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Review

Micro Fuel Cells for the Portable Applications

Go Young Moon† and Won Ho Lee

Corporate R & D, Research Park, LG Chem., Ltd, Science Town, Yu Seong, Daejeon Korea, 305-380

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Abstract: Due to the increasing intelligence, the increasing connectivity, and always-on characteristics energy needs for the portable electronics cannot be managed by the state-of-art battery technology. Micro fuel cell fuelled by aqueous methanol is gaining lots of interest from the new energy storage developers since it has the potential to offer the longer operation time to the portable electronic devices. Although the technical barriers to the commercialization exit, it is expected that the micro fuel cell technology bring huge benefits to the current energy storage market once it matures. In the article, benefits, challenges and market players of the direct methanol fuel cell arena is briefly reviewed.

Keywords: *direct methanol fuel cell, micro fuel cell, membrane, electrode, system miniaturization*

1. What is Micro Fuel Cell?

Micro fuel cells are classified into two types according to the fueling methods: the direct methanol fuel cell and the PEMFC with a micro reformer as shown in Figure 1. Their power range is normaly less than 100 wattage.

Direct methanol fuel cell fueled with aqueous methanol and air has been favored unanimously and has been developed extensively due to its many potential benefits over the hydrogen fueled PEMFC. Thus in this article benefits, barriers and perspectives of DMFC are illuminated.

Since PEMFC needs the expensive fuel reformer or bulky hydrogen storage, which resulting in the high cost and space limitation in the transportation application, DMFC has been illuminated as a reasonable alternative regardless of several disadvantages, e.g., low kinetic response time, high cost as a result of high precious metal catalyst loading, and methanol crossover etc.

There are a number of applications where the direct methanol fuel cell can provide real benefit based on its high energy density (pure methanol's energy density is 4,758 Wh/L, note that Li ion battery has 471 Wh/L energy density) and instantaneous refueling time with the simple exchange of the fuel cartridge.

For examples, the next generation of high bandwidth mobile devices, battery charger and military applications are good niche markets for DMFC since these applications require the supply of higher power density than existing batteries can provide. Power range according to the applications can be categorized as shown in Figure 2. Consequently, the need for a better battery with a longer operating time is a top priority to the portable electronic device industries and will drive the development of micro DMFC among various technologies. However safety precautions are at the forefront since methanol is toxic, inflammable, and prohibited in the public transportation like aircraft.

2. Market Expectations

Like today's rechargeable batteries, fuel cells can generate enough power to run energy-hungry electronic devices like notebook computer. But one does not need a wall outlet to recharge methanol in the small

†Author for all correspondences
(e-mail : gmoon@lgchem.com)

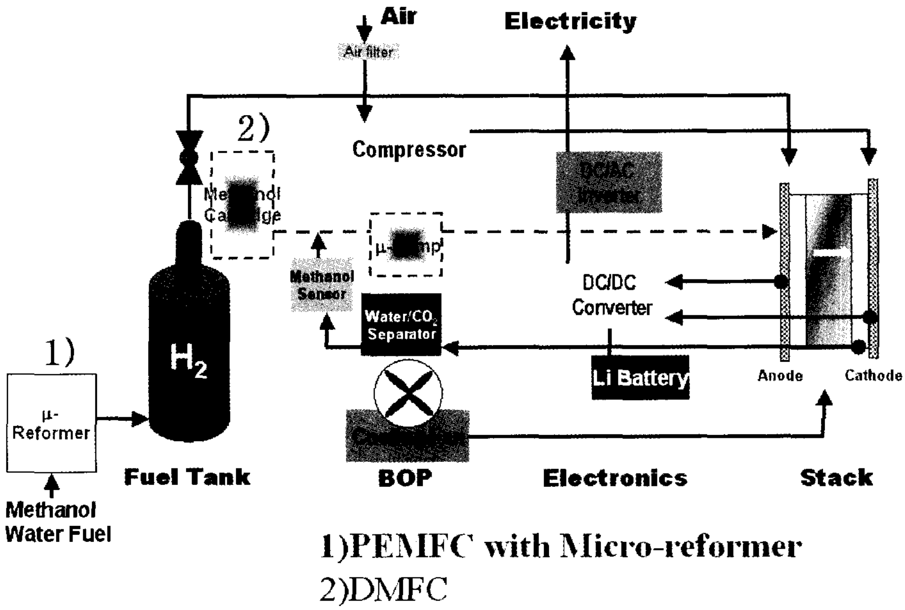


Fig. 1. Schematic of micro fuel cell systems.

