Fuel cells – the future of electricity generation for portable applications

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ABSTRACT

Fossil fuels, including crude oil, coal and natural gas are currently the key resources for world energy supply. Hence, the majority of electrical energy production is realized via combustion of conventional fuels, such as: coal, methane and petroleum. However, increasing emissions of pollutants and greenhouse gases from fossil fuel-based electricity production (especially with respect to SO_2, NO_x and CO_2 discharge) bring about major environmental concerns. In addition, the status of conventional (fossil) fuel reserves is still uncertain. Thus, production of "clean" electrical energy, especi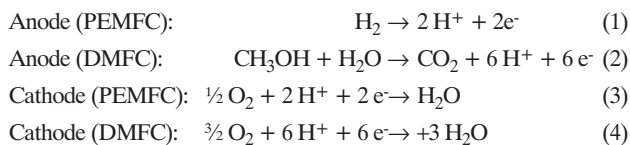ally from renewable resources, such as: biomass, solar, photovoltaic, geothermal, hydro and wind energy sources becomes of significant importance to the world's economy. Fuel cells (FCs) are electrochemical cells, which convert a source fuel (e.g. H_2, CH_4, alcohols, etc.) into an electric current. They generate electricity inside a cell via electrochemical reactions between a fuel and an oxidant, in the presence of an electrolyte. In general, most of fuel cells can be operated as emission-free devices, based on fuels produced from renewable resources. With a variety of possible FC types, fuel cells could potentially serve in stationary, transportation or portable applications. This work is a review of the *state-of-the-art* in fuel cell technology, with respect to FC employment in portable applications.

INTRODUCTION TO FUEL CELL TECHNOLOGIES

Electrical energy is typically produced at a power station by electromechanical generators driven by heat engines. A primary source of heat that is supplied to these engines comes from burning of fossil fuels, such as coal, petroleum or natural gas. For conventional steam turbines, these are directly driven by steam generated through combustion of a fuel, giving an overall process efficiency below 50%. Nevertheless, increasing concerns about shrinking reserves of fossil fuels, continuous oscillation of oil price, as well as stringent environmental regulations (especially with respect to excessive emissions of pollutants and greenhouse gases) are driving the world towards new sources of "clean" and renewable energy (Owen et al. 2010; Shafiee and Topal 2009; Wang and Wan 2009).

Fuel cells (FCs) are electrical energy converters, which change chemical energy of a fuel (through electrode reactions between this fuel and an oxidant, in the presence of an electrolyte medium) into electrical energy. Fuel cells can be operated on a continuous basis, as long as the reactant flow is maintained into the cell (while reaction products flow out of the cell). In this regard, FCs represent a thermodynamically open system, in contrast to conventional batteries, which are typical energy storage and conversion devices (a thermodynamically-closed system). Basically, all fuel cell assemblies comprise two electrodes (anode and cathode), separated with a layer of electrolyte. Operation of fuel cells is based on two electrochemical reactions that simultaneously occur at interfaces between the ionically conductive electrolyte and electrically conductive electrodes. There are many fuel cell types, with respect to their design and possible combinations of fuels. However, in practice FCs could be classified as: *low-* and *high-temperature* devices. The so-called *low-temperature* fuel cells are typically PEM (*Proton Exchange Membrane*) type systems, where the electrolyte is composed of a proton-conducting membrane (made of perfluorocarbon-sulfonic acid ionomer, e.g. *Nafion* type), which separates the cathode (Pt-based) and anode (Pt/Ru-based) sides. These types of fuel cells (where protons are conducted through the membrane) are generally run on pure hydrogen fuel or simple aliphatic alcohols, such as methanol (DMFC - *Direct Methanol Fuel Cell*) or ethanol (DEFC - *Direct Ethanol Fuel Cell*), at operational temperatures between ca. 60 and 120 °C. An overall, electrical plus thermal efficiency of such systems approaches 80-90 %. Anodic (fuel oxidation) and cathodic (oxygen reduction) reactions, characteristic to hydrogen PEMFC and methanol-fuelled DMFC devices are presented in equations 1 through 4 below. Also, a schematic diagram of PEMFC (H_2/O_2) in operation and its stack assembly are shown in Figure 1.

