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Low temperature fuel cells: Interactions between catalysts and engineering design

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Abstract

For many potential applications of fuel cells, especially road transport, it is highly desirable to use liquid fuels. In this paper it is shown that whether direct fuel cell systems (methanol/air) or indirect, hydrogen reformer to hydrogen are chosen, catalyst performance and cost plays a dominant role in the overall design. Notably, the maximum current densities which can usefully be employed are limited by the conductivity of low cost intercell plates in bipolar designs. Thus to attain respectable volume power densities, thin cell stack designs are essential. Considerations of overall simplicity, cooling and water control together with the need to operate at atmospheric pressure because of the cost, noise and inefficiency of air compressors all favour operating at 100°C or below. Although a number of systems could be constructed with known technology, costs are still too high for all but specialised applications. While useful engineering design work can be done using existing catalysts, present costs are far too high to justify widespread application. The recent discovery in the authors' laboratory of a base metal catalyst for the electrolytic oxidation of methanol together with past workers who have presented data on effective non-platinum air cathodes in acid electrolytes suggest that the quest is worthwhile. Bearing in mind the need to reduce total costs, while some system engineering development is worthwhile to provide solutions to the various physical problems involved, the authors argue that the primary effort on fuel cells should be in the fields of catalysis and electrode structure. © 1997 Elsevier Science B.V.

Keywords: Fuel cell; Engineering design; Catalyst performance; Low temperature

1. Introduction

Historically the development of catalysts for fuel cells has been almost entirely empirical and despite numerous fundamental electrode studies and the development of ingenious electroanalytical techniques, remains so. Although virtually all of the catalysts used today had been developed in the early 1960s, great strides have been made in their effective and economical application. Nevertheless there is still considerable scope for further improvement.

Thermodynamic considerations determine that fuel cells are essentially low voltage high current devices and this in turn necessitates the use of strong electrolytes to avoid the adverse effects of concentration polarisation [1]. In the first hydrogen–oxygen fuel cells developed by Grove sulphuric acid was the chosen electrolyte and it was again used by Mond and Langer; subsequently alkaline electrolytes received much attention as the problems of corrosion were considerably less than in an acidic environment while the performance of oxygen electrodes is substantially better than in acidic media. More recently attention has switched to acid media. It should

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however be noted that carbonate/bicarbonate aqueous electrolytes were investigated as they potentially offered the acceptance of carbon dioxide coupled with inexpensive materials of construction [2]. Unfortunately adequate electrode performance appeared to be unattainable.

Before considering catalyst performance in more detail it is useful to review the options and constraints facing people developing fuel cells. The chosen fuel is of great significance. Pure hydrogen is the most attractive fuel from the construction point of view as its anodic oxidation is readily catalysed. This option has been chosen in both buses and smaller vehicles suitable for use from centralised depots where recharging of cylinders on the vehicles can be contemplated [3]. For more widespread application liquid fuels are much more convenient and initially attention was directed to producing pure hydrogen from methanol by reaction with steam and purifying the resultant mixture of gases by diffusion through a Johnson Matthey palladium silver diffuser [4]. This was an expensive route although its cost could be reduced by supporting a much thinner membrane on a porous medium, this might still be an attractive option. At this point attention was directed towards the use of impure hydrogen. The problem here is that platinum, the most effective electrocatalyst for anodic oxidation of the fuel is poisoned by CO present in hydrogen which has been derived from methanol or hydrocarbons either by catalytic reforming or thermal cracking. Three alternative approaches to this problem have been attempted. By using phosphoric acid absorbed on a suitable matrix as electrolyte the International Fuel Cells Corporation (IFC) were able to operate at temperatures in the region of 200°C and tolerate modest amounts of CO. Steam-reformed hydrocarbons, chiefly natural gas, were firstly passed over a shift catalyst and CO further reduced by methanation. Although complex thus approached has lead to some impressive developments ranging into the multimegawatt range. An alternative pioneered by Shell in 1960s was to replace pure platinum by Adams platinum–ruthenium alloy [5] which at admittedly high loadings of the order 10 mg cm^{-2} allowed the use of up to 2% CO in the fuel supply. More recently much more efficient use of this catalyst has been achieved by Johnson Matthey. A third approach by Telefunken was to replace the anode catalyst by tungsten carbide [6] which appeared to be immune to CO poisoning although outputs were modest. It should be noted that the tungsten carbide used was sub-stoichiometric. A catalyst life of 30 000 h was obtained at 60°C.

