



# Towards operating direct methanol fuel cells with highly concentrated fuel

T.S. Zhao\*, W.W. Yang<sup>1</sup>, R. Chen<sup>1</sup>, Q.X. Wu<sup>1</sup>

Department of Mechanical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

## ARTICLE INFO

### Article history:

Received 2 September 2009  
Received in revised form 3 November 2009  
Accepted 20 November 2009  
Available online 11 December 2009

### Keywords:

Fuel cell  
Direct methanol fuel cell  
Concentrated fuel  
Methanol crossover  
Water crossover  
Water recovery

## ABSTRACT

A significant advantage of direct methanol fuel cells (DMFCs) is the high specific energy of the liquid fuel, making it particularly suitable for portable and mobile applications. Nevertheless, conventional DMFCs have to be operated with excessively diluted methanol solutions to limit methanol crossover and the detrimental consequences. Operation with diluted methanol solutions significantly reduces the specific energy of the power pack and thereby prevents it from competing with advanced batteries. In view of this fact, there exists a need to improve conventional DMFC system designs, including membrane electrode assemblies and the subsystems for supplying/removing reactants/products, so that both the cell performance and the specific energy can be simultaneously maximized. This article provides a comprehensive review of past efforts on the optimization of DMFC systems that operate with concentrated methanol. Based on the discussion of the key issues associated with transport of the reactants/products, the strategies to manage the supply/removal of the reactants/products in DMFC operating with highly concentrated methanol are identified. With these strategies, the possible approaches to achieving the goal of concentrated fuel operation are then proposed. Past efforts in the management of the reactants/products for implementing each of the approaches are also summarized and reviewed.

© 2009 Elsevier B.V. All rights reserved.

## 1. Introduction

A direct methanol fuel cell (DMFC) directly converts the chemical energy stored in methanol to electricity. Because of its significant advantages, including its simple structure as well as easy storage/handling and the high specific energy of the liquid fuel, DMFCs have been identified as a leading contender to compete with conventional battery technology for powering portable electronic devices. Although extensive efforts have been made in developing DMFC technology over the past decade, the overall cell performance has not reached the expected level for powering most energy-hungry electronic devices [1–4].

Technically, besides the sluggish kinetics of the methanol oxidation reaction (MOR) [5–7], the permeation of methanol from the anode to the cathode, which is known as methanol crossover, is a key barrier that has hampered the development of DMFC technology [8]. Methanol crossover not only causes a mixed potential on the cathode, decreasing the cathode potential, but also leads to a waste of fuel which lowers the overall efficiency of the cell. The ultimate solution to the problem of methanol crossover calls for the development of low-methanol-crossover membranes [9,10]

and highly active anode electrocatalysts [5–7]. Extensive efforts have been expended to modify existing Nafion<sup>®</sup> membranes to limit methanol crossover, but almost all the measures taken so far to suppress methanol crossover have caused a side effect that decreases the proton conductivity and increases the cell internal resistance, hence degrading the cell performance. On the other hand, although Pt–Ru has exhibited the best performance for the MOR among all the catalysts currently available, its activity is still not sufficiently high to reduce the rate of methanol crossover. Under such a circumstance, a simple method to alleviate the impact of methanol crossover on cell performance is to feed a diluted methanol solution (i.e., 1–2 M for active fuel-supply systems and 3–5 M for passive fuel-supply systems) [11–15] to DMFCs. Although a DMFC operating with diluted methanol solutions can yield fairly high performance, a serious problem with this operation is that the low specific energy of the fuel cell system, annuls the most striking feature of the high specific energy of liquid fuel. This problem can further be understood by referring to Fig. 1, which compares in the specific energy between Li-ion batteries and DMFCs operating with different methanol concentrations. The variation in the specific energy of the methanol solution with the fuel concentration, represented by the dashed line, indicates that the specific energy of methanol solution with a concentration greater than 2.0 M will be higher than that of existing Li-ion batteries (~350 Wh L<sup>-1</sup> [3]) and the specific energy of pure methanol is as high as 4900 Wh L<sup>-1</sup> [16,17], i.e., 14 times higher than that of Li-ion batteries. However, the data in Fig. 1 also show that when the overall energy-conversion

\* Corresponding author. Tel.: +852 2358 8647; fax: +852 2358 1543.

E-mail addresses: [metzhao@ust.hk](mailto:metzhao@ust.hk) (T.S. Zhao), [yangww@ust.hk](mailto:yangww@ust.hk) (W.W. Yang), [merchen@ust.hk](mailto:merchen@ust.hk) (R. Chen), [jeffwqx@ust.hk](mailto:jeffwqx@ust.hk) (Q.X. Wu).

<sup>1</sup> Tel.: +852 2358 8660.

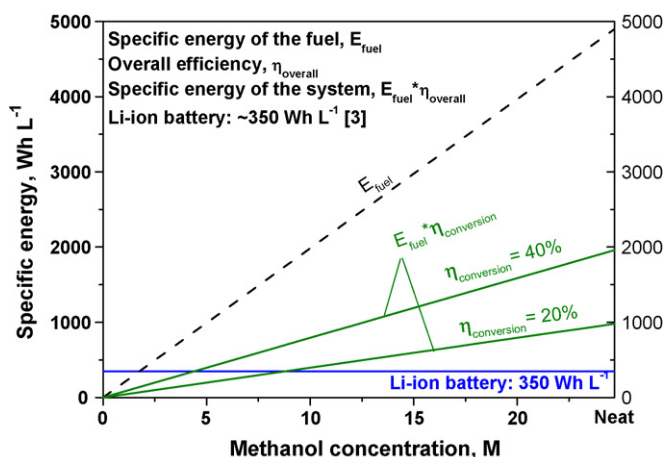


Fig. 1. Variation in specific energy of a DMFC system with methanol concentration.

efficiency of the DMFC system ( $\eta_{\text{overall}}$ ) is taken into account, only a small portion of the energy stored by the fuel solution can be converted into net power output and the overall specific energy of the DMFC system will be greatly reduced. Taking the system efficiency of 20% as an example, the specific energy of a DMFC system can be higher than that of Li-ion batteries only if the concentration of the methanol solution in the fuel cartridge is higher than 9.0 M. Hence, it is important to recognize that the high specific energy of a DMFC would become remarkable only if this type of fuel cell would operate with concentrated fuel (>9.0 M).

In conventional DMFC designs, an increase in the feed methanol concentration will lead to an increase in the rate of methanol crossover, thereby decreasing the cell voltage. As the rate of methanol crossover depends primarily on the methanol concentration in the anode catalyst layer, the strategy to increase the specific energy of the DMFC system is to use concentrated methanol, but in the meantime to maintain the fuel concentration in the anode catalyst layer at an appropriate level so that the rate of methanol crossover can be minimized and thus the cell voltage can be maximized. Although this strategy is challenging, some progress has been made over the past few years. The purposes of this article are to review the recent efforts in developing DMFCs that operated with highly concentrated methanol to maximize both the specific energy of the fuel cell system and cell performance and to provide an overview of this emerging research direction. The remainder of this article is organized as follows: Section 2 gives a general description of DMFC systems; key issues associated with transport of the reactants and products in DMFCs operating with concentrated fuel are elaborated in Section 3; Section 4 presents possible approaches to achieving the goal of concentrated fuel operation and reviews past efforts on the management of the individual reactants and products for implementing each of the presented approaches. Several DMFC prototypes that operate with pure methanol are presented in Section 5. Finally, a summary is given in Section 6.

## 2. General description of DMFC systems

Typical DMFC systems include a fuel cell stack that consists of a number of unit cells, a fuel reservoir, and other components to supply/remove and manage reactants/products. As the heart of a DMFC system, the unit cell, as illustrated in Fig. 2, typically consists of a membrane electrode assembly (MEA) that is sandwiched by an anode and a cathode bipolar plate (BP). The BP not only functions as a flow-field to deliver reactants and to remove products, but also collects the current generated in the cell. The MEA is an integrated multi-layered structure that is composed of, in the fol-

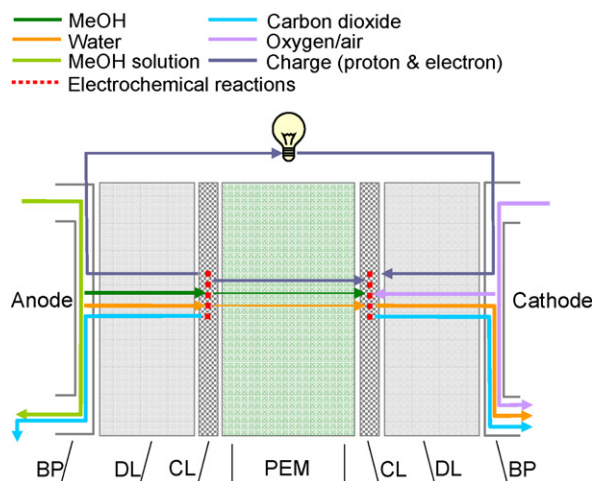
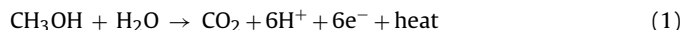
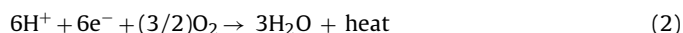


Fig. 2. Illustration of transport processes of different species in a liquid-feed DMFC system.