Power range	Typical Applications
<10 W	Digital cameras, PDAs, Portable audio, Mobile phones, Camcorders, and Handheld computers
11-50 W	Camcorders, Digital cameras, Notebook computers
51-100 W	Notebook computers

Fig. 2. Typical applications of micro fuel cells.

cartridge similar to the ink cartridge of today's inkjet printer is chemically transformed into electrons. A traveler could bring enough fuel in his carry-on to compute his way around the globe, and the only waste products he would produce are the same found in human breath - heat, carbon dioxide, and water.

According to the recent market study[1], the largest market for small fuel cells is in mobile phones, followed by notebook computers and personal digital assistants (PDAs). The report notes that the cost of the fuel cells will decrease faster than the cost of lithium ion batteries and will remain at a premium, but that this should not limit fuel cell sales. This report also forecasts a $2 billion market for portable power fuel cells by 2011. In spite of the broad debates, the development of efficient DMFC is still of prime importance to many energy storage developers such as Hitachi, NEC, Toshiba, Sony, Casio etc.

In the viewpoint of pricing, since no commercial micro fuel cell products are available in the market yet, the 5kW residential fuel cell system ($1,700 per kW) is chosen for price comparison (note that a diesel generator costs $800 to $1,500 per kilowatt, and a natural gas turbine can be even less). It is believed that the state-of-the-art DMFC costs even more than $10,000/kW presently. As shown in Figure 3, early small (micro or compact) fuel cell applications are critical to provide stepping-stones to cost reduction and wider commercialization of stationary and automobile fuel cells.

Even this high price declines rapidly through 2010, some people doubt the market penetration of micro fuel cell into the early niche markets. Who are the users? They are the innovators who are the first to adopt any new technology and early adopters (pilot line and production managers) looking for a competitive

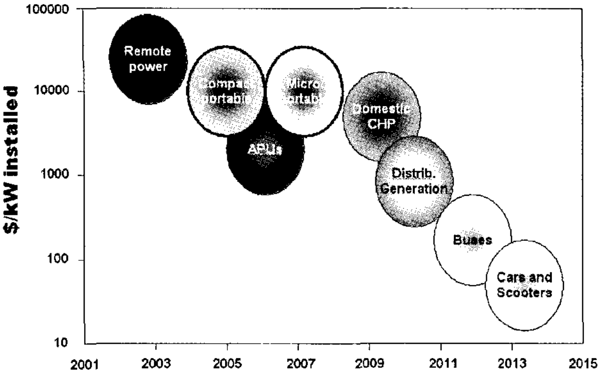


Fig. 3. Commercial introduction points for fuel cell applications [2].

advantage and comfortable with managing new technologies etc[1].

3. Barriers to a Broad Commercialization of DMFCs

It is frequently mentioned that cost is a barrier for all types of fuel cells across all applications. Of course significant cost reductions in the catalyst, membrane and manufacturing process of MEA and stack have to be realized. However it is not simple to address cost issue separately since cost is also related to the durability, performance and fuel infra issues. Thus authors will briefly touch the technical barriers to the commercialization of DMFC.

It seems that there are several main research streams to overcome DMFC's low performance. The first is to develop novel anode and cathode catalysts to reduce the kinetic loss. The second is to develop novel membranes having low methanol crossover. And the third is to design, fabricate, and operate the system efficiently.

3.1. Electrodes

DMFC normally uses the aqueous methanol fuel and a fraction of methanol is electrochemically oxidized at the anode. As known widely the electrochemical oxidation of methanol to CO_2 generates six electrons. However due to the sluggish kinetics and CO poisoning of catalyst many scientists are looking for the new Pt alloy catalyst, novel catalyst supports, the optimized ionomer content in the electrode formulation, the novel coating methods, the novel electrode geometry.

Pt-Ru black has been utilized most widely as the anode catalyst. Pt-Ru catalyst supported by novel carbon supports improves the catalyst activity, thus resulting in the catalyst reduction significantly. However the use of supported catalyst is detrimental to the methanol crossover, which means Pt/Ru black is more beneficial in terms of the reduction of methanol crossover than that of supported catalyst.

