# International activities in DMFC R&D: status of technologies and potential applications

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## Abstract

Technological improvements in direct methanol fuel cells (DMFCs) are fuelled by their exciting possibilities in portable, transportation and stationary applications. In this paper, a synopsis of the worldwide efforts resulting in inventions of a plethora of DMFC prototypes with low, medium and high power capacities by a number of Companies, Research Institutions and Universities is presented. The most promising short term application of DMFCs appears to involve the field of portable power sources. Recent advances in the miniaturization technology of DMFCs devices make these systems attractive to replace the current Li-ion batteries. In the field of electrotraction recent demonstration of DMFC stacks with specific power densities and efficiencies approaching those of the combined system methanol reformer-polymer electrolyte fuel cell (PEMFC) have stimulated further investigation on the development of materials with higher performance and lower cost. The most appropriate range of operation temperatures for applications in transportation appears to lie between 100 and 150 °C. These operating conditions may be sustained by using new high temperature electrolyte membranes or composite perfluorosulfonic membranes containing inorganic materials with water retention properties at high temperature. The most challenging problem for the development of DMFCs is the enhancement of methanol oxidation kinetics. At present, there are no practical alternatives to Pt-based catalysts. High noble metal loading on the electrodes and the use of perfluorosulfonic membranes significantly contribute to the cost of these devices. Critical areas include the design of appropriate membrane electrode assemblies for specific DMFC applications and the reduction of methanol cross-over. This latter aspect is strictly related to the use of membrane alternatives to Nafion, but it may also be conveniently addressed by the development of methanol-tolerant oxygen reduction catalysts.
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## 1. Introduction

Most of the world energy requirements are presently addressed by burning fossil fuels in low efficiency thermal processes. Related consequences in terms of atmospheric pollution, global warming, green house effect etc. are the objects of many debates between developed countries that are searching for a common legislation to properly restrict the polluting emissions and protect the environment. Transportation represents a significant portion of world energy consumption and contributes considerably to the atmospheric pollution. Although modern cars emit a lower amount of toxic gases and particulate than their older predecessors, their increasing number result in growing levels of pollution from transportation sources.

Reduced levels of transportation related pollution may be achieved by replacing a significant number of internal combustion engine vehicles with electric cars in the near future. In this regard, polymer electrolyte fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) have been envisaged as suitable power sources for electric cars. DMFCs which directly employ methanol as fuel have good potentialities since they eliminate the need of a complex reformer unit in the system [1]. Furthermore, since methanol is fed with large amount of water to the anode it also avoids complex humidification and thermal management problems associated to PEMFCs. DMFCs provide the advantage of smaller system sizes and weight in relation to other fuel systems and the concept of the DMFC device may be extended to alternative fuels obtained from natural gas (e.g., dimethylether) or from biomasses as well as fermentation of agricultural products such as ethanol reducing the dependence on insecure energy resources. DMFC devices presently suffer from methanol crossover across polymer electrolyte membranes (crossover

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affects the performance of the cathode as well as fuel efficiency) and poor methanol electro-oxidation kinetics [1]. Other relevant aspects are the cost of materials (noble metal catalysts, perfluorosulfonic membranes) and the cost of production of the various components of the device which are presently higher than conventional energy conversion systems. Automation and large-scale production, however, may significantly reduce the latter. Although DMFC systems have been primarily investigated for their potential use in portable power and electro-traction applications, fundamental research into distributed power sources for residential applications have shown exciting progress. Different applications imply different system design characteristics, operation parameters as well as materials employed in the device. The aim of the present DMFC review is to provide an overview on the international state of the art, recent progress, R&D focal areas and current problems to be solved for the different applications.

## 2. Current status of technology and potential applications

### 2.1. Portable power

Several organizations are actively engaged in the development of low power DMFCs for cellular phone, laptop computer, portable camera and electronic game applications [2–6]. The initial goal of this research is to develop proof of concept DMFCs capable of replacing high performance rechargeable batteries in the US$ 6-billion portable electronic devices market. 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 longer conversation times using cell phones, longer times for use of laptop computers between 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. Noteworthy accomplishments in these areas are reported below and in Table 1.

Motorola Labs—Solid State Research Center (US), in collaboration with Los Alamos National Laboratory ((LANL), US), is actively engaged in the development of low power DMFCs (greater than 300 mW) for cellular phone applications [7]. Motorola has recently demonstrated a prototype of a miniature DMFC (Fig. 1) based on a membrane electrode assembly (MEA) set between ceramic fuel delivery substrates. Motorola utilized their proprietary low temperature co-fired ceramic (LTCC) technology to create a ceramic structure with embedded microchannels for methanol/water mixing and delivery to the MEA and, exhausting by-product $CO_2$. In addition, processing of the
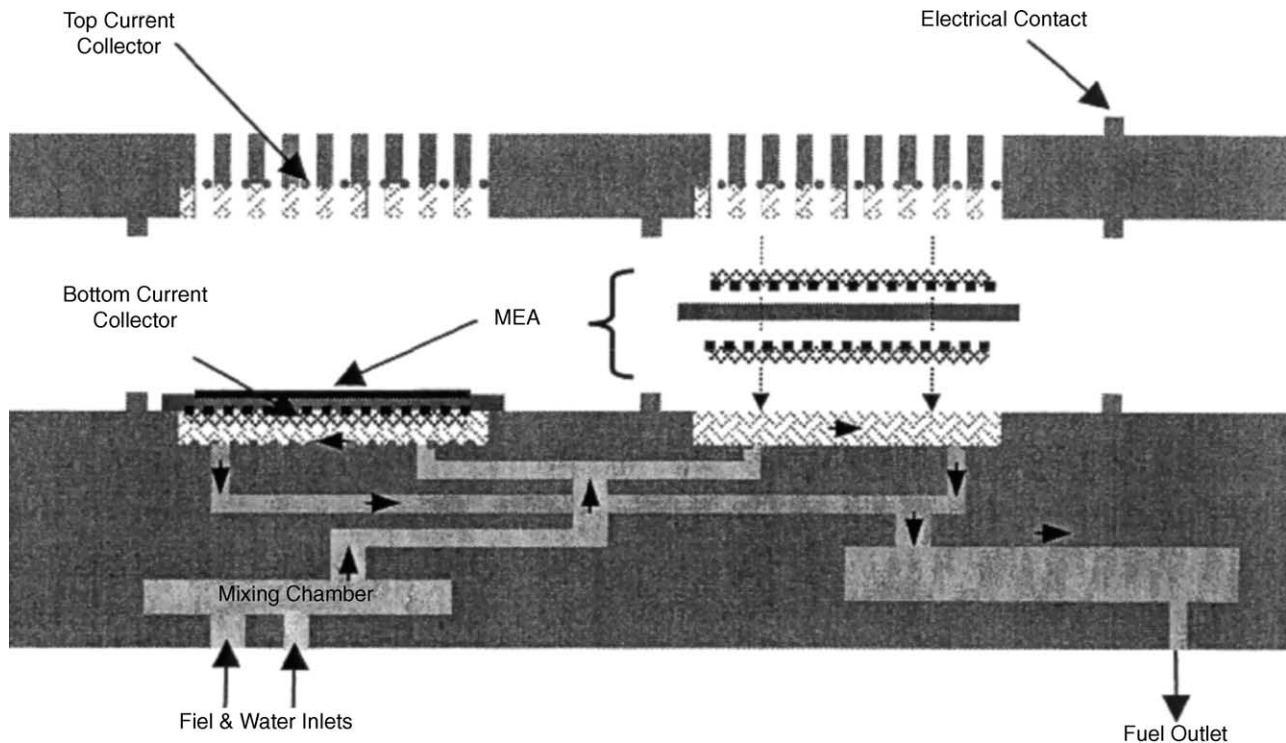


Fig. 1. Schematic of Motorola's miniature DMFC prototype [7].