Alternatives to hydrogen gas are the liquid fuels methanol and hydrazine hydrate, both of which can be reacted directly at the anode in a low temperature fuel cell. Methanol presents formidable challenges in the field of catalysis if cost effectiveness and efficiency are to be achieved. Hydrazine although highly reactive is both expensive and very toxic.

The electrolyte in a fuel cell may be either free liquid, absorbed on a porous membrane such as asbestos in the case of alkali or glass mat, or other inert material for acid, or a solid polymer cationic exchange membrane (SPM). Since it lends itself to recirculation, the free liquid has the advantages of relatively simple water control, ease of heat removal and ready removal of contaminants by replacement. The immobilised acidic and alkaline electrolytes offer lower internal resistance but present difficulty in cooling and controlling the water content. The SPM provides very low internal resistance but presents difficult cooling and water control problems although they have evidently been solved by Ballard [3]. If allowed to dry out, the membrane cracks and the expensive cell is ruined. Nevertheless because of the impressive results already demonstrated, this type of cell is receiving the major amount of attention at the moment in the hope that its outstanding problems can be solved.

For terrestrial use the cathode needs to be fed by air. In order to enhance cell output operation at 3 atmospheres or so is frequently demonstrated [7]. This does however involve problems of complexity, noise and reduced overall efficiency and it would be desirable to reduce operating pressure to atmospheric. One problem common to all fuel cells is the need to establish a stable three phase interface at the gas electrode. In the ensuing sections we consider this problem together with the various challenges facing those attempting to develop viable fuel cell power systems.

2. The air cathode

In alkaline electrolytes catalysis of the oxygen or air electrode is readily achieved and a wide variety of catalysts is effective. Carbon itself is quite active [8] but its activity is markedly enhanced by using it as a support for silver, platinum or palladium or a variety of spinels. Bacon used nickel oxide rendered semiconducting with lithium and operated at 200°C under 4 atmospheres of pressure with pure oxygen and was able to achieve a cell operating at close to reversible potential (1.23 V). For cells operating at temperatures below 100°C on grounds of cost, performance and life palladium seems to be a good choice and as mentioned below, air electrodes operating within 22.5 mV of the oxygen electrode at atmospheric pressure were achieved.

As already noted, a problem common to all gas electrodes is the necessity to establish a stable gas/liquid interface. Furthermore as the three phases gas, electrode and electrolyte can only meet in a line, two must combine if a significant reaction is to occur; normally the gas dissolves in the electrolyte. Because of the very low rates of diffusion it is essential to maximise the length of the interface. In the Bacon cell the interface was established within a biporous nickel electrode using a small differential pressure [9]. In a similar manner the Shell electrodes based on microporous plastics also use a small differential pressure [10]. Most electrodes nowadays depend on the hydrophobic properties of polytetrafluoroethylene to establish an interface.

The overall reaction at the cathode of a fuel cell operating in an acid environment is:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

Almost invariably platinum is used as the catalyst for the oxygen electrode in acid media. Damjanovic and Rao [11] listed the following six different reactions that could be involved in establishing the potential of the oxygen electrode in acid.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (E_0 = 1.23\,\mathrm{V(SHE)}) \tag{1}$$

$$PtO_2 + 2H^+ + 2e^- \rightarrow Pt(OH)_2 \quad (E_0 = 1.1\,\mathrm{V(SHE)}) \tag{2}$$

$$Pt(OH)_2 + 2H + 2e^- \rightarrow Pt + 2H_2O \quad (E_0 = 0.98\,\mathrm{V(SHE)}) \tag{3}$$

$$PtO + 2H^+ + 2e^- \rightarrow Pt + H_2O \quad (E_0 = 0.88\,\mathrm{V(SHE)}) \tag{4}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (E_0 = 0.68\,\mathrm{V(SHE)}) \tag{5}$$

