



Review

Overview on the challenges and developments of micro-direct methanol fuel cells (DMFC)

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Abstract

Interests in the feasibility of micro-direct methanol fuel cells (DMFC) for commercialization, especially in the portable applications area, have encouraged the R&D sections in companies and institutions to create a better, simpler and more economical prototype. Despite the increase in knowledge on how to handle this type of cells, many challenges still remain to be conquered. There is also the question of individuality for each prototype created, which is similar to what is faced in MEMS with its lack of a single driving market, and until one dominant application can be established, fuel cell designs will continue to evolve and bringing with each of them a host of pros and cons. This paper will draw out the current challenges and development of micro-DMFC. Besides that, this paper will also show some marketing prediction in term of economics view.

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Keywords: Micro-DMFC; Micro-fuel cell; Methanol**Contents**

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1. Introduction

Energy needs for portable electronics are rising rapidly in the past few years due to the increasing functionalities of portable devices, especially cell phones. The age of simple cell phone is fading fast, giving way to new “do-all/be-all” cell phone which incorporates graphics and games, internet service, instant messaging and even to find a restaurant or museum. Unfortunately, battery technology is unlikely to keep pace with these growing power demands. Realistic projections suggest that evolutionary improvements in batteries cannot adequately accommodate these kinds of energy needs. The lifetime of portable devices is still limited to how long they can operate as truly portable by the quantity of energy that can be stored within the batteries [1]. Fuel cell system allows portable devices to operate for longer times of period without being plugged into an electrical outlet [2]. Therefore, micro-fuel cells are being considered as a possible solutions to replace the current battery as the dominant power provider for portable application, at least at a theoretical level. The striking feature of micro-fuel cells is their higher inherent potential of higher energy densities compared to batteries [3].

The possibility of the hydrogen-fed proton exchange membrane fuel cell (PEMFC) for portable application is impaired by the yet unsolved problem of safe and reliable hydrogen storage system and also the lack of established infrastructure for the distribution of hydrogen. As such, micro-DMFC inevitably stands out as the most promising candidate due to some factors such as its high energy density and its simpler and safer handling since it is in liquid form at ambient condition [1]. Theoretical, pure methanol could achieve energy as high as 6 kWh kg^{-1} and 5 kWh l^{-1} [4]. Liquid fuel usage also eliminates the need for complicated fuel reforming system and bulky balance-of-plant (BOP), which simplifies the system considerably. Micro-DMFC can also be operated at ambient temperature, which significantly reduces the thermal management challenges for small systems [5].

2. Challenges and developments

In the making of micro-fuel cell systems, it is imperative to increase the power and energy density while maintaining the reliability equivalent to the reliability of batteries. For portable applications, the micro-fuel cells are designed to deliver power in the range of 0.5–20 W. The fuel cell units must be small in order to fit them into portable devices. However, miniaturization is not a simple scaling down of the larger system. Rather, each component of the fuel cell must be redesigned with an eye towards miniaturization [2]. Power density generated by a fuel cell system must also be given high priority and it is proportional to its stack size and active cell area. There are some boundary conditions considered and these include operation at ambient conditions, air-breathing cathodes and as few peripheral devices as possible such as pumps, valves and fans [6]. There are several technological challenges that have to be worked out before the micro-DMFC can be truly attractive for commercialization. These challenges and the respective efforts carried out to improve the system are discussed in the following section.

2.1. Methanol crossover

Methanol crossover in micro-DMFC is still the most important fundamental problem to solve in order to stimulate the development of micro-DMFC system. High concentration of methanol provides higher achievable energy density, but it also causes severe methanol crossover to the electrolyte membrane and results in mix potential at the cathode and therefore, presents low cell performance. By this mechanism, methanol molecules diffuse through the membrane and directly oxidized by oxygen on the cathode catalytic surface. The rate of crossover decreases with increasing current density, due to higher rate of methanol consumption at the anode. This induces the concentration gradient of methanol through membrane from the anode to the cathode. Apart from the high rate of diffusion transport from anode to cathode, one also encounters the electro-osmotic transport similar to the case of a water molecule being strongly bound to a proton, i.e. methanol is carried with the proton (ion–dipole interaction). Methanol crossover causes two detrimental consequences: self-discharge of methanol, which provides additional heat instead of electricity, and drastic reduction of the cathode voltage. In other words, this is like a “chemical short circuit” [4]. The current method chooses to limit the methanol concentration to approximately 5 wt.% with loss in performance [7]. Higher operating temperatures and lower methanol concentrations in the feed stream can also reduce the rate of methanol crossover in a DMFC. However, this can be a problem for micro-fuel cell.

Perfluorinated ionomer membrane is deemed as the state-of-the-art for electrolyte membrane in fuel cell applications. They are probably the most studied membranes in the PEMFC development activities for years, both industrially and academically. It consists of a perfluoroalkyl side chain and perfluoro alkyl ether side chain with a sulfonic acid group at its end. The most well-known materials of this category are the DuPont product, i.e. Nafion[®], and the Dow product, i.e. Dow membranes [8]. Existing polymer electrolyte membranes that are currently used as DMFC-electrolytes generally suffer from high methanol permeability and high electro-osmotic drag coefficient [9]. The commercially available electrolyte membrane, i.e. Nafion[®], is no exception. One common approach to deal with methanol crossover is the development of new proton-conducting membranes. The new polymers include polybenzimidazoles, polyamides, polyether imides, polysulphones, polyphenylene sulphides, polyetheretherketones and polyphenylquinoxalines [8]. Nevertheless, Schaffer et al. argued that even though these new types of polymer electrolytes will reduce the methanol crossover, they show low ionic conductivity [10].

Another approach is the modification of Nafion membranes to make them suitable for micro-DMFC-utilization. By blending different types of polymers to form hybrid membranes, such as the one being done with zirconium and phosphate, it is shown that the inorganic compound reduces the methanol permeability while the phosphate layer allows for more water to permeate rather than methanol [11]. Acid doped polybenzimidazole (PBI) is said to have low methanol crossover characteristic and recorded a power density of 210 mW cm^{-2} at 200°C when

operated on fairly concentrated methanol [7]. Meanwhile, the incorporation of inorganic material that can suppress methanol crossover, such as metallic layers like Palladium and Tantalum, may result in losses from electrochemical charge transfer over potentials [10]. This is due to the charge transport in a fuel cell takes place primarily by hydrogen ions. These can be reduced on the surface of the metallic layer which faces the anode, cross the metallic layer in their atomic state and finally oxidized on the surface of the metallic layer facing the cathode. Thus, formally an electric compensation current crosses the metallic layer diametrically opposed to the hydrogen flow. Methanol which is dissolved in the electrolyte between the anode and metallic layer does not react at the metallic surface and will not penetrate, provided the layer contains no defects.

