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Electrocatalysts for fuel cells

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The chemical and physical composition of the catalysts used in fuel cells are determined by the type of cell for which they are intended and its operating conditions. The six types of fuel cell presently in use or under development are described in the context of their electrocatalyst requirements.

The important features of the current–voltage characteristics of fuel cells and the extent to which these depend upon the electrocatalysts and electrode structures are described. The limitations of electrocatalysts presently used in fuel cell developments and opportunities for improving their performance are discussed and analysed.

Following this overview of electrocatalyst developments for fuel cells, the paper concludes with details of the development of precious metal based electrocatalysts for proton exchange, solid polymer fuel cells.

1. Introduction

There are now six fuel cell systems under development for providing electrical power in applications such as space vehicles, consumer electronics, motor vehicles, on site and distributed power. These fuel cells are characterized and described by their electrolytes as shown in table 1. These in turn largely determine the operating parameters of temperature and pressure of each type of cell. The development of electrocatalysts and the associated electrode materials of necessity reflect the individual electrode processes, the specific fuel cell type and its operating conditions and is the subject of this paper.

While the electrocatalysts are a key component of a fuel cell system, it should be noted that they are not the only application for catalysts in this field. For example, as fuel cell technology is presently positioned, fuel cells achieve superior performance, as defined by their current–voltage characteristics, when operated with hydrogen or hydrogen rich gas as the fuel. Hydrogen rich gas is presently provided by incorporating a catalytic reformer or partial oxidation reactor into the fuel cell system. Collectively, this makes fuel cells and their potential wide scale uses one of the major new applications for catalysis.

2. The role of electrocatalysts in fuel cells

The intrinsic activity of the anode and cathode electrocatalyst materials used in a particular type of cell is fundamental to the performance of the cell and, with it, the total fuel cell system. However, it is not the only parameter that a satisfactory material must satisfy for commercial applications. Trace levels of carbon monoxide

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Table 1. *Types of fuel cells*

type	electrolyte	operating temperature/ °C
alkaline	potassium hydroxide	50–90
proton exchange membrane	polymeric	50–125
phosphoric acid	orthophosphoric acid	190–210
molten carbonate	lithium/potassium carbonate mixture	630–650
solid oxide	stabilized zirconia	900–1000
biological	sodium chloride	ambient
direct methanol	sulphuric acid or polymer	50–120

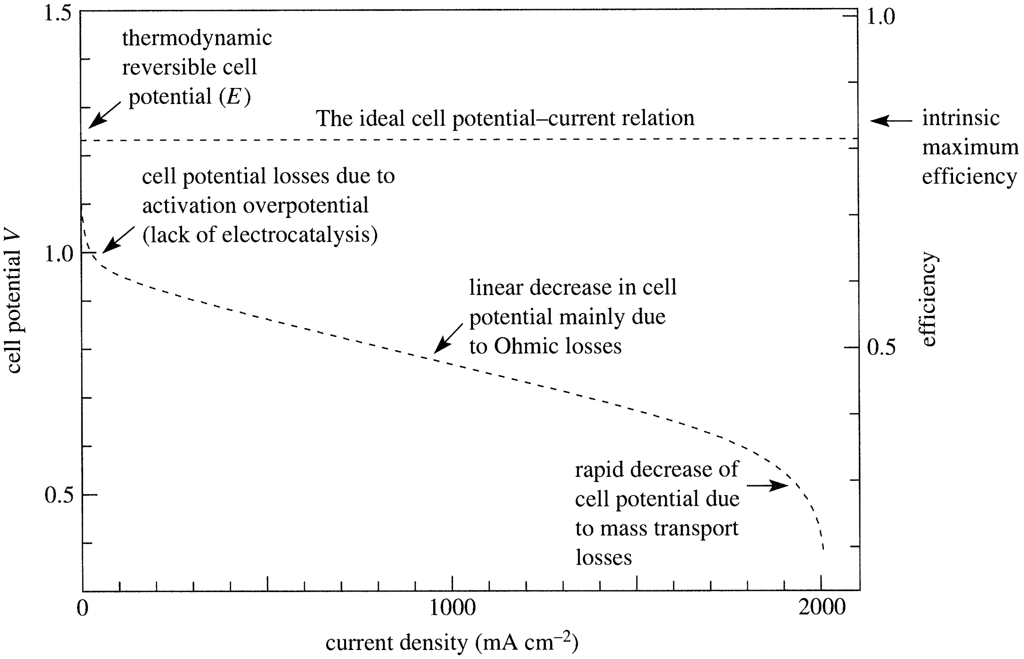

Figure 1. The current–voltage characteristics of fuel cell.

resulting from hydrocarbon reforming are a particular challenge in the development of electrocatalysts for ‘low temeprature’ cells. It remains to be seen how tolerant ‘high temperature’ cells are to sulphur in the fuel supply.

