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Catalysis Today 38 (1997) 393–400

CATALYSIS TODAY

Electrocatalysts for fuel cells

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Abstract

A brief description of the six main types of fuel cell which are currently under research and development is given. The discussion focuses on recent developments in the polymer electrolyte-based proton exchange membrane fuel cell with description of the limitations imposed by current electrocatalysts and the benefits offered by the development of improved materials. © 1997 Elsevier Science B.V.

Keywords: Fuel cell; Electrocatalyst; Platinum; Hydrogen; Methanol; Reformer

1. Introduction

The six main fuel cell systems are currently in various stages of development. These fuel cell systems are listed in Table 1. With the exception of the direct methanol fuel cell (DMFC), characterisation and nomenclature of these is by the electrolyte and associated operating temperature. These features also govern the requirements of the electrocatalysts which control the reactions. The DMFC stands alone in involving a carbonaceous fuel (methanol) fed directly to the anode; all others use hydrogen as the anode fuel, either as a pure gas, or as a hydrogen-rich gas mixture. A catalytic steam reformer, or partial oxidation reactor, fed with methanol (or methane) is used to generate the hydrogen-rich gas mixture suitable for the fuel cell anode. This reformer/fuel cell system, fed with methanol, is sometimes referred to as the indirect methanol fuel cell, since in contrast to the DMFC, it is still hydrogen that is ultimately oxidised on the fuel cell anode. The nature of the electrolyte in any fuel cell, and the associated operating temperature, are crucial features of consideration for effective catalysts. The nature of the electrolyte also determines the identity of the dominant migrating ion, as listed in Table 2. Electrocatalysis, whilst extremely important in fuel cells, is not the only application of catalysis in the field. Processing of the fuel stream in order to generate an appropriate hydrogen source prior to admission to the fuel cell also involves its own catalysts in a reformer or partial oxidation reactor. Carbon monoxide resulting from reforming hydrocarbons acts as a poison for anode electrocatalysts in the low temperature fuel cells, and its removal from the fuel source is a challenging work for the fuel processing catalysts. In addition, other potential contaminants such as sulphur may pose further and new requirements for catalysts and their development.

Apart from exhibiting electrocatalytic activity towards the electrode reactions (the fuel anode as well

PII S0920-5861(97)00050-3

Table 1
The main types of fuel cell. With the exception of the direct methanol fuel cell, these are classified according to the electrolyte

Fuel cell type	Common abbreviation	Electrolyte	Operating temperature, °C
Alkaline	AFC	Potassium hydroxide	50–90
Proton exchange membrane	PEMFC	Solid proton conducting polymer	50–125
Phosphoric acid	PAFC	Orthophosphoric acid	190–210
Molten carbonate	MCFC	Lithium/potassiun carbonate mixture	630–650
Solid oxide	SOFC	Stablised zirconia	900–1000
Direct methanol	DMFC	Sulphuric acid or solid polymer	50–120

Table 2
Fuel cell systems showing anodic and cathodic reactions, and the dominant mode of ion transport in the electrolyte

Fuel cell	Anode reaction	Net ion transport	Cathode reaction
AFC	$H_2+2OH^- \rightarrow 2H_2O+2e^-$	$\leftarrow OH^-$	$O_2+2H_2O+4e^- \rightarrow 4OH^-$
PEMFC	$H_2 \rightarrow 2H^++2e^-$	$H^+ \rightarrow$	$O_2+4H^++4e^- \rightarrow 2H_2O$
PAFC	$H_2 \rightarrow 2H^++2e^-$	$H^+ \rightarrow$	$O_2+4H^++4e^- \rightarrow 2H_2O$
MCFC	$H_2+CO_3^{2-} \rightarrow H_2O +CO_2+2e^-$ $CO+CO_3^{2-} \rightarrow 2CO_2+2e^-$	$\leftarrow CO_3^{2-}$	$O_2+2CO_2+4e^- \rightarrow CO_3^{2-}$
SOFC	$H_2+O^{2-} \rightarrow H_2O+2e^-$ $CO+O^{2-} \rightarrow CO_2+2e^-$ $CH_4+4O^{2-} \rightarrow 2H_2O+CO_2+8e^-$	$\leftarrow O^{2-}$	$O_2+4e^- \rightarrow 2O^{2-}$