It is generally believed that the certain carbon supports are contributed to the catalytic activity affirmatively. Finding novel carbon supports such as carbon nanotube, nanofiber etc. is attractive research topics for DMFC developers.

Searching for the novel electrocatalysts has been undertaken continuously. Most of efforts are alloying Pt with other transition metals. But it is hard to find better catalyst than Pt/Ru alloy combination. More elaborate review was published and interested readers are recommended to consult with them[3,4].

3.2. Methanol Crossover

Methanol crossover depends on a number of factors, the most important ones are the membrane permeability/thickness, the methanol concentration in the feed fuel, the electrode thickness, the operating temperature, and the performance of the anode catalyst etc[5].

In the view point of the membrane methanol crossover is the problem that anode fuel, the mixture of methanol and water, diffuses through the ion exchange membrane, typically Nafion of Dupont and reacts with the cathode catalysts as shown below in equation 1 under the electrochemical operating condition so that overall electrochemical efficiency reduces significantly.

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \qquad (1)$$

Nafion, developed in 1960s, have been a standard membrane in fuel cell area as well as chloro-alkali industry. Its fuel cell performance, ionic conductivity, longevity, physical and chemical properties became a sole benchmark to the membrane researchers. However, its successful adoption in proton exchange membrane fuel cell was hesitated in direct methanol fuel cell because of the methanol crossover. Now there are numerous research activities in fuel cell arena developing novel membranes satisfying the operating condition of the direct methanol fuel cell at low expense.

Driving forces for methanol crossover are the methanol concentration gradient through the membrane involving the higher fuel concentration the larger crossover and the electro-osmotic drag related to the proton transport from anode to cathode which becomes substantial at high current densities[3].

Methanol reacting with the cathode catalyst not only reduces the oxygen reduction efficiency but also creates the water flooding which results in the poor mass transport of the air within the gas diffusion layer structure.

In practice, the effects of methanol crossover can be reduced to a large extent by careful design of the MEA structure or by the application of novel membrane materials or cathode catalysts[4] as well as by optimizing the cell operating conditions such as the cathode hydraulic pressure, the temperature and concentration of the feed fuel, methanol.

Since current study is part of our efforts to mitigate the methanol crossover by means of Nafion modifications, we review the previous efforts related to the Nafion modifications although there have been significant amounts of reports exploiting novel DMFC membranes other than Nafion. Materials investigated for DMFC application are polyaryl-blend-membranes[6], PVA/PSSA blend membranes[7], PES/sulfonated PSf or sulfonated PEEK blend membranes[8], sulfonated SEBS[9] copolymer and hydrophilic 2-acrylamido-2-methylpropanesulfonic acid and hydrophobic 2-hydroxyethyl methacrylate[10] copolymer, inorganic modification of sulfonated PEK and PEEK with SiO_2, TiO_2 or ZrO_2[11].

However, a trade off phenomena between the methanol crossover and ionic conductivity is unavoidable in most of above studies, so practical applications of those membranes are limited. Scott et al.'s work[12] obtained the promising MEA performances based on the PSSA-graft-ETFE or LDPE membranes although the de-lamination of catalyst layer was a major issue. Other than the efforts to find inexpensive alternatives among hydrocarbon based materials, porous silica inorganic base membranes filled with ionomers were proposed by Yamaguchi et al[13].

Since Nafion has been known to be only accessible commercial fuel cell membrane currently, significant efforts to endow enhanced barrier properties to Nafion while keeping its high ionic conductivity by means of the modification have been widely executed, e.g., deposition of hydrocarbon or fluoro polymer barrier film onto Nafion by plasma polymerization[14,15] and coating of PVA barrier layer on both sides of Nafion [16], incorporation of inorganic powders in Nafion matrix, which resulting in the retention of more water due to hydrophilic nature of fillers and the better exclusion of methanol[17]. Although most of the modification efforts were successful in reducing the methanol crossover, it is very common to find out the results sacrificing the ionic conductivity. It is interesting to note that study of Dimitrova et al[17]. showed the enhancement of the conductivity with the sacrifice of methanol permeation rate in spite of the higher crystallinities of the inorganic modified membranes with SiO_2 and molybdophosphoric acid. Yang et al[18]. have shown that the Nafion impregnated with zirconium phosphate is capable of the promising performance at high temperature up to 150°C without the cathode humidification, which is attributed to the improved water retention characteristics of the composite membrane. Similar approach[19] impregnating Nafion's pores with 1-methylpyrrole to reduce the size of the diffusion channel in the matrix of Nafion achieved the reduction of methanol crossover while maintaining the competitive ionic conductivity.