It is accepted that NafionTM has a dual structure with a hydrophobic region interspersed with an ion-rich hydrophilic domains. Methanol diffuses primarily through the water-rich domains. Thus, selectively “sealing” water-rich domains on the surface of NafionTM membranes, which are constructed by $-\text{SO}_3^-$ clusters, is a promising method to suppress methanol crossover. The use of Pd nano-particles should be able to block the SO_3^- sites without adverse effect on the proton conductivity of the NafionTM membranes because Pd is highly permeable to hydrogen and capable to obtain a methanol-blocking proton exchange membrane.

The assembly of Palladium nano-particles onto the Nafion membrane surface yields a good result in reducing methanol crossover up to 8 orders of magnitude compared to the unmodified membrane, and with no reduction in its ionic conductivity. Methanol permeating across the resulting NafionTM membranes (Pd loading of self-assembled membrane was about $1.73 \mu\text{g cm}^{-2}$) was $1.3 \times 10^{-15} \text{ mol cm}^{-2} \text{ s}^{-1}$, comparing with the value of pure NafionTM membranes (self-assembled for 0 h) of $1.4 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$. The results demonstrate the promises of the application of such Pd-PDDA nano-particle self-assembled NafionTM membrane in DMFC [12].

2.2. Management of heat

A standard optimum value for fuel concentration still remains unknown. The optimum concentration of methanol in passive micro-DMFC is a result of a compromise between temperature, methanol transport rate and mixed potential, which is influenced by the methanol concentration. The optimum methanol concentration for a passive micro-DMFC is much higher than that in an active cell, which has an appropriate concentration of around 1 M. This higher optimum concentration can be attributed to two factors. One is the slower mass transport rate of methanol in a passive cell featuring a natural convection, as compared with a forced convection in an active cell. This means a higher methanol concentration is needed to compensate for it.

The other factor is the temperature rise in the cell due to the oxidation of crossover methanol at the cathode that releases heat. Methanol crossover increases with the increased methanol concentration, thus increasing the cell temperature which leads to enhanced reaction kinetics at both the anode and cathode. Moreover, the actual practical electrochemical energy recoverable

from a micro-DMFC system is much lower than the theoretical value. From the total energy, less than about 30% can be expected as electricity, while the rest is converted into heat [4]. The heat produced has to be dissipated, or else the accumulated heat in system might be a strong disadvantage for compact portable systems. However, despite the rather low energy conversion efficiency, micro-DMFC still offers an overall advantage over batteries in terms of energy density terms.

2.3. Relatively low power density

Ideally, the micro-DMFC should be a passive system, i.e. it is not operated under steady-state conditions. This is done by eliminating the fuel pump and air blower from the design. The methanol concentration, temperature and the extent of water and CO_2 accumulation in the cell vary with time on stream and this can cause a certain degree of deviation in the experimental data [4]. No external peripheral is required because the fuel is to be supplied to the anode from a built-in fuel reservoir in which methanol is stored. However, this simple design also causes lower system performance due to the difficulty in getting a continuous supply of fuel homogeneously to the anode. The lack of flowing force to remove the bubbles that constantly build up from the formation of CO_2 will also hinder further oxidation of fuel at the anode surface. At the cathode, water droplet tends to build up and block the active surface, thus reducing the oxygen supply even more.

Previous workers argued that the optimum methanol concentration for a passive micro-DMFC is 5 M [14,15]. At this concentration value, Tang et al. reported that a maximum value of power density as high as 43 mW cm^{-2} could be achieved [13], while Bae et al. reported that their system could achieve 20 mW cm^{-2} [14]. At a concentration higher than this value, the performance will decline due to the increased over potential at the cathode. This is because methanol crossover can deteriorate cell performance by generating a mixed potential and poisoning the catalyst at the cathode. However, the power density available from the methanol oxidation at the anode is still lower compared to the equivalent hydrogen-fed proton exchange membrane fuel cell (PEMFC), i.e. about 1/10. The cell stack cannot be made too small as the achievable power is in proportion with the active cell area. When a smaller system is considered, the energy density decreases drastically. This has limited the application of DMFC system in micro-size portable devices.

2.4. Management of water

System control associated with water and methanol management adds considerably to the complexity of micro-DMFC systems, particularly those being developed for portable applications [15]. It is desirable to recycle the water produced at cathode to anode for dilution of fuel, but there is very little information disclosed by established fuel cell manufacturers on their advanced prototypes. Some works have been done to improve water management in micro-DMFC. Usually gas diffusion layers for cathode are typically wet-proofed with a PTFE (Teflon) coating to ensure that the pores of the layer do

not become congested with liquid water. Yao et al. designed a system that recycles water from cathode to anode to give minimal water supply from outside the cell, i.e. ensures a small water storage space [16]. Their compact-shaped fuel cell design is made possible despite the incorporation of useful features needed for the design, such as the hydrophobic–hydrophilic coating layers, micro-pump and passive liquid–gas separator for CO₂ removal, through the MEMS-based fabrication process on the same silicon wafer. A net output of 10 mW with an energy efficiency of 35% and an overall size of 1 cm³ inch was achieved.

2.5. Slow reaction kinetics of methanol electro-oxidation

In micro-DMFC, anode suffers from high activation over potentials due to the slow kinetics of methanol oxidation reaction. This detrimental effect limits the rate of electrode reactions, which reduces the cell voltage and severely affects the voltage efficiency of the system. In practice, methanol oxidation at anode is promoted most effectively by platinum-based electro-catalyst. Micro-DMFC generally needs higher loading of catalyst, sometimes more than ten times higher than the hydrogen-fed PEMFC, due to the slow kinetics of methanol electro-oxidation reaction and severe methanol crossover to the cathode side. Unfortunately, platinum-based electro-catalyst is high in cost, and this dampens the progress commercialization of micro-DMFC. The passive micro-DMFC systems require even more catalyst loading than the active ones [17].

2.6. Unknown durability and projected lifetime

The ability of the micro-fuel cell to operate under a wide range of operating conditions with different system characteristics is described by the term, “fuel cell operational flexibility”. Optimum fuel cell operational flexibility must take into account both specified and an estimated amount of unexpected, or “out-of-specification” conditions over the fuel cell target lifetime. Some of the conditions to consider include: reactant flow rates and composition, operating and environmental temperature, operating and environmental pressure, humidification levels, peak load requirements and turn-down ratios, duty-cycle characteristics (including percentage of time at different load points), and required rate of transient responses.

However, micro-DMFC development is still relatively new compared to the more established PEMFC. Thus, the aging mechanism of micro-DMFC system has yet to be fully investigated, even though it is generally known that the operational conditions can affect fuel cell lifetime and durability, such as fuel flow rate and operating temperature [18]. There is also little reported information regarding the projected lifetime of a micro-DMFC system. To date there are few commercial products and almost certainly no large-scale manufacturing, although portable electronics manufacturers like Toshiba, Hitachi, Motorola and Fujitsu have given some press releases to show their prototypes at various advanced states of development. Workers choose Au for current collector layers because reliable long-term performance of DMFC operation is achieved with pure Au layers only [19].

