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Direct Methanol Fuel Cells: History, Status and Perspectives

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1.1

Introduction

Significant efforts in recent decades have been focused on the direct electrochemical oxidation of alcohol and hydrocarbon fuels. Organic liquid fuels are characterized by high energy density, whereas the electromotive force associated with their electrochemical combustion to CO_2 is comparable to that of hydrogen combustion to water [1–3]. Among the liquid organic fuels, methanol has promising characteristics in terms of reactivity at low temperatures, storage and handling. Accordingly, a methanol-feed proton exchange membrane fuel cell (PEMFC) would help to alleviate some of the issues surrounding fuel storage and processing for fuel cells. Technological improvements in DMFCs are, thus, fuelled by their perspectives on applications in portable, transportation and stationary systems especially with regard to the remote and distributed generation of electrical energy [4, 5]. Methanol is cheap and can be distributed by using the present infrastructure for liquid fuels. It can be obtained from fossil fuels, such as natural gas or coal, as well as from sustainable sources through fermentation of agricultural products and from biomasses. Compared with ethanol, methanol has the significant advantage of high selectivity to CO_2 formation in the electrochemical oxidation process [1–3]. However, despite these practical system benefits, DMFCs are characterized by a significantly lower power density and lower efficiency than a PEMFC operating with hydrogen because of the slow oxidation kinetics of methanol and methanol crossover from the anode to the cathode [1–3].

This chapter deals with an analysis of the history, current status of technology, potential applications and techno-economic challenges of DMFCs. The basic aspects of DMFC operation are presented with particular regard to thermodynamics, performance, efficiency and energy density characteristics. The historical development of DMFC devices and components is analyzed with special regard to the study of catalysts and electrolytes. The section on fundamentals is focused on the electrocatalysis of the methanol oxidation reaction (MOR) and oxygen electroreduction. The

current knowledge in the basic research areas is presented and particular emphasis is given to required breakthroughs. The technology section deals with the fabrication methodologies for the manufacturing of membrane electrode assemblies membrane electrode assembly (MEA), stack hardware and system design. Recent efforts in developing DMFC stack for both portable and electro-traction applications are reported.

1.2

Concept of Direct Methanol Fuel Cells

1.2.1

Principles of Operation

1.2.1.1 DMFC Components

The core of the present DMFCs is a polymer electrolyte ion exchange membrane. The electrodes (anode and cathode) are in intimate contact with the membrane faces (Figure 1.1). The electrodes usually consist of three layers: catalytic layer, diffusion layer and backing layer. The catalytic layer is composed of a mixture of catalyst and ionomer and it is characterized by a mixed electronic-ionic conductivity. The catalysts are often based on carbon supported or unsupported PtRu and Pt materials at the anode and cathode, respectively. The membrane as well as the ionomer consist, in most cases, of a perfluorosulfonic acid polymer. The diffusion layer is usually a mixture of carbon and polytetrafluoroethylene (Teflon®) with hydrophobic properties necessary to transport oxygen molecules to the catalytic sites at the cathode or to favor the escape of CO₂ from the anode. The overall thickness of a 'membrane and electrode assembly' (MEA) is generally smaller than one millimeter. Several cells are

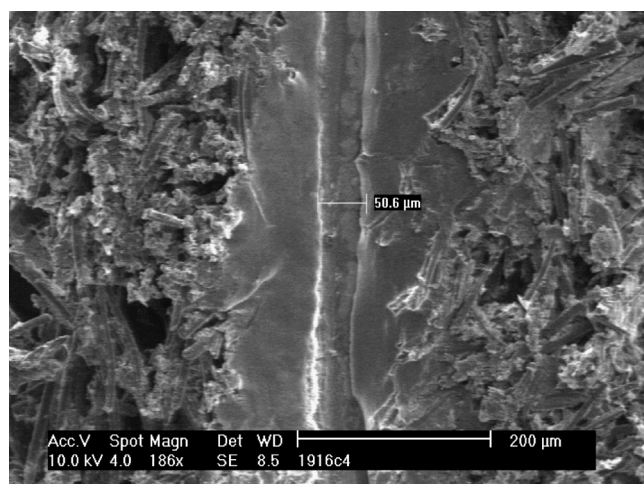


Figure 1.1 SEM micrograph of a DMFC membrane and electrode assembly equipped with Nafion 112 membrane.

usually connected in series to form a fuel cell stack that is integrated in a system which contains the auxiliaries, allowing stack operation and delivery of the electrical power to the external load.

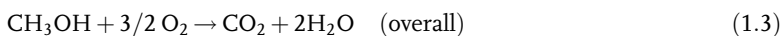
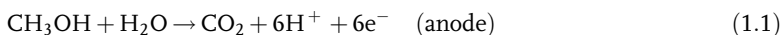
1.2.1.2 DMFC Operation Mode

In the literature, a distinction is usually made between 'active' and 'passive' operation mode [5]. In the active mode, the auxiliaries such as pumps, blowers, sensors, and so on are used to supply reactants and to control the stack operation in order to optimize working conditions. This allows the achievement of the most appropriate electrical characteristics. In the passive mode, there are no energy consuming auxiliaries (excluding step-up DC/DC converters) and the reactants reach the catalytic sites by natural convection, the effect of the capillary forces or due to the concentration/partial pressure gradient. The system is simpler than in the active mode; no significant amount of power from the stack is dissipated on auxiliaries, but, the operating conditions may not be optimal to achieve the best efficiency and performance.

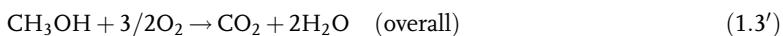
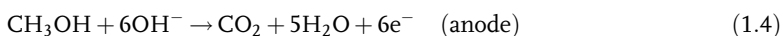
1.2.1.3 Fuel Cell Process

Protonic electrolyte based DMFCs are directly fed with a methanol/water mixture at the anode. Methanol is directly oxidized to carbon dioxide although the possible formation of compounds such as formaldehyde, formic acid or other organic molecules is not excluded. The formation of such organic molecules decreases the fuel use.

A scheme of the overall reaction process occurring in a DMFC equipped with a proton conducting electrolyte is outlined below:



In the presence of an alkaline electrolyte, this process can be written as follows:



The thermodynamic efficiency of the process is given by the ratio between the Gibbs free energy, that is, the maximum value of electrical work (ΔG°) that can be obtained, and the total available energy for the process, that is, the enthalpy (ΔH°). Under standard conditions:

$$\eta_{\text{rev}} = \Delta G^\circ / \Delta H^\circ; \text{ reversible energy efficiency} \quad (1.6)$$

with

$$\Delta G^\circ = \Delta H^\circ - (T \times \Delta S^\circ); \quad (1.7)$$

and

$$\Delta G^\circ = -nF \times \Delta E_{\text{rev}} \quad (1.8)$$

ΔE_{rev} is the electromotive force. At 25 °C, 1 atm and with pure oxygen feed, the reversible potential for methanol oxidation is 1.18 V [3]. It does not vary significantly in the operating range 20–130 °C and 1–3 bar abs. pressure.

1.2.2

Performance, Efficiency and Energy Density

1.2.2.1 Polarization Curves and Performance

Usually, the open circuit voltage of a polymer electrolyte DMFC is significantly lower than the thermodynamic or reversible potential for the overall process. This is mainly due to methanol crossover that causes a mixed potential at the cathode and to the irreversible adsorption of intermediate species at electrode potentials close to the reversible potential [6–19]. The coverage of methanolic species is large at high cell potentials, that is, at low anode potentials. This determines a strong anode activation control that reflects on the overall polarization curve (Figure 1.2). In Figure 1.2, the terminal voltage of the cell is deconvoluted into the anode and cathode polarizations:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}. \quad (1.9)$$

Anode, cathode and cell potentials can be measured simultaneously by a dynamic hydrogen electrode (DHE). Alternatively, the anode polarization can be measured in the driven mode and the cathode curve is calculated from Equation 1.9. In the driven mode, hydrogen is fed to the cathode that acts as both counter and reference

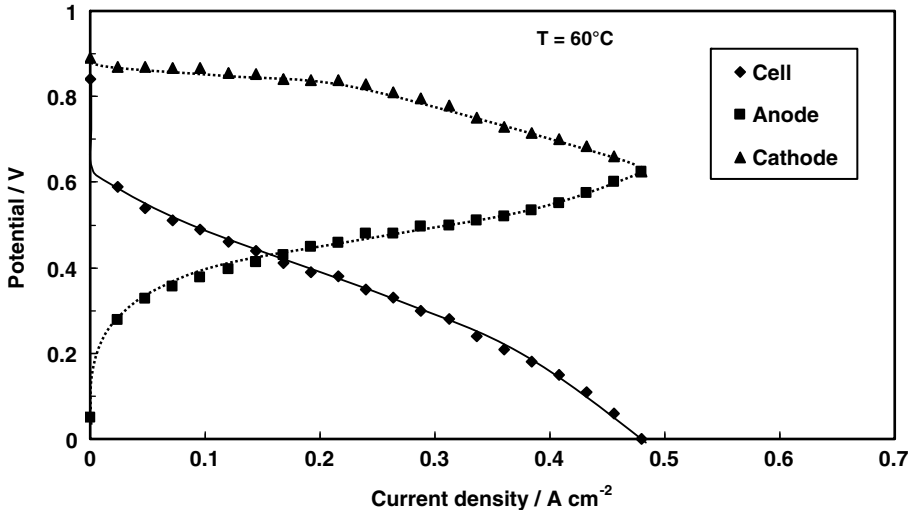


Figure 1.2 Single cell and *in situ* half-cell electrode polarizations for a DMFC operating at 60 °C, ambient pressure, with 1 M methanol at the anode and air feed at the cathode.

electrode. This is also the usual mode to carry out *in situ* cyclic voltammetry experiments for the anode.

Besides the strong activation control at the anode, the effect of the mixed potential on the cathode polarization curve is clearly observed in Figure 1.2. The onset potential for oxygen reduction in the presence of methanol crossover is below 0.9 V versus the reversible hydrogen electrode (RHE). This is much lower than the reversible potential for oxygen reduction in the absence of methanol, which is, 1.23 V vs. RHE. The methanol adsorption on the cathode mainly influences the region of activation control for oxygen reduction. In fact, at high cathode potentials, oxygen reduction is slow and oxidation of methanol permeated through the membrane is enhanced by the elevated potential. The two opposite reactions compete with each other and no spontaneous current is registered above 0.9 V (Figure 1.2).

At high currents (Figure 1.2), both anodic and cathodic polarization curves show the onset of mass transport constraints due to the removal of CO₂ from the anode and the effect of flooding at the cathode. In the protonic electrolyte methanol fuel cell, the flooding of the cathode is not only due to the water formed by the electrochemical process; it occurs, especially, as a consequence of the fact that a water/methanol mixture permeates the hydrophilic membrane.

The polarization curves of a DMFC device can be registered at different temperatures in order to study in detail the activation behavior (Figure 1.3), which clearly shows the presence of a strong effect of the temperature on the activation process. Temperature, pressure and methanol concentration are the most important variables determining performance and efficiency. Performance is often reported in terms of maximum power density under defined operating conditions.

1.2.2.2 Fuel Utilization

In a polarization diagram, beside the terminal voltage and the power density, it is also useful to report variations of the ohmic resistance and the crossover current (equivalent current density) as functions of the electrical current density. Usually, internal resistance does not vary significantly in the current density range of a DMFC whereas the equivalent current density is quite important for the methanol fuel cell because it determines the fuel use and influences the overall performance. It represents the current corresponding to the methanol permeation rate. A direct comparison with the effective (measured) electrical current permits evaluation of the fuel lost due to the crossover (Figure 1.4). The crossover or permeation rate of methanol can be determined *in situ* by the so-called CO₂ sensor method. Alternatively, chromatographic analyses can be used. In the presence of a Pt based catalyst, almost all the methanol that is permeated to the cathode is oxidized to CO₂ at high electrochemical potentials. From the CO₂ flow rate, the MOR and Faraday law, the equivalent current density is calculated according to the following equation:

$$I_{\text{cross over}} = \text{mol}_{\text{MeOH cross-over}} \cdot 6 \cdot F \quad (1.10)$$

Where $\text{mol}_{\text{MeOH crossover}}$ is the rate of methanol permeation to the cathode per unit of time and geometric electrode area ($\text{moles min}^{-1} \text{cm}^{-2}$).

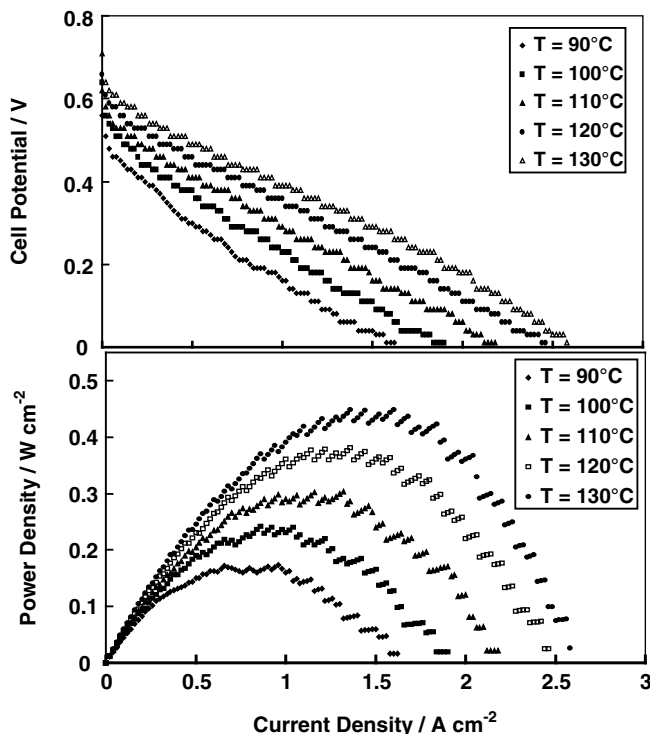


Figure 1.3 Galvanostatic polarization data for the DMFC equipped with CNR-ITAE Pt-Ru (anode) and 90% Pt/C (cathode) catalysts; 2 M CH_3OH , oxygen feed, interdigitated flow field [75].

The CO_2 -sensor based crossover measurement is instantaneous and it is carried out simultaneously with the polarization experiment. It takes into proper account the effect of the electro-osmotic drag. However, possible CO_2 permeation from the anode compartment through the membrane may cause some interference at high electrical current densities in the presence of thin membranes. Alternatively, the permeation can be measured in a separate experiment. An inert gas is fed to the cathode compartment and the electrode is polarized anodically while the methanol electrode is polarized cathodically. The measured anodic current is related to the methanol permeation rate through the membrane. This procedure discards two relevant phenomena that usually occur during practical fuel cell operation: electro-osmotic drag and methanol concentration gradient at the anode-electrolyte interface. Such effects are not reproduced in the driven mode. By using the CO_2 sensor method, it is observed that the equivalent current density usually decreases as a function of the electrical current density due to the methanol consumption at the anode/electrolyte interface, which reduces the methanol concentration gradient between the anode and the cathode (Figure 1.4).

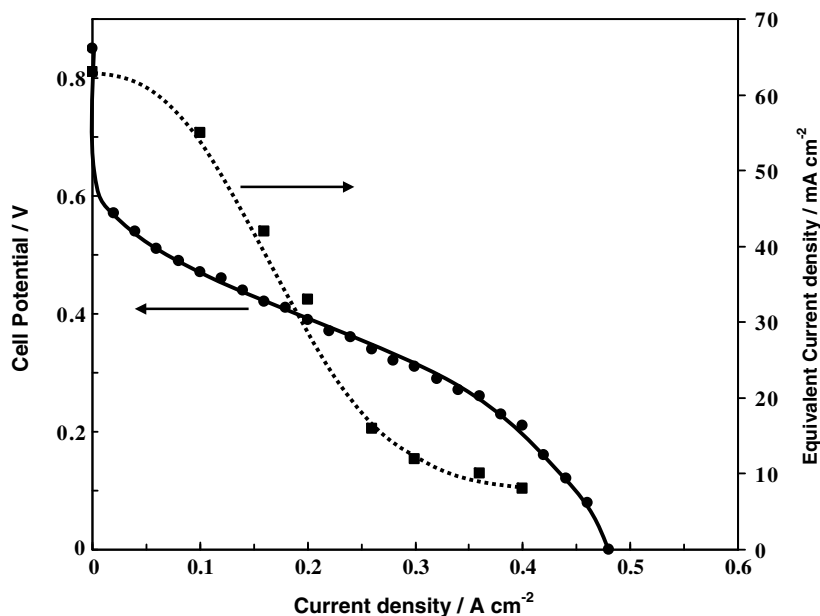


Figure 1.4 Cell potential and equivalent current density (due to methanol crossover) as a function of electrical current density for a DMFC operating at 60 °C.

1.2.2.3 Cathode Operating Conditions

Air is usually fed at stoichiometry of 2 in the active mode. If the system operates at ambient pressure, the power consumption by the blower, in the case of a large air flow, is not as significant as in the case of a compressor (pressurized DMFC). An increase of air flow produces better performance and it is not unusual to see DMFC experiments reported with an air flow corresponding to a stoichiometry of 5 or even higher.

A similar effect is produced by the cathode pressure. The negative effects of methanol poisoning at the cathode can be counteracted by an increase of oxygen partial pressure. The Temkin adsorption isotherm is often used to model the adsorption of oxygen at the cathode in PEMFCs [20]. Accordingly, an increase of oxygen partial pressure significantly influences the coverage of adsorbed oxygen species. This process is in competition with the adsorption of methanol permeated through the membrane, on the cathode surface. It appears that the increase of air stoichiometry especially favors the physical removal from the cathode of the liquid mixture of water/methanol that permeates through the membrane or is formed by the reaction (water) avoiding the electrode flooding. The flooding of the cathode is more significant in a protonic electrolyte DMFC than in a PEMFC due to the supply of plenty of liquid water together with methanol to the anode that permeates to the cathode through the hydrophilic membrane. This effect is less dramatic in a vapor-fed DMFC.

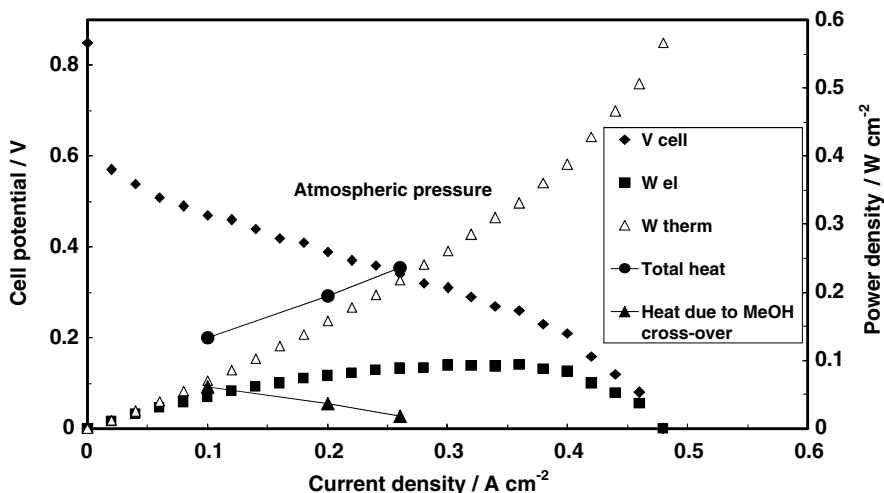


Figure 1.5 Electrical and thermal characteristics of a DMFC operating at 60 °C under atmospheric pressure.

1.2.2.4 Heat Production

For several applications, it is quite important to know how much heat is released during fuel cell operation. Thus, another useful polarization diagram to qualify the behavior of the fuel cell should include the heat released in the process deconvoluted into the heat produced by both the electrochemical process and that produced by the chemical reaction associated with methanol crossover (Figure 1.5). We are not aware of the use of such a plot in the literature. We have reported in Figure 1.5 the results of the heat release calculation that we carried out in the framework of European Community project called Morepower, which dealt with the development of a DMFC system for portable applications [21]. For sake of simplicity, the calculation reported here concerns single cell behavior.

The heat produced per unit of time by the electrochemical process only is derived from the reaction enthalpy and the methanol consumption rate from the following formula:

$$Q = \text{mol}_{\text{MeOH}}(\Delta H_r - nF\Delta E_{\text{cell}}); \quad (1.11)$$

mol_{MeOH} are the number of moles of methanol which are consumed per unit of time. This term is calculated from the electrical current density and the Faraday law; ΔE_{cell} is the cell voltage at the operating current density.

The redox process occurring at the cathode, associated with the methanol crossover, can be assumed as a chemical oxidation to CO_2 by the effect of the oxygen molecules, mediated by the Pt catalyst, since there is no electrical work produced:

$$Q = \text{mol}_{\text{MeOH}}\Delta H_r; \quad (1.12)$$

In Figure 1.5 the effect of heat release due to the electrochemical process is compared with that related to methanol crossover for a device operating at 60 °C with 1 M methanol and air feed at the cathode. The crossover decreases significantly as a

function of electrical current density; accordingly, the amount of heat released diminishes. The heat due to the crossover is comparable to the heat due to the electrochemical process at 0.1 A cm^{-2} whereas the effect of crossover is much less significant above 250 mA cm^{-2} . The chemical energy that is dissipated as heat represents a net loss of efficiency. The heat released increases exponentially as a function of current and it reaches a maximum at the short circuit.

1.2.2.5 Cell Efficiency

At a defined current density, the voltage efficiency is thus defined as the ratio between the terminal cell voltage and the reversible potential for the process at the same temperature and pressure.

$$\eta_v = \Delta V / \Delta E_{\text{rev}} \quad (1.13)$$

As a consequence of crossover, the current delivered by the DMFC device is smaller than that calculated on the basis of overall methanol consumption. The ratio between the measured electrical current (I) and that calculated from the Faraday law on the basis of the total methanol consumption (I_{total}) is defined as fuel efficiency:

$$\eta_f = I / I_{\text{total}} \quad (1.14)$$

A determination of the fuel efficiency based only on the methanol crossover may represent a source of error if there are other side effects such as a loss of methanol by evaporation. For a passive DMFC, the overall efficiency can thus be expressed as:

$$\eta = \eta_{\text{rev}} \times \eta_v \times \eta_f \quad (1.15)$$

In the active mode, the amount of energy consumed by the auxiliaries (pumps, blowers etc.) as compared with that delivered by the stack must be taken into consideration when the system efficiency is calculated.

1.2.2.6 Energy Density

Besides the performance and efficiency of the DMFC device, the energy density of the fuel plays a significant role in several practical applications, including transportation and portable power sources. It is also a relevant factor for stationary generation since it determines which infrastructure is appropriate for fuel distribution [22].

The energy density of a fuel is defined with respect to the weight (kWh/kg) or volume (kWh/l) as

$$W_e = (-\Delta G / 3600 M) \text{ or } W_s = (-\Delta G \rho / 3600 M); \quad (1.16)$$

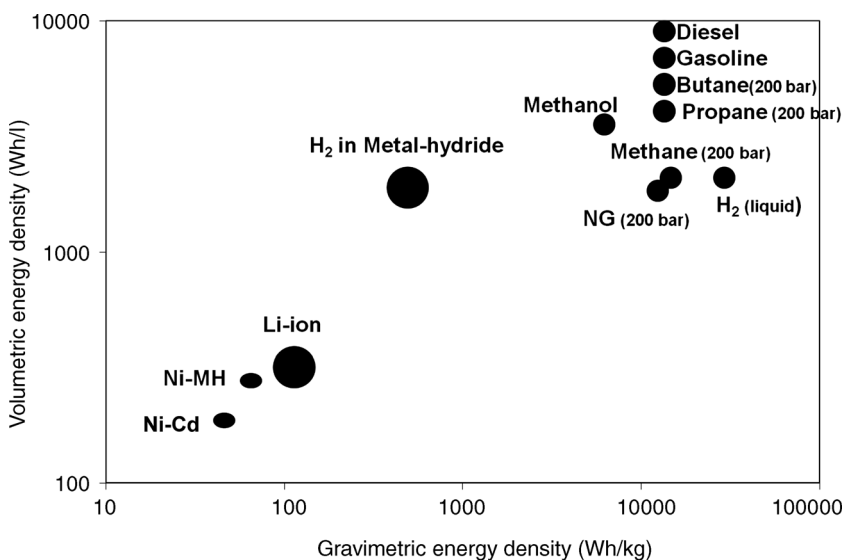
where M is the molecular weight (g/moles) and ρ the density (g/l).

Table 1.1 summarizes the energy density for various fuels. The gravimetric energy density of pure methanol is about one order of magnitude larger than that of H_2 stored in a pressurized tank (e.g., at 200 bar) and in a metal hydride system (4–5%). Similar considerations can be made with regard to the volume. The energy density of pure methanol is also much higher than Li-Ion batteries but lower than conventional liquid fuels used in transportation, such as gasoline and diesel (Figure 1.6).

To use all the potential energy density associated with methanol combustion, a tank with pure methanol should be used. When considering the range, that is, the driving

Table 1.1 Volumetric and gravimetric energy density for various fuels of technical interest for low temperature fuel cells.

Fuels	Volumetric Energy density (kWh l^{-1})	Gravimetric Energy density (kWh kg^{-1})
Diluted Hydrogen (1.5%)	—	0.49
Hydrogen	0.18 (@ 1000 psi, 25 °C)	—
Methanol	4.82 (100 wt.%)	6.1
Ethanol	6.28 (100 wt.%)	8
Formic acid	1.75 (88 wt.%)	—
Dimethyl ether (DME)	5.61 (in liquid of 100 wt.%)	8.4
Ethylene glycol	5.87 (100 wt.%)	5.3

**Figure 1.6** Gravimetric and volumetric energy density of various fuels/devices.

distance, of a fuel cell car compared with an internal combustion engine or the operating time of a methanol portable power source compared with a Li-battery, besides the energy density, the overall efficiency of the process should also be considered.

1.3

Historical Aspects of Direct Methanol Fuel Cell Development and State-of-the-Art

1.3.1

Historical Development of Methanol Oxidation Catalysts

The methanol electro-oxidation process was explored for the first time by E. Muller in 1922 [23]. However, the concept of methanol fuel cells started to be investigated in the

early 1950s by Kordesch and Marko [24] as well as by Pavela [25]. Accordingly, much research on the anode and cathode electrocatalysts for such an application was initiated at the same time [1, 26]. Alkaline electrolytes were initially used for methanol fuel cells; the search for the active anode and cathode catalysts mainly regarded nickel or platinum for the MOR and silver for the oxygen reduction process [25, 26]. Parallel investigations of the MOR were conducted in acidic electrolytes such as sulfuric acid in the same period [3, 23]. It was observed that the kinetics of methanol electro-oxidation was slower in an acidic environment compared with the alkaline electrolyte. However, better perspectives were envisaged for the acid electrolyte based DMFCs. The main issue of a liquid alkaline electrolyte, such as KOH, was its chemical interaction with the reaction product of methanol oxidation, that is, carbon dioxide, to give rise to the formation of carbonate.

Among the pioneering studies carried out on catalysts for methanol oxidation in acidic media, the work of Cathro [27] that investigated the Pt-Sn system and that of Jansen and Molhuysen [28] represented the first attempts to make a screening of bimetallic catalysts using a systematic approach. Pt-Sn and Pt-Ru were isolated as the most promising anode formulations [28]. In effect, PtSn was initially a better catalytic system than PtRu [28]; this was essentially due to the use of the ad-atoms approach for both the formulations. Successive studies by Watanabe and Motoo [29] in the 1960s showed the large potentialities of the Pt-Ru system especially when Pt and Ru were combined in a solid solution (face centered cubic (fcc) alloy).

Research on DMFCs initially addressed the search of active anode formulations; half-cell studies proved that the methanol oxidation process was slower than the oxygen reduction; thus, the anode reaction attracted more interest as the rate determining step (r.d.s.) of the overall DMFC process [1, 2]. The first decades of activity on anode catalysts mainly addressed the investigation of the mechanism and the search for new or improved catalyst formulations. One of the first attempts to rationalize the methanol oxidation process was by Bagotzky and Vassiliev [30]. Their work was essentially carried out on pure platinum; they proposed some relevant kinetic equations for the methanol electro-oxidation rate as a function of the coverage of methanolic residues and oxygen species adsorbed on the electrodes. These studies served as a basis for the successive formulation of the bifunctional theory [29] for bimetallic catalysts. Also worth mentioning is the work of Shibata and Motoo on the effect of ad-atoms [31] that individuated the influence of steric effects. Of relevant interest also were the successive attempts of McNicol [32], Parsons and Vander-Noot [33] and Aramata [34] to further rationalize the mechanism of methanol oxidation by electrochemical studies. However, an in-depth analysis of the methanol oxidation process, initially at smooth electrode surfaces, was made possible by the use of spectro-electrochemical methods. This work was carried out by several groups including those of Lamy [35], Bockris [36] and Christensen [37]. These studies essentially investigated adsorbed methanolic residues by infrared spectroscopy whereas, for the adsorbed oxygen species, ellipsometry gave appropriate results [38]. Further knowledge of the methanol oxidation process was provided by the use of *in situ* mass spectrometry. This method allowed detection of the anode potentials at which CO₂ was formed. In the late 1980s and beginning of the 1990s, a relevant

amount of work addressed the amelioration of catalyst formulations and investigated further the structural, surface and electronic properties of the most promising formulations, essentially Pt-Ru. The work carried out by Goodenough, Hamnett and Shukla in the 1980s and 1990s [39, 40] was of relevant interest in this regard. They focused their attention not only on the catalyst but also on the electrode structure (including diffusion and backing layers). Mc Breen and Mukerjee [41], Ross *et al.* [42] used advanced physico-chemical tools such as extended X-ray absorption fine structure (EXAFS), Low-energy ion scattering spectroscopy, Auger and X-ray photoelectron spectroscopy (XPS) to characterize model and practical anode and cathode catalysts.

