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2006

Nguyen, N. T., & Chan, S. H. (2006). Micromachined polymer electrolyte membrane and direct methanol fuel cells:a review. *Journal of Micromechanics and Microengineering*, 16(4).

<https://hdl.handle.net/10356/93879>

<https://doi.org/10.1088/0960-1317/16/4/R01>

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[<http://dx.doi.org.ezlibproxy1.ntu.edu.sg/10.1088/0960-1317/16/4/R01>].

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Micromachined Polymer Electrolyte Membrane and Direct Methanol Fuel Cells —a Review

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Abstract. This review reports recent progress of the development of micromachined membrane-based fuel cells. The review first discusses the scaling law applied to this type of fuel cells. Impacts of miniaturization on the performance of membrane-based fuel cells are highlighted. This review includes only the two most common micro fuel cell types: proton exchange membrane micro fuel cells (PEM μ FC) and direct methanol micro fuel cell (DM μ FC). Furthermore, we only consider fuel cells with active area of a single cell less than one square inch. Since the working principles of these fuel cell types are well known, the review only focuses on the choice of material and the design consideration of the components in the miniature fuel cell. Next, we compare and discuss the performance of different micro fuel cells published recently in the literature. Finally, the review gives an outlook on possible future development of micro fuel cell research.

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1. Introduction

With the advance of micro machining technologies, miniaturization of power sources has been the focus of many research groups. Based on the advantages of the scaling laws, miniaturization promises higher efficiency and performance of power generating devices [1]. Epstein et al. [2] proposed the miniaturization of heat engines to convert thermal energy of fuel combustion into mechanical energy and then into electricity. Since reaction conditions and other physical effects in microscale differ from what have been used in the large scale, miniaturization of power generation requires complex technologies, high-temperature materials, and therefore poses a number of other challenges [3]. Another approach for micro-scale power generation is to scale down electrochemical devices such as battery [4] and fuel cell. Fuel cells are electrochemical devices that convert chemical energy of a fuel directly into electricity. Fuel cells have gained renewed interest for applications in high-power consumption portable electronic devices such as data acquisition and communication devices. Since energy is stored as a "reservoir" of fuel rather than as an integral part of the power source, fuel cells have numerous advantages over batteries. Dyer [5] discussed briefly the portable applications of fuel cells. This review only focused on the system-level performance, cost, convenience and safety of fuel cells for these applications. Another recent review on fuel cell technology was reported by de Bruijn [6]. Heller reviewed miniature biofuel cells which use enzymes as the catalyst [7]. All these reviews are rather general and do not address the design and fabrication of miniature fuel cells for portable applications.

A miniature fuel cell power source can be realized through an approach that combines thin film materials with micro technologies. Micro fuel cells (μ FCs), which can be fabricated with micro technologies, have micro structures and generally generate less than 5 W of electricity are the recent focus of fuel cell research community.

Recently, there were a number of papers on membraneless laminar flow-based microfluidic fuel cells [8, 9, 10], which contain no proton exchange membrane. These micro fuel cells utilize the liquid/liquid interface between the fuel and the oxidant. Due to the dominant laminar convective transport, fuel crossover can be avoided. Planar design of this micro fuel cell allows a larger interface [11] and the implementation of air-breathing design [13]. This novel concept promised further miniaturization of fuel cells.

In this paper, the authors review only the fuel cells based on proton exchange membrane and with the active area of a single cell less than one square inch. The devices, defined in this review as micro fuel cells, are actually membrane-based micro fuel cells. The review first discusses the impact of scaling law and miniaturization on the performance of these devices. Next, the paper discusses the working principles of proton exchange membrane micro fuel cells (PEM μ FC) and direct methanol fuel cells (DM μ FC), which are most suitable for low-temperature, low-power portable applications. Based on the research works in the last three years, design considerations of micro fuel cells are analyzed and illustrated by the published prototypes. They μ FCs

are compared according to their performances. Finally, future trends and potential research focus on μ FCs are discussed.

2. Scaling law for micro fuel cells

Since micro structures are available in micro fuel cells, the impact of miniaturization can be derived from the so-called scaling law. Assuming a scaling factor of S , the ratio of the surface area to the volume scales is given as:

$$\frac{\text{surface}}{\text{volume}} \propto \frac{S^2}{S^3} = S^{-1}. \quad (1)$$

That means, with miniaturization ($S < 1$ and $S^{-1} > 1$) surface effects will become dominant in micro fuel cells. Similarly, for a constant flow rate, the pressure drop scales as:

$$\Delta p \propto S^{-3} \quad (2)$$

The Peclet number, a dimensionless number describing the ratio of convection to molecular diffusion scales is given as:

$$\text{Pe} = \frac{UL}{D} \propto S, \quad (3)$$

where the mean velocity U and the diffusion coefficient D are assumed to be constant. The same law applies to Reynolds number, which describes the ratio of inertial force to viscous force:

$$\text{Re} = \frac{UD_h}{\nu} \propto S, \quad (4)$$

where D_h is the hydraulic diameter of the channel, and ν is the kinematic viscosity. Based on the above scaling analysis, the advantages and drawbacks of miniaturization for fuel cells can be drawn as follows:

- The dominant surface effects improve reaction conditions and thus increase the cell performance.
- The high pressure drop increases the pressure across the diffusion layer, thus improves diffusion of the fuel and the oxidant to the membrane.
- The dominant surface effect and better reaction conditions also improves water formation and may lead to flooding of the electrodes.
- Diffusion coefficient D of liquids is about 3 orders of magnitude smaller than kinetic viscosity ν , while for gases these two properties are on the same order of magnitude. Thus, the relationship between the Peclet number and the Reynolds number are $\text{Pe} \approx 1000\text{Re}$ for liquids and $\text{Pe} \approx \text{Re}$ for gases, respectively. The relatively large Peclet number in a DM μ FC means a dominant convection transport, which may prevent fuel from diffusing toward the PEM. A relatively small Peclet number in a PEM μ FC may lead to insufficient water removal. A large Peclet number in liquid-based devices may lead to the possibility of removing the proton exchange

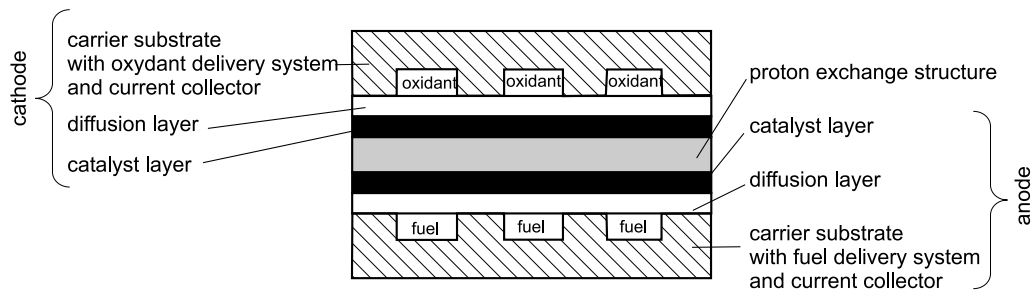


Figure 1. Basic components of a typical micro fuel cell.

membrane from the fuel cell design. In the membraneless micro fuel cells mentioned above [9], the Peclet number is on the order of 10,000, which prevents fuel cross over in the micro fuel cell.