as the air or oxygen cathode), the electrocatalysts must be stable within the working cell. For the alkaline fuel cell (AFC) this is relatively easy since many electrocatalytic materials are adequately stable in alkaline solutions. The fact that the AFC is very sensitive to the presence of CO_2, either in the fuel stream or in the air stream, has limited its application substantially to those situations where very pure hydrogen and very pure oxygen can be supplied. For the fuel cells employing acidic electrolytes, stability of the electrocatalyst is much more difficult to realise. Many electrocatalysts have been examined over many years for their application to fuel cells; the nature of preferred electrocatalysts is critically dependent on the nature of the fuel cell. The high temperature molten carbonate and solid oxide fuel cells (MCFC and SOFC) present difficulties of thermal stability as well as compatibility with the electrolyte. Currently preferred electrocatalysts for the various cells are listed in Table 3. Since most electrocatalysts for fuel cells are made from noble metals, particularly platinum, it is of practical importance, to minimise the loadings of the electrocatalysts over the electrodes and to maximise their effective utilisation in the electrode structure.

Table 3
Preferred electrocatalysts for the main fuel cell systems

Fuel cell	Anode catalyst	Cathode catalyst
AFC	Pt/Au, Pt, Ag	Pt/Au, Pt, Ag
PEMFC	Pt, Pt/Ru	Pt
PAFC	Pt	Pt/Cr/Co, Pt/Ni
MCFC	Ni, Ni/Cr	Li/NiO
SOFC	Ni/ZrO_2	$LaSrMnO_3$

2. Electrochemical characteristics of the fuel cell

The basic electrochemical characteristics of the fuel cell are shown in Fig. 1, depicted for the proton exchange membrane fuel cell (PEMFC). The 'theoretical' cell voltage, or thermodynamically reversible cell voltage is the potential difference between the equilibrium potential of the fuel and that of the oxidant (for example, 1.23 V for pure hydrogen and pure oxygen at 25°C). The cell voltage deviates increasingly from the theoretical voltage as greater current is drawn through the cell and the components are polarised. The performance of the anode and cathode electrocatalysts play an important role in polarising the cell away from thermodynamic equilibrium. For a hydrogen/air (oxygen) cell, the air electrode has by far the bigger activation overpotential as shown in Fig. 1.

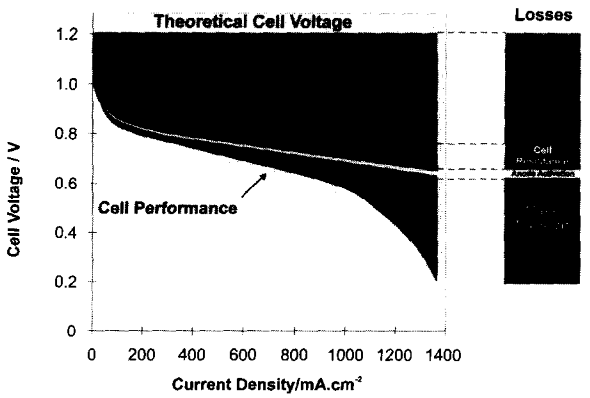

Fig. 1. Voltage/current relationship and cell performance losses for the PEMFC.

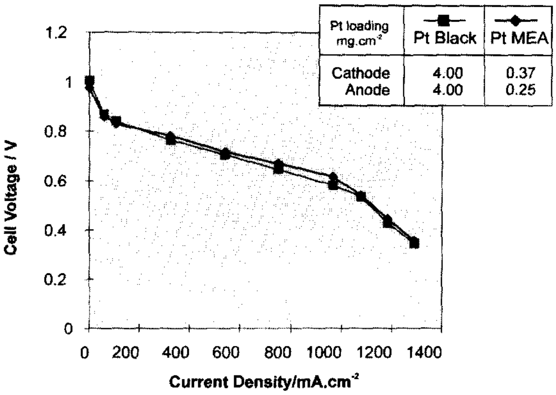

Fig. 2. PEMFC single cell performance of high and low platinum loading membrane electrode assemblies (MEAs). 240 cm^2 cell; Dow XUS13204.10 membrane; H_2/air, 30/30 psig, 1.5/2.0 stoichiometry; 75°C.