The 1990s opened a new era for the DMFCs; the investigation of catalysts formulations in polymer electrolyte single cells progressively replaced the half-cell studies in liquid electrolytes. The number of anodic formulations investigated reduced consistently. More attention addressed the behavior of the catalyst inserted in a practical MEA in a single cell. It was observed that operation at high anode potentials often caused Ru dissolution and migration through the membrane to the cathode [43]. The extensive use of combinatorial catalyst discovery studies in the 1990s suggested that multifunctional catalysts could be of significant importance [44].

It had been established in the 1970s and 1980s that the activity of a methanol oxidation catalyst depends on several factors, including catalyst formulation, support, electrode structure and operating conditions. Most of the work was concentrated on examining the effect of changing the catalyst formulation as a means of enhancing catalytic activity; alloys of various compositions were used as electrode materials although most of these alloys were based on Pt. It was evident that the reaction rate was improved by electrocatalysts adsorbing water and/or oxygen species at potentials similar to the reversible potential of the CH_3OH oxidation reaction and/or able to minimize poisoning by the methanolic residue [45, 46].

It was recognized that the presence of an alloying metal or ad-atom either: (i) modified the electronic nature of the surface; (ii) modified the physical structure; (iii) blocked the poison formation reactions; (iv) adsorbed oxygen/hydroxyl species which take part in the main oxidation reaction.

The following analysis tries to bring to a 'rationale' the main features of different bimetallic Pt-based electrocatalysts, including ad-atoms [46] (Figures 1.7–1.9). The following aspects are considered: (a) the influence of the interaction energies of CO on transition metals; (b) the influence of electronegativity; (c) possible steric and electronic effects, reflected by the influence of atomic radius and ionic potential values. As for the involvement of different poisons in the oxidation mechanism, spectroelectrochemical methods in the 1980s established that the two most probable adsorbed species were $-\text{CHO}$ and CO with evidence to support both possibilities [33]. On the whole, the evidence for CO as the poisoning species appeared to be, however, more conclusive, coming from various '*in situ*' spectroscopic techniques. Accordingly, both linear and bridge-bonded CO species have been detected on the electrode surface. Furthermore, the potentials where the poison was oxidized also corresponded very closely to those where adsorbed species from pure CO were oxidized in separate experiments [33]. A plot of several electro-catalytic activity results [28, 46–48] as a function of the adsorption heat of CO on transition metals taken from

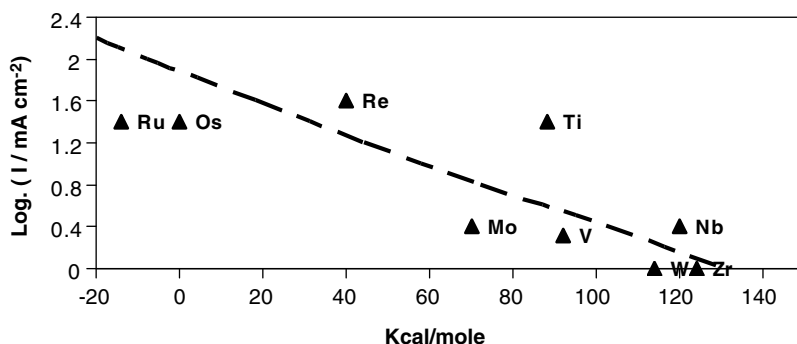


Figure 1.7 Methanol electrocatalytic activity vs. calculated interaction energy of CO adsorption on various Pt alloyed transition metals.

Miyazaki [49] is reported in Figure 1.7. It appears that higher electro-oxidation activity is found in metals having low interaction energies with the CO molecule. The experiments of Shibata *et al.* [31] on the enhancement of CO oxidation on Pt by the electronegativity of ad-atoms showed that a strong interaction between the ad-atom site and either the hydrated hydrogen ion or the adsorbed CO molecule was required to obtain high enhancement effects. Yet, such evidence was not observed for the CH_3OH oxidation reaction (Figure 1.8); in our opinion, this can be explained by the detrimental effects of non-transition elements upon the methanol dehydrogenation which, as is well known, constitutes the first step in the overall electro-oxidation reaction [2, 50]. Accordingly, the positive influence of the more electronegative elements still holds for transition metals which are known to favor CH_3OH dehydrogenation. According to the ad-atoms theory, two distinct effects were identified from a catalytic view-point in enhancing the electro-oxidation of organic molecules; the first was related to the modification of the electronic environment of the adsorption site, the other was linked to the steric factor which also influenced both the extent and the strength of the adsorption process. As for the latter, a correlation

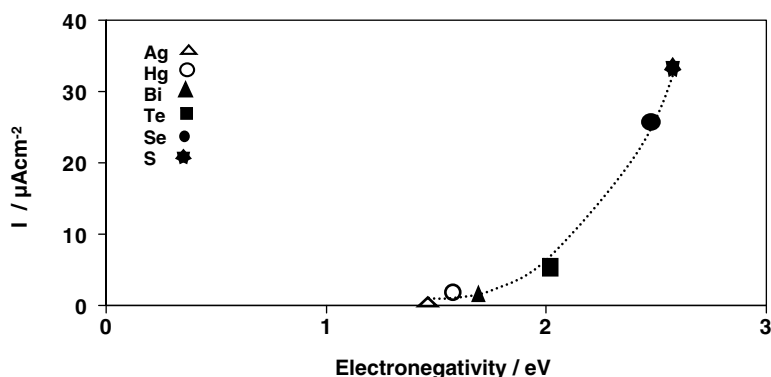


Figure 1.8 Methanol electro-oxidation activity vs. electronegativity of the ad-atoms used for Pt modification.

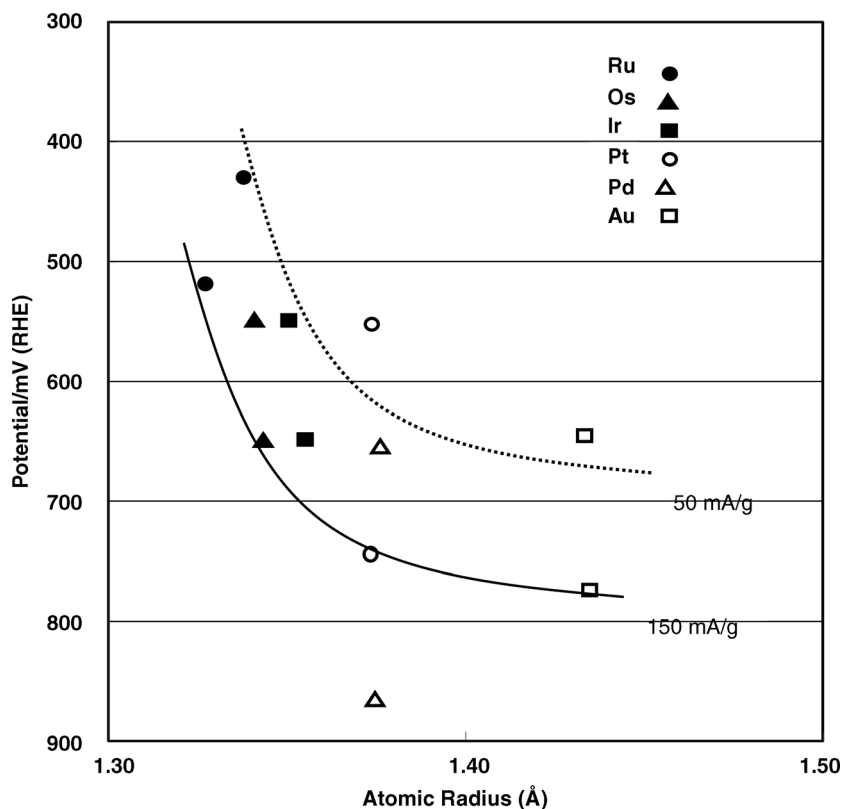


Figure 1.9 Methanol electro-oxidation activity vs. atomic radius of various metals used to form Pt-alloys.

between the overpotential at which a sustained current is obtained for CH_3OH electro-oxidation and the atomic radius of the alloyed metal with Pt was envisaged (Figure 1.9). The combination of labile adsorption intermediates with a large metal area for use was recognized to be favored by the small dimensions of the alloyed element. Regarding the influence of ad-atoms on the modification of the electronic environment of Pt, the literature predicted that the positive catalytic effects of Pt-Ru and Pt-Sn formulations were due to the adsorption, by these elements, of active oxygen on the catalyst surface at low potentials. These species were identified in the late 1980s as adsorbed OH species by using spectro-electrochemical methods.

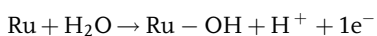
1.3.2

Status of Knowledge of Methanol Oxidation Process and State-of-the-Art Anode Catalysts

1.3.2.1 Oxidation Mechanism

The detailed mechanism of methanol oxidation has been elucidated in the last three to four decades by using a variety of experimental procedures [1, 2, 8, 33, 51–63]. This

mechanism is discussed in detail in several reviews [1, 2]. Studies found that the electrochemical oxidation of methanol on Pt involves several intermediate steps: dehydrogenation, CO-like species chemisorption, OH (or H₂O) species adsorption, chemical interaction between adsorbed CO and OH compounds, and CO₂ evolution [2]. One of these steps is the rate determining step (r.d.s.) depending on the operation temperature and particular catalyst surface (crystallographic orientation, presence of defects, etc.) [37, 64–66]. The state-of-the-art electrocatalysts for the electro-oxidation of methanol in fuel cells are generally based on Pt alloys supported on carbon black [51, 52, 67] or high surface area unsupported catalysts [68]. The electrocatalytic activity of Pt is known to be promoted by the presence of a second metal, such as Ru or Sn, acting either as an ad-atom or a bimetal [2]. According to the bifunctional theory, water discharging occurs on Ru sites with formation of Ru–OH groups on the catalyst surface [38]:



The final step is the reaction of Ru–OH groups with neighboring methanolic residues adsorbed on Pt to produce carbon dioxide [2]:



1.3.2.2 Pt-Ru Catalysts

The Pt-Ru binary alloy electrocatalyst appears as the most promising formulation. Pt sites in Pt-Ru alloys are especially involved in both the methanol dehydrogenation step and strong chemisorption of methanol residues. Although, the subject still remains controversial [29, 54, 55, 63, 69], an optimal Ru content of 50 at.% in carbon supported Pt-Ru catalysts for the MOR at high temperatures (90–130 °C) was found [70]. The optimum Ru surface composition is referable to the relevant synergism accomplished by a Pt-Ru surface with 50% atomic Ru in maximizing the product of θ_{OH} (OH coverage) and k (intrinsic rate constant), assuming the surface reaction between CO_{ads} and OH_{ads} as r.d.s. At low temperatures, adsorption of methanol on Pt requiring an ensemble of three neighboring atoms appears as the r.d.s. Gasteiger *et al.* [69] have observed that methanol oxidation occurs more readily at room temperature on pure Pt-Ru alloys having low Ru content ($\approx 10\%$) whereas at intermediate temperatures (60 °C) the reaction is faster on alloys with increased Ru content ($\approx 33\%$). At both intermediate and high temperatures, the removal of strongly adsorbed carbon monoxide by OH species is usually considered the r.d.s.

The synergistic promotion exerted by Pt-Ru alloys is supported by X-ray absorption analysis [41]. Accordingly, an increase of Pt d-band vacancies is produced by alloying with Ru; possibly, this modifies the adsorption energy of methanolic residues on Pt. Such evidence suggests that the reaction rate is not only dictated by the bifunctional mechanism but it is also influenced by electronic effects occurring on account of the interaction between Pt and Ru [41, 71].

The promoting effect of the RuO_x species for the MOR has been extensively investigated by several authors [72–74]; a very high performance was obtained in a DMFC with unsupported Pt-RuO_x anode electrocatalyst [9]. It was suggested that

facile oxygen transfer from Ru to Pt rich regions where adsorption of CO-like residues preferentially occurs could enhance the catalytic oxidation of methanol [74, 75].

The formation of oxidized species of Pt and Ru as well as the electronic properties of the active phase are also influenced by the metal-support interaction. Various catalysts characterized by different concentrations of metal phase on carbon have been investigated [76]. A comparison of the *in situ* stripping behavior of adsorbed methanolic residues for three Pt-Ru/C catalysts at various temperatures is shown in Figure 1.10 [76]. As the temperature increased above 90 °C, the stripping area of the

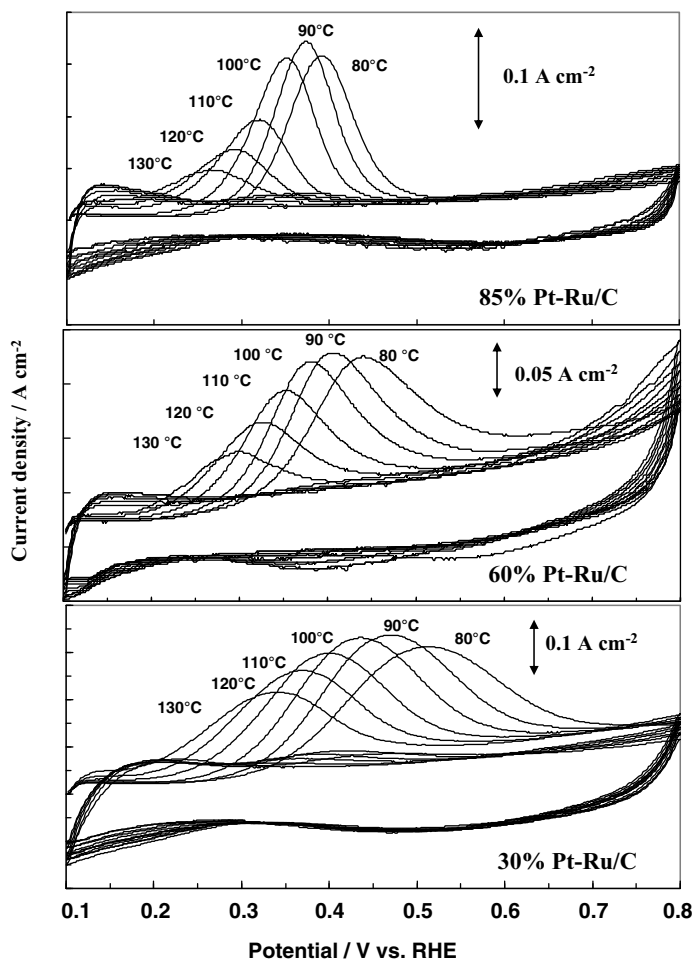


Figure 1.10 *In situ* stripping voltammetry of methanol residues at the various carbon-supported Pt-Ru catalyst/Nafion 117 membrane interfaces, at various temperatures under the DMFC configuration. Anode: 1 M methanol, 1 atm rel. adsorbed for 30 min; cathode: H₂ feed 1 atm rel. [76].

methanolic residues decreased progressively for all catalysts, whereas the peak shifted towards lower potentials on account of the decrease of the activation energy for CO removal. By comparing the behavior of the various catalysts, it was observed that the 30% Pt-Ru/C sample was characterized by the largest stripping area per unit of weight. Yet, the stripping peak potential at each temperature was shifted towards negative values for the 85% PtRu/C catalyst. XPS analysis of Pt 4f spectra (Figure 1.11)

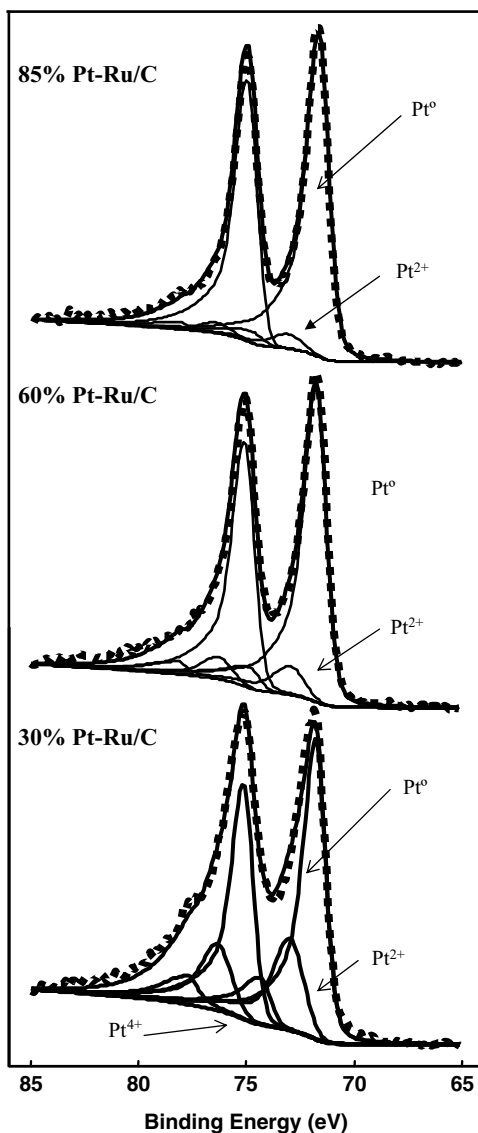


Figure 1.11 X-ray photoelectron spectra of Pt-Ru catalysts (Pt 4f doublet) [76].

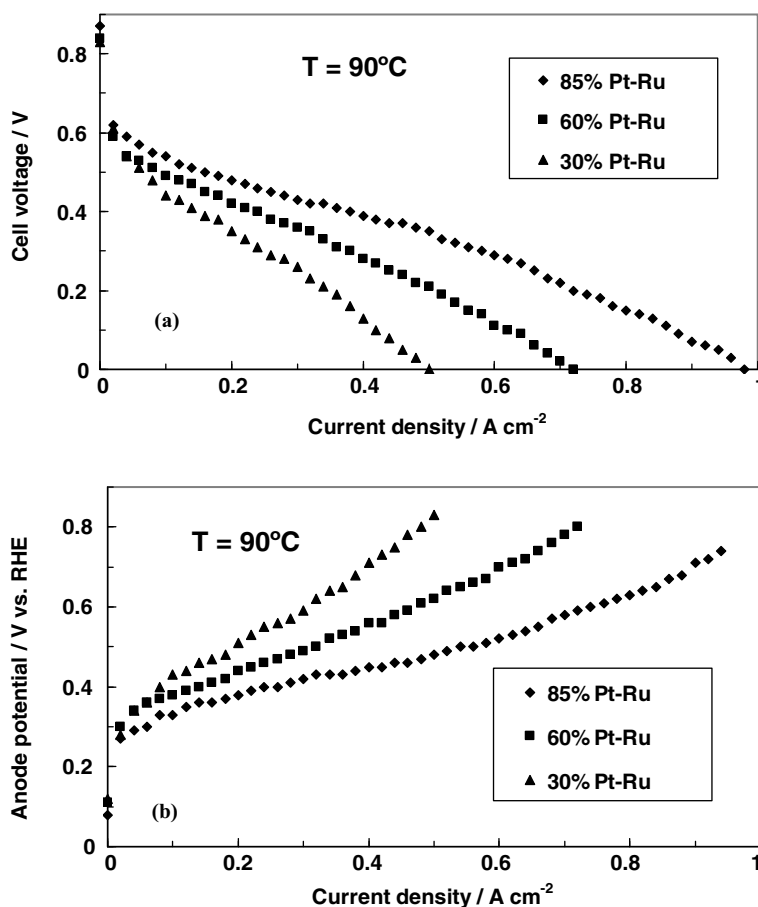


Figure 1.12 DMFC single cell (a) and anodic half-cell polarization behavior (b) at 90 °C for various Pt-Ru/C catalysts. Anode: 1 M methanol, 1 atm rel.; cathode: air feed 2.5 atm (a), H₂ feed 1 atm rel. (b) [76].

showed a shift to higher binding energies with a larger fraction of oxidized species for the catalysts with lower concentrations of metallic phase on carbon, that is, 30 and 60% Pt-Ru/C as an effect of metal support interaction. By comparing the behavior of the three different catalysts either in terms of single cell and half-cell polarization curves at 90 °C (Figure 1.12) [76], better performance was achieved for the catalyst showing both lower stripping peak potentials (as expected) but also lower coverage of methanolic residues. Thus, the higher intrinsic catalytic activity (lower activation barrier) appears to be more relevant than catalyst dispersion.

Significant interest has recently addressed the development of decorated catalysts [77, 78]. Pt-nanoparticles on the surface of a less expensive metal, which participates in the reaction, may represent a useful approach to reduce the incidence

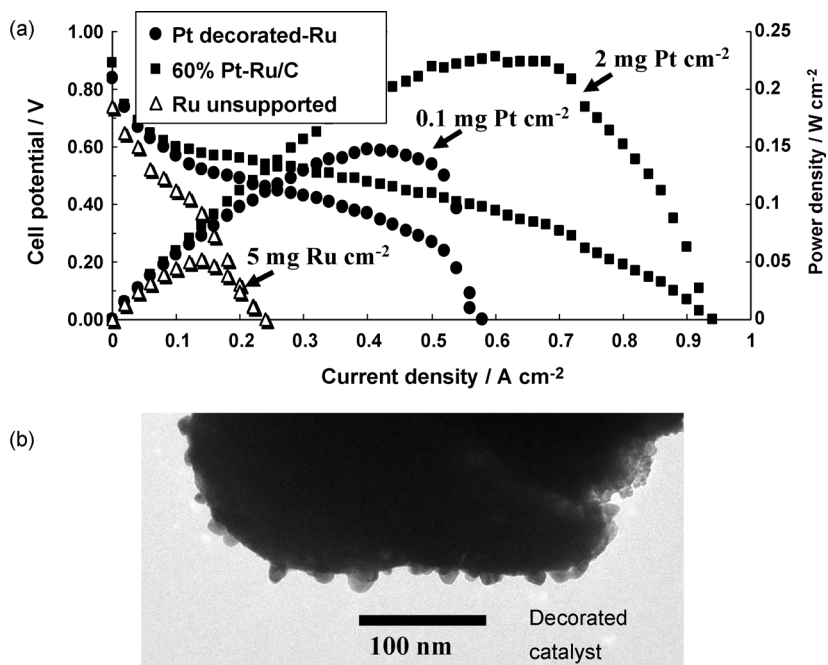


Figure 1.13 (a) DMFC single cell polarizations at 130 °C for commercial Pt-Ru/C, Pt-decorated and bare unsupported Ru catalysts. Anode: 1 M methanol, 2 atm rel.; cathode: air feed 2.5 atm., (b) transmission electron micrograph of Pt-decorated Ru catalyst [80].

of the catalyst cost in DMFC devices. Figure 1.13 shows a comparison of the DMFC polarization curves in the potential range of technical interest for the decorated (0.1 mg Pt cm⁻²), carbon supported Pt-Ru alloy (2 mg Pt cm⁻²) and bare unsupported Ru catalysts [79, 80]. The carbon supported Pt-Ru alloy based electrode shows lower potential losses in the activation controlled region than the decorated catalyst. However, the Pt loading in the decorated catalyst based anode is 20 times lower.

1.3.2.3 Alternative Anode Formulations

Only a few electrocatalyst formulations, alternative to Pt, have been proposed for methanol electro-oxidation in an acidic environment. These are mainly based on non-noble transition metal alloys like NiZr [81], transition metal oxides and tungsten-based compounds [82–84]. All these materials showed lower reaction rates than Pt-based electrocatalysts and, thus, such unsatisfactory preliminary results have not stimulated much work in these directions.

1.3.2.4 Practical Anode Catalysts

In the case of methanol electro-oxidation on carbon-supported Pt electrocatalysts, two different trends were observed. For what concerns anode catalyst morphology,

McNicol *et al.* [8] observed in their Pt electrocatalysts maximum activity at about $80 \text{ m}^2/\text{g}$ surface area. Another group has shown that the specific activity increases as a function of particle size [85]. Thus, a maximum in mass activity vs. particle size should be observed as in the case of oxygen reduction [86]. On the other hand, Watanabe *et al.* [87] found that the specific activity for methanol oxidation on a carbon supported Pt electrocatalyst does not change for a particle size above 2 nm (Pt fcc structure); thus, the mass activity increases as the dispersion of the metal phase is increased [87]. These latter findings have been in part confirmed for the Pt-Ru system for a particle size above 3 nm [88]. A poor catalytic performance was observed for catalysts with mean size of about 1–1.5 nm compared with the conventional catalysts; it was also observed that the structure is mainly amorphous in that range of particle size [89].

A high Pt wt.% on the carbon substrate will significantly decrease the anode thickness for the same Pt loading per geometric electrode area (e.g., 1 mg m^{-2}). Thus, it is possible to enhance mass transport through the electrode and, at the same time, reduce the ohmic drop. However, it has been found that an increase in Pt loading (above 40 wt.%) on the carbon support decreases the dispersion of the electrocatalyst, due to some particle agglomeration.

The synthesis of a highly dispersed electrocatalyst phase in conjunction with a high metal loading on carbon support is one of the goals of the recent activity in the field of DMFCs. The mostly used carbon blacks were: Acetylene Black (BET Area: $50 \text{ m}^2/\text{g}$), Vulcan XC-72 (BET Area: $250 \text{ m}^2/\text{g}$) and Ketjen Black (BET Area: $\sim 900 \text{ m}^2/\text{g}$) [40].

1.3.2.5 Anode Catalysts for Alkaline DMFC Systems

The methanol oxidation rate is accelerated at high pH values. Thus, from a kinetic viewpoint, it is advantageous to carry out methanol oxidation in alkaline electrolytes [90]. Furthermore, because the corrosion constraints are less significant in alkaline media, in principle, a wider number of catalyst formulations can be investigated for methanol oxidation than for proton conducting electrolytes. Despite these promising aspects, studies on the development of anode catalysts for alkaline DMFCs are less numerous than in acidic electrolytes. Due to the enhanced reaction rate at high pHs, alkaline DMFCs can employ non-precious transition metals, for example, Ni [90], which are characterized by low intrinsic activity. Although the reaction rates are usually faster for Pt-Ru than Ni, the increase of reaction kinetics due to the increased pH compensates, in part, for this gap in intrinsic activity [90]. The Ni-based catalysts can operate suitably in combination with a liquid electrolyte containing a concentrated base such as 5 M KOH or NaOH, characterized by a high pH. For practical purposes, anion exchange membranes have recently been preferred to the liquid electrolyte [91]. However, due to carbonation occurring during steady-state operation, the electrolyte in the anode compartment turns progressively into a carbonate/bicarbonate mixture with corresponding lower pH than the KOH solution. Furthermore, the conductivity decreases. Pt-electrocatalysts have mainly been considered for operation in conjunction with anion exchange membranes. These include the conventional Pt/C catalyst, platinized Ti electrodes [92] and Pt-Ru

alloys [90]. Platinized mesh anodes have shown higher catalytic activities than conventional Pt/C electrodes. Due to the open area of the mesh, the liquid can easily reach the interface reducing mass transport resistance [92]. The typical activation losses recorded for methanol oxidation at PtRu in acidic systems are less accentuated in alkaline media. The methanol oxidation rate at PtRu electrodes in a carbonate/bicarbonate mixture is about 8 and 2.5 times larger than in sulfuric acid, at 0.35 and 0.45 V RHE, respectively [90]. However, the reaction kinetics in the presence of a Nafion®-type ionomer are faster than in sulfuric acid due to the absence of sulfate anion adsorption on the catalyst surface.

1.3.3

Technological Advances in Electrolyte Development for DMFCs

The electrolytes that were first used in DMFC devices in the 1950s consisted of a concentrated alkaline solution for example, KOH which contained dissolved methanol [3, 25, 26, 93, 94]. Although some attempts were also carried out with anion exchange membranes onto which the electrodes were pressed [95], using an approach similar to the modern PEMFCs, the best results in terms of output power were achieved with 5 M KOH [94].

Alkaline instead of protonic electrolytes were initially selected because methanol oxidation in alkaline media is faster than in the presence of acidic electrolytes [95]. This made possible the use of low cost catalysts, for example, Ni at the anode and silver at the cathode [94]. Unfortunately, there were several practical constraints that convinced most of the DMFC developers to abandon the alkaline electrolyte approach [2, 3, 90, 96] and focus their attention on protonic electrolytes. This approach was undertaken despite the fact that the number of possible catalyst formulations was restricted to those stable in acidic environments [90, 96]. The main problem of alkaline electrolytes consisted of the acid–base reaction between CO₂ and the alkaline solution with carbonate precipitation in the catalyst pores. The lack of adequate alkaline polymer electrolyte membranes with conductivity comparable to Nafion [97, 98] retarded the development of a new generation of anionic membrane direct methanol fuel cells (AMDMFC) [95]. Most of the anion-exchange membranes used in the past required KOH recirculation at the anode [90, 95]. Regeneration of this electrolyte due to carbonation and dilution was considered a significant constraint for practical applications. The use of carbonate/bicarbonate media instead of KOH partly reduced the kinetic advantage of alkaline media over protonic electrolytes for methanol electro-oxidation [95]. Proton conducting solid polymer electrolyte membranes for hydrogen-fed fuel cells were initially developed at General Electric for the Gemini Earth-orbiting program in the early 1960s [99]. These devices were based on a polystyrene sulfonic acid membrane that exhibited poor oxidative stability, thus no suitable long-term performance [99]. The poor stability was due to the oxidation of the C–H bonds occurring at high potentials at the cathode, especially in the presence of hydrogen peroxide-type radicals. A large improvement in terms of stability was achieved when Nafion replaced the sulfonated polystyrene-divinylbenzene membrane in the late 1960s [97, 98]. Nafion was originally developed for chloro-alkali

electrolyzers; its peculiar characteristics rely on the excellent chemical, electrochemical stability and high proton conductivity that is derived from its unique chemical structure [99].