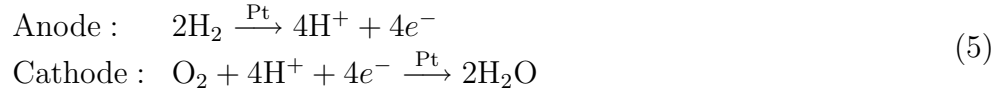
For a given micro fuel cell design, there is an optimal channel dimensions for fuel/oxidant delivery. Too small or too large fuel delivery channels may lead to decrease in fuel cell performance. For instance, Cha et al. [14] reported an optimal channel cross section of about $100\ \mu\text{m} \times 100\ \mu\text{m}$.

3. Membrane-based micro fuel cell types

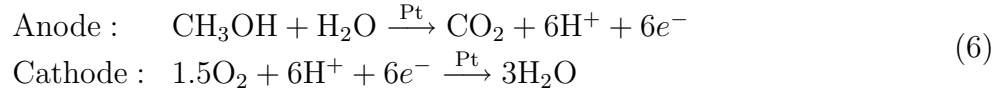
In a microengine, energy losses are caused by heat lost from the combustion reactions. Microengines require another step to convert the mechanical energy into the electrical energy. The high temperature involved in a microengine is a big challenge for material selection and fabrication technology. In contrast, the oxidation reaction in fuel cells converts the chemical energy directly into the electrical energy at a relatively low temperature, and even at room temperature. Depending on the type of fuel and electrolytes used, fuel cells are categorized as alkali fuel cell (AFC), phosphoric acid fuel cell (PAFC), solid oxide fuel cell (SOFC), and solid polymer fuel cell (SPFC). Since the electrolyte of SPFC is made of polymer, it can only work at relatively low temperature. Micro fuel cells are most likely used in portable applications at low temperature. Therefore SPFC is the best candidate for low temperature applications. In this review, the authors only focus on two common SPFC types: proton exchange membrane micro fuel cell (PEM μ FC) and direct methanol micro fuel cell (DM μ FC). Since proton exchange membrane can be made of non-polymeric porous material, we use PEM μ FC and DM μ FC as the two generic terms in this review.

Figure 1 depicts the basic components of a typical micro fuel cell. The design and fabrication of the components in Fig. 1 will be reviewed and discussed in the subsequent sections. The central part of a micro fuel cell is the electrolyte working as the proton conducting media, which is in contact with a porous anode and a porous cathode on either side. The anode and cathode each consists of several layers such as carrier substrate, current collector, diffusion layer and catalyst layer. The

fuel is fed continuously to the anode and an oxidant such as oxygen from air is supplied continuously to the cathode. The electrochemical reactions are activated at the electrodes by catalysts. For fuel cell fed with hydrogen and oxygen, the reactions at the anode and cathode are:



Protons pass through the electrolyte, while the electrons generate a current externally across the electrodes that can be used by a load. In the case of methanol as the fuel, the reaction at the anode and cathode are:



From the above fuel types, methanol is the better candidate for portable application because of the higher energy content. Compared to hydrogen, methanol is cheaper to produce and easy to store. However the fuel crossover problem and poor electrode kinetics are two key challenges to the success of applications.

The ideal efficiency of a micro fuel cell can be estimated as:

$$\eta_{\text{ideal}} = \eta_{\text{max}} \frac{V_{\text{cell}}}{V_{\text{max}}}, \quad (7)$$

where η_{max} is the maximum thermal efficiency, which is 83% and 97% for hydrogen and methanol, respectively. The maximum cell voltages of hydrogen and methanol at 25 °C are 1.23 V and 1.21 V, respectively.

4. Design considerations for micro fuel cells

4.1. Carrier substrate

For micro electromechanical systems, silicon was a preferred material because of the availability of current micro technologies. Basic silicon-based micromachining technologies include anisotropic etching, deep reactive ion etching (DRIE), deposition of various materials using chemical vapor deposition (CVD) and physical vapour deposition (PVD). These micro techniques allow the miniaturization of fuel/oxidant delivery system as well as the deposition of electrodes and electrolyte materials. Silicon/glass based system are mechanically more stable than conventional polymer-based membranes. Silicon and glass can withstand much higher operating temperature and do not suffer from swelling as in the case of its polymer-based counterparts. However, silicon is brittle and prone to fracture because most of the silicon-based micro fuel cells are assembled by press-fit and have a relatively large size in the order of centimetres. Figure 2(a) shows the common fabrication steps of bulk micromachining on a single substrate.

Stainless steel is an alternative to silicon. Stainless steel foils are available commercially and has been used widely for micro reactors. This substrate can be machined by etching, laser machining or punching. Hahn et al. [15] used stainless steel

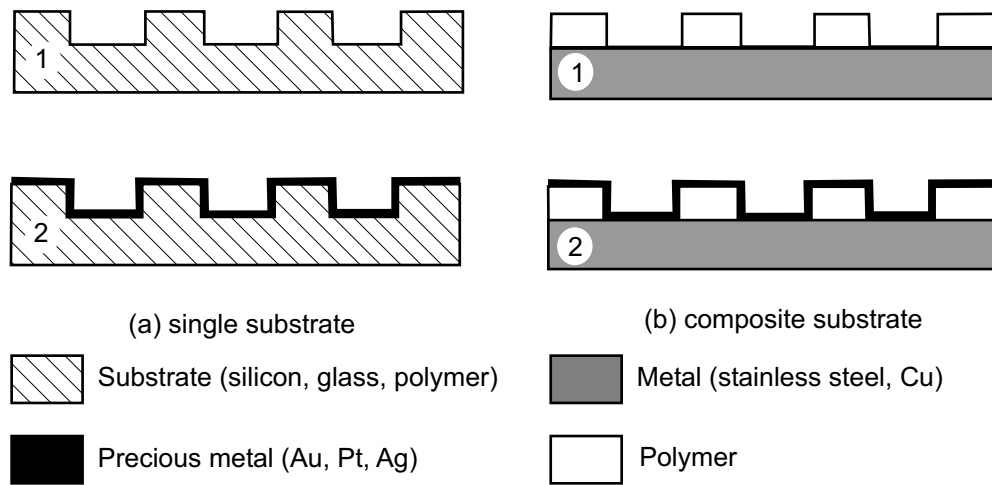


Figure 2. Fabrication steps of carrier substrates with fuel/oxidant delivery channels and current collector: (a) bulk machining on a single substrate (etching, laser machining, hot embossing, moulding), (b) Micro machining of a composite substrate.

laminated with a polyimide film as the substrate for their micro fuel cells. Fuel delivery microchannels were formed into the polyimide film by reactive ion etching (RIE). Gold was sputtered on this stainless steel/polyimide composite to form the current collector. Hsieh et al. [16] fabricated fuel delivery microchannels in SU-8 on a copper film as shown in Fig. 2(b). Their approach is similar to that of Hahn et al. [15]. Instead of using stainless steel, a copper foil was adopted as the substrate material. SU-8, a thick film photo resist [17], was spin coated and structured on top of the copper substrate. Silver was then sputtered on the copper/SU-8 composite to make the current collector. A similar work was reported by Cha et al. [18].