However, further detailed methodologies to eliminate methanol crossover and dilution requirements remain proprietary [7].

2.7. Membrane electrode assembly

For a micro-DMFC, membrane electrode assembly (MEA) is the most important part that enables electricity generation from chemical energy in methanol. In order to realize the commercialization of micro-DMFC, the quest to devise a more effective and suitable MEA for micro-DMFC application is inevitable. While extensive research has been conducted on the MEAs for hydrogen-fed PEMFC, relatively very few studies for DMFC have been reported so far.

2.7.1. Membrane thickness

It was found that the thickness of the Nafion membrane is one of the most essential factors in determining the methanol crossover rate, i.e. the methanol crossover becomes less as the membrane thickness increases. Unfortunately, the thick membrane reduces the power density due to its high ohmic loss [20].

Liu et al. investigated the effect of methanol thickness on the performance of a passive micro-DMFC using various membranes, namely Nafion 117, 115 and 112 with respective thicknesses of 175 μm, 125 μm and 50 μm [14]. The findings show that when the cell was tested with low methanol concentration (2.0 M), the thicker membrane gave a better performance at low current densities; whereas at higher current densities, the cell with the thinner membrane yielded a better performance. At high methanol concentration, the three membranes exhibit similar cell voltages over a wide range of current densities. From these results, it can be concluded that thicker membranes are recommended for passive micro-DMFC with high methanol concentration because even though they give more or less the same cell performance as thinner membranes, it would yield higher cell efficiency.

On the other hand, the membrane thickness only has a slight effect on the cell performance [13]. However, the operating time of the cell could be affected by it because the methanol crossover rate is directly proportional to the membrane thickness. A comparison was done using Nafion 115 and Nafion 117. It was found that the duration time is inversely proportional to the rate of methanol consumption, i.e. it increases as the electric load decreases and the membrane thickness increases. It was later argued that thicker membranes are preferred and membranes that give lower methanol crossover should be used to increase energy efficiency, and thus operating time.

2.7.2. Catalyst loading

High loading is difficult to achieve with a thin catalyst layer. Therefore, it is relatively difficult to fabricate a homogeneous catalyst layer for micro-DMFC using the conventional methods such as the doctor-blade technique, decal method, and brushing method. The systematic errors in a preparation process have made reproducibility of catalyst layer extremely difficult, especially with the doctor-blade casting method. The cell performance is not proportional to the catalyst loading but reaches a plateau or even declines with an increase in the catalyst loading

[5]. This is usually associated with thicker catalyst layer, and by reducing the layer thickness in the MEA fabrication process, power density can be significantly improved. Higher catalyst loading can produce a larger active surface area that improves performance, but it also causes detrimentally higher mass transport resistance against methanol transport and gives a less steep concentration gradient for methanol, i.e. an excessive resistance against methanol supply to and carbon dioxide removal from the anode [21].

Conventionally, Pt/Ru catalyst is used for anode, while Pt catalyst is used for cathode. Incorporation of Ru in anode catalyst is to cope with the poisoning of catalyst caused by the intermediates of methanol electro-oxidation, such as carbon monoxide. Shimizu et al. gave the optimum Pt/Ru and Pt loading as 2.5 mg cm^{-2} , but as the loading was increased further, the cell performance started to decline [5]. Bae et al. Gave the optimum catalyst loading as 8 mg cm^{-2} with a maximum power density of 45 mW cm^{-2} . The difference between these two findings could be attributed to lower methanol concentration and the supported catalyst type used by [5]. A supported catalyst makes for a much thicker electrode than an unsupported black catalyst and this imparts an additional resistance to methanol transport at high catalyst loadings [13].

2.7.3. Diffusion layer

Generally, the gas diffusion layer is the electrical conductor that transport electron to and from the catalyst layer. It is made porous to ensure that reactants effectively diffuse to the catalyst layer. The gas diffusion layer also assists in water management by allowing an appropriate amount of water to reach, and be held at, the membrane for hydration.

Some alternative materials have been proposed to substitute the conventional carbon material. Stainless steel cloth is selected due to its adequate corrosion resistance and it shows a better performance compared to carbon cloth and paper, probably because of its smaller pores and thicker material. The resistance is lower than all the carbon materials. Although it does not have separate paths for gas and liquid transport, it shows equally good properties regarding mass transport. Studies are being carried out on sintered stainless steel fiber felt as a gas diffusion layer in a passive micro-DMFC. Liu et al. Has reported that the cell using sintered stainless steel felt gives a better performance than that of carbon paper, even though the thickness and porosity of these two materials are similar, due to the higher electrical conductance in metal [22]. Metal fiber might be more hydrophilic compared to that of carbon fiber in the carbon paper due to its coarser surface, and this makes methanol supply easier.

3. Miniaturized system design

The micro-fuel cell system must be made small and compact for portable application. Each application has different power, voltage, geometric design requirements. Significant effort for future commercialization has to be put in developing systems that can achieve the optimum balance of cost, efficiency, reliability and durability. Fuel cells built to exploit micro-scale phenomena would be smaller, make better use of volume and could

obtain improved heat and mass transfer [19]. Two approaches are currently considered: scaling down of fuel cell system using conventional assembling method, or to redesign every component in the system using MEMS technology.

3.1. Conventional DMFC design

By using the conventional method, a fuel cell system can be fabricated by hot-pressing the sandwich structure of gas diffusion layer, electrodes and electrolyte membrane. The MEA is mounted in a casing usually made from Perspex or polycarbonate and then bonded mechanically. Basically the method is the same as the one used to assemble a typical DMFC that produces a few watts, with the size being the only difference. Since the achievable power density is proportional to the active surface area of MEA, only limited power can be generated from a miniaturized or micro-DMFC. There are several reports regarding the development of micro-DMFC using conventional assembling method. Shimazu et al. developed a pump less small DMFC [5]. The performance of this 36 cm^2 , passive, air-breathing micro-DMFC, which was operated at room temperature, is encouraging. It was run successfully with methanol concentration ranging from 0.5 M to 4 M and does not need any external pump or ancillary devices. The methanol solution is stored in a built-in reservoir. It could achieve 11 mW cm^{-2} with 4 M methanol at current densities as high as 36 mA cm^{-2} and at a voltage of 0.3 V. A smaller cell with 7.5 cm^2 active area was also developed and the highest power density obtained was 3 mW cm^{-2} at 10 mA cm^{-2} . However, the durability of the system is not mentioned (Fig. 1).