Table 1
Portable power

| Single cell/stack developer | Power density | Temperature (°C) | Oxidant | Methanol concentration (M) | Anode catalyst | Membrane electrolyte | Cathode catalyst | Number of cells/surface area |
|---|---|---|---|---|---|---|---|---|
| Motorola Labs | 12–27 mW/cm$^2$ | 21 | Ambient air | 1 (0.45 ml/min) | Pt/Ru alloy, 6–10 mg/cm$^2$ | Nafion 117 | 6–10 mg/cm$^2$ | 4/13–15 cm$^2$ planar stack |
| Energy Related Devices | 3–5 mW/cm$^2$ | 25 | Ambient air | 1 (pure) | Pt/Ru alloy | Nafion | Pt | planar stack |
| Jet Propulsion Lab | 6–10 mW/cm$^2$ | 20–25 | Ambient air | 1 | Pt/Ru alloy, 4–6 mg/cm$^2$ | Nafion 117 | Pt, 4–6 mg/cm$^2$ | 6/6–8 cm$^2$ flat-pack |
| Los Alamos National Labs | 300 W/l | 60 | Air flowed at 3–5 times stoichiometry | 0.5 | Pt/Ru, 0.8–16.6 mg/cm$^2$ | Nafion | Pt, 0.8–16.6 mg/cm$^2$ | 5/45 cm$^2$ |
| Forschungszentrum Julich GmbH | 45–55 mW/cm$^2$ | 50–70 | 3 atm O$_2$ | 1 | Pt/Ru, 2 mg/cm$^2$ | Nafion 115 | Pt, 2 mg/cm$^2$ | 40/100 cm$^2$ bipolar plate |
| Samsung Advanced Institute of Technology | 10–50 mW/cm$^2$ (single cell) | 25 | Ambient air | 2–5 | Pt/Ru | Hybrid membrane | Pt | 12/24 cm$^2$ monopolar |
| Korea Institute of Energy Research | 121–207 mW/cm$^2$ | 25–50 | Ambient pressure, O$_2$ (300 cc/min) | 2.5 | Pt/Ru/C metal powder | Nafion115 & 117 | Pt-black | 6/52cm$^2$ bipolar |
| Korea Institute of Science & Technology | 3–9 mW/cm$^2$ | 25 | Ambient air | | Pt/Ru, 8 mg/cm$^2$ | Nafion 117 | Pt, 8 mg/cm$^2$ | 15/90 cm$^2$ monopolar |
| More Energy Ltd. | 60–100 mW/cm$^2$ | 25 | Ambient air | 30–5% methanol | Pt/Ru | Liquid Electrolyte | Pt | /20cm$^2$ |

ceramic material into a grid screen design facilitated the delivery of ambient air to the MEA. Substrates are processed in multiple layers after aligning, tacking and laminating at approximately $3.45 \times 10^6$ Pa. The final monolithic integrated ceramic substrate is formed after sintering at 850 °C.

In the current design as represented in Fig. 1, the MEA is mounted between two porous ceramic plates. Thin films of electrocatalysts were applied in a proprietary process using carbon cloth gas diffusion layers. For the anode, an unsupported Pt/Ru (1:1) alloy at a high loading of 6–10 mg/cm$^2$, and for the cathode Pt black were used as electrocatalysts. Nafion 117 membranes were used as the electrolyte and were hydrated by running deionized (DI) water through the cell for 18 h. The active electrode area for a single cell is approximately 3.5–3.6 cm$^2$. In the stack assembly, four cells are connected in series in a planar configuration with a MEA area of 13–14 cm$^2$, the cells exhibited average power densities between 15–22 mW/cm$^2$. Four cells (each cell operating at 0.3 V) are required for portable power applications because DC–DC converters typically require 1 V to efficiently step up to the operating voltage for electronic devices. The fuel cell consumed oxygen from ambient air (21 °C and 30% RH) and the fuel from 1.0 M methanol pumped at a rate of 0.45 ml/min using a peristaltic pump. Variations in time of operation, temperature, fuel mixing, flow rate and humidity gradually led to improved performance characteristics of the system. In addition, 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, US) is working in alliance with Manhattan Scientific Inc., US) to develop miniature fuel cells for portable electronic applications [2,8]. A relatively low-cost sputtering method, similar to the one used by the semiconductor industry for production of microchips, is being used for deposition of electrodes (anode and cathode) on either side of a microporous plastic substrate; the micropores (15 nm to 20 μm) are etched into the substrate using nuclear particle bombardment. Micro-fuel arrays, with external connections in series, are precisely fabricated and have a thickness of about a millimeter. The principal advantages of the cell include the high utilization of catalyst, controlled pore geometry, low-cost materials and minimum cell thickness and weight. A MicroFuel Cell$^{TM}$ was reported to have achieved a specific energy density of 300 Wh/kg using methanol and water and, air as the anodic and cathodic fuels, respectively.

Fig. 2 describes the schematic cross section of the fuel cell. The anode design is a critical new advance in the development of a cost-effective pore-free electrode that is only permeable to hydrogen ions. 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 forms a plug in the pore of the
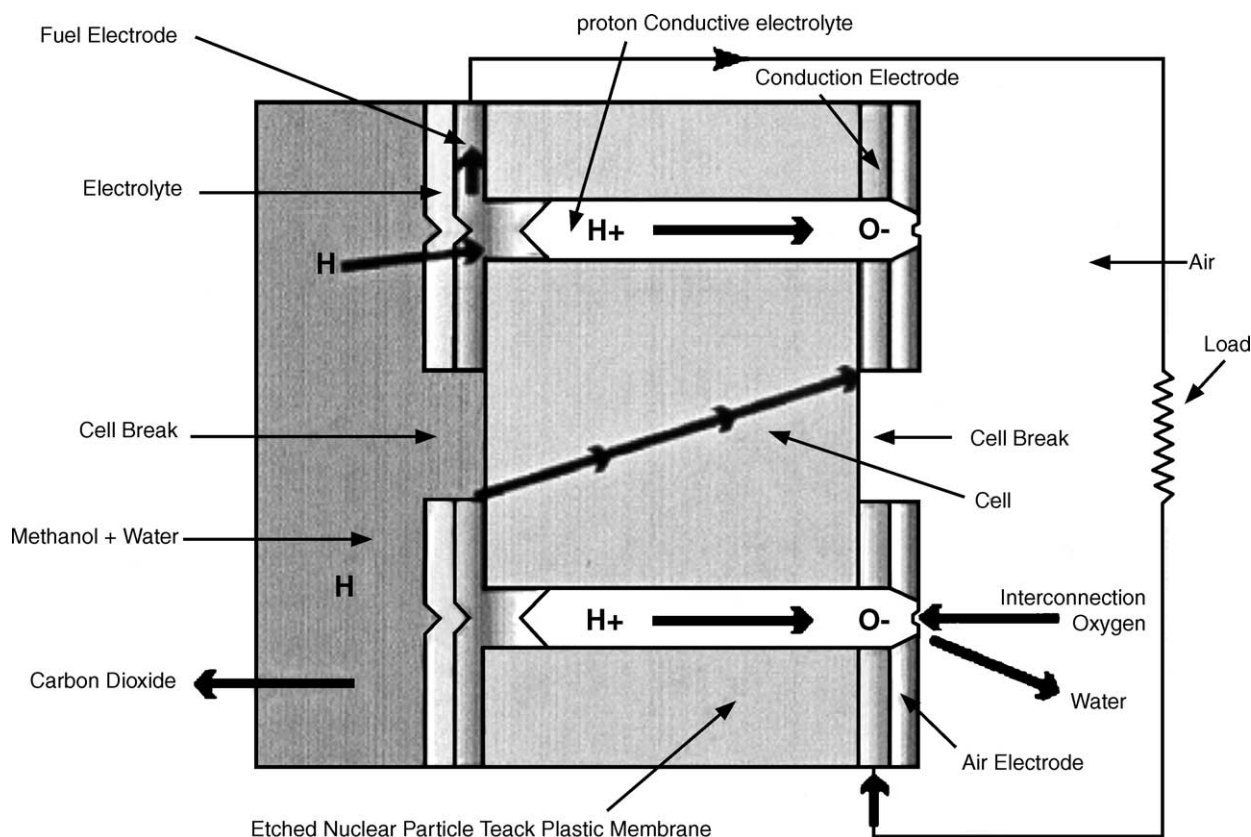
Fig. 2. MicroFuel Cell[TM] schematic cross sectional view [2,8].

