



Improved Durability and Cost-effective Components for New Generation Solid Polymer Electrolyte Direct Methanol Fuel Cells

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DELIVERABLE REPORT

D.7.2 – STATE OF THE ART ON HIGH TEMPERATURE DMFCs AND PORTABLE APPLICATIONS DMFCs

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R	Report	X
P	Prototype	
D	Demonstrator	
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SUMMARY	
Keywords	<i>Catalysts, Membranes, Stack, Portable Applications, High Temperature</i>
Abstract	The objective of this deliverable is to define the current state of the art of direct methanol fuel cells technology as a baseline to assess the progress achieved during the project. This overview deals with both low and high temperature DMFC applications. The most relevant areas for early market applications such as portable power sources and assisted power units are considered.

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D.7.2 – DIRECT METHANOL FUEL CELLS: STATE OF THE ART

1. Introduction

Fuel cells represent an important technology for a large variety of applications including micro power, auxiliary power, transportation, stationary power for buildings and other distributed generation applications, and central power [1]. The candidate fuel for fuel cells is usually considered hydrogen. However, at present, no suitable large-scale infrastructure exists for hydrogen production, storage and distribution. Significant efforts have been addressed in the last decades to the direct electrochemical oxidation of alcohol and hydrocarbon fuels [2-5]. Organic liquid fuels are characterised by high energy density (Table 1), whereas, the electromotive force associated to their electrochemical combustion to CO₂ is comparable to that of hydrogen combustion to water. Among the liquid organic fuels, methanol has promising characteristics in terms of reactivity at low temperatures, storage and handling.

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

Table 1. Volumetric and Gravimetric Energy density for various fuels of technical interest for low temperature fuel cells

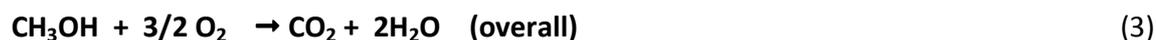
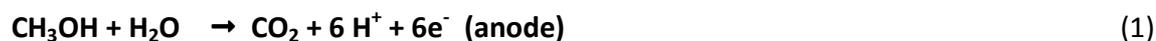
Accordingly, a direct methanol fuel cell (DMFC) would help to alleviate some of the issues surrounding fuel storage and processing for fuel cells. Methanol is cheap and it can be distributed by using the present infrastructure for liquid fuels. It can be obtained from fossil fuels, such as natural gas or coal, as well as from sustainable sources through fermentation of agricultural products and from biomasses. With respect to ethanol, methanol has the significant advantage of high selectivity to CO₂ formation in the electrochemical oxidation process. In general, liquid-fuelled fuel cells are a promising alternative to hydrogen fuelled devices as electrochemical power sources in particular for application in portable technology due to the low power required by these systems.

2. Fundamental Aspects of Direct Methanol Fuel Cells

2.1 DMFC Components and Processes

The core of the direct methanol fuel cell is a polymer ion exchange membrane. The electrodes (anode and cathode) are in intimate contact with the membrane faces. The electrodes usually consist of three-layers: catalytic layer, diffusion layer and backing layer but there are also several different configurations. The catalytic layer is composed by a mixture of catalyst and ionomer and it is characterised 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). The hydrophobic properties of this layer are fundamental to allow the transport of oxygen molecules to the catalytic sites at the cathode or to favour the escape of CO₂ from the anode. The package formed by electrodes and membrane is called “membrane and electrode assembly” (MEA).

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



The free energy associated with the overall reaction at 25°C and 1 atm and the electromotive force are:

$$\Delta G = -686 \text{ kJ mol}^{-1}_{\text{CH}_3\text{OH}}; \quad \Delta E = 1.18 \text{ V} \quad [2]$$

Usually, the open circuit voltage of a polymer electrolyte direct methanol fuel cell is significantly lower than the thermodynamic or reversible potential for the process. This is mainly due to methanol cross-over that causes a mixed potential at the cathode and to the irreversible adsorption of intermediate species at electrode potentials close to the thermodynamic values. The coverage of methanolic species is larger at high cell potentials, i.e. at low anode potentials. This determines a strong anode activation control that reflects on the overall polarization curve (Fig. 1). This can be observed in a polarization plot (Fig. 1) where the terminal voltage of the cell is deconvoluted into the anode and cathode polarizations according to the equation:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \quad (4)$$

Besides the strong activation control at the anode, the effect of the mixed potential on the cathode polarization curve is clearly observed in Fig. 1. The onset potential for the oxygen reduction in the presence of methanol cross-over is below 0.9 V versus the reversible hydrogen electrode (RHE). This is much lower than the reversible potential for the oxygen reduction in the absence of methanol, i.e. 1.23 V vs. RHE. As it was pointed out above, such a result is mainly due to the effect of the mixed potential. In addition, the cathode polarization curve in the presence of cross-over does not present a clear sigmoidal shape as in hydrogen-fed PEMFCs since 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 each other and no spontaneous current is registered above 0.9 V (Fig. 1). At high currents, both anodic and cathodic polarization curves show the onset of mass transport constraints due to the removal of the CO_2 from the anode and the effect of flooding at the cathode. In the methanol fuel cell, the flooding of the cathode is not only due to the water formed by the electrochemical process; but, it especially occurs as a consequence of the fact that a liquid or a vapour (and not a humidified gas) is fed to the anode and this water/methanol mixture permeates through the hydrophilic membrane to the cathode.

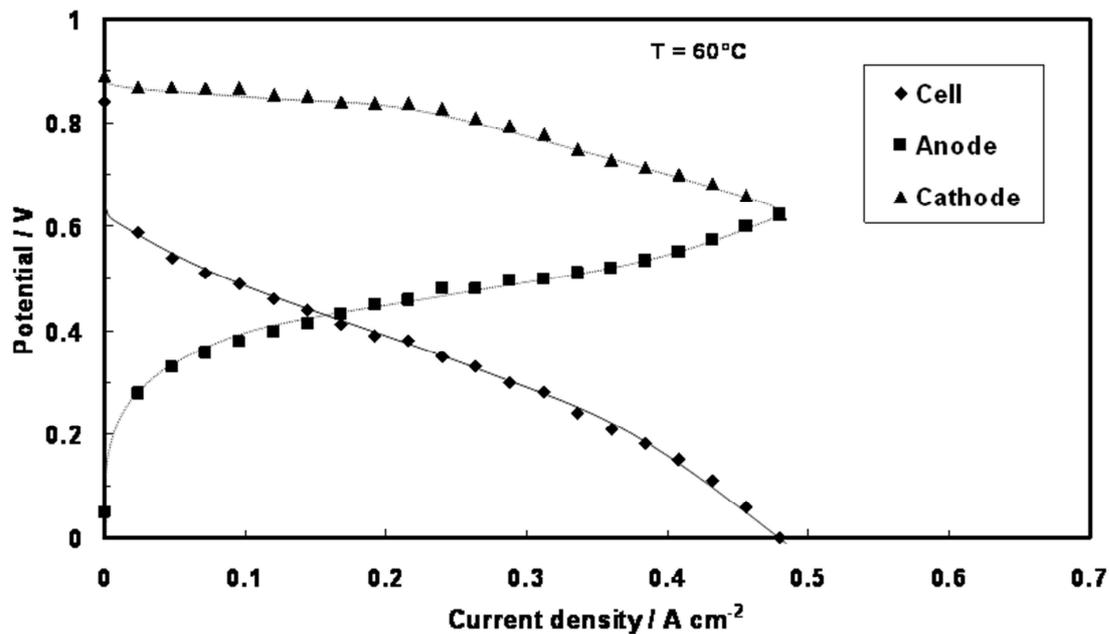


Figure 1. Single cell and in-situ half-cell electrode polarizations for a DMFC operating at 60 °C, ambient pressure, with 1 M methanol at the anode and air feed at the cathode.