Despite the large methanol crossover shown by Nafion membranes, these membranes were the most used electrolyte in DMFCs in the 1990s [97]. Nafion 117 is still considered a standard electrolyte to compare the performance, conductivity, and methanol crossover of alternative or newly developed membranes for DMFCs [1, 2]. As alternative to Nafion, Hyflon[®] was employed with success in DMFCs especially at high temperatures [100]. Hyflon is characterized by the presence of short side chains and an equivalent weight smaller than Nafion [100, 101]. The peculiar characteristic of Hyflon is a glass transition temperature higher than Nafion, which makes this polymer more stable at high temperatures [100]. Prior to the advent of Nafion in DMFCs, which essentially occurred in the late 1980s, various acid electrolytes were used for DMFCs, such as sulfuric acid and phosphoric acid. In these devices, the anode and cathode were separated by a ceramic matrix, for example, a porous silicon carbide separator impregnated with the acidic electrolyte. The electrodes were impregnated with the same acid. Yet, due to extremely high levels of methanol crossover, this concept was abandoned in favor of Nafion. However, in the late 1990s, a similar approach was developed by Peled *et al.* at Tel Aviv University using a nanoporous membrane based on poly(ethylene oxide) (PEO) filled with silica nanoparticles and impregnated with sulfuric acid or trifluoromethanesulfonic acid (TFMFSA) [102]. The projected cost of this nanoporous membrane filled with sulfuric acid was considered quite low compared with Nafion. However, the best performance was achieved with TFMFSA due to the lower adsorption of anionic species from the electrolyte on the electrode [103].

The strong activation control of the MOR indicated in the high temperature operation, the most useful strategy to improve performance. High temperature operation allowed the achievement of high current densities with consequent fast methanol consumption at the anode/electrolyte interface. This effect reduces the concentration gradient, allowing a decrease in methanol crossover. In this regard, the use of thin membranes like Nafion 112 was sometimes adopted for high temperature operation [9, 104]. The most promising strategies to increase the operating temperatures concerned the use of phosphoric acid-doped polybenzimidazole membranes operating at about 180–200 °C [105] and composite perfluoro-sulfonic acid membranes operating up to 145 °C, containing inorganic fillers such as silica, zirconium phosphate, heteropolyacid-doped silica, and titanium oxide [106, 107]. In several attempts, the filler was formed *in situ*, for example, silica was synthesized inside the membrane by using a sol-gel type procedure using tetraethyl orthosilicate (TEOS) as precursor [108]. Although both approaches were demonstrated to be appropriate for extending the operating temperature range, the main constraint of phosphoric acid-doped polybenzimidazole was represented by the leaching of acid molecules from the membrane in the presence of hot methanol whereas a composite membrane operated properly at 145 °C in the presence of 3 bar abs. pressure [107]. Subsequently, it was shown that the water retention properties in composite membranes were promoted by the presence of acidic functionalities

on the filler surface [107]. Operation at high temperature (145 °C) and reasonable pressure (1.5 bar abs) with acceptable level of performance was made possible by amelioration of membrane properties [107–109]. The composite membrane approach was also extended to membranes alternative to Nafion such as sulfonated poly(ether ether ketone) (S-PEEK) and polysulfone-type [110].

Regarding membrane stability, some aspects related to the operating conditions appear less critical in a DMFC than in a hydrogen-fed fuel cell. For example, in a methanol fuel cell, the cathode never experiences electrochemical potentials above 1 V. Furthermore, the formation of hydrogen peroxide radicals, which can cause significant membrane degradation, occurs mainly in a PEMFC by effect of hydrogen crossover to the cathode. On the other hand, it is observed that the presence of hot concentrated methanol in DMFCs may increase membrane swelling. However, due to the lower electrochemical stability requirements, the range of membranes explored for DMFCs appears larger than that for PEMFCs [2, 101]. Recently, partially fluorinated, non-fluorinated aromatic polymers, radiation grafted ethylene tetra-fluoroethylene (ETFE)-based membranes, acid–base blends and so on [2, 101], have been explored as alternatives to Nafion. Several excellent reviews have already been published on this topic [96, 101]. Most of these alternative electrolytes have the characteristics of lower methanol crossover but also less conductivity than Nafion (as mentioned above these aspects are often interrelated), and, especially, the projected costs appear quite promising compared with classic perfluorosulfonic membranes. Among the various proposed membranes, S-PEEK [111], despite its promising properties in terms of conductivity, fuel permeation and costs, still seems affected by significant swelling; the properties of sulfonated poly(aryl-ether)-type membranes such as polysulfone or polyimide ionomer membranes as well as acid–base blends appear more promising [99, 110, 112].

More recently, several attempts have been carried out to develop a new generation of alkaline anion exchange membranes (AAEMs). The availability of new anionic polymers, with conductivity approaching values that are half of the conductivity of Nafion [91, 92], but characterized by much lower methanol crossover, has given new emphasis to the development of alkaline methanol fuel cells. The new membranes significantly reduced the drawbacks associated with conventional aqueous KOH electrolyte fuel cells that is, carbonate formation and the need to frequently regenerate the electrolyte. OH^- ions, necessary for ion conduction, are formed at the cathode by the water added to humidify the oxidant. These ions migrate to the anode reducing methanol crossover by the electro-osmotic drag. The alkaline environment allows the use of non-noble metal catalysts (usually unstable in the acidic environment); in fact, catalyst corrosion and membrane degradation problems are significantly mitigated due to the high pH [91]. Accordingly, cheap catalysts and hydrocarbon-only membranes have been explored [90, 91, 95, 96]. There are, however, some drawbacks which concern the formation of a pH gradient between anode and cathode [95], the need of cathode humidification (protonic membranes based DMFCs are usually fed by dry air) and the need to increase the operating temperature to enhance conductivity, which may be not useful for portable applications.

1.3.4

State-of-the-Art DMFC Electrolytes**1.3.4.1 General Aspects of DMFC Electrolyte Development**

It is widely recognized that the electrolyte is a key component in DMFCs. The electrolyte determines the fuel permeation rate and the choice of the catalysts, and influences the reaction rate. The standard electrolyte membrane for DMFCs is usually a perfluorosulfonic acid membrane such as Nafion, which is also widely used in PEMFCs. Most of the electrolyte alternatives to Nafion, both the proton-conducting and alkaline type, are cheaper than the classic perfluorosulfonic membranes used in PEMFCs; in some cases, they are also characterized by lower methanol crossover; however, life-time characteristics similar to those shown by Nafion-type membranes in fuel cells (60 000 h of operation) have not been achieved yet with the alternative membranes [97, 98]. Concerning conductivity, only recently membrane alternatives to Nafion-type have shown similar levels of performance. One critical aspect is related to the fact that the presence of water is a requirement of low-temperature DMFCs for the occurrence of the electrochemical reactions and to promote ion conductivity. As methanol is highly soluble in water, the transport of water through the membrane is commonly associated with methanol permeation. This effect is more critical with protonic membranes because, besides methanol transport due to the concentration gradient (diffusion), there is an effect due to the electro-osmotic drag. High ionic conductivity is often associated with the presence of high levels of water uptake by the membrane whereas what is required is a low water uptake. These aspects are mainly related to polymer electrolyte membrane DMFCs. No drawbacks in terms of methanol crossover with consequent cathode poisoning and poor anode reaction kinetics are envisaged in intermediate temperature solid oxide fuel cells (IT-SOFCs) which employ dense ceramic anionic electrolytes and operate at 500°–750 °C. However, such devices are less suitable for most of the applications of methanol fuel cells including portable and assisted power units (APU). Thus, the research efforts on low temperature methanol fuel cell membranes have addressed improving the conductivity, reducing the crossover of methanol and catalyst degradation. The latter regards, for example, dissolution of Ru and Ru ion migration from the anode to the cathode [43], Co or Fe dissolution from the cathode into the membrane (e.g., in the case of a PtCo or PtFe alloy cathode) and so on. Other important aspects are the increase of chemical and electrochemical stability, reduction of water uptake and swelling, extension of the operating temperature range and finally cost reduction for market application.

1.3.4.2 Proton Conducting Membranes

In the present section, we have restricted our discussion to the characteristics of membranes that are actually considered for commercial DMFC systems. Several excellent reviews have been published on this topic [101, 113–116]. Perfluorosulfonic polymer electrolyte membranes are currently used in H₂/air and methanol/air fuel cells because of their excellent conductivity and electrochemical stability [98]. Unfortunately, they suffer several drawbacks such as methanol crossover and

membrane dehydration. The latter severely hinders fuel cell operation above 100 °C, which is a prerequisite for high rate oxidation of small organic molecules involving the formation of strongly adsorbed reaction intermediates such as CO-like species [2]. Since methanol is rapidly transported across perfluorinated membranes and is chemically oxidized to CO₂ and H₂O at the cathode, there is a significant decrease in coulombic efficiency for methanol consumption, as much as 20% under practical operating conditions [117]. Thus, it is very important to modify these membranes by, for example, developing composites or finding alternative proton conductors with the capability of inhibiting methanol transport. It is generally accepted that a solid-state proton conductor is preferable for liquid fuel fed DMFCs because it hinders corrosion and rejects carbon dioxide (produced during the methanol oxidation). However, there are some prerequisites that should be properly considered. The polymer electrolyte should have a high ionic conductivity ($5 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$) under working conditions and low permeability to methanol (less than $10^{-6} \text{ moles min}^{-1} \text{ cm}^{-2}$). Furthermore, it must be chemically and electrochemically stable under operating conditions. These requirements appear, potentially, to be met by new classes of solid polymer electrolytes that show promising properties. Alternative membranes based on poly(arylene ether sulfone) [118], sulfonated poly(ether ketone) [119] or block co-polymer ion-channel-forming materials as well as acid-doped polyacrylamide and polybenzimidazole have been suggested [116, 118–120]. Various relationships between membrane nanostructure and transport characteristics, including conductivity, diffusion, permeation and electro-osmotic drag, have been observed [121]. Interestingly, the presence of less connected hydrophilic channels and the wider separation of sulfonic groups in sulfonated poly(ether ketone) reduces water/methanol permeation and electro-osmotic drag with respect to Nafion while maintaining high protonic conductivity [121]. Furthermore, an improvement in thermal and mechanical stability has been shown in nano-separated acid–base polymer blends obtained by combining polymeric N-bases and polymeric sulfonic acids [119].

The perfluorinated polymers such as polysulfones, polyetherketones, and polyimides usually combine reduced crossover and appropriate conductivity levels. However, the conduction mechanism in these systems is not very different from that in Nafion. Thus, methanol crossover cannot be eliminated completely. It appears that the main advantage of these polymers is cost reduction with respect to Nafion. Alternatively, membranes such as phosphoric acid impregnated-polybenzimidazole (PBI) which do not need water transport to maintain high proton conductivity may represent a valid approach [105, 122]. However, these electrolytes still present methanol crossover effects; moreover, suitable DMFC life-time for such membranes has not been yet demonstrated. Other issues are cold start-up and low temperature operation.

In principle, the water uptake properties of sulfonic acid-based membranes may be modulated by selecting the proper concentration and distribution of sulfonic groups inside the polymer. Such an objective is generally pursued in the preparation of grafted polymer membranes [123]. The application of the radiochemical grafting technique to the production of DMFC membranes has been explored in the

framework of the Nemecel European program (see Section 1.4.2). In this procedure the material properties may be properly tailored by varying a few parameters in the synthesis while maintaining the process characteristics and plants for large scale production. The main efforts are addressed to reduce the cost of production through a flexible preparation process and the proper selection of cheap base materials. For this purpose films of ETFE (which has C_2H_2 and C_2F_2 groups with 1/1 ratio and nearly perfect alternance) have been selected as substrate material; the films were radio-chemically grafted with styrene and subsequently sulfonated in order to obtain sulfonic acid anchored groups. The present cost of the base irradiated ETFE material compares favorably with the average industrial cost of the commercial perfluorinated sulfonic membranes. In order to improve the mechanical strength properties of the polymer, increase the thermal resistance and reduce the crossover of gases or liquids (such as methanol) through it, while maintaining suitable conductivity, appropriate crosslinking was made during the grafting step by adding a crosslinking agent [123].

Considerable efforts in the last decade have addressed the development of composite membranes. These include ionomeric membranes modified by dispersing insoluble acids, oxides, zirconium phosphate, and so on, inside their polymeric matrix; other examples are ionomers or inorganic solid acids with high proton conductivity embedded in porous non-proton-conducting polymers [120]. In an attempt to reduce the drawbacks of perfluorosulfonic membranes, nanoceramic fillers have been included in the polymer electrolyte network. Stonehart, Watanabe and co-workers [124] have successfully reduced the humidification constraints in PEMFCs by the inclusion of small amounts of SiO_2 and Pt/TiO_2 (~ 7 nm) nanoparticles to retain the electrochemically produced water inside the membrane. This approach was used in DMFCs to increase operating temperatures (up to $145^\circ C$) and reduce methanol crossover by increasing the tortuosity factor for methanol permeation [106]. Although it has been hypothesized [116, 120] that the inorganic filler induces structural changes in the polymer matrix, the water retention mechanism and protonic conductivity appear favored in the presence of acidic functional groups on the surface of nanoparticle fillers [107].

1.3.4.3 Membranes for High Temperature Applications

A rational analysis of filler effects on structural, proton transport properties and the electrochemical characteristics of composite perfluorosulfonic membranes for DMFCs was reported [107, 125]. It was observed that a proper tailoring of the surface acid–base properties of the inorganic filler for application in composite Nafion membranes allows appropriate DMFC operation at high temperatures and reduced pressure [107]. An increase in both the strength and amount of acidic surface functional groups in the fillers enhances water retention inside the composite membranes through an electrostatic interaction in the presence of humidification constraints, in the same way as for the adsorption of hydroxyl ions in solution [107, 109, 125].

The DMFC performance of various MEAs based on composite membranes that contain fillers with different acid–base characteristics improves as the pH of the slurry of the inorganic filler decreases (Figure 1.14). As expected, the surface

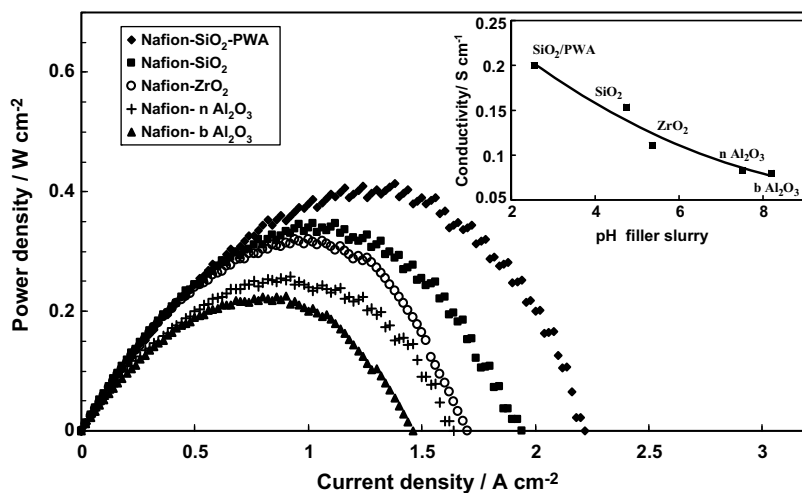


Figure 1.14 DMFC power density curves at 145 °C for MEAs containing different inorganic fillers. Methanol feed 2 M, 2.5 atm; oxygen feed 2.5 atm. Pt loading $2 \pm 0.1 \text{ mg cm}^{-2}$. The inset shows the variation of membrane conductivity at 145 °C as a function of the pH of slurry of the filler [109].

properties play a more important role than the crystalline structure of the filler, since the water molecules, acting as promoters towards the proton migration, are effectively coordinated by the surface groups. The conductivity and performance of composite perfluorosulfonic membranes in DMFCs are strongly related to the surface acidity, which, in turn, influences the characteristics of the water physically adsorbed on the inorganic filler surface. It has been observed that the more acidic the filler surface, the larger its capability of undergoing a strong interaction with water through the formation of hydrogen bonds (Figure 1.15). This latter effect produces a decrease in the O–H stretching and bending frequencies in the physically adsorbed water. Furthermore, an increase in the water uptake in the composite membrane and an enhancement of proton conductivity are observed in the presence of acidic fillers [107, 125]. The proton migration inside the membrane appears to be assisted by the water molecules on the surface of the nanofiller particles and could also be promoted by the formation and breaking of hydrogen bonds [109, 125].

Conventional ion-exchange perfluoropolymer membranes such as the well-known Nafion membrane are based on long-side-chain polymers (LSC). In the last few decades, Solvay Solexis has developed a new short-side-chain (SSC) proton conducting perfluoropolymer membrane, that is, Hyflon Ion, characterized by excellent chemical stability and equivalent weight (850 g/eq.) lower than conventional Nafion 117 (1100 g/eq.) [100]. Besides the improved conductivity related to the higher degree of sulfonation, the short-side-chain Hyflon Ion ionomer is characterized, in the protonic form, by a primary transition at around 160 °C whereas the conventional Nafion shows this transition at about 110 °C. This characteristic of the Hyflon Ion membrane ensures proper operation at high temperatures (100–150 °C) provided

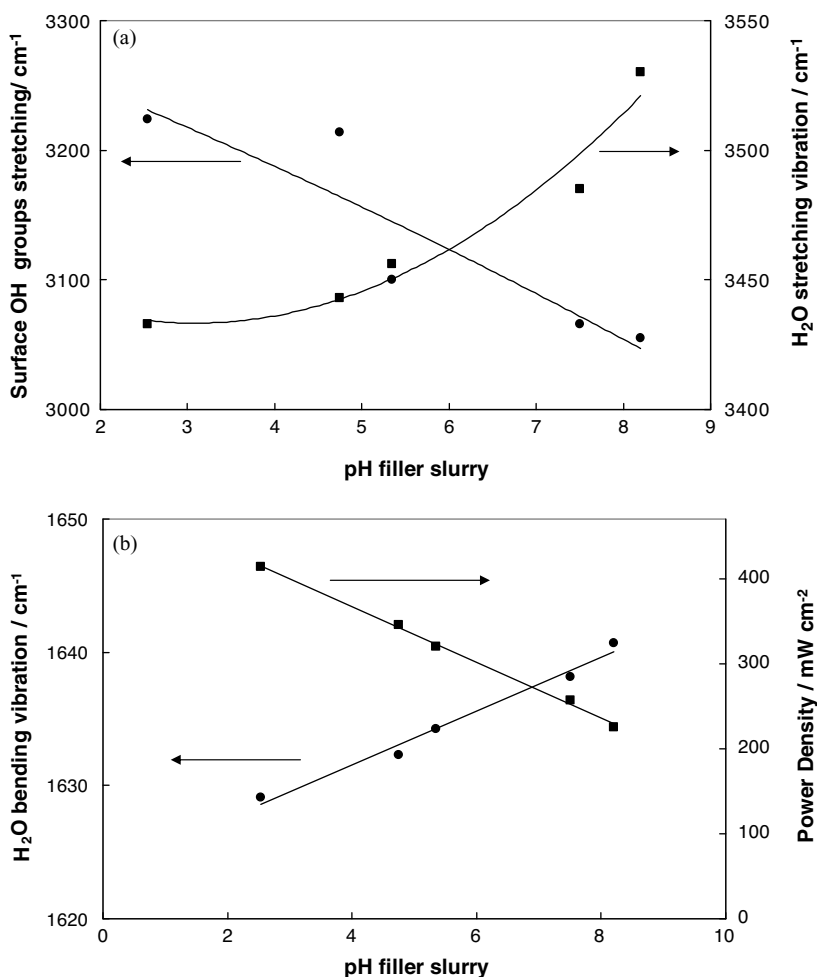


Figure 1.15 Variation of O–H stretching vibration frequencies for surface OH functionalities and physically adsorbed water versus the pH of slurry of the fillers (a); variation of O–H bending vibration frequencies of physically adsorbed water and DMFC maximum power density versus the pH of slurry of the fillers (b) [109].

that a sufficient amount of water is supplied to the membrane or retained inside the polymer under these conditions.

Hyflon Ion membranes have been investigated for applications in DMFCs operating between 90° and 140°C in the European FP5 Dreamcar project, which is described in the transportation section. DMFC assemblies based on these membranes showed low cell resistance and promising performances compared with conventional membranes. The peak power density reached about 290 mW cm^{-2} at 140°C and 3 bars abs. with 1 M methanol and air feed (Figure 1.16).

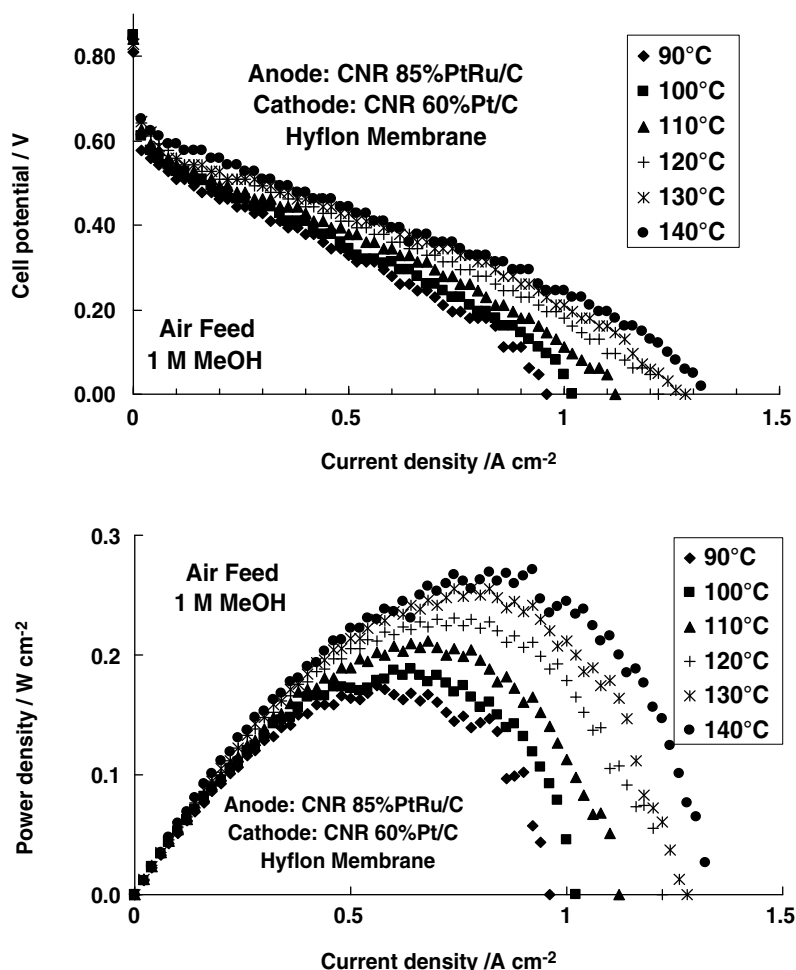


Figure 1.16 DMFC polarization and power density curves for a Hyflon Ion membrane-based MEA [100].

1.3.4.4 Alkaline Membranes

As is well known, the major drawbacks of proton-conducting electrolyte-based DMFCs concern slow reaction kinetics and fuel crossover. A large amount of precious catalysts is necessary and this has a considerable impact on the cost of these devices. Furthermore, catalyst corrosion and membrane degradation at low pH values limit the number of materials that can be selected for long-term stability [101]. On the other hand, the liquid alkaline electrolytes that were initially preferred for DMFCs [94] are affected by practical constraints such as potassium or sodium carbonate formation and precipitation in the catalyst pores, the need to frequently regenerate the electrolyte and liquid electrolyte leakage through the electrode. Some of the drawbacks associated with the behavior of liquid alkaline electrolytes in fuel cells can be

solved by using new anion exchange membranes [90, 96]. In anionic polymer electrolytes, OH^- ions, responsible for ionic conduction, are formed at the cathode by the water fed to humidify the oxidant stream according to Equation 1.5. The OH^- ions are transported through the membrane to the anode where they react with methanol to form CO_2 (Equation 1.4). The CO_2 reaction product reacts easily with OH^- ions to form carbonate/bicarbonate ($\text{CO}_3^{2-}/\text{HCO}_3^-$) anions [90]. In the membrane region in contact with the anode, the $\text{CO}_3^{2-}/\text{HCO}_3^-$ ions neutralize the positive charge fixed on the polymeric membrane, for example, quaternary ammonium functionalities, affecting conductivity and causing a variation of the local pH in the anode compartment with respect to the cathode [90]. The decrease of pH at the anode causes a positive shift of the redox potential (in the absolute potential scale) for the oxidation process, thus diminishing the electromotive force. In other words, the pH difference will reduce the voltage thermodynamically. The thermodynamic voltage loss can be 290 mV in the presence of a pH difference of about 4 at 80 °C [90]. This loss decreases by increasing the operating temperature. High temperature operation restricts the number of anionic polymers that can be used. Furthermore, the high temperature approach might not be appropriate for portable applications. Besides these aspects, there are several advantages in using anion exchange membranes. As discussed above, the main advantage concerns with the favorable reaction rates in alkaline media with respect to acidic electrolytes for both oxygen electro-reduction and methanol electro-oxidation reactions [90, 96]. Methanol is oxidized to carbon dioxide in both acid and alkaline electrolytes in the presence of proper catalysts for example, PtRu [90]. The significant reduction of activation overpotential in alkaline media can compensate for the voltage loss due to the thermodynamic effects associated to the pH gradient [90]. However, the enhanced reaction kinetics may allow the use of cheaper materials and, possibly, non-noble metals. In alkaline media, Ni anodes and Ag cathodes represent a suitable compromise in terms of activity and cost [25, 26, 50]. In general, a significant reduction of the catalyst cost may be envisaged.

The OH^- ions migrate from the cathode to the anode; this pathway is the opposite direction to the electro-osmotic drag in proton exchange membrane DMFCs. Thus, the electro-osmotic drag does not contribute to the methanol crossover in alkaline systems. However, it should be pointed out that even at high current densities (in the cell voltage region of technical interest), the contribution of the electro-osmotic drag to methanol crossover, in protonic electrolyte-based DMFCs is quite small with respect to the concentration gradient (diffusion). OH^- migration in the membrane is assisted by water as it occurs for protons in the analogous acidic polymer electrolyte. Thus, methanol crossover cannot be completely eliminated by the anion exchange membranes; however, in principle, it can be reduced. In general, the alkaline electrolyte causes lower corrosion problems. This allows the investigation of a large number of catalyst formulations, especially with regard to methanol tolerance characteristics.

Another important aspect is membrane stability. One of the main degradation mechanisms of proton exchange membranes during fuel cell operation is caused by the hydrogen peroxide-type radicals formation during oxygen electroreduction in an

acidic environment. This process is less effective at high pH values [90, 96]. Thus, as occurs for the catalysts, there is a wider range of polymers that can be potentially used as anionic electrolytes in DMFCs. Cheap hydrocarbon-only membranes may be selected [96]; yet, these systems are less appropriate than the fluorinated membranes in terms of high temperature stability. Besides the above mentioned thermodynamic effect due to the pH gradient, another significant problem associated with the use of anion exchange membranes is the low ionic conductivity. This is essentially caused by the lower mobility of anions such as OH^- or the carbonate-type with respect to the protons. The lack of appropriate anionic membranes with conductivity characteristics similar to Nafion has practically hindered the development of alkaline DMFCs for several decades. It should be mentioned that several researchers such as Ogumi *et al.* [126] and Yu and Scott [92] have reported interesting results with anionic membranes but alkaline solutions were indeed used in those studies to enhance membrane conductivity. Recirculation of the liquid electrolyte through the device not only enhances conductivity but significantly reduces the pH gradient. Thus, electrolyte recirculation eliminates the thermodynamic constraints and enables an extension of the three-phase reaction zone from the electrode/membrane interface to the bulk of the electrode, favoring the presence of a mixed conductivity in the catalytic layer. This aspect is quite important in the absence of a suitable ionomer solution. In this regard, there is considerable interest in the synthesis of perfluorinated anion exchange membranes that can be dissolved in non-volatile solvents, enabling the preparation of mixed conductivity (ionic and electronic) catalytic layers as occurs for conventional PEMFCs and DMFCs. Perfluorinated anion-exchange membranes are also of interest for their perspectives to extend the operating range to higher temperatures [90]. Of course, these are significantly more expensive than hydrocarbon membranes containing C–H bonds in the backbone.

One of the reasons why an increasing number of DMFC developers have recently been showing interest in alkaline membranes is especially due to the development of new polymers that show appropriate conductivities in a range from ambient temperature to 80 °C [91, 92]. Although these conductivity values are still lower than those of conventional perfluorosulfonic membranes, since the alkaline membranes are less affected by methanol permeation, they can be used in a thinner form. This compensates, in part, for the effect of high cell resistance [90, 96]. Among the various types of anion-exchange membranes recently proposed, significant interest has been stimulated by radiation grafted alkaline membranes [91]. Radiation-grafting of styrene into non-fluorinated (LDPE), partially fluorinated (PVDF) and fully fluorinated (FEP) films has been considered widely for PEMFCs and DMFCs [91, 101]. Lower methanol crossover with respect to Nafion and the issue of high temperature operation has been demonstrated in DMFCs with grafted protonic membranes [123]. The radiation grafting process is also appealing for anionic membranes. This process is generally carried out on commercial preformed films; several parameters can be modulated such as the process temperature, the level of grating, radiation dose, and thickness to obtain particular membrane properties [96]. Methanol crossover can be further diminished by using appropriate crosslinking procedures.

Interesting results were obtained by Yu and Scott using Morgane ADP, a commercial anion exchange membrane produced by Solvay (Belgium) [92]. The main drawbacks concerned with conductivity and stability. Another interesting commercial membrane is produced by Tokyzama (Japan) [90, 96]. Recently, high conductivity anion exchange membranes were prepared by the radiation grafting of vinylbenzylchloride (VBC) into FEP with a subsequent amination with triethylamine and an ion exchange with KOH [91]. These membranes were characterized by a degree of grafting of about 20% and conductivities of $2 \cdot 10^{-2} \text{ S cm}^{-1}$ at 50°C in aqueous solutions. The conductivities are 20% of the values obtained for state-of-the-art perfluorosulfonic acid membranes. The activation energy for OH^- migration in the membrane was twice compared with that observed for protons in fully hydrated Nafion indicating that OH^- mobility is strongly temperature dependent [92].