As reviewed above, development of novel DMFC membrane is quite challenging task since high barrier property inevitably reduces the ionic conductivity as well as the stability (durability) which is one of the

Table 1. DMFC development status of Japanese companies

	NEC	Hitachi	Honda	Yuasa	Toshiba	Casio	Sony	Sanyo
Market yr.	The second half of 2004	By 2005	-	2003	In 2004	In 2005	-	In 2005
Feature	CNH as electrode	Sulfoalkylated aromatic membrane	Silicon Micro-Fab.	500 W portable	Methanol diluted with formed water	Ultrafine MeOH reformer	$C_{60}(OH)_{12}$ as electrolyte	-
Cell Type	DMFC	DMFC	H_2	DMFC	DMFC	PEMFC with reformer	DMFC	DMFC
Continuous operation time	Laptop PC	Laptop PC	Robots	Yamaha Motor bicycle	Cellular PDA Laptop	Laptop PC and PDA	Laptop PC	-

important characteristics of the membrane in the fuel cell operation but frequently forgotten.

When we mention the possibility to develop the fuel cell membranes, chance of DMFC membranes is a lot high compared to the PEMFC membranes that are exposed to much harsh operating conditions.

3.3. System Miniaturization

Most of prototype DMFC systems suffer from the low power density of around 50 mW/cm^2 these days; to be competitive in the market 100 mW/cm^2 of power density is critical in the lightweight and compact systems. Many companies and universities are working on the system miniaturization issue by revealing the prototypes.

Among many miniaturization concepts and prototypes technologies utilizing silicon wafer process[20-23] for microelectronics attract lots of interest. System design implemented on silicon wafer has high potential to alleviate the production cost and to miniaturize the system by reducing length scale. However there are many system level issues to be addressed in developing a complete fuel cell system such as air supply, fuel delivery including sensor, thermal management, power management, system integration and system operation logic etc.

Another interesting micro fuel cell technology is based on printed circuit board (PCB) technology. PCB provides the fuel flow field, current collection and electrical interconnection for the fuel cell array. Driving forces of PCB technology are that PCB is a well-known low cost technology and a rapid prototyping technology. Fraunhofer group of Germany[24] and Stanford group of USA[25,26] are active in this technology.

In addition to silicon and PCB substrates, catalyst layer, current collector and electrical interconnector can be deposited by sputter and CVD on ceramic[27], flexible foil and flexible plastic substrates.

Task left to the fuel cell engineers is to increase the power density (more than 100 mW/cm^2) with proven reliability and durability, which to the best knowledge is not realized by any parties.

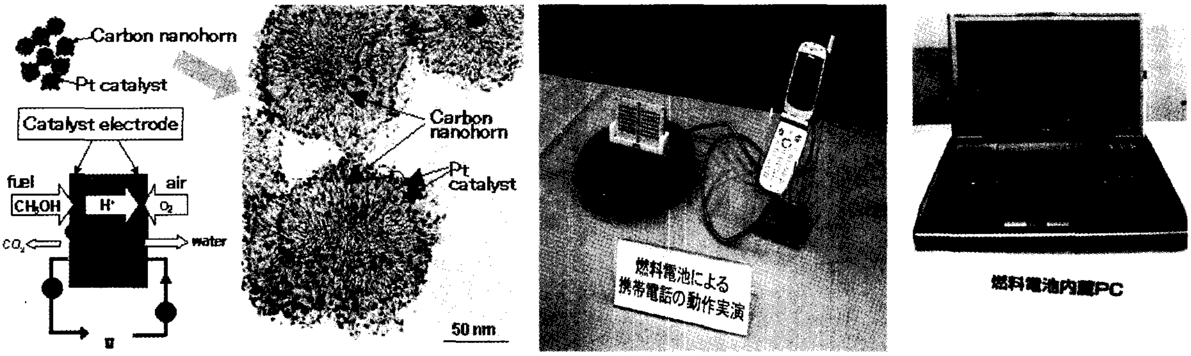
4. Major Players in the Micro Fuel Cell Arena

Although many R & D programs are ongoing on DMFC technology over the world, not many serious prototypes were unveiled up to now. Among them Japanese electronic companies are leading the state of art DMFC technologies. Their efforts and current status are listed in Table 1.