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) is deposited to mitigate the hydration induced cracking that occurs in many of these films. The third layer is deposited over the structural metal film and is the most significant layer because it needs to be catalytically active to methanol and capable of accepting hydrogen ions. An alternate method of forming the electrode is to include on the surface of the metal films powder catalyst particles (Pt/Ru on activated carbon) to enhance the catalytic properties of the electrode. Between the anode electrode and the cathode electrode is the electrolyte filled pore, the cell interconnect and the cell break. In the pores of the membrane the electrolyte (Nafion) is immobilized and ERD claims this collimated structure results in improved protonic conductivity. Each of the cells is 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 is formed by first sputter depositing a conductive gold film onto the porous substrate followed by a platinum catalyst film. The electrode is 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 utilize their fuel cell as a simple charger in powering a cellular phone. The fuel cell is configured into a plastic case that is in close proximity to a rechargeable battery. Methanol is delivered to the fuel cell via fuel needle and fuel ports, which allow methanol to wick or evaporate out into the fuel manifold, and is delivered to the fuel electrodes.

The Jet Propulsion Laboratory (JPL, US) has been actively engaged in the development of "miniature" DMFCs for cellular phone applications over the last 2 years [4,9]. 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 requirements fluctuates between 800–1800 mW. In the JPL DMFC the anode is 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 platinum-ruthenium catalyst onto the carbon substrate. The preferred electrolyte is Nafion 117; however, other materials may be used to form proton-conducting membranes. Air is 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 is the hydrophobic Teflon polymer
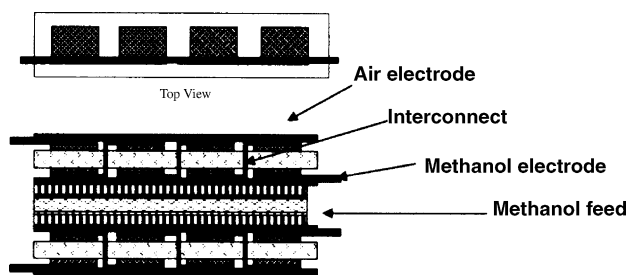
Fig. 3. Schematic of JPL's interconnected cells in a flat-pack DMFC design [4,9].

utilized to create a three-phase boundary and to achieve efficient removal of water produced by 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 may be prepared by pressing the anode, electrolyte and cathode at $8.62 \times 10^6$ Pa and 146 °C.

JPL opted for a "flat-pack" instead of the conventional bipolar plate design, but this resulted in higher ohmic resistances and non-uniform current distribution. In this design the cells are externally connected in series on the same membrane, with through membrane interconnect and air electrodes on the stack exterior. Two "flat packs" can be deployed in a back to back configuration with a common methanol feed to form a "twin-pack" (Fig. 3). Three "twin-packs" in series will be needed to power a cellular phone. In the stack assembly, six cells are connected in series in a planar configuration, which exhibits 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 of configuration and interconnect design have resulted in improved performance characteristics of the six cell "flat-pack" DMFC. Based on the results of the current technology, the JPL researchers predict that a 1 W DMFC power source, with the desired specifications for weight and volume and having 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 [10]. A 30-cell DMFC stack, with electrodes having an active area of 45 cm$^2$, was constructed, an important feature of this stack being a narrow width (i.e., 2 mm) of each cell. MEAs are made by the decal method; that is, thin film catalysts bonded to the membrane resulting in superior catalyst utilization and overall cell performance. Anode catalyst loading of Pt between 0.8–16.6 mg/cm$^2$ in unsupported PtRu and carbon supported PtRu are used. A highly effective flow field for

air made it possible to use a dry air blower for operation of 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 estimate of an energy density of 200 Wh/kg was made 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 [11]. The FJG system consists of the cell stack, a water/methanol tank, a pump and ventilators as auxiliaries. The stack is designed in the traditional bipolar plate configuration, which results in lower ohmic resistances but heavier material requirements. To circumvent the weight limitations current collectors are manufactured from stainless steel (MEAs are mounted between current collectors) and are inserted into plastic frames to reduce stack weight. The 6 mm distance between MEAs (cell pitch) reveals very tight packaging of the stack design. Each frame carries two DMFC single cells that are connected in series by external wiring (Fig. 4). MEAs are fabricated in house with 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 allows 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 45–55 mW/cm$^2$. The cathode uses air at ambient or elevated pressures, when the stack operates at temperatures above 60 °C the air is fed into the cathode by convection forces. Further evaluation of the system revealed that current collectors made of stainless steel showed an inhomogeneous distribution of contact resistance and as a result single cells displayed fluctuating power densities. It was postulated that the pressure of the current collectors on the MEAs is not high enough to prevent delamination of the electrocatalyst layer. 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 and although it is not air-breathing it works with low air stoichiometric rates (more efficient cathodic flow distribution structure). The short stack was tested under ambient pressure (a low power-consuming compressor provided air to the cathode) and operated at 45 °C.
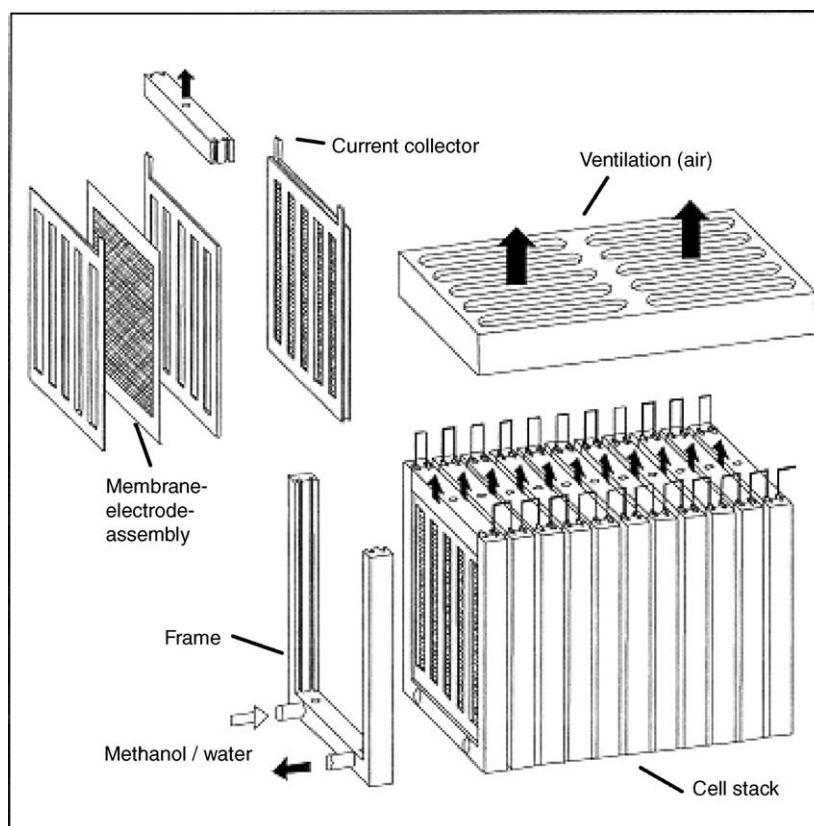
Fig. 4. Schematic of the Forscungszentrum Julich GmbH 50 W DMFC stack [11].