Anode (PEMFC): $\qquad\qquad\qquad H_2 \rightarrow 2\,H^+ + 2e^-$ (1)

Anode (DMFC): $\qquad CH_3OH + H_2O \rightarrow CO_2 + 6\,H^+ + 6\,e^-$ (2)

Cathode (PEMFC): $\tfrac{1}{2}\,O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O$ (3)

Cathode (DMFC): $\tfrac{3}{2}\,O_2 + 6\,H^+ + 6\,e^- \rightarrow +3\,H_2O$ (4)

PEM-based fuel cells can generate power from Watts to hundreds of kilowatts and as such they are projected to serve a variety of potential applications, from portable electronic appliances and backup power generators to transportation (passenger cars, buses, utility vehicles, etc.) and high-power stationary applications (up to 250 kW).
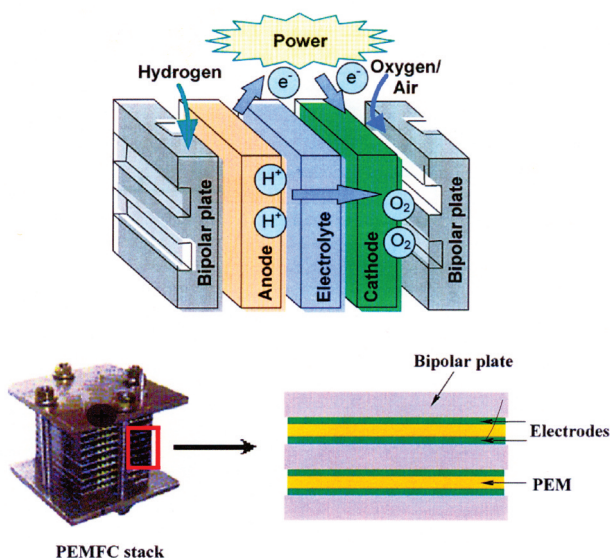

Figure 1. Schematic diagram of low-temperature (H_2/O_2) PEMFC in operation and its stack assembly.
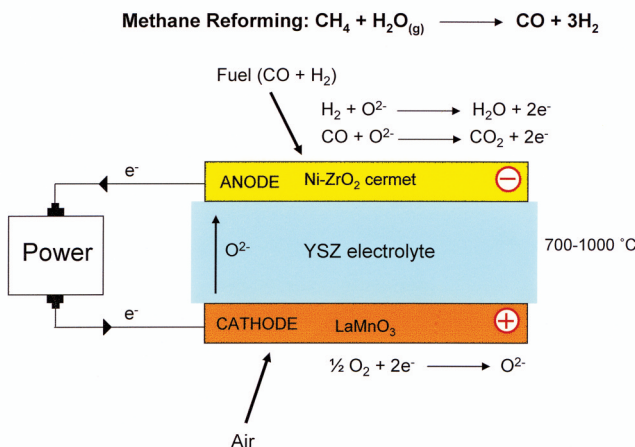

Figure 2. Schematic diagram of high-temperature SOFC device and its operational details.

On the other hand, *high-temperature* fuel cell, such as SOFC - *Solid Oxide Fuel Cell* (see Figure 2) uses a solid oxide electrolyte made from a ceramic material - yttria stabilized zirconia (YSZ: Y_2O_3/ZrO_2), which at the fuel cell's operational temperature (700-1000 °C) acts as a conductor of oxide ions. This material allows oxygen atoms to be converted to oxide (O^{2-}) ions on the porous surface of $LaSrMnO_3$ (LSM) cathode and then to be transported through the ceramic electrolyte to a fuel-based anode zone ($Ni\text{-}ZrO_2$ cermet), where the oxide ions react with fuel (H_2 or/and CO), giving up electrons to an external circuit (see Figure 2 for details). Another type of high-temperature fuel cell (MCFC - *Molten Carbonate Fuel Cell*) is operated in a similar way, except that its electrolyte consists of molten Li and K carbonates, and the fuel cell's operational temperature range is 600-700 °C. Unlike PEM fuel cells, the high-temperature FCs (both SOFC and MCFC systems) use much cheaper catalyst materials (principally Ni-based). In addition, high-temperature operation eliminates the need for external fuel reforming; also it leads to production of high-temperature heat as a by-product to the electrical power. This heat can conveniently be utilized in the so-called *Combined Heat and Power* (CHP) systems, or additionally it can be used to drive a gas turbine, in order to produce more electricity. Therefore, SOFC and MCFC systems are envisaged for large (over 100 kW) stationary power or transportation (buses, trains) applications (Barbir 2005; Carrette et al. 2001; Singhal and Kendall 2003).