Recent advances in polymeric micromachining [17] make polymers an attractive material for micro fuel cells. Polymeric micro machining technologies such as reactive ion etching, polymeric surface micromachining, hot embossing, soft lithography and laser machining are readily available [17]. Polymethylmethacrylate (PMMA) [19, 20], polydimethylsiloxane (PDMS)[21, 22], SU-8 [16] or other materials can work as carrier substrates for micro fuel cells. Hsieh et al. [20] used excimer laser to machine delivery microchannels in the PMMA substrate. The cross section of the channel was in rectangular shape. Copper as current collector was sputtered on PMMA. Chan et al. [19] used CO₂ laser machining to create fuel/oxidant delivery microchannels, gold film as current collector was coated directly on PMMA. In contrast to the rectangular cross section made by excimer laser, the special Gaussian shape of the channel cross section and consequently a current collector without discontinuities allows the CO₂ laser machined micro fuel cell to achieve a very low internal resistance. Sha et al. [21] reported the use of PDMS as the substrate material for micro fuel cells. PDMS can be fabricated by casting the prepolymers on a master. This technique is also known as soft lithography [17]. Since PDMS is a soft material, current collector was sputtered on the

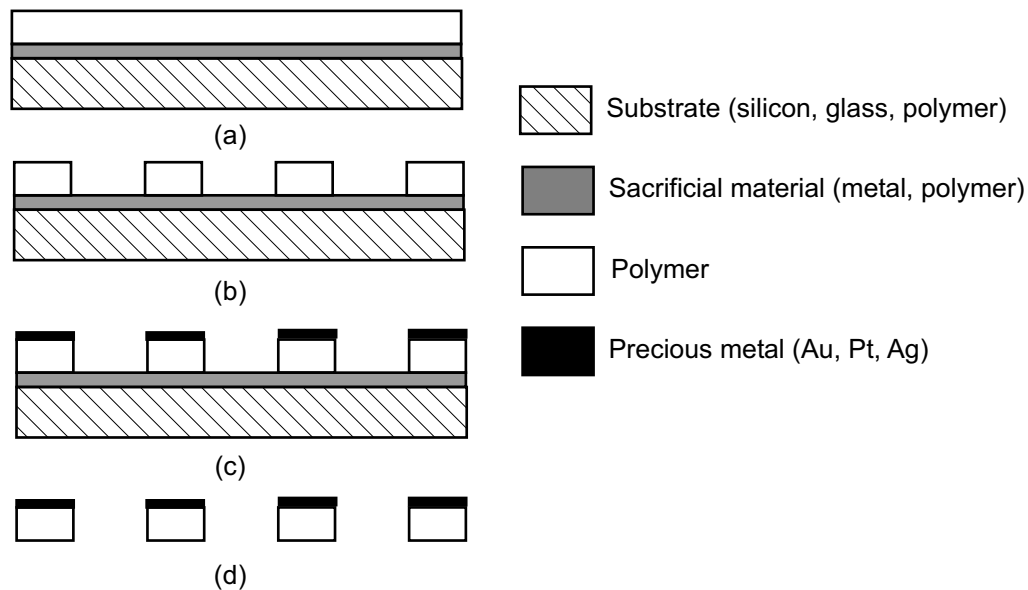


Figure 3. Fabrication steps of carrier substrates with polymeric surface micromachining: (a) coating of sacrificial material and the functional polymer material, (b) structuring of the functional material, (c) sputtering of current collector layer, (d) releasing the polymer part by etching or dissolving the sacrificial material.

membrane electrode assembly (MEA). Stanley et al. [22] also used a similar approach to form the microchannels. The PDMS part was glued to the MEA by a silicon rubber adhesive. Cha et al. [23] fabricated SU-8 using polymeric surface micromachining [17] with a glass wafer as both carrier substrate and sacrificial material. Platinum was sputtered directly on SU-8 and acts as the current collector. The fabrication steps of a carrier substrate with polymeric surface micromachining is shown in Fig. 3.

4.1.1. Proton exchange structure The central part of a micro fuel cell is the proton exchange membrane (PEM). Nafion (DuPont) membrane is usually used as the solid electrolyte. With adoption of micro technology, porous membranes made of silicon or other material have also become attractive. The biggest challenge in the mass production of micro fuel cell is the monolithic integration of all components in a single process. Because Nafion is incompatible to silicon processes and swells during operation makes the integration of this material in a monolithic manner extremely difficult. However, micro and nanotechnologies make the fabrication of nano-porous membrane[24] and nanochannels [25] in silicon possible. These nano structures could be an alternative to the Nafion-based PEM. Recently, Mitrovski et al. [26] introduced a novel proton exchange concept using liquid electrolyte confined inside a microchannel network. This concept may potentially solve the problem of dehydration in PEM-based micro fuel cells.

In nanoscale geometries such as nanopores and nanochannels, the overlap of electric double layer (EDL) occurs and improves proton conductivities. These nanostructures can be fabricated with common micromachining technologies. Porous silicon can be

fabricated in an anodization process in a buffered HF solution. Gold et al. [24] fabricated sulphuric acid loaded nano porous silicon membrane with thickness ranging from 40 to 70 μm and proton conductivities in the order of 10^{-2} to 10^{-1} S/cm. These characteristics are comparable to commercial Nafion membranes. Liu et al. [25] recently fabricated nanochannels in glass substrate. The channels are 1 mm long and 100 μm wide but only few hundreds nanometer in depth. These channels also achieved conductivities in the order of 10^{-2} to 10^{-1} S/cm. However, because of the planar configuration and the small number of available nanochannels the current density and power density of the micro fuel cell with nanochannels are limited. Stanley et al. [22] used porous glass loaded with Nafion as the membrane. The porous glass membrane was made of compressed glass fibre immersed in Nafion solution. This membrane has a proton conductivity of 40×10^{-3} S/cm, which is lower than the conventional Nafion membrane. Kanamura et al. [27] synthesized macroporous silica using 474-nm polystyrene beads as the colloidal template. A mixture of colloidal silica and polystyrene beads were heated at 890 $^{\circ}\text{C}$, where the beads were burnt away and silica was sintered to a porous silica membrane. The pores in the membrane were then filled with a gel polymer (AMPS, 2-acrylamido-2methyl-1propanesulfonic acid) to offer proton conduction. Proton conductivities from 2×10^{-2} to 7×10^{-2} S/cm were achieved with this membrane.