As with most catalysts, durability with respect to maintaining electrode performance is particularly important. Present requirements for stationary power applications require the fuel cell stack to have a minimum life of five years.

Last, but by no means least, electrocatalyst materials must be compatible with electrode materials in systems where different materials are used and with the electrolyte with which they are in intimate contact.

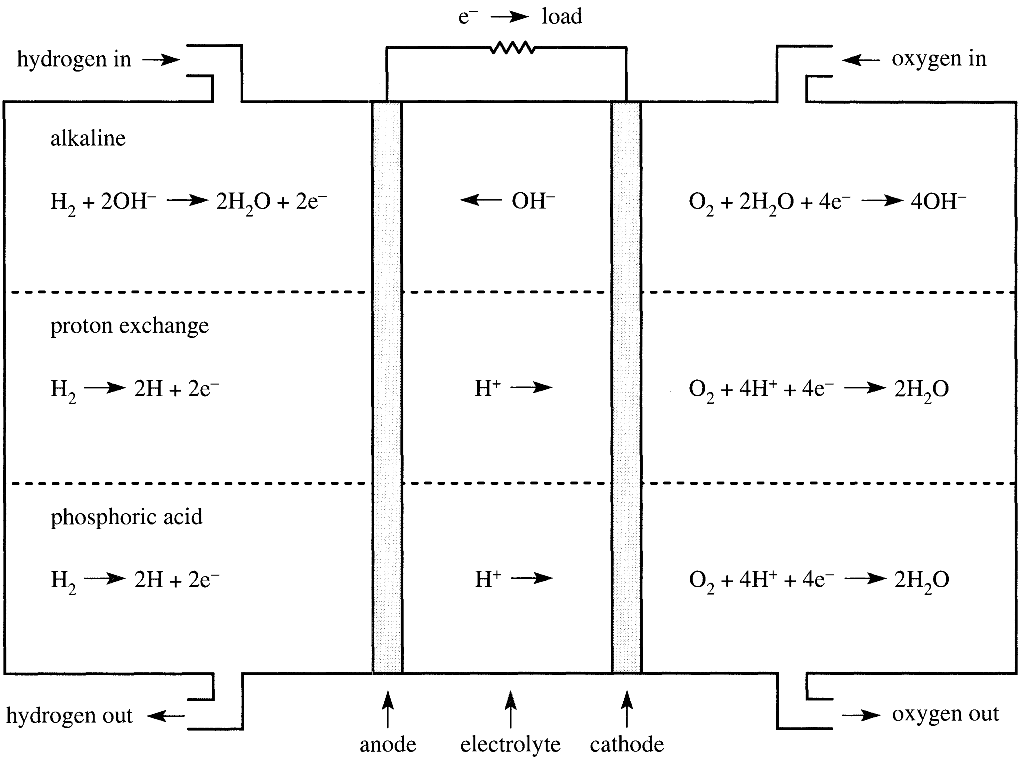

Figure 2. Low temperature fuel cell systems.

(a) *The current–voltage characteristics of a fuel cell*

A typical current–voltage curve for a fuel cell is shown in figure 1 together with the relationship between cell potential, V and the conversion efficiency of fuel to electrical power.

The thermodynamic reversible cell potential, E, is generally in the range 1–1.5 V. It is a function of the type of cell, the elctrode processes and operating temperature and determines the intrinsic maximum efficiency. This typically is greater than 80% (Krumpelt 1994).

The cell potential V, decreases as the current drawn from the cell increases and increasingly diverges from the ideal cell potential–current relationship and maximum efficiency. The performance of the anode and cathode electrocatalysts play a significant but not a sole role in determining the shape of this curve. Of particular significance is the performance of the electrocatalysts in the initial stages of the cell voltage–current curve when voltage losses due to activation overpotential result in a significant and often dominating impact on cell performance (Krumpelt 1994). It is in addressing this limitation in electrocatalyst performance that most work has been focused in recent years.