In the absence of poisoning species, the hydrogen overpotential on a Pt catalyst is low. Overpotentials are also required to overcome the cell resistance, chiefly the electrolyte resistance, giving an ohmic response. At very high current densities, the output of the cell becomes limited by mass transport processes that are associated with reactant diffusion towards, and product diffusion from, the reaction sites in the electrode structures. For the PEMFC, operating on air as the source of oxygen, these are dominated by the increased difficulty in the diffusion of reactant oxygen, diluted in nitrogen, counterflow to the diffusion of product water. Typical of the PEMFC as well as other low temperature systems fuelled by hydrogen, is the fact that the cathode polarisation at all current densities, and the mass transport limitations at high current densities govern the performance of the fuel cell.

3. Catalyst utilisation

The heart of the PEMFC where the energy conversion reactions take place is the membrane electrode assembly (MEA). This is constructed from the anode and cathode comprising the electrocatalysts bonded to the faces of a solid polymer electrolyte film. This solid state fuel cell designed for low temperature operation can be fed with hydrogen or methanol as the fuel and pure oxygen, but usually air, as the oxidant. As indicated above, the electrocatalysts for the PEMFC are invariably based on platinum and as such it is imperative to design electrode structures to minimise the loadings of the electrocatalysts by maximising their effective utilisation in the electrode structure. The dramatic progress made in this direction in recent years can be seen in Fig. 2, which illustrates the performance of MEAs in a 240 cm^2 active area Ballard Mark 5 single cell. For the same cell performance, it has been possible to reduce the electrode platinum loadings by more than an order of magnitude. This has been achieved by replacing the unsupported platinum black based electrodes at 4.0 mg cm^{-2} Pt loading, with carbon supported, platinum catalysts of higher surface area using loadings as low as 0.1 mg cm^{-2} Pt.

4. The cathodic reaction in low temperature fuel cells

Despite the very high current densities obtained from the PEMFC, as demonstrated in Fig. 2, there are still cell performance losses which can in principle be overcome. These losses are dominated by kinetic and mass transport issues at the oxygen reduction cathode. The reduction of oxygen is itself a complex electrochemical process, as shown in Fig. 3. Two basic paths can be identified, following adsorption onto the electrocatalyst surface. If the O_2 molecule is adsorbed so that its axis is parallel to the catalyst

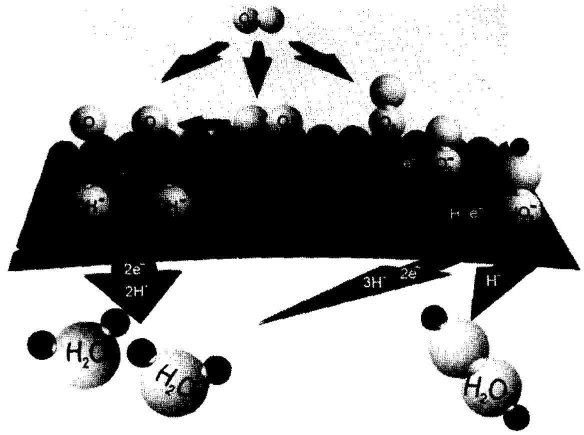

Fig. 3. Reaction pathways for electrochemical reduction of oxygen in acidic electrolytes.

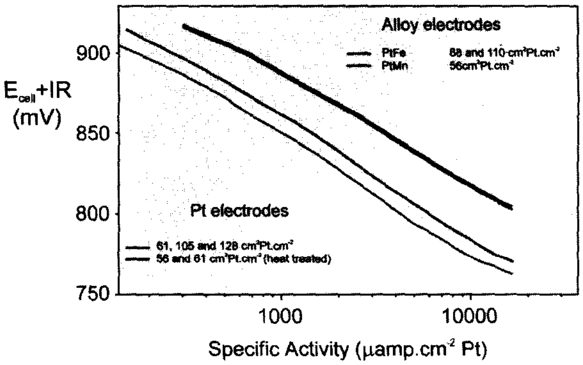

Fig. 4. PEMFC single cell performance of MEAs with platinum and platinum alloy cathode electrocatalysts. 25 cm^2 cell; Dow XUS13204.10 membrane; H_2/O_2, 30/40 psig, 300/300 $cm^3\ min^{-1}$; 75°C.