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 [12]. Single cell are constructed with a PtRu black anode electrode (a methanol flow field and a capillary wicking structure are part of the anode structure), a hybrid membrane material (ionomer/ZrO(HPO$_4$)$_2$, ionomer/BaTiO$_3$ or ionomer laminated material) and a Pt black cathode electrode with an air flow field (breathing structure). The catalyst layers have been fabricated by magnetron sputtering methods on Nafion membrane surfaces. Single cell experiments at room temperature utilizing 2–5 M methanol and ambient air result in power densities on the order of 10–50 mW/cm$^2$ (air-breathing and air blowing). The cellular phone used to test the DMFC prototype is reported to be functional for up to 40 days on standby and 20 h of talk time.

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 of 52 cm$^2$ total electrode area [13]. The stack was tested at 25–50 °C using 2.5 M methanol supplied without a pumping system and at ambient pressure O$_2$ at a flow rate of 300 cc/min. 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/C metal powders and Pt-black for anode and cathode electrodes, respectively.

Korea Institute of Science and Technology (KIST, South Korea) has developed a 15-cell monopolar stack of 90 cm$^2$ total electrode area and a maximum power density of 3.2 mW/cm$^2$ [14]. The MEAs were fabricated by hot pressing catalyst layered carbon paper and Nafion 117 membrane, catalyst layers were formed by spray-coating catalyst ink. Anode electrocatalyst loading of 8 mg PtRu/cm$^2$ and cathode electrocatalyst loading of 8 mg Pt/cm$^2$ are utilized in this system. The performance tests were conducted at room temperature under static feed conditions: air was fed only through natural convection and the methanol solution was stored in the engraved plate that contacted the MEA on the anode side. Single cell tests at various methanol concentrations resulted in maximum power density of 9 mW/cm$^2$. The poor performance of the stack power density was attributed to the poor air diffusion into the cathode with a resulting mass transfer limitation at that electrode.

More Energy Ltd. (MEL, ISRAEL) a subsidiary of Medis Technologies Ltd. (MDTL, US) is developing a direct liquid methanol (DLM) fuel cells (a hybrid PEM/DMFC system) for portable electronic devices [15]. 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

Table 2
Transportation

| Single cell/stack developer | Power/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 (pure) | Pt/Ru | Nafion | Pt | – |
| IRD Fuel Cell A/S | 100 mW/cm$^2$ | 90–110 | 1.5 atm air | – | Pt/Ru | Nafion | Pt | 4/154 cm$^2$ bipolar |
| Thales CNR-ITAE Nuvera Fuel Cells | 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) | 110 (80) | 3 atm O$_2$ (1.5 atm air) | 0.5 (0.5) | Pt/Ru | Nafion 117 | Pt-black, 4 mg/cm$^2$ | 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 |

a proprietary liquid electrolyte that acts as the membrane in place of a solid polymer electrolyte (Nafion) and (iii) novel polymer and electrocatalyst 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 under way 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.

## 2.2. Transportation

DMFC technology offers a solution for transportation applications in the 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 has been well established that the infrastructure for methanol distribution and storage can be easily modified 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 costs 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 5 years) have become actively engaged in the devel-

opment of DMFCs for transport applications. The most remarkable results achieved in this field are summarized in Table 2. These institutions have directed their resources toward improving every facet of the DMFC in the 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 [16]. Daimler–Chrysler (Germany) demonstrated this system for the 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 our private communication with Ballard revealed that they have 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 at this time with respect to the stack design and performance of the DMFC power source. However, the patent literature indicates fabrication techniques for producing DMFC electrodes [17].

The anode was prepared by first oxidizing the carbon substrate (carbon fiber paper or carbon fiber non-woven) via electrochemical methods in acidic aqueous solution (0.5 M sulfuric acid) prior to incorporation of the proton-conducting ionomer. Oxidation results in the formation of various acidic surface oxide groups on the carbonaceous substrate and can be achieved by constructing a simple electrochemical cell comprising the carbonaceous electrode substrate as the working electrode. During the treatment of the carbon substrate a voltage of greater than 1.2 V and more than 20 coulombs/cm$^2$ was used in the process. The second step involves the impregnation of a proton-conducting ionomer such as a poly(perfluorosulfonic acid) into the carbon substrate and then drying off the carrier solvent; the amount impregnated into the substrate was usually greater than 0.2 mg/cm$^2$. 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, the catalyst is applied to the periphery of the electrode where it will be utilized 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 the more intimate contact of an ionomer coating with 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 occurred via conventional methods, that is, hot pressing the anode and cathode to a solid polymer membrane electrolyte. Oxygen and methanol flow fields are subsequently pressed against cathode and anode substrates, respectively but details of this assembly have not been forthcoming.

IRD Fuel Cell A/S (Denmark) has developed DMFCs primarily for transportation applications (0.7 kW) [18]. 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 have an active cell area of 154 cm$^2$ with cell dimensions of 125 mm$^2$. 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.

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 with financial support of the European Union Joule Program [19]. Bipolar plates were utilized in the stack design and MEAs were fabricated using Nafion as the solid polymer electrolyte and high surface area carbon supported Pt-Ru and Pt electrocatalyst for methanol oxidation and oxygen reduction, respectively. The electrode area was 225 cm$^2$ and 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$^2$. Fig. 5 shows the overall stack performance. A comparison of the polarization curves for single cells in the stack and a prototypal cell is shown in Fig. 6. The different diffusion characteristics of the cells in the stack indicate that the stack fluidodynamics should be enhanced in terms of homogeneity of distribution of reactant over the electrodes.