Kim et al. work on a passive, air-breathing micro-DMFC in their effort to develop the MEA and design monopole stacks that operate under passive conditions [22]. A monopolar, as shown in Fig. 2, was assembled by putting six sets of an anode–cathode pair on each side of the membrane and connecting the anodes and cathodes in series using wires. The anode side plate has channels and a large open space for delivering and storing methanol solu-

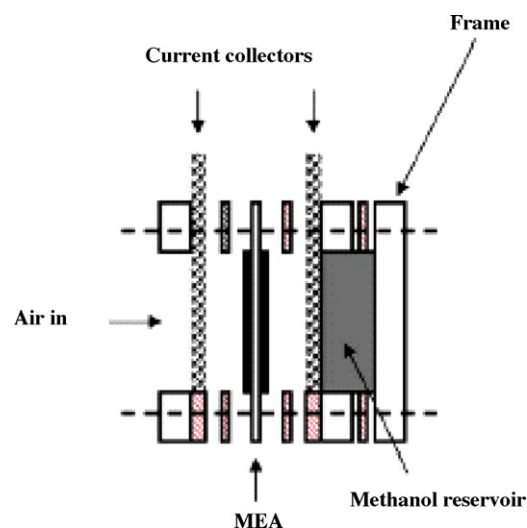


Fig. 1. Small air passive micro-DMFC assembled with conventional method [5].

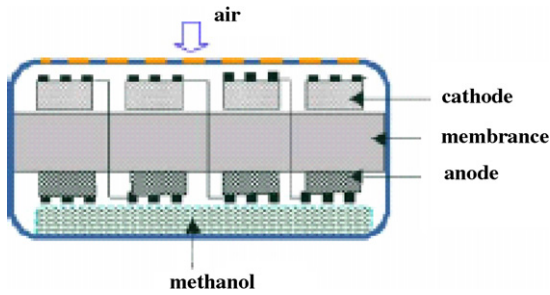


Fig. 2. A schematic diagram of a passive monopolar stack with a built-in methanol reservoir [23].

tion while the cathode side plate has many holes for air diffusion. Whereas a single cell with active area of 6 cm^2 can generate a maximum power density of 40 mW cm^{-2} at 4 M methanol under ambient conditions, the stack can produce a power output of 1000 mW with a total active area of 27 cm^2 . Stacking up the cells enables it to power LCD panel (600 W) and also a toy car (2400 W).

Blum et al. has developed a pump-less micro-DMFC that can manage water loss to the environment and the water flux through the electrolyte membrane in a flat micro-DMFC without using any mechanical recycling system and obtained a 90–95% fuel utilization for 1 M methanol [15]. The membrane used was made of PVDF and nano-powder SiO_2 . The development is based on the nano-porous proton-conducting membrane (NP-PCM). This membrane has several advantages over the commercial Nafion membrane—lower cost, higher conductivity and lower fuel crossover. Crossover current density for Nafion 117 at 20°C was found to be 40 mA.

The novelty of this system is that water flux through the membrane was managed by the use of a liquid–water leak-proof system. It consists of several hydrophobic sub layers made from PVDF and carbon powder paste and placed on both side of the cathode current collectors. The paste is inserted into the pores

of the wet-proofed Toray paper to form a layer inside the paper, close to its surface. Several insertions are made, and then it is cured at high temperature. Then the MEA was hot-pressed in the conventional way. They achieved a 70–90% reduction in water loss (to the environment) with maximum power of 12.5 mW cm^{-2} and a stable operation of up to 900 h.

Henzel et al. has explored the possibilities of several concepts in construction techniques [6]. For example, a series connection of a certain number of cells would enable a high voltage. The exterior dimension of their membrane fuel cell system can be determined by the arrangement of series-connected cells in a stack or plane of a membrane, as shown by the banded structure. Several different possible concepts are shown in Fig. 3. For portable applications, the boundary conditions are

- operation at ambient conditions (pressure, temperature),
- air-breathing cathodes, and
- as few peripheral devices as possible (pumps, valves, fans, etc.).

At the same time, a high power density and a reliable operation in the hands of the customer is required. Thus, the development of portable fuel cells as energy supply systems for electronic devices still is a challenge.

Meanwhile, Liu et al. has developed a passive, air-breathing, liquid-fueled direct methanol fuel cell with no external pumps or any other auxiliary device to investigate the effect of methanol concentration and membrane thickness on the performance of cell (Fig. 4) [14]. The MEA was sandwiched between two electrical current collectors, which were made of 316 stainless steel plates of 1.0 mm in thickness. A plurality of parallel channels was machined by a wire cutting technique for both current collectors, serving as the passages of fuel and oxidant, which resulted in an open ratio of 48%. A 200-nm platinum layer was sputtered onto the surface of 316 stainless steel plates to reduce the contact resistance with the electrodes. The cell was held

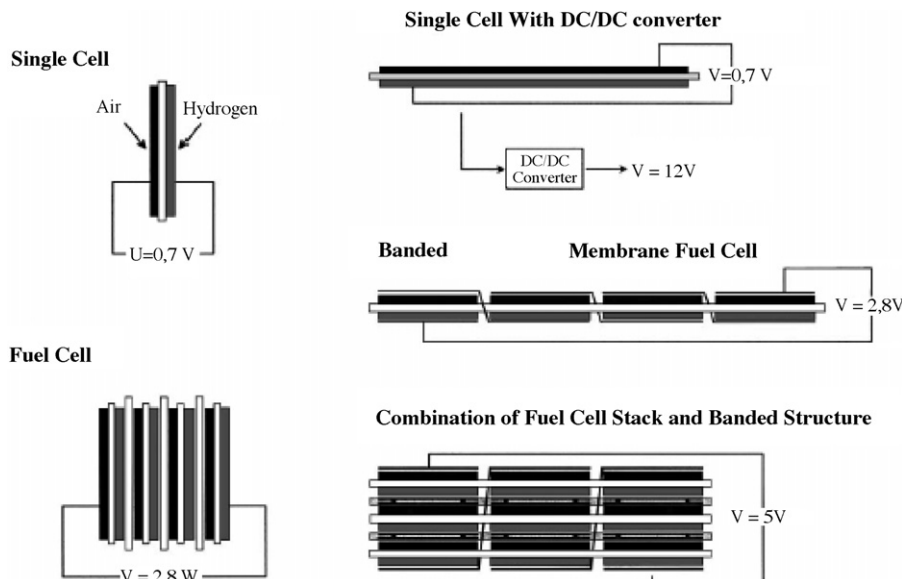


Fig. 3. Construction method of membrane fuel cells at Fraunhofer Institute of Solar Energy Systems [6].

