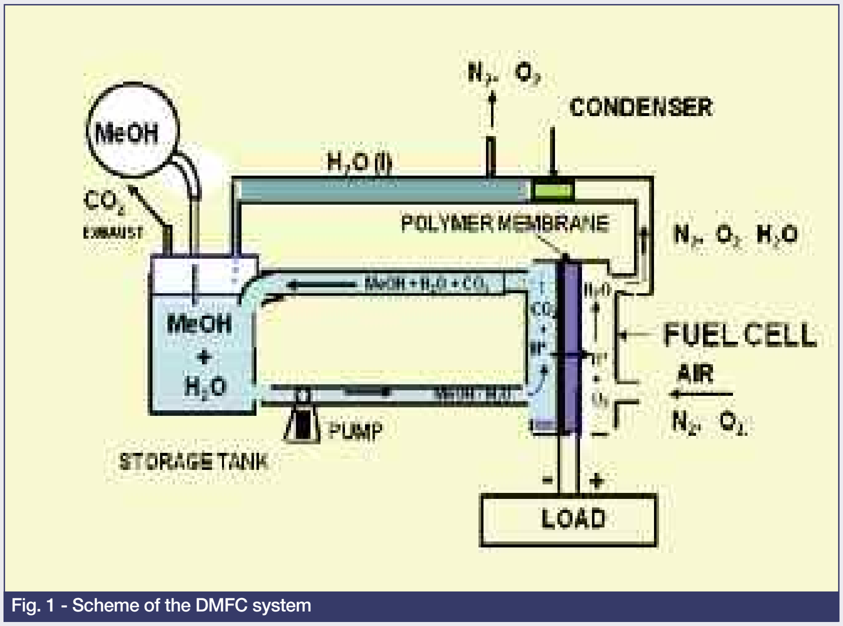


Fig. 1 - Scheme of the DMFC system

Vincenzo Baglio,
Vincenzo Antonucci,
Antonino S. Aricò
CNR-ITAE
Messina
vincenzo.baglio@itae.cnr.it

FUEL CELLS FOR PORTABLE APPLICATIONS

Direct methanol fuel cells (DMFCs) are promising power sources for portable applications due to their high energy density, light-weight, simplicity as well as easy handling and recharging. This review deals with an analysis of the current status of technology and potential applications of DMFCs. The status of knowledge in the basic research areas is presented and particular emphasis is given to required breakthroughs.

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]. Several types of fuel cells are in advanced stage of development. They can be classified into different categories, depending on the type of fuel and oxidant, whether the fuel is processed outside (external reforming) or inside (internal reforming) the fuel cell, the type of electrolyte, the temperature of operation, whether the reactants are fed to the cell by internal or external manifolds, etc. Generally, fuel cells are distinguished on the basis of the electrolyte. If there is an ion exchange membrane the fuel cell is called Polymer Electrolyte Fuel Cell (PEFC). This technology is now approaching commercialization. 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 (Tab. 1), whereas, the electromotive force associated to their electrochemical combustion to CO_2 is comparable to that of hydrogen combustion to water. Yet, very high overpotentials are always required in fuel cells operating at low temperatures to break the fuel apart, significantly degrading cell performance. Among the liquid organic fuels, methanol has promising characteristics in terms of reactivity at low temperatures, storage and handling. Accordingly, a direct methanol proton exchange membrane fuel cell (DMPEMFC) would help to alleviate some of the issues surrounding fuel storage and processing for fuel cells. Technological improvements in direct methanol fuel cells (DMFCs) are thus fuelled by their perspectives of applications in portable, transportation and stationary systems especially with regard to the remote and distributed generation of electrical energy. 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 CO_2 formation in the electrochemi-

Tab. 1 - Volumetric and gravimetric energy density for various fuels of technical interest for low temperature fuel cells

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

cal 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.

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, it 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 (Fig. 1). Methanol, which is characterized by low cost, easy storage and handling, and high energy density, appears well-suited for portable fuel cells.

Fundamental aspects of direct methanol fuel cells

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 CO_2 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:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \qquad \text{(anode)}$$
$$3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \qquad \text{(cathode)}$$

$$CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O \qquad \text{(overall)}$$

The free energy associated with the overall reaction at 25 °C and 1 atm and the electromotive force are $\Delta G = -686\ \text{kJ mol}^{-1}{}_{CH3OH}$; $\Delta E = 1.18$ V [2].