4.2. Diffusion layer

The diffusion layer serves several functions: bringing fuel and oxidant to the proton exchange structure, removing water from the membrane and conducting the current. Thus, the diffusion layers are often made of electrically conductive porous materials such as the carbon paper. The conductivity of carbon paper can be further improved by filling it with electrically conducting powder such as carbon black [22]. To remove water from the pores of diffusion layer, the diffusion layer can be further treated with a hydrophobic material such as polytetrafluoroethylene (PTFE) [28]. Heinzl et al. used Toray carbon paper filled with carbon black and PTFE to make the diffusion layer of their micro fuel cell [56]. Similarly, Lee et al. [29] used carbon paper treated with carbon-supported platinum as the diffusion layer. Cha et al. [23] used a polymeric frame filled with carbon black and PTFE as the diffusion layer. Many micro fuel cell designs forego the diffusion layer by using a thin catalyst layer sputtered directly on the PEM [20, 16, 21, 30].

Miniaturization and the associated scaling laws may lead to novel ways of designing a diffusion layer. As already mentioned at the beginning of this review, the interface between fuel and oxidant flows can replace both the PEM and the diffusion layer [8]. Furthermore, gas-permeable elastomer such as PDMS can also work as the diffusion layer for liquid-electrolyte-based proton exchange structure [26]

4.3. Catalyst layer

Platinum (Pt) and ruthenium (Ru) are the common catalyst materials for micro fuel cells. Hsieh et al. sputtered a 20 to 60nm platinum layer directly on the PEM made of Nafion 117 [20]. Shah et al. [21] deposited a 5 nm platinum layer on the Nafion membrane as the catalyst. However, the cost of pure platinum would possibly hinder the commercialization of this fuel cell. Thus, using other material to support platinum can reduce the cost of the catalyst layer. The catalyst layer can be made of Nafion bonded platinum on carbon, which extends the three-phase boundary area (gas-catalyst-electrode) for improved electrochemical reaction [31, 32, 22, 33].

Instead of deposition on the PEM, Yeom et al. [34] deposited the catalyst layer on top of the current collector and the carrier substrate. The current collector acts as a seed layer for electroplating a platinum layer using hexachloroplatinate solution ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$). This concept is compatible to the batch process of micromachining. Cha et al. used the same concept to fabricate their catalyst layer onto the diffusion layer. The SU-8 frame was filled with a catalyst ink consisting of Nafion solution, water, isotropyl alcohol, platinum back as well as Pt-Ru alloy [23].

Instead of carbon powder (carbon black), carbon nanotubes can be used as the support material for platinum nanoparticles to make the catalyst layer [35, 36, 37, 38, 39, 41]. All these works reported a better fuel cell performance compared to these using carbon powder. Li et al. [42] improved this technique further by aligning carbon nanotubes. This new concept first deposited 2.8-nm platinum nanoparticles onto the carbon nanotubes, then used filtration method to align them. The aligned nanotubes improved electrical conductivity and hydrophobicity of the catalyst layer.

4.4. Fuel and oxidant delivery system

4.4.1. Bipolar and planar design Currently, there are two basic design approaches for delivery of fuel and oxidant in microfuel cells: the traditional bipolar design and the planar design. The Bipolar design is based on the stacking concept where all the components of a micro fuel cell are layered in a stack. Fuel and oxidant supplies are separated by the PEM. Most micro fuel cells based on bipolar design have separated fuel/oxidant delivery systems. The general bipolar design is depicted in Fig. 4. Bipolar design ensures the separation of fuel and oxidant and avoids them from coming into contact with each other before reaction. The bipolar design is only suitable for hybrid integration of the fuel cell components. That means, the components are fabricated separately and assembled together into a complete device. The planar design depicted in Fig. 4(b) is more suitable for monolithic integration, because both fuel and oxidant are delivered through channel networks located at a single side of the PEM. The fuel and oxidant channels are interdigitated, so that reaction can occur between them. Compared to the bipolar design, the planar design is two-dimensional and requires a larger surface area to deliver the same performance.

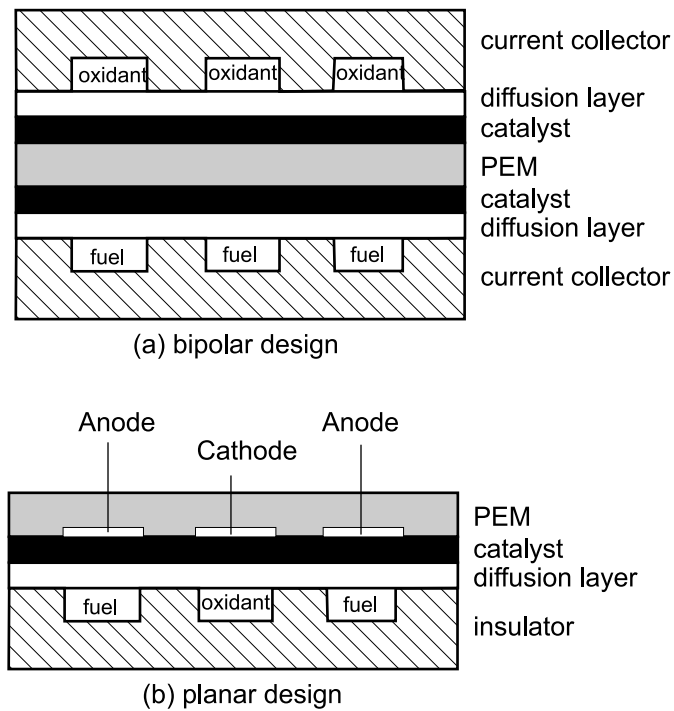


Figure 4. Two basic designs of micro fuel cells: (a) bipolar, (b) planar (not to scale).

4.4.2. Fuel delivery system Based on the different concepts of fuel delivery and fuel handling, micro fuel cell can be categorized as passive and active types. While active micro fuel cells need external pumps and mixers for delivering and conditioning fuels, passive micro fuel cells do not need any external accessories. Designing a passive micro fuel cell is a big challenge because of the need of water management such as water removal at the cathode and humidification as well as dilution of the fuel at the anode. Most of the published research works on micro fuel cell rely on external active fuel delivery. A number of fuel delivery designs was reported in the literatures. In this context, the authors categorize them based on their geometry as: direct supply design, parallel design, serpentine design, serpentine/parallel design, spiral design, interdigitated design and spiral/interdigitated design. Figure 5 depicts these basic designs. Cha et al. [14] used numerical simulation to compare the performance of the several channel designs.

Direct supply design does not need channel structure to guide the fuel. Fuel is fed directly to the PEM, Fig. 5(a). To increase the pressure across the PEM, this concept can be combined with the diffusion layer by using a porous material. Kumar and Reddy used metal foam to increase the pressure drop across the fuel delivery system and improved the performance of the fuel cell [43].