surface, it divides into adsorbed oxygen atoms; these can then be reduced and protonated to give water. This constitutes the left-hand mechanism in Fig. 3. The right-hand side shows the oxygen molecule adsorbed with its axis perpendicular to the catalyst surface. In this case the O_2 molecule does not cleave; instead the peroxide anion (HO_2^-) is formed by partial reduction as an adsorbed intermediate. This intermediate can then be further reduced to water as shown, or it can be protonated and leave the surface as hydrogen peroxide. Because of the complexity of this reaction, the cathode reaction requires a significant overpotential, as shown in Fig. 1. The usual electrocatalyst for this reaction is platinum. However, in recent years it has been found that the intrinsic kinetics for the reaction can be significantly enhanced by the use of platinum alloy catalysts in which transition metals such as Cr, Mn, Fe, Co and Ni are incorporated into the platinum crystal lattice. The performance of some of these can be seen in Fig. 4, shown for a 75°C fuel cell operated at 30/40 psig H_2/O_2, and plotted in terms of the activity of the cell per unit surface area of platinum available in the electrode. The near logarithmic response between current and cell voltage arises from correction for the ohmic potential drop component, and indicates that under this condition the cell was operating under purely kinetic control. The enhancement in performance of some 30 mV represents an increase in the intrinsic kinetics of the platinum catalyst surface by a factor of 2–3 times.

Transport processes are also complex at the cathode. A typical cathode comprises a catalyst layer deposited on to a porous conducting substrate such as carbon fibre paper. Apart from the reaction itself, oxygen must diffuse through the porous substrate, through the catalyst layer and through the electrolyte local to the catalyst surface. This oxygen must be humidified and, if air is used, it also contains nitrogen. All these components must have free access through the substrate, and thermal gradients must be accommodated. These processes, together with the proton and water transport through the polymeric electrolyte, are illustrated in Fig. 5. In this case a porous electrically conducting substrate, 150 μm thick, must allow free transport of O_2 to the underlying electrocatalyst layer. The catalyst layer, 40 μm thick lies in contact with the solid phase layer (150 μm) PEM electrolyte. The water balance throughout this system is critical. Reduction of oxygen from air at high current densities leaves a residue chiefly of nitrogen, and this must be transported away from the cathode if fresh air is to reach the cathode electrocatalyst to continue the reaction. This blanketing effect of the nitrogen residue is not experienced when pure oxygen is fed to the cathode. Even with rapid transport of nitrogen, it must be expected that operation of the cathode at high current densities will necessitate a reduced proportion of oxygen in the cathode gas stream. Effective design of the cathode to minimise blanketing by nitrogen is paramount.

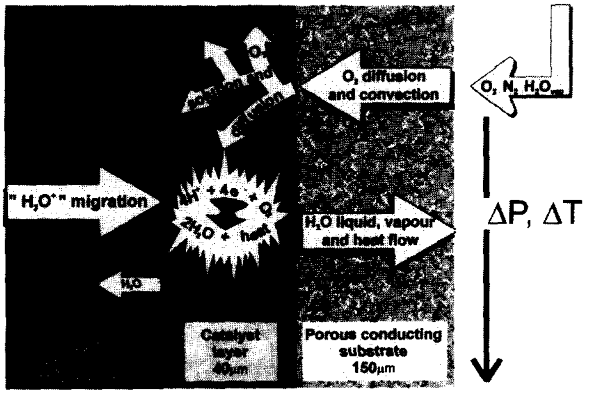

Fig. 5. Transport processes at PEMFC oxygen reduction cathode.