1.3.4.5 Effects of Crossover on DMFC Performance and Efficiency

Methanol crossover through the polymer membrane is known to be one of the most challenging problems affecting the performance of DMFCs [88]. The overall efficiency of a methanol fuel cell is determined by both voltage and faradaic efficiency for the consumption of methanol [12]. The faradaic efficiency is influenced mainly by methanol crossover through the membrane. The methanol crossover is usually measured indirectly by determining the amount of CO_2 produced at the cathode by the oxidation of methanol on the Pt surface [88]. This CO_2 can be monitored on line by using an IR-detector. A more accurate method consists of a chromatographic analysis of aliquot samples of the cathode outlet stream [106, 117].

The crossover of methanol is influenced by both membrane characteristics and temperature, as well as by the operating current density [88, 117]. In general, an increase in temperature causes an increase in the diffusion coefficient of methanol and determines a swelling of the polymer membrane. Both effects contribute to an increase in the methanol crossover rate. The crossover includes both methanol permeability due to a concentration gradient and molecular transport caused by electro-osmotic drag in the presence of a proton conducting electrolyte. The latter is directly related to the proton migration through the membrane and it increases with the current density [127]. For DMFCs equipped with an alkaline electrolyte, the electro-osmotic drag is directed towards the anode. Thus, it does not contribute to the crossover. Methanol permeability, caused by the concentration gradient at the anode-electrolyte interface, depends on the operating current density. In a polarization curve, the onset of diffusional limitations occurs when the rate of reactant supply is lower than the rate of its electrochemical consumption. Thus, if the anode is sufficiently active to oxidize methanol electrochemically to CO_2 at a rate comparable to or higher than the rate of the methanol supply, the methanol concentration gradient between anode/electrolyte and cathode/electrolyte interfaces could be reduced significantly [11, 88, 117]. Membranes that are very thick are effective barriers for reducing methanol crossover; conversely, an increase in thickness causes an increase of ohmic overpotentials. In some cases, it may be more productive to use a thinner membrane with reduced ohmic limitations and select appropriate operating conditions which limit the methanol crossover.

1.3.5

Historical Development of Oxygen Electroreduction in DMFCs

Regarding the development of catalysts for the oxygen reduction process in methanol fuel cells during the last few decades, it should be mentioned that silver was considered mainly at the beginning, especially for operation in conjunction with alkaline electrolytes [25, 26]. Silver is used presently in oxygen depolarized cathodes for industrial chloro-alkali cells which use a liquid electrolyte (KOH) [128] whereas Pt and its alloys were employed for oxygen reduction in the presence of acidic electrolytes both in unsupported and carbon supported form. The development of cathode catalysts for proton conducting electrolyte based DMFCs was initially influenced by similar studies carried out on phosphoric acid fuel cells (PAFCs). The catalytic layer was essentially a mixture of Pt/C catalysts and PTFE binder sintered at around 350 °C. These hydrophobic electrodes were useful in reducing the flooding caused by liquid electrolytes. However, the need to use a methanol tolerant cathode catalyst was quickly discerned. Accordingly, the research was also directed towards alternative catalytic systems including non-noble metals.

In the late 1980s, the development of methanol tolerant oxygen reduction catalysts became of practical interest with the development of metal chalcogenides [129], phthalocyanines and porphyrins [130] -based cathodes with catalytic activities approaching those of Pt in the presence of methanol poisoning.

As for the development of non-noble metal catalysts for the oxygen reduction reaction (ORR), essentially three classes of materials were investigated in the first decades of DMFC development. These included oxides, chalcogenides other than oxides and organometallic compounds. Metal oxides were initially considered being these materials the most obvious candidates as Pt substitutes in electrocatalysis. Oxides are present on the surfaces of all non-noble metals at potentials useful for oxygen reduction. It was assumed that oxygen reduction occurred by the exchange of oxygen atoms between molecular oxygen, surface oxide, and water (referred to as a regenerative mechanism). Several non-noble metal oxides with metallic conductivity are available; a few are stable in acid electrolytes. These include mainly tungsten oxides as a possible candidate. Only recently, Co-oxides with a perovskite structure similar to that used in intermediate temperature solid oxide fuel cells (IT-SOFCs) have been considered [131].

1.3.6

Status of Knowledge of Oxygen Reduction Electrocatalysis and State-of-the-Art Cathode Catalysts**1.3.6.1 Oxygen Reduction Process**

Although Pt/C electrocatalysts are, at present, the most widely used materials as cathodes in proton conducting electrolyte-based low temperature fuel cells, due to their intrinsic activity and stability in acidic solutions, there is still great interest in developing more active, selective and less expensive electrocatalysts for oxygen reduction. However, there are a few directions that can be investigated to reduce

the costs and to improve the electrocatalytic activity of Pt, especially in the presence of methanol crossover. One is to increase Pt use; this can be achieved by increasing its dispersion on carbon and the interfacial region with the electrolyte. Another successful approach to enhance the electrocatalysis of O_2 reduction is by alloying Pt with transition metals. This enhancement in electrocatalytic activity has been interpreted differently, and several studies were done to analyze in depth the surface properties of the proposed alloy combinations [132–134]. Although a comprehensive understanding of numerous reports has not been reached yet, the observed electrocatalytic effects have been ascribed to several factors (interatomic spacing, preferred orientation, electronic interactions) which play, under fuel cell conditions, a favorable role in enhancing the ORR rate [135–143].

Also, there is an increasing interest in developing methanol tolerant catalyst alternatives to Pt for oxygen reduction; however, it should be taken into account that if the methanol which permeates through the membrane is not completely oxidized at the cathode surface to CO_2 , it would contaminate the water at the outlet of the cathode compartment. This could cause several environmental problems in the absence of a proper technical solution, which could be a single chamber DMFC with highly selective anode and cathode catalysts. Alternatively, a proper catalytic burner should be used at the cathode outlet.

As discussed in a previous section, various studies carried out in the past, especially on carbon supported Pt electrocatalysts for oxygen reduction in phosphoric acid fuel cells, showed that the electrocatalytic activity (mass activity, $mA\ g^{-1}\ Pt$, and specific activity, $mA\ cm^{-2}\ Pt$) depends on the mean particle size. The mass activity for oxygen reduction reaches a maximum at a dimension of about 3 nm, corresponding closely with the particle size at which there is a maximum in the fraction of (1 1 1) and (1 0 0) surface atoms on Pt particles of cubo-octahedral geometry [144]. Platinum atoms at edge and corner sites are considered less active than Pt atoms on the crystal faces. Accordingly, both mass and specific activity should decrease significantly as the relative fraction of atoms at edge and corner sites approach unity [144]. This situation occurs with Pt particles smaller than 1–2 nm in diameter.

In the case of DMFCs, an additional aspect should be considered, which is methanol crossover through the membrane. Methanol oxidation and oxygen reduction in the cathode compartment compete for the same sites, producing a mixed potential which reduces the cell open circuit potential.

In the case of methanol oxidation at the cathode, three neighboring Pt sites in a proper crystallographic arrangement will favor methanol chemisorption. Since at high cathodic potentials the water discharging reaction is largely favored, oxidation of the methanolic residues adsorbed on the surface proceeds very fast producing a parasitic anodic current on this electrode.

When the particle size of the electrocatalyst is very small or one has an amorphous Pt electrocatalyst for the oxygen reduction, methanol chemisorption energy could be lower and hence the cathode less poisonable. At the same time, however, due to the fact that only the inactive edge and corner atoms will be present and dual sites of the proper orientation will not be available, the activity of such an electrocatalyst for oxygen reduction will be lower. The best compromise is to modulate the structure and

the particle size between amorphous and crystalline in order to decrease the poisoning by methanol and enhance oxygen reduction. A second possibility is to use a promoting element for oxygen reduction that simultaneously hinders the methanol chemisorption still maintaining the proper structure and particle size.

1.3.6.2 Pt-Based Catalysts and Non-noble Metal Electrocatalysts

The intrinsic electrocatalytic activity of Pt alloys (Pt-Cr, Pt-Ni, Pt-Co, Pt-Cu, Pt-Fe) with a lattice parameter smaller than that of Pt was found to be higher than on the base metal [132–140, 145, 146]. This effect is related to the nearest neighboring distance of Pt-Pt atoms on the surface of the fcc crystals. The r.d.s. involves the rupture of the O–O bond through a dual site mechanism; a decrease of the Pt–Pt distance favors the dual site O₂ adsorption. Leaching of non-noble elements produces a roughening of the surface with a corresponding increase of the Pt surface area.

Many investigations in PEMFCs have shown that enhanced electrocatalytic activity for the ORR of some binary Pt based alloy catalysts, such as Pt–M, (where M = Co, Fe, etc.), in comparison with pure Pt [147–152] can be also interpreted in terms of increased Pt d-band vacancy (electronic factor) and its relative effect on the OH chemisorption from the electrolyte [153].

Methanol chemisorption and ORRs require an appropriate geometrical arrangement of Pt atoms. Both processes are favored on a Pt (1 1 1) surface, which possesses the reasonable nearest Pt–Pt interatomic distance. Thus, the poisoning effect of methanol crossover should be more significant on the Pt (1 1 1) surface. However, it is difficult to quantify the compensation effect due to the increased methanol oxidation rate at the sites where oxygen reduction is favored. Beside these aspects, a recent work has also taken into consideration the role played by the promoting element (Co, Cr) for the removal of strongly bonded oxygenated species on Pt through an intra-alloy electron transfer [142]. Chemisorption of oxygen molecules occurs more easily on oxide-free Pt surfaces [142], but, as reported in cyclic voltammetry studies [64], methanol adsorption and oxidation are favored on a reduced Pt surface rather than on platinum oxide. The addition of Co and Cr to Pt appears to simultaneously favor both ORRs and MORs. For example, the promoting effect of Cr on Pt for methanol electro-oxidation has already been reported [98, 141]. Furthermore, the presence of electropositive elements alloyed to Pt favors the chemisorption of OH species on neighboring Pt sites. In the absence of oxygen, a small but noticeable promoting effect for methanol oxidation in a wide range of anodic overpotentials has been observed by Cr, Fe and other elements usually selected as catalytic enhancers for the ORR in PEFCs [6]. At present, it is difficult to establish if the beneficial effect on oxygen reduction is prevailing with respect to the promoting effect on methanol oxidation at the DMFC cathode. For the Pt-Fe system, Watanabe *et al.* reported that after electrochemical testing of a Pt-Fe alloy the catalyst was covered by a thin Pt skin of less than 1 nm in thickness [150, 151]. Moreover, they suggested that during the adsorption step, a p orbital of O₂ interacts with empty d orbitals of Pt and, consequently, back donation occurs from the partially filled orbital of Pt to the p* (anti-bonding) molecular orbital of O₂. The increase in d-band vacancies on Pt by alloying produces a strong metal–O₂ interaction. This interaction weakens the O–O bonds,

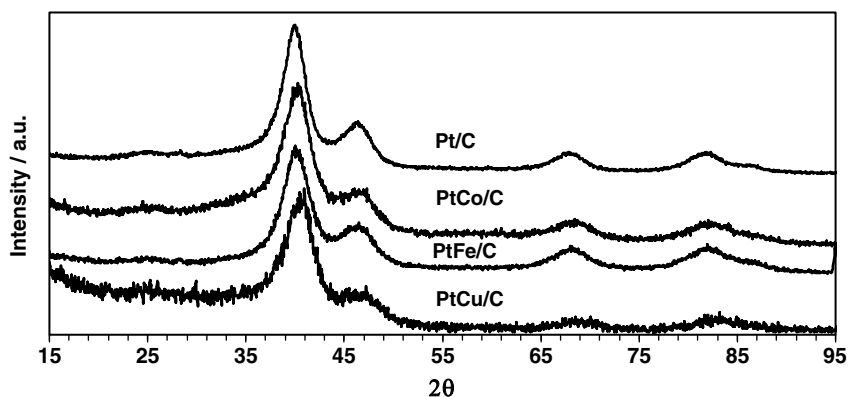


Figure 1.17 XRD patterns of Pt and Pt-based bimetallic catalysts for the oxygen reduction reaction in DMFCs [154].

resulting in bond cleavage and bond formation between O and H^+ of the electrolyte, thus improving the ORR. The leaching of Fe ions into the membrane may cause an increase in resistance and accelerate the degradation reactions of the polymer.

Recently, cathode catalysts synthesized by a low-temperature colloidal-incipient wetness route characterized by a high concentration of metallic phase on carbon black and a particle size smaller than 3 nm have been investigated [154, 155]. The new approach allowed carbon-supported bimetallic nanoparticles with a particle size of about 2–2.5 nm and a suitable degree of alloying, to be obtained. X-ray diffraction (XRD) patterns of these Pt/C and Pt-M/C catalysts are reported in Figure 1.17. These showed the typical fcc crystallographic structure of Pt. A moderate degree of alloying was found in Pt-Fe catalysts whereas the degree of alloying was slightly higher for Pt-Co/C and significantly larger for Pt-Cu/C compared with Pt-Fe, using the same procedure. These findings were derived from a decrease of the lattice parameter.

In terms of polarization behavior, the Pt-Fe/C (2.4 nm) performed better than the Pt/C, Pt-Cu/C and Pt-Co/C catalysts with similar particle sizes (2.1–2.8 nm) at 60 °C (Figure 1.18). This was also confirmed by cathode polarization curves (Figure 1.18). Methanolic residues stripping analysis of these catalysts (Figure 1.19) showed that this enhanced activity was possibly derived from better methanol tolerance and higher intrinsic catalytic activity for oxygen reduction. The presence of a significant current density in the hydrogen desorption region ($E < 0.4$ V RHE) for the Pt-Fe even after methanol adsorption, which was not observed for the other catalysts, indicated suitable methanol tolerance properties. The positive shift of the potential for Pt-Oxide reduction was associated with better intrinsic catalytic activity. The electrochemical active surface area derived from the methanolic residues stripping analysis was larger for catalysts with a smaller particle size, for example, PtCu/C. Yet, it appeared that the small increase of electrochemically active surface area in PtCu did not play the same role of the increase of methanol tolerance and intrinsic catalytic activity in PtFe.

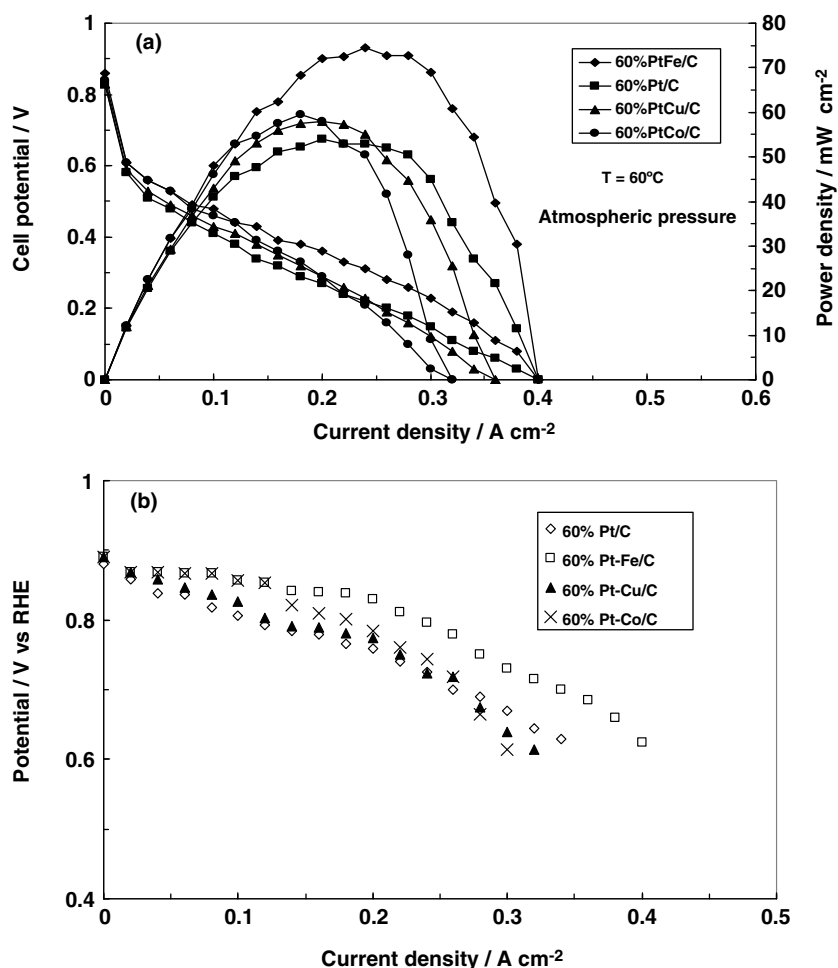


Figure 1.18 (a) Polarization and power density curves for the DMFCs equipped with the various cathode catalysts at 60 °C under atmospheric pressure, and (b) cathodic polarization curves for DMFCs based on the different cathode catalysts recorded at the same operating conditions [154].

1.3.6.3 Alternative Cathode Catalysts

Alternatively to platinum, organic transition metal complexes are known to be good electrocatalysts for the ORR. Transition metals, such as iron or cobalt organic macrocycles from the families of phenylporphyrins, phthalocyanines and azoannulenes have been tested as O₂-reduction electrocatalysts in fuel cells [130, 156–159]. One major problem with these metal organic macrocyclics is their chemical stability under fuel cell operation at high potentials. In many cases, the metal ions dissolve irreversibly in the acid electrolyte. However, if the metal-organic macrocyclic is

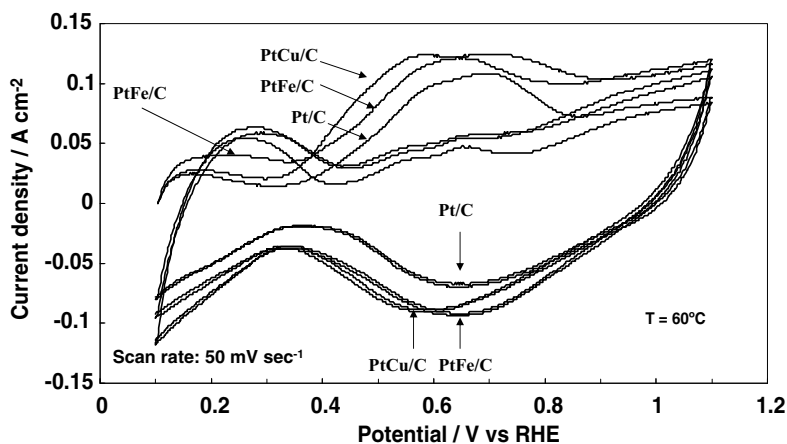


Figure 1.19 Adsorbed methanolic residues stripping voltammetry at a scan rate of 50 mV s^{-1} for the different cathode catalysts at 60°C [154].

supported on high surface area carbon and treated at high temperatures (from 500 to 800°C), the residue exhibits promising electrocatalytic activity without any degradation in performance, from which one may infer the good stability of the metal in the electrocatalyst [158].

In some other studies, a few inorganic materials have been proposed as suitable substitutes for platinum in methanol fuel cells due to their selectivity for oxygen reduction, even in the presence of methanol. These materials consist mainly of the Chevrel-phase type ($\text{Mo}_4\text{Ru}_2\text{Se}_8$), transition metal sulfides ($\text{Mo}_x\text{Ru}_y\text{S}_z$, $\text{Mo}_x\text{Rh}_y\text{S}_z$) or other transition metal chalcogenides ($(\text{Ru}_{1-x}\text{Mo}_x)\text{SeO}_z$) [129, 160]. Some of these possess semiconducting properties, thus, in theory, they could introduce an additional ohmic drop in the electrode. However, their activity for oxygen reduction is significantly lower than Pt [2]. Carbon supported Ru electrocatalysts are reported to exhibit high selectivity for oxygen reduction in the presence of methanol but their activities are significantly lower [161]. The tolerance of these materials to methanol is due to the absence of adsorption sites for methanol dehydrogenation. In the case of Ru/carbon, at high potentials, the surface is covered mainly by Ru oxides on which methanol chemisorption is hampered [161]. Regarding the development of cathode catalysts for alkaline DMFCs, it should be pointed out, as for the anode catalyst, that corrosion problems are minimized by the operation at high pH values. Thus, due to the large variety of catalytic formulations that may be screened, it should be easier to discover a methanol tolerant cathode catalyst. The reaction kinetics for oxygen reduction at the cathode are more favorable in alkaline media. This allows the replacement of Pt with less noble or non-precious catalysts with significant advantages in terms of cost reduction. Among the various cathode formulations, Ag and MnO_2 catalysts have shown suitable methanol tolerance and catalytic activity for oxygen reduction [90].

1.3.7

DMFC Power Sources in the 'Pre-1990 Era'

Even though from the 1960s to the 1980s the development of DMFCs was a 'Fuel Cell Researcher's Dream' [97], only in the last two decades have the attractive features of DMFC power sources (portable liquid fuel with an energy density of about half that of gasoline, environmentally friendly technology, a 10-fold increase in power density with a proton exchange membrane electrolyte) clearly indicated their possible application in transportation, portable power and power generation/cogeneration applications.

There were only a few attempts to develop DMFC stacks/systems in the decades preceding the 1990s. The first attempts to develop methanol fuel cells [23, 24] were carried out by Kordesch and Marko in 1951 on the basis of earlier studies by E. Muller. The DMFC devices initially developed were based on alkaline electrolytes, Ni-based or Pt-Pd-based anodes, and silver cathodes [25, 26]. One of the first DMFC stacks of reasonable power was based on alkaline electrolytes and developed in the 1960s by Murray and Grimes at Allis-Chalmers in 1963 [94]. It was operating at 50 °C and consisted of an aqueous alkaline electrolyte (5 M KOH) Pt-Pd anode and Ag cathode catalysts. A porous Ni sheet was used as the backing layer for the electrode. The stack was composed of 40 cells and provided maximum electrical power of 750 W at 9 V with an average cell power density of about 40 mW/cm². The approach of using concentrated KOH as electrolyte was similar to that of hydrogen-fed alkaline fuel cells developed in the same period for space applications mainly [97–99]. However, the problem of an acid–base reaction between the electrolyte and the reaction product at the anode, that is, CO₂ with formation of potassium carbonate, was quickly recognized. This caused carbonate precipitation inside catalyst pores with occlusion and consequent increase of mass transport constraints. The increase of resistance over time and the need to regenerate the cell (excess of carbonate removal) induced most of the DMFC developers to address their efforts towards the development of DMFCs based on proton conducting electrolytes. Some attempts addressed the use of carbonate electrolytes working at high temperature or anion exchange membranes [95]. Unfortunately, the performance achieved by using the latter approach was not satisfying in the past [95]. In recent years, however, the approach of anion exchange membranes for DMFCs has been reconsidered. The new anionic membranes show proper conductivity values even in the absence of KOH recirculation [91].

DMFC devices based on acidic electrolytes were initially developed in the mid-1960s by leading laboratories such as Shell, Exxon and Hitachi [2]. In all these cases, 1–2 M sulfuric acid was used as the electrolyte and unsupported platinum black was initially used as electrocatalyst. However, studies conducted by researchers at Shell in 1968 selected Pt-Ru as one of the most effective anode electro-catalysts and developed a 300 W prototype [23]. Esso developed a 100 W stack for communication applications [23]. In terms of stack development, another highlight in terms of performance was the development of a 50 W DMFC stack at Hitachi [2]. Interest in developing DMFCs was stimulated in the early 1990s when the sulfuric acid electrolyte was replaced by a solid-state proton conductor (Nafion). There were two significant

effects, (a) an increase in electro-catalytic activity of the electrodes, and (b) improved open circuit potential of the cell due to reduced methanol crossover. In addition, an enhanced oxygen electrode performance was observed because of the replacement of the liquid electrolyte with the perfluorosulfonic acid solid polymer.

Interest in stack development initially focused on transportation applications. Recently, due to the lower efficiency and power densities of DMFCs compared with PEMFCs and the higher projected costs of DMFC power sources (mainly because of the significantly higher noble metal loading), short-term projected applications were directed towards portable applications [4].

Due to the poor anode reaction kinetics and cathode poisoning by methanol crossover, high noble metal loading was initially used in both electrodes (about 10 mg/cm² unsupported catalysts); this decreased progressively up to reach 2 mg cm⁻² and even lower.

After the use of unsupported catalysts, high concentration carbon supported catalysts (e.g., 85% PtRu and 60%Pt) were used in practical stacks [162]. One recent approach involves the use of decorated catalysts with ultra-low Pt loadings [80].

1.4

Current Status of DMFC Technology for Different Fields of Application

1.4.1

Portable Power Sources

The potential market for portable fuel cell systems deals mainly with the energy supply for electronic devices, but it also includes remote and micro-distributed electrical energy generation. Accordingly, DMFC power sources can be used in mobile phones, lap-top computers, as well as energy supply systems for weather stations, medical devices, auxiliary power units (APU) and so on. Direct methanol fuel cells (DMFCs) are promising candidates for these applications because of their high energy density, light weight, compactness, and simplicity as well as their easy and fast recharging [24, 163–165]. Theoretically, methanol has a superior specific energy density (6000 Wh/kg) in comparison with the best rechargeable battery, lithium polymer and lithium ion polymer (theoretical, 600 Wh/kg) systems. This performance advantage translates into more conversation time using cell phones, more time for the use of laptop computers between the replacement of fuel cartridges, and more power available on these devices to support consumer demand. In relation to consumer convenience, another significant advantage of the DMFC over the rechargeable battery is its potential for instantaneous refueling. Unlike rechargeable batteries that require hours to charge a depleted power pack, a DMFC can have its fuel replaced in minutes. These significant advantages make DMFCs an exciting development in the portable electronic devices market.

Several organizations (Table 1.2) are actively engaged in the development of low power DMFCs for cellular phone, laptop computer, portable camera and electronic game applications [104, 163–166]. The primary goal of this research is to develop

Table 1.2 DMFC power sources for portable applications.

Developer	Number/area of cells	Power density	Temperature (°C)	Oxidant	Methanol concentration (M)	Anode catalyst and loading	Electrolyte	Cathode catalyst and loading
Motorola Labs	4 cells (planar stack)/13–15 cm ²	12–27 mW/cm ⁻²	21	Ambient air ^a	1	PtRu alloy, 6–10 mg cm ⁻²	Nafion 117	6–10 mg cm ⁻²
Energy Related Devices	Planar stack	3–5 mW/cm ⁻²	25	Ambient air ^a	1	PtRu alloy	Nafion	Pt
Jet Propulsion Lab	6 cells (flat pack)/6–8 cm ²	6–10 mW/cm ⁻²	20–25	Ambient air ^a	1	PtRu alloy, 4–6 mg cm ⁻²	Nafion 117	Pt, 4–6 mg cm ⁻²
Los Alamos National Labs	5 cells/45 cm ²	300 W/l	60	Air (3–5 times stoichiometry)	0.5	PtRu alloy, 0.8–16.6 mg cm ⁻²	Nafion	Pt, 0.8–16.6 mg cm ⁻²
Forschungszentrum Jülich	40 cells/100 cm ²	45–55 mW/cm ⁻²	50–70	O ₂ (3 atm)	1	PtRu, 2 mg cm ⁻²	Nafion 115	Pt, 2 mg cm ⁻²
GmbH	12 cells (monopolar)/2 cm ²	23 mW/cm ⁻²	25	Ambient air ^a	5 Passive mode	PtRu, 3–8 mg cm ⁻²	Hybrid membrane	Pt, 3–8 mg cm ⁻²
Samsung advanced Institute of Technology	6 cells (bipolar)/52 cm ²	121–207 mW/cm ⁻²	25–50	O ₂ (300 ml min ⁻¹), ambient pressure	2.5 Active mode	PtRu/C	Nafion 115 & 117	Pt black
Korea Institute of Science & Technology	6 cells (monopolar)/6 cm ²	40 mW/cm ⁻²	25	Ambient air ^a	4 Passive mode	PtRu	Nafion 115	Pt
More Energy Ltd.	20 cm ²	60–100 mW/cm ⁻²	25	Ambient air ^a	30–5%	PtRu	Liquid electrolyte	Pt
Institute for Fuel Cell Innovation, Canada	3 cells (monopolar)	8.6 mW/cm ⁻²	25	Ambient air ^a	2 Passive mode	80% PtRu, 4 mg cm ⁻²	Nafion 117	Pt black, 4 mg cm ⁻²

(Continued)

Table 1.2 (Continued)

Developer	Number/area of cells	Power density	Temperature (°C)	Oxidant	Methanol concentration (M)	Anode catalyst and loading	Electrolyte	Cathode catalyst and loading
University of Connecticut, USA	4 cells/18–36 cm ²	30 mW/cm ²	25	Ambient air ^a	2–5 Passive mode	PtRu alloy, 7 mg cm ⁻²	Nafion 117	Pt, 6.5 mg cm ⁻²
Honk Kong University	Single cell/4 cm ²	28 mW/cm ²	22	Ambient air ^a	4 Passive mode	PtRu, 4 mg cm ⁻²	Nafion 115	40% Pt/C, 2 mg cm ⁻²
The Pennsylvania State University, USA	Single cell/5 cm ²	93 mW/cm ²	85	Air (700 ml min ⁻¹ and 15 psig)	2 Active mode	PtRu, 4 mg cm ⁻²	Nafion 112	40% Pt/C, 1.3 mg cm ⁻²
Harbin Institute of Technology	Single cell	9 mW/cm ²	30	Ambient air ^a	2 Passive mode	40% PtRu/C, 2 mg cm ⁻²	Nafion 117	40% Pt/C, 2 mg cm ⁻²
Tel-Aviv University, Israel	Flat fuel cell/6 cm ²	12.5 mW/cm ²	25	Ambient air ^a	1–6 in H ₂ SO ₄ Passive mode	PtRu, 5–7 mg cm ⁻²	NP-PCM	Pt, 4–7 mg cm ⁻²
Tekion Inc., USA	Single cell/5 cm ²	65 mW/cm ²	60	Ambient air ^a	2 Active mode	PtRu	Nafion	Pt
University of California, USA	μ-Single cell/1.625 cm ²	16–50 mW/cm ²	25–60	Air (88 ml min ⁻¹)	2 Active mode	PtRu, 4–6 mg cm ⁻²	Nafion 112	40% Pt/C, 1.3 mg cm ⁻²
Waseda University, Japan	μ-Single cell/0.018 cm ²	0.8 mW/cm ²	25	O ₂ (10 μl min ⁻¹) sat. in H ₂ SO ₄	2	PtRu, 2.85 mg cm ⁻²	Nafion 112	Pt, 2.4 mg cm ⁻²
Institute of Microelectronic of Barcelona-CNM, Spain	μ-Single cell	11 mW/cm ²	25	Ambient air ^a	4–5 Passive mode	PtRu, 4 mg cm ⁻²	Nafion 117	Pt, 4 mg cm ⁻²
Yonsei University, Korea	Multi-cell structure (monopolar)	33 mW/cm ²	80	O ₂ (30 ml min ⁻¹)	2	60% PtRu/C, 4 mg cm ⁻²	Nafion 117	60% Pt/C, 4 mg cm ⁻²
CNR-ITAE, Italy	3 cells (monopolar)/4 cm ²	20 mW/cm ²	21	Ambient air ^a	5 Passive mode	PtRu, 4 mg cm ⁻²	Nafion 117	Pt, 4 mg cm ⁻²

^aAmbient air usually refers to the air breathing mode.

proof of concept DMFCs capable of replacing high performance rechargeable batteries in the US\$ 6-billion portable electronic devices market.