In order to be competitive within the portable market, the DMFC must be reasonably cheap and capable of delivering long operation time. At present, there are a few challenging drawbacks in the development of such systems. These mainly consist in finding i) electrocatalysts which can effectively enhance the

electrode-kinetics of methanol oxidation ii) electrolyte membranes which have high ionic conductivity and low-methanol cross-over and iii) methanol-tolerant electrocatalysts with high activity for oxygen reduction.

2.2 Methanol oxidation electrocatalysts

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 [6], even if the use of high surface area unsupported catalysts is preferable for some applications [7]. 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 adatom or a bimetal [8-10]. The alloying of Sn and Ru with Pt gives rise to electrocatalysts which strongly promote the oxidation of methanol. Since the complete oxidation of methanol to CO₂ involves the transfer of 6 electrons to the electrode, the overall reaction mechanism involves several steps including dehydrogenation, chemisorption of methanolic residues, rearrangement of adsorbed residues, chemisorption of oxygenated species (preferentially on the alloying element) and surface reaction between CO and OH to give rise to CO₂. On a pure Pt surface, the dissociative chemisorption of water on Pt is the rate determining step at potentials below ≈ 0.7 V vs. RHE, i.e. in the potential region that is of technical interest [11]. It is generally accepted that an active catalyst for methanol oxidation should give rise to water discharging at low potentials and to "labile" CO chemisorption. Moreover, a good catalyst for methanol oxidation should also catalyze the oxidation of carbon monoxide. Even if various theories have been put forward to explain the promoting effect of the additional elements [5, 12-14], the subject remains controversial. Transition metal promoters and adatoms are seen as a means to improve the electrocatalytic behaviour of electrodes, either by minimizing the poisoning reaction or enhancing the main oxidation reaction. Besides, three main hypotheses have been made. A first hypothesis suggests that the metal promoters and adatoms either alter the electronic properties of the substrate or act as redox intermediates [14-16]. This hypothesis, supported by experimental evidences, also leads to the influence of a possible steric effect on the enhanced oxidation rate [16]. A second hypothesis envisages ad-atoms as blocking agents for the poison forming reaction, assumed to occur on a number of sites greater than those required for the main reaction [16]. A third hypothesis based on the bifunctional theory invokes a mechanism by which the oxidation reaction of either the fuel or the poisoning intermediate is enhanced by the adsorption of oxygen or hydroxyl radicals on promoters or adatoms adjacent to the reacting species [5]. Combining the electronic and bifunctional theories it is derived that the role of the second element is to increase the OH adsorption on the catalyst surface, at lower overpotentials, and to decrease the adsorption strength of the poisoning methanolic residues.

Both Pt-Ru and Pt-Sn systems have been reported to be promising catalysts for electro-oxidation of methanol in direct methanol fuel cells [17-19]. But although there is a conclusive evidence on catalytic promotion of methanol electro-oxidation on the Pt-Ru system in relation to Pt, contradictory results have been reported in the literature on the promotional effect of Sn for this reaction [12, 20-23]. It is generally accepted that Pt sites in Pt-Ru alloys are especially involved in both the methanol dehydrogenation step and strong chemisorption of methanol residues. At suitable electrode potentials (0.2 V vs. RHE), water

discharging occurs on Ru sites with formation of Ru-OH groups at the catalyst surface [24]. The final step is the reaction of Ru-OH groups with neighboring methanolic residues adsorbed on Pt to give carbon dioxide.

One of the main requirements for an optimal alloy electrocatalyst, such as Pt-Ru (the most performing at the moment), is its high dispersion. The mass activity (A/g Pt) of the catalyst for methanol electro-oxidation is strictly related to the degree of dispersion, since the reaction rate is generally proportional to its active surface area [25]. For this reason, usually the metal particles are dispersed onto a carbon support in order to avoid the agglomeration of particles and the decrease of surface area. Different carbon blacks are used for this purpose; actually, the most used is Vulcan XC-72 (BET Area: 250 m²/g), which appears to be the best compromise with the presence of a small amount of micropores and a reasonable high surface area sufficient to accommodate a high loading of the metal phase.

2.3 Oxygen reduction electrocatalysts

Although Pt/C electrocatalysts are, at present, the most widely used materials as cathodes in low temperature fuel cells, due to their intrinsic activity and stability in acidic solutions, there is still great interest to develop more active, selective and less expensive electrocatalysts for oxygen reduction. 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 cross-over. One is to increase Pt utilization; this can be achieved either by increasing its dispersion on carbon and the interfacial region with the electrolyte. Another successful approach to enhance the electrocatalysis of O₂ reduction is by alloying Pt with transition metals. This enhancement in electrocatalytic activity has been differently interpreted, and several studies were made to analyze in depth the surface properties of the proposed alloys combinations [26-36]. Although a comprehensive understanding of the numerous reported evidences has not yet been reached, the observed electrocatalytic effects have been ascribed to several factors (interatomic spacing, preferred orientation, electronic interactions) which play, under fuel cell conditions, a favourable role in enhancing the ORR rate [16]. A higher activity of Pt-Fe alloy electrocatalysts compared to platinum for oxygen reduction in the presence of methanol was obtained in half-cell and DMFC experiments (Fig. 2), although a partial Fe dissolution was observed [35].

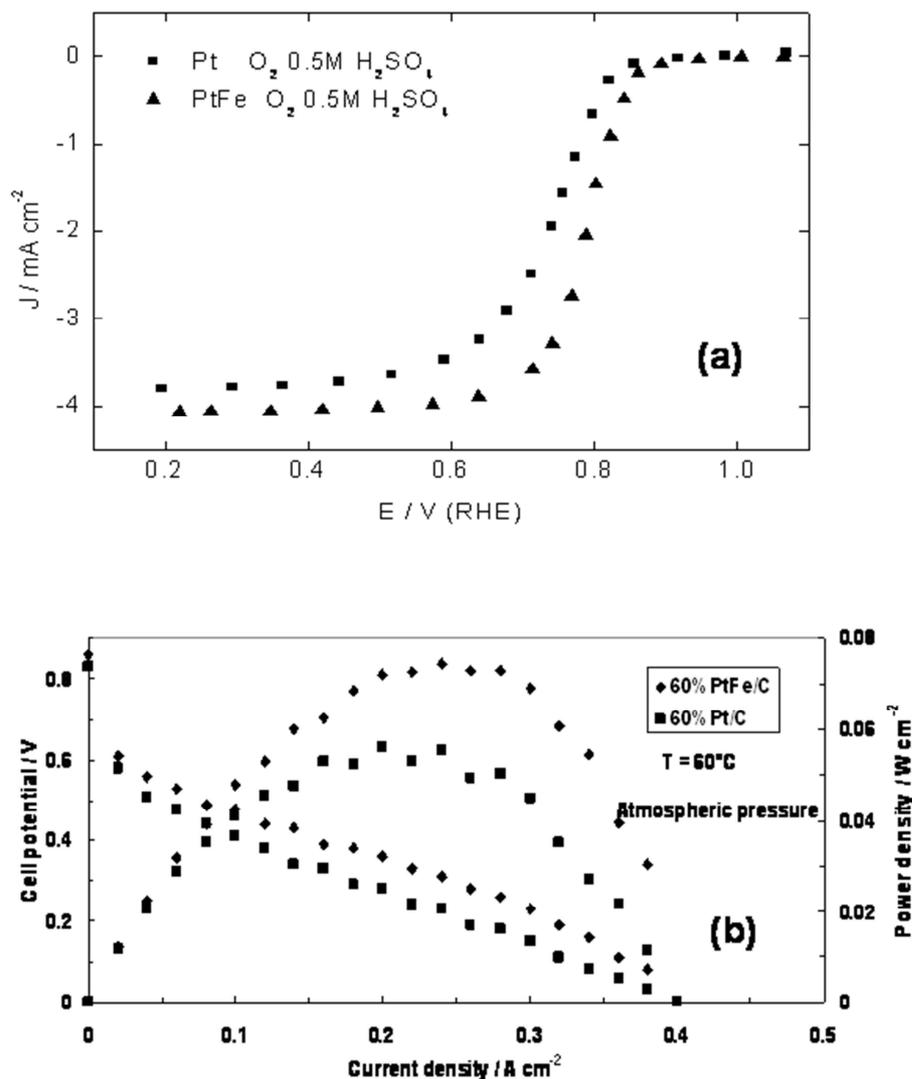


Figure 2. Polarization curves for ORR in 0.5 M H₂SO₄ (a) and polarization and power density curves in DMFC (b) for Pt/C and Pt–Fe/C cathode catalysts at 60°C [34, 35].