FUEL CELLS FOR PORTABLE APPLICATIONS

Portable fuel cells can be divided into two categories, namely: microfuel cells (battery replacements for mobile phones, laptops, camcorders, digital cameras, etc. with power capabilities under 100 W) and portable power generators (up to several kW), applicable to recreational, industrial and military applications.

Laptop computer and mobile phone electronic appliances are likely the most promising market segments for commercialization of PEM microfuel cells. Some of the first prototypes of DMFC devices, built to power portable laptop computers, were presented by Toshiba and SFC *Smart Fuel Cell* AG companies in 2003, and later by Matsushita Battery in 2006 (Matsushita Battery Industrial 2006; SFC *Smart Fuel Cell* AG 2003; Toshiba company 2003). An idea behind replacing a Li-ion (or earlier NiMeH) battery with a portable fuel cell system was primarily related to the emergence of new, rigorous requirements with respect to energy-density (see Figure 3) and the device's operational time between consecutive recharges. In addition to their superior energy-density characteristics (Figure 3), DMFC devices can maintain their original electrochemical performance for a much longer period of time than conventional Li-ion batteries, where significant electrochemical deterioration can already be observed after 12 to 18 months of their

operation. In contrast, direct methanol fuel cells are expected to be fully operational for thousands of hours, which does translate to operational lifetimes of over 5 years. For microfuel cells, DMFC systems are far superior to those hydrogen-fuelled cells. This is because the storage and supply of hydrogen fuel (e.g. from high-pressure cylinders or metal hydrides) at portable (or micro) level becomes impractical. Conversely, DMFCs are fuelled with methanol solution, typically supplied in small (*ca.* 50 cm^3) disposable cartridges, which allows to run the computer for over 5 hours on a single cartridge (compare with ca. 2 hours for an average lithium-ion battery set).
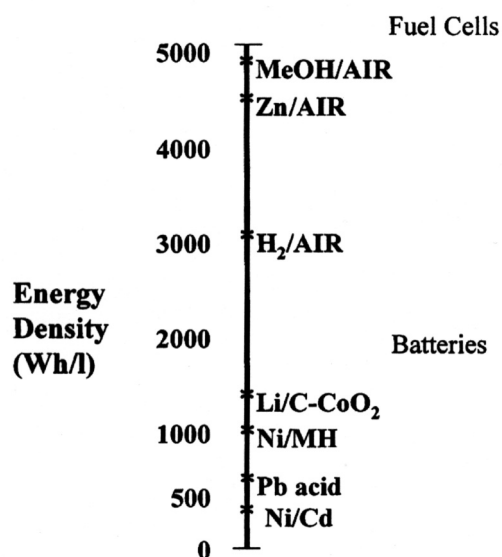

Figure 3. Theoretical energy densities for the selected power delivery systems (reproduced from Dyer 2002, with permission from International Journal of Hydrogen Energy).

Recently, more research attention (Andreadis and Tsiakaras 2006; Basu et al. 2008; Fujiwara et al. 2008; Li et al. 2009) has been given to another type of direct alcohol fuel cell: DEFC system. When compared with methanol, ethanol appears significantly less toxic and thus more environmentally-friendly fuel. Also, ethanol can easily be produced from a variety of available agricultural products and biomass substrates. In addition, C_2H_5OH provides about 30 % greater energy-density than methanol (compare 8,030 Wh·kg^{-1} with 6,100 Wh·kg^{-1}, respectively), whereas its oxidation by-products (i.e. acetaldehyde and acetic acid) are significantly less detrimental to health than methanol itself, or its oxidation by-products.

Direct alcohol fuel cell systems seem very well suited to other portable electronic devices, such as: mobile phones, camcorders, digital cameras, PDAs (Portable Digital Assistants) and some cordless tools. However, most of these appliances are much smaller than portable computers. Thus, introduction of a viable FC technology into this market will strongly depend on how small these microfuel cells could actually be manufactured. Nevertheless, current market forecasts on the introduction of microfuel cells are quite optimistic. Table 1 (reproduced from Agnolucci 2007, with permission from International Journal of Hydrogen Energy) shows the worldwide size of electronic devices market, which is potentially available to microfuel cells.