$$HO_2 \rightarrow O_2 + H^+ + e^- \quad (E_0 = 0.13\,\mathrm{V(SHE)}) \tag{6}$$

Although the work was published in 1964 and much has been written about the subject since, the overall understanding of the process has not advanced significantly. One may note however the empirical observation that the behaviour of the oxygen electrode in strongly alkaline electrolytes is much better than in strongly acidic media. As hydrogen peroxide is much more stable in acidic than alkaline media [12] so Eq. (5) plays a significant role in the poor performance in acid. Platinum is certainly a good catalyst for the decomposition reaction

$$2H_2O_2 \rightarrow 2H_2 + O_2 \tag{7}$$

One may note in passing that the enzyme catalase (containing no platinum) is very effective in decomposing hydrogen peroxide [13]. Unfortunately it is most effective in the pH range 6.5–7 while it is slowly destroyed itself when promoting the reaction. Nevertheless this suggested that the search for a non-platinum catalyst for oxygen reduction is worthwhile. This was borne out by the work reported by Baudendistel et al. [6] using "activated charcoal" further treated with ammonia at 900–1000°C. Since carbon itself appears to be inactive in acidic media [9], one may infer that there was an unidentified contaminant which promoted the necessary reactions.

There have been a number of further attempts to find alternatives to platinum, not only because of its cost, but also as it is a catalyst for methanol oxidation, any fuel reaching the cathode causes a deterioration in performance [14]. As McNicol [15] pointed out, chelates such as phthalocyanines and porphyrins have structures similar to catalase and it has been suggested that planar structures such as these macrocyclic compounds favour minimum interaction between oxygen and the central transition metal ion [13]. Since they are poor electronic conductors chelates are normally supported on conducting carbon with basic surface oxides [16]. If supported on a metal such as gold, little activity was found [17] suggesting that interaction between the chelate and the carbon was essential for the development of substantial catalytic activity. It has also been established that the nature of the central ion in such chelates has a strong influence on activity [18]. For instance in phthalocyanines the most active are those where the central ion is iron or cobalt [19]. The binding of the chelate to the carbon support via electron conduction bridges has been shown to benefit performance [20]. It has been shown [21] that chelates behave as both oxygen reduction catalysts as well as promoting hydrogen peroxide decomposition.

It has been suggested [15] that the bonding between oxygen and the central metal ion occurs via the d_z^2 orbital of the metal ion, and that back-bonding into the anti-bonding π^* orbitals of the oxygen molecule can take place via the d_{xz}, d_{yz} orbitals of the metal if they are occupied. In this way the O=O bond is weakened. In order to activate the oxygen molecule back-bonding is essential. The role of support, central metal ion, substituents on organic skeleton and different ligands on activity can be understood in this model. It may also be possible via doping of the supported chelate catalyst with electropositive entities to enhance this back-bonding effect analogous to the way N_2 and CO dissociation is enhanced in ammonia synthesis and Fischer–Tropsch synthesis catalysts [15].

In terms of practical electrodes there have been interesting developments in carbon supported chelates whose activity and stability are both markedly enhanced by heat treatment. For instance, when tetramethoxyphenylporphrinato-cobalt(II) was heated between 88°C and 1200°C its performance was significantly improved [22]. It was proposed that the carbon generated in the pyrolysis of the chelate was responsible for its electrochemical activity. In tests in 2.25 M sulphuric acid a catalyst prepared by heat treatment at 800°C was stable over 10 000 h at potentials $\geq$700 mV at a current of 5 mA cm^{-2}.

Van Veen and Visser [21] studied a series of phthalocyanine complexes supported on Norit BRX carbon and showed that the activity varied with central metal ion as follows the order Fe>>Co>Ru>Mn, Pd, Pt>Zn. Stability on the other hand, decreases in the order Co>Fe>Ru. The authors also established that carbon pretreatment to produce basic surface groups prior to emplacement of the catalyst produced the highest activity chelate catalyst. Heat treatment at 700°C increased activity 50 fold as well as increasing