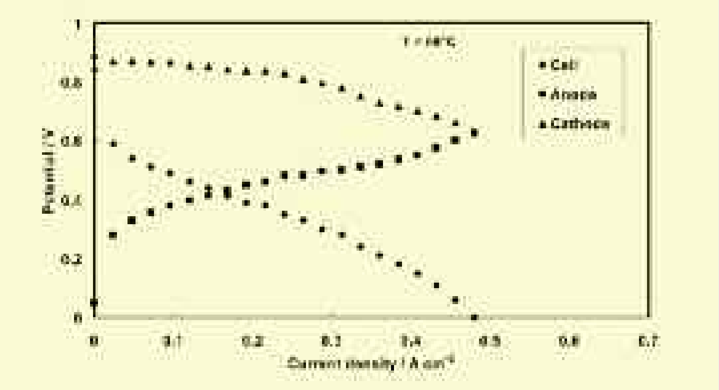


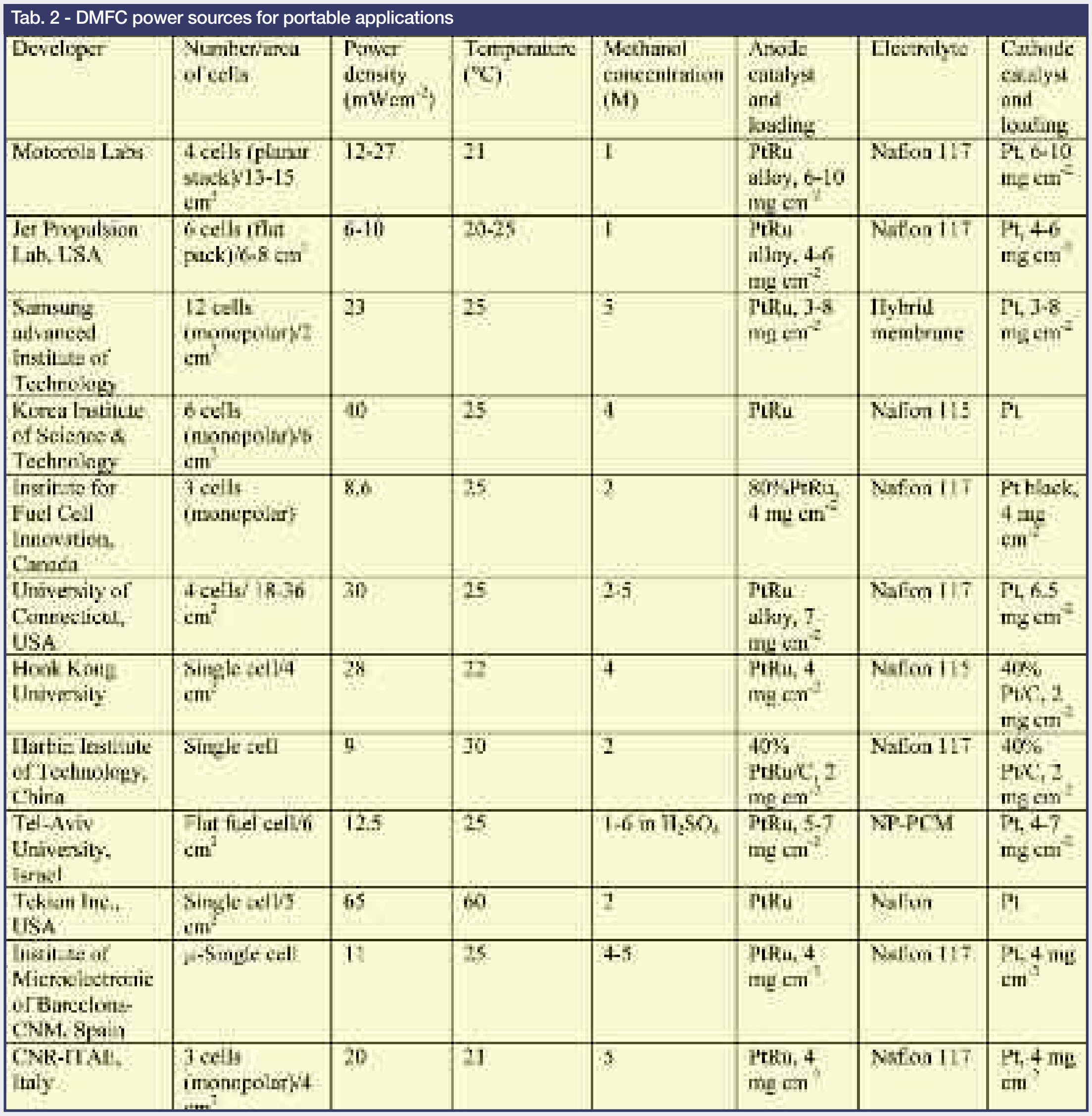
Fig. 2 - Single cell and in-situ half-cell electrode polarizations for a DMFC operating at 60 °C, ambient pressure, with 1 M methanol at the anode and air feed at the cathode