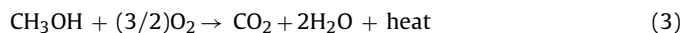
lowing order, an anode diffusion layer (DL), an anode catalyst layer (CL), a polymer electrolyte membrane (PEM), a cathode CL, and a cathode DL. The function of the membrane is to conduct protons from the anode to the cathode, and it simultaneously serves as an electronic insulator between the anode and the cathode. Typically, perfluorinated sulfonic acid ion exchange membranes developed by DuPont and trademarked as Nafion<sup>®</sup> are used in DMFCs. The function of each DL is to provide support for the corresponding CL, to evenly distribute reactants over the CL, and to conduct electricity to the current-collector, i.e., BP. The DLs at both the anode and cathode usually consist of two layers, a backing layer that is made of carbon cloth or carbon paper, and a micro-porous layer (MPL) that is composed of hydrophobic polymer and carbon powder. Different from the DLs, both the CLs are made of catalysts mixed with ionomer to provide triple-phase boundaries for the methanol oxidation and oxygen reduction reactions and thereby facilitate the simultaneous transport of protons, electrons, reactant and products. A methanol/water solution is directly supplied to the anode as the fuel, while oxygen/air is supplied to the cathode as the oxidant. At the anode, methanol reacts with water in the presence of a catalyst, typically a Pt–Ru catalyst, to produce carbon dioxide, protons and electrons, i.e.:



The protons migrate to the cathode through the polymer electrolyte membrane, while the electrons travel to the cathode through an external circuit where electric power is delivered. At the cathode, the protons, electrons and oxygen molecules are combined in the presence of a catalyst, typically a Pt catalyst, to form water, namely:



The two electrochemical reactions (1) and (2) form the following overall cell reaction:



In addition, in a DMFC, methanol may permeate through the membrane from the anode to the cathode, which is known as ‘methanol crossover’. The methanol that crosses over reacts with oxygen at the cathode, which reduces the fuel utilization efficiency and cathode potential, with the result that less power is generated by the fuel cell. In addition to methanol, water also crosses through the membrane. This ‘water crossover’ is driven at least in part by electro-osmotic drag and diffusion, with the result that significant amounts of water are lost from the anode.

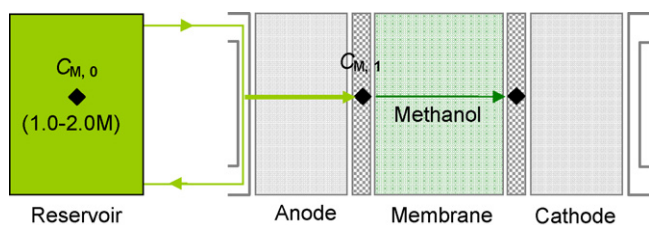


Fig. 3. Illustration of transport process of methanol in a diluted methanol-feed DMFC.

A typical active DMFC system also includes a liquid pump to supply/remove the anode reactant (fuel)/product ( $\text{CO}_2$ ) to/from the anode flow-field, and a gas blower/compressor to supply/remove the cathode reactant (oxygen)/product (water) to/from the cathode flow-field. This type of DMFC system with liquid pumps and gas blowers/compressors is known as an active DMFC. On the other hand, a DMFC system that does not include liquid pumps and gas blowers/compressors is referred to as a passive DMFC. In passive DMFCs, the reactant supply and product removal fully rely on passive forces such as diffusion, capillarity, gravity, and natural convection.

### 3. Critical issues in the supply/removal of reactants/products in DMFC systems

This section describes the supply, removal and transport of reactants and products in a DMFC that include methanol, water, oxygen, and carbon dioxide. The emphasis is placed on identifying the critical issues for managing the supply/removal of the reactants/products so that both the cell performance and the specific energy of DMFCs can be maximized.

#### 3.1. Methanol

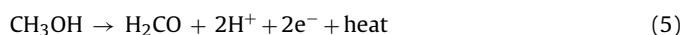
The transport of methanol in a conventional DMFC design is shown in Fig. 3. Methanol stored in the fuel reservoir ( $C_{M,0}$ ) is supplied to the anode flow-field. It then transfers through the anode DL to the anode CL, where the concentration of methanol drops to  $C_{M,1}$  due to the mass-transport resistance in the anode DL. In the anode CL, part of the methanol is consumed by the anode MOR, as indicated by Eq. (1), while the remainder permeates through the membrane and arrives at the cathode, where it is oxidized to create a so-called mixed potential, which decreases the cathode potential. Hence, the rate of methanol crossover needs to be minimized in order to achieve a higher cell voltage. As the transport of methanol through the membrane is dominated by molecular diffusion, reducing the methanol concentration in the anode CL can thus reduce the rate of methanol crossover. On the other hand, too low-methanol concentration in the anode CL will result in a large concentration overpotential, which also decreases the cell voltage. Therefore, it is critical to maintain an adequate methanol concentration ( $C_{M,1}$ ) in the anode CL, which depends on the methanol concentration in the fuel reservoir ( $C_{M,0}$ ) and the mass-transfer resistance in the anode DL.

For a given conventional DL made of carbon paper/cloth, the maintenance of an adequate methanol concentration in the anode CL requires the methanol concentration in the fuel reservoir ( $C_{M,0}$ ) to be relatively low (i.e., 1–2 M for active fuel-supply systems [11,12] and 3–5 M for passive fuel-supply systems [13–15]) so that the cell performance can be maximized. On the other hand, a low fuel concentration in the fuel reservoir means that the specific energy of the fuel cell system will be low. To increase the specific energy of the fuel cell, more concentrated methanol or pure methanol is desired. Hence, how to maintain an adequate methanol

concentration ( $C_{M,1}$ ) in the anode CL with highly concentrated methanol carried in the fuel reservoir is critical to achieve both high cell performance and high system specific energy. Unfortunately, it is difficult to achieve this balance point, as the transport of methanol is intrinsically coupled with the transport of water and  $\text{CO}_2$ . A change in one of the three mass-transport processes of methanol, water and  $\text{CO}_2$  will cause a change in the other two.

#### 3.2. Water

As indicated by Eqs. (1) and (2), water is a reactant on the DMFC anode, but a product on the cathode. In addition, water is also needed in the membrane to ensure the transport of protons. Eq. (1) suggests that the MOR requires the molecular ratio of water to methanol to be 1:1. It is known, however, that the molecular ratio of water to methanol has to be much higher than the stoichiometric 1:1 ratio so that a complete 6-electron anodic oxidation to  $\text{CO}_2$  can be completed [18]. Otherwise, if the water level in the anode CL is insufficient, the MOR will be incomplete to form either formic acid or formaldehyde, i.e.,



The above partial MORs suggest that insufficient water in the anode CL not only results in low cell performance, but also leads to the generation of other hazardous products, for example, formaldehyde. Hence, the molecular ratio of water to methanol must be maintained to be much higher than 1:1. This requirement can be readily met in conventional DMFCs operating with diluted methanol solutions, as sufficient water is contained in the fuel solution. When, however, a DMFC is fuelled with pure methanol or a highly concentrated methanol solution, in which no or little water is carried by the fuel cell system, a critical question is: what is the source of the water required for the MOR?

The cathode ORR, shown in Eq. (2), indicates that 3 mole of water are produced when 1 mole of methanol and 1 mole of water are consumed in the MOR (Eq. (1)). This fact suggests that if one of the 3 mole of water produced on the cathode could be recovered to the anode, the DMFC would operate with pure methanol without additional water to the anode fuel. The critical issue then is how to recover part of the water produced on the cathode and return it back to the anode.

Another issue related to water in a DMFC is the potential problem of water flooding at the cathode, which is particularly true for DMFCs with low-concentration methanol feed [19–21]. Under typical operating conditions, the product water on the cathode needs to be transported to the flow channel and vented out of the cell. If the mass-transport resistance of water from the cathode catalyst layer to the flow-field is too large, the liquid water will accumulate on the cathode to give rise to the so-called water flooding problem, which increases substantially the mass-transfer resistance of oxygen and lowers the cell voltage. In particular, the water flooding problem becomes more serious with increasing current and may eventually lead to a limiting current due to the mass-transport limitation of oxygen. It should be recognized that for a DMFC fed with low-concentration methanol, the presence of high water content at the anode will increase the rate of water crossover through the membrane, thus exaggerating the cathode flooding problem. Therefore, water management that suppresses water crossover and reduces water flooding in the cathode is another critical issue in sustaining DMFC operation.

In summary, in order to make a DMFC operate with concentrated fuel, water in the fuel cell system needs to be managed (i) to maintain a new water balance in a cell when the total water removal from the cell does not exceed the net production of water,

and (ii) to recover some of the produced water from the cathode to the anode.

### 3.3. Carbon dioxide

As a product of the anode MOR,  $\text{CO}_2$  needs to be vented from a DMFC system. If a diluted methanol solution is fed to a DMFC, the presence of gas  $\text{CO}_2$  in the anode flow-field and anode DL may lead to an increase in the methanol-transport resistance from the anode flow-field to the anode CL, resulting in the concentration loss of methanol [22,23]. Also, the presence of gas  $\text{CO}_2$  in the anode flow-field can increase the flow resistance, thus increasing the pumping power of the auxiliary liquid pumps [24] and thereby decreasing the overall efficiency of the fuel cell system. Hence, under the condition of diluted methanol operation, in order to reduce the concentration loss of methanol and the extra pumping work, a faster removal of gas  $\text{CO}_2$  from the DMFC anode is necessary. It should be recognized, however, that if a DMFC operates with pure methanol or highly concentrated methanol, a faster removal of gas  $\text{CO}_2$  from the DMFC will not be required for the following reason. If highly concentrated methanol is supplied to the anode flow-field, a large mass-transport resistance of methanol from the anode flow-field to the anode CL is needed to make the methanol concentration in the anode CL adequate (i.e., sufficiently low to reduce the rate of methanol crossover). As the presence of gas  $\text{CO}_2$  in the anode flow-field and anode DL can increase the mass-transport resistance of methanol from the flow-field to the CL, appropriately controlling the  $\text{CO}_2$  removal from the DMFC anode makes it possible for a DMFC to be operated with a higher concentration of methanol. In addition, a large amount of gas ( $\text{CO}_2$ ) coverage in the anode CL can greatly reduce the local water concentration in the anode CL so that the diffusion flux of water to the cathode can be reduced [25–28], which not only reduces the anode water loss, but also alleviates the problem of cathode flooding. The above discussion indicates that for a given methanol concentration, a proper control of gas  $\text{CO}_2$  removal is required to maintain an adequate methanol concentration in the anode CL. Hence, the critical issue is how to manage the  $\text{CO}_2$  transport process to achieve an optimum gas  $\text{CO}_2$  distribution in the DMFC anode so that a DMFC can operate with concentrated fuel and yield high performance.