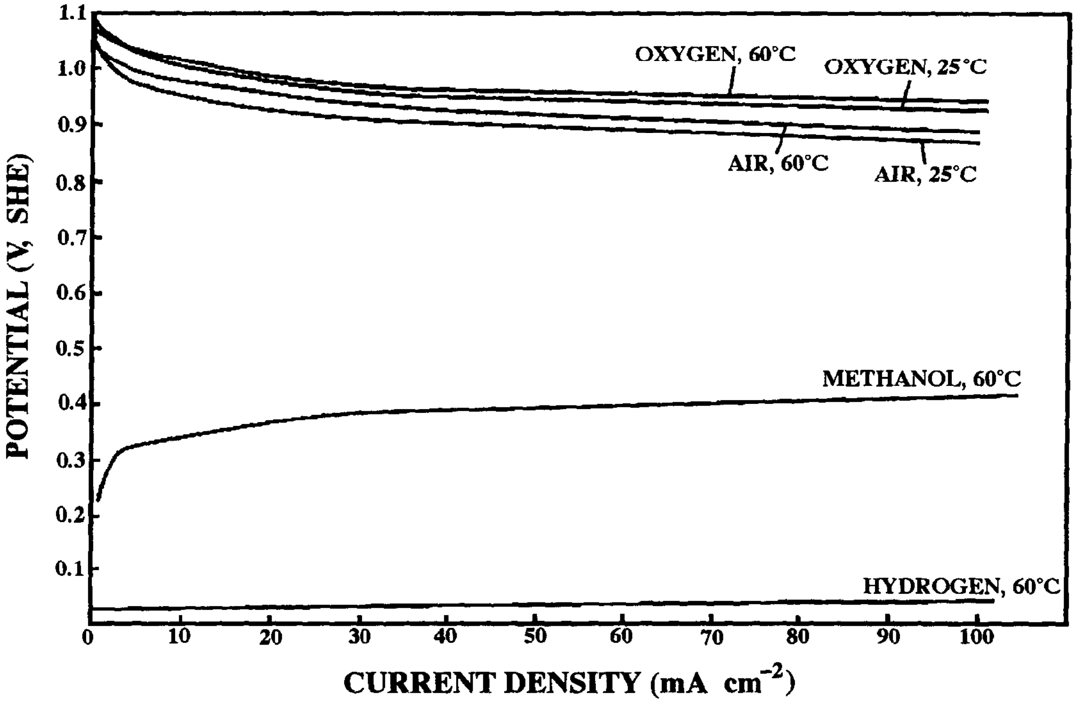


Fig. 1. Performance of Shell electrodes on substrates made from gold-coated microporous polyvinylchloride in 3 M H_2SO_4.

stability. The effect of the heat treatment is not understood although it is possible that highly stable complexes containing a CoN_4 unit can be formed [23].

If the Nernst equation applies to the oxygen electrode at equilibrium, then the difference in equilibrium potentials in air (E_0(air)) and in pure O_2 ($E_0(O_2)$) would be given by

$$E_0(O_2) - E_0(\text{air}) = \frac{RT}{2F}\ln\frac{p(O_2)}{p(\text{air})} = 0.02\,\text{V},$$

where p is the appropriate pressure of O_2. As Liebhafsky and Cairns [18] point out, this condition is almost attained with "Shell" microporous electrodes in alkaline electrolytes, where under high currents, the corresponding potential difference, ($E(O_2)$–E(air)) was observed to be approx. 0.02 V. The fact that the Nernst equation appears to be observed so far from equilibrium suggests that the potential is a function of a complex combination of reactions. Nevertheless the result showed that with the good catalysis achievable in alkaline solution coupled with a favourable electrode structure, high performance on air is achievable. That the structure of the electrode is significant is evident from the high performance of the Shell electrodes on air (Fig. 1). The specific activity of the Shell electrode at 0.9 V SHE was 10 A g^{-1} Pt while Hards et al. [40] reported about 2 A g^{-1} under similar conditions for an electrode on a SPM. The Shell electrodes were very thin and had a high platinum content per unit volume being made of Adams platinum (ex Johnson Matthey) and nitrogen blanketing of the pores was thus minimised by direct access of air to the surface. The SPM cell used a supported carbon and current collection via a carbon paper which could limit the escape of nitrogen. When the thickness of the Shell electrodes was increased by using platinum supported on carbon the specific activity fell markedly and was inferior to that reported by Hards et al.