Alternatively to platinum, organic transition metal complexes are known to be good electrocatalysts for the oxygen reduction reaction. Transition metals, such as iron or cobalt organic macrocycles from the families of polypyrroles, phenylporphyrins, phthalocyanines and azoannulenes have been tested as O₂-reduction electrocatalysts in fuel cells [37-42]. 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 are irreversibly dissolved in the acid electrolyte. However, if the metal-organic macrocyclic is supported on a high surface area carbon and treated at high temperatures (from 500 to 800 °C), the residue exhibits electrocatalytic activity comparable to that of Pt without any degradation in performance, from which one may infer the good stability of the metal in the electrocatalyst [41]. Recently, B. Piela et al. [42] reported interesting

results for the operation of these compounds in solid polymer electrolyte fuel cells, showing a high selectivity for oxygen.

Pd is also interesting as it is at least fifty times more abundant on the Earth than Pt. For these reasons, Pd could be used (and it has been tested) in fuel cells as a Pt co-catalyst and as a Pt-free catalyst [43].

In some other studies, a few inorganic materials have recently 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 mainly consist of carbon nitrides [44], 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 ($(\text{Ru}_{1-x}\text{Mo}_x)\text{SeO}_z$) [45, 46]. Some of these possess semiconducting properties, thus, in theory, they could introduce an additional ohmic drop in the electrode. However, their activities for oxygen reduction are significantly lower than Pt [47, 48]. Carbon supported Ru electrocatalysts are reported to exhibit high selectivity for oxygen reduction in the presence of methanol but their activities are significantly lower [49].

2.4 Proton exchange membranes

Nafion membranes are currently used as electrolytes in DMFCs; yet, since methanol is rapidly transported across perfluorinated membranes, commonly used in polymer electrolyte membrane fuel cells, and is chemically oxidized to CO_2 and H_2O at the cathode, there is a significant decrease in coulombic efficiency for methanol consumption by as much as 20% under practical operation conditions. Thus, it is very important to modify these membranes by, as example, developing composites [50-52] or finding alternative proton conductors with the capability of inhibiting methanol transport. The polymer electrolyte should have a high ionic conductivity ($5 \cdot 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$) 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 to be potentially met by new classes of solid polymer electrolytes that show promising properties even though there has been no clear demonstration of their use in DMFC. Some of the membranes investigated so far are: sulfonated poly-ether-ether-ketone [53, 54] and poly-sulfone [55], polyvinylidene fluoride [56], styrene grafted and sulfonated membranes [57], zeolites gel films (tin mordenite) and/or membranes doped with heteropolyanions [58]. Some recent results obtained from CNR-ITAE, Messina, Italy, using polysulfone membranes are reported in Fig. 3.

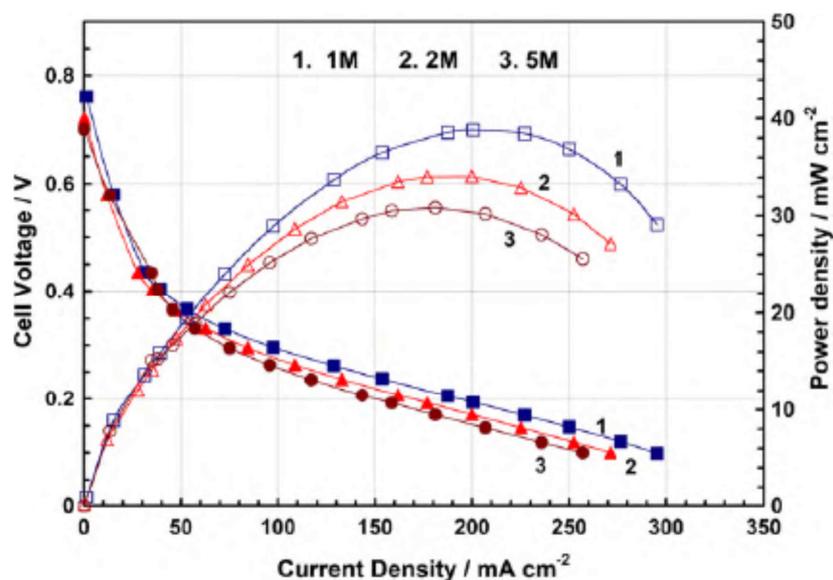


Figure 3. Polarization and power density curves recorded for active-mode DMFC single cell on a sulfonated polysulfone (66% sulfonation) membrane (70 μm) at room temperature with different methanol concentrations [55].

Alternatives to these membranes and Nafion are acid-doped polyacrylamid and polybenzimidazole [59–63]. The main question about these membranes is the extent of leaching of acids of small molecular weight (H_3PO_4) entrapped in the polymer, during operation of a fuel cell fed with a hot methanol/water mixture as the anode reactant. In fact these polymers usually swell at high temperature in the presence of water and methanol. Probably these problems may be better addressed by using a high molecular weight superacid (such as phosphotungstic acid) that may be physically entrapped in the polymer structure. However, in this case, the uptake of water by the polymer should not be significantly reduced since water is essential for the protonic conduction.

Some investigations have regarded the development of composite membranes [50, 64, 65]. Composite recast Nafion-silica membranes have shown excellent properties in terms of mechanical characteristics, water retention at high temperature, resilience to methanol cross-over and ionic conductivity [65]. These electrolytes allow DMFCs operation at 145 $^\circ\text{C}$ with a significant enhancement in methanol oxidation kinetics [65]. The only drawback, at the present time, appears to be the high cost of production, primarily determined by the expensive perfluorinated ionomer necessary for their fabrication. Some variations of this procedure include the use of heteropolyacid doped silica entrapped into recast Nafion or zirconium phosphate/ extruded Nafion membranes [50, 51].

2.5 Electrode and MEA preparation

Direct methanol fuel cell electrodes mainly consist of gas diffusion electrodes similar to those used in H₂-fuelled proton exchange membrane fuel cells (PEFCs) [7, 66-68]. Typically, such an electrode is made up of a first macroporous layer, which is a carbon cloth or paper. This is the conductive support onto which the microporous gas diffusion layer and thereafter the catalytic layer are deposited. In most electrode configurations, the gas diffusion layer is formed by Polytetrafluoroethylene (PTFE) and carbon black; whereas, the composite catalytic layer consists of carbon supported Pt or Pt alloy catalysts and Nafion ionomer. The function of PTFE in the diffusion layer is to provide a network for gas transport and to give structural integrity to the layer. The catalytic layer, containing Nafion in an amount ranging between 15 and 33 wt%, is hot pressed or deposited onto the perfluorosulfonic electrolyte membrane [7, 67, 69]. Such an electrode structure was originally developed for operation at about 80°C since the development of DMFC for transportation was historically considered to provide the main perspectives for large-scale application of such devices. In low temperature liquid-fuelled Direct Methanol Fuel Cells (DMFCs) finalized to the development of portable systems, this electrode configuration suffers from mass-transport limitations. These constraints mainly occur at the anode due to the low diffusion coefficient of methanol in water and the release of carbon dioxide gas bubbles [70, 71]. The influence of PTFE content, in the anode diffusion layer, on cell performance was investigated for high temperature DMFCs. The optimal PTFE amount was found to be between 13 and 20 wt% [72]. Some recent studies have been addressed to replace the carbon cloth or carbon paper support with a titanium net [71] to enhance mass transport. Alternatively, some attempts have been addressed to enhance the morphology of the conventional electrode structure. As well known, a correlation between the amount of ionomer, in the catalytic layer, and catalyst porosity exists [69]. The ionomer content influences the hydrophobic and hydrophilic pore distribution in the catalyst layer. Hydrophilicity increases as a function of the Nafion content. DMFCs are generally operated with aqueous methanol solution at different concentrations; therefore, in order to have a better reactant distribution, a good hydrophilicity is important for the anode side. On the other hand, hydrophobic pores have an important role for CO₂ removal from the catalytic layer. The optimization of the structure of the electrode and/or MEA also requires an appropriate investigation of the microstructure of the carbon support, in order to ideally distribute the ionomer on the carbon surface containing Pt or Pt-Ru particles. In this way, Pt loading could be significantly reduced if Pt utilization increased.