The region where the cell potential approximates to a linear relationship with current density is influenced by the ohmic resistance of the cell materials. The electrocatalyst materials may contribute to ohmic losses but are generally not the most significant factors. The rapid loss of cell potential at high current density is attributed to mass transport of fuel, oxygen and reaction products in the cell structure. Again,

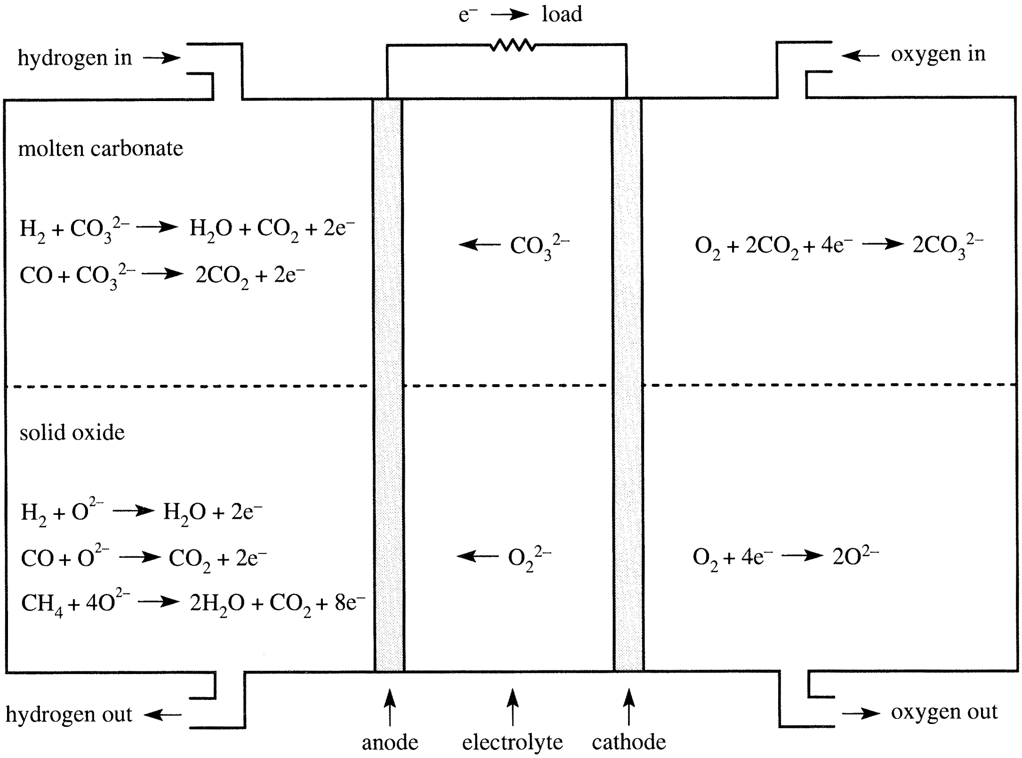

Figure 3. High temperature fuel cell systems.

the electrocatalysts may contribute to mass transport losses but in practice are not the principle factors.

Poisoning of the electrocatalyst or decreasing activity with increasing time of operation of the cell result in further losses of cell voltage, V as the current delivered by the cell increases. In addition to reducing the power density, poisoning and poor durability of the electrocatalysts result in reduced cell efficiency if power density is maintained by increasing current density.

3. The six fuel cell systems

Although the overall equation representing the conversion of hydrogen or hydrocarbons and oxygen in a fuel cell to water, carbon dioxide and electrical power is the same for each of the six fuel cell systems, the reactions occurring at the anode and cathode are different depending upon the electrolyte and the current carrying ion. These reactions are illustrated schematically in figures 2 and 3 (Cameron 1990).

Further the products of the reaction may arise at either the cathode or anode. It is therefore not surprising that these factors together with the different temperature regimes in which the six fuel cell systems operate result in the preferred electrocatalysts for each system being significantly different.

Table 2. *Preferred electrocatalysts*

type	anode	cathode
AFC	Pt/Au, Pt, Ag	Pt/Au, Pt, Ag
SPFC	Pt, Pt/Ru	Pt
PAFC	Pt	Pt/Cr/Co, Pt/Ni
MCFC	Ni, Ni/Cr	Li/NO
SOFC	Ni/ZrO_2	$LaSrMnO_3$

(*a*) *Electrocatalysts used in fuel cells*

Electrocatalysts are produced and used in a wide range of compositions and physical forms: metal foam, gauze or thin film; metal powders or blacks; supported metals; simple oxides; mixed oxides.