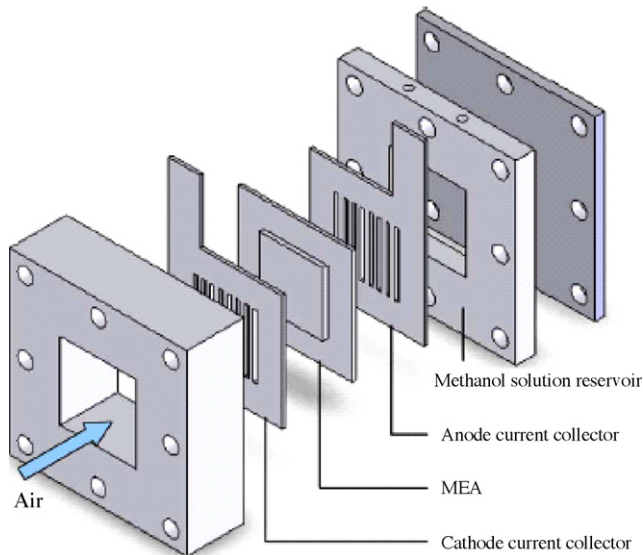


Fig. 4. Schematic diagram of a passive, air-breathing [14].

together between an anode and a cathode fixture, both of which were made of transparent acrylic plates. A 3.0 ml methanol solution reservoir was built in the anode fixture. 2.0 M or 4.0 M methanol was diffused into the catalyst layer from the built-in reservoir, while oxygen, from the surrounding air, was diffused into the cathode catalyst layer through the opening of the cathode fixture. Power density as high as 20 mW cm^{-2} could be achieved with 5 M methanol, and it was found that the passive DMFC with the thicker membrane exhibited higher efficiency.

3.2. Micro-DMFC design using MEMS technology

Successful application of MEMS technology, which is traditionally used in the semiconductor industry, in various systems such as internal sensors, biomedical and optical systems, has made it a promising candidate for the miniaturization of fuel cell system, especially PEMFC and DMFC. Several works have been conducted to investigate the feasibility of MEMS technology in micro-DMFC system. This technology provides a possibility of economical future mass production and has the potential to solve problems which are critical in the conventional stack technology such as the fabrication of micro-porous membranes optimized for two phase transport, the plasma polymerization of ion conducting polymers and the fabrication of transport optimized micro-flow fields with varying dimensions [19]. MEMS technology can control the fine and precise flows of the fuel, air and water in the electrodes, which may improve the current and power densities in a small fuel cell [24]. The prospective potential of MEMS technology for miniaturization of fuel cell system has stimulated interests from researchers and industries. Apart from the drastically decreased size, the application of MEMS technology in a fuel cell production usually results in the change of cell materials, such as the silicon wafer, instead of the conventional graphite, for bipolar plates. In fact, the major advantage of MEMS technology is in making the bipolar plate smaller and with higher precision, coupled with the potential of mass production.

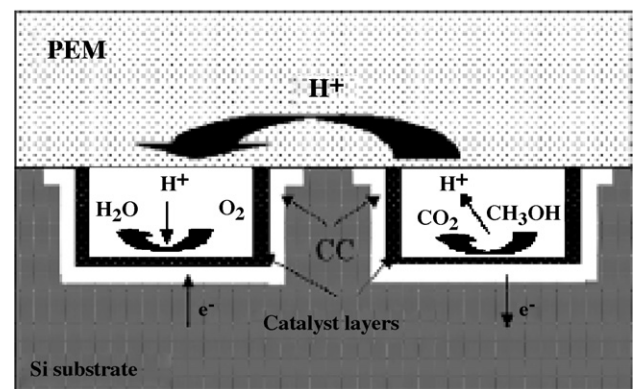
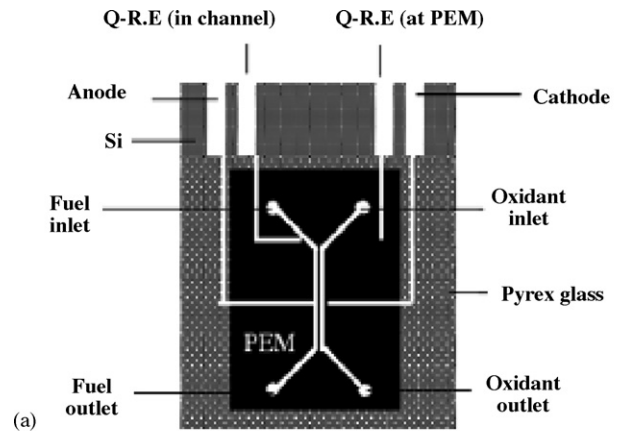


Fig. 5. Schematic diagram of in-plane micro-DMFC system: (a) top view of design; (b) cross-sectional view with working principle [28].

The use of silicon wafer in micro-fuel cells enables more variation in MEA fabrication. The silicon material system also encompasses a range of materials used in the semiconductor integrated circuit industry such as silicon oxides, nitrides and carbides as well as metals like aluminum and titanium [25]. Nafion membranes are inadequate to standard micro-fabrication techniques, i.e. they cannot be easily patterned with standard photolithography and their volumetric variations due to hydration are a real problem for the assembly with silicon substrates [26]. Regardless of the MEA used in cell system, the common fabrication processes in MEMS technology are more or less the same. Firstly, micro-fluid channels and feed holes are inscribed onto the wafer by applying various etching methods, such as deep reactive ion etching (DRIE) with a negative photo resist that acts as an etching mask, or wet chemical etching. Then a layer of Au or Cu/Au is sputtered on silicon wafer as the current collector, with titanium/tungsten layer as adhesive. There are two options for the application of catalysts, either to coat the catalyst on the electrodes and hot-press it with the membrane or to coat it directly onto the surface of the silicon substrates. Current approaches for MEMS assembly are using single or double Si wafers for substrates and a combination of novel materials.

The design of the micro-DMFC and its working principle are depicted in Fig. 5. The fuel solution ($\text{CH}_3\text{OH}/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$) is fed to the anode side of the unit cell where the catalyst promotes the CH_3OH to release electrons, carbon dioxide, and protons.

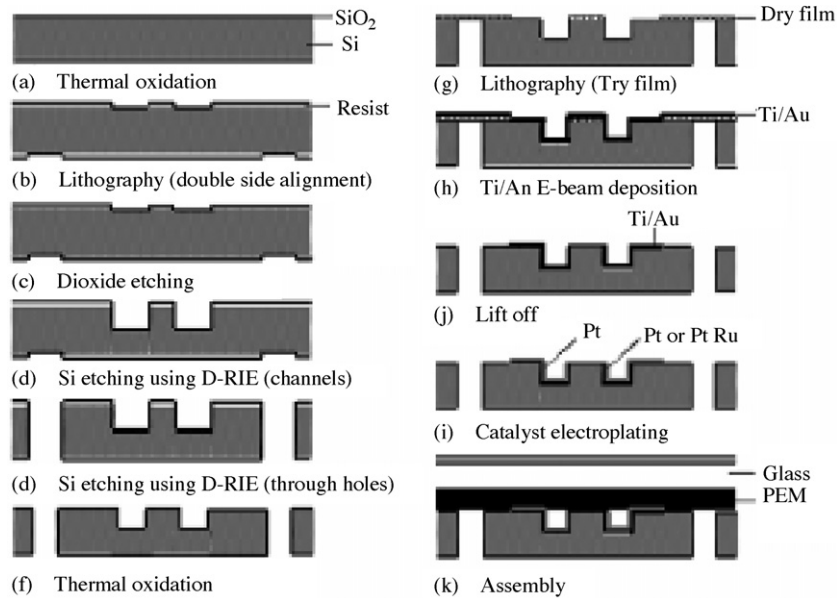


Fig. 6. Schematic of fabrication of micro-DMFC chip [28].