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. 2). This can be observed in a polarization plot (Fig. 2) where the terminal voltage of the cell is deconvoluted into the anode and cathode polarizations according to the equation:

$$E_{cell} = E_{cathode} - E_{anode}$$

Besides the strong activation control at the anode, the effect of the mixed potential on the cathode polarization curve is clearly observed in Fig. 2. 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. As it was pointed out above, such a result is mainly due to the effect of the mixed potential. The potential loss observed at the cathode originates also from the sluggishness of the oxygen reduction reaction (ORR). 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. 2). 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.

Tab. 2 - DMFC power sources for portable applications



Developer	Number/area of cells	Power density (mWcm^{-2})	Temperature (°C)	Methanol concentration (M)	Anode catalyst and loading	Electrolyte	Cathode catalyst and loading
Motorola Labs	4 cells (planar stack)/13-15 cm^2	12-27	21	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	20-25	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	25	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	25	4	PtRu	Nafion 115	Pt
Institute for Fuel Cell Innovation, Canada	3 cells (monopolar)	8.6	25	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	25	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	22	4	PtRu, 4 mg cm^{-2}	Nafion 115	40% Pt/C, 2 mg cm^{-2}
Harbin Institute of Technology, China	Single cell	9	30	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	25	1-6 in H_2SO_4	PtRu, 5-7 mg cm^{-2}	NP-PCM	Pt, 4-7 mg cm^{-2}
Tekion Inc., USA	Single cell/5 cm^2	65	60	2	PtRu	Nafion	Pt
Institute of Microelectronic of Barcelona-CNM, Spain	μ-Single cell	11	25	4-5	PtRu, 4 mg cm^{-2}	Nafion 117	Pt, 4 mg cm^{-2}
CNR-ITAE, Italy	3 cells (monopolar)/4 cm^2	20	21	3	PtRu, 4 mg cm^{-2}	Nafion 117	Pt, 4 mg cm^{-2}

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.

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 has recently gained momentum [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].

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 [11]. 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 m^2/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.

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 O_2 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 [12-14]. Recently, success was met in the development of ORR electrocatalysts consisting of bimetal carbon nitrides [15, 16]. 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 [17].

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 [18-20] or finding alternative proton conductors with the capability of inhibiting methanol transport. The polymer electrolyte should have a high ionic conductivity ($5x10^{-2}$ ohm^{-1} cm^{-1}) under working conditions and low permeability to methanol (less than 10^{-6} moles min^{-1} 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 [21, 22] and poly-sulfone [23], polyvinylidene fluoride [24], styrene grafted and sulfonated membranes [25], zeolites gel films (tin mordenite) and/or membranes doped with heteropolyanions [26].

A critical area to improve overall cell performance is the fabrication of MEAs. In fact, the performance of a DMFC is strongly affected by the fabrication procedure of the membrane-electrode assembly. Progress on preparation of high performance MEAs has been made by preparing thin electrocatalyst layers (about 10 μm thick) composed of the electrocatalyst and ionomer in the electrode substrate [27]. Problems caused by barrier layer effects of nitrogen for access of oxygen to the catalytically active sites and electrode flooding need further investigations. Possible solutions to these problems are heat treatments of the recast Nafion gel in the electrocatalytic layer to make it hydrophobic or pore formers to increase porosity.