### 3.4. Oxygen/air

At the cathode, oxygen/air is transported from the cathode flow-field to the cathode CL, where it reacts with the protons and electrons, coming from the anode, to form water. At high current densities, the mass-transport loss of oxygen through the DMFC cathode may become a factor that limits cell performance. Since the concentration of oxygen/air is fixed, the mass transport of this species depends on the mass-transport resistance only. Hence, the critical issue in the design of the DMFC cathode is how to minimize the oxygen transport resistance from the flow-field to the cathode CL.

Oxygen transport is coupled to the counter-current water transport in the cathode DL. Cathode water flooding in the cathode DL and the flow-field can increase the mass-transport resistance of oxygen from the flow-field to the cathode CL [19–21,29]. A common method to alleviate water flooding is to increase the flow rate of cathode gas to enhance the removal of water and to force oxygen/air flow into the cathode CL so that the overall mass-transport resistance of oxygen through the cathode can be lowered [30]. It should be pointed out that in a DMFC operating with highly concentrated methanol, increasing the gas flow rate to alleviate water flooding may not be a good choice since it will lead to an increase in the rate of water removal from the cathode. As discussed in Section 3.2, however, water is an anode reactant and therefore has to be

recovered from the cathode under pure methanol or highly concentrated methanol operations. Hence, the increased water removal as a result of the cathode gas flow rate will cause the fuel cell operation to move away from the water-neutral operation point. Hence, it is critically important to recognize that in a DMFC operating with pure methanol or highly concentrated methanol, the enhancement of oxygen/air transport has to be considered together with the issue of the water recovery from the cathode so that both oxygen transport loss and water loss can be minimized.

## 4. Approaches to achieving concentrated fuel operation of DMFCs

The discussion in the preceding section suggests that with given catalyst and electrolyte materials, the maximization of both the system specific energy and cell performance in a DMFC system can be achieved if the following design requirements can be met.

- (i) The fuel cell system carries a high-concentration fuel or pure methanol, but little or no water.
- (ii) The fuel cell system should control the delivery of the fuel in such a way that the fuel concentration in the anode CL can be maintained at the appropriate level to minimize the voltage losses due to methanol crossover and methanol transport.
- (iii) The fuel cell system should change ‘water crossover’ in conventional dilute-methanol operating systems to ‘water recovery’ from the cathode to the anode to compensate for the water consumed in the MOR.

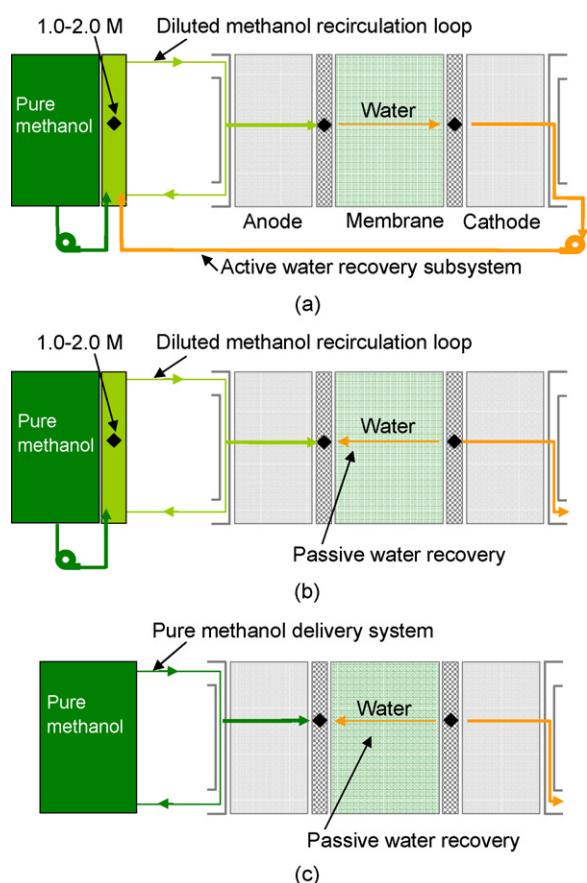
Based on these design requirements, three possible approaches that enable DMFCs to operate with pure methanol are described as follows.

*Approach I:* A diluted methanol recirculation loop with an active water-recovery subsystem.

As is illustrated in Fig. 4a, pure methanol is stored in a reservoir, but no additional water is carried in the fuel cell system. To bring the methanol concentration in the anode CL to an appropriate level, a diluted methanol recirculation loop is interposed between the reservoir and the anode flow-field, in which pure methanol from the reservoir is diluted by the water recovered from the cathode through an active water-recovery subsystem. The diluted methanol (1.0–2.0 M) is then directed to the anode flow-field. The key issue in this approach is how to devise an active water-recovery system such that sufficient water can be collected from the cathode and externally pumped back to the diluted methanol loop. The disadvantage of this system design is that while neat methanol can be carried in the cartridge, the system suffers from excessive complexity due to the need for condensing, pumping and recirculating the water, which results in significant parasitic power losses and an increase in system volume. Such power losses can be particularly severe, relative to fuel cell power output, in the case of small-scale power sources.

*Approach II:* A diluted methanol recirculation loop with passive water recovery through the membrane.

As shown in Fig. 4b, the second approach is essentially similar to Approach I, except that the active water-recovery system in Approach I is changed to a passive process: the water consumed by the anode MOR is provided by pushing liquid water from the cathode back to the anode CL through the membrane. This passive water recovery from the cathode can be realized by an optimum design of MEA, such as increasing the hydrophobicity of the cathode microporous layer (MPL) and DL and utilizing a thinner membrane. In Approach II, since the cathode water is directly recovered to the anode CL (unlike in Approach I) and consumed by the anode MOR, the methanol concentration (i.e., 1.0–2.0 M) in the diluted methanol



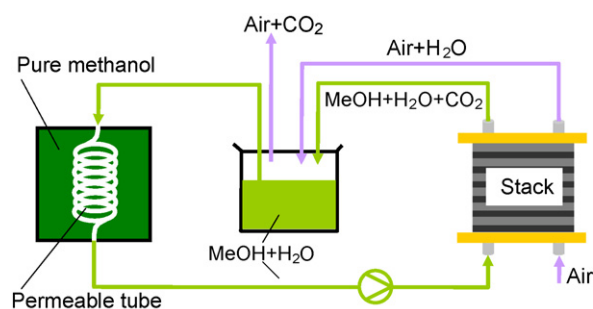
**Fig. 4.** Illustration of three approaches to operate a DMFC with pure methanol. (a) Approach I: diluted methanol recirculation loop with active water-recovery subsystem; (b) Approach II: diluted methanol recirculation loop with passive water recovery through the membrane; (c) Approach III: pure methanol feed with passive water recovery through the membrane.

recirculation loop can be maintained by pure methanol taken from the fuel reservoir. The key issue in the success of this approach is how to configure the MEA to ensure that sufficient of the water generated at the cathode can be pushed back to the anode to achieve the water-neutral operation point. As compared with Approach I, Approach II does not include a pumping system to recover the water from the anode to the cathode, thus making the parasitic power losses smaller.

**Approach III:** A pure methanol feed with passive water recovery through the membrane.

As illustrated in Fig. 4c, the third approach is to introduce pure methanol directly to the anode flow-field, thereby eliminating the diluted methanol recirculation loop in Approaches I and II. As the methanol concentration gradient from the reservoir to the anode CL is excessively steep in this design, the key to the success is how to devise a methanol mass-transport barrier that provides an optimized rate of fuel delivery from a reservoir to the anode CL such that the methanol concentration in the anode CL is maintained at an adequate level. Compared with Approaches I and II, Approach III eliminates both the diluted methanol recirculation loop and the active pumping system to recover the water from the cathode. Hence, Approach III provides the most compact fuel cell system with no parasitic power losses resulting from pumping and recirculation subsystems.

In principle, the three approaches described here enable a DMFC to operate with pure methanol. Practically, however, it is not easy to achieve these approaches, as the transport of methanol and water in a fuel cell needs to be well managed. Moreover, as the transport



**Fig. 5.** An example of Approach I to operate a DMFC stack with pure methanol passively diffused into the diluted methanol-feed tube [32].

of the methanol and water is intrinsically coupled to the transport of CO<sub>2</sub> and oxygen, attention has to be paid to carbon dioxide and oxygen management. Specifically, the transport of gas CO<sub>2</sub> should be well optimized such that both the methanol and water can be appropriately distributed in the DMFC anode to maximize cell performance; at the same time, oxygen/air should be supplied at such a flow rate that minimizes the concentration loss of oxygen and the water loss from the cathode so that sufficient water can be recovered to the anode to sustain the anode MOR. It should be mentioned that each of the approaches described in this article has specific advantages that are best realized in specific situations. In the following, the past efforts to manage the transport of each of the reactants and products (methanol, water, carbon dioxide and oxygen) to achieve the goal of operating DMFCs with concentrated fuel are summarized and discussed.