Lee et al. [29] implemented the distribution pillars design shown in Fig. 5(b). The distribution pillars were etched in silicon using DRIE. A chromium/gold layer was deposited as the current collector. The only advantage of this design is low supplying pressure. However, the drawbacks are the low pressure applied on the PEM and the

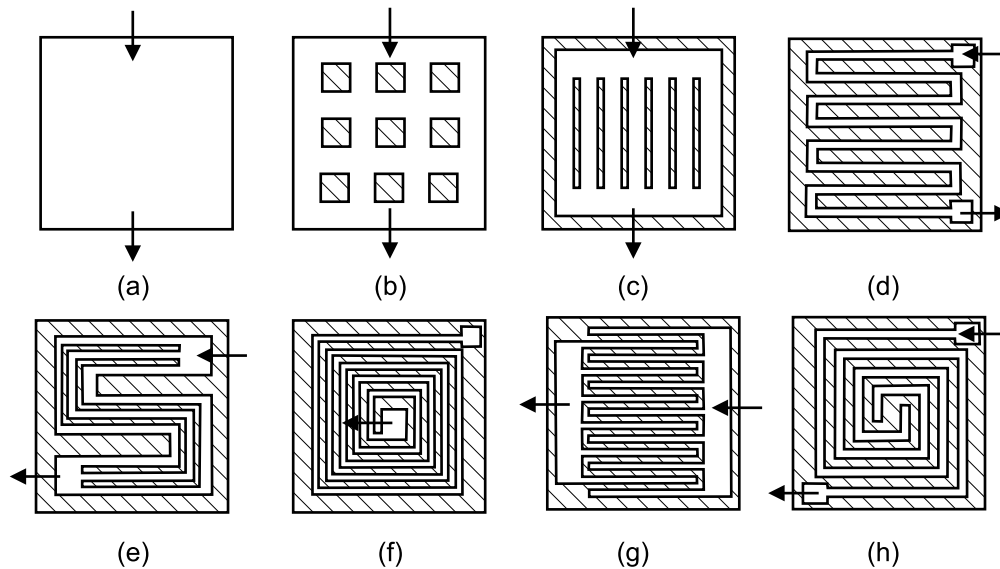


Figure 5. Typical fuel delivery designs: (a) direct supply, (b) with distribution pillars, (c) parallel microchannels, (d) serpentine microchannel, (e) parallel/serpentine microchannel, (f) spiral microchannel, (g) interdigitated microchannel, (h) spiral/interdigitated microchannel.

sharp edges, which may lead to breakages in the current collector layer and consequently increasing the internal electrical resistance of the fuel cell.

Parallel design (Fig. 5(c)) is popular among published works on micro fuel cells. The parallel channels reduce the supplying pressure and decrease the mean fuel velocity at a constant flow rate. The lower velocity leads to a longer residence time and better fuel diffusion. This design was implemented by Cha et al. [18] in SU-8, by Hahn et al. [15] in polymer/steel composite, by Wozniak et al. [44] in silicon, by Müller et al. in metal foil [45] and in carbon paper [46].

The serpentine design depicted in Fig. 5(d) increases the channel length and thus the pressure drop. The higher pressure forces the fuel to go directly into the diffusion layer, leading to better fuel permeability and consequently better performance. Wong et al. implemented a single serpentine microchannel of $500\ \mu\text{m} \times 500\ \mu\text{m}$ in cross section on the stainless steel [47]. Testing results showed that for the same operating condition with methanol as the fuel, the micro fuel cell with a serpentine channel delivers a higher power density. The high fuel consumption at the entrance may lead to fuel deficiency and non-uniform current density distribution in the area around the end of the channel [14]. Because of this problem, many micro fuel cells incorporate the parallel/serpentine design shown in Fig. 5(e). This design reduces the pressure drop by using numerous parallel channels. Yen et al. [48, 49] used DRIE system to etch 3 parallel/serpentine microchannels of $750\ \mu\text{m} \times 400\ \mu\text{m}$ in silicon. Hsieh et al. [20] used excimer laser to machine 4 parallel/serpentine microchannels in PMMA. Each channel is $200\ \mu\text{m}$ in depth and $400\ \mu\text{m}$ in width. The same design was implemented in SU-8 with a channel

cross section of $200\ \mu\text{m} \times 200\ \mu\text{m}$. Lee et al. [50] implemented 3 parallel/serpentine micro channels on a stainless steel substrate. The microchannels measuring $50\ \mu\text{m}$ in depth, $100\ \mu\text{m}$ and $200\ \mu\text{m}$ in width were formed by electroplating with a SU-8 mould.

The spiral design shown in Fig. 5(f) has the same advantage as the serpentine design. However, the spiral design keeps the fuel-depleted region at the channels' end close to the fuel-rich entrance. Thus, current density is more evenly distributed. Chan et al. [19] implemented this design on a PMMA substrate. The channel is dead-ended, thus forcing all the fuel through the diffusion layer to the PEM. Together with a special channel shape, the reported fuel cell showed an excellent performance.

A typical interdigitated design is shown in Fig. 5(g). The delivery channel is of dead-ended design. The fuel is forced to enter the diffusion layers before exiting the fuel cell through the interdigitated channel systems [14]. The disadvantage of this design is that the fuel is almost depleted while travelling through the exit side. Half of the active membrane area is therefore not fully utilized. Cha et al. [14] proposed the spiral/interdigitated design depicted in Fig. 5h. This design actually shows the dead-ended spiral design reported by Chan et al. [19].

4.5. Oxidant delivery system

Oxidants for micro fuel cell are usually pure oxygen or air. For practical applications, air is the most favourable oxidant. Theoretically, oxidant delivery system can follow the same designs shown in Fig. 5. The use of external pumps, fans or compressors would improve the performance but these parasitic losses offset the net power output of the fuel cell. Passive concepts such as self-breathing are most preferred for micro fuel cell design. Hahn et al. [15] used holes machined on the current collector of the cathode as air access. Modroukas et al. [32] micromachined the air breathing cathode in silicon. The openings are $55\ \mu\text{m} \times 55\ \mu\text{m}$ square holes. Self-breathing micro fuel cells rely on free convection to remove water vapour and supply fresh air to the cathode. In high-current-density applications, oxygen concentration near the membrane could quickly deplete. The higher water content in the case of methanol as fuel can further increase the diffusion barrier for oxygen. In such cases, a large "breathing" area is required for the cathode. For special environment where air is either not available (underwater) or too low in density, hydrogen peroxide or sodium percarbonate can be used as the source of oxygen.

4.6. Water management

Water management is an important factor for the performance of a micro fuel cell. On one hand, polymeric PEM relies on water for the proton transport. Hydrogen as fuel needs to be humidified before entering the PEM, while in the case of methanol, it has to be diluted for optimal utilization. On the other hand, too much water will cause flooding at the electrodes thus blocking fuel and oxygen from reaching the PEM. Active water control such as taking water from the cathode to feed the anode could replace external

humidification. However, because of the space constrains as well as the small amount of available energy in micro fuel cells, active water management is always difficult. Since water can diffuse from the cathode back to the anode, passive water management is more likely the solution for micro fuel cells. Despite the importance of water management, no detailed design optimization has been reported in the literature. The spiral design of the fuel delivery system reported by Chan et al. [19] allows water to diffuse quickly across the entire membrane. This design is one of the factors contributing to the cell's high performance. Both numerical simulation [51] and visualization [52] of water production and distribution will help to optimize water management in micro fuel cells.