DMFCs for portable applications

In practice, fuel cells do not operate as single units; rather, they are connected in a series to additively combine the individual cell potentials and achieve a greater, and more useful, potential. A collection of single cells in series is known as a "stack". For conventional actively-driven fuel cells, the most popular means of interconnection are the "bipolar plates". These connect one cathode to the anode of the next cell; furthermore, the bipolar plates serve as a means of feeding oxygen to the cathode and fuel to the anode. The fuel cell stack consists of a repeated, interleaved structure of membrane electrode assemblies (MEAs), gas diffusion layers (GDLs) and bipolar plates. All these components are clamped together with significant force to reduce electrical contact resistance. The fuel and oxidant are provided with manifolds to the correct electrodes, and cooling is provided either by the reactants or by a cooling medium. Usually, this type of fuel cell works with forced airflow on the cathode side and forced fuel flow on the anode side, requiring various auxiliary components and a rather complicated control system. Such a fuel cell does not fit the requirements for low-power-battery replacement applications. For such applications, the key challenges are to provide acceptable power output and high-energy efficiency under conditions convenient to the user. The desired operating conditions include, for example, an operating temperature near room temperature, no forced airflow, and no recirculation fuel pump. It is well known that a forced air design with an external blower is unattractive for use in small fuel cell systems, as the parasitic power losses from the blower are estimated at 20-25% of the total power output. To this scope, the concept of passive-feed DMFCs has been the object of significant interest [28]. Under this configuration, DMFCs operate without any external devices for feeding methanol and blowing air into the cells. Oxygen can diffuse into the cathode from the ambient due to an air-breathing action of the cell (partial pressure gradient); whereas, methanol can reach the catalytic layer from a reservoir driven by a concentration gradient between the electrode and the reservoir and through capillary force action of electrode pores. The use of low cost miniaturised "step-up" DC/DC converters allows to suitably increase the stack potential with a very small dissipation of power (~90% efficiency). This approach does not require extensive miniaturisation of the DMFC stack favouring the development of low cost DMFC stack architectures with practical electrode area. The unique

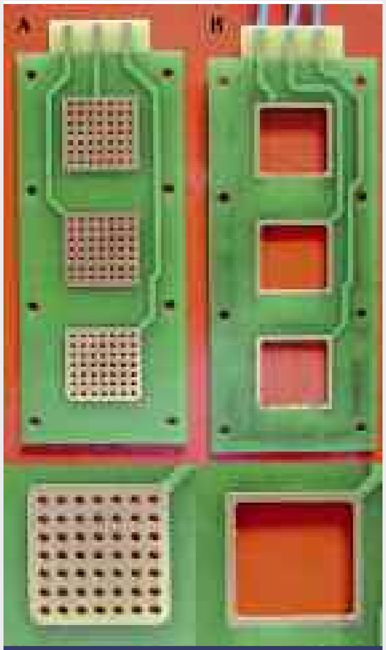


Fig. 3 - Pictures of two different monopolar plates for application in a DMFC three-cell stack operating under passive mode

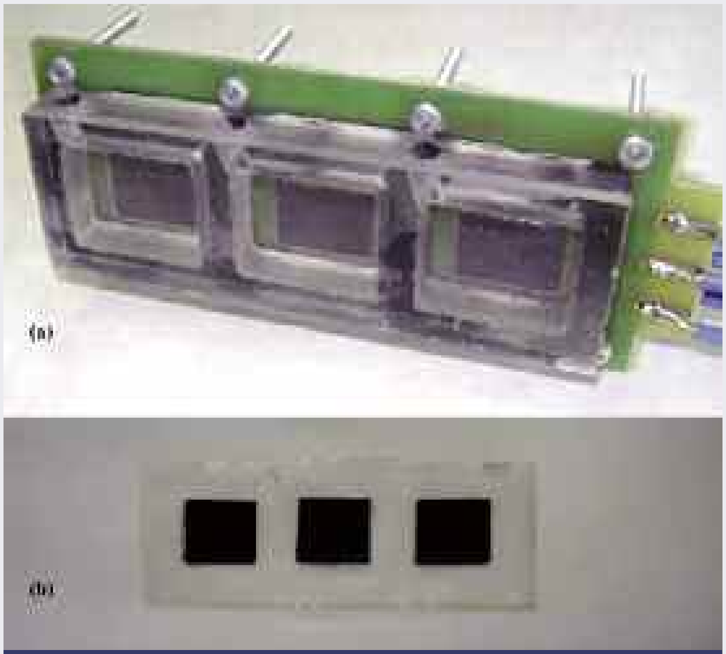


Fig. 4 - Pictures of the DMFC design B used for a three-cell stack (a) and MEA formed by a single membrane and three couples of electrodes (b)