The operation of DMFCs with air requires the development of a proper cathode layer. In fact, when air is fed to the cathode side, while oxygen reacts to produce water, the nitrogen contained in the feed stream remains entrapped in the pores of the electrode; the entrapped nitrogen is a diffusion barrier for the incoming oxygen, and results in mass transport overpotential performance losses even at intermediate current densities. Furthermore, the transport of this gas to the reaction sites is retarded by flooding of the electrocatalyst layer [73]. A few approaches have been proposed to enhance the oxygen transport properties when air is used as the feed stream. Some examples are heat treatments of the recast Nafion gel in the electrocatalytic layer to make it hydrophobic [74] or to use pore formers to increase porosity [75, 76].

3. Current status of DMFC technology for portable power sources applications

Portable power is becoming important for many electronic devices, such as notebook computers, personal digital assistants (PDAs), music systems and cellular telephones. Currently, these devices are powered by primary and secondary batteries. While the power source is often the largest component of the device and, in fact, is the limiting factor in efforts toward miniaturization, the runtime and functionality of the devices remain limited by the quantity of energy that can be stored and carried within them. Thus, advances in the development of portable fuel cells will have a great impact on the use and development of modern electronic devices. Unlike primary and secondary batteries, where the reactants and products are contained within the battery, fuel cells employ reactants that are continuously supplied to the cell; byproducts also are continuously removed. Methanol, which is characterized by low cost, easy storage and handling, and high energy density, appears well-suited for portable fuel cells [77-80]. 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 for charging 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 are actively engaged in the development of low power DMFCs for cellular phone, laptop computer, portable camera and electronic game applications [81-95]. The primary goal of this research is to develop proof of concept DMFCs capable of replacing high performance rechargeable batteries in the portable electronic devices market. Manhattan Scientific Inc (MSI) expects that methanol-based micro fuel cell technology will replace obsolete small batteries and will provide power for cell phones on standby for 6 months and 1 week talk time when compared to 2 weeks and 5 ours talk time with lithium-ion batteries. The Darnell group estimated that fuel cells market will be increased to 463.8 million unit sales for cell phones in 2009. Polyfuel website states that 73% of laptop users are likely to select a fuel cell technology vs. a laptop offering only a conventional battery.

Polyfuel estimates that the markets for μ DMFC will be over 140 million units in 2012. Commercial market demands for fuel cells are anticipated to be \$2.6 billion in 2009 and will reach \$13.6 billion by 2014. The world fuel cell spending (which includes R & D and commercial sales) is expected to be \$10.8 billion in 2009 [84]. This represents a range of applications such as PC, cell phones, military and healthcare.

A comprehensive list of various companies working on μ DMFC technology is presented in Table 2.

Company's Name	Maximum power density and total power	Potential applications
Toshiba	300 mW	Flash-based MP3 player
Polyfuel	56 W	Laptop
Antig	16 W	Laptop, portable electronics
NEC corporation	70 mW cm ⁻²	Laptop
Neahpower	70 W	Laptop, military
Motorola	100 mW	Mobile phone/recharger
Fujitsu	Maximum 15 Wh	Mobile phone, Laptop (8–10 h)
Giner	150 W	Cellphones, PDA, Laptops
Ultra cell, USA	25 W	Laptops, run for 2 days and portable electronic devices
MTI micro fuel cell	800 mW (max. 1 W), 35 Wh	To military and consumer electronic devices
Jadoo power, USA	100 W	To military and other applications
Samsung, Korea	20 W	Laptop for 6 h, Handphone

Table 2: Different companies working in the development of μ DMFC (Reproduced from Ref. [81]).

Toshiba has developed prototype DMFC units having an output power of 100 mW and 300 mW to a flash-memory-based digital audio player and a hard disk drive device based digital audio player, respectively. Polyfuel Company has developed a cheaper membrane to use in DMFC when compared to its competitor Dupont. Antig is developing fuel cell stacks and number of stacks is determined by the requirement of power supply. This company has announced in April 2008 that it has received Underwriters Laboratories (UL) approval to use its stack in portable electronic equipment. The membrane developed by Neah power is based on the silicon layer instead of majority of the companies developed technology on polymer based. MTI microfuel cell company has developed a technology to eliminate the need for cumbersome water management micropumps and micro-plumbing subunits, which has distinctive advantages such as maximize the amount of fuel within the power pack by use of 100% methanol as fuel and minimizing the percentage of dilution of the fuel. The water required for the process on the fuel side is used up from the regenerated water on the air side of the cell without any external pumps. Jadoo power is the number one provider of portable fuel cell for military and other applications. Smart Fuel Cell Company has developed 80% weight reduction with extremely high power density of 1200 Wh per Kg for military applications.

At a meeting held in 2005 in Canada, the International Civil Aviation Organization's Dangerous Goods Panel (ICAO DGP) voted to allow passengers to carry and use micro fuel cells and methanol fuel cartridges on-board airplanes to power their laptop computers and other consumer electronic devices. The ICAO DGP action would allow passengers to carry micro fuel cells in the cabin only and not stowed in checked baggage and up to two spare fuel cartridges per person will be allowed [96]. The United States has approved in May 2008, the use of micro fuel cells in airlines to as early as May 30, 2008 and takes effect October 1, 2008. This is a boon to the companies and this removes the major barrier keeping micro fuel cells out of electronic devices [97].

At Motorola, a portable direct methanol fuel cell prototype has been presented, which is capable of powering communications devices such as PDAs, or performing as a desktop charger for a cell phone. The fuel cell is packaged using low-temperature cofired ceramic (LTCC) technology. This ceramic medium is suitable for producing specialized design features such as the channelization requirements for fuel delivery and distribution as well as those required for oxygen intake and for water recovery. Rapid prototyping of the ceramics is a real advantage, allowing assessment of major design changes in only a few days with

minor adjustments in hours. The 100 mWe fuel cell prototype showed sustained and stable performance for approximately a week [98].

The Jet Propulsion Laboratory (JPL), USA, has been actively engaged in the development of “miniature” DMFCs for cellular phone applications [99, 100]. According to their analysis, the power requirement of cellular phones during 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 platinum-ruthenium alloy particles, either as fine metal powders (unsupported) or dispersed on high surface area carbon. Alternatively, a bimetallic powder made up of submicron platinum and ruthenium particles was reported to give better results than the platinum-ruthenium alloy. Another method describes the sputter-deposition of a platinum-ruthenium 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 was prepared by applying platinum ink to a carbon substrate. Another component of the cathode was the hydrophobic Teflon polymer utilized to create a three-phase boundary and to achieve efficient removal of water produced by the electro-reduction 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 4–6 mg cm⁻². The MEA was prepared by pressing the anode, electrolyte and cathode at 8.62×10^6 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 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”. 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 6–10 mW cm⁻². The fuel cell was typically run at ambient air, 20–25 °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.