Details of the material composition of electrocatalysts currently preferred for use in specific fuel cell systems are given in table 2.

Significant progress has been made in recent years in all aspects of fuel cell technology including electrocatalysts. Demonstrations in stationary power applications ranging from 50 kW to 11 MW have been successful (Shibata 1994). More recently fuel cell technology has advanced to the stage where it can be demonstrated as an emissions free system in transport applications (Prater 1996). However, for fuel cells to compete with other power generation technologies, further improvements to the activity and durability of the electrocatalysts for most fuel cell systems are being sought and are the subject of worldwide development programmes.

Further, as progress is made towards acceptable electrocatalyst performance for specific applications, the need to consider materials and manufacturing costs become increasingly significant.

Highlights and a brief summary of specific opportunities for further improvements to electrocatalysts follow by reference to the specific fuel cell systems.

(i) *Alkaline fuel cells*

The principle application for alkaline fuel cells is in space exploration. Here fuel cells have provided the power and drinking water for manned space flights utilizing liquid hydrogen and oxygen as the fuel sources. Exceptionally high current densities can be achieved using high loadings of precious metal based electrocatalysts with durability more than adequate for the application.

Alkaline fuel cells suffer from the major disadvantage of the electrolyte reacting with carbon dioxide and this has limited their development for other applications. However, of significance concerning electrocatalyst development, cathode performance using the preferred precious metal catalysts is superior to that in all other fuel cell systems where cathode performance with current electrocatalysts is comparatively poor (Appleby 1994). Electrocatalyst development for alkaline fuel cells is therefore not a priority area.

(ii) *Proton exchange membrane fuel cells*

This all solid state system which has already been demonstrated as having the capability to achieve power densities of $1\ \mathrm{kW\ l^{-1}}$ using hydrogen as the fuel (Prater

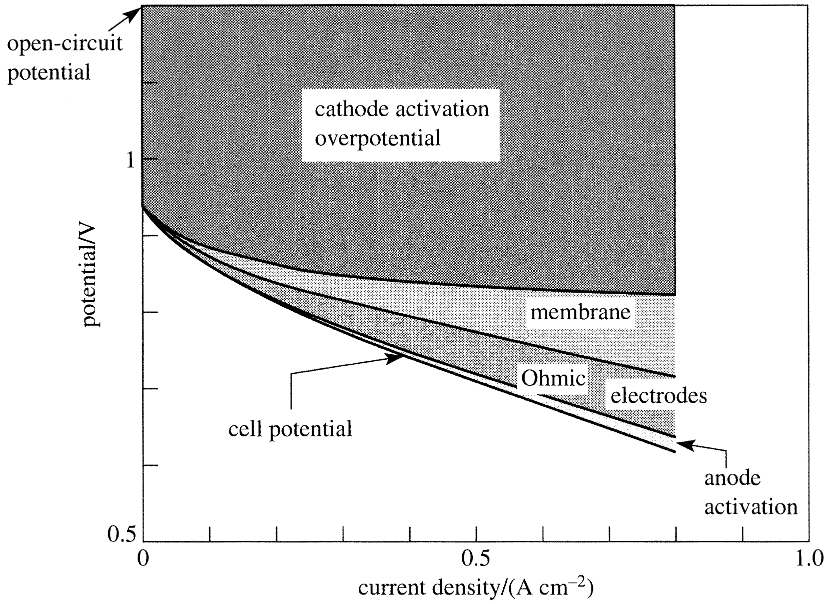

Figure 4. Fuel cell performance losses.

1996) is presently the first choice system for transport applications. Opportunities for further improvements in the cell's performance include the development of anode catalysts with increased resistance to carbon monoxide poisoning and cathode performance using air as the oxidant. The preferred catalysts for both anode and cathode are supported platinum. For transport applications where cost is a major factor, good platinum utilization is essential. With developments leading to a tenfold improvement now having been achieved (Ralph *et al.* 1995), platinum loadings are no longer a significant issue for transport applications.

Further improvements in cell performance are possible from developments in cathode electrocatalyst performance as described in § 4.