Portable power generators are usually sold to industrial and recreational, and military users, to power a wide range of electronic devices (or to be used as battery chargers). Fuel cell-based power generators offer extremely clean, highly-efficient and silent operation, as compared to conventional diesel or gas-powered generators. Therefore, such FC devices are particularly attractive to the military market, where price issues are usually of less importance. For the civil sector, the FC-based power generator market is currently confined to unique applications, e.g. at locations with very rigorous environmental (or noise-related) regulations, such as those of California. For portable power generators (several kW), both direct alcohol as well as hydrogen-fuelled FC systems can commercially be envisaged (Agnolucci 2007; Cowey et al. 2004; Dyer 2002).

Table 1. Worldwide total available market for microfuel cells, given in millions of units (reproduced from Agnolucci 2007, with permission from Elsevier Science).

	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	AGR
Camcorders	10	11	13	15	18	20	23	27	31	36	15.2
Digital cameras	7	9	12	15	19	25	33	42	54	70	28.9
Mobiles	305	322	344	371	408	447	483	522	563	608	8
Laptops	34	37	41	47	54	62	71	80	90	102	13.1
PDAs	13	17	20	24	29	36	44	53	65	79	21.9

Sales for 2008-2011 are estimated using the 2002-2007 annual growth rate (AGR).

THE COST OF PEM-BASED PORTABLE POWER

Current cost of fuel cell technology is still a major and critical factor, which prevents the PEM-based fuel cell power systems from their full commercialization. In fact, the PEMFC-based 1 kW Ballard-Coleman portable power generator is about 7 times as expensive as its conventional, ICE (*Internal Combustion Engine*) diesel-powered 1 kW competitor from Honda (Cropper 2004). Similar trends are observed for microfuel cells, when their prices are compared to those of the competitive Li-ion batteries.

The primary expense to manufacture the PEM fuel cell is associated with the cost of manufacture of its *Membrane Electrode Assemblies* (MEAs). A fuel-cell electrode is essentially a thin catalyst layer (a location, where electrochemical reactions take place) pressed between the ionomer membrane and porous, electrically conductive substrate. The most common catalyst in PEM fuel cells (for both hydrogen oxidation and oxygen reduction reactions) is platinum or Pt-Ru alloys for oxidation of alcohols (e.g. methanol or ethanol). Pt catalyst is very expensive; thus, a number of research activities concentrate on lowering its loading on the surface of carbon powder-supported electrode (currently at ca. 0.3-0.4 mg $Pt \cdot cm^{-2}$). Furthermore, much cheaper and based on non-noble metals, nanostructured electrocatalysts have recently been developed.

All these activities aim at reducing the price of PEM-type FC units, in order to reach the target price of 400 U\$ and 1,000 U\$ for 20 W and 50 W DMFC laptop docking stations, correspondingly (Agnolucci 2007; Barbir 2005; Carrette et al. 2001). One might possibly assume that the cost of microfuel cells would significantly drop if mass production of these systems were achieved.

TECHNICAL DIFFICULTIES AND SYSTEM CONSTRAINTS

Direct alcohol fuel cell systems

A major aspect which is linked to the performance of a DMFC (or DEFC) device arises from the permeability of polymer membranes to alcohols. Both water and alcohol molecules are transported through the membrane to the cathode side, which is realized by means of electro-osmotic forces, as well as by diffusion. Then, a mixed potential results at the cathode, which causes a more or less significant depolarization effect. The alcohol crossover phenomenon (which also leads to reduction of fuel utilization) is typically dealt with by optimization of alcohol concentration, in addition to taking care of these parameters which are related to the structure of the membrane and those directly linked to the fuel cell's operation (e.g. see works by Barbir 2005 and by Carrette et al. 2001).