Motorola Labs—Solid State Research Center, USA, [4] in collaboration with Los Alamos National Laboratory (LANL), USA, is actively engaged in the development of low power DMFCs (greater than 300 mW) for cellular phone applications [167]. Motorola has recently demonstrated a prototype of a miniature DMFC based on a MEA set between ceramic fuel delivery substrates [4]. Motorola used their proprietary low temperature co-fired ceramic (LTCC) technology to create a ceramic structure with embedded microchannels for mixing and delivering methanol/water to the MEA and exhausting the by-product CO_2 . The active electrode area for a single cell was approximately $3.5\text{--}3.6\text{ cm}^2$. In the stack assembly, four cells were connected in series in a planar configuration with an MEA area of $13\text{--}14\text{ cm}^2$; the cells exhibited average power densities between $15\text{--}22\text{ mW cm}^{-2}$. Four cells (each cell operating at 0.3 V) were required for portable power applications because DC/DC converters typically require 1 V to efficiently step up to the operating voltage for electronic devices. Improved assembly and fabrication methods have led to peak power densities greater than 27 mW cm^{-2} . Motorola is currently improving their ceramic substrate design to include micro-pumps, methanol concentration sensors and supporting circuitry for second generation systems.

Energy Related Devices Inc. (ERD), USA, is working in alliance with Manhattan Scientific Inc., (USA) to develop miniature fuel cells for portable electronic applications [163, 168]. A relatively low-cost sputtering method, similar to the one used by the semiconductor industry for the production of microchips, was used for the deposition of electrodes (anode and cathode) on either side of a microporous plastic substrate; the micropores (15 nm to $20\text{ }\mu\text{m}$) are etched into the substrate using nuclear particle bombardment. Micro-fuel arrays with external connections in series were fabricated precisely and had a thickness of about a millimeter. The principal advantages of the cell include the high use of catalyst, controlled pore geometry, low-cost materials and minimum cell thickness and weight. A MicroFuel Cell[®] was reported to have achieved a specific energy density of 300 Wh/kg using methanol/water and air as the anodic and cathodic reactants, respectively [4].

The anode design that was developed by MicroFuel Cell has represented a critical new advance in the development of a cost-effective pore-free electrode that is permeable to only hydrogen ions [4]. This increases the efficiency of a methanol fuel cell because it blocks the deleterious effect of methanol crossover across the membrane. The first layer of the anode electrode formed a plug in the pore of the porous membrane; an example is a 20 nm thick palladium metal film on a Nuclepore[®] filter membrane with 15 nm diameter pores. The second layer (platinum) was deposited to mitigate the hydration induced cracking that occurs in many of these films. The third layer was deposited over the structural metal film and was the most significant layer because it needed to be catalytically active to methanol and capable of accepting hydrogen ions. An alternative method of forming the electrode was to include powder catalyst particles (Pt/Ru on activated carbon) on the surface of the metal films to enhance the catalytic properties of the electrode. Between the anode electrode and the cathode electrode was the electrolyte filled pore, the cell

interconnect and the cell break. In the pores of the membrane the electrolyte (Nafion) was immobilized and ERD claims this collimated structure results in improved protonic conductivity. Each of the cells was electrically separated from the adjacent cells by cell breaks, useless space occupying the central thickness of the etched nuclear particle track plastic membrane. The cathode was formed by sputter depositing a conductive gold film onto the porous substrate first, followed by a platinum catalyst film. The electrode was subsequently coated with a Nafion film. Alternatively, platinum powder catalyst particles were added to the surface of the electrode via an ink slurry of 5% Nafion solution. A hydrophobic coating was then deposited onto this Nafion layer in order to prevent liquid product water from condensing on the surface of the air electrodes. ERD developed a novel configuration to use their fuel cell as a simple charger in powering a cellular phone. The fuel cell was configured into a plastic case that was in close proximity to a rechargeable battery. Methanol was delivered to the fuel cell via fuel needle and fuel ports, which allowed methanol to wick or evaporate into the fuel manifold, and be delivered to the fuel electrodes.

The Jet Propulsion Laboratory (JPL), USA, has been actively engaged in the development of 'miniature' DMFCs for cellular phone applications over the last 2 years [165, 169]. According to their analysis, the power requirement of cellular phones during the standby mode is small and steady at 100–150 mW. However, under operating conditions the power requirement fluctuates between 800–1800 mW. In the JPL DMFC, the anode was formed from Pt-Ru alloy particles, either as fine metal powders (unsupported) or dispersed on high surface area carbon. Alternatively, a bimetallic powder made up of submicron Pt and Ru particles was reported to give better results than the Pt-Ru alloy. Another method describes the sputter-deposition of a Pt-Ru catalyst onto the carbon substrate. The preferred electrolyte was Nafion 117; however, other materials may be used to form proton-conducting membranes. Air was delivered to the cathode by natural convection and the cathode is prepared by applying a platinum ink to a carbon substrate. Another component of the cathode was the hydrophobic Teflon polymer used to create a three-phase boundary and to achieve efficient removal of water produced by the electroreduction of oxygen. Sputtering techniques can also be used to apply the platinum catalyst to the carbon support. The noble metal loading in both electrodes was $4\text{--}6\text{ mg cm}^{-2}$. The MEA was prepared by pressing the anode, electrolyte and cathode at $8.62 \times 10^6\text{ Pa}$ and 146°C . JPL opted for a 'flat-pack' instead of the conventional bipolar plate design, but this resulted in higher ohmic resistance and non-uniform current distribution. In this design the cells were externally connected in series on the same membrane, with through membrane interconnect and air electrodes on the stack exterior. Two 'flat packs' were deployed in a back to back configuration with a common methanol feed to form a 'twin-pack' [4]. Three 'twin-packs' in series were needed to power a cellular phone. In the stack assembly, six cells were connected in series in a planar configuration, which exhibited average power densities between $6\text{--}10\text{ mW cm}^{-2}$. The fuel cell was typically run at ambient air, $20\text{--}25^\circ\text{C}$ with 1 M methanol. Improvements in the configuration and interconnect design have resulted in improved performance characteristics of the six cell 'flat-pack' DMFC. Based on the results of current technology, the JPL

researchers predict that a 1 W DMFC power source with the desired specifications for weight and volume and an efficiency of 20% for fuel consumption can be developed for a 10 h operating time, prior to replacement of methanol cartridges.

As stated earlier, Los Alamos National Laboratory (LANL) has been in collaboration with Motorola Labs—Solid State Research Center to produce a ceramic based DMFC, which provides better than 10 mW cm^{-2} power density. LANL researchers have also been engaged in a project to develop a portable DMFC power source capable of replacing the 'BA 5590' primary lithium battery used by the US Army in communication systems [170]. A 30-cell DMFC stack with electrodes having an active area of 45 cm^2 was constructed, an important feature of which was the narrow width (i.e., 2 mm) of each cell. MEAs were made by the decal method, that is, thin film catalysts bonded to the membrane resulting in superior catalyst use and overall cell performance. An anode catalyst loading of Pt between $0.8\text{--}16.6 \text{ mg cm}^{-2}$ in unsupported PtRu and carbon supported PtRu were used. A highly effective flow field for air made it possible to use a dry air blower to operate the cathode at three to five times stoichiometry. The stack temperature was limited to 60°C and the air pressure was 0.76 atm, which is the atmospheric pressure at Los Alamos (altitude of 2500 m). To reduce the crossover rate, methanol was fed into the anode chamber at a concentration of 0.5 M. Since water management becomes more difficult at such low methanol concentrations, a proposed solution was to return water from the cathode exhaust to the anode inlet, while using a pure methanol source and a methanol concentration sensor to maintain the low methanol concentration feed to the anode. The peak power attained in the stack near ambient conditions was 80 W at a stack potential of 14 V and approximately 200 W near 90°C . From this result, it was predicted that this tight packed stack could have a power density of 300 W/l. An energy density of 200 Wh/kg was estimated for a 10 h operation, assuming that the weight of the auxiliaries is twice the weight of the stack.

Forschungszentrum Julich GmbH (FJG), Germany, has developed and successfully tested a 40-cell 50 W DMFC stack [171]. The FJG system consisted of the cell stack, a water/methanol tank, a pump, and ventilators as auxiliaries. The stack was designed in the traditional bipolar plate configuration, which results in lower ohmic resistances but heavier material requirements. To circumvent the weight limitations current collectors were manufactured from stainless steel (MEAs were mounted between the current collectors) and were inserted into plastic frames to reduce the stack's weight. The 6 mm distance between MEAs (cell pitch) revealed a very tight packaging of the stack design. Each frame carried two DMFC single cells that were connected in series by external wiring [4]. MEAs were fabricated in house with an anode loading of 2 mg cm^{-2} PtRu black, catalyst loading of 2 mg cm^{-2} Pt black and cell area of 100 cm^2 for each of the 40 cells. At the anode a novel construction allowed the removal of CO_2 by convection forces at individual cell anodes. The conditions for running the stack were 1 M methanol, 60°C and 3 bar O_2 which led to peak energy densities of $45\text{--}55 \text{ mW cm}^{-2}$. The cathode used air at ambient or elevated pressures; when the stack operated at temperatures above 60°C the air was fed into the cathode by convection forces. Recent developments include a three-cell short stack design which has reduced the cell pitch to only 2 mm. The individual cell area of this design

is larger, 145 cm^2 , than the previous prototype's and although it is not air breathing, it works with low air stoichiometric rates (more efficient cathodic flow distribution structure).

Samsung Advanced Institute of Technology (SAIT), South Korea, has developed a small monopolar DMFC cell pack (2 cm^2 , 12 cells, CO_2 removal path, 5–10 M methanol, air breathing and room temperature) of 600 mW for mobile phone applications [172, 173]. Unsupported PtRu and Pt catalysts were coated onto a diffusion electrode of porous carbon substrate of anode and cathode, respectively. In order to allow methanol wicking and air breathing, short and capillary paths were designed as the diffusion layer. Catalyst loading was around $3\text{--}8 \text{ mg cm}^{-2}$. Ternary alloys with low binding energy for CO adsorption were investigated with the aid of quantum chemical methods. Inorganic phase dispersed hybrid membranes based on Nafion or Co-PTFS were prepared and applied to the MEA to attain high fuel efficiency and prevent a voltage loss on the cathode. A monopolar structure was investigated; 12 cells of 2 cm^2 were connected in series within a flat cell pack. Fuel storage was attached to the cell pack and power characteristics were measured on the free-standing basis without any fuel and air supply systems. A power density of 50 mW cm^{-2} at 0.3 V was achieved in the normal diffusion electrode design. For application in portable electronic devices, methanol wicking and air breathing electrodes were required. A monopolar design consisting of 12-cell flat pack was assembled and tested. Each cell had an active area of 2 cm^2 and the pack was equipped with a path for CO_2 removal at the anode. The maximum power output was 560 mW at 2.8 V, close to that required by the cellular phone. For this cell pack condition with small active area, the unit cell power density was 23 mW cm^{-2} .

The Korea Institute of Energy Research (KIER, South Korea) has developed a 10 W DMFC stack (bipolar plate, graphite construction) fabricated with six single cells with a 52 cm^2 electrode area [174]. The stack was tested at $25\text{--}50^\circ\text{C}$ using 2.5 M methanol, supplied without a pumping system, and O_2 at ambient pressure, at a flow rate of 300 cc min^{-1} . The maximum power densities obtained in this system were 6.3 W (121 mW cm^{-2}) at 87 mA cm^{-2} at 25°C and 10.8 W (207 mW cm^{-2}) at 99 mA cm^{-2} at 50°C . MEAs using Nafion 115 and 117 were formed by hot pressing and the electrodes were produced from carbon supported Pt-Ru metal powders and Pt-black for anode and cathode electrodes, respectively.

More Energy Ltd. (MEL), Israel, a subsidiary of Medis Technologies Ltd. (MDTL, USA), is developing direct liquid methanol (DLM) fuel cells (a hybrid PEM/DMFC system) for portable electronic devices [175]. The key features of the DLM fuel cell are as follows: (i) the anode catalyst extracts hydrogen from methanol directly, (ii) the DLM fuel cell uses a proprietary liquid electrolyte that acts as the membrane in place of a solid polymer electrolyte (Nafion) and (iii) novel polymers and electrocatalysts enable the fabrication of more effective electrodes. The company's fuel cell module delivers approximately 0.9 V and 0.24 W at 60% of its nominal capacity for eight hours. This translates into energy densities of approximately 60 mW cm^{-2} with efforts underway to improve that result to 100 mW cm^{-2} . The high power capacity of the cell is attributed to the proprietary electrode's ability to efficiently oxidize methanol. In addition Medis claims the use of high concentrations of

methanol (30%) in its fuel stream with plans for increasing that concentration to 45% methanol.

At the Institute for Fuel Cell Innovation in Vancouver, Canada, a passive (air breathing) planar three-cell DMFC stack was designed, fabricated and tested [176]. In order to maintain design flexibility, polycarbonate was chosen for the plate material whereas 304 stainless steel mesh current collectors were used. In order to test the DMFC in different electrical cell configurations (single cell, multiple cells connected in series or in parallel), a stainless threaded rod was attached to each mesh current collector on the anode and cathode sides to allow for an external electrical connection. Commercial electrodes from E-TEK were used. The catalyst loading was 4 mg cm^{-2} and consisted of an 80% Pt: Ru alloy on optimized carbon. Unsupported Pt black with a 4 mg cm^{-2} loading was used for the cathode. A Nafion 117 membrane was used as the electrolyte. A power density of 8.6 mW cm^{-2} was achieved at ambient temperatures and under passive operation. Stacks with a parallel connection of the single cells showed a significantly lower performance than in a series configuration. High electrical resistance proved to be the dominant factor in the low performance as a result of the stainless steel hardware and poor contact between the electrodes and current collectors.

At the University of Connecticut, USA, the group of Z. Guo and A. Faghri developed a design for planar air breathing DMFC stacks [177]. This design incorporated a window-frame structure that provided a large open area for more efficient mass transfer with modular characteristics, making it possible to fabricate components separately. The current collectors had a niobium expanded metal mesh core with a platinum coating. Two four-cell stacks, one with a total active area of 18 cm^2 and the other with 36 cm^2 , were fabricated by inter-connecting four identical cells in series. These stacks were suitable for portable passive power source application. Peak power outputs of 519 and 870 mW were achieved in the stacks with active areas of 18 and 36 cm^2 , respectively. A study of the effects of methanol concentration and fuel cell self-heating on fuel cell performance was carried out. Power density reached its highest value in this investigation when 2 and 3 M methanol solutions were used.

At the Honk Kong University of Science and Technology, China, the group of R. Chen and T.S. Zhao [178–181] studied the effect of methanol concentration on the performance of a passive DMFC single cell. They found that cell performance improved substantially with an increase in methanol concentration; a maximum of power density of 20 mW cm^{-2} was achieved with 5.0 M methanol solution. The measurements indicated that better performance with higher methanol concentrations was attributed mainly to the increase in the cell's operating temperature, a result of the exothermic reaction between permeated methanol and oxygen on the cathode. This finding was subsequently confirmed by the fact that cell performance decreased when the cell that was running with higher methanol concentrations, cooled down to room temperature. Moreover, they proposed a new MEA, in which the conventional cathode gas diffusion layer (GDL) is eliminated while using a porous metal structure made of a metal foam for transporting oxygen and collecting current. They showed theoretically that the new MEA [180] and the porous current collector enabled a

higher mass transfer rate of oxygen and, thus, better performance. The improved performance of the porous current collector was attributed to the increased operating temperature, a result of the lower effective thermal conductivity of the porous structure and its fast water removal, a result of the capillary action [181].

Another group at the Honk Kong University, H.F. Zhang *et al.* [182], reported on a flexible graphite-based integrated anode plate for DMFCs operating at high methanol feed concentrations under active mode. This anode structure made of flexible graphite materials not only played a dual role for the liquid diffusion layer and flow field plate but also served as a methanol blocker by decreasing methanol flux at the interface of the catalyst and membrane electrolyte. DMFCs incorporating this new anode structure exhibited a much higher open circuit voltage (OCV) (0.51 V) than that (0.42 V) of a conventional DMFC at a 10 M methanol feed. Cell polarization data showed that this new anode structure significantly improved cell performance at high methanol concentrations (e.g., 12 M or above).

M.A. Abdelkareem and N. Nakagawa from Gunma University, Japan, [183] studied the effect of oxygen and methanol supply modes (passive and active supplies of methanol, and air-breathing and flowing supplies of oxygen) on the performance of a DMFC. The experiments were carried out with and without a porous carbon plate (PCP) under ambient conditions using methanol concentrations of 2 M for the MEA without PCP and 16 M for that with PCP. For the conventional MEA, flowing oxygen and methanol were essential to stabilize the cell's performance, avoiding flooding at the cathode and depletion of methanol at the anode. As a result of flowing oxygen, methanol and water fluxes, the conventional MEAs performance increased more than double compared with that obtained from the air-breathing cell. For the MEA with a porous plate, MEA/PCP, the flow of oxygen and methanol had no significant effect on cell performance, because porous carbon plate, PCP, prevented the cathode from flooding by reducing the mass transport through the MEA.

The effect of operating conditions on the energy efficiency of a small passive DMFC was analyzed by D. Chu and R. Jiang from the US Army Research Laboratory, Adelphi, USA [184]. Both faradaic and energy conversion efficiencies decreased significantly with increasing methanol concentration and environmental temperatures. The faradaic conversion efficiency was as high as 94.8%, and the energy conversion efficiency was 23.9% at an environmental temperature low enough (10 °C) and under a constant voltage discharge at 0.6 V with 3 M methanol for a DMFC bi-cell using Nafion 117 as the electrolyte. Although higher temperatures and higher methanol concentrations allowed higher discharge power, they resulted in considerable losses of faradaic and energy conversion efficiencies using the Nafion electrolyte membrane.

Various research groups have focused their attention on the critical aspects which need to be addressed for the design a high-performance DMFC. These are CO₂ bubble flow at the anode [185] and water flooding at the cathode [186]. Lu and Wang from Pennsylvania State University, USA, [187] developed a 5 cm² transparent cell to visualize these phenomena *in situ*. Two types of MEA based on Nafion 112 were used to investigate the effects of backing pore structure and wettability on cell polarization characteristics and two-phase flow dynamics. One employed carbon paper backing

material and the other, carbon cloth. Experiments were performed with various methanol feed concentrations. The transparent fuel cell reached a peak power of 93 mW cm^{-2} at 0.3 V, using a Toray carbon-paper based MEA with 2 M methanol solution preheated to 85°C . For the hydrophobic carbon paper backing, it was observed that CO_2 bubbles nucleated at certain locations and formed large and discrete bubble slugs in the channels. For the hydrophilic carbon cloth backing, the bubbles were produced more uniformly and were smaller in size. It was thus shown that the anode backing layer of uniform pore size and more hydrophilicity was preferable for gas management in the anode. Flow visualization of water flooding on the cathode side of the DMFC was also carried out. It showed that the liquid droplets appeared more easily on the surface of carbon paper due to its reduced hydrophobicity at elevated temperatures. For the single-side ELAT carbon cloth, liquid droplets tended to form in the corner between the current collecting rib and GDL since ELAT is highly hydrophobic and the rib (stainless steel) surface is hydrophilic. Even if this study was performed at a relatively high temperature (85°C), a basic understanding of its results is indispensable for portable DMFC design and optimization.

Lai *et al.* [188] investigated the long-term discharge performance of passive DMFCs at different currents with different cell orientations. Water produced in the cathode was observed from the photographs taken by a digital camera. The results revealed that the passive DMFCs with anodes facing upward showed the best long-term discharge performance at high currents. A few independent water droplets accumulated in the cathode when the anode faced upward. Instead, in the passive DMFC with vertical orientation, a large amount of the water produced flowed down along the surface of current collector. The passive DMFC with vertical orientation performed relatively well at low currents. It was concluded that the cathode produced less water in a certain period of time at lower currents. In addition, the rate of methanol crossover in the passive DMFC with the anode facing upward was relatively high, which lead to a more rapid decrease of methanol concentration in the anode. The passive DMFC with the anode facing downward resulted in the worst performance because it was very difficult to remove CO_2 bubbles produced in the anode.

Water loss and water recycling in direct-methanol fuel cells (DMFCs) are significant issues that affect the complexity, volume and weight of the system and become of greater concern as the size of the DMFC decreases. A research group at Tel-Aviv University, Israel, [189] developed a flat micro DMFC in a plastic housing with a water-management system that controlled the flux of liquid water through the membrane and the loss of water during operation. These cells contained a nanoporous proton-conducting membrane (NP-PCM). Methanol consumption and water loss were measured during operation in static air at room temperature for up to 900 h. Water flux through the membrane varied from negative to zero to positive values as a function of the thickness and the properties of the water-management system. The loss of water molecules (to the air) per molecule of methanol consumed in the cell reaction (defined as the w factor) varied from 0.5 to 7. When w was equal to 2 (water flux through the membrane was equal to zero), there was no need to add water to the DMFC and the cell was operating under water-neutral conditions. On the other hand, when W was smaller than 2, it was necessary to remove water from the cell and when

it was larger than 2, water was added. The cell showed stable operation up to 900 h and its maximum power was 12.5 mW cm^{-2} .

At the Korea Institute of Science and Technology (KIST), Kim *et al.* [190] developed passive micro-DMFCs with capacities under 5 W to be used as portable power sources. Research activities were focused on the development of MEAs and the design of monopolar stacks operating under passive and air-breathing conditions. The passive cells showed many unique features, much different from the active ones. Single cells with an active area of 6 cm^2 showed a maximum power density of 40 mW cm^{-2} at 4 M of methanol concentration at room temperature. A six-cell stack with a total active area of 27 cm^2 was constructed in a monopolar configuration and it produced a power output of 1000 mW (37 mW cm^{-2}). Effects of experimental parameters on performance were also examined to investigate the operational characteristics of single cells and monopolar stacks.

Tekion Inc., Champaign, USA, [191] has developed an advanced air breathing DMFC for portable applications. A novel MEA was fabricated to improve the performance of air-breathing DMFCs. A diffusion barrier on the anode side was designed to control methanol transport to the anode catalyst layer, thus suppressing methanol crossover. A catalyst coated membrane with a hydrophobic gas diffusion layer on the cathode side was employed to improve the oxygen mass transport. The advanced DMFC achieved a maximum power density of 65 mW cm^{-2} at 60°C with 2 M methanol solution. The value was nearly twice that of a commercial MEA. At 40°C , the power densities operating with 1 and 2 M methanol solutions were over 20 mW cm^{-2} with a cell potential at 0.3 V.

Pennsylvania State University together with the University of California in Los Angeles, USA, [192] developed a silicon-based micro-DMFC for portable applications. Anode and cathode flow-fields with a channel and rib width of $750 \mu\text{m}$ and a channel depth of $400 \mu\text{m}$ were fabricated on Si wafers using microelectromechanical system (MEMS) technology. A MEA was specially fabricated to mitigate methanol crossover. This MEA features a modified anode backing structure in which a compact microporous layer is added to create an additional barrier to methanol transport, thereby reducing the rate of methanol crossing over the polymer membrane. The cell with the active area of 1.625 cm^2 was assembled by sandwiching the MEA between two micro-fabricated Si wafers. Extensive cell polarization testing demonstrated a maximum power density of 50 mW cm^{-2} using 2 M methanol feed at 60°C . When the cell operated at room temperature, the maximum power density was about 16 mW cm^{-2} with both a 2 and 4 M methanol feed. It was further observed that the present μDMFC still performed reasonably with 8 M methanol solution at room temperature.

The Waseda University, Japan, proposed a new concept for μDMFC (0.018 cm^2 active area) based on MEMS technology [193]. The μDMFC was prepared using a series of fabrication steps from a micro-machined silicon wafer including photolithography, deep reactive ion etching, and electron beam deposition. The novelty of this structure is that anodic and cathodic micro-channels arranged in plane were fabricated, dissimilar to the conventional bipolar structure. The first objective of the experimental trials was to verify the feasibility of this novel structure on the basis of

MEMS technology. The methanol anode and oxidant cathode were prepared by electroplating either Pt-Ru or Pt and Pt, respectively, onto the Ti/Au electrodes. A Nafion 112 membrane was used as the electrolyte. The performance of the μ DMFC was assessed at room temperature using 2 M $\text{CH}_3\text{OH}/0.5$ M $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ as the fuel and $\text{O}_2\text{-sat.}/0.5$ M $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ as the oxidant. The fuel supply was by means of a microsyringe pump connected to the μ DMFC unit. The OCV for the Pt cell was 300 mV while it was 400 mV for the Pt-Ru cell. The maximum power density was 0.44 mW cm^{-2} at 3 mA cm^{-2} at the Pt electrode while, maximum power density reached 0.78 mW cm^{-2} at 3.6 mA cm^{-2} for the cell with the Pt-Ru anode. The reason for this low performance could be due to a non-optimal composition of Pt-Ru anode catalyst.

The Institute of Microelectronics of Barcelona-CNM (CSIC), Spain, presented a passive and silicon-based micro DMFC [194]. The device was based on a hybrid approach composed of a commercial MEA consisting of a Nafion 117 membrane with a 4.0 mg cm^{-2} Pt-Ru catalyst loading on the anode side and 4.0 mg cm^{-2} Pt on the cathode (E-TEK ELAT) sandwiched between two microfabricated silicon current collectors. The silicon plates were provided with an array of vertical squared channels, 300 micrometers in depth, that covered an area of $5.0 \times 5.0 \text{ mm}$. In order to provide the current collectors with an appropriate electrical conductivity, a 150 nm Ti/Ni sputtered layer was deposited covering the front side of the wafer. This conductive layer was used as a seed layer for the 4 mm thick Ni layer that was electrodeposited afterwards. This layer enhanced the electrical conductivity of the current collector; it was then covered by a thin Au layer to prevent oxidation. The cell was equipped with a 100 ml methanol reservoir. The cell was tested at room temperature and different methanol concentrations. It was found that methanol concentration had little impact on the fuel cell's maximum power density, which reached a value of around 11 mW cm^{-2} and was comparable to values reported in the literature for larger passive and stainless-steel fuel cells.

A research group at Yonsei University, Korea, developed a DMFC on printed circuit board (PCB) substrates by means of a photolithography process [195]. The effects of the channel pattern, channel width and methanol flow rate on the performance of the fabricated DMFC were evaluated over a range of flow-channel widths from 200 to $400 \mu\text{m}$ and flow rates of methanol from 2 to 80 ml min^{-1} . A μ DMFC with a cross-stripe channel, zig-zag and serpentine-type patterns. A single cell with a $200 \mu\text{m}$ wide channel delivered a maximum power density of 33 mW cm^{-2} when using 2 M methanol feed at 80°C .