5. The anodic reaction in low temperature fuel cells

Pure hydrogen provides the best fuel for the fuel cell anode. Because of the fact that reduced hydrogen does not occur in nature its manufacture from reformed natural gas or methanol provides a viable source. The reforming reaction does not, however, provide pure hydrogen; rather it produces a mixture of gases as output : H_2, CO_2, N_2 and CO. This mixture is hydrogen rich, but the other components can restrict the performance of the anodes severely. Of most significance here is the production of carbon monoxide. Carbon monoxide is a severe anode catalyst poison, as shown by the data in Fig. 6. The diagram, from half-cell measurements, shows that at PEMFC temperatures the Pt anode catalyst is heavily poisoned by as little as 100 ppm CO in H_2. Fig. 7 shows that CO is itself very difficult to oxidise electrocatalytically at low overpotentials. Primarily, the effect appears to involve the adsorption of the CO to the electrocatalyst; once adsorbed, it is difficult to remove. The data show very clearly that it is carbon monoxide which poisons the hydrogen anode catalysts. The effect of CO on the complete cell performance is shown in Fig. 8. These data, again obtained on the Ballard Mk V cell show the impact of 10, 40 and 100 ppm CO in the hydrogen fuel stream on the performance of a platinum based anode, at a Pt loading of 0.37 mg cm^{-2}. High performance levels attained using pure hydrogen as fuel are progressively and severely reduced by increasing concentrations of CO.

One method of combating poisoning of hydrogen electrodes by CO is to modify the catalyst using an approach in which the relative strength of the chemisorbed CO bond is reduced. Fig. 9 shows the anode half-cell performance of pure Pt, Pt/Ni and Pt/Ru fuelled with hydrogen carrying 100 ppm CO. Of these, Pt/Ru is shown to be the least polarised by the presence of CO: the presence of Ru dissolved in a Pt matrix reduces the degree of anode poisoning. Fig. 10 illustrates the marked tolerance to CO caused by the use of the Pt/Ru anode, at a Pt loading of 0.34 mg cm^{-2}, in the complete single cell tests. It is more than 30 years since the discovery of Pt/Ru as an electrocatalyst which is relatively tolerant of carbon monoxide (relative to pure Pt), and no significantly

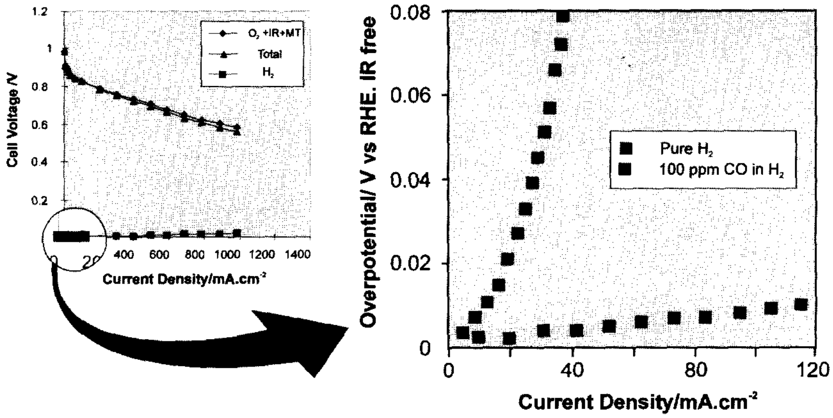

Fig. 6. Anode half-cell performance of platinum catalyst with pure hydrogen and 100 ppm carbon monoxide in hydrogen. Nafion-coated anode; 1.0 M H_2SO_4; 80°C; 0.25 mg cm^{-2} Pt.

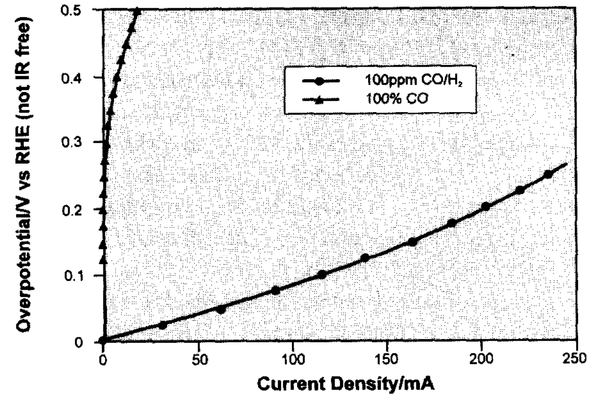

Fig. 7. Anode half-cell performance of platinum catalyst with 100 ppm carbon monoxide in hydrogen and pure carbon monoxide. Nafion-coated anode; 1.0 M H_2SO_4; 80°C; 0.25 mg cm^{-2} Pt.

better electrocatalytic system has yet been found for the anode reaction. Despite the effectiveness of the Pt/Ru alloy in tolerating CO, this catalyst poison remains a problem for the low temperature fuel cell yet to be solved viably.