Siemens Ag (Germany) optimized its DMFC system (high oxygen pressure operation) for a niche market and, examined DMFCs in the low temperature, low pressure air operation for more general purposes [20]. MEAs in single cells experiments are constructed using a Nafion 117 membrane, Pt-black with a catalyst loading of 4 mg/cm$^2$ for the cathode and a high surface area Pt-Ru alloy (either unsupported or carbon supported) for the anode (2 mg/cm$^2$). A maximum power density of ~250 mW/cm$^2$ is achieved for operating conditions of 110 °C, 3 bars O$_2$, 0.5 M methanol
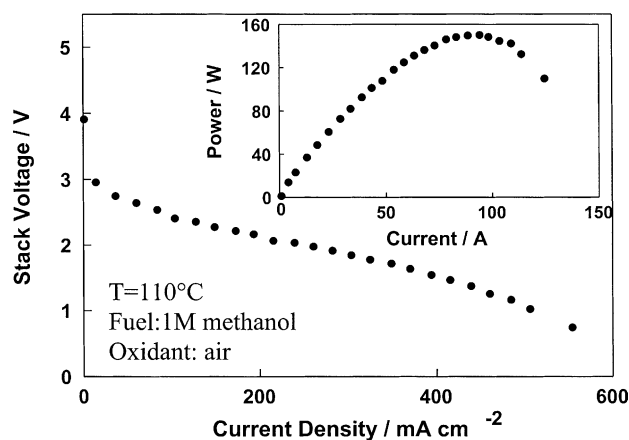


Fig. 5. Galvanostatic polarisation and power density for a five-cell air-feed DMFC stack at 110 °C. Electrolyte: Nafion 117. Catalysts: 85% Pt-Ru/C and 85% Pt/C; 2 mg Pt cm$^{-2}$; methanol 1 M, electrode surface 225 cm$^2$ [19].
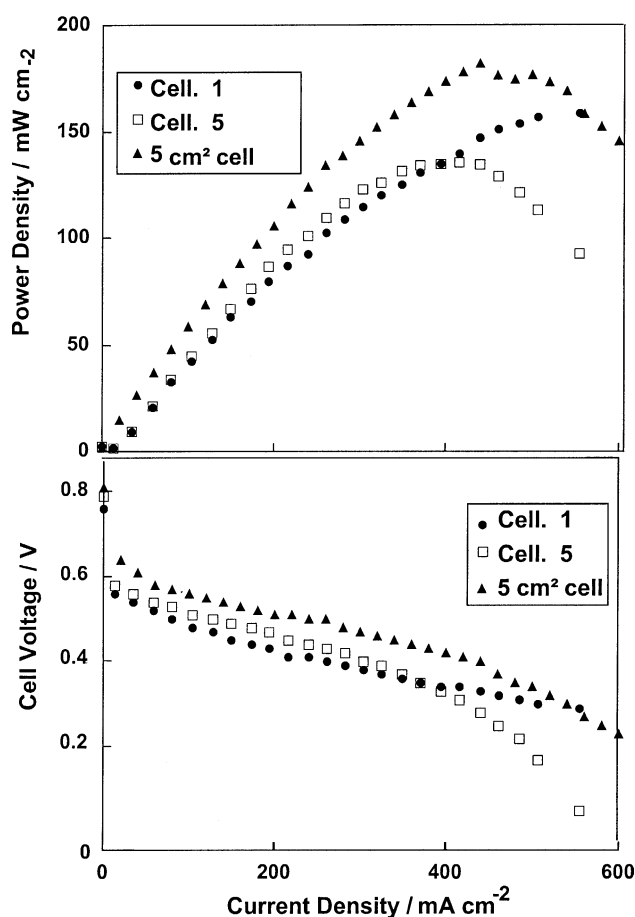


Fig. 6. Galvanostatic polarisation data and power densities at 110 °C for two 225 cm$^2$ cells along a 150 W air-fed DMFC stack section (from the reactant inlet) and comparison with a 5 cm$^2$ graphite single cell operating under same conditions and equipped with the same M&E assembly. Electrolyte: Nafion 117. Catalysts: 85% Pt-Ru/C and 85% Pt/C; 2 mg Pt cm$^{-2}$; methanol 1 M [19].

and an electrode surface area of 3 cm$^2$. Single cell experiments exploring operating conditions at lower temperatures, lower pressures and air being supplied to the cathode electrode utilize similar MEA components as described previously. A maximum power density of ~90 mW/cm$^2$ is achieved for operating conditions of 80 °C, 1.5 bar air and 0.5 M methanol. These conditions result in a maximum power density that is significantly lower than results obtained for previous experiments using O$_2$ as the cathodic fuel. We should also note that there is a positive correlation between the air flow rate (25–100 standard cubic centimeter per minute (sccm)) and the cell performance.

Siemens AG in Germany, in conjunction with IRF A/S in Denmark and Johnson Matthey Technology Center in the United Kingdom has developed a DMFC stack with an electrode area of 550 cm$^2$ under the auspices of the European Union Joule Program [21–23]. The projected cell performance is 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 has been demonstrated by operating at a temperature of 110 °C and a pressure of 1.5 atm and using 0.75 M methanol, this stack exhibited a performance level of 175 mA/cm$^2$ at 0.5 V per cell; 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 is to improve the design to lower the air stoichiometric flow to the desired value of about a factor of two. A 0.85 kW air-fed stack composed of 16 cells and operating at 105 °C was successively demonstrated with 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 cm$^2$ per cell has been demonstrated [24]. The cells were 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%.
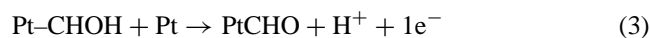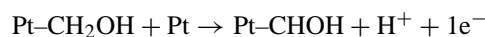
## 3. Status of knowledge in basic research areas and needed breakthroughs

### 3.1. Electrode kinetics and electrocatalysis of methanol oxidation

#### 3.1.1. Overall reaction, intermediate steps and rate determining step

Since methanol is the most electroactive organic fuel for fuel cells, extensive, fundamental studies have been carried out to elucidate the reaction mechanism in a multitude of

laboratories in the USA, England, Russia, France, Germany and Japan starting as early as the 1960s. Two recent reviews cover in detail the analyses of the reaction mechanisms as well as the conflicting views that still exist on reaction pathways and rate determining steps [25,26]. Thus, only a summary of the present status of knowledge and a survey of the current international activities is presented in this section. The electrooxidation of methanol to carbon dioxide is a six-electron transfer reaction; due to the slow kinetics of this reaction (even on the best possible electrocatalysts) and poisoning by adsorbed intermediates, partial oxidation to products such as formaldehyde, formic acid and methyl formate occurs. A generally accepted schematic for the reaction pathways leading to the partial or complete oxidation of methanol on Pt-Ru catalysts is reported below:

$$CH_3OH + Pt \rightarrow Pt–CH_2OH + H^+ + 1e^-$$

$$Pt–CH_2OH + Pt \rightarrow Pt–CHOH + H^+ + 1e^-$$

$$Pt–CHOH + Pt \rightarrow PtCHO + H^+ + 1e^- \tag{3}$$

A surface rearrangement of the methanol oxidation intermediates gives carbon monoxide, linearly bonded to Pt sites, as following:

$$PtCHO \rightarrow Pt–C{\equiv}O + H^+ + 1e^- \tag{4}$$
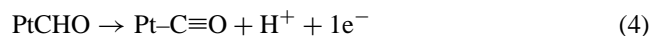
In presence of Ru as promoter, water discharging occurs at low anodic overpotentials on Ru with formation of Ru-OH species at the catalyst surface.