Another, key technical difficulty to overcome for direct alcohol fuel cells refers to the so-called "CO poisoning effect" (Carrette et al. 2001; Conway and Tilak 1992), related to the formation of carbon monoxide during a sequence of oxidation reactions at Pt or Pt-based catalysts (see equations 5 and 6 below for oxidation of methanol at Pt).

$$6\,Pt + CH_3OH \quad \rightarrow \quad Pt_3COH + 3\,PtH \qquad (5)$$
$$Pt_3COH \quad \rightarrow \quad PtCO + 2\,Pt + H^+ + e^- \qquad (6)$$
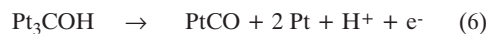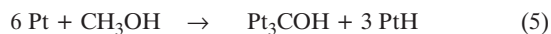
Such-formed CO species (equation 6) is very strongly adsorbed on the Pt catalyst surface, which causes complete blocking of CO-occupied platinum sites for any further electrochemical reactivity. The above problem can to a great extent be solved through incorporation of specific activity promoters (typically Ru, Sn, Os, W and Mo) in the catalyst matrix.

PEM (H_2/O_2) fuel cells

The proton-exchange membranes of PEM fuel cells should always be kept hydrated, in order to ensure high conductivity for proton transfer. As PEM fuel cells are fed with gaseous fuels (hydrogen at anode and oxygen/air at cathode side), water management in the membrane becomes a key issue for this FC system. A common way to improve the water management in PEMFCs is to provide constant humidification to the streams of gases incoming to the fuel cell (see again works by Barbir 2005 and by Carrette et al. 2001).

A major technical difficulty for operation of PEM fuel cells is related to fuel processing, i.e. to production and further (safe) storage of hydrogen. Hydrogen can be obtained from a variety of substances, including: alcohols (e.g. by partial oxidation or steam reforming of CH_3OH), various hydrocarbons (e.g. through catalytic steam reforming, partial oxidation and coal gasification processes), decomposition of ammonia and water electrolysis (Carrette et al. 2001). Unfortunately, most of these processes would require high temperatures and quite expensive (and complex) apparatus in place, in order to be carried-out. In addition, subsequent hydrogen clean-up procedures would also be necessary, if a *ready-to-go* fuel (by this type of fuel processing methods) were to be obtained. Ideally, one would like to produce ultra-pure hydrogen gas (e.g. via alkaline water electrolysis) by means of hydro-electric or solar power plants.

Also, a relatively new method for hydrogen production is based on anaerobic fermentation of widely available, renewable biomass substrates. These processes typically lead to the generation of highly energetic biogas, which largely consists of methane and hydrogen gas mixture (Demirel et al. 2010; Wang and Wan 2009).

Hydrogen storage for the purpose of PEM fuel cells can be realized by a number of available storing methods. Gaseous hydrogen has a relatively low energy density; thus, a preferred way to store pure hydrogen would be either in highly-compressed cylinders or in a liquid (cryogenic) form (by cooling H_2 down to –253 °C). Regrettably, these two forms of hydrogen storage appear quite expensive and would

require (for a fully commercialized system) a network of high-tech refuelling stations. In addition, direct storage of large amounts of highly-explosive gas (e.g. on vehicle's board) could raise some serious safety concerns.

Hydrogen can also be (indirectly) stored in metals, in the form of metal hydrides (similarly to that of rechargeable NiMeH batteries). More recently, H storage has also been realized by means of carbon nanotube materials (Cheng et al. 2001; Li et al. 2006; Liu et al. 2010; Panella et al. 2005). Nanostructured carbon materials have a very unique, tubular structure; they possess large surface areas and extraordinary chemical/thermal stability. Specific carbon nanotube materials can currently provide the hydrogen storage capacity of nearly 2 wt. %. However, according to the U.S. Department of Energy (Deng et al. 2004), a carbon nanostructured material needs to store at least 6.5 % of its own weight in hydrogen, in order to make PEM fuel cells practical in transportation applications.

CONCLUSIONS

Transition from the fossil fuel-based economy to the fuel cell-based energy system seems the most probable scenario for the future energy market. This transformation will not be immediate and will be driven in parallel by depletion of fossil fuels reserves, as well as by more stringent environmental standards.

PEMFC-based power sources have significant potential to power portable and small electronic devices, primarily due to their high electrical efficiency and "zero-emission", environmentally-friendly operational characteristics. However, it seems apparent that further, commercial development of this technology will strongly depend on the ability to initiate mass production of price-competitive fuel-cell devices, which are able to compete with current leaders of the portable power market.

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