3. The fuel anode

In alkaline electrolytes pure hydrogen is the principal fuel used and the catalysts chosen are nickel, platinum or palladium, the latter two normally being supported on carbon. The inherent stability of the platinum metals coupled with the fact that relatively low loadings are needed make them the preferred choice. Palladium is less expensive than platinum and appears to offer a better performance coupled with adequate stability. It is perfectly possible to use nickel in Raney form for hydrogen electrodes and this was notably achieved by Justi and Winsel [24].

A number of fuel cells were built in the 1960s using alkaline electrolytes and hydrazine hydrate as fuel [25], which although highly reactive, is both expensive and highly toxic. Both platinum and palladium catalyse the reaction:

$$N_2H_4 \rightarrow 4H^+ + 4e^-$$

Nickel is equally effective and Shell made electrodes by diffusing evaporated aluminium into expanded nickel mesh at 1000°C and then leaching out the aluminium with KOH solution leaving a coating of Raney nickel.

In acidic electrolytes platinum is the preferred catalyst for hydrogen electrodes as it combines activity with stability. Normally the platinum is dispersed on carbon and effective electrodes are now made with loadings below 1 mg cm^{-2}. However if carbon monoxide is present, it is essential to use a platinum/ruthenium alloy or some other catalyst resistant to poisoning by carbon monoxide.

If methanol is the chosen fuel an acidic electrolyte must be used to reject carbon dioxide. The anodic oxidation of methanol proceeds as

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad (E_0 = 0.04\,\text{V(SHE)}) \qquad (8)$$

Unlike the hydrogen electrode which is almost perfectly reversible, methanol electrodes based on platinum are strongly polarised (Fig. 1). In studies of the methanol reaction on smooth platinum foil catalysts in ultra-pure sulphuric acid using electrochemical pulse techniques [26,27], the initial currents decay by five orders of magnitude in going from the initial to the pseudo-steady state, defined as that reached after five minutes on load. Even after this period the current continues to decline and the true steady state is reached only after many hours. This decline in performance is attributed to an adsorbed methanolic residue on the catalyst surface which is only removed at potentials where oxygen in one form or another is adsorbed. Thus the challenge appears to be the development of catalysts which retard the formation of dehydrated residue, or adsorb oxygen at lower potentials than that of pure platinum.

The nature of the methanolic residue has been extensively studied and comprehensively reviewed by Parsons and Vandernoot [28] and more recently by Potter and Hards [29]. The consensus appears to be that the short term poisoning of the catalytic surface is by CO. Longer term effects may be due to polymerisation of intermediates [14].

The sequence of reactions for the oxidation of methanol suggested by Bagotsky et al. [30] still seems reasonable although no doubt there are additional subtleties. It is shown below (reactions (9) through (13)) using multiple site adsorption for intermediates.

$$3Pt + CH_3OH \rightarrow Pt_3COH + 3H^+ + 3e^- \qquad (9)$$

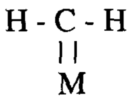
$$3Pt + 3H_2O \rightarrow 3PtOH + 3H^+ + 3e^- \qquad (10)$$

$$Pt_3COH + PtOH \rightarrow Pt_2CO + H_2O + 2Pt \qquad (11)$$

$$Pt_2CO + PtOH \rightarrow PtCOOH + 2Pt \qquad (12)$$

$$PtCOOH + PtOH \rightarrow CO_2 + H_2O + 2Pt \qquad (13)$$

Supporting evidence for this sequence which implies triple site adsorption of the methanol is that the overall reaction goes through a peak as the platinum dispersion is increased implying that a minimum area of platinum is required [31]. Additionally Williams et al. [14] operating a 300 W DMFC detected the presence of organic acids in the electrolyte which they attributed to an attack of a radical on a methanol molecule analogous to that postulated for Fischer–Tropsch synthesis of organic compounds from carbon monoxide and hydrogen:



$$\begin{array}{c} H-C-H \\ \| \\ M \end{array}$$

This type of residue may well account for the long-term decay in performance, which again implies multiple site adsorption.