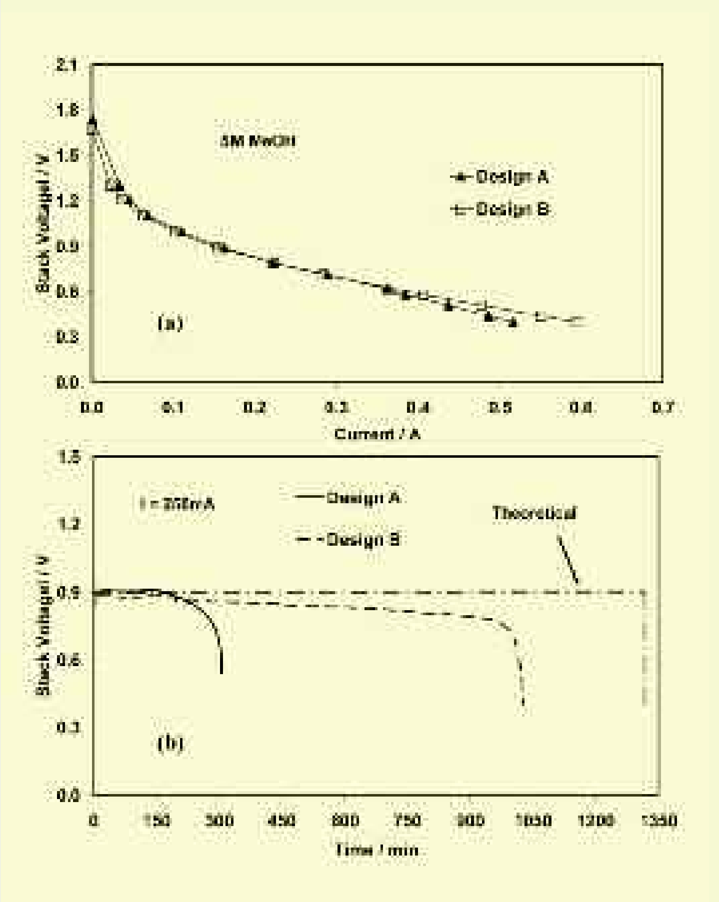


Fig. 5 - Comparison between the polarization curves obtained with the two different designs with a Pt loading of 4 mg cm^{-2} on each electrode and 5 M methanol solution (a), and chrono-potentiometric results at 250 mA obtained with the two designs using a Pt loading of 4 mg cm^{-2} and 5 M methanol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

requirements of air breathing small fuel cells have led to several alternative designs [28-32]. Several organizations are actively engaged in the development of low power DMFCs for cellular phone, laptop computer, portable camera and electronic game applications [33-48]. The initial goal of this research is to develop proof of concept DMFCs capable of replacing high performance rechargeable batteries. Accomplishments in this area are reported in Tab. 2. Also our group (CNR-ITAE, Messina, Italy) has developed passive DMFC mini-stacks for portable applications, based on a simple approach [33]. Essentially, two designs of flow-fields/current collectors for a passive DMFC monopolar three-cell stack were developed and investigated (see Fig. 3). 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 (Fig. 4a). 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 (Fig. 4b), afterwards they were sandwiched between two PCBs. The geometrical area of each electrode was 4 cm^2 and the total area of the stack was 12 cm^2. The cells were connected in series externally through the electric circuit. The electrochemical characterization was carried out varying the catalyst loading and methanol concentration. A loading of 4 mg cm^{-2} Pt loading provided the best electrochemical results in the presence of unsupported catalysts [33]. This appeared to be the best compromise between electrode thickness and amount of catalytic sites. Similar performances in terms of maximum power were recorded for the two designs; whereas, better mass transport characteristics were obtained with 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}. The use of highly concentrated methanol solutions caused a significant decrease of OCV that reflected on the overall polarization curve. 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 CO_2 removal from the anode and better mass transport properties.