NEC's micro fuel cell is based on a carbon nanohorn as the electrode catalyst support. Using carbon nanohorn technology they insisted that 20% increase of the MEA performance was achieved. NEC's continuous prototypes are shown in Figure 4.

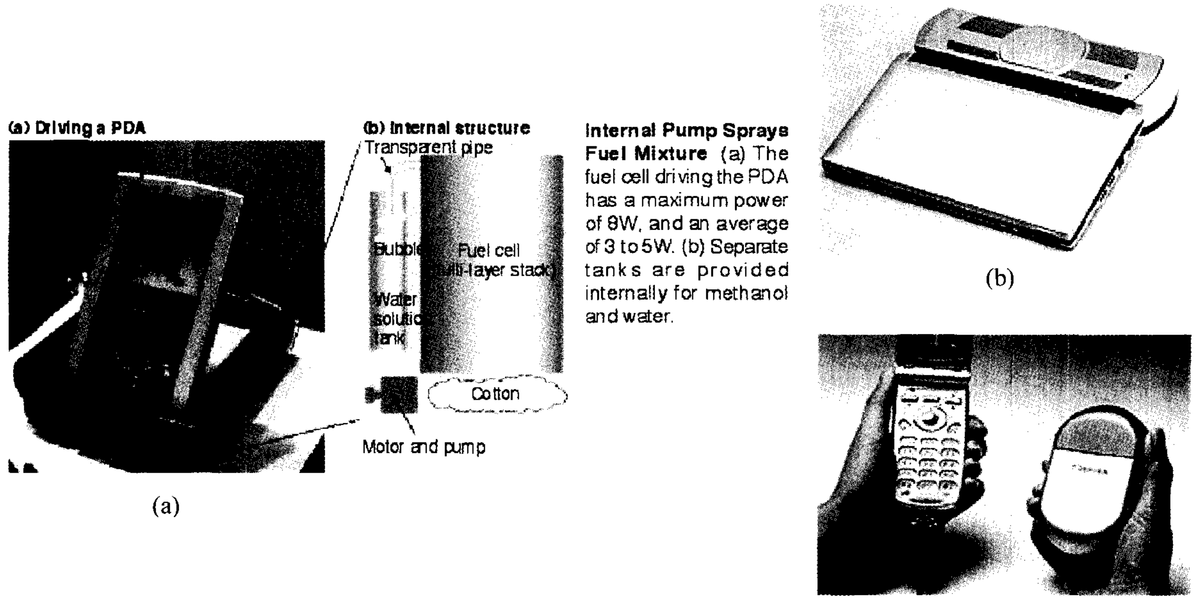
Toshiba also is developing the DMFC systems for PDA or notebook application. The feature is the fuel circulation system diluted with formed water in the cathode. With this way one can reduce the size of the fuel tank, which means the increase of energy density of the system. Recent prototypes are shown in Figure 5.

Casio has taken a different approach in its fuel cell



(a) (b) (c)

Fig. 4. NEC's DMFC technologies (Source: NEC); a) carbon nanohorn electrode, b) cellular phone application, c) notebook application, 2003.

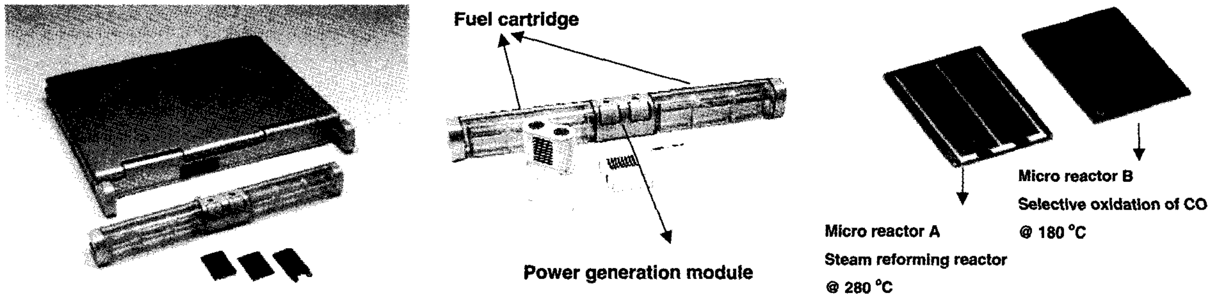


(c)

Fig. 5. Toshiba's DMFC development (Source: Toshiba); a) PDA application, b) Notebook application, c) mobile phone application.