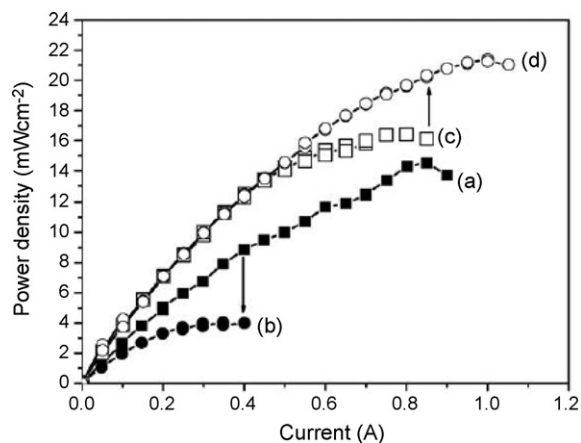
#### 4.1. Methanol management

This section reviews the past efforts to manage the supply and transport of methanol in such a way that maintains the methanol concentration in the anode CL at an appropriate level. Past work is reviewed by dividing it into two subsections. Section 4.1.1 deals with methanol management in a DMFC system with a diluted methanol recirculation loop (i.e., Approaches I and II), while Section 4.1.2 focuses on methanol management in a DMFC system with pure methanol introduced directly to the anode (i.e., Approach III).

##### 4.1.1. Systems with diluted methanol recirculation loops (Approaches I and II)

The key to realizing both Approaches I and II is how to utilize the water produced from the fuel cell system to dilute the pure methanol carried by the fuel cell system before being directed to the anode flow-field. A number of DMFC systems [31–39] that use Approaches I and II have been reported in the open literature. Xie et al. [31] demonstrated a 2-W active DMFC system, in which before being fed to the anode flow-field, a diluted methanol solution was obtained from a mixing chamber where pure methanol from the fuel cartridge was mixed with the liquid water that was actively pumped from the cathode and with the exhausted methanol solution recovered from the anode outlet. A methanol sensor was used to monitor the resulting methanol concentration from the mixing chamber. If the concentration was below the pre-set value (e.g., 1.0M), the liquid pump was started to add pure methanol to the mixing chamber. Another liquid pump was then used to feed the diluted methanol solution to the stack.

A similar diluted methanol recirculation loop was proposed by Oedegaard and Hentschel [32] and is illustrated in Fig. 5. The low-concentration methanol solution from a diluted methanol tank was pumped through a tube to the stack. The novelty of this design was that a portion of the tube was made of a methanol-permeable material (Nafion® tube) and it was passed through a pure methanol tank



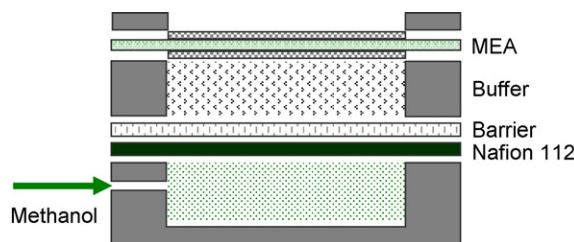
**Fig. 6.** Performance of passive DMFC with fuel reservoir filled with hydrogels [40]: (a) operation with 4.0-M methanol without hydrogels; (b) operation with 8.0-M methanol without hydrogels; (c) operation with 4.0-M methanol soaked in hydrogels; (d) operation with 8.0-M methanol soaked in hydrogels.

such that pure methanol could passively diffuse into the tube. This passive methanol addition eliminates the use of the pure methanol pump in the system described in Ref. [31]. Hence, the overall system can be more compact and consumes less parasitic power. The problem with this system design is that the methanol in the pure methanol tank is continuously diluted by the water permeated from the low-concentration loop, which causes the methanol solution fed to the stack to be gradually reduced. Note that, in order to maintain high and stable cell performance, the methanol concentration in the diluted methanol recirculation loop in DMFC systems [31–39] using Approaches I and II should be accurately and stably controlled at an appropriate level.

#### 4.1.2. Systems without diluted methanol recirculation loops (Approach III)

As discussed earlier, in Approach III, pure methanol is directly transported to the anode CL without going through a diluting process as in Approaches I and II. Hence, the key to the success of this approach is how to devise a methanol mass-transport barrier that provides an optimized rate of fuel delivery from a reservoir so that the methanol concentration in the anode CL can be maintained at an appropriate level. In line with this understanding, various strategies have been proposed [18,40–52] and some of them are highlighted as follows.

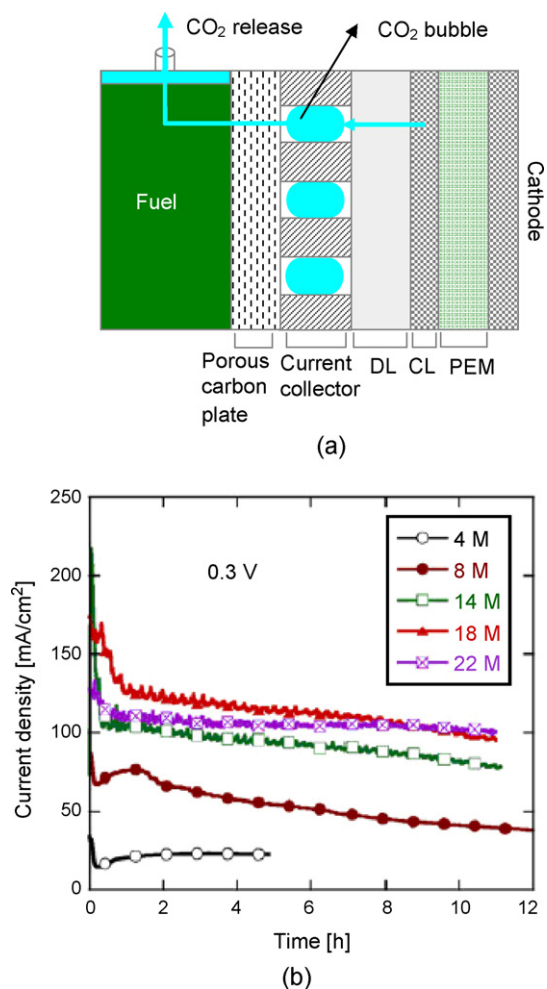
Kim et al. [40,41] developed passive DMFC systems that could operate with 6.0–8.0 M methanol solutions. In their design, the fuel reservoir was filled with hydrogels soaked with methanol. As the release of methanol from the methanol-soaked hydrogels can be extremely slow, the methanol transfer rate to the anode electrode can be very small. Fig. 6 [40] compares the performance obtained with methanol supplied by the methanol-soaked hydrogels or by methanol solutions. For methanol supplied by methanol solutions, it is seen that the maximum power density decreases from 14 to 4  $\text{mW cm}^{-2}$  when the methanol concentration is increased from 4.0 to 8.0 M; the substantial reduction in the performance is obviously due to the problem of methanol crossover. By contrast, when the methanol is supplied by methanol-soaked hydrogels, the power density increases from 16.5 to 21.5  $\text{mW cm}^{-2}$  when the methanol concentration is increased from 4.0 to 8.0 M. This result indicates that the formation of methanol-soaked hydrogels is one way to control the methanol transport from the fuel reservoir to the fuel cell. Another study by the same authors [41] indicated that when a passive DMFC was used to power a cellular phone, it could run for about 40 min at a maximum power of 2.4 W with 18  $\text{cm}^3$  6-M methanol-soaked hydrogels.



**Fig. 7.** Passive DMFC with fuel deliver rate controlled with a pervaporation film (Nafion® 112 herewith) [42].

Another way to control the fuel-delivery rate from a pure methanol reservoir is to evaporate the liquid methanol into the vapour phase and control the evaporation rate. A simple way to evaporate the liquid methanol is to use a so-called “pervaporation” membrane [53], which allows a liquid to permeate through it and evaporate into the vapour phase. For instance, Kim [42] devised the concentrated fuel feed system shown in Fig. 7, which consists of a porous foam, a Nafion® 112 membrane (the pervaporation film), a barrier, and a buffer. With the membrane and a proper design of the barrier and buffer, the fuel cell was able to operate with pure methanol and achieved a maximum power density of 36  $\text{mW cm}^{-2}$ . It was also shown that the fuel cell could continuously operate at power densities that ranged from 25 to 30  $\text{mW cm}^{-2}$  for 360 h which indicated that the system could well control the transport rate of methanol from the pure methanol reservoir to the anode CL. Another example is the work by Eccarius et al. [43,44]. In their designs, in addition to the use of a phase separation membrane as the pervaporation film, a perforated plate was attached to the membrane so that the methanol delivery rate could be finely controlled by adjusting the open ratio of the perforated plate. A similar idea of using a pervaporation membrane to evaporate the liquid fuel to the vapour phase and to limit the fuel-delivery rate has also been described in some patents [18,45].

The fuel-delivery rate can also be controlled by managing the release of the  $\text{CO}_2$  that is produced on the anode CL. For instance, Nakagawa and his co-workers [47–50] devised a fuel-delivery system that consisted of a fuel reservoir, a porous plate, and a perforated current-collector, as shown in Fig. 8a. During operation, methanol can be transported from the fuel reservoir to pass through the porous plate and the openings of the current-collector to arrive at the anode. Simultaneously, the  $\text{CO}_2$  produced at the anode electrode is transported through the same components but in the reverse direction. When the pore size of the porous plate is sufficiently small, the resistance of  $\text{CO}_2$  release becomes large. As such, with proper design of the pore size of the porous carbon plate and the pore size of the perforated current-collector,  $\text{CO}_2$  can be accumulated in the holes of the current-collector to form a gas slug in each hole of the current-collector and thereby create a gas-rich barrier. Consequently, methanol and water in the reservoir have to diffuse as a vapour phase through this gas-rich barrier to the anode electrode such that the transport rate of the methanol to the anode CL can be limited. Hence, a higher methanol concentration can be used. Fig. 8b [49] shows the transient current density of a passive DMFC with the fuel-delivery system shown in Fig. 8a, in which the 1-mm porous plate is made of amorphous carbon (referred to as PCPY1). It is interesting to note that this DMFC system can operate with almost pure methanol (22.0 M) to give fairly high performance. The stable discharge behaviour indicates that the rate of methanol delivery to the anode electrode can be stably regulated by the system. Nevertheless, it should be pointed out that one disadvantage of the above-described fuel-delivery system is that methanol crossover can be serious at low current densities and under open-circuit conditions, because the rate



**Fig. 8.** Passive DMFC with fuel delivering rate controlled by managing release of CO<sub>2</sub> using a porous plate [49]: (a) sketch of cell structure; (b) discharge current densities at constant voltage of 0.3 V for different methanol-feed concentrations.