An alternative method of approaching the poisoning effect of carbon monoxide is to clean up the reformed fuel stream prior to admission to the fuel cell. An example of this is illustrated in Fig. 11. The fuel, in this case methanol, is fed to a reforming processor (Hot Spot™ reactor) which produces a gas stream containing 55% H_2, the required fuel mixed with 22% CO_2, 21% N_2 and 2% CO. The remarkably small dimensions of this reactor make it a viable proposition for its 625 $dm^3 h^{-1}$ H_2 output. The small size is achieved by combining the exothermic partial oxidation reaction with an endothermic steam reforming reaction over the same catalyst particles. This achieves a very high rate of internal heat transfer and a very easily controlled reactor. The reformer output is then fed to a 'clean-up' reactor (Selox™) where the fuel is reacted further with air to reduce the CO content from 2% to 10 ppm, a far more viable concentration for the electrocatalysts used in the low temperature fuel cell. Note that this is carried out at the expense of a marginal loss of the hydrogen fuel, and a marginal increase in the CO_2 component.

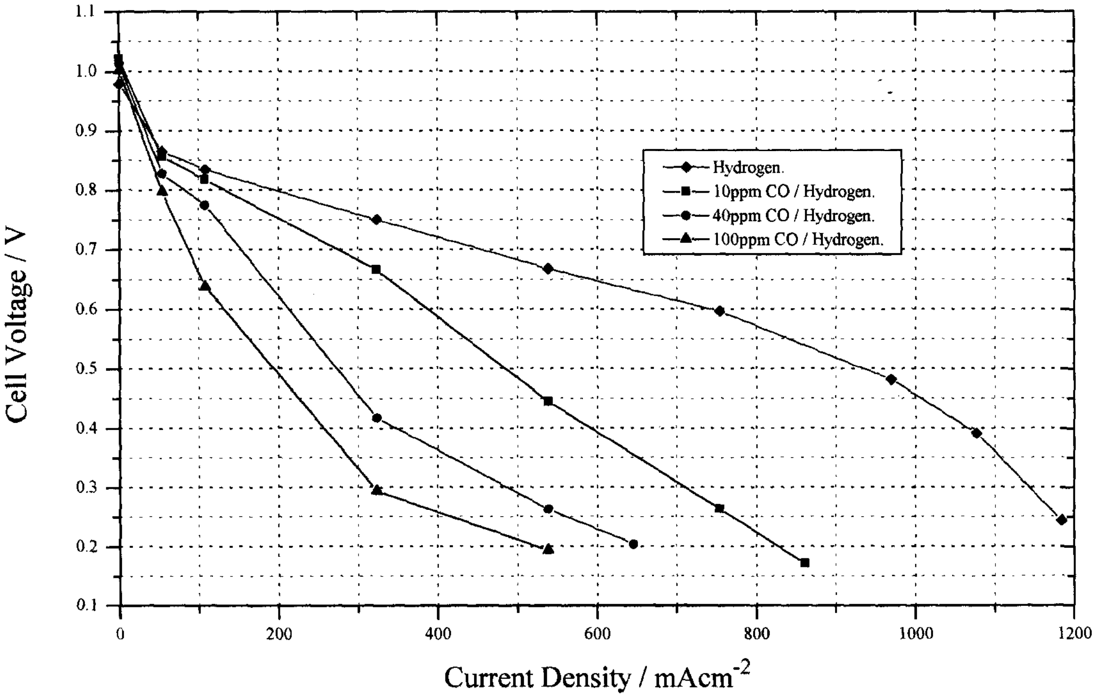

Fig. 8. Effect of CO content in hydrogen on PEMFC single cell performance. 240 cm^2 cell; anode: 0.37 mg cm^{-2} Pt; cathode: 4.0 mg cm^{-2} Pt; Nafion 115 membrane; H_2/air, 30/30 psig, 1.5/2.0 stoichiometry; 80°C.