4.7. Temperature control

Temperature is another important parameter affecting the performance of a micro fuel cell. Both vapour pressure at the cathode and the anode and the reaction kinetics depend on the operating temperature. Humidification of PEM depends directly on the temperature. Too high the temperature accelerates evaporation and dries out the PEM. Too low temperature promotes the formation of water droplets and may lead to flooding of the electrodes. In addition, the conductivity of the membrane is improved with increased temperature. Hence, the water and temperature managements are inter-related. High temperature may cause the membrane itself to dehydrate and increases the fuel crossover rate [53]. If the micro fuel cell is to be deployed in extreme climates or un-conditioned environments, active temperature control is needed for stable operation.

Active temperature control for the micro fuel cell is a complex task. The simplest system consists of a heater and a temperature sensor. None of the reported works implemented active temperature control. He et al. [54] implemented a thin-film temperature sensor on the PEM. A structured gold film was used as temperature sensor on the Nafion membrane. Because the high strain on the membrane, the sensor was protected between two parylene layers. The temperature sensor was able to monitor the operating temperature of the fuel cell. If a heater can be fabricated in the same process, active temperature control can be realised.

5. Performance comparison

Table 1 and Table 2 compare the basic parameters of the reviewed fuel cells. The authors only considered fuel cells with active area of a single cell less than one square inch. In addition, at least one of the components of the fuel cell should be machined with micromachining technology and have sub millimetre features.

Figure 6 shows the reported maximum power density of a single cell versus the corresponding current density. Most of the proton exchange membrane micro fuel cells operated at room temperatures (20 °C to 25 °C), the best three micro fuel cells [19],[33] and [50] worked at 24 °C and 25 °C. Most of the direct methanol micro fuel cells operated between 60 °C and 70 °C. We assume that the authors selected the most

Table 1. Proton exchange membrane micro fuel cells A_{total} : total size in mm \times mm; A_{active} : active area in cm 2 ; P_{max} : maximum power density in mW/cm 2 ; I : current density at maximum power density in mA/cm 2 ; T : operating temperature in $^{\circ}$ C.

Ref.	First author	Year	A_{total}	A_{active}	Substrate	Design	PEM	P_{max}/I	H $_2$ a); oxidant b)	T
[19]	Chan	2005	25 \times 25	3.2	PMMA	spiral	Nafion 115	82/205	10 psi; 50 air	24
[18]	Cha	2004	n/r	2	SU-8	serpentine	Nafion 115	315/901	10 psi; 20 O $_2$	24
[15]	Hahn	2004	10 \times 10	0.18	polymer/steel	parallel	Nafion	0.09/0.3	30; 30 air	50
[54]	He	2005	22 \times 22	3	n/r	parallel/serpentine	Nafion	80/225	0.5; breathing	60
[56]	Heinzel	2005	n/r	n/r	graphite	direct	Nafion 117	87.3/175	n/r	80
[20]	Hsieh	2004	22.5 \times 22.5	5	PMMA	parallel/serpentine	Nafion 117	42/60	20 ml/min; 50 O $_2$	25
[16]	Hsieh	2005	22.5 \times 22.5	5	SU8	parallel/serpentine	Nafion 117	32/100	8; breathing	25
[29]	Lee	2002	22 \times 22	n/r	silicon	direct	Nafion 115	20/80	10; breathing	25
[50]	Lee	2005	40 \times 40	4	steel	parallel/serpentine	Nafion 112	20/60	n/r; n/r	25
[31]	Meyers	2002	n/r	n/r	silicon	n/r	Nafion	150/250	50-300; O $_2$	25
[32]	Modroukas	2005	25 \times 25	1	silicon	direct	Nafion 112	63/200	n/r	25
[45]	Müller	2003	14 \times 14	1	metal foil	parallel	Nafion	130/200	15; n/r	38
[21]	Shah	2004	31 \times 16	1.7	PDMS	direct	Nafion	50/150	20; 50	25
[22]	Stanley	2005	n/r	n/r	PDMS	direct	glas fiber/PTFE	0.28/1	0.1; breathing	60
[34]	Yeom	2005	n/r	n/r	silicon	n/r	Nafion 112	3.2/10	100; n/r	30
[33]	Yu	2003	n/r	5.1	silicon	n/r	Nafion 112	35/60	7; 7	20
						n/r	Nafion 112	194.5/450	50; 50	25

n/r: not reported

a) in ml/min otherwise the given as supply pressure

b) in ml/min with type of oxidant (air or O $_2$)

Table 2. Direct methanol micro fuel cells A_{total} : total size in mm \times mm; A_{active} : active area in cm²; P_{max} : maximum power density in mW/cm²; I : current density at maximum power density in mA/cm²; T : operating temperature in °C.

Ref.	First author	Year	A_{total}	A_{active}	Substrate	Design	PEM	P_{max}/I	methanol ^{a)} /oxidant ^{b)}
[63]	Blum	2003	n/r	6	polymer	n/r	PVDF/SiO ₂ powder	12.5/55	1M;n/r
[14]	Cha	2004	25.1 \times 25.1	1.8	SU-8	direct	Nafion 115	8/37	2M;0.8
[40]	Kelley	2000	n/r	0.25	silicon	direct	Nafion 117	60/300	0.5M, 200;200 air
[57]	Kelley	2002	n/r	0.25	silicon	direct	Nafion 117	90/300	0.5M, 200;200 O ₂
[55]	Li	2004	n/r	0.045	n/r	direct	Nafion 117	0.015/0.075	n/r
[49]	Lu	2004	n/r	1.625	n/r	parallel/serpentine	Nafion 112	50/200	2M 0.283; 88
[59]	Lu	2005	n/r	1.625	steel	parallel/serpentine	Nafion 112	100/375	2M 2.2; 375
[60]	Motokawa	2004	n/r	0.018	silicon	planar	Nafion 112	0.78/3.6	2M 0.01; 0.01
[30]	Aravamudhan	2005	n/r	n/r	silicon	direct	Nafion 115	8.1/35	n/r
[47]	Wong	2005	n/r	1	silicon	serpentine	Nafion	100/400	2M 0.8;n/r
[44]	Wozniak	2004	n/r	0.25	silicon	parallel	Nafion	0.3/2.5	6M;n/r
[48]	Yen	2003	n/r	1.625	silicon	parallel/serpentine	Nafion 112	47.2/220	1M 0.283; 80
[39]	Kim	2004	n/r	6	n/r	n/r	Nafion 115	40/140	4M passive; passive