Perspectives and Concluding Remarks

(i) The most challenging problem for the development of DMFCs has been, and still is, a significant enhancement of electrocatalytic activities for the 6-electron transfer electro-oxidation of methanol. The sluggishness of the reaction is caused by the very strong chemical adsorption of CO-type species on an electrocatalyst which enhances the dissociative adsorption of methanol (Pt is the best known electrocatalyst for this step). A neighboring chemisorbed labile OH species is vital for the electrooxidation of the strongly adsorbed CO species. At present, a Pt-Ru electrocatalyst (50:50 at. %) has shown the best results [49].

(ii) The performance for the oxygen reduction reaction with a platinum electrocatalyst is affected by the cross-over of methanol from the anode to the cathode through the proton conducting membrane.

Firstly, the open circuit potential is reduced by about 200 mV and the second effect is due to the competitive adsorption of dissociated methanol and oxygen species. At present, there is no clear evidence of catalytic enhancement in oxygen reduction for alloys of Pt with Cr, Co and Ni in the presence of methanol cross-over [50]. Non-platinum electrocatalysts, such as heat-treated phthalocyanines and porphyrins [51], as well as transition metals chalcogenides [52], have some chances of methanol tolerance but have considerably lower activities than platinum and also problems of stability. The near term prospects of replacing platinum as an electrocatalyst is very slim but a great challenge is to reduce the noble metal loading in both electrodes by a factor of about 10 to reduce its cost to about $10/kW.

(iii) The perfluorosulfonic acid polymer electrolyte in the DMFC is an equally expensive material. There has been a lot of research on alternative proton conducting membranes for PEMFCs (sulfonated polyetherketone, polysulfone, radiation grafted polystyrene, zeolites, electrolytes doped with heteropolyacids and sulfonated polybenzimidazole [21-26]) but it is still a challenge to attain sufficiently high specific conductivity and stability in the DMFC environment. In recent studies, some Nafion-based composite membranes with silicon oxide [19] and zirconium hydrogen phosphate [18] have shown beneficial effects on operation up to about 150 °C with enhanced performance (lower activation and ohmic overpotentials).

(iv) The development of DMFC stacks for portable applications has gained momentum in the last two-three years. The applications of DMFC in portable power sources cover the spectrum of cellular phones, personal organizers, laptop computers, military back power packs, etc. The infusion of semiconductor technology [53, 54] into the development of micro and mini fuel cells by leading organizations such as LANL [34], JPL [35], Motorola [36], has provided an awakening of DMFCs replacing the most advanced type of rechargeable batteries, i.e., lithium ion. For several of these applications, a DMFC working at room temperature and ambient pressure with an efficiency of only about 20% may be sufficient to have a strikingly higher performance than the lithium ion batteries, in respect to operating hours between refueling/recharging because of the high energy density of methanol. Further, the refueling in the case of DMFCs is instantaneous, whereas it requires about 3-5 hrs for lithium ion batteries. There is still a challenge in reducing the weight and volume of the DMFC to a level competitive with lithium ion batteries, as needed for say the cellular phone and laptop applications. What is most attractive in the portable power applications, as compared with the transportation and stationary applications is that the cost per kW or cost per kWh could be higher by a factor of 10 to 100. For this application, there is hardly any competition for lithium ion and DMFCs from any other type of power source; yet, the Pt loadings are still high in the DMFCs. Reducing the loading of noble metals is actually one of the breakthroughs which may allow the DMFC to increase its competitiveness on the market of power sources.

In the near-term the high energy density of DMFCs and the recent advances in the technology of the realization of miniaturized fuel cells make these systems attractive to replace 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 successful utilization of such systems; the progress made in manufacturing DMFCs for portable systems may also stimulate new concepts and designs which may aid the further development of these systems for electro-traction.

Vincenzo Baglio is a researcher at CNR-ITAE of Messina, Italy. He obtained a B.Sc. degree in chemistry from University of Messina (Italy) and a PhD in "Materials for Environment and Energy" from University of Rome "Tor Vergata" (Italy). His current research is focused on energy conversion and storage.

Vincenzo Antonucci is the chief of the fuel cell section of the CNR-ITAE Institute of Messina, Italy. He is author of more than 130 articles on International Journals involving electrochemistry, materials science, catalysis and photovoltaics.

Antonino S. Aricò is SOFC/DMFC project leader at the CNR-ITAE Institute. He is involved in research programs related to the development of low and high temperature fuel cells. He has published about 130 articles on International Journals. He has been involved in several EU projects.

References

[1] L. Carrette, K.A. Friedrich. U. Stimming, *ChemPhysChem*, 2000, **1**, 163.