Our group (CNR-ITAE, Messina, Italy) investigated two designs of flow-fields/current collectors for a passive DMFC monopolar three-cell stack (Figure 1.20) [196]. The first design (A) consisted of two plastic plates covered by thin gold film current collectors with a distribution of holes through which methanol (from a reservoir) and air (from the atmosphere) could diffuse into the electrodes. The second design (B) consisted of thin gold film deposited on the external borders of the fuel and oxidant apertures in the PCBs where electrodes were placed in contact. A 21 ml methanol reservoir with 3 small holes in the upper part to fill the containers and to release the produced CO_2 , was attached to the anode side (Figure 1.21). The MEAs for the two stack designs (3 cells) were manufactured by assembling, simultaneously, three sets

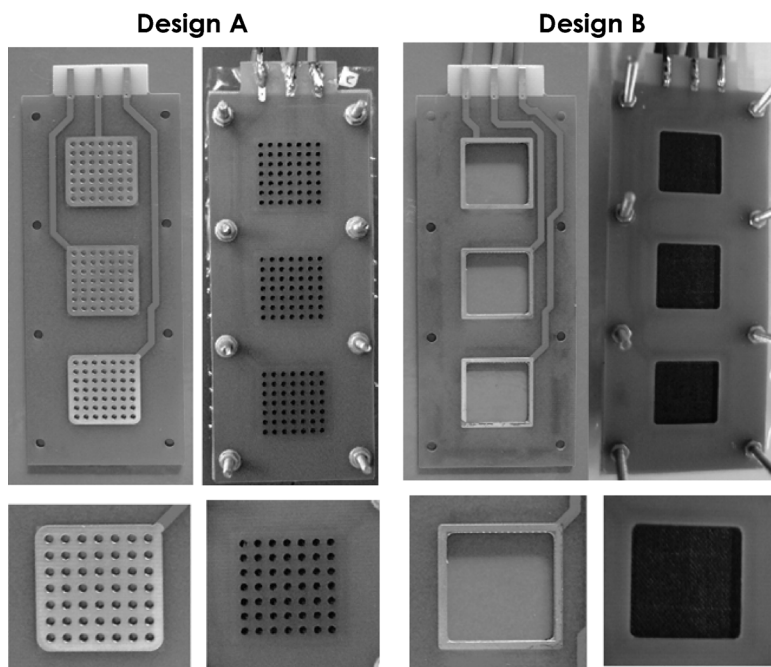


Figure 1.20 Pictures of two different monopolar plates for application in a DMFC three-cell stack operating under passive mode.

of anode and cathode pairs onto the membrane (Figure 1.21b); afterwards they were sandwiched between two PCBs. The geometrical area of each electrode was 4 cm^2 and the total area of the stack was 12 cm^2 . The cells were connected in series externally through the electric circuit. The electrochemical characterization was carried out varying the catalyst loading and methanol concentration. A 4 mg cm^{-2} Pt loading provided the best electrochemical results in the presence of unsupported catalysts. This appeared to be the best compromise between electrode thickness and the amount of catalytic sites. Similar performances in terms of maximum power were recorded for the two designs whereas better mass transport characteristics were obtained with design B. On the contrary, OCV and stack voltage at low currents were higher for design A as a consequence of lower methanol crossover. Maximum power of 220–240 mW was obtained at ambient temperatures for the three-cell stack with 5 M methanol corresponding to a power density of about 20 mW cm^{-2} . An investigation of the discharge behavior of the two designs was carried out (Figure 1.22). A longer discharge time (17 h) with unique MeOH charge was recorded with design B at 250 mA compared with design A (5 h). This was attributed to easier CO_2 removal from the anode and better mass transport properties. In fact, in design A, CO_2 did not escape easily from the anode, which hindered methanol diffusion to the catalytic sites by natural convection. When the small stack based on A design was mechanically agitated, the effect of this forced convection increased the discharge time.

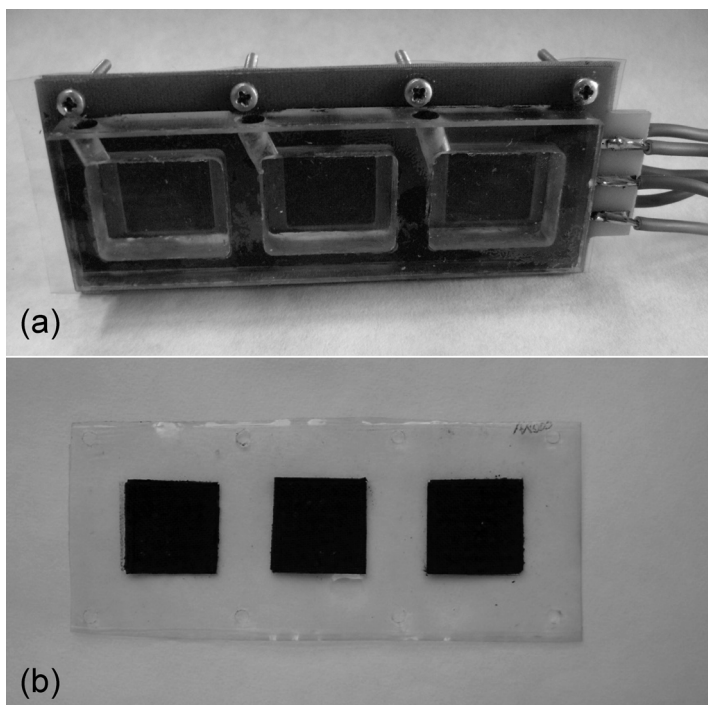


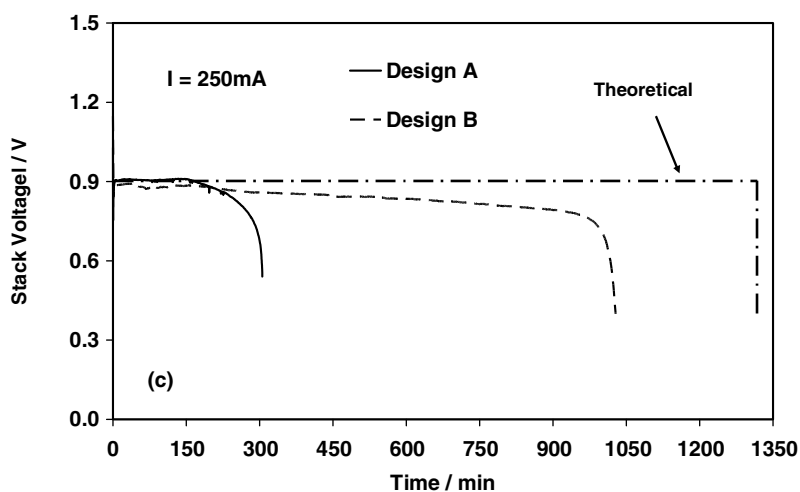
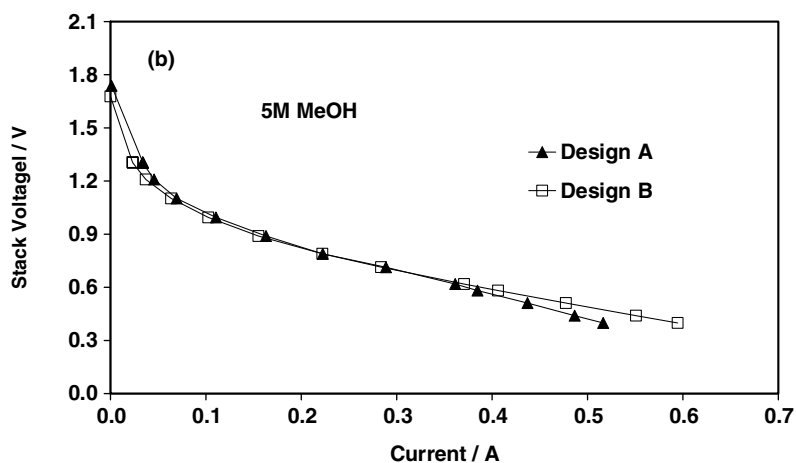
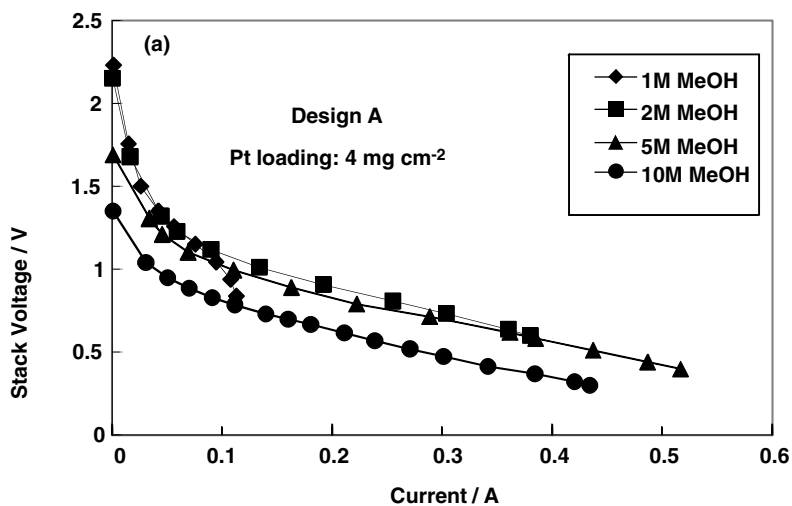
Figure 1.21 Pictures of the DMFC design B used for a three-cell stack (a) and MEA formed by a single membrane and three couples of electrodes (b).

A recent European project called Morepower addressed the development of a low cost, low temperature (30–60 °C) portable DMFC device of compact construction and modular design. The project was coordinated by GKSS (Germany) and included, as partners, Solvay, Johnson Matthey, CNR-ITAE, CRF, Polito, IMM and NedStack. The electrical characteristics of the device were 40 A, 12.5 V (total power 500 W). Single cell performance approached 0.2 A cm^{-2} at about 0.5 V/cell at 60 °C and atmospheric pressure [21]. Several new membranes were investigated in this project. One of the most promising was a low-cost proton exchange membrane produced by Solvay using a radiochemical grafting technology (Morgane CRA type membrane) which showed a suitable compromise in terms of reduced methanol crossover and suitable ionic conductivity [111]. Inorganic filler-modified S-PEEK membranes were also developed in the same project by GKSS (Germany) to reduce the permeability to alcohol while maintaining high proton conductivity [111].

1.4.2

Transportation

Though the application of fuel cells in transportation has drawn great enthusiasm and stimulated interest since the late 1970s, it is still considered a formidable venture



if fuel cell powered vehicles are to compete with the conventional internal combustion and diesel engine powered vehicles. This is not surprising since fuel cell development is still in its infancy, compared with the highly advanced IC or diesel engine technology which has taken over 100 years to reach high levels of performance with respect to operating characteristics (start-up time, acceleration, lifetime, considerable reduction in level of environmental pollutants, etc.). The impetus for developing battery and fuel cell-powered vehicles derived from the energy crisis in 1973; in the late 1980s and 1990s, environmental legislation to reduce greenhouse gas emissions provided further stimulation. The United States Partnership for new Generation of Vehicles Program was implemented to make 'Quantum Jumps' in the performance of automobiles, such as (i) tripling efficiency of fuel consumption, (ii) reaching a range of 500 km between refueling, and (iii) ultra low or zero emissions of pollutants, while remaining cost competitive with the current automobile technology [2, 4]. Similar objectives have been addressed in European Research Programs FP5 and FP6. The only types of vehicle that have the potential of reaching these goals are IC or diesel engine/battery and fuel cell/battery hybrid vehicles. The former type of power plants are more advanced than the latter and, in fact, Toyota and Honda have commercialized IC engine/battery hybrid vehicles in the last few years. Other companies have also started commercialization of diesel engine/battery hybrids [2, 4]. Nowadays, however, due to the considerable progress made in this field, DMFCs appear much more ready for application in electrotraction systems. With the development of highly active catalysts and appropriate ionomeric membranes, these systems have been successfully operated at temperatures close to or above 100 °C, allowing the achievement of interesting performances [104, 170]. In particular, it was shown that the overall efficiency of recent DMFC devices is comparable or superior to the combination of reformer-H₂:air fuel cells [171]. These aspects, together with the intrinsic advantages of methanol fuel cells with respect to hydrogen-consuming devices, which are due mainly to the liquid fuel feed and the absence of a cumbersome reformer, would claim for a close demonstration of DMFCs in electric vehicles. Yet, DMFC devices may be employed in a fuel cell vehicle if they fulfill specific requirements in terms of power density, durability, cost and system efficiency. Accordingly, more active catalysts need to be developed together with high temperature and crossover resilient membranes. In addition, a great deal of attention should be devoted to bipolar plates and flow-fields both in terms of design and materials.

Practically all worldwide activities on fuel cell/battery hybrid vehicles (Daimler/Chrysler/Ballard, Ford, Toyota, General Motors/Opel, Honda, Volkswagen, Fiat) are essentially on PEMFC or PEMFC/battery hybrid vehicles [2, 4]. In several demonstration vehicles, hydrogen was the fuel carried on board, mostly as a compressed gas



Figure 1.22 Polarization curves for the design A stack with a Pt loading of 4 mg cm⁻² on each electrode at different methanol concentrations (a), comparison between the polarization curves obtained with the two different designs with a Pt loading of 4 mg cm⁻² on each electrode and 5 M methanol solution (b), and chrono-potentiometric results at 250 mA obtained with the two designs using a Pt loading of 4 mg cm⁻² and 5 M methanol solution (c).

or as a metal hydride. However, in order to meet the technical targets of the vehicle and to minimize problems caused by changes needed in the infrastructure and fuel distribution network, emphasis has been on carrying conventional gasoline fuel or methanol on board and processing it into hydrogen. However, due to (i) the efficiency losses in fuel processing, (ii) the significant weight of the fuel processing system and (iii) the progress made in DMFC technology with respect to efficiency, specific power and power density, there has been an increasing interest in developing DMFCs in recent years; a 3 kW DMFC in a one-passenger vehicle prototype was demonstrated by Daimler-Chrysler/Ballard [2, 4]. Though DMFC technology is quite promising, major breakthroughs are still needed if it is to compete with PEMFC technology even though the latter has the burden of carrying a heavy fuel processor to produce hydrogen from gasoline or methanol or compressed hydrogen fuel [2, 4].

DMFC technology offers a solution for transportation applications in transition towards a zero emission future. Using methanol as a fuel circumvents one of the major hurdles plaguing PEMFC technology, that is the development of an inexpensive and safe hydrogen infrastructure to replace the gasoline/diesel fuel distribution network. It is well established that the infrastructure for methanol distribution and storage can be easily adapted from the current gasoline intensive infrastructure. Another drawback in using PEMFC technology is the need to store hydrogen (at very high pressures) or carry a bulky fuel processor to convert the liquid fuel into hydrogen on board the vehicle. Methanol is an attractive fuel because it is a liquid under atmospheric conditions and its energy density is about half of that of gasoline. Despite the compelling advantages of using DMFCs in transportation applications, major obstacles to their introduction remain. These barriers include the high cost of materials used in fabricating DMFCs (especially the high cost of platinum electrocatalysts), the crossover of methanol through the electrolyte membrane from the anode to the cathode, and the lower efficiency and power density performance of DMFCs in comparison to PEMFCs.

Despite these obstacles a number of institutions (particularly in the last ten years) have become actively engaged in the development of DMFCs for transportation applications. The most remarkable results achieved in this field are summarized in Table 1.3. These institutions have directed their resources toward improving every facet of the DMFC in a quest for competitive balance with PEMFCs, as stated below. Ballard Power Systems Inc. (BPSI, Canada) in collaboration with Daimler-Chrysler (Germany) recently reported the development of a 3 kW DMFC system that is at a very preliminary stage in comparison to Ballard's PEMFC products [197]. Daimler-Chrysler (Germany) demonstrated this system for transportation application in a small one-person vehicle at its Stuttgart Innovation Symposium in November, 2000. The DMFC go-cart weighed approximately 100 kg, required an 18 V/1 Ah battery system for starting the electric motor on its rear wheels, and had a range of 15 km and a top speed of 35 km/h. The stack used 0.5 l methanol (the concentration of methanol was unclear) as fuel and operated at approximately 100 °C. In January, 2001 Ballard revealed that they had built and operated a 6 kW stack (60 V) based on the same stack design as the prototype shown in Stuttgart. No details are available with respect to the

Table 1.3 DMFC prototypes for stationary, APU and automotive applications.

Single Cell/Stack Developer	Power/Cell Power density	Temperature (°C)	Oxidant	Methanol Concentration (M)	Anode Catalyst	Membrane Electrolyte	Cathode catalyst	Number of cells/ Surface area (cm ²)
Ballard Power Systems, Inc.	3 kW	100	Air	1	Pt/Ru	Nafion	Pt	—
IRD Fuel Cell A/s	100 mW/cm ⁻²	90–100	1.5 atm air	—	Pt/Ru	Nafion	Pt	4/154 cm ² bipolar
Thales, CNR-ITAE, Nuvera FCs	140 mW/cm ⁻²	110	3 atm air	1	Pt/Ru	Nafion	Pt	5/225 cm ² bipolar
Siemens Ag	250 mW/cm ⁻² / 90 mW/cm ⁻²	110/80	3 atm O ₂ (1.5 atm air)	0.5 (0.5)	Pt/Ru	Nafion 117	Pt-black	3 cm ² per cell
Los Alamos National Labs	1 kW/l	100	3 atm air	0.75	Pt/Ru	Nafion 117	Pt	30/45 cm ² bipolar
Thales, CRF-Fiat, CNR-ITAE, Solvay (DREAMCAR Project)	5 kW/160 mW/cm ⁻²	130	3 atm air	1–2	85% PtRu/C	Hyflon	60%Pt/C	100/300 cm ² bipolar

stack design and performance of the DMFC power source. However, the patent literature indicates fabrication techniques for producing DMFC electrodes [198]. The anode was prepared by first oxidizing the carbon substrate (carbon fiber paper or carbon fiber non-woven) via electrochemical methods in an acidic aqueous solution (0.5 M sulfuric acid) prior to the incorporation of the proton-conducting ionomer. The second step involves the impregnation of a proton-conducting ionomer such as a poly(perfluorosulfonic acid) into the carbon substrate. The anode preparation is completed by applying aqueous electrocatalyst ink to the carbon substrate without extensive penetration in the substrate. This method ensures that less electrocatalyst is used and that the catalyst is applied to the periphery of the electrode where it will be used more efficiently. The performance enhancements associated with the treatment of the carbonaceous substrate may be related to the increase in the wettability of the carbonaceous substrate. This may result in more intimate contact between the ionomer coating and the electrocatalyst, thereby improving proton access to the catalyst. Another theory concludes that the presence of the acidic groups on the carbon substrate itself may improve proton conductivity, or the surface active acidic groups may affect the reaction kinetics at the electrocatalyst sites. The assembly of the MEA and single cell was carried out via conventional methods, that is, hot pressing the anode and cathode to a solid polymer membrane electrolyte.

IRD Fuel Cell A/S (Denmark) has developed DMFCs primarily for transportation applications (0.7 kW) [199]. The stack was constructed with separate water and fuel circuits and the bipolar flow plates are made of a special graphite/carbon polymer material for corrosion reasons. The MEAs had an active cell area of 154 cm^2 . The air pressure was 1.5 bar at the cathode. A nominal cell voltage of 0.5 V was observed for IRDs stack at a current density at 0.2 A/cm^2 and electric power was generated at 15 W per cell. More recently, IRD has developed a 3 kW DMFC stack.

A consortium composed of Thales-Thompson (France), Nuvera Fuel Cells (Italy), LCR (France) and Institute CNR-ITAE (Italy) has developed a five-cell 150 W stainless steel based air fed DMFC stack in the framework of the Nemecel project with the financial support of the European Union Joule Program [200]. Bipolar plates were used in the stack's design and MEAs were fabricated using Nafion as the solid polymer electrolyte and high surface area carbon supported Pt-Ru and Pt electrocatalysts for methanol oxidation and oxygen reduction, respectively. The electrode area was 225 cm^2 and the stack was designed to operate at 110°C , using 1 M methanol and 3 atm air achieving an average power density of 140 mW/cm^2 .

Siemens AG in Germany, in conjunction with IRF A/S in Denmark and Johnson Matthey Technology Center in the United Kingdom developed a DMFC stack with an electrode area of 550 cm^2 under the auspices of the European Union Joule Program [201–204]. The projected cell performance was a potential of 0.5 V at a current density of 100 mA/cm^2 with air pressure at 1.5 atm and the desirable stoichiometric flow rate. A 3-cell stack was demonstrated operating at a temperature of 110°C and a pressure of 1.5 atm using 0.75 M methanol; this stack exhibited a performance level of 175 mA/cm^2 at 0.5 V per cell, and at 200 mA/cm^2 the cell potential was 0.48 V.

These performances were obtained at a high stoichiometric air flow rate (factor of 10) but in order to reduce auxiliary power requirements, one of the goals at Siemens was to improve the design to lower the air stoichiometric flow to the desired value of a factor of about two. A 0.85 kW air-fed stack composed of 16 cells and operating at 105 °C was demonstrated successively with a maximum power density of 100 mW cm⁻².

Los Alamos National Laboratory (LANL) is also actively pursuing the design and development of DMFC cell stacks for electric vehicle applications. According to the latest available information, a five-cell short stack with an active electrode area of 45 cm² per cell has been demonstrated [104, 170, 205]. The cells operated at 100 °C, an air pressure of 3 atm and a methanol concentration of 0.75 M. The maximum power of this stack was 50 W, which corresponds to a power density of 1 kW/l. At about 80% of the peak power, the efficiency of the cell stack with respect to the consumption of methanol was 37%.

Among the recent European community projects dealing with the development of DMFCs for automotive and APU applications, the Dreamcar project (ERK6-CT-2000-00315) that was carried out in the framework of the FP5 EC program should be mentioned. Dreamcar was the acronym of Direct Methanol Fuel Cell System for Car Applications; the project was coordinated by Thales Engineering & Consulting (France) and CRF- FIAT (Italy) and included, as partners, CNR-ITAE (Italy), Solvay (Belgium) and TAU-Ramot (Israel) [162]. The main objective of the project was to design, manufacture and test a 5 kW stack at high temperatures (up to 140 °C). There were three main research topics in the Dreamcar project: higher operating temperatures (up to 140 °C) to enhance the electrochemical reactions; development of new fluorinated (improvement of the membranes developed in the framework of a previous project, Nemecel JOE3-CT-0063) and hybrid inorganic-organic membranes; development of new carbon supported Pt-alloy catalysts to increase the efficiency of the electrodes and power density [162].

The Solvay Solexis Hyflon membrane was selected for the final stack. In order to allow stack operation at high temperatures with the Hyflon membrane, the operating pressure was 3 bar abs. The performance of the MEAs was first investigated in a single cell configuration based on the same materials of the final stack. In the framework of the same project, a nanoporous proton conducting membrane (NP-PCM) that showed superior performance in the presence of a liquid TFMSA acid electrolyte was also developed [103]. Yet, the use of an acidic liquid electrolyte, necessary to make the NP-PCM membrane conductive, was considered incompatible with the materials used in the construction and testing of the final stack (severe problems with corrosion and fluid management) [162].

The final stack (Figure 1.23) consisted of 100 cells of 300 cm² and provided an output electrical power of about 5 kW. The specific power output was 110 W/l. The average single cell performance in the final stack was about 160 mW cm⁻² compared with 300 mW cm⁻² that was almost achieved in the single cell with the same membrane/electrode materials [162]. The main drawbacks concerned methanol crossover and heat management since significant heat/energy dissipated during operation at 130/140 °C at 3–4 bar using an external radiator [162].

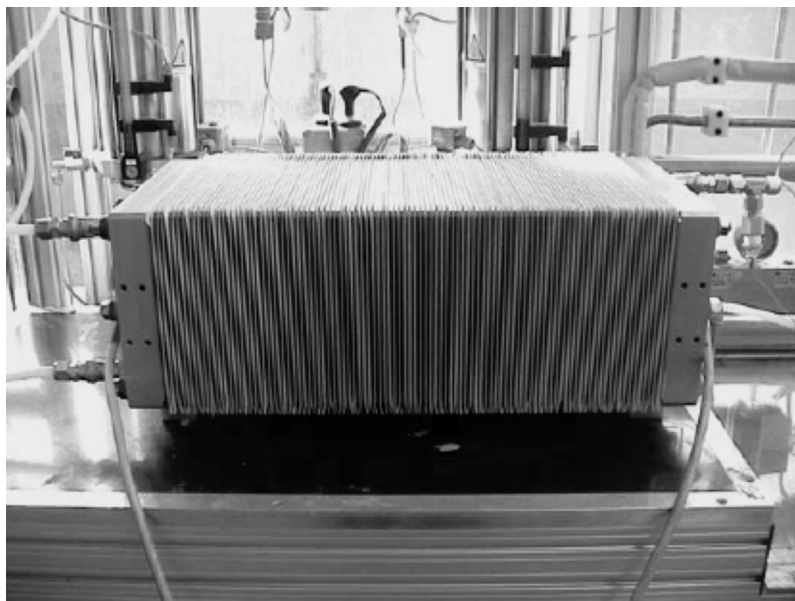


Figure 1.23 A 5 kW DMFC stack developed in the framework of the Dreamcar project.

Technology that is presently considered promising for electro-traction consists of a hybrid system using both pure hydrogen-fed PEMFCs and advanced Li-batteries [206]. To make DMFCs competitive with regard to this technology, it is essential to increase the power density, decrease methanol crossover and reduce costs. Regarding the electrolyte, an appropriate membrane operating in a range that varies from sub-zero to 130 °C at ambient pressure is required. The same requirements apply to membranes for PEMFCs. In general, high temperature stack operation would simplify heat and water management.

1.4.3

Technology Development

1.4.3.1 DMFC Technology

MEAs are usually considered the most important components of a DMFC power source. They contain backing layers, gas diffusion layers, catalytic layers and membranes. However, a significant role is also played by the flow field/current collector, reactant manifold and the stack's housing. A stack module is usually formed by a connected series of cells (e.g., through bipolar plates). Several modules can be connected to each other in series or in parallel depending on the required electrical characteristics of the power source. Furthermore, several auxiliaries are necessary for thermal and water management, start-up, shut-down and normal operation. These include compressor/blowers, fuel tank and liquid pumps, methanol concentration sensors, gas/liquid separation devices, eventually catalytic burner, and

DC/DC (step-up) and DC/AC converters. All the above components form a DMFC system and they are the subject of development and integration studies.

1.4.3.2 Catalyst Preparation

The synthesis of a highly dispersed electrocatalyst phase in conjunction with a high metal loading on a carbon support is one of the present goals in DMFCs [2]. One of the main requirements for an optimal electrocatalyst is its high dispersion. The mass activity ($A\ g^{-1}$) of the catalyst for an electrochemical reaction is directly related to the degree of dispersion since the reaction rate is generally proportional to the active surface area. The main routes for the synthesis of Pt-Ru/carbon electrocatalysts include impregnation, colloidal procedures, self-assembling methods, decoration and so on [2].

1.4.3.3 Electrode Manufacturing and Membrane Electrode Assemblies Membrane Electrode Assembly (MEAs)

The performance of a DMFC is also strongly affected by the fabrication procedure of the MEA. Conventional technology that was used two decades ago consisted of the preparation of gas-diffusion electrodes having suitable polytetrafluoroethylene (PTFE) content in both diffusion and catalyst layers. Nafion ionomer was spread onto the electrocatalyst layer, followed by the preparation of membrane-electrode assembly by a hot-pressing procedure [19]. A disadvantage of this procedure is the poor electrochemically active area between electrocatalyst particles and ionomer, thus decreasing the catalyst use [207].

One of the approaches that has recently been used, especially for PEMFCs, concerns the direct deposition of the catalyst onto the membrane to form a catalyst coated membrane (CCM) [208]. The diffusion and backing layers are added subsequently for example, during cell and stack assembling. In this configuration, there is an intimate contact between the catalytic layer and the membrane whereas the diffusion layer is put in contact with the catalytic layer only.

Regarding the cathode operation, while oxygen reacts to produce water, nitrogen contained in the air stream remains entrapped in the pores of the electrode; the entrapped nitrogen is a diffusion barrier for the incoming oxygen, and it results in mass transport overpotential with, consequently, performance losses even at intermediate current densities. Furthermore, although it is known that oxygen permeability through the ionomer is high at high current densities, transport of this gas to the reaction sites is retarded by flooding of the electrocatalyst layer [2]. Due to this flooding of the active layer, the ionomer swells until it is saturated with water, thus increasing the hydrophilicity of the layer. Such drawbacks have been conveniently reduced in air feed-SPE fuel cells by using thin film electrodes. These are characterized by low electrocatalyst loadings ($0.05\text{--}0.1\text{ mg cm}^{-2}$) [208]. Due to the lower performance of the oxygen electrode with such low Pt loadings in DMFCs, alternative solutions should be investigated. Gas channels allowing a fast transport of the reaction gas and easy removal of the excess N_2 can be realized in the cathode layer by means of PTFE-carbon composite ducts [209]. This configuration does not affect electrocatalyst use or the continuity of ionomer in the catalyst layer, thus improving

the mass-transport properties of the electrode. Another approach is to use pore formers such as $(\text{NH}_4)_2\text{CO}_3$ to increase the porosity in the active layer of the cathode [210, 211].

1.4.3.4 Stack Hardware and Design

The architecture of a DMFC stack for transportation and stationary applications, including the remote and distributed generation of electrical energy, is essentially similar to that of a PEFC stack for the same applications [5, 97, 98]. In contrast, a large variety of approaches and designs has been adopted for portable fuel cell stacks [4, 5]. Requirements for stacks vary depending on the applications. Compact size, fast start-up procedure and high performance are required for transportation applications [7]. Easy handling, miniaturization and rapid fuel refilling are especially important for portable applications [4, 5].

The conventional PEMFC stack architecture [97, 98] for transportation and stationary applications is based on bipolar plates connecting the various cells (MEAs) in series. There are also two end plates enabling current collection, a manifold, and appropriate gaskets which together with the flow-fields in the bipolar plates allow distribution of the reactants over the various cells. The flow fields are often based on flow channels machined into graphite (generally composite graphite is used) or consist of corrosion resistant alloy bipolar plates; a flow field can also be a corrosion resistant metal foam or a stamped flow pattern in a metal plate. The machined graphite flow field can be a simple design of dots, parallel channels, serpentine or interdigitated design [2]. The flow configuration may be cross-flow, co-flow or counter-flow. All these aspects significantly influence mass transport and thermal management by favoring diffusion or forced convection of the reactants to the catalytic sites and heat removal. In DMFC stacks cooling cells are not strictly required because efficient heat removal can be obtained either by increasing the recirculation rate of the liquid mixture of water and methanol at the anode or using an external radiator.

Significant progress has been made by improving the characteristics of the electrode backing layer in terms of composition and thickness to reduce mass transport limitations. Some investigations have focused on the design of reactant flow fields [11]. The most widely employed flow field in advanced fuel cells is based on the serpentine configuration. The reactant molecules have access to the electrocatalytic sites through diffusion across the so-called diffusion layer, that is, the backing layer, made of carbon cloth and carbon black, hydrophobized by the appropriate addition of PTFE.