As already noted, Shell workers [32,33] discovered that platinum/ruthenium alloys were something like two orders of magnitude more effective than platinum alone in promoting the electro-oxidation of methanol. Although other alloys have shown some promise, platinum/ruthenium still appears to be the catalyst of choice for DMFCs. Shell in the 1960s used Adams Pt/Ru in their stacks but subsequently effective electrodes were made by depositing the catalyst metals on high surface area carbon papers [33]. Others have made very effective electrodes from active carbon powders on which the catalyst is deposited. Very recently in the authors' laboratory we have found a non-platinum catalyst for the oxidation of methanol in acid media [34].

Although the long-term deterioration in performance might present a real difficulty, fortunately under intermittent operation characteristic of transport applications McNicol [35] has shown that during shutdown periods these adsorbed poisons are desorbed and operation over thousands of hours is possible with a free electrolyte which can be changed at intervals. Nevertheless the search for more effective and cheaper catalysts should be encouraged. As long as Pt/Ru remains the catalyst of choice the obvious route to improvement is to increase operating temperatures; this however raises further problems. If in order to preserve overall efficiency, pressures are limited to atmospheric then with aqueous electrolytes, whether as free acids or hydrated membranes, temperatures are limited to below 100°C.

4. Cell and stack design

Because fuel cells are high current low voltage devices internal resistance is a critical matter. The most significant sources of internal resistance are: (a) the electrolyte; (b) current collection at the electrode; and (c) the intercell connection.

Designers of fuel cells with an alkaline electrolyte have a much free hand than is the case for acid electrolytes. Not only are the necessary catalysts much cheaper, but relatively inexpensive base metals such as nickel and nickel-plated mild steel can be used in construction. Even silver can be used in modest quantities without undue expense. The good performance of inexpensive air electrodes operating at atmospheric pressure means that it is possible to lose a few millivolts through higher internal resistance without sacrificing too much efficiency. Thus whereas in acidic electrolytes through connections must be made over the whole electrode surface, in alkali edge collection is feasible, particularly if annular electrodes are employed, thus simplifying cell design and improving reliability.

In both acidic and alkaline cells, the thinner the electrolyte, the lower the internal resistance. This fact has been successfully exploited in the membrane cells operating on hydrogen and oxygen. In the case of the DMFC, while low internal resistances can certainly be achieved by this means, as already noted the thinner membranes allow greater diffusion of methanol to the air electrode with loss of both columbic efficiency and reduced effectiveness of the cathode catalyst. This suggests that a radically different membrane might be more successful. The other potential problem with the membrane cell is that reaction side-products may be difficult to remove while liquid electrolytes can readily be changed.

It is also evident that the higher the current density at which the cell operates, the higher is the ohmic loss. The high cost per unit area of existing membranes, approx. \$500 m^{-2} [36] is another encouragement to operate at high current densities. With liquid electrolytes such as sulphuric acid cost is not a significant factor, although obviously the higher the current density, the more compact and hopefully, more cost-effective is the cell.

The diffusion of methanol from anode to cathode with a free electrolyte can be minimised by a microporous membrane between electrodes as in the Shell DMFC where the electrodes were formed on opposite faces of microporous PVC. One would also expect that by operating at above the boiling point of methanol (65°C at atmospheric pressure) diffusion would be limited. However these uncertainties reinforce the need for demonstrations on a large enough scale to evaluate the respective merits and problems of different systems.