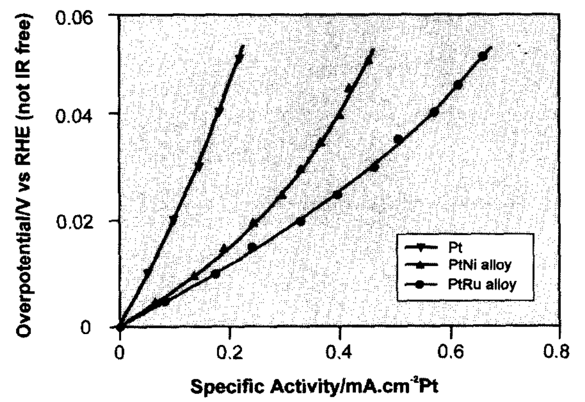

Fig. 9. Anode half-cell performance of Pt, Pt/Ni alloy and Pt/Ru alloy catalysts with 100 ppm CO in H_2. Nafion-coated anode; 1.0 M H_2SO_4; 80°C; 0.25 mg cm^{-2} Pt.

The role of carbon dioxide also needs to be considered in the same light. Fig. 12 shows the single cell performance obtained when the anode is fed with hydrogen containing 25% CO_2. It can be seen that at current densities above 500 mA cm^{-2}, the platinum based anode shows a marked decrease in cell voltage. Again the use of the Pt/Ru anode helps to alleviate some of this poisoning effect, but is still some 20–30 mV below the pure hydrogen performance. Whilst the effect of CO_2 is nowhere near as large as the effect of carbon monoxide, the reasons for the losses need to be better understood and overcome, as even these relatively minor losses cannot be tolerated by the fuel cell stack developer, as they represent a system efficiency penalty of some 1–2%. However, the main difficulty in the application of a reformed hydrogen fuel in the low temperature fuel cell remains the effect of carbon monoxide on the anode catalyst. The generation of CO and its effects on anode catalyst performance is probably also one of the major impediments to efficient operation of the low temperature direct methanol fuel cell. It is interesting to note here that Pt/Ru is in this case also the most effective anode electrocatalyst to date.