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 a 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 [101, 102]. A 30-cell DMFC stack with electrodes with an active area of 45 cm² 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 utilization and overall cell performance. An anode catalyst loading of Pt between 0.8–16.6 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 cross-over 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 50W DMFC stack [103]. 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 resistance but heavier material requirements. To circumvent the weight limitations, current collectors were manufactured from stainless steel (MEAs were mounted between the current collectors) and 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. MEAs were constructed 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 cm² for each of the 40 cells. At the anode a novel construction allowed the removal of CO₂ by convection forces at individual cell anodes. The conditions for running the stack were 1M methanol, 60 °C and 3 bar O₂, which led to peak energy densities of 45–55 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 cm², than the previous prototype's and although it is not air-breathing, it works with low air stoichiometric rates (a more efficient cathodic flow distribution structure).

Samsung Advanced Institute of Technology (SAIT), South Korea, has developed a small monopolar DMFC cell pack (2 cm², 12 cells, CO₂ removal path, 5–10 M methanol, air breathing and room temperature) of 600 mW for mobile phone applications [104, 105]. Unsupported PtRu and Pt catalysts were coated onto a diffusion electrode of porous carbon substrate of the 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 3–8 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 for attaining high fuel efficiency and preventing a voltage loss on the cathode. A gas chromatography (GC) method was utilized in situ during the electrochemical polarization. In this way, the cathode output stream gas was analyzed and it was calculated the amount of carbon dioxide produced by the permeated methanol, which is consumed at the cathode. A monopolar structure was investigated; 12 cells of 2 cm² 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 or 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; the MEA having this novel diffusion electrode showed 10 mW cm^{-2} at 0.3 V of power density without the aid of any external fueling system. In this MEA, the anode contained a microlayer for the methanol flow field with capillary wicking structure and the cathode-contained a microlayer for the air flow field with breathing structure. A hybrid membrane with inorganic phase dispersions was utilized. This was operated as methanol blocking medium in the hydrophilic channel of the ionomer assisting to reduce the amount of methanol cross-over. As measured by GC, the hybrid membrane allowed a 20–40% reduction of methanol permeation, at the nominal potential of 0.3 V, within the various range of methanol concentrations from 1 to 5 M. If a conductivity approaching that of plain Nafion i.e. near 10^{-1} S/cm , could be achieved with this system, such a process offers the possibility of the development of functional membranes for DMFCs. A monopolar design consisting of 12 cells flat pack was assembled and tested in the severest condition that is methanol wicking and air breathing at room temperature. Each cell had the active area of 2 cm^2 and the pack was equipped with a path of 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} , which is rather higher than that achieved in the single MEA test (10 mW cm^{-2}). This result could be attributed to the uniform fuel distribution and efficient current collecting design of smaller single cells.

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 [106]. The stack was tested at 25–50 °C using 2.5 M methanol, supplied without a pumping system, O_2 at ambient pressure and 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 a direct liquid methanol (DLM) fuel cells (a hybrid PEM/DMFC system) for portable electronic devices [107]. 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 construction 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 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. The increased concentration of methanol in the feed stock results in concentration gradients that should lead to higher methanol crossover rates. However, this technical concern is not mentioned in the company's literature.

At the Institute for Fuel Cell Innovation in Vancouver, Canada, a passive (air breathing) planar three-cell DMFC stack was designed, fabricated and tested [108]. 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 side 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 utilized as electrolyte. A power density of 8.6 mW cm^{-2} was achieved at ambient temperature and passive operation. Stacks with a parallel connection of the single cells showed a significantly lower performance than in a series configuration. It was also identified that high electrical resistance was 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 University of Connecticut, USA, the group of Z. Guo and A. Faghri developed a design for planar air breathing DMFC stacks [109]. This design incorporated a window-frame structure that provided a large open area for more efficient mass transfer with modular characteristics, making 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. The 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 [110-113] studied the effect of methanol concentration on the performance of a passive DMFC single cell. They found that the cell performance was 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 the better performance with higher methanol concentrations was mainly attributed to the increase in the cell operating temperature caused by the exothermic reaction between permeated methanol and oxygen on the cathode. This finding was subsequently confirmed by the fact that the cell performance decreased, when the cell running with higher methanol concentrations was cooled down to room temperature. Moreover, they proposed a new membrane-electrode assembly (MEA), in which the conventional cathode gas diffusion layer (GDL) is eliminated while utilizing a porous metal structure, made of a metal foam, for transporting oxygen and collecting current. They showed theoretically that the new MEA [112] and the porous current collector enabled a higher mass transfer rate of oxygen and thus better performance. The measured polarization and constant-current discharging behavior showed that the passive DMFC with the new MEA and new current collector yielded better and much more stable performance than did the cell having the conventional MEA and the conventional perforated-plate current collector, in particular with high methanol concentration. The EIS spectrum analysis further demonstrated that the improved performance with the new MEA was attributed to the enhanced transport of oxygen as a result of the reduced mass transfer resistance in the fuel cell system; whereas, the improved performance

for the porous current collector was attributed to the increased operating temperature as a result of the lower effective thermal conductivity of the porous structure and its fast water removal as a result of the capillary action [113].

Another group at the Honk Kong University, H.F. Zhang et al. [114], reported on a flexible graphite-based integrated anode plate for DMFCs operating at high methanol feed concentration under active mode. This anode structure which was made of flexible graphite materials not only provided 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 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 10 M methanol feed. Cell polarization data showed that this new anode structure significantly improved the cell performance at high methanol concentrations (e.g. 12 M or above).

M.A. Abdelkareem and N. Nakagawa from Gunma University, Japan, [115] 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 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 MEA performance increased by more than twice as compared to 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 the cell performance, where the porous carbon plate, PCP, prevented the cathode from flooding by reducing the mass transport through the MEA. Methanol and water fluxes through the MEA/PCP were not affected by flowing oxygen at 0.1 l min^{-1} . However, the increase in oxygen flow rate from 0.1 l min^{-1} to 1 l min^{-1} had a negative effect on the cell performance either for the conventional MEA or for the MEA/PCP. This was probably due to the cooling effect for conventional MEA and the drying effect for the MEA/PCP. A moderate supply of oxygen to the cathode, like air-breathing, was appropriate for the DMFC with a PCP.

The effect of operating conditions on energy efficiency for a small passive DMFC was analyzed by D. Chu and R. Jiang from U.S. Army Research Laboratory, Adelphi, USA [116]. Both Faradic and energy conversion efficiencies decreased significantly with increasing methanol concentration and environmental temperature. The Faradic conversion efficiency was as high as 94.8%, and the energy conversion efficiency was 23.9% in the presence of an environmental temperature low enough (10°C) under constant voltage discharge at 0.6 V with 3 M methanol for a DMFC bi-cell using Nafion 117 as electrolyte. Although higher temperature and higher methanol concentration allowed to achieve higher discharge power, they resulted in considerable losses of Faradic and energy conversion efficiencies by using Nafion electrolyte membrane. Their conclusion was that the development of alternative highly conductive membranes with a significantly lower methanol crossover is necessary to avoid loss of Faradic conversion efficiency with temperature and with fuel concentration.

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 [117] and water flooding at the cathode [118]. Lu and Wang from the Pennsylvania State University, USA [119], developed a 5 cm² transparent cell to visualize these phenomena in situ. Two types of membrane-electrode assembly (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 Toray carbon-paper based MEA under 2 M methanol solution preheated at 85°C. For the hydrophobic carbon paper backing, it was observed that CO₂ 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 of smaller 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 DMFC was also carried out. It was shown that the liquid droplets appeared more easily on the surface of carbon paper due to its reduced hydrophobicity at elevated temperature. 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 relatively high temperature (85°C), such a basic understanding is indispensable for portable DMFC design and optimization.