[2] A.S. Aricò, S. Srinivasan, V. Antonucci, *Fuel Cells*, 2001, **1**, 133.

[3] C. Lamy, J.-M. Léger, S. Srinivasan, Modern Aspects of Electrochemistry, J.O'M. Bockris, B.E. Conway (Eds.), 34, Plenum Press, New York, Chapter 3, 53 (2000).

[4] M. Shibata, S. Motoo, *J. Electroanal. Chem.*, 1985, **194**, 261.

[5] M. Watanabe, S. Motoo, *J. Electroanal. Chem*, 1975, **60**, 275.

[6] A. Hamnett, *Catalysis Today*, 1997, **39**, 445.

[7] X. Ren, M.S. Wilson, S. Gottesfeld, *J. Electrochem. Soc.*, 1996, **143**, L12.

[8] M. Gotz, H. Wendt, *Electrochim. Acta*, 1998, **43**, 3637.

[9] A.S. Aricò, Z. Poltarzewski, H. Kim, A. Morana, N. Giordano, V. Antonucci, *J. Power Sources*, 1995, **55**, 159.

[10] H.A. Gasteiger, N. Markovic, P.N. Ross Jr., E.J. Cairns, *J. Electrochem. Soc.*, 1994, **141**, 1795.

[11] N. Giordano, E. Passalacqua, L. Pino, A.S. Aricò, V. Antonucci, M. Vivaldi, K. Kinoshita, *Electrochim. Acta*, 1991, **36**, 1979.

[12] S. Mukerjee, S. Srinivasan, *J. Electroanal. Chem.*, 1993, **357**, 201.

[13] M. Watanabe, K. Tsurumi, T. Mizukami, T. Nakamura, P. Stonehart, *J. Electrochem. Soc.*, 1994, **141**, 2659.

[14] A.S. Aricò, A.K. Shukla, H. Kim, S. Park, M. Min, V. Antonucci, *Appl. Surf. Sci.*, 2001, 172, 33.

[15] V. Di Noto, E. Negro, R. Gliubizzi, S. Lavina, G. Pace, S. Gross, C. Maccato, *Adv. Funct. Mater.*, 2007, **17**, 3626.

[16] E. Negro, V. Di Noto, *J. Power Sources*, 2008, **178**, 634.

[17] V. Jalan, E.J. Taylor, *J. Electrochem. Soc.*, 1983, **130**, 2299.

[18] C. Yang, S. Srinivasan, A.S. Aricò, P. Cretì, V. Baglio, V. Antonucci, *Electrochem. Solid-State Lett.*, 2001, **4**, A31.

[19] A.S. Aricò, V. Baglio, A. Di Blasi, P. Cretì, P.L. Antonucci, V. Antonucci, *Solid State Ionics*, 2003, **161**, 251.

[20] V. Baglio, A.S. Aricò, A. Di Blasi, V. Antonucci, P.L. Antonucci, S. Licoccia, E. Traversa, F. Serraino Fiory, *Electrochim. Acta*, 2005, **50**, 1241.

[21] L. Li, J. Zhang, Y. Wang, *J. Membrane Sci.*, 2003, **226**, 159.

[22] B. Bauer, D.J. Jones, J. Roziere, L. Tchicaya, G. Alberti, M. Casciola, L. Massinelli, A. Peraio, S. Besse, E. Ramunni, J. New Mat. *Electrochem. Sys.*, 2000, **3**, 93.

[23] F. Lufrano, V. Baglio, P. Staiti, A.S. Aricò, V. Antonucci, *J. Power Sources*, 2008, **179**, 34.

[24] E. Peled, T. Duvdevani, A. Aharon, A. Melman, *Electrochem. Solid-State Lett.*, 2000, **3**, 525.

[25] S. Hietala, M. Koel, E. Skou, M. Elomaa, F. Sundholm, *J. Mater. Chem.*, 1998, **8**, 1127.

[26] A.S. Aricò, P.L. Antonucci, N. Giordano, V. Antonucci, *Material Letters*, 1995, **24**, 399.

[27] M.S. Wilson, S. Gottesfeld, *J. Appl. Electrochem.*, 1992, **22**, 1.

[28] W. Qian, D.P. Wilkinson, J. Shen, H. Wang, J. Zhang, *J. Power Sources*, 2006, **154**, 202.