A different approach to the flow of reactants and products within the electrode structure, that is, an interdigitated design, was proposed by Nguyen [212] and Wilson *et al.* [205] for H_2 – O_2 solid polymer electrolyte fuel cells (SPEFCs). In practice, the reactant gases are forced to enter and exit the electrode pores under a gradient pressure achieved by making the inlet and outlet channels dead-ended. As pointed out by Nguyen [212], the flow through the electrode in an interdigitated design is no longer governed by diffusion but becomes convective in nature. The forced-flow-through characteristics created by the interdigitated flow fields in SPEFCs have been also investigated for DMFCs [11]. In general, it has been shown that enhanced mass transfer characteristics are achieved with the interdigitated flow field in DMFCs but

these beneficial effects are especially observed only at high current densities, which correspond to low values of cell potential. At high cell potentials, that is, under practical operating conditions (above 0.5 V), higher efficiency for fuel use is obtained with the classical serpentine flow fields due to the lower methanol crossover.

In fuel cell stacks of significant size, graphite bipolar plates are being replaced with the more economic carbon based composite materials or by metallic foams [213, 214]. With composite materials, the same design of graphite plates may be reproduced whereas metallic foam operates, conceptually, under conditions similar to serpentine flow fields in that the reactant distribution over the electrocatalyst layer is controlled by diffusion. Alternative stack designs have been investigated by Scott and co-workers [215]. These authors analyzed the possibility of using more open structures at the anode (e.g., dots or open channels) to favor the diffusion of methanol. In other cases, the parallel flow channel pattern has been preferred due to an optimal combination of simplicity of design and suitable performance. Graphite or carbon composite based bipolar plates exhibit minimal corrosion. In the case of stainless-steel or metallic alloy-based materials, an appropriate evaluation of the chemical and electrochemical stability in the presence of hot methanol/water mixtures is necessary. In some cases surface treatments or special alloys are required to minimize corrosion.

DMFC stacks for portable applications may have different architectures [4, 5] especially if the power output is smaller than 50–100 W and passive mode operation is required. Several configurations have been proposed for the passive DMFC stacks; the most common are the bi-cell and monopolar-type [5]. In the bi-cell type, the methanol tank is allocated in between two anodes which belong to two different cells and the cathodes of these two cells are exposed to air [5]. Bi-cell units are grouped in a stack by leaving a gap between two cathodes belonging to two different bi-cells; the series connection of the various bi-cells is made externally. In the monopolar configuration all electrodes of the same type, for example, all anodes, are allocated on one face of the membrane and the cathodes on the other face. Each couple of electrodes forms a cell; the membrane is the same for all the cells. Series connection between two cells is created by an electric conductor passing through the membrane or by an external circuit [4, 5].

A planar architecture is often used for μ DMFC stacks [216]. For example, a catalyzed membrane integrated on a silicon or polymeric matrix through micromachining processes has recently emerged as a possible way to fabricate miniaturized DMFCs [217, 218]. Thanks to integrated-circuit (IC) technology [219], micro-channel patterns of μ DMFCs bipolar plates, into which reactants are fed, can be featured on an Si or polymeric matrix with high resolution and good repeatability. Basically, the μ DMFC has a conventional single cell structure in which the MEA is sandwiched between two current collectors, made of gold, with fuel/air channels. These designs take advantage of the full wafer-level process capability. Alternatively, micro-channels can be created on a polymeric substrate, such as polycarbonate, by mechanical erosion with a numerical control mechanical device [193].

Micropumps can be used for fuel delivery in μ DMFC stacks. For the passive mode operation, several approaches can be used for the methanol feed to the anode. These have been reviewed recently by Qian *et al.* [5]. Such approaches are based on natural

circulation [220], capillary action [221] or self-pressurization using a controlled three-way valve [222]. It is appropriate to use a non-diluted fuel tank and to control the methanol and water feeds by valves, metering, orifices or pumps. Water should be recovered from the cathode, for example, by favoring back-diffusion through the membrane from the cathode.

1.4.3.5 DMFC Systems

The DMFC stack plant is generally designed on the basis of the power output level and the desired application. An interesting DMFC system design was proposed in a recent European project called Morepower [21]. The project investigated the development of a low-cost, low temperature, portable DMFC system of compact construction and modular design with nominal power 250 W for the potential markets of weather stations, medical devices, signal units, gas sensors and security cameras. The system was designed by the Institut für Microtechnik of Mainz (Germany) and the modeling was carried out by Specchia *et al.* at the Politecnico of Turin (Italy) to evaluate heat, mass fluxes and pressure drops, for the integration and optimization of the DMFC components in a portable Auxiliary Power Unit [223]. The system design and components are reported in Figure 1.24 [224]. These consist of the DMFC stack, the radiator (E-201) to cool the fuel solution downstream the DMFC anode, the gas-liquid separator (S-201, an atmospheric adiabatic flash unit) to dump up the produced CO_2 , the catalytic burner (R-401) to burn the residual MeOH vapor before

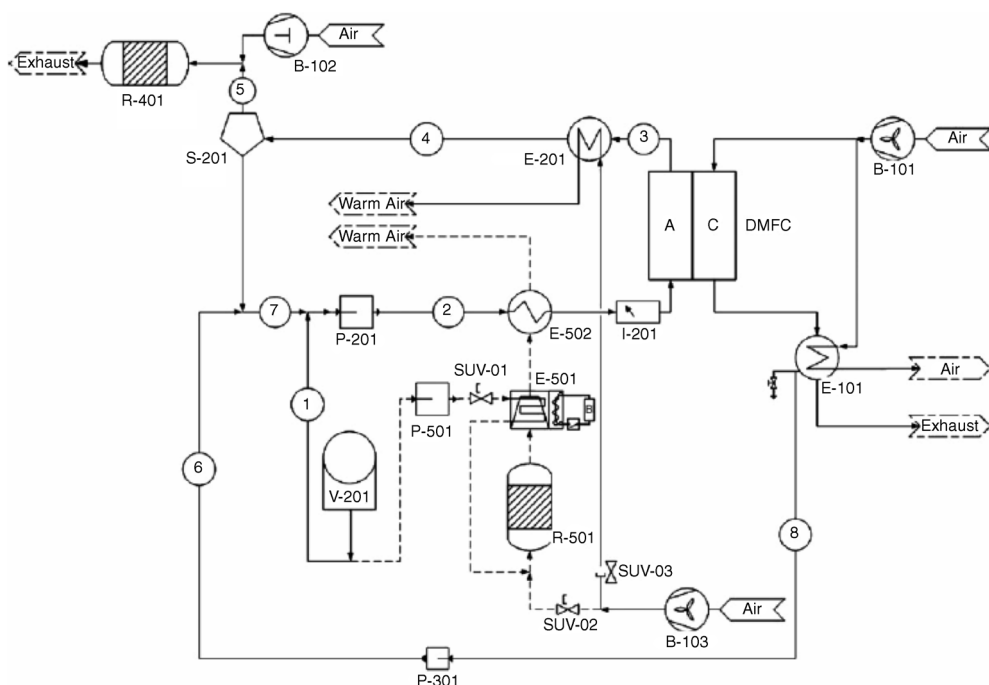


Figure 1.24 DMFC process scheme developed in the framework of the Morepower project [223].

releasing the anode exhausts in the atmosphere, the pump (P-201) to feed the fuel solution to the DMFC anode, the MeOH cartridge (V-201) to feed fresh MeOH into the system, the water condenser (E-101) to recover and make-up the water lost during operation, and the blower (B-101) to feed the fresh air necessary for the cathode reactions. The addition of fresh feed solution from the MeOH cartridge (V-201) to the exhaust solution is controlled via an MeOH sensor (I-201) [224, 225]; the controlled composition feed solution is then pumped into the DMFC where overall electrochemical reactions between the fuel and air produce power and heat. All the systems and sub-components necessary for the start-up are also present in the DMFC system. A small fraction of pure MeOH, taken directly from the MeOH cartridge (V-201) via a dedicated pump (P-501), is fed to an evaporator (E-501, electrically heated during the initial phase of the start-up procedure). The MeOH vapor obtained is then burned into a burner (R-501) with fresh air (B-103); the flue gas produced is used to heat-up the solution to be fed to the DMFC in the start-up heat exchanger (E-502).

The complexity of this design is determined by the characteristics required in terms of system control and rapid start-up and shut-down. A simpler system can be designed if a self-start up is preferred to rapid start-up; the burner (R-501) with its associated auxiliaries that is, evaporator (E-501), pump (P-501), blower (B-103) and relative valves in Figure 1.24 can be removed from the scheme. A concentrated methanol solution, for example, 10 M, remains liquid even at several degrees below zero. In terms of CO₂ escape, the use of a highly selective hydrophobic membrane can allow the removal of the catalytic burner (R-401) with the associated air supply (B-102) in Figure 1.24; furthermore, the radiator (E-201) may be more compact if no loss of water/methanol vapor occurs through the selective membrane even at high temperatures. In such a case, there is no need to cool down the unreacted fuel mixture significantly. Accordingly, it would not be necessary to spend much energy in the E-502 pre-heater. The heat released from the stack should be properly used to heat-up the methanol solution fed to the anode. The device necessary for recovering water from the cathode condenser to the anode may be quite compact if part of the water permeates or back-diffuses from a highly hydrophobic cathode to the anode through a membrane containing proper hydrophilic channels.

A simple passive methanol fuel cell stack usually does not need auxiliaries; on the other hand, miniaturized DMFCs may require some auxiliaries such as micropumps and so on. Miniaturized systems can also be quite complex. DMFC stacks and systems for portable uses have recently been reviewed [5]. Of course, a simplification of the systems allows a reduction in production costs. In some cases, the proper development of materials for MEAs and auxiliaries may help to simplify DMFC systems.

1.5

Perspectives of Direct Methanol Fuel Cells and Techno-Economical Challenges

The most challenging problem in the development of DMFCs has been, and still is, that significant enhancement of electrocatalytic activity for the 6-electron transfer

electro-oxidation of methanol is needed. On the other hand, research in this area has encouraged many scientists and engineers to use highly sophisticated electrochemical surface science and material science techniques to unravel the mysteries of the reaction path, rate determining steps and physicochemical characteristics (electronic and geometric factors, adsorption/desorption energies and electrocatalyst/support interaction) which influence the activities of the various types of electrocatalysts. The sluggishness of the reaction, especially in the presence of protonic electrolytes, is caused by a strong chemical adsorption of CO-type species on an electrocatalyst subsequent to the dissociative adsorption of methanol (Pt is the best known electrocatalyst for this step). A neighboring chemisorbed labile OH species is vital for the electro-oxidation of the strongly adsorbed CO species. To date, the Pt-Ru electrocatalyst (50:50 at. wt%) has shown the best results. There has been little success with alternatives to Pt and its alloys in proton conductive electrolytes; those tested include transition metal alloys, oxides, and tungsten bronzes. One achievement has been using carbon-supported electrocatalysts, which help reducing the Pt loading by a factor of about two to four.

The reaction rates are higher in alkaline environments with respect to protonic electrolytes. This fact and the lower corrosion constraints in alkaline media allow the replacement of Pt with non-precious metal catalysts for example, Ni. Alternatively, PtRu can be used in an alkaline electrolyte to take advantage of the lower overpotentials. However, no significant enhancement in terms of power density has been achieved because this kinetic advantage is counteracted by the carbonation drawback and reduced ionic conductivity unless concentrated alkaline solutions are used.

The performance of the ORR on a platinum electrocatalyst is affected by the crossover of methanol from the anode to the cathode through the ion exchange membrane. The open circuit potential is reduced by about 200 mV due to the competitive adsorption of dissociated methanol and oxygen species. At present, for Pt alloys there is no clear evidence of catalytic enhancement in oxygen reduction when methanol crossover occurs. Non-platinum electrocatalysts, such as heat-treated phthalocyanines and porphyrins, as well as transition metal chalcogenides, have some chance of methanol tolerance but have considerably lower activity than platinum and also raise questions of stability. The short term prospect of replacing platinum as an electrocatalyst is very slim but the greater challenge is to reduce the noble metal loading in both electrodes by a factor of about 10 in order to reduce its cost to about \$10/kW.

If an anion exchange membrane is used instead of a protonic electrolyte, Pt-based cathode electrocatalysts can be replaced by silver or MnO_2 , which are much less expensive and methanol tolerant. Although the oxygen reduction in alkaline media is faster than an acidic electrolyte, the performance enhancement achieved with anion exchange membranes is quite limited due to both the absence of a suitable ionomer to extend the triple-phase boundary in the electrode bulk and the low anionic conductivity.

The perfluorosulfonic acid polymer electrolyte in the DMFC is an equally expensive material (about \$300/kW, based on state-of-the-art performance). There has been a lot of research on alternative proton conducting membranes which allow CO_2

rejection (sulfonated polyetherketone, polyether sulfone, radiation grafted polystyrene, zeolites, electrolytes doped with heteropolyacids and sulfonated polybenzimidazole), but it is still a challenge to attain sufficiently high specific conductivity and stability in the DMFC environment. Nafion-based composite membranes with silicon oxide and zirconium hydrogen phosphate have enhanced performance in operation up to about 150 °C (lower activation and ohmic overpotentials); these can also operate suitably under ambient conditions with reduced crossover due to an increase of the tortuosity factor.

Alternatively, new emphasis has recently been placed on anion exchange membranes. Both anodic and cathodic reaction rates are enhanced in alkaline media. Yet, the kinetic advantage is counteracted by a thermodynamic loss due to the presence of a pH gradient between the anode and the cathode. This is caused by a carbonation process occurring at the anode. This drawback can be overcome by recirculating KOH or carbonate solution through the device, but several technical problems arise under these conditions, that is, precipitation of carbonate on the electrode pores, the need to frequently regenerate the electrolyte and so on. Other drawbacks of anion exchange membranes concern low anionic conductivity (about five times lower than Nafion at low temperatures), higher activation energy for ion conduction than Nafion, no proper ionomer solution to enable an extension of the three-phase reaction zone in the electrode bulk, and reduced stability at high temperatures. Some of these problems can be solved by improving the characteristics of the anionic polymer electrolyte. Regarding methanol crossover, there is no effect from electro-osmotic drag with anion exchange membranes. Yet, as is well known, most of the methanol crossover is due to the concentration gradient between the anode and the cathode and the hydrophilic properties of the present membranes.

A critical area to improve overall cell performance in is the fabrication of MEAs. Progress in the preparation of high performance MEAs has been made by preparing thin electrocatalyst layers (about 10 μm thick) composed of the electrocatalyst and ionomer in the electrode substrate or directly deposited onto the membrane (CCM). Problems caused by the barrier layer effects of nitrogen on oxygen access to the catalytically active sites and electrode flooding need further investigation. Possible solutions to these problems are heat treatments of the recast Nafion gel in the electrocatalytic layer to make it hydrophobic or the use of pore formers to increase porosity.

Direct methanol single cell development in the last decade has achieved very interesting results. Maximum power densities of about 500 mW cm^{-2} and 300 mW cm^{-2} under oxygen and air feed operation, respectively, and 200 mW cm^{-2} at a cell potential of 0.5 V have been reported for cells operating at temperatures close to or above 100 °C under pressurized conditions, with Pt loadings of 1–2 mg cm^{-2} . At ambient temperatures in passive mode operation, the power density ranges between 10 and 40 mW cm^{-2} .

The development of DMFC stacks for both transportation and portable applications has gained momentum in recent years. The rated power output of the DMFC stack varies from a few watts in the case of portable power sources up to a few kW for remote power generator and hybrid battery-fuel cell vehicles. The best results achieved with DMFC stacks for electrotraction are 1 kW/l power density with an

overall efficiency of 37% at 0.5 V/cell. These performances make the DMFCs quite competitive with respect to the reformer-H₂/air SPE fuel cell, especially if one considers the complexity of the whole system; yet, the Pt loadings are still high in DMFCs (around 1–2 mg cm⁻²). Reducing the loading of noble metals or using cheap non-noble metal catalysts is actually one of the breakthroughs which may allow an increase in DMFC competitiveness on the power source market.

In the short-term the high energy density of DMFCs and recent advances in the technology of miniaturized fuel cells make these systems attractive in terms of replacing the current Li-based batteries in cellular phones, lap top computers and other portable systems. This field appears the most promising for the near-term and a successful use of such systems is envisaged; the progress made in manufacturing DMFCs for portable systems may also stimulate new concepts and designs which may aid further development of these systems for electrotraction.

Table 1.4 summarizes the main drawbacks of DMFCs together with some potential solutions. Unfortunately, several proposed approaches create new drawbacks. For

Table 1.4 Drawbacks and potential solutions of DMFC devices.

Drawback	Potential solution	Present approach
Low power density	Enhance oxidation kinetics	-Multifunctional catalysts -Increase the operating temperature and pH -Highly dispersed catalysts
	Improve electrode performance	-Thin film electrodes -Optimization of the MEA
Fuel crossover	Membranes impermeable to methanol	-Anion exchange membranes -Composite membranes -Polyarylsulfonic membranes -Polyvinyl alcohol treated membranes
	Methanol tolerant oxygen reduction catalysts	-Chevrel-phase type (Mo ₄ Ru ₂ Se ₈), transition metal sulfides (Mo _x Ru _y S _z , Mo _x Rh _y S _z) or other transition metal chalcogenides -Pt-alloys
High cost	Reduce noble metal loading	-Non-noble metal catalysts (anode and cathode) in conjunction with alkaline electrolytes -Oxide catalysts -Cathode catalysts based on iron or cobalt organic macrocycles (phenylporphyrins, phthalocyanines) -Cobalt polypyrrole-carbon composite catalysts (Co-PPY-C) -Decoration (anode catalyst)
	Membranes alternative to Nafion	-Anion exchange membranes -Grafted membranes -S-PEEK, SPSf, and so on

example, an increase in operating temperature to enhance the reaction kinetics causes membrane dehydration with most conventional membranes. This results in a significant increase of ohmic constraints. On the other hand, the membranes which allow high temperature operation, such as phosphoric acid doped polybenzimidazole, do not appear appropriate in terms of suitable conductivity under low temperature operation, a pre-requisite for portable power sources. The use of non-noble metal catalysts is presently possible in DMFCs using alkaline electrolytes. However, low conductivity, carbonation and thermodynamic constraints limit the practical applications of this approach. The methanol tolerant cathode catalysts such as Chevrel-phase type or transition metal chalcogenides, do not allow oxidation to CO_2 of the methanol permeated through the membrane; the cathode outlets thus, contains traces of unreacted methanol that cannot be released in the atmosphere. This requires modification of the system and/or cell concept. Reduction of the catalyst layer thickness to reduce mass transport constraints can be achieved by increasing the concentration of the active phase on the support. However, this approach reduces catalyst use. The use of highly hydrophobic cathodes that favor oxygen transport and reduce flooding by water permeated through the membrane or formed by the reaction increases the resistance and reduces the interface between catalyst and ionomer (triple phase boundary).

These examples show that there are no unequivocal or radical solutions and a compromise is often necessary to enhance device characteristics. Furthermore, it also appears that materials should be tailored to specific applications. A chemical and dimensional stable electrolyte with high conductivity in a wide temperature range would be more appropriate if the conduction mechanism is not assisted by water. Methanol crossover is often associated with water permeation; these effects cause cathode poisoning and flooding. From a practical point of view, a carbon dioxide rejecting electrolyte appears more appropriate but new efforts should address the development of multifunctional catalysts with reduced noble metal loadings. Significant progress in the development of materials would be also beneficial to reduce system complexity.

The applications of DMFCs in portable power sources cover the spectrum of cellular phones, personal organizers, laptop computers, military back power packs, and so on. The infusion of semiconductor technology into the development of micro and mini fuel cells by leading organizations such as LANL, JPL, Motorola, has created an awareness of DMFCs replacing the most advanced type of rechargeable batteries, that is, lithium ion. For several of these applications, a DMFC working at room temperature and ambient pressure with an efficiency of only about 20% may perform strikingly better than lithium ion batteries with respect to operating hours between refueling/recharging because of the high energy density of methanol. Further, refueling in the case of DMFCs is instantaneous whereas it requires about 3–5 hrs for lithium ion batteries. There is still the challenge of reducing the weight and volume of DMFCs to a level competitive with lithium ion batteries, necessary, for instance, for cellular phone and laptop applications. What is most attractive about the portable power applications, compared with transportation and stationary applications, is that the cost per kW or cost per kWh could be higher by a factor of 10 to 100

without compromising the market application. For this application, there is hardly any competition for lithium ion and DMFCs from any other type of power source.

The present analysis indicates that the targets for each application may be achieved through thoughtful development of materials, innovative device design, and through an appropriate choice of operating conditions.

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References

- 1 Wasmus, S. and Kuver, A. (1999) *J. Electroanal. Chemistry*, **461**, 14–31.
- 2 Arico, A.S., Srinivasan, S. and Antonucci, V. (2001) *Fuel Cells*, **1** (2), 133–161.
- 3 Lamy, H., Léger, J.-M. and Srinivasan, S. (2000) Direct methanol fuel cells—from a 20th century electrochemists' dream to a 21st century emerging technology, in *Modern Aspects of Electrochemistry*, **34** (eds J.O'.M. Bockris and B.E. Conway), Plenum Press, New York, Ch 3, p. 53.
- 4 Dillon, R., Srinivasan, S., Arico, A.S. and Antonucci, V. (2004) *J. Power Sources*, **127** (1–2), 112–126.
- 5 Qian, W., Wilkinson, D.P., Shen, J., Wang, H. and Zhang, J. (2006) *J. Power Sources*, **154** (1), 202–213.
- 6 Bockris, J.O'.M. and Srinivasan, S. (1969) *Fuel Cells: Their Electrochemistry*, McGraw- Hill Book Company, New York.
- 7 Shukla, A.K., Arico, A.S. and Antonucci, V. (2000) *Renew. Sust. Energ. Rev.*, **5**, 137–155.
- 8 McNicol, B.D., Rand, D.A.J. and Williams, K.R. (1999) *J. Power Sources*, **83** (1–2), 15–31.
- 9 Ren, X., Wilson, M.S. and Gottesfeld, S. (1996) *J. Electrochem. Soc.*, **143** (1), L12–L15.
- 10 Arico, A.S., Cretì, P., Kim, H., Mantegna, R., Giordano, N. and Antonucci, V. (1996) *J. Electrochem. Soc.*, **143**, 3950–3959.
- 11 Arico, A.S., Cretì, P., Baglio, V., Modica, E. and Antonucci, V. (2000) *J. Power Sources*, **91** (2), 202–209.
- 12 Moore, R.M., Gottesfeld, S. and Zelenay, P. (1999) Proton Conducting Membrane Fuel Cells – Second International Symposium, Electrochemical Society, Pennington, New Jersey, Proceedings

- 98–27 (eds S. Gottesfeld and T.F. Fuller), pp. 365–379.
- 13 Narayanan, S.R., Chun, W., Valdez, T.I., Jeffries-Nakamura, B., Frank, H., Surampudi, S., Halpert, G., Kosek, J., Copley, C., LaConti, A.B., Smart, M., Wang, Q., Surya Prakash, G. and Olah, G.A. (1996) Program and Abstracts, 1996 Fuel Cell Seminar, pp. 525–528.
 - 14 Baldauf, M. and Preidel, W. (1999) *J. Power Sources*, **84** (2), 161–166.
 - 15 Shukla, A.K., Christensen, P.A., Hamnett, A. and Hogarth, M.P. (1995) *J. Power Sources*, **55** (1), 87–91.
 - 16 Scott, K., Taama, W.M., Argyropoulos, P. and Sundmacher, K. (1999) *J. Power Sources*, **83** (1–2), 204–216.
 - 17 Jung, D.H., Lee, C.H., Kim, C.S. and Shin, D.R. (1998) *J. Power Sources*, **71** (1–2), 169–173.
 - 18 Ravikumar, M.K. and Shukla, A.K. (1996) *J. Electrochem. Soc.*, **143** (8), 2601–2606.
 - 19 Srinivasan, S., Mosdale, R., Stevens, P. and Yang, C. (1999) *Annu. Rev. Energy Environ.*, **24**, 281–285.
 - 20 Aricò, A.S., Antonucci, V., Alderucci, V., Modica, E. and Giordano, N. (1993) *J. Appl. Electrochem.*, **23** (11), 1107–1116.
 - 21 EU funded project MOREPOWER (compact direct methanol fuel cells for portable applications), project nr. SES6-CT-2003-502652 (2004).
 - 22 Carlstrom, C., Craft, J., Fannon, M., Manning, M., Marvin, R., Modi, A., Reichard, J., Scartozzi, P., Dolan, G. and Sievers, B. (2006) DMFC Prototype Demonstration for Consumer Electronic Applications in U.S. Department of Energy Hydrogen Program: Hydrogen, Fuel Cells & Infrastructure, Technologies, Annual Review, May 16–19, Arlington, Virginia.
 - 23 Apanel, G. and Johnson, E. (2004) *Fuel Cells Bull.*, **11**, 12–17.
 - 24 Kordesch, K. and Simader, G. (1996) *Fuel Cells and their Applications*, Wiley-VCH Verlag GmbH, Weinheim.
 - 25 Pavela, T.O. (1954) *Ann. Acad. Sci. Fennicae AII*, **59**, 7–11.
 - 26 Justi, E.W. and Winsel, A.W. (1955) Brit. Patent 821, 688.
 - 27 Cathro, K.J. (1969) *J. Electrochem. Soc.*, **116** (11), 1608–1611.
 - 28 Janssen, M.M.P. and Moolhuysen, J. (1976) *Electrochim. Acta*, **21** (11), 861–868.
 - 29 Watanabe, M. and Motoo, S. (1975) *J. Electroanal. Chem.*, **60** (3), 275–283.
 - 30 Bagotzky, V.S. and Vassiliev, Yu.B. (1967) *Electrochim. Acta*, **12** (9), 1323–1343.
 - 31 Shibata, M. and Motoo, S. (1985) *J. Electroanal. Chem.*, **194** (2), 261–274.
 - 32 McNicol, B.D. and Short, R.T. (1977) *J. Electroanal. Chem.*, **81** (2), 249–260.
 - 33 Parsons, R. and VanderNoot, T. (1998) *J. Electroanal. Chem.*, **257** (1–2), 9–45.
 - 34 Aramata, A., Kodera, T. and Masuda, M. (1988) *J. Appl. Electrochem.*, **18** (4), 577–582.
 - 35 Beden, B., Kardigan, F., Lamy, C. and Leger, J.M. (1981) *J. Electroanal. Chem.*, **127** (1–3), 75–85.
 - 36 Chandrasekaran, K., Wass, J.C. and Bockris, J. O'M. (1990) *J. Electrochem. Soc.*, **137** (2), 518–524.
 - 37 Christensen, P.A., Hamnett, A. and Troughton, G.L. (1993) *J. Electroanal. Chem.*, **362** (1–2), 207–218.
 - 38 Ticianelli, E., Berry, J.G., Paffet, M.T. and Gottesfeld, S. (1977) *J. Electroanal. Chem.*, **81** (2), 229–238.
 - 39 Goodenough, J.B., Hamnett, A., Kennedy, B.J., Manoharan, R. and Weeks, S. (1988) *J. Electroanal. Chem.*, **240** (1–2), 133–145.
 - 40 Ravikumar, M.K. and Shukla, A.K. (1996) *J. Electrochem. Soc.*, **143** (8), 2601–2606.
 - 41 Mc Breen, J. and Mukerjee, S. (1995) *J. Electrochem. Soc.*, **142** (10), 3399–3404.
 - 42 Markovic', N., Widelov, A., Ross, P.N., Monteiro, O.R. and Brown, I.G. (1997) *Catal. Lett.*, **43** (1–2), 161–166.
 - 43 Piela, P., Eickes, C., Brosha, E., Garzon, F. and Zelenay, P. (2004) *J. Electrochem. Soc.*, **151**, A2053–A2059.
 - 44 Gurau, B., Viswanathan, R., Liu, R.X., Lafrenz, T.J., Ley, K.L., Smotkin, E.S., Reddington, E., Sapienza, E.A., Chan, B.C., Mallouk, T.E. and Sarangapani, S.