Lai et al. [120] investigated the long-term discharge performance of passive DMFC 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 anode facing upward showed the best long-term discharge performance at high current. A few independent water droplets accumulated in cathode when the anode faced upward. Instead, in the passive DMFC with vertical orientation, a large amount of produced water flowed down along the surface of current collector. The passive DMFC with vertical orientation showed relatively good performance at low current. It was concluded that the cathode produced less water in a certain period of time at smaller current. In addition, the rate of methanol crossover in the passive DMFC with anode facing upward was relatively high, which led to a more rapid decrease of the methanol concentration in anode. The passive DMFC with anode facing downward resulted in the worst performance because it was very difficult to remove CO₂ 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, realized 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 [121]. 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, through 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 resulted 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. [122] developed passive micro-DMFCs with capacities under 5 W to be used as portable power sources. Research activities were focused on the development of membrane–electrode assemblies (MEAs) and 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 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 having 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 the performance were also examined to investigate the operation characteristics of single cells and monopolar stacks. Application of micro-DMFCs as portable power sources were demonstrated using small toys and display panels powered by the passive monopolar stacks.

Tekion Inc., Champaign, USA, has developed an advanced air breathing direct methanol fuel cell for portable applications [123]. A novel MEA was fabricated to improve the performance of air-breathing direct methanol fuel cells. A diffusion barrier on the anode side was designed to control methanol transport to the anode catalyst layer and thus suppressing the 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 mWcm^{-2} at $60 \text{ }^\circ\text{C}$ with 2 M methanol solution. The value was nearly two times more than that of a commercial MEA. At $40 \text{ }^\circ\text{C}$, 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 University of California at Los Angeles, USA, developed a silicon-based micro DMFC for portable applications [124]. Anode and cathode flow-fields with channel and rib width of $750 \text{ }\mu\text{m}$ and channel depth of $400 \text{ }\mu\text{m}$ were fabricated on Si wafers using the microelectromechanical system (MEMS) technology. A membrane-electrode assembly (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 $60 \text{ }^\circ\text{C}$. When the cell was operated at room temperature, the maximum power density was shown to be about 16 mW cm^{-2} with both 2 and 4 M methanol feed. It was further observed that the present μDMFC still produced reasonable performance under 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 [125]. The μDMFC was prepared using a series of fabrication steps from 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 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. The electroplating solution for Pt was 20 mM $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and 0.5 mM $(\text{CH}_3\text{COO})\text{Pb} \cdot 3\text{H}_2\text{O}$. The deposition was carried by applying a current density of 30 mA cm^{-2} during 10 min. The mass loading of Pt was 2.4 mg cm^{-2} . The Pt–Ru for methanol oxidation was obtained from a solution containing 20 mM $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ + 20 mM $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$. The deposition was performed at -0.15 V vs. Ag/AgCl for 5 min. The mass loading of Pt–Ru was 2.85 mg cm^{-2} . The electroplating process was carried out at $25 \text{ }^\circ\text{C}$ for both electrodes. Energy dispersive X-ray (EDX) analysis showed a platinum/ruthenium of 90/10 atomic ratio. A Nafion 112 membrane was used as electrolyte. The performance of the μDMFC was assessed at ambient temperature using 2 M $\text{CH}_3\text{OH}/0.5 \text{ M H}_2\text{SO}_4/\text{H}_2\text{O}$ as the fuel and $\text{O}_2\text{-sat.}/0.5 \text{ M H}_2\text{SO}_4/\text{H}_2\text{O}$ as the oxidant. The O_2 saturated solution was prepared by using oxygen bubbling into 0.5 M $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solution. The supply of fuel was made by means of a microsyringe pump connected to the fabricated μDMFC unit. The OCV for the Pt cell was 300 mV while it was 400 mV for Pt–Ru cell. The maximum power density was 0.44 mW cm^{-2} at 3 mA cm^{-2} at Pt electrode. While, the maximum power density reached 0.78 mW cm^{-2} at 3.6 mA cm^{-2} for cell with Pt–Ru anode. The reason of this low performance could be due to the not optimal composition of Pt–Ru anode catalyst.

The Institute of Microelectronics of Barcelona-CNM (CSIC), Spain, presented a passive and silicon-based micro DMFC [126]. The device was based on a hybrid approach composed of a commercial Membrane Electrode Assembly (MEA) consisting of a Nafion® 117 membrane with 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 of 300 micrometers depth that covered an area of $5.0 \times 5.0 \text{ mm}$. The fabrication process of the silicon plates started with a double-side polished Si wafer 500 mm thick. A first photolithography was done on the front side to define an array of squared windows with 80 mm size. Subsequently, a second photolithography was performed on the back side to define the cavity for the fuel container. Then, a deep reactive ion etching (DRIE) was realized first on the front side to obtain 200 mm-deep channels, and continued at the back until the wafer was completely perforated. These channels allowed fuel transport to the electrode surface and their dimensions were set to $80 \times 80 \text{ micrometers}$ in order to ensure the prevalence of the capillary force versus gravity in the anode side regardless of device orientation. 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. Finally, the wafer was cut into $10 \times 14 \text{ mm}$ chips. In order to guarantee uniform pressure over the active area of the cell, two micromilled methacrylate pieces tightened with four bolts were used as external casing. In addition to provide a mechanical support while testing, the cell was equipped with a 100 ml methanol reservoir. The cell was tested at ambient temperature and different methanol concentrations. It was found that methanol concentration had low impact on the fuel cell maximum power density, which reached a value around 11

$\text{mW}\cdot\text{cm}^{-2}$ and was comparable to values reported in the literature for larger passive and stainless-steel fuel cells. Temperature measurements were performed; the fuel cell temperature did not change significantly and was independent from the methanol crossover rate.

A research group of Yonsei University, Korea, realized a DMFC on printed circuit board (PCB) substrates by means of a photolithography process [127]. The effects of 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 μm and flow rates of methanol from 2 to 80 ml min^{-1} . A μDMFC with a cross-stripe channel pattern gave superior performance compared with zig-zag and serpentine type of pattern. A single cell with a 200 μm wide channel delivered a maximum power density of 33 mW cm^{-2} when using 2 M methanol feed at 80°C.

CNR-ITAE, Italy, developed passive DMFC mini-stacks for portable applications [128-130] based on simple designs. Essentially, two designs of flow-fields/current collectors for a passive DMFC monopolar three-cell stack were investigated (see Fig. 4). The first design (A) consisted of two plastic plates (printed circuit boards - PCBs) covered by thin gold film current collectors with a distribution of holes through which methanol (from a reservoir) and air (from ambient) 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 the electrodes were placed in contact. A big central hole allowed a direct exposure of electrodes to ambient air (cathodes) and methanol solution (anodes). A methanol reservoir (containing in total 21 ml of methanol solution and divided in three compartments), 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. The electrodes were composed of a commercial gas-diffusion layer-coated carbon cloth HT-ELAT and LT-ELAT (E-TEK) at the anode and cathode, respectively. Unsupported Pt-Ru (Johnson-Matthey) and Pt (Johnson-Matthey) catalysts were mixed with 15 wt.% Nafion ionomer (Ion Power, 5 wt.% solution) and deposited onto the backing layer for the anode and cathode, respectively. Nafion 117 (Ion Power) was used as electrolyte. The MEAs for the two stack designs (3 cells) were manufactured by assembling simultaneously three sets of anode and cathode pairs onto the membrane, 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.