[29] A. Heinzel, C. Hebling, M. Muller, M. Zedda, C. Muller, *J. Power Sources*, 2002, **105**, 250.

[30] A. Faghri, Z. Guo, *Appl. Thermal Engineering*, 2008, **28**, 1614.

[31] D. Kim, E.A. Cho, S.-A. Hong, I.-H. Oh, H.Y. Ha, *J. Power Sources*, 2004,**130**, 172.

[32] R. Chen, T.S. Zhao, *Electrochem. Comm.*, 2007, **9**, 718.

[33] V. Baglio, A. Stassi, F.V. Matera, A. Di Blasi, V. Antonucci, A.S. Aricò, *J. Power Sources*, 2008, **180**, 797.

[34] S.C. Thomas, X. Ren, S. Gottesfeld, P. Zelenay, *Electrochim. Acta*, 2002, **47**, 3741.

[35] T.I. Valdez, S.R. Narayanan, *Proceedings of The Electrochemical Society*, 2005, **31**, 506.

[36] J. Pavio, J. Hallmark, J. Bostaph, A. Fisher, B. Mylan, C.G. Xie, *Fuel Cells Bulletin*, 2002, **43**, 8.

[37] R. Chen, T.S. Zhao, *Electrochim. Acta*, 2007, **52**, 4317.

[38] H.F. Zhang, I.-M. Hsing, *J. Power Sources*, 2007, **167**, 450.

[39] M.A. Abdelkareem, N. Nakagawa, *J. Power Sources*, 2007, **165**, 685.

[40] D. Chu, R. Jiang, *Electrochim. Acta*, 2006, **51**, 5829.

[41] H. Yang, T.S. Zhang, Q. Ye, *J. Power Sources*, 2005, **139**, 79.

[42] G.Q. Lu, C.Y. Wang, *J. Power Sources*, 2004, **134**, 33.

[43] Q.-Z. Lai, G.-P. Yin, J. Zhang, Z.-B. Wang, K.-D. Cai, P. Liu, *J. Power Sources*, 2008, **175**, 458.

[44] A. Blum, T. Duvdevani, M. Philosoph, N. Rudoy, E. Peled, *J. Power Sources*, 2003, **117**, 22.

[45] D. Kim, E.A. Cho, S.-A. Hong, I.-H. Oh, H.-Y. Ha, *J. Power Sources*, 2004, **130**, 172.

[46] Y.H. Pan, *J. Power Sources*, 2006, **161**, 282.

[47] G.Q. Lu, C.Y. Wang, T.J. Yen, X. Zhang, *Electrochim. Acta*, 2004, **49**, 821.

[48] N. Sabate, J.P. Esquivel, J. Santander, N. Torres, I. Gracia, P. Ivanov, L. Fonseca, E. Figueras, C. Canè, *J. New Materials for Electrochem. Sys.*, 2008, **11**, 143.

[49] A.S. Aricò, P.L. Antonucci, E. Modica, V. Baglio, H. Kim, V. Antonucci, *Electrochim. Acta*, 2002, **47**, 3723.

[50] E. Antolini, T. Lopes, E.R. Gonzales, *J. Alloys and Compounds*, 2008, **461**, 253.

[51] G.R. Sun, J.T. Wang, R.F. Savinell, *J. Appl. Electrochem.*, 1998, **28**, 1087.

[52] N. Alonso-Vante, *H. Tributsch, Nature*, 1986, **323**, 431.

[53] G. D'Arrigo, C. Spinella, G. Arena, S. Lorenti, *Fuel Cells Bulletin*, 2003, **4**, 10.

[54] S. Motokawa, M. Mohamedi, T. Momma, S. Shoji, T. Osaka, *Electrochem. Comm.*, 2004, **6**, 562

ABSTRACT

Celle a combustibile per applicazioni portatili

Le celle a metanolo diretto (DMFC) hanno recentemente suscitato notevole interesse non solo per la loro semplicità ma anche per le caratteristiche ottimali, in termini di densità di energia e compatibilità ambientale. Le proprietà sopra elencate rendono le celle a metanolo particolarmente adatte al settore della tecnologia portatile (laptop, cellulari ecc.). Questo articolo tratta lo stato dell'arte e le potenziali applicazioni delle celle DMFC, con particolare riguardo alle problematiche e alle possibili soluzioni.