The electrons travel in the form of an electric current that can be utilized before it returns to the cathode side of the fuel cell where the oxidant solution (O_2 -sat./ H_2SO_4/H_2O) has been fed. On the other hand, molecular oxygen reacts at the cathode with proton being transported through the membrane from the anode and produces water, thereby completing the oxidation–reduction process. The anode to cathode contact is the thickness of the Nafion ($50\ \mu\text{m}$) as illustrated in Fig. 5. Here, the path length from anode to cathode is the clearance between the two micro-channels, which is $100\ \mu\text{m}$. Connecting both the anode and the cathode to an external load makes it possible to produce electric power.

The approach shown in Fig. 5 has several advantages and differs in many ways from previous designs:

- It is of planar structure and essentially an unfolded fuel cell as shown in Fig. 5, which integrates the anode and cathode onto a single Si surface. Whereas, the bilayer design uses separate Si wafers with channels for the anode and cathode.
- The fuel and oxidant are supplied to the cell in isolated, separate micro-channels. Both the fuel and oxidant are distributed in micro-channels throughout the wafer, and they both possess an exhaust. The isolation of fuel and oxidant precludes one from crossing the fuel and oxidants streams.
- The characteristic length of the system that is the distance that the protons must travel from anode to cathode is very short. This makes the system less sensitive to ohmic impedance effect.
- The efficiency of the current collectors is high, because the catalyst layers are supported on the metal directly. In addition, the current collectors are directly deposited in the micro-channels. The current does not need to be pulled out by relatively large metal lines.
- Catalyst electrodes are directly fabricated in the bottom and sidewalls of the micro-channels.

Conventionally, a bipolar structure is used in the DMFC design consisting of two Si wafers and the MEA to make up a cell [17,30]. However, there have been some novel designs by previous workers. Motokawa et al. designed a micro-DMFC using a series of fabrication steps from micro-machined silicon wafer including photolithography, DRIE, and electron beam deposition as shown in Fig. 6 [28]. The anodic and cathodic micro-channels are fabricated using a single Si wafer and this enables the system to be made extremely small (active area = $0.018\ \text{cm}^2$) and with less substrate material. A conventional electrolyte membrane (DuPont's Nafion membrane) and catalysts (Pt–Ru for anode and Pt for cathode) were used. Current collectors, namely Ti/Au, were formed by electron beam deposition and lift-off method. Preliminary testing results show that this micro-system generates $0.78\ \text{mW cm}^{-2}$ at $3.6\ \text{mA cm}^{-2}$. The low attainable power might be due to the non-optimal composition of catalyst and the pretreated Nafion membrane being placed between the patterned silicon layer and glass substrate where the whole structure was only clamped mechanically without any high pressure bonding.

Methanol is not suitable to be used in medical applications because it is toxic and volatile and cannot be transported on common carriers. An alternative fuel to be used in portable devices is ethanol, especially for biomedical applications. Aravamudan et al. has developed a novel micro-direct ethanol fuel cell system [29]. The comparison between the conventional system and this new system design is shown in Fig. 7. Fig. 7(a) illustrates the cross-sectional view of the porous silicon-based micro-DEFC stack. This structure consists of a porous silicon anode (fuel micro-column) and a porous silicon cathode (air micro-column) sandwiching a proton exchange membrane. The anode micro-columns serve as built-in fuel reservoir, while the cathode micro-columns are exposed to the atmosphere. Platinum is deposited on both the micro-columns to act both as an electro-catalyst and as a current collector. Nafion 115TM membrane acts

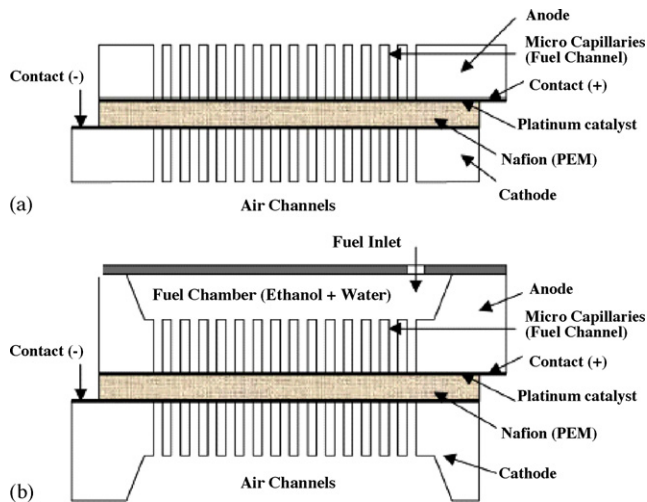


Fig. 7. (a) Cross-sectional view of the porous silicon-based micro-DEFC stack. (b) Alternative design for the porous silicon-based micro-DEFC stack [29].

as the PEM for the fuel cell. The fuel supply system uses porous silicon and the porous silicon structure also serves as a built-in fuel storage reservoir. The pore diameter and porosity of the silicon are carefully controlled. The capillary force generated by the pores has the ability to wick the fuel towards the electrode irrespective of the orientation of the cell and these results in a uniform and regulated supply of the fuel and eliminates the need for a micro-pump. At room temperature and 8.5 M ethanol solution, the cell could achieve a maximum power density of 8.1 mW cm^{-2} . As shown in Fig. 7(b), an alternate structure with $50 \mu\text{m}$ depth trench in the porous silicon substrate has also been designed for additional fuel storage.

Current techniques for micro-fuel cell are usually co-planar fabrication based on silicon-glass technology and conventional carbon-supported platinum electrodes. Silicon has been the material of choice for micro-electromechanical systems mostly because of the extensive infrastructure in the electronic integrated circuits (IC) industry. However, silicon has a few disadvantages. It has high resistivity and faces difficulties in reducing process cost and achieving good cell performance by sustaining good adhesion with the PEM used. Micro-fabrication processing with Si is costly due to the time required for dry etching (rate = $3.0 \mu\text{m min}^{-1}$) and the high expense of the dry etching system. The fragility of the silicon wafer makes it difficult to compress the cell for good sealing and for lowering the contact resistance between MEA and Si-based bipolar plates. Silicon wafer is also nearly electrically insulated. Conductivity for current collection fully depends on the thickness of the conductive layer coated on these substrates, which will increase the cost significantly in order to minimize the resistance required in high power application.