Turning now to the electrodes, connection between the active reaction site and the intercell collectors is complex. Clearly the catalyst itself must be an electronic conductor. In SPM cells the catalyst is usually deposited on the membrane itself with a Nafion® binder. Collection from the catalyst is usually by means of carbon cloth or paper and then to graphite intercell bipolar plates with alternate lands and gas channels. In the case of a free electrolyte, with the Shell electrodes the basis was a thin sheet (0.7 mm) of microporous plastic the surface of which was made conducting by a thin (approx. 1 μm) layer of gold onto which a catalyst was deposited using a suitable binder [10,32]. In the case of air, which was supplied to the catalyst side of the electrode, a stable interface was established by means of a small differential pressure (3–4 kN m^{-2}). The gold layer provided lateral conductivity. Connection between the electrode and the intercell plate was provided by either gold-plated polyethylene mesh (Netlon) or expanded niobium mesh. This type of open construction lends itself to release of unwanted products from the electrode surface: carbon dioxide at the fuel electrode, nitrogen and water vapour at the air electrode. In current SPM cells the intercell connection is a very expensive component. Machined graphite plates at a cost of £770 per kW [36] in hydrogen air cells and presumably considerably more in DMFCs are prohibitively expensive for widespread use. Niobium, platinised titanium or gold-plated stainless steel are possible alternatives but again very expensive, particularly as both reactants being in the gas phase and liquid cooling must thus be provided within the plates. The cheap alternative of a carbon filled plastic component presents problems of significantly lower conductivity. Typically graphite has a specific resistance of 3×10^{-3} ohm cm; for niobium the figure is 1.25×10^{-5} ohm cm. We understand that at present the lowest resistance that can be achieved with carbon-filled plastic is about 0.3 ohm cm or 1% the conductivity of graphite.

To give perspective to these figures, if an intercell separator plate had 1 mm ridges on either side of a 0.5 mm diaphragm and the spacing of ridges was 1 cm the resistance between cells would be about 0.75 ohm cm^{-2} and the resistive loss at 100 mA cm^{-2} would be 75 mV. At higher current densities the loss would be more. While closer spacing of the lands would reduce resistive loss, it would probably be at a cost of reduced electrode performance. Thus in order to achieve acceptable performance with low cost separators current densities should be limited particularly if this also implies lower catalyst costs. As the performance of platinum based catalysts is to a first order approximation directly proportional to catalyst loading [7], this appears to be the case. Yet another problem arises from cell cooling. The rate of heat removal from the cell stack is considerable, at least equal to the electrical power output and probably considerably more in the case of the DMFC. This in turn necessitates use of a liquid coolant which presents no problem with a circulating free liquid electrolyte. However with a membrane cell and both reactants, air (or oxygen) and methanol in the gas phase a complex intercell plate is needed which would probably be more expensive and higher in resistance.

5. Discussion

Despite the potentially low cost of fuel cells using alkaline electrolytes and their superior performance on air as cathode and some other work in Belgium conducted by the firm ZEVCO based on a system previously developed by Elenco, nowadays these systems appear to be neglected. Undoubtedly concerns about carbonation of the electrolyte have played a part, but provided that the electrolyte is circulated (desirable from the point of cooling), and the air is scrubbed, this should not be a problem.

Work on hydrogen/air cells is dominated by the SPM cells. High outputs can be achieved by operating under pressure of 3 atmospheres or so [7], overall costs are high and overall efficiencies are probably low at part load operation, which is often encountered in transport operation. It has been suggested [36] that exhaust gas from the cell could be used to power a turbine driven compressor, but this sounds very expensive and not particularly efficient. If operation at atmospheric pressure is accepted then much higher overall efficiencies could be achieved. At present costs are dominated not by the platinum catalysts but by the intercell plates costing £720 per kW, leading to an estimated total cost of £10 715 per kW [30]. This represents a severe engineering challenge which should not be beyond solution. If the graphite intercell plates can be replaced by a simple injection moulded component and the cost of the membrane reduced then an economic solution might well be in sight. Alternatively there is quite a lot to be said for exploring the alternative of a free sulphuric acid electrolyte which would ease cooling and water control problems while existing materials would permit the construction of a low-cost cell from simple injection moulded components.

Considering fuel supply, distribution of pure hydrogen and storage in pressured containers is feasible but inconvenient and not without hazard. The alternative of operating on pure hydrogen generated from methanol in a transportable 5 kW unit was demonstrated by Shell in 1964 with a start-up time of 15 min and thenceforth instantaneous response to load [2]. Much more recently the US Department of Transport has demonstrated a larger unit with phosphoric acid cells fed from a methanol/water reactor without a palladium/silver diffusion unit as used by Shell but much more sluggish response. Neither of these approaches is ideal and recently attention has returned to the use of cracked methanol which was first used by Telefunken [6]. An very compact methanol cracker has been demonstrated which starts up in about a minute and if used with a platinum/ruthenium catalysed SPM cell would still require further CO reduction.

