, has also been used in the construction of batteries. Both designs of cell are shown schematically in Figure 3. With both types of battery internal electrical connections from the electrodes to the conducting cell separators were made from gold-plated plastic mesh. Thus series electrical connection is built into the batteries. The mesh chosen allows the free passage of gas past the air electrodes, escape of carbon dioxide bubbles from the electrolyte and current collection from the surface rather than from the periphery of the

electrodes. The construction of this type of cell is described elsewhere<sup>5</sup> and Figure 4 shows a 300 watt methanol-air battery of 40 cells.

During operation of an 8-cell prototype methanol-air fuel cell using 6N sulphuric acid, the fuel-electrolyte mixture developed an ester-like smell. The electrolyte was extracted with ether and the extract analysed by gas-liquid chromatography. In addition to the intermediates normally encountered (formaldehyde and formic acid), traces of acetic, propionic, butyric and isobutyric acids were detected together with some unidentified compounds. These materials were not present in either the methanol used as fuel or in the ether used for the extraction.

These side products are present in small quantities but may be strongly adsorbed on the electrocatalyst thereby causing the observed slow decline in electrical output with time. Experiments in which small quantities of these materials were deliberately introduced into a fresh electrolyte - fuel mixture showed that they had a poisoning effect on the methanol electrode.

We have carried out some preliminary experiments to determine the source of these poisons. The first possibility that occurred to us was that these materials might arise as a result of attack by the acid electrolyte on one or other of the plastics present in the cell (polystyrene, Perspex, P.V.C., or polyethylene). We were able however to detect traces of these organic acids after prolonged anodic oxidation of methanol in 6N sulphuric acid in all-glass apparatus with a platinized-platinum anode.

DISCUSSION

In spite of the difficulties of choosing inexpensive, acid-resistant constructional materials, developing suitable electrocatalysts and minimizing the effects of impurities on the electrodes, we have built a series of satisfactory methanol-air batteries. The first battery - a small 8-cell prototype - was built in September 1963 and is still operational, giving 2.85 watts at 1 amp compared with its initial performance of 3.15 watts at the same current density. This testifies to the longevity of the system, for the only servicing the battery has received is an occasional wash with distilled water.

Since the prototype was built we have been able to build larger batteries using improved electrocatalysts and this work has led to the construction of a 40-cell battery delivering 300 watts at 12 volts at 60°C. With this battery, as with all the other batteries we have constructed, there has always been an ester-like smell and organic acids have been detected frequently. It is interesting to speculate on the origins of these materials.

Whilst radical dimerizations are frequently encountered in electrochemical processes<sup>6</sup>, this type of reaction does not seem likely here. If a radical were polymerizing then the expected yields of acids would be butyric << propionic << acetic. Even though the isolation of the organic acids is only qualitative it seems that they are present in quantities which decrease only slowly as one goes up the homologous series. Thus the likely route appears to be an attack of a radical on a methanol molecule.

The existence of the radical  $\text{H} - \underset{\text{M}}{\overset{\text{O}}{\text{C}}} - \text{OH}$  has been postulated in the

Fischer-Tropsch synthesis<sup>7</sup> of organic compounds from carbon monoxide and hydrogen. Formaldehyde, which has been detected in solution by several workers<sup>8,9</sup>, might have this structure in the adsorbed state and, by progressive condensations with methanol and subsequent rearrangements, would lead to aldehydes which, under the anodic conditions present, would be electrochemically oxidized to the organic acids which have been detected. However, until a more thorough investigation of the spectrum of products is available, the reaction mechanism must remain obscure.

Finally, although these side reactions cause some trouble, the longevity of our prototype battery testifies to the fact that they do not have a disastrous effect on cell life. However, attention will have to be devoted not only to improving the efficiency of electro-catalysts for the methanol oxidation but also to the suppression of side reactions. Probably, if a catalyst is sufficiently good for the overall reaction of methanol to carbon dioxide, the side products will be formed in negligible quantities.

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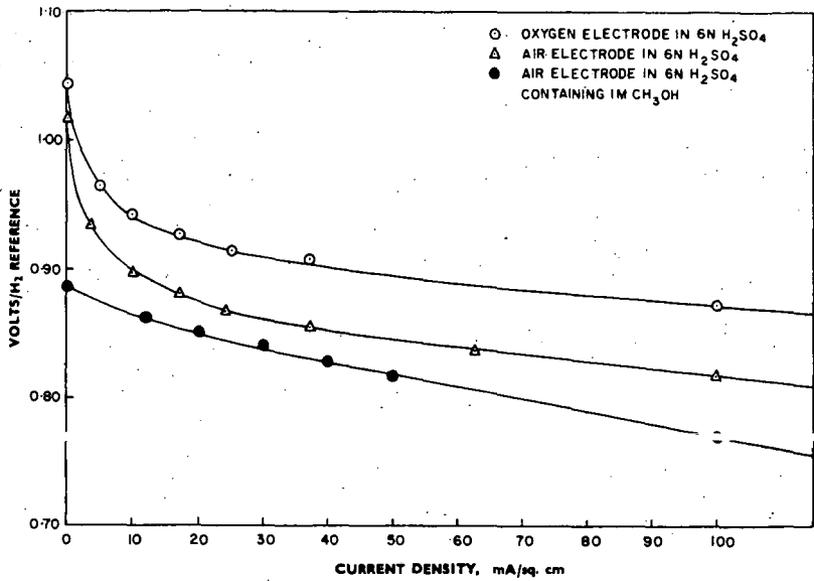


FIG. 1—Polarization curves for oxygen and air electrodes in sulphuric acid solution at 25°C