n/r: not reported

a) in ml/min with the concentration in M

b) in ml/min

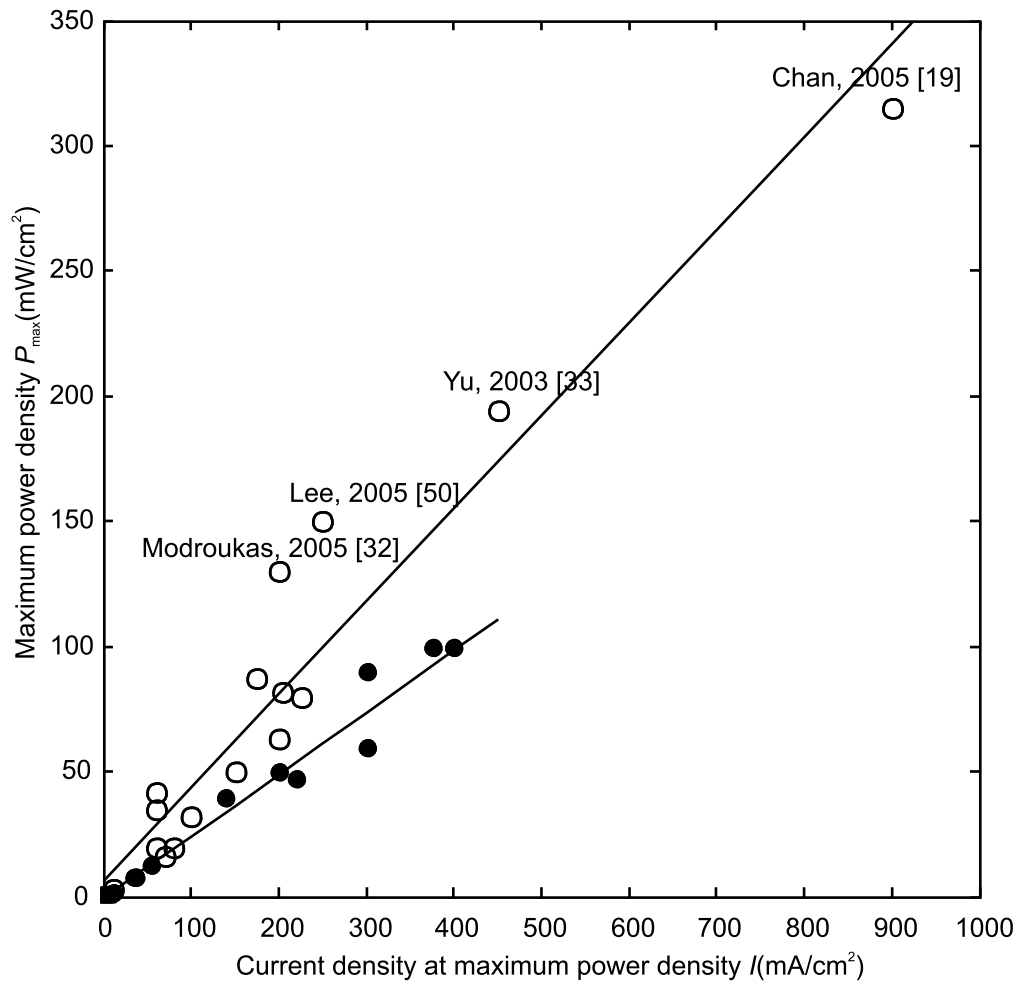


Figure 6. Maximum power density versus current density (white circles and black circles represent proton exchange membrane micro fuel cells and direct methanol micro fuel cells, respectively).

suitable fuel/oxidant flow condition and presented their best achievable results. The data in Fig. 6 show the progress of the maximum power density improvement in recent years. Since the theoretical maximum potential of hydrogen fuel cell of 1.23 V is higher than 1.21 V of methanol and the cell potential at peak power is approximately half of the maximum potential, PEM μ FC and DM μ FC should have different characteristics on the maximum power density versus current density diagram. Fig. 6 shows clearly the separated characteristics of hydrogen-based PEM μ FC and methanol-based DM μ FC. Despite the higher operating temperature, DM μ FC delivers a lower maximum power density than PEM μ FC under the same current density.

The cell potential and the current density at the peak power density of the reviewed micro fuel cells are plotted in Fig. 7. This diagram confirms, that DM μ FCs generally supply a lower cell potential at their peak power density. Fig. 7 also shows that there is a certain limit for the cell to reach. The top right corner in the diagram in Fig. 7) is though desirable but difficult to achieve. All reported micro fuel cells occupy the

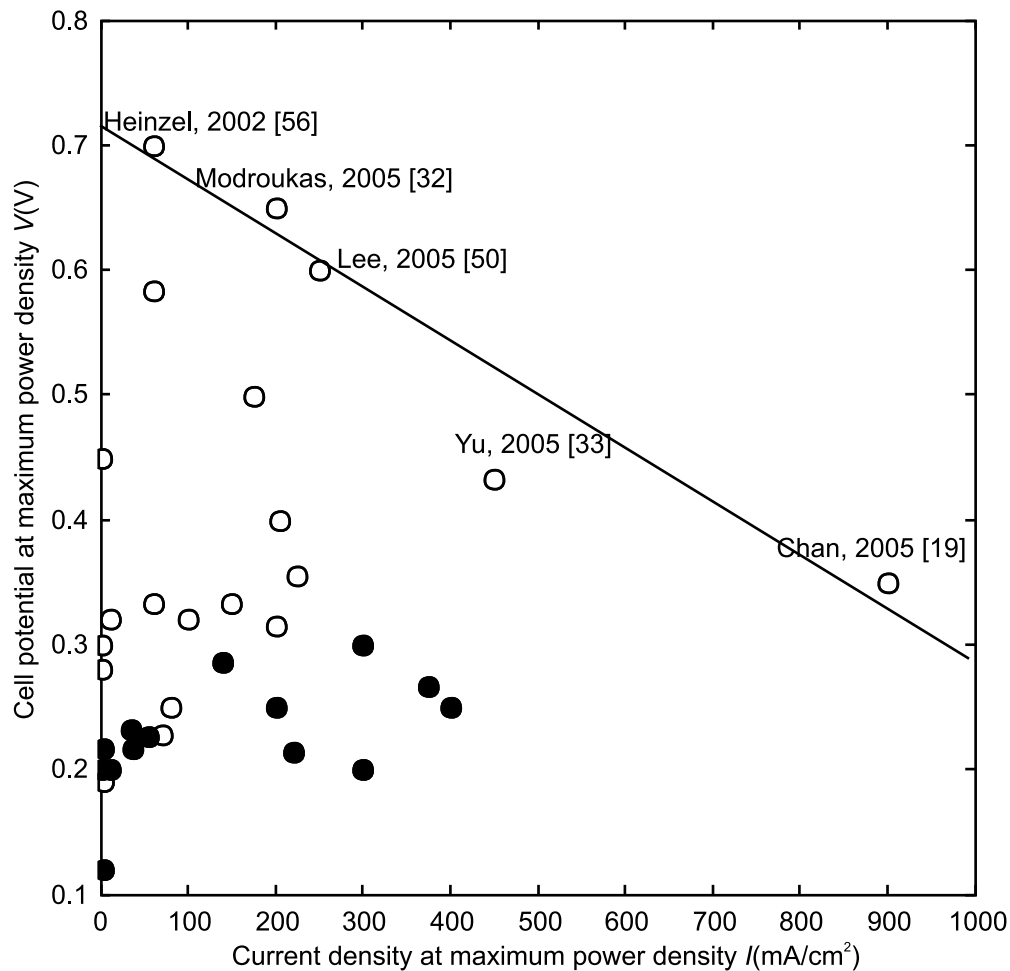


Figure 7. Cell potential versus current density at maximum power density (white circles and black circles represent proton exchange membrane micro fuel cells and direct methanol micro fuel cells, respectively).

bottom left corner of the diagram. Chan et al. [19] achieved a high current density with the special Gaussian shapes of fuel delivery microchannels. This gradual surface allows the fabrication of a smooth current collector. Due to the constrain in micro fabrication technology, all other micro fuel cells have microchannels with sharp edges, which may cause breakages and high electrical resistance in the current collector.