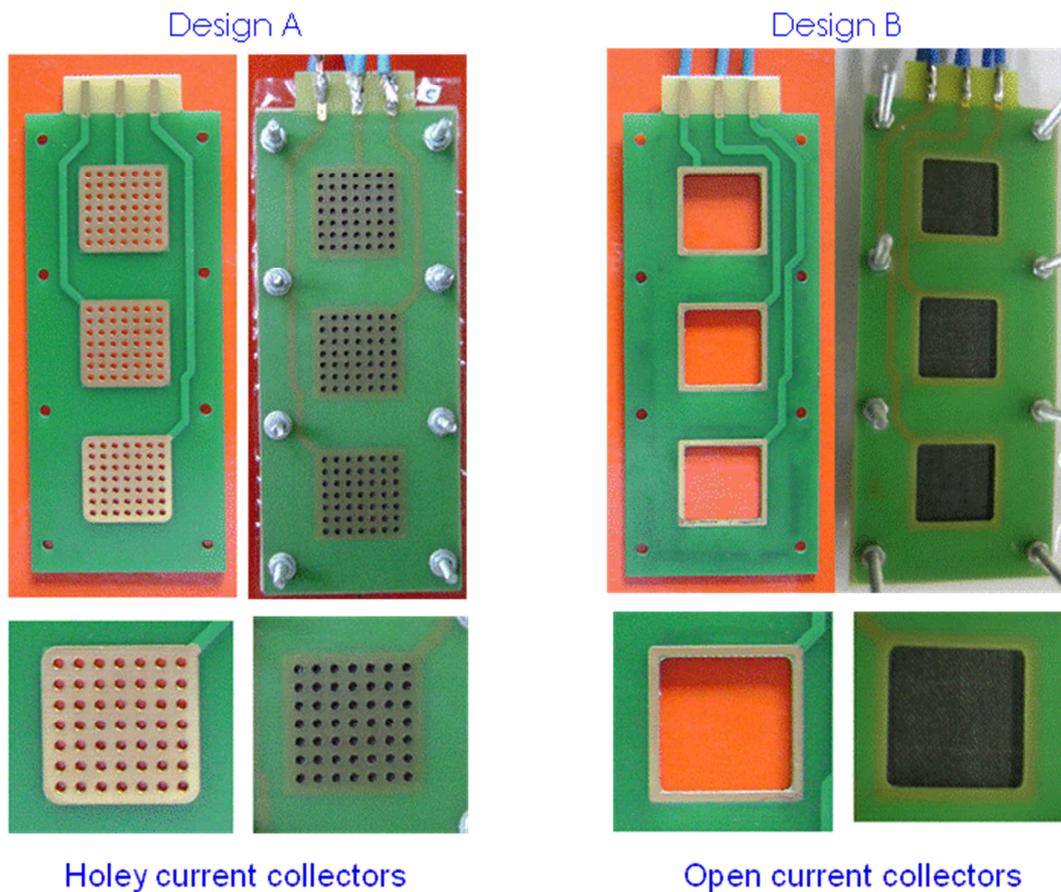


Figure 4. Pictures of two different DMFC-three-cell-stack designs.

The electrochemical characterization was carried out varying the catalyst loading and methanol concentration. A loading of 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 amount of catalytic sites.

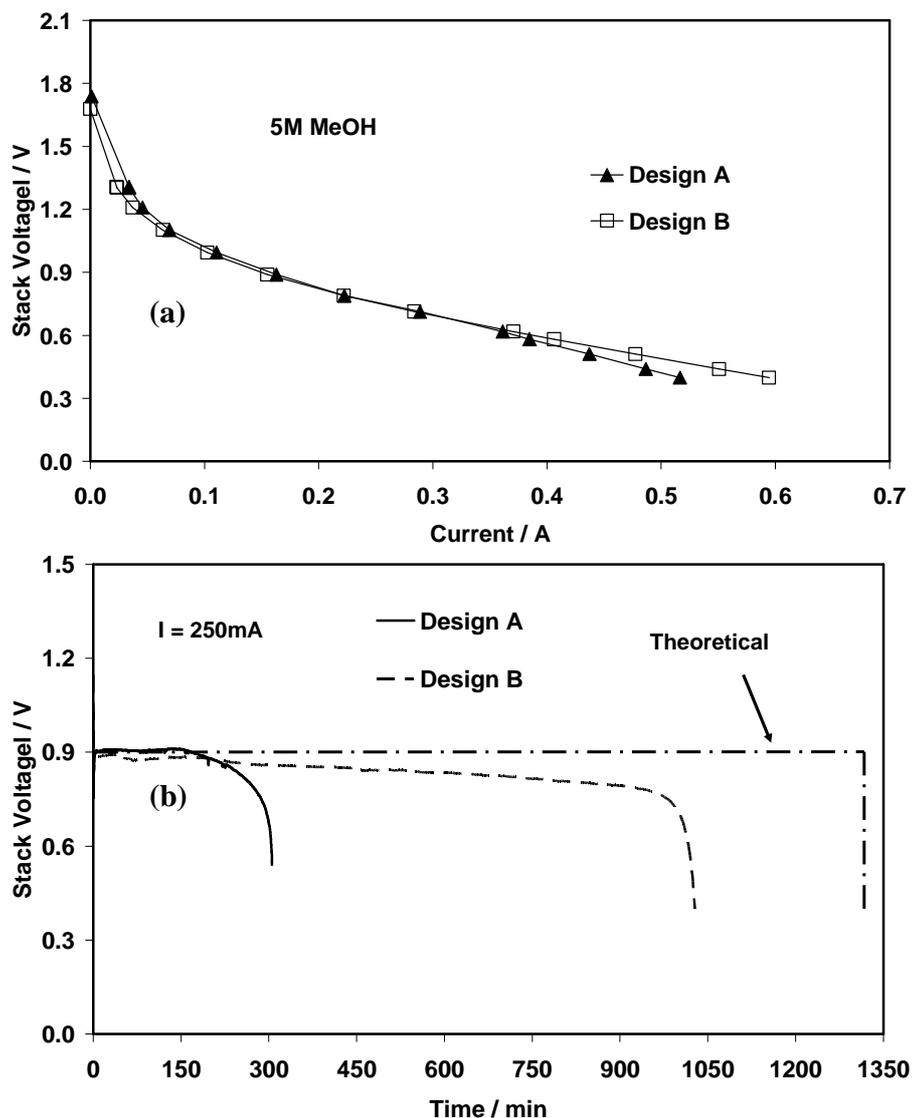


Figure 5. Comparison between the polarization curves obtained with the two different designs with a Pt loading of 4 mg cm^{-2} on each electrode and 5 M methanol solution (a), and chrono-potentiometric results at 250 mA obtained with the two designs using a Pt loading of 4 mg cm^{-2} and 5 M methanol solution (b) [129].

Similar performances in terms of maximum power were recorded for the two designs; whereas, better mass transport characteristics were obtained with the design B (Fig. 5a). On the contrary, OCV and stack voltage at low current were higher for the design A as a consequence of lower methanol cross-over. A maximum power of 220-240 mW was obtained at ambient temperature for the three-cell stack with 4 mg cm^{-2} Pt loading on each electrode using both 2 M and 5 M methanol concentration at the anode, corresponding to a power density of about 20 mW cm^{-2} [128, 129]. The use of highly concentrated methanol solutions caused a significant decrease of OCV that reflected on the overall polarization curve; however, the activation losses were similar to diluted methanol solutions. A longer discharge time (17 h)

with an unique MeOH charge was recorded with design B (Fig. 5b) at 250 mA compared to the design A (5 h). This was attributed to an easier CO₂ removal from the anode and better mass transport properties. In fact, in the design A, CO₂ did not escape easily from the anode hindering the methanol diffusion to the catalytic sites by natural convection. When the small stack based on the A design was mechanically agitated, the effect of this forced convection increased the discharge time [129]. As a further optimization, Titanium-grid current collectors with proper mechanical stiffness were added [130]. They allowed a significant increase of the performance by reducing contact resistance even in the case of significant swelling. The performance obtained with Nafion 117 membrane and Ti grids was 32 mWcm⁻² [130].

Cao et al. [131] designed, fabricated and tested silicon-based micro-DMFC stacks that consisted of six unit cells; the results showed that a stack with double serpentine-type flow-fields generated a peak power of 151mW at a voltage of 1.5 V.