$$Ru + H_2O \rightarrow RuOH + H^+ + 1e^- \tag{5}$$
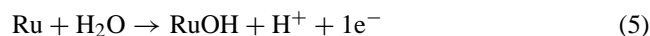
The final step is the reaction of Ru-OH groups with neighboring methanolic residues to give carbon dioxide:

$$RuOH + PtCO \rightarrow Pt–Ru + CO_2 + H^+ + 1e^- \tag{6}$$

On the better electrocatalysts, such as a Pt-Ru alloy, CO$_2$ is the main product, while on an inferior electrocatalyst such as Pt small amounts of formic acid and formaldehyde have been detected. In situ product analyses have been carried out by on-line gas or liquid chromatography by Lamy and coworkers [27] and differential electrochemical mass spectrometry by Vielstich et al., Bonn University [28]. Another method used by Lamy and coworkers is in situ fourier transform infrared reflectance spectroscopy, used as single potential alteration infrared spectroscopy [29]. A similar technique, electrochemically modulated infrared spectroscopy, was used by this group to identify intermediate species strongly adsorbed on the electrode [29]. The strongly adsorbed CO species was identified as the main poisoning species, blocking the electrode sites for further intermediate formation during methanol oxidation. The vital step appears to be the formation of the ($^\bullet$CHO)$_{ads}$ species, which facilitates the overall reaction; it subsequently forms the strongly adsorbed CO species. The rate determining step is the oxidation of adsorbed CO with adsorbed OH species, according to the publications of Swathirajan and
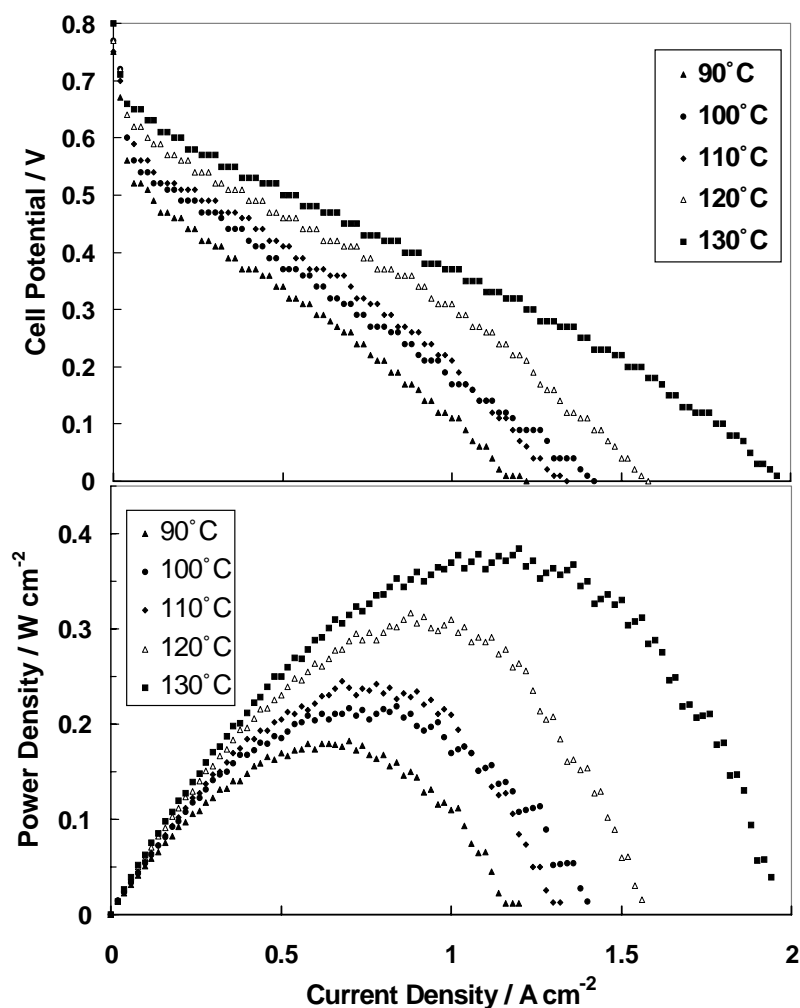
Fig. 7. Galvanostatic polarisation data for a DMFC equipped with CNR-ITAE Pt-Ru (anode) and E-TEK 30% Pt/C (cathode) catalysts; 2 M CH$_3$OH, oxygen feed.

Mikhail at General Motors [30], Bockris and Kahn, Texas A&M University [31] and Kauranen et al. [32].

Increase of operation temperature produces a significant increase in DMFCs performance. This effect is nearly related to the faster CO removal from electrocatalyst surface as revealed by CO stripping analysis [33]. Fig. 7 shows DMFC polarization curves in presence of a Pt-Ru anode catalyst and Nafion 112 membrane at various operating temperatures.

### 3.1.2. Electrocatalysis

The interest in the electrocatalytic oxidation of methanol is only surpassed by investigations of the hydrogen and oxygen electrode reactions. Platinum and platinum ruthenium alloys have been the most investigated electrocatalysts. For a more complete review of electrocatalyst studies and the conclusions reached, the reader is referred to the aforementioned review articles. Highlights of recent and ongoing investigations may be summarized as follows: (i) with a Pt-Ru alloy electrocatalyst, the water discharge occurs at low potentials on Ru sites while methanol chemisorption requires three neighboring Pt sites. The removal of carbon monoxide needs the presence of OH species on adsorbed Ru sites. According to work at Los Alamos National Laboratory by Dinh et al. [33], the above processes are accelerated by the presence of low index planes; (ii) a ruthenium content of 50% is optimal for methanol oxidation; (iii) X-ray absorption spectroscopic studies by McBreen and Mukerjee at Brookhaven National Laboratory [34] have shown that an increase in d band vacancy is produced by alloying Pt with Ru and this modifies the adsorption energy of methanol residues on Pt. Thus, the reaction rate is not only influenced by the bifunctional mechanism but also by electronic effects; (iv) promotional effects of Ru and Sn with Pt have also been extensively analyzed—Aricò et al. [35], at the CNR-TAE Laboratory in Italy observed a shift by 1.1 eV in the X-ray near edge spectrum (XANES) of the Pt-Sn/C electrocatalyst, which suggests that Sn atoms in Pt-Sn donate electrons to Pt atoms and are thereby oxidized. A charge transfer from Sn to Pt was also shown using XPS analysis by Shukla and coworkers in an International Collaboration with CNR-ITAE in Italy, Indian Institute of Science and Seoul National University Korea [36]; (v)

Iwasita et al., Bonn University [37] have attributed the shift towards higher frequencies for CO stretching in their FTIR experiments to a lower chemisorption energy for CO on the Pt-Ru alloy; (vi) in a related study at Eindhoven University in The Netherlands, Frelink et al. [38] have observed a shift to higher frequencies at various coverage's due to changes in binding energies to the alloy surface, induced by Ru through a ligand effect on Pt; (vii) a combinatorial catalytic approach was used at Pennsylvania State University and the Illinois Institute of Technology [39]; and (viii) several studies have been carried out and are ongoing as well to elucidate the morphologic aspects of electrocatalysts. Significant information has also been obtained on the behavior of ternary as well as multifunctional catalysts which aided the interpretation of the role of the various promoting elements [40].