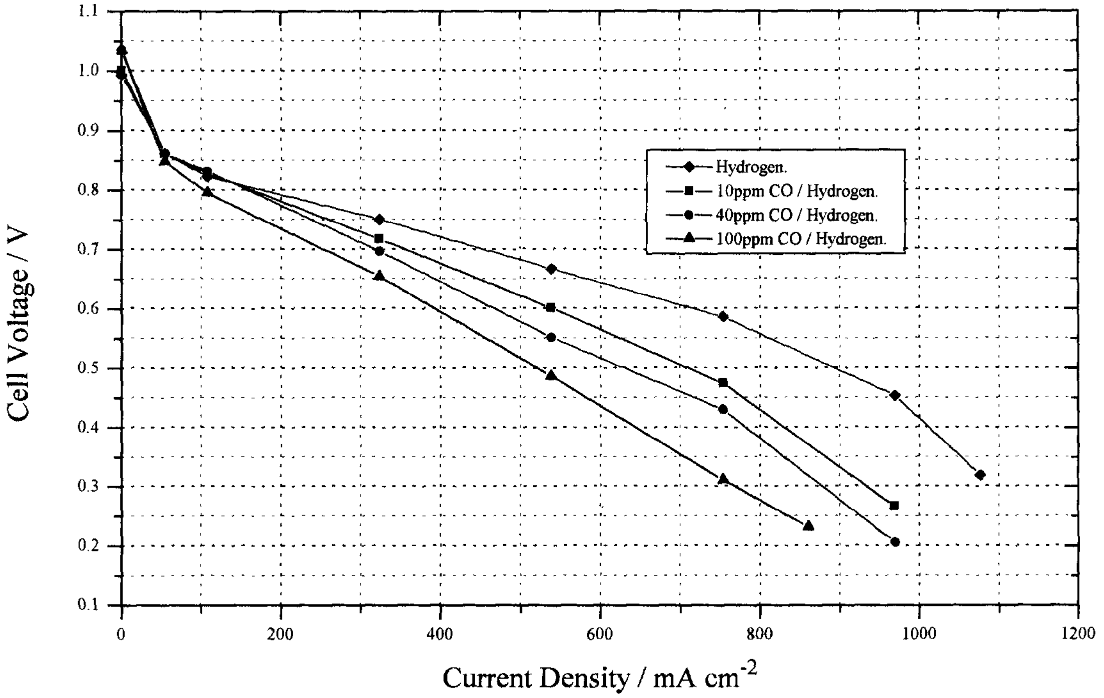

Fig. 10. Effect of CO content in hydrogen on PEMFC single cell performance with Pt/Ru anode electrocatalyst. 240 cm^2 cell; anode: 0.34 mg cm^{-2} Pt; cathode: 4.0 mg cm^{-2} Pt; Nafion 115 membrane; H_2/air, 30/30 psig, 1.5/2.0 stoichiometry; 80°C.

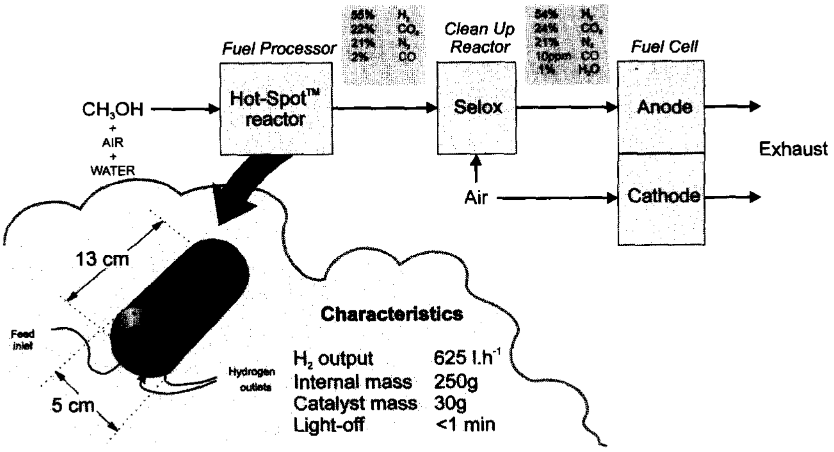

Fig. 11. PEMFC and HotSpot™ partial oxidation reformer system.

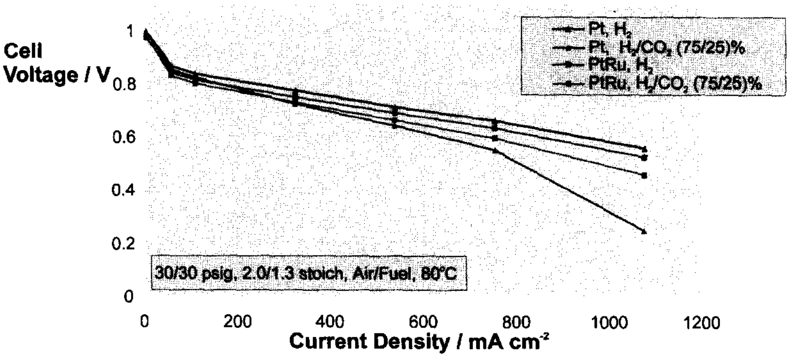

Fig. 12. Effect of carbon dioxide in hydrogen on PEMFC single cell performance. 240 cm^2 cell; anode: 0.25 mg cm^{-2} Pt; cathode: 4.0 mg cm^{-2} Pt; Nafion 117 membrane; H_2/air: 30/30 psig, 1.5/2.0 stoichiometry; 75°C.

6. Conclusion

Electrocatalysts are vital components of fuel cell systems. Much progress has been made over the years in improving their effectiveness both for anode and cathode reactions. There is nevertheless scope for considerable improvement in the performance of the electrocatalysts, particularly at the air cathode, where large activation overpotentials should be overcome. With the anode reaction also, electrocatalysts more tolerant to carbon monoxide should allow the use of less pure hydrogen and stimulate performance. Improved electrocatalysts must still retain compatibility with the fuel cell system. These are the acidic electrolytes in low temperature cells, up to ca 200°C. There is much room for improvement in the design of catalysts for use in fuel cells, both in activity and in durability. Application of platinum-based electrocatalysts require a high utilisation of the available material, and there remains scope for raising this.