Fuel cells which can use hydrocarbon fuels directly without reforming have been a challenge to electrocatalyst and cell development for many years (Cameron 1987). As a result of recent work the most promising system to emerge is the direct methanol fuel cell using a proton exchange membrane electrolyte in preference to sulphuric acid. In this cell, anode performance is a limiting factor. Platinum promoted with ruthenium is the preferred anode electrocatalyst. Further improvements to the performance of this system are required notably for transport applications.

(iii) *Phosphoric acid fuel cells*

Systems for stationary power applications using phosphoric acid fuel cells are the most advanced of the fuel cell systems. Pre-commercial units ranging from 50 kW to 11 MW are installed on sites around the world (Ramm 1996). Performance and reliability of the current generation of units have been outstanding. However, despite extensive work to develop improved promoters and stabilizers for the supported platinum cathode electrocatalyst further improvements in both activity and durability are desired. Anode activity and platinum utilization are satisfactory.

Table 3. *EPSA of low low Pt loading 'Nafion ink' cathodes from ex situ cyclic voltammetry*
(All 'Nafion ink' cathodes used 20 wt% Pt/XC72R with a metal area of 100 m^2 (g Pt)$^{-1}$.)

cathode	Pt loading (mg Pt cm^{-2})	Pt utilization (%)	EPSA (cm^2 Pt cm^{-2})
Nafion ink	0.11	43	45
	0.22	54	103
	0.33	42	132
E-Tek	0.52	11	46
Pt black	4.0	est. 5	50

(iv) *Molton carbonate fuel cells*

Nickel based electrocatalysts are the preferred materials for both anode and cathode. Nickel based anodes are subject to dissolution in the molten carbonate electrolyte. More stable electrocatalysts such as nickel/chrome have been developed to minimize the effect of the electrolyte. The success of these developments can be assessed when the 2 MW Santa Clara demonstration unit goes on stream later this year.

LiO/Ni is presently the preferred cathode electrocatalyst. However, like other fuel cell systems, with the exception of the alkaline fuel cell, there remains considerable scope for improving cathode performance.

(v) *Solid oxide fuel cells*

The solid oxide fuel cell using yttria stabilized zirconia as the electrolyte has an operating temperature in the range 900–1000 °C. Much of the work in recent years on this system has been concerned with the development of cell structures that will enable stacks to be constructed and scaled up. Tubular, planar and monolith systems are being constructed and evaluated for durability and manufacturing potential. Nickel/zirconia is the preferred anode material and lanthanum strontium manganese oxide the cathode material. These materials have adequate if not outstanding electrocatalyst performance using hydrogen or hydrogen rich gas as the fuel. Methane may also be used directly as the fuel with these materials with some loss in cell performance.

The principal development in solid oxide technology is concerned with the evaluation of electrolyte materials which have better oxygen ion conductivity at lower temperatures preferably in the range 550–650 °C. The development of such systems which have now been reported (Steele 1993) requires new electrocatalysts for the cathode to be found. Not only do they need to have cathode activity at least as good as those used at higher temperatures, but also have to be compatible with the electrolyte.

4. Improved cathode electrocatalysts for proton exchange membrane fuel cells

A diagram illustrating the main factors contributing to the decrease in cell potential with increasing current density is shown in figure 4 (Verbrugge 1992). It is