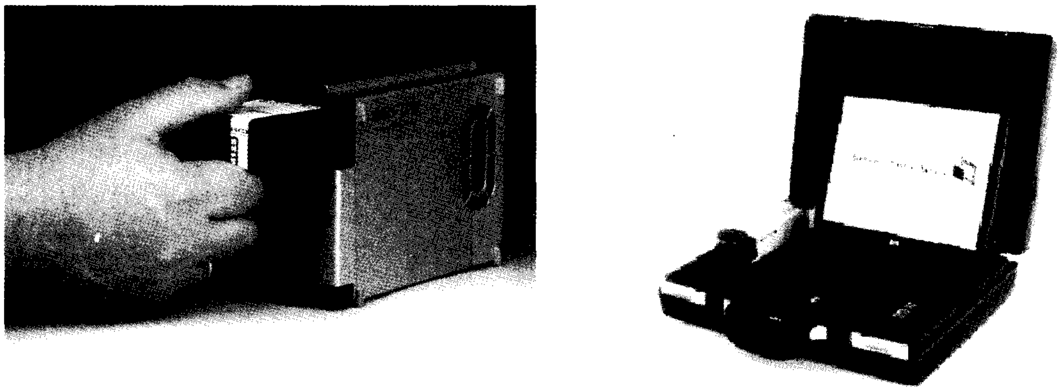
development. Since DMFC system suffers from the poor power generation efficiency, Casio utilized a micro reformer generating hydrogen from the methanol based on its silicon technology. With this way, it could achieve high power density than DMFC system. But several problems such as the complexity of the system, the encapsulation of reformer's high temperature as well as the durability of the system have to be solved before going to the market. Casio's PEMFC with a micro reformer is shown in Figure 6. Hitachi is also a player in micro DMFC. The feature of this company is hydrocarbon-based membrane instead of perfluoroalkyl membrane. This membrane can reduce the methanol crossover significantly compared to the perfluorosulfonic acid membranes.

In Germany, there is a company called Smart Fuel Cell developing and marketing micro DMFC system. It is known in the market that this company sells a briefcase-size 25 W system for IT devices to affluent campers who use it to recharge their battery-powered devices. The products from this company are shown in Figure 7.



(a) (b) (c)

Fig. 6. Casio's micro fuel cell with a micro reformer (Source: Casio Web).



(a) (b)

Fig. 7. DMFC systems from Smart Fuel Cell, Germany (Source: Smart Fuel Cell); a) compact external power supply for IT devices, b) fuel cell briefcase for mobile computing.

Another important player in this arena is MTI Micro Fuel Cells located in USA. This company is exclusively using the MEA and components of Dupont and targeting on the portable electronics applications.

5. Conclusions

Micro fuel cell is widely viewed as the promising power generator for the electronic devices because of the longer operation time and high energy density. However it has to clear the several barriers ahead for the full acceptance to the energy storage market.

Fuel cell should prove clear benefits over battery technology in light of the energy density and no disposal problems as well as the instant refueling. Currently battery reveals around the 471 Wh/L energy density, thus to be competitive the fuel cell has to show much higher energy density than that of the battery. There is no sole solution for this. High catalytic performance of the electrode catalyst, the new membranes permeating much less methanol, and smart system operation logic have to be realized altogether.

The developers of DMFC have to agree on what concentration of methanol to use and how it will be packaged and distributed in order to make the users access to the fueling infra easily[28]. The greatest challenge of all could be price. Although the price will fall with gaining a significant market share and finding the broad application, initial price must be reasonable enough to attract the early users in niche markets. This is the usual chicken and egg problem.

It is hard to forecast how the fuel cell market will proceed. However it is interesting to hear frequently the news releases saying major developers will launch the early micro fuel cells from 2004 to 2005. It is expected that the micro fuel cell industry grow dramatically in the next 2 or 3 years.

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