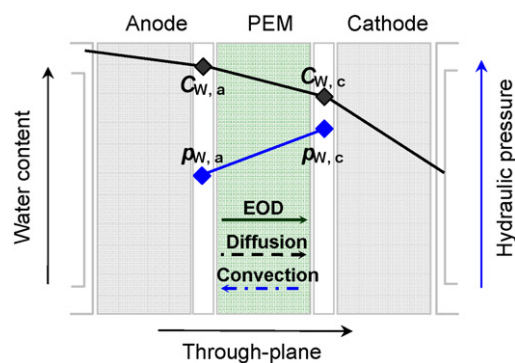
of CO<sub>2</sub> generation is too low to form the gas-rich barrier in the anode.

Still, another way to limit the rate of methanol transport from a fuel source to the anode CL is to increase the mass-transport resistance of the anode DL by using porous materials with excessively small pores and by thickening the layer [51,52]. For example, Zhang and Hsing [51] developed an active DMFC system, in which a single flexible graphite plate was used to form the anode flow-field and DL. As the permeability of this material is rather small, the anode diffusion layer can significantly resist methanol transport from the flow-field to the anode CL. It should be pointed out that the way to increase the mass-transport resistance of the anode DL is limited by the availability of excessively low permeability, electronically conducting, porous materials and by the fact that the DL cannot be too thick.

In addition to the management of methanol delivery and transport discussed above, the successful operation of a DMFC with concentrated fuel also depends on the management of the water. This is addressed next.

#### 4.2. Water management

This section reviews the past work on water management in DMFC systems that are operating with pure methanol. More specifically, consideration is given to the recovery of the water that is produced on the cathode to the anode. The discussion is



**Fig. 9.** Typical profiles of water concentration and pressure across the membrane in a DMFC operating with diluted methanol solution.

divided into two subsections. Section 4.2.1 deals with an active water-recovery system (i.e., Approach I), whereas Section 4.1.2 is concerned with passive water recovery through a membrane (i.e., Approaches II and III).

##### 4.2.1. Active water recovery (Approach I)

In accordance with the concentrated fuel DMFC operation described in Approach I, the water required for the anode MOR is recovered actively from that produced at the cathode. Examples of actively recovering the water from the cathode include the work by Xie et al. [31] and that by Oedegaard and Hentschel [32], in which the product water (mostly in the vapour phase, but also including the liquid water droplets), along with the exhausted air, flowing through the cathode flow-field was pumped to a mixing chamber on the anode. The water vapour was then condensed into the liquid phase and delivered to the diluted methanol recirculation loop, whereas the remaining gases were vented. One disadvantage of this type of active water-recovery subsystem is that it suffers from excessive complexity due to the pumping and condensing components that not only result in significant parasitic power losses, but also increase the system volume. Such power losses can be particularly severe, relative to the fuel cell power output, in the case of small-scale power sources.

Different from the above-described active systems, Yao et al. [54] developed an air-breathing DMFC system, in which water was collected by the cathode current-collector. The water vapour vented from the cathode was condensed at the outer surface of the current-collector and flowed towards a collecting point under the influence of gravity. The liquid water was pumped to the anode. One disadvantage of this system is that the cathode is exposed to the ambient environment and some water may be lost to ambient environment. As a result, the recovered water might not be sufficient to dilute the methanol solution on the anode. Hence, the system cannot operate when the fuel is too concentrated. Another problem with this water-recovery design is that the system renders an orientation-dependent operation, as the water is collected by taking the advantage of gravity. Moreover, the presence of liquid water on the cathode surface may hinder the transport of oxygen to the cathode electrode, thus lowering the cathode potential.

It should be recognized that in the DMFC systems using Approach I, such as [31–37,54], a diluted methanol solution is actually fed to the fuel cell stack although the fuel cell system carries highly concentrated or pure methanol. The typical distributions of water content and pressure across the MEA when its anode is fed a diluted methanol solution are illustrated in Fig. 9. A higher water content at the anode can significantly increase the rate of water crossover from the anode to the cathode through the membrane although a slightly higher liquid pressure can be built up on the DMFC cathode by the capillary action that tends to force

water to flow back to the anode [55–60]. A higher rate of water crossover means a higher rate of water loss from the anode. This fact means that the rate of water recovered from the cathode needs to be increased in response to the anode water loss. Hence, water crossover increases the pumping work of the active water-recovery system and this results in a lower overall fuel cell efficiency. In addition, a higher rate of water crossover can exaggerate the problem of cathode flooding, thus deteriorating the cell performance. For these reasons, the rate of water crossover has to be reduced. Theoretically, the rate of water crossover is determined by electro-osmotic drag (EOD), the water concentration gradient ( $\nabla \cdot C_{W,N}$ ) and the hydraulic pressure difference across the membrane ( $\Delta p_{W,c-a}$ ) as expressed by [25]:

$$N_{W,CR} = \underbrace{n_d \frac{I_{cell}}{F}}_{\text{EOD flux}} - \underbrace{D_{W,N} \nabla \cdot C_{W,N}}_{\text{diffusion flux}} - \underbrace{\frac{\rho_l K_{mem}}{M_W \mu_l} \frac{\Delta p_{W,c-a}}{\delta_{mem}}}_{\text{convection flux}} \quad (6)$$

where  $n_d$  is the electro-osmotic drag coefficient which can reach as high as 2.5 when the membrane is fully hydrated [55]. Therefore, lowering the water content and liquid pressure in the anode CL, or increasing the water content and liquid pressure in the cathode CL can help limit water crossover to the cathode. It has been found [25,61,62] that the water content and liquid pressure in both the anode and the cathode CL can be manipulated by changing the DL, MPL, and CL material properties such as hydrophobicity, permeability and porosity. Based on this understanding, extensive efforts [26–28,52,61,63,64] have been made to reduce the rate of water crossover by optimizing the MEA structure. If the rate of water crossover in the DMFC systems using Approach I can be reduced, the need to recover water from the cathode by an active water-recovery subsystem can be alleviated, thereby minimizing the parasitic power losses associated with the pumping device. Further, if a net flux of water can be internally pushed through the membrane back to the anode by the hydraulic pressure difference created between the anode and cathode DL, the active water-recovery system in Approach I can then be eliminated. This passive water recovery is desired, as the fuel cell system parasitic power losses can be minimized.

#### 4.2.2. Passive water recovery through the membrane (Approaches II and III)

In Approaches II and III, the water required for the anode MOR is internally recovered from the cathode through the membrane. Eq. (1) indicates that to sustain the anode MOR, one of the 3 mole of the water produced by the cathode ORR needs to be recovered, which means that only 2 mole of the water produced on the cathode are allowed to be vented from the cathode (known as cathode water loss). In other words, a critical point in DMFC systems operating with concentrated fuel with the passive water recovery is that the cathode water loss cannot be too large to ensure that sufficient water is recovered to the anode to sustain the MOR. Several studies [43,44,48] have confirmed the importance of controlling the cathode water loss in the DMFCs with a passive water recovery configured MEA. For instance, Eccarius et al. [44] examined the influence of cathode air flow rates (at stoichiometries of 2, 4 and 6 with a minimum flow rate of 40 sccm) on both the anode and cathode potential losses (or cathode overpotential) in a vapour-feed DMFC operating with concentrated fuel. As shown in Fig. 10a, the cathode potential loss decreases with increasing air flow rate as a result of the enhanced mass transport of oxygen to the cathode CL. By contrast, however, Fig. 10b shows that the anode potential loss increases with the air flow rate, as a higher air flow rate leads to a larger cathode water loss which, in turn, causes the water recovery from the cathode to the anode to become insufficient. More interestingly, Fig. 10b shows that the limiting current density of the MOR

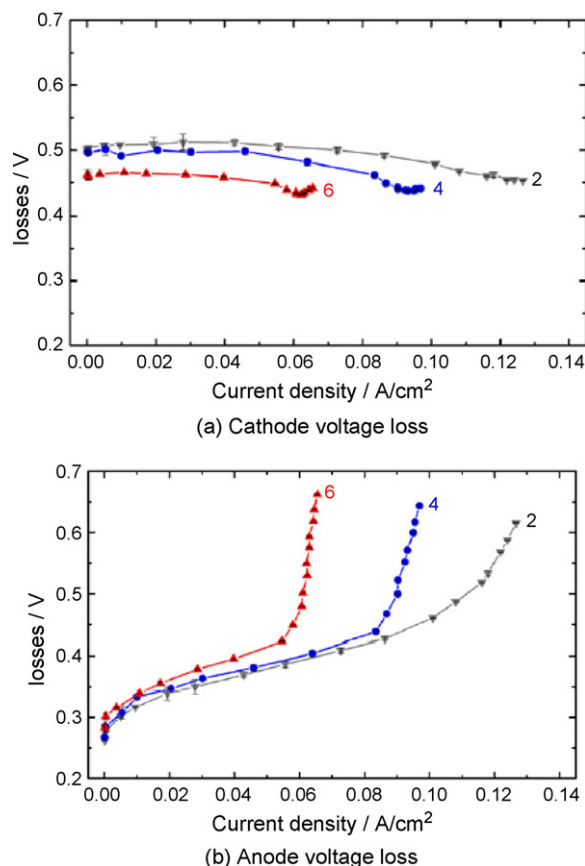


Fig. 10. Effects of cathode air flow rates (at stoichiometries of 2, 4 and 6 with minimum flow rate of 40 sccm) on: (a) cathode voltage loss; (b) anode voltage loss (temperature: 50 °C) [44].

dramatically decreases from 130 to 60 mA cm<sup>-2</sup> when the cathode air stoichiometry is tripled. As the supply of methanol vapour to the anode CL remains the same, the decrease in limiting current density is solely attributed to the decrease in the water flux recovered from the cathode. The result implies that an increase in the cathode air flow rate will increase the water loss from the cathode, thus annulling the water flux recovered from the cathode. As a result, measures should be taken to control the rate of cathode water loss in DMFC systems with passive water recovery MEA.