Kim et al. [132] developed a passive DMFC stack of six unit cells and investigated the influence of operating conditions such as the cell temperature and methanol concentration on stack performance. It was found that with increasing methanol concentration: (i) the open-circuit voltage (OCV) decreased as a result of the higher rate of methanol crossover; (ii) the cell operating temperature increased and caused an improvement in cell performance.

Recently, Chan et al. [133] designed, fabricated and tested a small passive DMFC stack and investigated the effect of methanol concentration on stack performance and the effect of cell operating temperature on water flooding. The performance of the stack increases with increasing methanol concentration as a result of the increased cell operating temperature caused by the exothermic reaction between the permeated methanol and oxygen at the cathode. On the other hand, the increased operating temperature reduced water flooding at the air-breathing cathode on account of the increased water evaporation rate, which further increased the cell voltage and operation stability. It was also found that with the same methanol concentration, the stack exhibited a much higher cell operating temperature (50–53 °C) than the unit cell (27–29 °C), which tends to increase the performance.

In summary, to maximize water and oxygen transport to the air-breathing cathode, the monopolar arrangement is widely used in formation of passive DMFC stacks. The stack performance is affected by many design parameters and operating conditions, including methanol concentration, catalyst loading, MEA and current-collector design. The most promising results are summarized in Table 3.

Developer	Number/area of cells	Power density (mWcm ⁻²)	Methanol concentration (M)	Anode catalyst and loading	Electrolyte	Cathode catalyst and loading
Motorola Labs	4 cells (planar stack)/13-15 cm ²	12-27	1	PtRu alloy, 6-10 mg cm ⁻²	Nafion 117	Pt, 6-10 mg cm ⁻²
Jet Propulsion Lab, USA	6 cells (flat pack)/6-8 cm ²	6-10	1	PtRu alloy, 4-6 mg cm ⁻²	Nafion 117	Pt, 4-6 mg cm ⁻²
Samsung advanced Institute of Technology	12 cells (monopolar)/2 cm ²	23	5	PtRu, 3-8 mg cm ⁻²	Hybrid membrane	Pt, 3-8 mg cm ⁻²
Korea Institute of Science & Technology	6 cells (monopolar)/6 cm ²	40	4	PtRu	Nafion 115	Pt
Institute for Fuel Cell Innovation, Canada	3 cells (monopolar)	8.6	2	80% PtRu, 4 mg cm ⁻²	Nafion 117	Pt black, 4 mg cm ⁻²
University of Connecticut, USA	4 cells/ 18-36 cm ²	30	2-5	PtRu alloy, 7 mg cm ⁻²	Nafion 117	Pt, 6.5 mg cm ⁻²
Honk Kong University	Single cell/4 cm ²	28	4	PtRu, 4 mg cm ⁻²	Nafion 115	40% Pt/C, 2 mg cm ⁻²
Harbin Institute of Technology, China	Single cell	9	2	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	1-6 in H ₂ SO ₄	PtRu, 5-7 mg cm ⁻²	NP-PCM	Pt, 4-7 mg cm ⁻²
Institute of Microelectronic of Barcelona-CNM, Spain	μ-Single cell	11	4-5	PtRu, 4 mg cm ⁻²	Nafion 117	Pt, 4 mg cm ⁻²
CNR-ITAE, Italy	3 cells (monopolar)/4 cm ²	32	5	PtRu, 2.5 mg cm ⁻²	Nafion 117	Pt, 2.5 mg cm ⁻²

Table 3: DMFC power sources for portable applications

As mentioned above, the potential market for portable fuel cell devices mainly concerns with small electronic devices, mobile phones and lap-top computers but it also includes weather stations, medical devices, signal units, auxiliary power units (APU), gas sensors units, etc. In this regard, a recent European project called MOREPOWER was addressing the development of a low cost, low temperature (30–60°C) portable direct methanol fuel cell device of compact construction and modular design in the range of hundred Watts power. 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). The single cell performance was approaching $0.2 \text{ A}\cdot\text{cm}^{-2}$ at about 0.5 V/cell at 60 °C and atmospheric pressure [134]. Several new membranes were investigated in this project. One of the most promising was a low-cost proton exchange membrane produced by SOLVAY by using a radiochemical grafting technology (Morgane® CRA type membrane) which showed a suitable compromise in terms of reduced methanol cross-over and suitable ionic conductivity [135]. Inorganic fillers-modified SPEEK membranes were also developed in the same project by GKSS (Germany) to reduce the permeability to alcohols while keeping high proton conductivity [135].

4. Current status of DMFC technology for transportation applications

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 500km between refueling, and (iii) ultra-low or zero emissions of pollutants, while remaining cost competitive with the current automobile technology [136]. Similar objectives have been addressed in European Research Programs. 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 [136]. 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 [101, 137]. 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 [103]. 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 fulfil 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, 136]. In several demonstration vehicles, hydrogen was the fuel carried on board, mostly as a compressed gas 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, 136]. 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, 136].

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 [138].

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) [139]. 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 [139].

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. The final stack 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 mWcm⁻² compared with 300 mWcm⁻² that was almost achieved in the single cell with the same membrane/electrode materials [139]. 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 [139].

A 71-cell direct methanol fuel cell (DMFC) stack has been developed at Forschungszentrum Julich [140]. The system consists of the stack, a water/methanol tank, a heat exchanger, a pump and compressors as auxiliary components. The auxiliary components are driven by the DMFC stack itself without external power sources. The DMFC stack consists of 71 cells with an area of 144 cm². The current collectors are manufactured of stainless steel (1.4571) with a cell pitch (distance between two membrane electrode assemblies (MEAs)) of only 2 mm. The MEAs are fabricated in-house by a combination of a decal and direct coating method. The thickness of each current collector is 0.3 mm. Each cell is provided with effective flow fields for a homogeneous flow distribution. The flow distribution has been calculated and approved by experiments. Therefore, the necessary stoichiometric air flow rate is only in the range of 2–3. The air compressor is designed to supply air with a maximum pressure of 1.5 bar absolute to the cell.

In the Optimet project [141], funded under the French Fuel Cell Network (Réseau PACo), the goal was to optimize the design and components of a direct methanol fuel cell stack for high-temperature operation using novel non-fluorinated membranes and non-commercial electrodes with low precious metal loading. The membranes selected after screening of various candidate hydrocarbon and heterocyclic ionomers were composite systems based on sulfonated polyetheretherketone (sPEEK) and incorporating zirconium hydrogen phosphate precipitated in situ from a multicomponent solution containing sPEEK and zirconyl propionate. Electrodes were prepared with 1.2 mg Pt (or PtRu) and membrane-electrode assemblies fabricated by in situ hot-pressing. The 30-cell stack was operated at 130°C for 8 h daily (shut down overnight) over two approximately one-month periods, providing stable power output (700 We) with no degradation even after an interim one-month shutdown. The results convincingly demonstrate that low Pt-loaded electrodes and composite sPEEK-ZrP membranes are viable options for high-temperature DMFCs.

A list of the main achievements in this field is reported in Table 4.

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	-
Thales et al. (Optimet project)	700 W	130	-	-	Pt/Ru (1.2 mg cm ⁻²)	SPEEK+ZrP	Pt (1.2 mg cm ⁻²)	30 bipolar
Thales, CNR-ITAE, Nuvera FCs	140 mW cm ⁻²	110	3 atm air	1	Pt/Ru	Nafion	Pt	5 / 225cm ² bipolar
Julich	500 W	70	1.5 atm air	1	Pt/Ru (3.9 mg cm ⁻²)	Nafion 115	Pt (2.3 mg cm ⁻²)	71 / 144 cm ² bipolar
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

Table 4. DMFC prototypes for APU and automotive applications

Technology that is presently considered promising for electro-traction consists of a hybrid system using both pure hydrogen-fed PEMFCs and advanced Li-batteries. 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 subzero 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.

5. Conclusions

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 utilization 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.

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