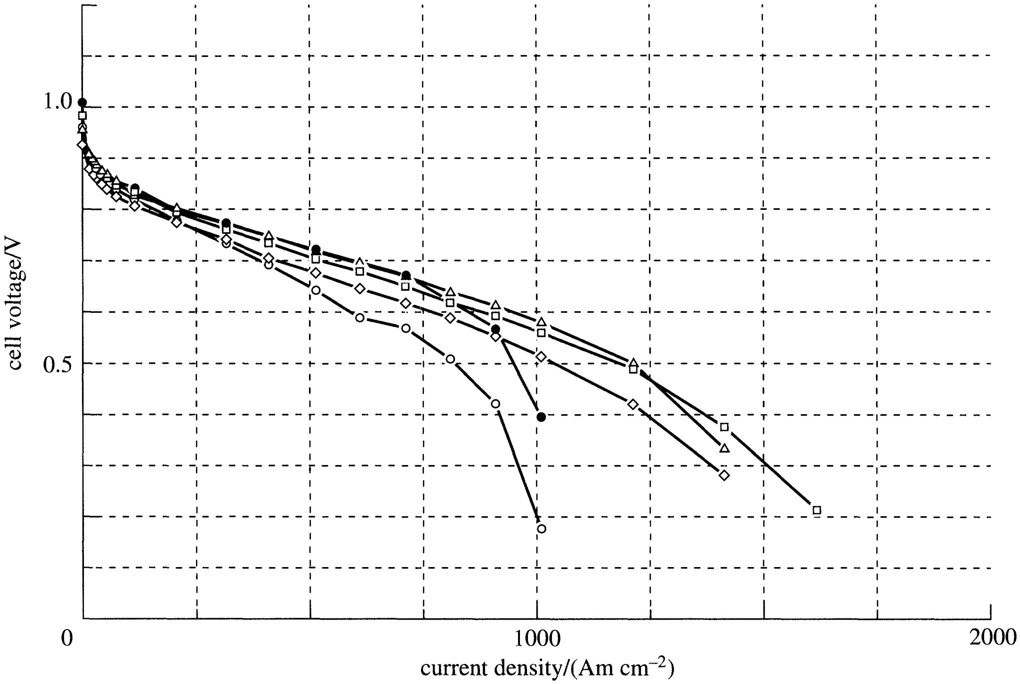

Figure 5. Single cell performance of Nafion ink cathodes, OE-Tech cathode 0.52 mg Pt cm^{-2}. ◇, Nafion ink cathode 0.11 mg Pt cm^{-2}; □, Nafion ink cathode 0.20 mg Pt cm^{-2}; △, Nafion ink cathode 0.33 mg Pt cm^{-2}; ●, Pt black cathode 4 mg Pt cm^{-2}.

immediately apparent from this diagram that more active cathode electrocatalysts would contribute to a significant improvement in cell performance.

Performance improvements of the carbon supported platinum cathode electrocatalyst, which is the preferred system for this cell, have been made by increasing platinum utilization and effective surface area, improving oxygen reduction kinetics by the development of promoters and improving the mass transport performance of the cathode.

(*a*) *Platinum utilization*

Until recently the platinum loadings of anode and cathode systems used in proton exchange membrane fuel cells have been substantially higher by a factor of ten than those which can be accepted for commercial applications.

Substantial progress has been made in the development of carbon supported platinum catalysts to replace the platinum black materials used in current stacks. A comparison of cathode systems and their respective platinum utilization and effective platinum surface areas is given in table 3.

Further, the performance of the low platinum loading ‘Nafion ink’ cathodes is compared with higher loading cathodes in figure 5.

(*b*) *Improved oxygen reduction kinetics*

Supported platinum metal alloy catalysts promoted with base metals have been developed and used as cathode electrocatalysts for phosphoric acid fuel cells. A similar approach to improving the activity of cathodes for proton exchange membrane cells has been undertaken. The specific activity of a range of platinum promoted