Watanabe et al. [41], Yamanashi University reported that the electrocatalytic activity for methanol oxidation does not increase with particle size above 20 Å. This means that the mass activity increases with the increasing dispersion of the electrocatalyst. Wieckowski and coworkers [42] at the University of Illinois found that the (1 1 1) Pt crystallographic plane, partially covered with Ru ad-atoms performs better than when Ru is adsorbed on any other plane; and (ix) studies to investigate the role of carbon black have shown, in the work of Kaurenan and Skou [43], Ravikumar and Shukla [44] from the Indian Institute of Science, and Goodenough et al., [45] New South Wales that (a) a low surface area carbon black (e.g., acetylene black) does not yield a high dispersion of metal phase, (b) a high surface area carbon black (e.g., Vulcan XC-72, Ketjen Black) accommodates a high amount of metal phase with a high degree of dispersion due to the significant amount of micropores. However, there will be no homogeneous distribution of the electrocatalyst—this leads to mass transport limitations of reactant and limited access to inner electrocatalytic sites; and (x) several alternatives to Pt or Pt alloy electrocatalysts have been investigated worldwide. These include transition metal alloys and transition metal oxide/metal combinations. The latter are attractive because they could assist the decomposition of water and facilitate a redox route for electrooxidation of metal. To date, problems encountered with the stability's of these materials in acid electrolytes have arisen. However, this approach needs further examination in the state of the art DMFC with a proton conductive membrane electrolyte.

### 3.2. Methanol cross-over

#### 3.2.1. Mechanism and its effects on DMFC performance

The cross-over of methanol from the anode to the cathode in a DMFC has serious consequences of reducing its coulombic and voltage efficiencies. The main reason for the cross-over is that the methanol fuel is soluble in water over the full range of composition from 0 to 100%. This is unlike the case of gaseous hydrogen and oxygen fuels oxidized and reduced at the anode and cathode electrodes, respectively. As a consequence, the diffusion rate of methanol from the anode to the cathode is extremely high (corresponding to an equivalent current loss larger than $100 \, mA/cm^2$ under open circuit conditions). This should be compared with a diffusion rate that results in an equivalent current loss of a few $mA/cm^2$ or less for hydrogen or oxygen in a proton exchange membrane fuel cell. Investigations in several laboratories in the USA, Japan, Canada, Korea and Germany have examined the extent of methanol cross-over in DMFC's as a function of operating temperatures and current density using electrochemical on-line gas chromatographic and mass spectrometry techniques [46–50]. Apart from the high rate of diffusion transport from anode to cathode, one encounters the electroosmotic transport whereby methanol is carried with the proton (ion–dipole interaction) as in the case of a water molecule being strongly bound to a proton. The rate of cross-over decreases with increasing current density, due to the higher rate of methanol consumption at the anode. This induces a concentration gradient in the active layer of the anode electrode and a considerably lower methanol concentration at the interface of the active layer with the membrane. Higher operating temperatures and a lower methanol concentration in the feed stream reduces the rate of methanol cross-over in DMFCs. As a compromise for optimizing performance and reducing cross-over, most researchers are using a concentration of 1M methanol. Apart from the crossover problem reducing the coulombic efficiency of a DMFC, its voltage efficiency is also decreased because of a lowering of the open circuit potential (OCV) (caused by the depolarizing of the oxygen electrode under open circuit conditions) and the poisoning effects of the Pt electrocatalyst by methanol derived species at this electrode.

#### 3.2.2. Methods for inhibition of methanol cross-over

The cross-over of methanol is due to its high rate of permeability through the membrane, caused by the high concentration gradient of methanol from the anode to the cathode. Several projects have been and are being carried out to minimize the permeation rate. Researchers at LANL [51] in the USA have shown that the permeation rate is markedly reduced at current densities above $300 \, mA/cm^2$. Researchers at CNR-ITAE [52] have also shown reduced methanol cross-over rates with thinner membrane electrolytes and higher temperature operations when the DMFC cell is working at high current density. Modified composite membranes (Nafion-silica), with $SiO_2$ particles entrapped in the polymeric structure [53], serves as a physical barrier for methanol crossover; even though the ohmic resistance is increased (depends on the concentration of silica). Low crossover rate (equivalent to $40 \, mA/cm^2$, at a DMFC operating current density of $500 \, mA/cm^2$) have been demonstrated in presence of Nafion-Silica composite membranes [54]. At Pennsylvania State University in the USA, Allcock and coworkers [55] are investigating phosphazene membranes, prepared by thin film casting of a poly(aryloxy) phosphazene from a solution of tetrahydrofuran, phosphorus oxychloride and water. The microporous membrane contained either phosphoric acid
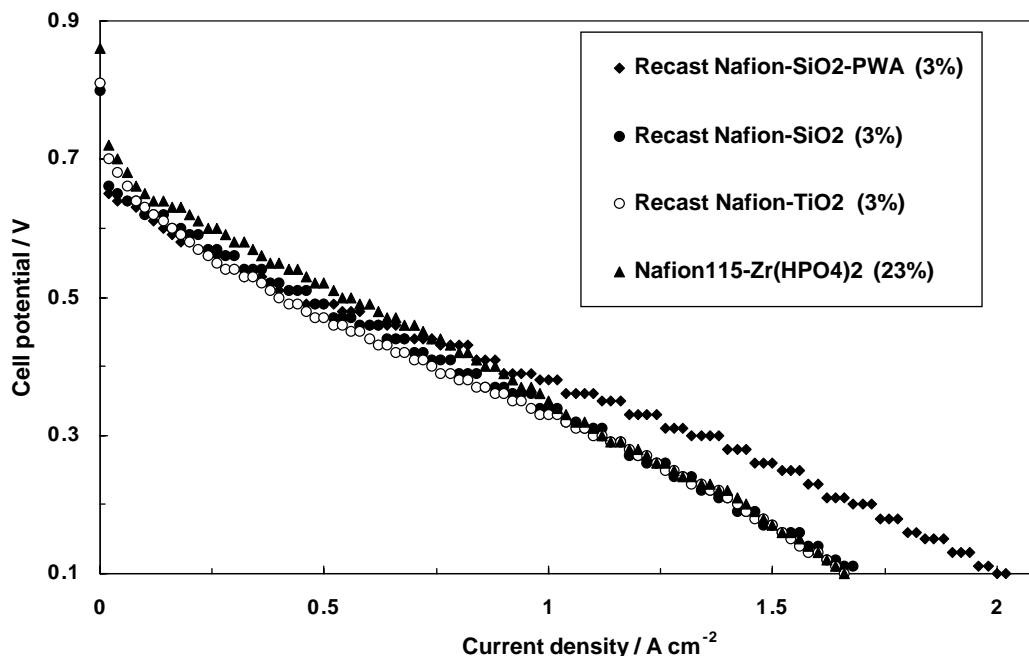
Fig. 8. Polarization curves for DMFC equipped with different composite Nafion membranes and operating at 145 °C. Catalysts: 60% Pt-Ru/C and 30% Pt/C (E-TEK); oxygen feed, methanol 2 M.

entrapped in the membrane or the acid coordinately bound in the polymer backbone. Another type of membrane was prepared by treating benzenoid side groups (the side groups are attached to a polyphosphazene mainchain) with sulfonating agents such as concentrated sulfuric acid, fuming sulfuric acid and sulfur trioxide. Although lower cross-over rates (by a factor of five), as compared with Nafion membranes, were reported the ohmic resistances were higher. Savinell and coworkers [56,57] at Case Western Reserve University imbibed polybenzimidazole membranes with a large amount of phosphoric acid (about 400% content) and found low cross-over rates at a temperature of 150–200 °C. Such a membrane in a DMFC environment exhibited a crossover rate of 5 to 10%. This membrane is akin to a silicon carbide matrix impregnated with phosphoric acid in a phosphoric acid fuel cell. International Fuel Cells, in USA had evaluated a fuel cell with the latter type of membrane and found that some methanol was consumed to form methyl phosphate and dimethyl ether. Researchers at Samsung Advanced Institute of Technology, Korea [58] are evaluating inorganic-organic hybrid polymer membranes—mainly composites of Nafion with silica, $TiO_2$ and zirconyl phosphate, prepared by hydrolysis or sol–gel reactions.