Efforts to find alternative materials for fabricating electrodes are still going on. Kuhnke et al., and Ito and Kunimatsu studied how to fabricate an alternative form of electrode using glassy carbon, a material which exhibits a high electrical conductivity and chemical inertness [31,32]. Ito and Kunimatsu utilized micro-machining technologies to come up with a novel design for their passive-type fuel cell [32]. To achieve a high voltage,

the micro-DMFCs are integrated on a single photosensitive glass substrate containing a micro-holes array. The substrate was processed using a wet etching technique with a high aspect ratio of about 20 with a $50 \mu\text{m}$ diameter cell and the array was fabricated using a photo-lithography technique. The maximum cell potential and power density achieved with the $50 \mu\text{m}$ diameter cell and surface area are $2.0 \times 10^{-5} \text{ cm}^2$ were 330 mV and $57 \mu\text{W cm}^{-2}$, respectively (Fig. 8).

A novel micro-fabrication method using multi stream laminar flow where two or more liquid streams merge into a single micro-fluidic channel is presented [33]. They chose this method to counter some technical issues related to the use of PEMs such as its tendency to dry out at higher temperatures required to run fuel cells more efficiently thereby reducing the effectiveness of proton conduction and its fuel crossover problem that results in the lowering of the cell performance due to a mixed potential at the cathode. The fuel and oxidant they used are formic acid and dissolved oxygen, respectively, and the fluid flow is pressure-driven and regulated with a syringe pump. With this design, they claimed that PEM-related issues of fuel crossover, anode dry-out and cathode flooding can be eliminated. It eliminates the issue of membrane-clogging by carbonates that will immediately be removed from the system by the flowing streams. Its flexibility also allows for a mixed-media configuration where the OCP achieved from the alkaline anode/acidic cathode configuration was as high as 1.4 V (Fig. 9).

Another novel design using polymer chips that play the roles of current collector, fuel-diffusion layer, and catalyst supporter was studied [34]. Simplified fabrication steps based on the low-cost wet process and friendly adhesion characteristics with the PEM, which reduces contact resistance between the membrane and the electrodes, are among the advantages of using these photosensitive polymers in a micro-DMFC system. A maximum power density of 8 mW cm^{-2} was obtained at the temperature of 68°C with the 2 M methanol used in the experiment.

Lu et al. Opted for stainless steel to be used as bipolar plates, which has flow fields machined by photochemical etching technology, as it is said to have much higher conductivity and mechanical strength [35]. The maximum power density achieved was 62.5 mW cm^{-2} at 40°C and 100 mW cm^{-2} at 60°C using 2 M methanol solution under ambient pressure. This is largely due to better compression because the cell can be secured more tightly thereby lowering contact resistance with the MEA as the sealing between both bipolar plates and MEA becomes more desirable. This is almost double what was achieved from the experiments using Si wafer as substrates in their previous DMFC design [27]. An effective sealing between the gasket and the diffusion layer also decreases the overall methanol crossover rate. However, they only focused on gross cell performance with the promise of further system optimization in a future publication.

Hahn et al. used a metal-polymer foil-type planar design for their passive MEMS-based micro-fuel cells, which is constructed without additional gas diffusion layers (GDL) [19]. The foils are fixed on a silicon-wafer during fabrication but the wafer is only used as carrier substrate. To reduce sealing problem, the interconnection between cells is performed on the outside of the membrane area and each individual cell is provided by outside

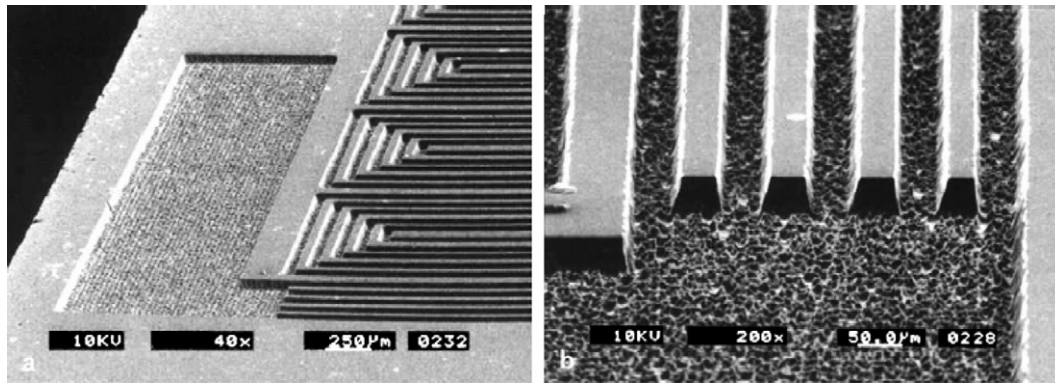


Fig. 8. SEM micrographs of channel structure with trapezoid cross-section and high roughness [31].

access with the help of electrical test pads. A micro-fuel cell of this assembly with the size of $1\text{ cm} \times 1\text{ cm}$ and $200\text{ }\mu\text{m}$ thickness gave an output current of 40 mA at 1.5 V with a stable long term operation at 80 mW cm^{-2} (Fig. 10).

4. Future for micro-fuel cells

Current generation lithium-ion (Li-ion) rechargeable battery technology capacity improvements are expected to be modest in the coming years (<5% per year) and will struggle to meet

ever-increasing power requirements [36]. Fuel cell technology is expected to be the most promising candidate to replace battery technology. In general terms, fuel-cell markets are broken down into three categories: portable (electronic devices), stationary (generators), and vehicle propulsion [37]. Micro-fuel cells, or more specifically, micro-direct methanol fuel cells (DMFCs), aim to cater to the first category, which includes devices such as mobile phones, laptop computers and PDA. North America (primarily the USA) is the dominant region of development and that there is a lag in the market from the time it was invented and developed with support from the US Defence Advanced Research Projects Agency (DARPA) in the early 1990s up to 2001 and 2002 where the graph shows a jump in the volume (refer to Fig. 11). However, this data is misleading as the jump is mostly caused by efforts from only a handful of companies, e.g. Ball Aerospace and Smart Fuel Cell, and a significant proportion of North American companies are working on military contracts rather than gearing up for commercialization.