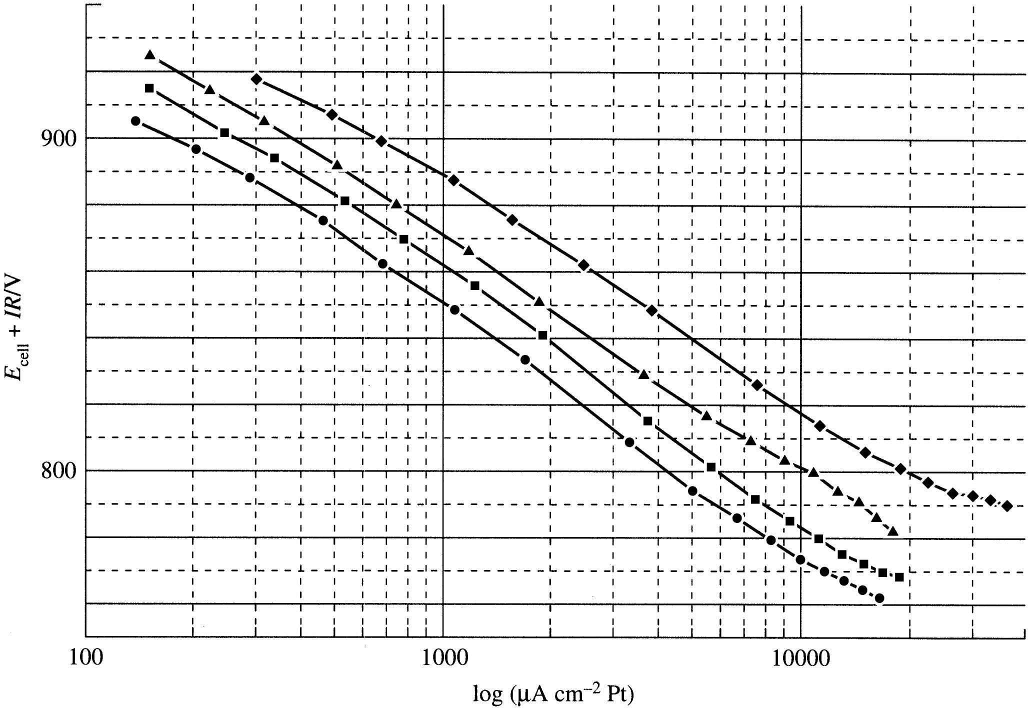

Figure 6. Tafel plots showing the perfomrances of Pt alloys versus pure Pt. ●, Pt; ■, Pt heat treated; ▲, Pt–Mn alloy; ◆, Pt–Ti alloy.

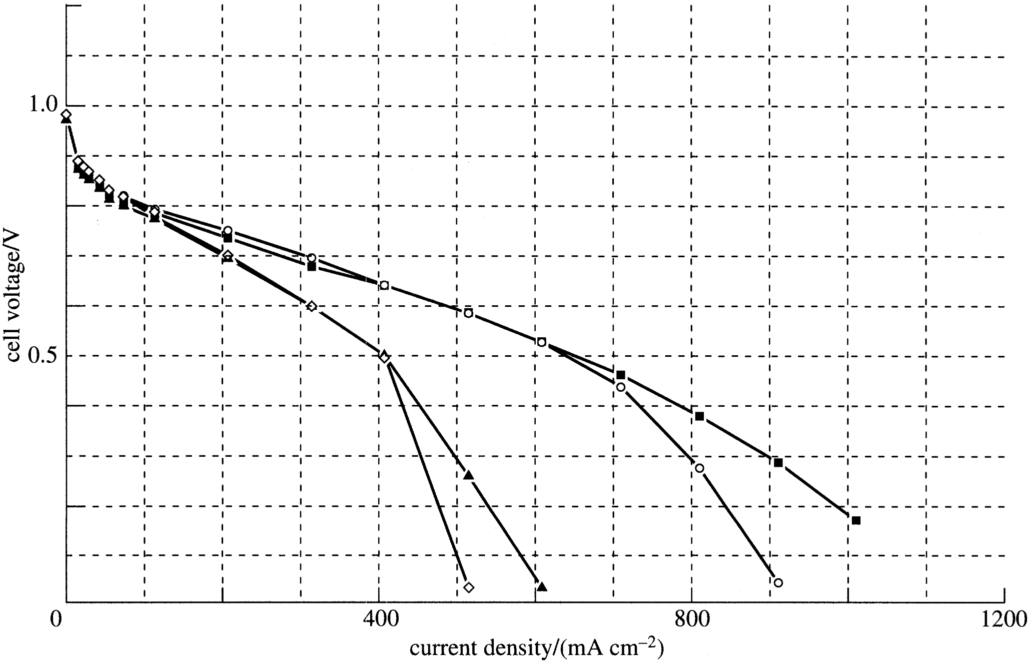

Figure 7. Effect of cathode backing structure on MEA performance. ■, bilayer cloth; ○, bilayer paper; ▲, single layer cloth; ◇, single layer paper.

catalysts is shown in figure 6. The catalysts contain 20 wt% Pt supported on Vulcan XC72R carbon in Nafion coated electrodes containing 0.5 mg Pt cm^{-2}. The single cell performance of the electrodes after correction for the resistance of the electrolyte and effective platinum surface area (EPSA) show that alloys do have an intrinsic benefit of at least 20 mV.

(c) *Mass transport in cathode structures*

Improvements in electrocatalyst performance are only reflected in single cell and stack performance if mass transport limitations are not the controlling factor. Traditionally electrocatalysts for proton exchange membrane fuel cells are supported on carbon cloth or paper to produce an electrode. The effect of the electrode support materials including the use of a separate uncatalysed carbon layer in a bilayer structure in figure 7.

5. Conclusions

Electrocatalysts play a key role in determining the overall performance of fuel cell systems. While much progress has been made in improving activity and durability, notably with respect to precious metal based systems as specifically described, there remains substantial scope for further improvements with particular emphasis on cathode systems.

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