With a minimum cathode water loss or sufficient water availability at the cathode, the issue now is how to create a sufficiently large pressure between the anode and cathode CL to drive water to the anode. Special attention should be paid to DMFCs that use Approach II, in which the higher water content at the anode creates a potential for water crossover from the anode to cathode as a diluted methanol is fed to the anode CL. In this case, a much higher cathode liquid pressure is required to drive the water flow to the anode to counteract both the water fluxes by EOD and diffusion. Several studies [65,66] have been reported to recover passively water from the cathode to the anode by designing the optimum cathode structure for low-concentration liquid-feed DMFCs. Peled et al. [65] proposed a highly hydrophobic liquid-water-proof structure for the DMFC cathode that was formed by coating several hydrophobic sub-layers on both sides of the cathode current-collector. Each sub-layer was a paste that consisted of 20–50 wt.% Teflon and carbon powders with a thickness of 20–50 μm. This structure can create very high hydraulic liquid pressure at the cathode. By applying such a liquid-water-proof structure to the air-breathing cathode of a low-concentration liquid-feed DMFC, Blum et al. [66] managed to decrease the factor  $W$  (the ratio of the



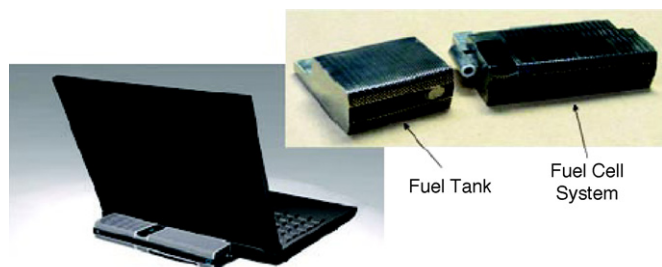


Fig. 11. Fully integrated DMFC for powering a laptop computer by PolyFuel Inc. [39].

molecules of water vented out from the cathode to the molecules of methanol consumed by the anode MOR) from 7 to 2. This means that the water required for the anode MOR at a certain discharging current is recovered internally from the cathode and only the remaining water is vented from the cathode diffusion mediums to the ambient environment. This result indicates that a water-neutral operation point can be achieved in a low-concentration liquid-feed DMFC by the optimized cathode structure, which enables the successful operation of a DMFC described in Approach II. PolyFuel Inc. [39] has recently demonstrated a DMFC prototype for powering a laptop computer, as shown in Fig. 11. The design of this prototype is based on Approach II, in which a novel MEA enables passive water recovery from the cathode to achieve operation with pure methanol [38].

Unlike Approach II, in which diluted methanol is fed to the anode CL, in Approach III, pure methanol is delivered directly to the anode CL. Consequently, the water distributions across the MEA for the two approaches are different. Fig. 12 shows the typical distributions of water concentration and hydraulic pressure across the MEA when the anode is directly fed with pure or highly concentrated methanol. Since little or no water is fed to the anode, the water content at the anode becomes relatively lower than that at the cathode, where water is produced by the cathode ORR and by the oxidation of the permeated methanol, and then water can naturally diffuse from the cathode through the membrane to the anode. In this case, water recovery by modifying the cathode DL becomes much easier [67,68]. For instance, Guo and Faghri [67] proposed a water-management system for a DMFC, in which the integration of the MPL, the hydrophobic backing layer and an air filter created a high water concentration and high liquid pressure at the cathode to recover water to the anode, thus enabling the DMFC to operate with pure methanol. With a charge of 5.1 g of pure methanol, the prototype system demonstrated a continuous operation of 18 h with a total power output of 1.56 Wh. Another example is the work by Kim [42], who developed a vapour-feed

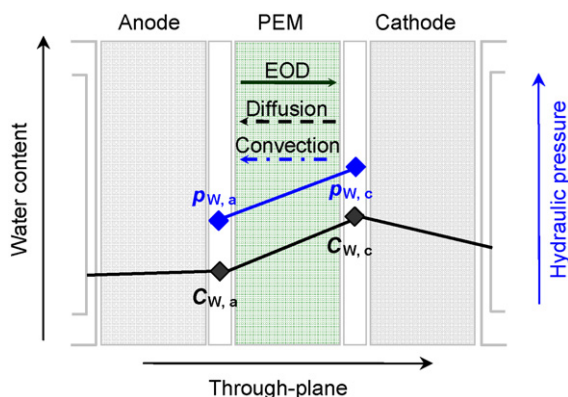


Fig. 12. Typical profiles of water concentration and pressure across the membrane in a DMFC operating with pure methanol.

passive DMFC that operated with pure methanol; after starting the fuel cell with pre-humidifying the MEA, it could run for 15 days at a stable power density of around  $25\text{--}30\text{ mW cm}^{-2}$ . This proved that the water required by the MOR could be continuously supplied by passive water recovery from the cathode.

In summary, it has been demonstrated that in DMFC systems using pure or highly concentrated methanol, the water required by the MOR can be supplied by either active or passive water-recovery systems. Passive water recovery is more desirable for cases where the system volume and weight, as well as the minimization of parasitic power losses, are critical.

#### 4.3. Carbon dioxide management

As the transport process of  $\text{CO}_2$  from the anode CL to the anode flow-field is intrinsically coupled with the transport of methanol and water, achieving an appropriate distribution of  $\text{CO}_2$  at the anode by controlling  $\text{CO}_2$  removal from the cell can help to obtain the distributions of methanol and water that are necessary for achieving high-concentration methanol operations [25–28,47–50,69–71]. For example, several studies [25–28] have indicated that increasing the gas-void fraction in the anode CL by optimizing the structures of the anode DL, MPL and CL, which decreases both the methanol concentration and the water content in the anode CL, can greatly reduce the rates of water crossover and methanol crossover. As discussed earlier in Section 4.1 and shown in Fig. 8a, the anode structure created by Nakagawa and his co-workers [47–50] was to control the delivery rate of the methanol from the reservoir to the anode electrode by controlling the transport of  $\text{CO}_2$  and its distribution in the anode. As a result, the DMFC could operate with pure methanol. In addition, the  $\text{CO}_2$  produced by the anode MOR was utilized to feed the methanol solution to the cell [69–71], which thus made the use of a liquid methanol pump in the DMFC system unnecessary, thereby offering the benefit of reducing both the system volume and the parasitic power losses.

#### 4.4. Oxygen/air management

The oxygen management in a DMFC system operating with highly concentrated fuel is somewhat different from that operating with a diluted methanol solution. In conventional active DMFC systems operating with diluted methanol, as water crossover is more serious and tends to exaggerate the cathode flooding problem, a high cathode gas flow rate is usually needed to enhance the oxygen transport and minimize the cathode potential loss associated with oxygen transport. A high gas flow rate will, however, cause a problem for the passive water recovery in DMFC systems operating with concentrated fuel as described in Approaches II and III, because increasing the cathode gas flow rate will augment the cathode water loss, which can cause the flux of water recovery to be insufficient for the MOR. Abdelkareem and Nakagawa [48] examined the impacts of both air-breathing and active oxygen supply modes on the flux of water recovery and the flux of methanol crossover through the membrane. The results are shown in Fig. 13a. It is interesting to note that when the oxygen flow rate was increased from 100 to 1000 sccm, the flux of the water recovery through the membrane reduced by half, but the flux of methanol crossover was nearly doubled. On the other hand, the air-breathing mode resulted in the largest flux of water recovery, but the smallest flux of methanol crossover. The transient cell discharging current density at a constant voltage corresponding to the different oxygen supply modes is shown in Fig. 13b [48]. As can be seen, for the DMFC that operates with 16.0-M methanol solution, the air-breathing mode results in the best performance, but the active oxygen supply at 1000 sccm leads to the worst performance although the high gas flow rate enhances the oxygen transport.

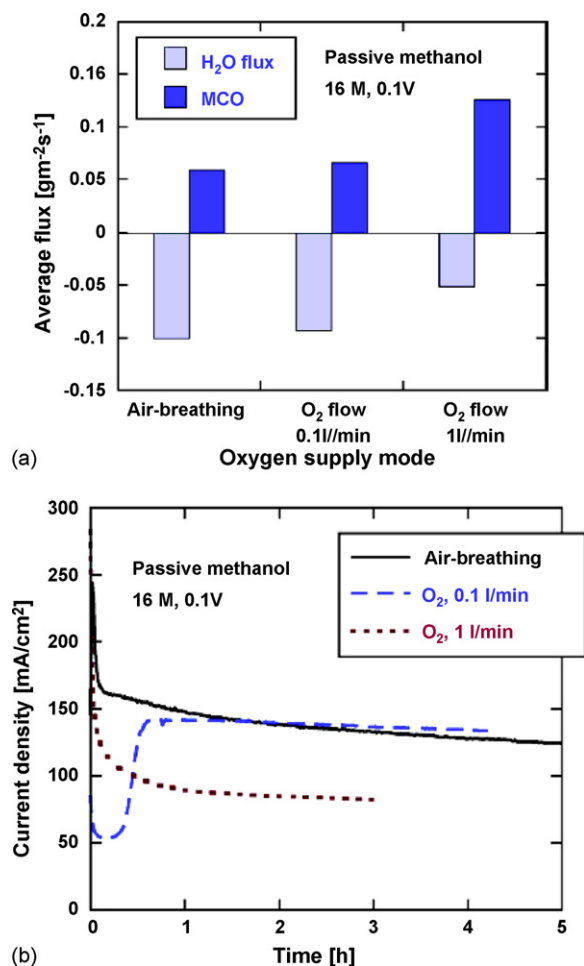


Fig. 13. Effect of oxygen flow rate on: (a) fluxes of methanol crossover and water recovery; (b) discharge current density of passive DMFC operating with 16 M and discharging at a constant voltage of 0.1 V [48].