According to a 2003 study released by Allied Business Intelligence (ABI), micro-fuel cells entered the commercial market in the 2004–2005 timeframe. Worldwide shipments are projected to reach 200 million units by 2011. The Darnell report estimates that worldwide fuel cells could account for 8.6 million unit sales for mobile phones in 2004, increasing to 463.8 million in 2009, a Compound Annual Growth Rate (CAGR) of 122.1%—if the right price points are achieved. Like others,

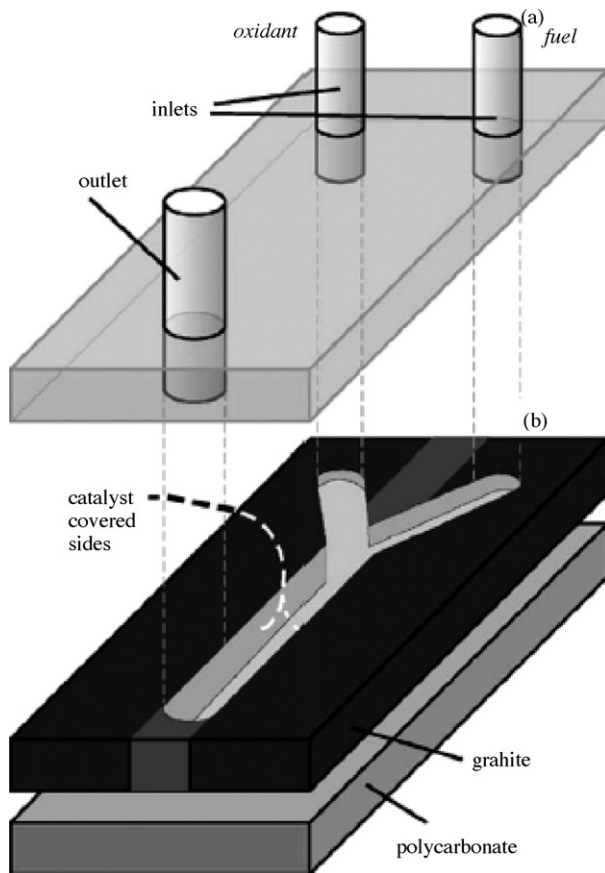


Fig. 9. Assembly scheme of a laminar flow-based fuel cell with graphite plates as the catalyst support, current collector, and defining structure for the geometry and dimensions of the channel [33].

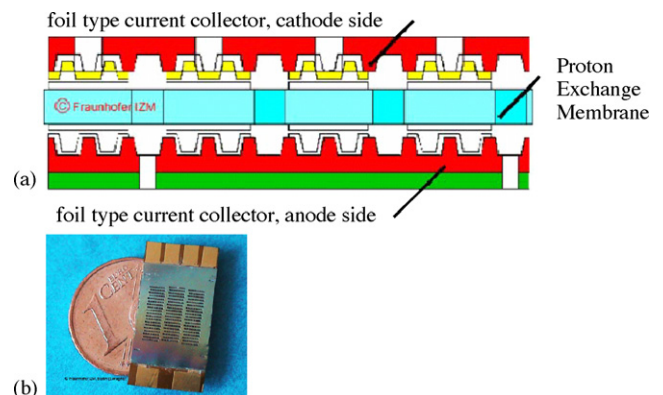


Fig. 10. (a) Cross-sectional view of micro-fuel cell and (b) micro-fuel cell with integrated serial connection of three cells [19].

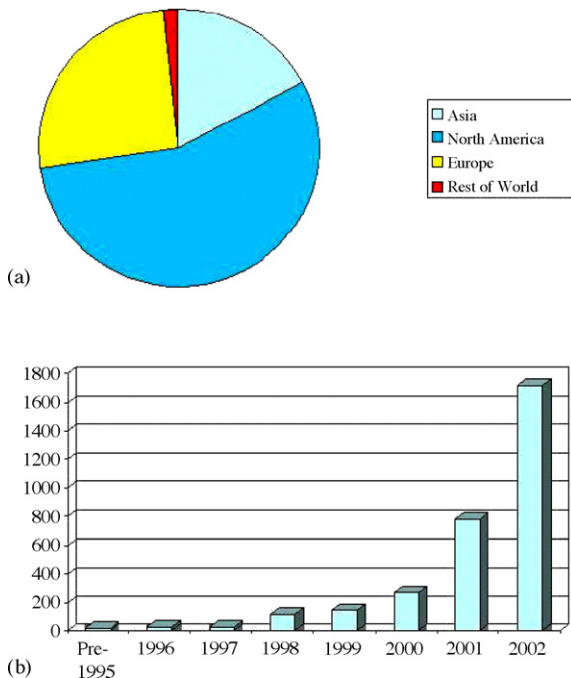


Fig. 11. (a) Development chart for fuel cells according to region and (b) portable systems built by cumulative numbers [38].

Darnell Group believes the direct-methanol fuel cell holds the most promise. It operates in a relatively low temperature range, making it attractive for tiny to mid-sized applications. The main technology is proton exchange membrane, and a majority of units sold through 2005 were PEMFC. The small portable and portable electronic markets are dominated almost entirely and in equal shares by PEMFC and DMFC technologies [39]. PEMFC technology is leading but in terms of R&D, the DMFC technology is receiving as much attention as the PEMFC technology [40].

A 2005 forecast given by the world's largest market research resource online (RESEARCHANDMARKETS) shows that the market demand for micro-fuel cells is building towards mass-market acceptance by 2008. Markets are anticipated to be US\$ 510 million worldwide by 2008, with the strong growth occurring in 2007–2008 and 145 million units in sales by 2010 [40] as technology becomes mature and products start to work. By 2013, micro-fuel cell markets are expected to reach US\$ 11 billion. This represents a range of PC, mobile phones, PDA, and digital device segments in a variety of industry, military, and health care segments [41]. The mobile phone is particularly looked into with interest due to the many features that it can carry within its slim and compact design. It is the device of choice for constant mobile communication and provides such broad services like email, text messaging (SMS), and digital photos and videos (MMS). It is also slowly becoming an entertainment center with the availability of music, movies, games and real-time sporting events. Future advances such as credit card transactions and airline ticketing also suggests a possible change in the users' lifestyles. Nokia notes that there are nearly 2 billion mobile phones in the global market and forecasts that number to rise to 3 billion by 2008.

5. Conclusions and suggestions

Conventional batteries are soon becoming inadequate for the increasing power and complexity of portable electronic devices and computers. The micro-DMFC is capable of replacing the conventional battery without recharging from the AC mains. It is smaller, better, less-costly, environmentally safe and much more efficient and mobile and can be used either in the plane, train, and car or in remote areas where there is no electricity as in some parts of emerging economies. The refueling of the micro-DMFC is fast and the fuel can last several months. The product is cost competitive due to the large market size and economies of scale. The micro-DMFC systems are eventually far less expensive than the alternative battery technologies in the long run.

However, methanol crossover is currently the biggest challenge faced by micro-DMFC designers as it has the most effect on the cell performance. Several common approaches to prevent it in terms of membrane modifications and novel cell/stack designs are currently being studied. Meyer and Maynard suggested that one must deliver a complete system, and not just the stack itself, when designing a useful model [2]. This complicates the situation for designers even further due to the many challenges that have to be faced such as system integration, peripheral system components that are necessary to ensure the cell activities but limit the overall cell performance, and also managements of air, water, fuel, power load and heat. Furthermore, as fuel cells depend on the environments in terms of input and output of fuel, air and water, many uncertainties and parameters have to be considered as well before an optimized design can be put in the market.

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