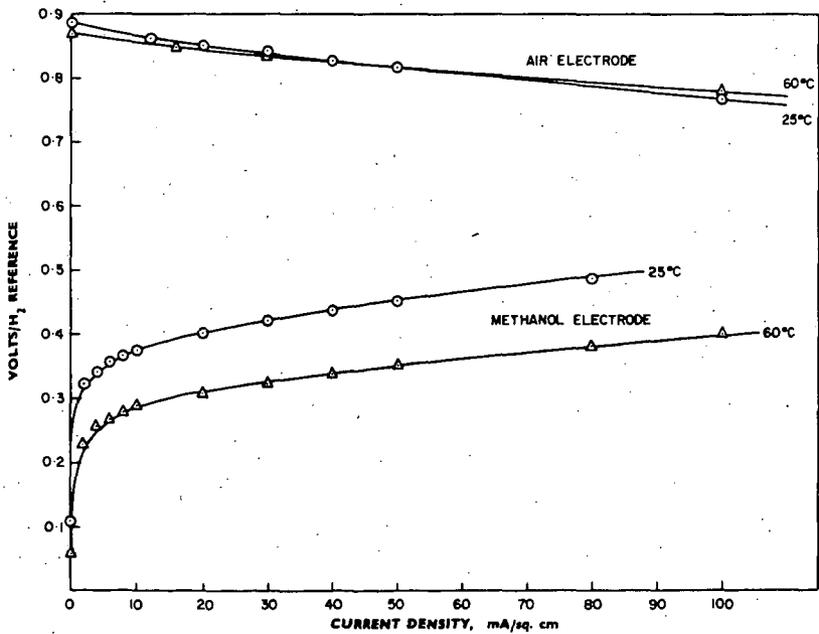


FIG. 2—Polarization curves for air and methanol electrodes in a 1M CH<sub>3</sub>OH-6N H<sub>2</sub>SO<sub>4</sub> mixture at 25° and 60°C

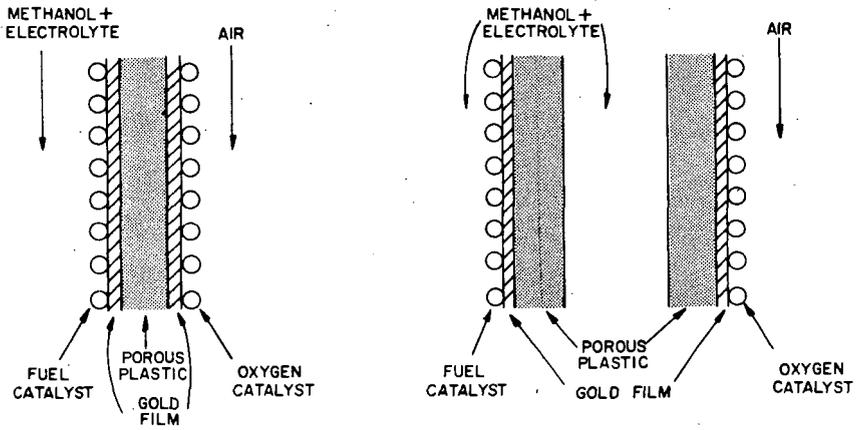
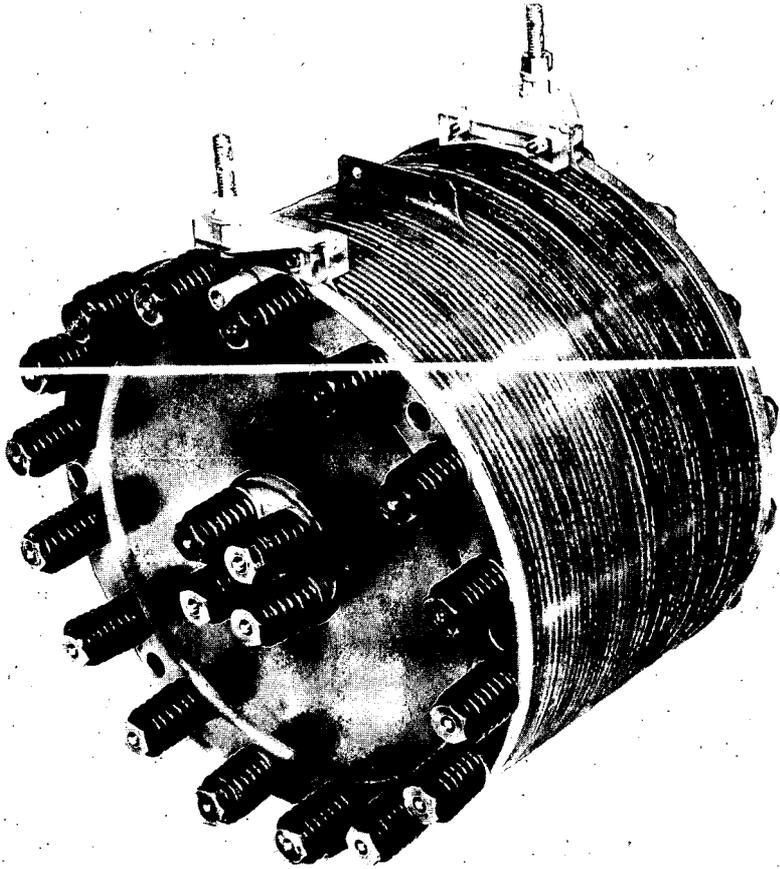


FIG. 3—Schematic drawing of two types of single cell



MH 1014

**FIG. 4-** 40-cell methanol-air fuel battery