Hence, in DMFC systems operating with concentrated fuel with passive water recovery (i.e., Approaches II and III), a low cathode gas flow rate or an air-breathing mode is preferable.

## 5. Prototypes

This section describes some DMFC prototypes that operate with pure methanol. Examples use the three approaches illustrated in Fig. 4. The 2-W DMFC system by Xie et al. [31] (Motorola Lab) belongs to Approach I, as sketched in Fig. 4a. Because of its active operation, the performance of such a system can be easily monitored. More importantly, the system capacity can be easily scaled



Fig. 14. Micro charger with removable fuel cartridge by MTI Micro Fuel Cells Inc. [73].

up by sandwiching more cell units together to service higher-power applications. To sustain the operation of such a system, however, several ancillary subsystems including a methanol dilution subsystem, a low-concentration methanol recirculation subsystem and active water-recovery subsystem, are required. By estimation, the ancillary subsystems take up almost 42% of the overall system volume. This reduces not only the specific energy and overall efficiency but also the design flexibility when the required size of the fuel cell system is small. To achieve 48-h continuous operation, a volume of 200-cc pure methanol will be required and the total system volume (including the fuel) will reach 0.694 L. The DMFC system can only provide a specific energy of  $155 \text{ Wh L}^{-1}$  and the overall system efficiency of 20%.

The DMFC prototype, as shown in Fig. 11, developed PolyFuel Inc. [39] belongs to Approach II shown in Fig. 4b. The prototype was applied for powering an all-day true wireless laptop computer. As the design allows passive water recovery through the membrane instead of using an active water-recovery subsystem, the DMFC system is greatly simplified and the overall system efficiency is improved. The prototype produced a net output of 15 W with a run time of 10 h with a single fuel cartridge. The system achieves a specific energy of  $325 \text{ Wh L}^{-1}$  with a single fuel cartridge and  $435 \text{ Wh L}^{-1}$  with two cartridges.

MTI Micro developed several DMFC prototypes [72–74] that belong to Approach III; the system is sketched in Fig. 4c. In this design, pure methanol is directly fed to the anode electrode by a novel fuel methanol delivery subsystem and the water required for the MOR is passively recovered through the membrane. Their latest prototype, a charger with a removable fuel cartridge is shown

Table 1  
Technical specifications of some DMFC prototypes.

	Application (power)	System volume-based energy (see Eq. (7))	Fuel volume-based energy (see Eq. (8))	Conversion efficiency (see Eq. (9))
Motorola Lab [31]	Charger (1 W) Charger (2 W)	$77 \text{ Wh L}^{-1}$ (62 h with 100-cc methanol) $155 \text{ Wh L}^{-1}$ (48 h with 200-cc methanol)	$\sim 620 \text{ Wh L}^{-1}$ $\sim 956 \text{ Wh L}^{-1}$	$\sim 13\%$ $\sim 20\%$
PolyFuel Inc. [39] MTI Micro Fuel Cells Inc. [73]	Laptop computer (15 W) Charger (1 W)	$325 \text{ Wh L}^{-1}$ (10 h on a single fuelling)	$\sim 1800 \text{ Wh kg}^{-1}$ $\sim 1420 \text{ Wh L}^{-1}$	$\sim 29\%$
LG Chem [75]	Laptop computer (25 W)	$\sim 250 \text{ Wh L}^{-1}$ (10 h with 200-cc methanol)	$\sim 1250 \text{ Wh L}^{-1}$	$\sim 26\%$
Toshiba [76]	Handheld device (1 W)	$143 \text{ Wh L}^{-1}$ (20 h with 25-cc methanol)	$\sim 800 \text{ Wh L}^{-1}$	$\sim 16\%$
Samsung [77]	Laptop computer	(100 Wh on a single fuelling)	$\sim 1000 \text{ Wh L}^{-1}$	$\sim 20\%$
SFC Smart Fuel Cell [78]	Electric vehicle	(11.1 kWh on a single fuelling)	$\sim 1110 \text{ Wh L}^{-1}$	$\sim 23\%$

in Fig. 14 [73]; it is capable of providing up to 25 Wh of handheld power with a single, pure methanol cartridge. The specific energy of this prototype can be as high as 1800 Wh kg<sup>-1</sup> (i.e., an energy density of about 1420 Wh L<sup>-1</sup>) at an overall energy-conversion efficiency of 29%. It should be mentioned here that in-series connected fuel cell stacks can be classified into two types: a bipolar stack and a monopolar stack. Passive DMFC stacks usually adopt the monopolar arrangement as this arrangement allows the air-breathing cathode to be completely exposed to ambient air to maximize oxygen transport. A monopolar stack has a smaller volumetric power density than a bipolar design. For this reason, the DMFC systems based on Approach III are more suitable for low-power applications.

In addition to the prototypes introduced above, many other companies [75–78] have also unveiled DMFC prototypes for powering different devices, such as handheld electronics, laptop computers, and even electric vehicles. The specifications of these prototypes are presented in Table 1, in which the second column shows the applications of the prototypes, the third column gives the system volume-based energy on a single fuelling, the fourth column is the fuel volume-based energy, and the fifth gives the overall energy-conversion efficiency. The system volume-based energy, the fuel volume-based energy, and the energy-conversion efficiency are defined, respectively, as:

$$E_{\text{System-volume}} = \frac{\text{electrical energy output with a single fuelling (Wh)}}{\text{volume of system including fuel cartridge (L)}} \quad (7)$$

$$E_{\text{Fuel-volume}} = \frac{\text{electrical energy output for an infinite number of fuelling (Wh)}}{\text{volume of fuels (L)}} \quad (8)$$

and

$$\eta_{\text{conversion}} = \frac{\text{electrical energy output (Wh)}}{\text{energy input of methanol (Wh)}} \quad (9)$$

As shown in the Table 1, the fuel volume-based energies of the prototypes operating with pure methanol are much higher than the energy density of a state-of-art Li-ion battery (about 350 Wh L<sup>-1</sup> [3]). Since the total volume of a stand-alone DMFC system is dominated by the volumes of the fuel cell stack and the ancillary subsystems (or components), the system volume-based energies (i.e., energy density) on a single fuelling of the DMFC prototypes are typically low. Hence, it is critically important to make the fuel cell system more compact. Moreover, it has been found that the energy-conversion efficiency of all the prototypes presented in the Table 1 is still low (below 30%). Therefore, effort is also needed to increase the energy-conversion efficiency of DMFC systems.

## 6. Concluding remarks

With a state-of-the-art polymer electrolyte membrane and electrocatalyst materials, the ability to use highly concentrated or pure methanol in direct methanol fuel cells with fairly high performance brings this type of fuel cell closer to commercialization, particularly for portable and mobile applications (e.g., notebook computers, mobile phones, personal data assistants). This article has provided a comprehensive review of past efforts on the design and optimization of DMFC systems that operate with concentrated methanol. Based on the understanding of the key issues associated with the transport of the reactants (methanol and water at the anode, as well as oxygen at the cathode) and products (CO<sub>2</sub> at the anode and water at the cathode) in the DMFC system structure, the strategies to operate DMFCs with concentrated fuel are: (i) limiting the delivery rate

of the fuel so that the fuel concentration is at the appropriate level when it comes into contact with the anode CL; (ii) changing ‘water crossover’ in conventional diluted methanol operating systems to ‘water recovery’ from the cathode to the anode to compensate for the water consumed by the MOR; (iii) optimizing the removal of CO<sub>2</sub> from the cell to help maintain the methanol concentration and the water content in the anode CL at an appropriate level and (iv) controlling the cathode oxygen flow rate to an appropriate level that minimizes the concentration loss of oxygen and the excessive water loss from the cathode so that sufficient water can be recovered for the anode.

The strategies for operating highly concentrated DMFCs have now become clear and some advances have been made over the past few years. Nevertheless, a number of published works to realize these strategies are limited. A rapid growth in publications about operating DMFCs with highly concentrated fuel is anticipated. Issues dealing with methanol transport from the highly concentrated fuel source to the anode CL have been addressed, but more extensive work in this direction is anticipated. Particularly, the understanding of the mechanisms of methanol evaporation and transport in counter-convected and diffused CO<sub>2</sub> in a porous electrode structure is limited. Attention also needs to be paid to how the fuel-delivery rate can be controlled in response to the fuel cell discharging current. With respect to water management, more extensive work has to be undertaken to optimize the MEA structure in such a way that both water recovery and removal can be managed to ensure sufficient water recovery for the MOR and also to avoid the problem of cathode water flooding. Little research has been conducted on the control of CO<sub>2</sub> release and transport to realize the desirable distributions of methanol and water in the anode for pure methanol operation. The key issue concerning the cathode oxygen/air supply in DMFCs operating with highly concentrated fuel is how to minimize both the concentration loss of oxygen and the water loss from the cathode. In addition, thermal management in DMFCs operating with concentrated fuel has still to be addressed. Particular attention needs to be directed towards finding a means to maintain an appropriate cell operating temperature that can maximize the cell performance. Finally, a scientifically sound numerical approach for designing and optimizing DMFCs operating with concentrated fuel should be developed to guide future efforts.

## Acknowledgement

The work described in this paper was fully supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. 623008).