Essentially two different approaches to the development of low-temperature DMFCs have been made, one involving the use of a free liquid electrolyte and the other solid polymers. Initially sulphuric acid was the electrolyte of choice and it had the advantages of low cost. Its circulation facilitated the removal of excess heat and exhaust carbon dioxide. Air electrode performance although reduced by the presence of methanol was still acceptable at atmospheric pressure. To date the only complete fuel cell power systems which operate in the stand-alone mode have used this approach with the fuel supplied in solution. The weakness of this approach has been the high cost of the catalyst and the relatively modest outputs achieved. Additionally above about 85°C sulphuric acid is reduced and poisons the catalyst. Recently most work reported on DMFCs has involved the use of SPM electrolytes which offer low internal resistance and operation at higher temperatures. Further, possibly because of the higher activity of water in the absence of free acid, better performance of the methanol electrode is achieved. Very good performance has been achieved but only when operating under pressure [37]. Apparently the oxygen (air) electrode only operates satisfactorily under pressure which would constrain the efficiency attainable. Also the thin polymer membrane apparently allows significant transfer of methanol to the air side where it is lost.

Catalytic problems are greatly reduced by operation at high temperatures and this is achieved in both the molten carbonate (MCFC) and solid oxide (SOFC) fuel cells. There are of course other difficulties and the MCFC is being considered primarily for power generation where corrosion and electrolyte stability problems have been tackled in order to attain the necessary longevity [3]. SOFCs are being considered for both stationary and mobile use. For stationary use these devices employ an yttria stabilised zirconia electrolyte and operate at about 900°C in order to achieve adequate conductivity [38]. The most effective application would be as a "topping" operation in which the high temperature exhaust was used to operate a steam turbine. In order to reduce the operating temperature to 650°C or so for mobile use, alternative electrolytes are being developed [38]. As very thin wafers of electrolyte have to be employed, those developing this type of fuel cell are facing some significant challenges. It is as yet early to predict the outcome of this work.

Before a fuel cell system can achieve commercial acceptance it must be available at a price that the customer perceives to be good value. Elements to be considered are total cost, capital investment, cost per kWh stored, cost per kW output and suitability for the operating environment. All of these vary widely with the intended application.

The gasoline engine represents a formidable financial target for the fuel cell to challenge. Bearing in mind that the elements of the total power system include the fuel cell stack, the air supply, fuel supply and control, to be competitive all components must be of low cost. It has already been argued that on grounds of cost, efficiency and noise operation an essentially atmospheric pressure is desirable. The most convenient source of air is a radial blower. Johnson [39] reported a power consumption of 6 W for one suitable for a 410 W hydrazine air stack of compact construction, requiring $0.43\ \mathrm{dm^3\,s^{-1}}$ at $0.98\ \mathrm{kN\,m^{-2}}$. This pressure drop can be considered satisfactory for a compact design (total individual cell thickness in stack 5 mm) suggesting that the blower for a well designed stack operating at atmospheric pressure consumes of the order of 1.2% of peak power. It is probable that a fan would be needed for the radiator to cool the electrolyte or circulating coolant. Nevertheless, Johnson's work showed that total parasitic losses for a liquid fuelled system operating at atmospheric pressure can be contained to within less than 5% of peak output. Similar losses would be expected for a hydrogen/air system operating at atmospheric pressure.

The present situation of fuel cells is intriguing. The impressive demonstrations of hydrogen powered vehicles in the US and Germany [3] illustrate the point that given an operable system, engineers can integrate fuel cells with vehicles. While pure hydrogen offers the possibility of pollution free operation in cities, costs are still very high but should be capable of reduction. If hybrid combinations of fuel cell and lead/acid battery are considered then it should be possible within existing knowledge to build a city bus operating on methanol which is cracked and then fed to a hydrogen cell. As matters stand there appear to be strong arguments for using a free acid electrolyte although this could change if massive cost reductions are achieved with SPM systems. The direct methanol system offers an attractive degree of simplicity and is probably capable of being demonstrated in a hybrid city bus albeit at a higher cost than the methanol cracker/free sulphuric acid type of unit. Certainly the rewards of success are so high that all reasonable avenues should be explored.

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