- (1998) *J. Phys. Chem. B*, **102** (49), 9997–10003.
- 45 Fritts, S.D. and Sen, R.K. (1988) Assessment of Methanol Electrooxidation for Direct Methanol-Air Fuel Cells. *DOE Report*, Contract DE AC0676 RLO 1830 by Battelle.
 - 46 Cameron, D.S., Hards, G.A., Harrison, B. and Potter, R.J. (1987) *Platinum Metals Rev.*, **31** (4), 173–181.
 - 47 Beden, B., Kadirgan, F., Lamy, C. and Leger, J.-M. (1981) *J. Electroanal. Chem.*, **127** (1–3), 75–85.
 - 48 Hamnett, A. and Kennedy, B.J. (1988) *Electrochimica Acta*, **33** (11), 1613–1618.
 - 49 Miyazaki, E. (1980) *J. Catal.*, **65**, 84–92.
 - 50 Goodenough, J.B., Hamnett, A., Kennedy, B.J., Manoharam, R. and Weeks, S.A. (1990) *Electrochimica Acta*, **35** (1), 199–207.
 - 51 Hamnett, A. (1997) *Catal. Today*, **38** (4), 445–457.
 - 52 Hogarth, M.P. and Hards, G.A. (1996) *Platinum Metal Rev.*, **40**, 150–155.
 - 53 Wang, K., Gasteiger, H.A., Markovic, N.M. and Ross, P.N. Jr (1996) *Electrochim. Acta*, **41** (16), 2587–2593.
 - 54 Frelink, T., Visscher, W. and Van Veen, J.A.R. (1995) *Surf. Sci.*, **335** (1–2), 353–360.
 - 55 Frelink, T., Visscher, W. and Van Veen, J.A.R. (1996) *Langmuir*, **12** (15), 3702–3708.
 - 56 Iwasita, T., Hoster, H., John-Anacker, A., Lin, W.F. and Vielstich, W. (2000) *Langmuir*, **16** (2), 522–529.
 - 57 Tong, Y.Y., Rice, C., Wieckowski, A. and Oldfield, E. (2000) *J. Am. Chem. Soc.*, **122** (6), 1123–1129.
 - 58 Gasteiger, H.A., Markovic, N., Ross, P.N. and Cairns, E.J. Jr (1994) *J. Phys. Chem.*, **98** (2), 617–625.
 - 59 Friedrich, A.K., Geyzers, K.P., Linke, U., Stimming, U. and Stumper, J. (1996) *J. Electroanal. Chem.*, **402** (1–2), 123–128.
 - 60 Schmidt, T.J., Noeske, M., Gasteiger, H.A., Behm, R.J., Britz, P., Brijoux, W. and Bonnemann, H. (1997) *Langmuir*, **13** (10), 2591–2595.
 - 61 Dinh, H.N., Ren, X., Garzon, F.H., Zelenay, P. and Gottesfeld, S. (2000) *J. Electroanal. Chem.*, **491** (1–2), 222–233.
 - 62 Schmidt, T.J., Gasteiger, H.A. and Behm, R.J. (1998) *Electrochem. Commun.*, **1**, 1–5.
 - 63 Takasu, Y., Fujiwara, T., Murakami, Y., Sasaki, K., Oguri, M., Asaki, T. and Sugimoto, W. (2000) *J. Electrochem. Soc.*, **147** (12), 4421–4427.
 - 64 Pletcher, D. and Solis, V. (1982) *Electrochim. Acta*, **27** (6), 775–782.
 - 65 Chrzanowski, W. and Wieckowski, A. (1998) *Langmuir*, **14** (8), 1967–1970.
 - 66 Kim, H. and Wieckowski, A. (1999) Third International Symp. On New Materials for Fuel Cells and Modern Battery Systems, Montréal, Canada (ed. O. Savadogo), pp. 125–126.
 - 67 Liu, L., Pu, C., Viswanathan, R., Fan, Q., Liu, R. and Smotkin, E.S. (1998) *Electrochim. Acta*, **43** (241), 3657–3663.
 - 68 Aricò, A.S., Shukla, A.K., El-Khatib, K.M., Creti, P. and Antonucci, V. (1999) *J. Appl. Electrochem.*, **29** (6), 671–676.
 - 69 Gasteiger, H.A., Markovic, N., Ross, P.N. Jr and Cairns, E.J. (1994) *J. Electrochem. Soc.*, **141** (7), 1795–1803.
 - 70 Aricò, F.A.S., Baglio, V., Creti, F.P. and Antonucci, V. (2000) Fuel Cell Seminar Abstracts, October 30–November, Portland, Oregon, pp. 75–78.
 - 71 Iwasita, T., Nart, F.C. and Vielstich, W. (1990) *Ber. Bunsenges Phys. Chem.*, **94** (9), 1030–1034.
 - 72 Rolison, D.R., Hagans, P.L., Swider, K.L. and Long, J.W. (1999) *Langmuir*, **15** (3), 774–779.
 - 73 Aricò, A.S., Monforte, G., Modica, E., Antonucci, P.L. and Antonucci, V. (2000) *Electrochem. Commun.*, **2** (7), 466–470.
 - 74 Hamnett, A., Kennedy, B.J. and Wagner, F.E. (1990) *J. Catal.*, **124** (1), 30–40.
 - 75 Aricò, A.S., Creti, P., Modica, E., Monforte, G., Baglio, V. and Antonucci, V. (2000) *Electrochim. Acta*, **45** (25–26), 4319–4328.
 - 76 Aricò, A.S., Baglio, V., Di Blasi, A., Modica, E., Antonucci, P.L. and

- Antonucci, V. (2003) *J. Electroanal. Chem.*, **557**, 167–176.
- 77 Maillard, F., Lu, G.-Q., Wieckowski, A. and Stimming, U. (2005) *J. Phys. Chem. B*, **109** (34), 16230–16243.
- 78 Brankovic, S.R., Wang, J.X. and Adzic, R.R. (2001) *Electrochem. Solid-State Lett.*, **4** (12), A217–A220.
- 79 Arico, A.S., Baglio, V., Di Blasi, A., Modica, E., Monforte, G. and Antonucci, V. (2005) *J. Electroanal. Chem.*, **576**, 161–169.
- 80 Arico, A.S., Baglio, V., Modica, E., Di Blasi, A. and Antonucci, V. (2004) *Electrochem. Commun.*, **6**, 164–169.
- 81 Hays, C.C., Manoharan, R. and Goodenough, J.B. (1993) *J. Power Sources*, **45** (3), 291–301.
- 82 Niedrach, L.W. and Zeliger, H.I. (1969) *J. Electrochem. Soc.*, **116** (1), 152–153.
- 83 Okamoto, H., Kawamura, G., Ishikawa, A. and Kudo, T. (1987) *J. Electrochem. Soc.*, **134** (7), 1653–1658.
- 84 Bashyam, R. and Zelenay, P. (2006) *Nature*, **443** (7107), 63–66.
- 85 Poirier, J.A. (1994) *J. Electrochem. Soc.*, **141** (2), 425–430.
- 86 Giordano, N., Passalacqua, E., Pino, L., Arico, A.S., Antonucci, V., Vivaldi, M. and Kinoshita, K. (1991) *Electrochim. Acta*, **36** (13), 1979–1984.
- 87 Watanabe, M., Saegusa, S. and Stonehart, P. (1989) *J. Electroanal. Chem.*, **271** (1–2), 213–220.
- 88 Ren, X., Zelenay, P., Thomas, S., Davey, J. and Gottesfeld, S. (2000) *J. Power Sources*, **86** (1), 111–116.
- 89 Garcia, G., Baglio, V., Stassi, A., Pastor, E., Antonucci, V. and Arico, A.S. (2007) *J. Solid State Electr.*, **11**, 1229–1238.
- 90 Wang, Y., Li, L., Hu, L., Zhuang, L., Lu, J. and Xu, B. (2003) *Electrochem. Commun.*, **5** (8), 662–666.
- 91 Slade, R.C.T. and Varcoe, J.R. (2005) *Solid State Ionics*, **176** (5–6), 585–597.
- 92 Yu, E.H. and Scott, K. (2004) *Electrochem. Commun.*, **6** (4), 361–365.
- 93 Wynn, J.E. (1960) *Proc. Ann. Power Sources Conf.*, **14**, 52–57.
- 94 Murray, J.N. and Grimes, P.G. (1963) *Fuel Cells, CEP Technical Manual*, American Institute of Chemical Engineers, 57–65.
- 95 Hunger, H.F. (1960) *Proc. Ann. Power Sources Conf.*, **14**, 55–59.
- 96 Varcoe, J.R. and Slade, R.C.T. (2004) *Fuel Cells*, **5** (2), 187–200.
- 97 Srinivasan, S., Dillon, R., Krishnan, L., Arico, A.S., Antonucci, V., Bocarsly, A.B., Lee, W.J., Hsueh, K.-L., Lai, C.-C. and Peng, A. (2003) in *Proceedings of the 1st International Fuel Cell Science, Engineering and Technology Conference*, April 21–23, 2003, Rochester, New York, 529–536.
- 98 Costamagna, P. and Srinivasan, S. (2001) *J. Power Sources*, **102** (1–2), 242–252.
- 99 Pivovar, B.S. et al. (2007) *Sulfonated Poly (aryl ether)-type Polymers as Proton Exchange Membranes: Synthesis and Performance in Membranes for Energy Conversion*, **2** (eds K.-V. Peinemann and S.P. Nunes), Wiley-VCH Verlag GmbH, Weinheim, pp. 1–46.
- 100 Arico, A.S., Baglio, V., Di Blasi, A., Antonucci, V., Cirillo, L., Ghielmi, A. and Arcella, V. (2006) *Desalination*, **199**, 271–273.
- 101 Neburchilov, V., Martin, J., Wang, H. and Zhang, J. (2007) *J. Power Sources*, **169** (2), 221–238.
- 102 Peled, E., Duvdevani, T., Aharon, A. and Melman, A. (2000) *Electrochem. Solid-State Lett.*, **3** (12), 525–528.
- 103 Peled, E., Livshits, V., Rakhman, M., Aharon, A., Duvdevani, T., Philosoph, M. and Feigling, T. (2004) *Electrochem. Solid-State Lett.*, **7**, A507–A510.
- 104 Arico, A.S., Antonucci, P.L., Modica, E., Baglio, V., Kim, H. and Antonucci, V. (2002) *Electrochim. Acta*, **47**, 3723–3732.
- 105 Wang, J., Wasmus, S. and Savinell, R.F. (1995) *J. Electrochem. Soc.*, **142**, 4218–4223.
- 106 Arico, A.S., Creti, P., Antonucci, P.L. and Antonucci, V. (1998) *Electrochem. Solid-State Lett.*, **1**, 66–68.

- 107 Aricò, A.S., Baglio, V., Di Blasi, A., Creti, P., Antonucci, P.L. and Antonucci, V. (2003) *Solid State Ionics*, **161**, 251–265.
- 108 Ruffmann, B., Silva, H., Schulte, B. and Nunes, S. (2003) *Solid State Ionics*, **162–163**, 269–275.
- 109 Aricò, A.S., Baglio, V., Di Blasi, A. and Antonucci, V. (2003) *Electrochem. Commun.*, **5**, 862–866.
- 110 Lufrano, F., Baglio, V., Staiti, P., Arico, A.S. and Antonucci, V. (2006) *Desalination*, **199** (1–3), 283–285.
- 111 Antonucci, V., Aricò, A.S., Baglio, V., Brunea, J., Buder, I., Cabello, N., Hogarth, M., Martin, R. and Nunes, S. (2006) *Desalination*, **200**, 653–655.
- 112 Miyatake, K. and Watanabe, M. (2007) Polyimide Ionomer Membranes for PEMFCs and DMFCs in *Membranes for Energy Conversion*, **2** (eds K.V. Peinemann and S.P. Nunes), Wiley-VCH Verlag GmbH, Weinheim, pp. 47–60.
- 113 Mauritz, K.A. and Moore, R.B. (2004) *Chem. Rev.*, **104**, 4535–4585.
- 114 Kreuer, K.D., Paddison, S.J., Spohr, E. and Schuster, M. (2004) *Chem. Rev.*, **104**, 4637–4678.
- 115 Savadogo, O. (2004) *J. Power Sources*, **127**, 135–161.
- 116 Savadogo, O. (1998) *J. New Mater. Electrochem. Sys.*, **1**, 47–66.
- 117 Cleghorn, S., Ren, X., Thomas, S. and Gottesfeld, S. (1997) Book of Extended Abstracts, ISE-ECS Joint Symposium, Paris, Sept., Abstract n. 182, pp. 218–219.
- 118 Nolte, R., Ledjeff, K., Bauer, M. and Mulhaupt, R. (1993) *J. Membr. Sci.*, **83**, 211–220.
- 119 Kerres, J., Ullrich, A., Meier, F. and Haring, T. (1999) *Solid State Ionics*, **125**, 243–249.
- 120 Alberti, G. and Casciola, M. (2003) *Annu. Rev. Mater. Res.*, **33**, 129–154.
- 121 Kreuer, K.D. (2001) *J. Membr. Sci.*, **185**, 29–39.
- 122 Li, Q. and Jensen, J.O. (2007) Membranes for High Temperature PEMFC Based on Acid-Doped Polybenzimidazoles in *Membranes for Energy Conversion*, **2** (eds K.-V. Peinemann and S.P. Nunes), Wiley-VCH Verlag GmbH, Weinheim, pp. 61–96.
- 123 Aricò, A.S., Baglio, V., Creti, P., Di Blasi, A., Antonucci, V., Brunea, J., Chapotot, A. et al. (2003) *J. Power Sources*, **123** (2), 107–115.
- 124 Watanabe, M., Uchida, H., Seki, Y., Emori, M. and Stonehart, P. (1996) *J. Electrochem. Soc.*, **143**, 3847–3852.
- 125 Aricò, A.S., Baglio, V. and Antonucci, V. (2007) Composite Membrane for High Temperature Direct Methanol Fuel Cells in *Membranes for Energy Conversion*, **2** (eds K.-V. Peinemann and S.P. Nunes), Wiley-VCH Verlag GmbH, Weinheim, pp. 123–168.
- 126 Ogumi, Z., Matsuoka, K., Chiba, S., Matsuoka, M., Iriyama, Y., Abe, T. and Inaba, M. (2002) *Electrochemistry*, **70** (12), 980–983.
- 127 Ren, X., Sringer, T.E. and Gottesfeld, S. (1999) Proton Conducting Membrane Fuel Cells – Second International Symposium, Electrochemical Society, Pennington, New Jersey, Proceedings 98–27 (eds S. Gottesfeld and T.F. Fuller), pp. 341–357.
- 128 Ichinose, O., Kawaguchi, M. and Furuya, F. (2004) *J Appl Electrochem.*, **34** (1), 55–59.
- 129 Alonso-Vante, N. and Tributsch, H. (1986) *Nature (London)*, **323**, 431–432.
- 130 Sun, J.R., Wang, J.T. and Savinell, R.F. (1998) *J. Appl. Electrochem.*, **28** (10), 1087–1093.
- 131 Imaizunii, S., Shimanoe, K., Teraoka, Y. and Yamazoe, N. (2005) *Electrochem. Solid-State Lett.*, **8** (6), A270–A272.
- 132 Paffet, M.T., Beery, G.J. and Gottesfeld, S. (1988) *J. Electrochem. Soc.*, **135** (6), 1431–1436.
- 133 Watanabe, M., Tsurumi, K., Mizukami, T., Nakamura, T. and Stonehart, P. (1994) *J. Electrochem. Soc.*, **141** (10), 2659–2668.
- 134 Freund, A., Lang, J., Lehman, T. and Starz, K.A. (1996) *Cat. Today*, **27** (1–2), 279–283.

- 135 Jalan, V. and Taylor, E.J. (1983) *J. Electrochem. Soc.*, **130**, 2299–2301.
- 136 Gottesfeld, S., Paffett, M.T. and Redondo, A. (1986) *J. Electroanal. Chem.*, **205**, 163–168.
- 137 Beard, B.C. and Ross, P.N. (1990) *J. Electrochem. Soc.*, **137**, 3368–3374.
- 138 Kim, K.T., Hwang, J.T., Kim, Y.G. and Chung, J.S. (1993) *J. Electrochem. Soc.*, **140** (1), 31–36.
- 139 Mukerjee, S., Srinivasan, S., Soriaga, M.P. and McBreen, J. (1995) *J. Electrochem. Soc.*, **142** (5), 1409–1422.
- 140 Neergat, M., Shukla, A.K. and Gandhi, K.S. (2001) *J. Appl. Electrochem.*, **31** (4), 373–378.
- 141 Takasu, Y., Iwazaki, T., Sugimoto, W. and Murakami, Y. (2000) *Electrochem. Commun.*, **2** (9), 671–674.
- 142 Aricò, A.S., Shukla, A.K., Kim, H., Park, S., Min, M. and Antonucci, V. (2001) *Appl. Surf. Sci.*, **172** (1–2), 33–40.
- 143 Baglio, V., Di Blasi, A., D'Urso, C., Antonucci, V., Aricò, A.S., Ornelas, R., Morales-Acosta, D., Ledesma-Garcia, J., Godinez, L.A., Arriaga, L.G. and Alvarez-Contreras, L. (2008) *J. Electrochem. Soc.*, **155**, B829–B833.
- 144 Kinoshita, K. (1992) *Electrochemical Oxygen Technology*, John Wiley & Sons, Inc., New York.
- 145 Antolini, E., Lopez, T. and Gonzalez, E.R. (2008) *J. Alloys and Compounds*, **461**, 253–262.
- 146 Dohle, H., Divisek, J., Mergel, J., Oetjen, H.F., Zingler, C. and Stolten, D. (2000) Fuel Cell Seminar Abstracts, October 30–November 2, Portland, Oregon, pp. 126–129.
- 147 Paulus, U.A., Wokaun, A., Scherer, G.G., Schmidt, T.J., Stamenkovic, V., Radmilovic, V., Markovic, N.M. and Ross, P.N. (2002) *J. Phys. Chem. B*, **106** (16), 4181–4191.
- 148 Koffi, R.C., Coutanceau, C., Garnier, E., Leger, J.-M. and Lamy, C. (2005) *Electrochim. Acta*, **50** (20), 4117–4127.
- 149 Xiong, L. and Manthiram, A. (2005) *J. Electrochem. Soc.*, **152** (4), A697–A703.
- 150 Uchida, H., Ozuka, H. and Watanabe, M. (2002) *Electrochim. Acta*, **47** (22–23), 3629–3636.
- 151 Toda, T., Igarashi, H. and Watanabe, M. (1999) *J. Electroanal. Chem.*, **460** (1–2), 258–262.
- 152 Shukla, A.K., Raman, R.K., Choudhury, N.A., Priolkar, K.R., Sarode, P.R., Emura, S. and Kumashiro, R. (2004) *J. Electroanal. Chem.*, **563** (2), 181–190.
- 153 Zinola, C.F., Castro Luna, A.M., Triaca, W.E. and Arvia, A.J. (1994) *J. Applied Electrochem.*, **24** (2), 119–125.
- 154 Baglio, V., Stassi, A., Di Blasi, A., D'Urso, C., Antonucci, V. and Aricò, A.S. (2007) *Electrochim. Acta*, **53**, 1360–1364.
- 155 Stassi, A., D'Urso, C., Baglio, V., Di Blasi, A., Antonucci, V., Aricò, A.S., Castro Luna, A.M., Bonesi, A. and Triaca, W.E. (2006) *J. Appl. Electrochem.*, **36** (10), 1143–1149.
- 156 Jasinski, R. (1965) *J. Electrochem. Soc.*, **112**, 526–530.
- 157 Franke, R., Ohms, D. and Wiesener, K. (1989) *J. Electroanal. Chem.*, **260** (1), 63–73.
- 158 Faubert, G., Lalande, G., Coté, R., Guay, D., Dodelet, J.P., Weng, L.T., Bertrand, P. and Dénés, G. (1996) *Electrochim. Acta*, **41** (10), 1689–1701.
- 159 Elzing, A., Van der Putten, A., Visscher, W. and Barendrecht, E. (1987) *J. Electroanal. Chem.*, **233** (1–2), 113–123.
- 160 Reeve, R.W., Christensen, P.A., Hamnett, A., Haydock, S.A. and Roy, S.C. (1998) *J. Electrochem. Soc.*, **145** (10), 3463–3471.
- 161 Schmidt, T.J., Paulus, U.A., Gasteiger, H.A., Alonso-Vante, N. and Behm, R.J. (2000) *J. Electrochem. Soc.*, **147** (7), 2620–2624.
- 162 Final report of the EU funded project DREAMCAR (direct methanol fuel cell system for car applications), project nr. ERK6-CT-2000-00315 (2005).
- 163 Hockaday, R.G., DeJohn, M., Navas, C., Turner, P.S., Vaz, H.L. and Vazul, L.L. (2000) Proceedings of the Fuel Cell Seminar, Portland, Oregon, USA, 30 October–2 November, pp. 791–794.

- 164 Kelley, S.C., Deluga, G.A. and Smyrl, W.H. (2000) *Electrochem. Solid-State Lett.*, **3** (9), 407–409.
- 165 Narayanan, S.R., Valdez, T.I. and Clara, F. (2000) Proceedings of the Fuel Cell Seminar, Portland, OR, USA, 30 October–2 November, pp. 795–798.
- 166 Jung, D.-H., Jo, Y.-H., Jung, J.-H., Cho, S.-Y., Kim, C.-S. and Shin, D.-R. (2000) Proceedings of the Fuel Cell Seminar, Portland, OR, USA 30 October–2 November, pp. 420–423.
- 167 Bostaph, J., Koripella, R., Fisher, A., Zindel, D. and Hallmark, J. (2001) Proceedings of the 199th Meeting on Direct Methanol Fuel Cell Electrochemical Society, Washington, DC, USA 25–29 March.
- 168 Hockaday, R.G. (1998) US Patent No. 5,759,712.
- 169 Witham, C.K., Chun, W., Valdez, T.I. and Narayanan, S.R. (2000) *Electrochem. Solid-State Lett.*, **3**, 11, 497–500.
- 170 Gottesfeld, S., Ren, X., Zelenay, P., Dinh, H., Guyon, F. and Davey, J. (2000) Proceedings of the Fuel Cell Seminar, Portland, OR, USA, 30 October–2 November, pp. 799–802.
- 171 Dohle, H., Mergel, J., Scharmaan, H. and Schmitz, H. (2001) Proceedings of the 199th Meeting Direct Methanol Fuel Cell Symposium, Electrochemical Society, Washington, DC, USA 25–29 March.
- 172 Chang, H. (2001) The Knowledge Foundation's Third Annual International Symposium on Small Fuel Cells and Battery Technologies for Portable Power Applications, Washington, DC, USA, 22–24 April.
- 173 Chang, H., Kim, J.R., Cho, J.H., Kim, H.K. and Choi, K.H. (2002) *Solid State Ionics*, **148**, 601–605.
- 174 Jung, D.H., Jo, Y.-H., Jung, J.-H., Cho, S.-H., Kim, C.-S. and Shin, D.-R. (2000) Proceedings Fuel Cell Seminar, Portland, OR, USA, 30 October–2 November, pp. 420–423.
- 175 Lifton, R.F. (2001) The Knowledge Foundation's Third Annual International Symposium on Small Fuel Cells and Battery Technologies for Portable Power Applications, Washington, DC, USA, 22–24 April.
- 176 Martin, J.J., Qian, W., Wang, H., Neburchilov, V., Zhang, J., Wilkinson, D.P. and Chang, Z. (2007) *J. Power Sources*, **164** (1), 287–292.
- 177 Guo, Z. and Faghri, H. (2006) *J. Power Sources*, **160**, 1183–1187.
- 178 Liu, J.G., Zhao, T.S., Chen, R. and Wong, C.W. (2005) *Electrochem. Comm.*, **7**, 288–293.
- 179 Chen, R. and Zhao, T.S. (2007) *J. Power Sources*, **167** (2), 455–460.
- 180 Chen, R. and Zhao, T.S. (2007) *Electrochem. Comm.*, **9** (4), 718–724.
- 181 Chen, R. and Zhao, T.S. (2007) *Electrochim. Acta*, **52** (13), 4317–4324.
- 182 Zhang, H.F. and Hsing, I.-M. (2007) *J. Power Sources*, **167** (2), 450–454.
- 183 Abdelkareem, M.A. and Nakagawa, N. (2007) *J. Power Sources*, **165** (2), 685–691.
- 184 Chu, D. and Jiang, R. (2006) *Electrochim. Acta*, **51** (26), 5829–5835.
- 185 Yang, H., Zhang, T.S. and Ye, Q. (2005) *J. Power Sources*, **139** (1–2), 79–90.
- 186 Di Blasi, A., Baglio, V., Denaro, T., Antonucci, E. and Aricò, A.S. (2008) *J. New Mater. Electrochem. Syst.*, **11**, 165–174.
- 187 Lu, G.Q. and Wang, C.Y. (2004) *J. Power Sources*, **134** (1), 33–40.
- 188 Lai, Q.-Z., Yin, G.-P., Zhang, J., Wang, Z.-B., Cai, K.-D. and Liu, P. (2008) *J. Power Sources*, **175** (1), 458–463.
- 189 Blum, A., Duvdevani, T., Philosoph, M., Rudoy, N. and Peled, E. (2003) *J. Power Sources*, **117** (1–2), 22–25.
- 190 Kim, D., Cho, E.A., Hong, S.-A., Oh, I.-H. and Ha, H.-Y. (2004) *J. Power Sources*, **130** (1–2), 172–177.
- 191 Pan, Y.H. (2006) *J. Power Sources*, **161** (1), 282–289.
- 192 Lu, G.Q., Wang, C.Y., Yen, T.J. and Zhang, X. (2004) *Electrochim. Acta*, **49** (5), 821–828.

- 193 Motokawa, S., Mohamedi, M., Momma, T., Shoji, S. and Osaka, T. (2004) *Electrochem. Comm.*, **6** (6), 562–565.
- 194 Sabate, N., Esquivel, J.P., Santander, J., Torres, N., Gracia, I., Ivanov, P., Fonseca, L., Figueras, E. and Canè, C. (2008) *J. New Mater. Electrochem. Syst.*, **11** (2), 143–146.
- 195 Lim, S.W., Kim, S.W., Kim, J., Ahn, J.E., Han, H.S. and Shul, Y.G. (2006) *J. Power Sources*, **161** (1), 27–33.
- 196 Baglio, V., Stassi, A., Matera, F.V., Di Blasi, A., Antonucci, V. and Aricò, A.S. (2008) *J. Power Sources*, **180** (2), 797–802.
- 197 Harris, D. (2000) Ballard Power Systems Inc. News Release, 9 November.
- 198 Zhang, J., Colbow, K.M. and Wilkinson, D.P. (2001) US Patent No. 6,187,467.
- 199 <http://www.ird.dk/product.htm/>.
- 200 Buttin, D., Dupont, M., Straumann, M., Gille, R., Dubois, J.C., Ornelas, R., Fleba, G.P., Ramunni, E., Antonucci, V., Arico, V., Creti, P., Modica, E., Pham-Thi, M. and Ganne, J.P. (2001) *J. Appl. Electrochem.*, **31** (3), 275–279.
- 201 Baldauf, M. and Preidel, W. (1999) *J. Power Sources*, **84** (2), 161–166.
- 202 Baldauf, M., Frank, M., Kaltschmidt, R., Lager, W., Luft, G., Poppinger, M., Preidel, W., Seeg, H., Tegeder, V., Odgaard, M., Ohlenschloeger, U., Yde- Andersen, S., Lindic, M.H., Drews, T., Nguyen, C.V., Tachet, I., Skou, E., Engell, J., Lundsgaard, J., Hogarth, M.P., Hards, G.A., Kelsall, I., Theobald, B.R.C., Smith, E., Thompsett, D., Gunner, A. and Walsby, N. (1996–1999) Publishable Final Report of The European Commission Joule III Programme.
- 203 Baldauf, M. and Preidel, W. (1999) Book of Abstracts, Proceedings of the Third International Symposium on Electrocatalysis: Workshop, Electrocatalysis in direct and indirect methanol PEM fuel cells, Portoroz, Slovenia, 12–14 September.
- 204 Baldauf, M. and Preidel, W. (2001) *J. Appl. Electrochem.*, **31** (7), 781–786.
- 205 Wilson, M.S., Sringer, T.E., Davey, J.R. and Gottesfeld, S. (1995) Proton Conducting Membrane Fuel Cells I, Electrochemical Society, Pennington, NJ, Proceedings 95–23 (eds S. Gottesfeld, G. Halpert and A. Langrebe), p. 115.
- 206 <http://world.honda.com/news/>.
- 207 Aricò, A.S., Creti, P., Giordano, N., Antonucci, V., Antonucci, P.L. and Chuvilin, A. (1996) *J. Appl. Electrochem.*, **26** (9), 959–967.
- 208 Wilson, M.S. and Gottesfeld, S. (1992) *J. Appl. Electrochem.*, **22** (1), 1–7.
- 209 Shukla, A.K., Stevens, P., Hamnett, A. and Goodenough, J.B. (1989) *J. Appl. Electrochem.*, **19** (3), 383–386.
- 210 Fisher, A., Jindra, J. and Wendt, H. (1998) *J. Appl. Electrochem.*, **28** (3), 277–282.
- 211 Gamburzev, S., Boyer, C. and Appleby, A.J. (1999) Proton Conducting Membrane Fuel Cells II -Second International Symposium, Electrochemical Society, Pennington, New Jersey, Proceedings 98–27 (eds S. Gottesfeld and T.F. Fuller), pp. 23–29.
- 212 Nguyen, T.V. (1996) *J. Electrochem. Soc.*, **143** (5), L103–L105.
- 213 Busick, D.N. and Wilson, M. (1999) Proton Conducting Membrane Fuel Cells – Second International Symposium, Electrochemical Society, Pennington, New Jersey, Proceedings 98–27 (eds S. Gottesfeld and T.F. Fuller), pp. 435–445.
- 214 Zawodzinski, C., Wilson, M.S. and Gottesfeld, S. (1999) Proton Conducting Membrane Fuel Cells – Second International Symposium, Electrochemical Society, Pennington, New Jersey, Proceedings 98–27 (eds S. Gottesfeld and T.F. Fuller), pp. 446–456.
- 215 Scott, K., Taama, W.M. and Argyropoulos, P. (1998) *J. Applied Electrochem.*, **28** (12), 1389–1397.
- 216 Min, K.B., Tanaka, S. and Esashi, M. (2002) *Electrochemistry*, **70** (12), 924–927.
- 217 D'Arrigo, G., Spinella, C., Arena, G. and Lorenti, S. (2003) *Mater. Sci. Eng. C*, **23**, 13–18.
- 218 Yao, S.-C., Tang, X., Hsieh, C.-C., Alyousef, Y., Vladimer, M., Fedder, G.K.

- and Amon, C.H. (2006) *Energy*, **31** (5), 636–649.
- 219** D'Arrigo, S., Coffa, C. and Spinella, C. (2006) *Sensors Actuators*, **99**, 112–118.
- 220** Ye, Q. and Zhao, T.S. (2005) *J. Power Sources*, **147** (1–2), 196–202.
- 221** Xie, C., Bostaph, J. and Pavio, J. (2004) *J. Power Sources*, **136** (2), 55–65.
- 222** Zhang, J., Colbow, K.M., Lee, A.N.L. and Lin, B. (2004) US Patent Pub. No. 20040131898.
- 223** Icardi, U.A., Specchia, S., Fontana, G.J.R., Saracco, G. and Specchia, V. (2008) *J. Power Sources*, **176** (2), 460–467.
- 224** Specchia, S., Icardi, U.A., Specchia, V. and Saracco, G. (2005) *Int. J. Chem. React. Eng.*, **3**, A24–A27.
- 225** Sgroi, M., Bollito, G., Innocenti, G., Saracco, G., Specchia, S. and Icardi, U.A. (2007) *J. Fuel Cell Sci. Technol.*, **4** (3), 345–349.