Figure 8 compares the reviewed micro fuel cells based on the type of fuel delivery systems. The depicted maximum power densities in each category was achieved with oxygen as oxidant and are therefore comparable. In general, direct supply and parallel channel systems deliver lower power density. Serpentine and spiral designs show higher performances. The reason may be due to the higher pressure drop, the better fuel distribution and the better utilization of active membrane area. While serpentine design may still have the problem of non-uniform current distribution between the exit and entrance due to the fuel depletion, the spiral design makes the current density more evenly distributed.

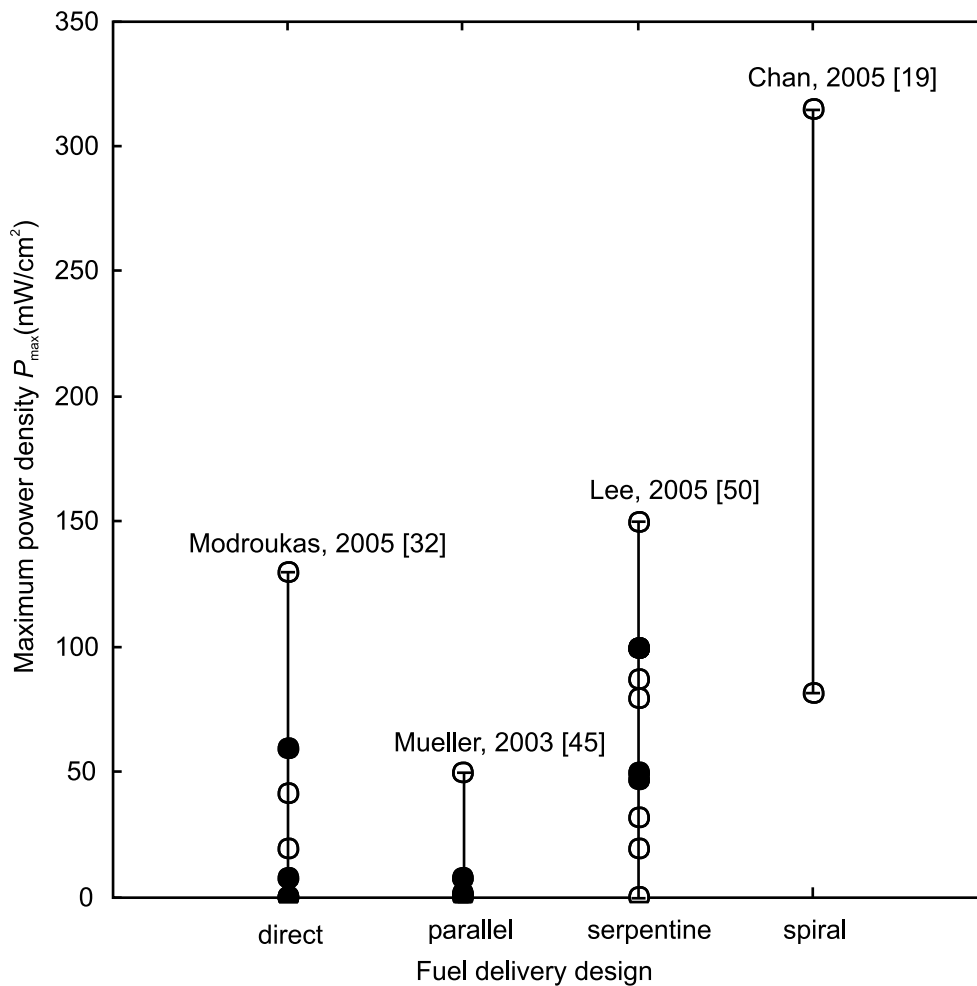


Figure 8. Maximum power density of the different fuel delivery designs (white circles and black circles represent proton exchange membrane micro fuel cells and direct methanol micro fuel cells, respectively).

6. Conclusion

This review discusses the design, fabrication technology and performance of membrane-based micro fuel cells. The fact, that the majority of reviewed papers were published in the last three years (2003-2005) showed that most research works on miniaturisation of membrane-based micro fuel cell are still in the preliminary stage. A huge research potential is still available in this field and new advances can be expected in the years to come. Since micro fuel cells are defined as being fabricated with micro technology and having micro structures, batch fabrication of micro fuel cells is desired. Similar to microelectronic devices and micro electromechanical systems (MEMS), batch fabrication would decrease the cost and makes complex fuel cells with integrated sensors possible. This paper shows that high performance can be achieved by careful design of fuel delivery, water/temperature management, and current collector and by minimising the contact resistance between parts.

Most published works were based on hybrid integration with Nafion as the material for the proton exchange membrane. This is a natural process as observed in the past decade in other fields of miniaturization such as MEMS and microfluidics. In the earlier stage, conventional concepts are simply miniaturized with the available micro technologies. Novel concepts utilizing the microscale effects will emerge in the next development stage. Membraneless laminar flow-based micro fuel cells are the first signals for this trend. Micro fuel cells based on Nafion was only the first step in the quest for fuel cell miniaturization. Breakthroughs can be expected in the research on proton exchange membrane, either in the MEA or directly cast on the electrodes. A solid proton exchange membrane is desired because polymer-based membranes such as Nafion would change significantly in size depending on the degree of their humidification. Furthermore, high process temperature may destroy the polymer structure. Variation in surface stress and low-temperature requirement make deposition of thin films on this structure very difficult. Making the proton exchange membrane based on porous silicon [24] and porous glass [22] are the first steps leading to solid proton exchange membranes. With the availability of a solid proton exchange membranes, deposition and patterning of thin films are possible. Similar to the past development in MEMS and microfluidics, monolithic integration of the fuel cell components can be achieved by deposition and selective etching. Batch fabrication also allows the integration of temperature [54] and humidity sensors. Automatic adjustment for the optimal operation would be then possible. Passive fuel delivery and self-breathing may not meet the power requirements of many portable appliances. Low-power active fuel delivery based on microfluidic technology could solve this problem and would be an interesting research topic for the near future.

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