## References

- [1] J. Larminie, A. Dicks, *Fuel Cell Systems Explained*, 2nd ed., Wiley, West Sussex, 2003.
- [2] R. Dillon, S. Srinivasan, A.S. Arico, V. Antonucci, *J. Power Sources* 127 (2004) 112–126.
- [3] *Fuel Cells Bull.* October (2007) 12–15.
- [4] U.A. Icardi, S. Specchia, G.J.R. Fontana, G. Saracco, V. Specchia, *J. Power Sources* 176 (2008) 460–467.
- [5] S. Wasmus, A. Küver, *J. Electroanal. Chem.* 461 (1999) 14–31.
- [6] H. Liu, C. Song, L. Zhang, J. Zhang, H. Wang, D.P. Wilkinson, *J. Power Sources* 155 (2006) 95–110.
- [7] E. Antolini, T. Lopes, E.R. Gonzalez, *J. Alloys Compd.* 461 (2008) 253–262.
- [8] A. Heinzel, V.M. Barragan, *J. Power Sources* 84 (1999) 70–74.
- [9] V. Neburchilov, J. Martin, H. Wang, J. Zhang, *J. Power Sources* 169 (2007) 221–238.
- [10] N.W. Deluca, Y.A. Elabd, *J. Polym. Sci. B: Polym. Phys.* 44 (2006) 2201–2225.
- [11] S. Surampudi, S.R. Narayanan, E. Vamos, H. Frank, G. Halpert, A. Laconti, J. Kosek, G.K. Surya Prakash, G.A. Olah, *J. Power Sources* 47 (1994) 377–385.
- [12] M.K. Ravikumar, A.K. Shukla, *J. Electrochem. Soc.* 143 (1996) 2601–2606.
- [13] R. Chen, T.S. Zhao, *J. Power Sources* 152 (2005) 122–130.
- [14] B. Bae, B.K. Kho, T. Lim, I. Oh, S. Hong, H.Y. Ha, *J. Power Sources* 158 (2006) 1256–1261.

- [15] J.G. Liu, T.S. Zhao, R. Chen, C.W. Wong, *Electrochem. Commun.* 7 (2005) 288–294.
- [16] C.K. Dyer, *Sci. Am.* (1999) 88–93.
- [17] W. Vielstich, *J. Braz. Chem. Soc.* 14 (2003) 503–509.
- [18] X. Ren, J.J. Becerra, R.S. Hirsch, S. Gottesfeld, US Patent 7407721 B2.
- [19] T.S. Zhao, C. Xu, R. Chen, W.W. Yang, *Prog. Energy Combust. Sci.* 35 (2009) 275–292.
- [20] T.S. Zhao, R. Chen, W.W. Yang, C. Xu, *J. Power Sources* 191 (2009) 185–202.
- [21] H. Li, Y. Tang, Z. Wang, Z. Shi, S. Wu, D. Song, et al., *J. Power Sources* 178 (2008) 103–107.
- [22] C.W. Wong, T.S. Zhao, Q. Ye, J.G. Liu, *J. Electrochem. Soc.* 152 (2005) A1600–A1605.
- [23] W.W. Yang, T.S. Zhao, C. Xu, *Electrochim. Acta* 53 (2007) 853–862.
- [24] M.D. Lundin, M.J. McCready, *J. Power Sources* 172 (2007) 553–559.
- [25] W.W. Yang, T.S. Zhao, *J. Power Sources* 188 (2009) 433–446.
- [26] Q.X. Wu, T.S. Zhao, R. Chen, W.W. Yang, *J. Power Sources* 191 (2009) 304–311.
- [27] C.E. Shaffer, C.Y. Wang, *ECS Trans.* 16 (2008) 1507–1518.
- [28] F.Q. Liu, C.Y. Wang, *Electrochim. Acta* (2008) 5517–5522.
- [29] C. Xu, T.S. Zhao, *Electrochem. Commun.* 9 (2007) 497–503.
- [30] F.Y. Zhang, X.G. Yang, C.Y. Wang, *J. Electrochem. Soc.* 153 (2006) A225–A232.
- [31] C. Xie, J. Bostaph, J. Pavio, *J. Power Sources* 136 (2004) 55–65.
- [32] A. Oedegaard, C. Hentschel, *J. Power Sources* 158 (2006) 177–187.
- [33] C.Y. Wang, G.Q. Lu, F.Q. Liu, T. Akiyama, US Patent 0141338 A1, 2006.
- [34] M. Takada, C.Y. Wang, US Patent 0190378 A1, 2007.
- [35] D.K. Sohn, S.K. Kang, K.H. Choi, Y.J. Kim, US Patent 0178358 A1, 2007.
- [36] H. Miyamoto, N. Tomimatsu, N. Shibuya, US Patent 0231649 A1, 2007.
- [37] T. Noh, G. Moon, US Patent 0224465 A1, 2007.
- [38] A. Mossman, B. Wells, R. Barton, H. Voss, US Patent 079529, 2008.
- [39] PolyFuel Inc., Annual Merit Review Proceedings Fuel Cells Hydrogen Program, DOE, USA, 2008, [http://www.hydrogen.energy.gov/annual\\_review08\\_fuelcells.html](http://www.hydrogen.energy.gov/annual_review08_fuelcells.html).
- [40] W.J. Kim, H.G. Choi, Y.K. Lee, J.D. Nam, S.M. Cho, C.H. Chung, *J. Power Sources* 157 (2006) 193–195.
- [41] W.J. Kim, H.G. Choi, Y.K. Lee, J.D. Nam, S.M. Cho, C.H. Chung, *J. Power Sources* 163 (2006) 98–102.
- [42] H.K. Kim, *J. Power Sources* 162 (2006) 1232–1235.
- [43] S. Eccarius, X. Tian, F. Krause, C. Agert, *J. Micromech. Microeng.* 18 (2008) 1–9.
- [44] S. Eccarius, F. Krause, K. Beard, C. Agert, *J. Power Sources* 182 (2008) 565–579.
- [45] X. Ren, F.W. Kovacs, K.J. Shufon, S. Gottesfeld, US Patent 2008/0032182 A1, 2008.
- [46] Y.H. Pan, *Electrochem. Solid-State Lett.* 9 (2006) A349–A351.
- [47] N. Nakagawa, M.A. Abdelkareem, K. Sekimoto, *J. Power Sources* 160 (2006) 105–116.
- [48] M.A. Abdelkareem, N. Nakagawa, *J. Power Sources* 165 (2007) 685–691.
- [49] M.A. Abdelkareem, N. Morohashi, N. Nakagawa, *J. Power Sources* 172 (2007) 659–665.
- [50] M.A. Abdelkareem, N. Nakagawa, *J. Power Sources* 162 (2006) 114–123.
- [51] H. Zhang, I.M. Hsing, *J. Power Sources* 167 (2007) 450–454.
- [52] F.Q. Liu, G.Q. Lu, C.Y. Wang, *J. Electrochem. Soc.* 153 (2006) A543–A553.
- [53] X. Feng, R. Huang, *Ind. Eng. Chem. Res.* 36 (1997) 1048–1066.
- [54] S.C. Yao, X. Tang, C.C. Hsieh, Y. Alyousef, M. Vladimer, G.K. Fedder, et al., *Energy* 31 (2006) 636–649.
- [55] X. Ren, W. Henderson, S. Gottesfeld, *J. Electrochem. Soc.* 144 (1997) L267–270.
- [56] R. Jiang, D. Chu, *J. Electrochem. Soc.* 155 (2008) B798–B803.
- [57] G.Q. Lu, F.Q. Liu, C.Y. Wang, *Electrochem. Solid-State Lett.* 8 (2005) A1–A4.
- [58] C. Xu, T.S. Zhao, *J. Power Sources* 168 (2007) 143–153.
- [59] S. Ge, B. Yi, P. Ming, *J. Electrochem. Soc.* 153 (2006) A1443–A1450.
- [60] W.W. Yang, T.S. Zhao, *J. Power Sources* 190 (2009) 216–222.
- [61] C. Xu, T.S. Zhao, Y.L. He, *J. Power Sources* 171 (2007) 268–274.
- [62] C. Xu, T.S. Zhao, W.W. Yang, *J. Power Sources* 178 (2008) 291–308.
- [63] G. Jewett, Z. Guo, A. Faghri, *J. Power Sources* 168 (2007) 434–446.
- [64] H.K. Kim, J.M. Oh, J.H. Kim, H. Chang, *J. Power Sources* 162 (2006) 497–501.
- [65] E. Peled, A. Blum, A. Aharon, M. Philosoph, Y. Lavi, *Electrochem. Solid-State Lett.* 6 (2003) A268–A271.
- [66] A. Blum, T. Duvdevani, M. Philosoph, N. Rudoy, E. Peled, *J. Power Sources* 117 (2003) 22–25.
- [67] Z. Guo, A. Faghri, *J. Power Sources* 160 (2008) 1142–1155.
- [68] F.Q. Liu, C.Y. Wang, *ECS Trans.* 2 (2007) 79–84.
- [69] Y.H. Chan, T.S. Zhao, R. Chen, C. Xu, *J. Power Sources* 176 (2008) 183–190.
- [70] Q. Ye, T.S. Zhao, *J. Power Sources* 147 (2005) 196–202.
- [71] S. Gottesfeld, US Patent 6686081 B2, 2004.
- [72] MTI Micro Fuel Cells Inc., Annual Merit Review Proceedings Fuel Cells Hydrogen Program, DOE, USA, 2008, [http://www.hydrogen.energy.gov/annual\\_review08\\_fuelcells.html](http://www.hydrogen.energy.gov/annual_review08_fuelcells.html).
- [73] *Fuel Cells Bull.* December (2008) 1.
- [74] <http://www.mtimicrofuelcells.com>.
- [75] *Fuel Cells Bull.* November (2005) 5.
- [76] *Fuel Cells Bull.* December (2003) 2.
- [77] *Fuel Cells Bull.* June (2004) 6.
- [78] *Fuel Cells Bull.* December (2008) 3.