In an international cooperation between Princeton University and CNR-ITAE [59], a composite Nafion 115 zirconium hydrogen phosphate (23%, w/w) membrane was investigated for application in DMFC at high temperatures (150 °C). This membrane shows lower methanol cross-over with respect to recast Nafion-SiO2 (3%, w/w) membrane due to the higher content of inorganic compound inside the polymer electrolyte channels acting as diffusion barrier

for methanol (Fig. 8). Yet, larger ohmic resistances were observed up to 150 °C due to the reduced proton/water mobility inside Nafion channels (Fig. 9). The resulting effect is a better performance for zirconium hydrogen phosphate based membrane in the activation controlled region and a lower performance in the ohmic and diffusion controlled region of the polarization curve with respect to the $SiO_2$ based membrane (Fig. 8). Further, increase of performance for the Nafion-$SiO_2$ membrane is achieved by adsorbing a strong acid on the surface of colloidal $SiO_2$ particles indicating that the surface acidity of the inorganic oxide is probably governing the conductivity and water retention properties at high temperature (Fig. 9). The highest conductivity for the Nafion-$SiO_2$ membrane is achieved at 145 °C; at higher temperatures water losses determine an increase of cell resistance. As opposite, the Nafion 115-zirconium hydrogen phosphate membrane shows a progressive decrease of cell resistance (Fig. 9). In fact, in presence of $ZrH(PO_4)_3$ which is a protonic conductor at intermediate temperatures, the proton mobility inside the system is strongly activated by temperature in presence of reduced water content inside the membrane.

### 3.3. Electrode kinetics and electrocatalysis of oxygen reduction

Worldwide research activities to elucidate the mechanism of the complex electrode reaction (both evaluation and reduction) of oxygen and to find the best electrocatalysts for low and intermediate temperature fuel cells have been very extensive—second most to the hydrogen electrode reaction.
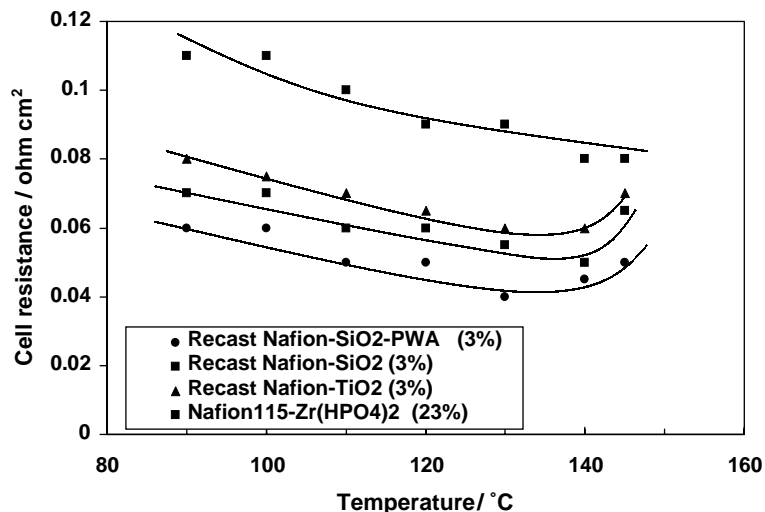
Fig. 9. Variation of cell resistance with temperature during DMFC operation with different composite Nafion membranes.

There have also been excellent reviews on these aspects as relevant to proton exchange membrane, alkaline and phosphoric acid fuel cells [60–62]. Thus, this sub-section will focus on mechanistic and electrocatalytic aspects, as relevant to DMFCs. The most significant effect of using methanol as a fuel in a fuel cell on the oxygen electrode Pt electrocatalyst is the significant decrease in its open circuit potential, caused by the cross-over of methanol from the anode to this electrode; loss of OCV could be as high as 0.2 V when using 1–2 M methanol as the fuel. Taking into consideration that the oxygen electrode has an open circuit potential about 0.2 V lower than the theoretical value of 1.23 V in a PEMFC, because of its high irreversibility and competing anodic reactions (Pt oxide formation, organic impurity oxidation), the efficiency loss under these conditions is as high as 30%. The second effect of methanol cross-over is in the kinetics of the electroreduction of oxygen. To date, there is no clear understanding of the mechanism of this effect, which slows down the rate of reaction, as evidenced by an increase of the Tafel slope and a decrease of the exchange current density.

In some cases low crossover values were recorded by operating the DMFC at higher temperatures—as illustrated by the LANL [51] (USA) and CNR-TAE [52] (Italy) researchers. This effect is mainly related to the higher achievable current densities which produces a fast methanol consumption at the anode/electrolyte interface and thus a lower methanol concentration gradient across the electrolyte. As stated in the preceding subsection, the crossover can be reduced by use of alternate or composite membranes. Apart from the as-mentioned effects of these methods to increase the coulombic efficiencies, other benefits are the increase of the open circuit potential of the oxygen electrode and the improvement of the kinetics of oxygen reduction. The latter is probably due to the decreased concentration of organic species (derived from methanol) adsorbed on the electrode. Research studies have revealed that Co and Fe porphyrins and phthalocyanins electrocatalysts are in-

sensitive to the presence of methanol, when functioning as oxygen electrodes [63–66]. These electrocatalysts were supported on a high surface area carbon (Vulcan XC 72R) and thermally treated at 800 °C. An alternative approach, used by these workers was to disperse these metal-organic macrocyclics in a film of a conducting polymer (poly aniline or polypyrrole) [67].

## 4. Conclusions

An analysis of the international activities carried out over the last 2 years in the field of DMFC stack and system development technology has been made. It is widely recognized that to reduce greenhouse gases and obey recent environmental laws it is necessary to develop highly efficient and low-cost energy conversion systems. Direct methanol fuel cells possess good potentialities in this regard due to intrinsically low polluting emissions and system simplicity. Recent results on DMFC stacks in terms of power density output ($\approx$1 kW/l) and overall conversion efficiency (37% at the design point of 0.5 V per cell) indicate that these systems are quite competitive with respect to the reformer-H2/air PEMFC units for application in electrotraction as well as in distributed power generation. Yet, significant progress is necessary to further decrease the gap that still exists with respect to conventional power generation systems in terms of power density and costs. The major hurdles concern the reduction of noble metal loading, methanol cross-over drawbacks and fabrication costs. At present, the most appealing application for DMFCs is in the field of portable power sources where device costs are less critical and power densities are close to those of Li-batteries. The present analysis indicates that the targets for each application may be achieved through a thoughtful development of materials device design as well as through an appropriate choice of operating conditions.

## Acknowledgements

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