BARRIERS TO COMMERCIALIZATION OF PASSIVE DIRECT METHANOL FUEL CELLS: A REVIEW

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Abstract

Fuel cells are electro-chemical reactors which realize the direct conversion of the chemical energy of reactants to electrical energy, with high efficiency and high environmental compatibility. This article is concerned with one of the most advance fuel cells- direct methanol fuel cells (DMFCs). We present a comprehensive review on the commercialization barriers of passive DMFCs. The paper also summarizes past research efforts and possible future directions towards these problems.

Keywords: direct methanol fuel cell; DMFC; passive; commercialization.

1. Introduction

Fuel cell is a device that converts the chemical energy stored in a fuel directly into electrical energy and heat through the electrochemical reactions. Fuel cell systems have received much attention in recent years because of the increasing price of petroleum and its potential for wide range of applications. Fuel Cells are expected to be the next generation of power sources with the advantages of high efficiency and low pollution. Today, Fuel cells are extensively being studied because of its potential for a wide range of applications.

Amongst the various types of fuel cells, the direct methanol fuel cells (DMFC) have attracted extensive interest from the research community and industry since its is simple in construction, which does not require use of reformers and humidifiers. ‘Passive’ DMFC, which does not have any external pumps or other ancillary device for reactant supply or product removal has been critically investigated recently. Since passive DMFCs have much simpler structures than conventionally active DMFCs (with fuel pumps and oxidant suppliers), and the parasitic power loss from ancillary devices is eliminated, they have been considered as more promising power sources for portable power sources.

The goal of this paper is to review the various critical issues that have been considered as barriers for commercialization of passive DMFC. Sluggish anode kinetics, methanol crossover, problems of species and heat management and high cost have been described in details with the summary of past research efforts. The general approach in this paper is to outline the issues and problems followed by approaches with examples.

2. Working Principle

Construction of the passive DMFC is shown in fig. 1. Its components are fuel reservoir, anode current collector (ACC), anode gas diffusion layer (AGDL), anode catalyst layer (ACL), membrane, cathode catalyst layer (CCL), cathode gas diffusion layer (CGDL), cathode current collector (CCC). The methanol water mixture from reservoir reaches to ACL mainly by diffusion, where electrochemical reaction occurs as:

\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} = 6\text{H}^+ + 6\text{e}^- + \text{CO}_2 + \text{heat} \]

Generated electron flows through external circuit, proton flows through PEM and both reaches to CCL where it reacts with oxygen and produces water. Carbon dioxide generated at anode and water generated at cathode is vented out of the cell by passive means. Cathode reaction is:

\[ 6\text{H}^+ + 6\text{e}^- + \frac{3}{2}\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O} + \text{heat} \]
3. Commercialization Barriers

3.1. Sluggish anode kinetics

The DMFC has one of the highest application prospects as an energy converter for zero-emission vehicles (ZEVs) and low power portable devices. However, the methanol oxidation reaction at the anode catalyst significantly limits the performance of the DMFC due to the relatively poor methanol oxidation kinetics with presently known catalyst materials (Pt:Ru bimetallic anode catalyst and Pt as cathode catalyst). Rate of methanol oxidation reaction at DMFC anode is quite slow as compared to that of hydrogen in PEM Fuel Cell anode. This leads to high “activation overpotential” and lower performance of the cell. To improve the anode kinetics high catalyst loading, 2mg/cm² or more is used [1]. But this also increases the cost of the cell.

To improve the methanol oxidation rate, the research splits in two directions:

- Development of new, more active, catalysts [3-7]. Hogarth and Ralph showed that the methanol electro-oxidation activity of PtRu/C was found to be the highest among the binary Pt-based alloys [7]. The authors of [3] proved the Pt–Ru–Mo as most active ternary catalyst among the Pt–Ru–X (X = Mo, Co, Sn, Cu, Fe, Ni, W) deposited on a polyaniline matrix. It was found ten times active than that of Pt–Ru at 0.4 V.
- Improving catalyst manufacturing methods so that the catalyst surface area can be increased, more ordered catalyst layer can be formed and platinum content can be reduced [8-10]. Moore et al. [11] prepared a Pt75Ru25/C nanocatalyst by using a single-source precursor \([\text{Ru}(2,3\text{-bis(2-pyridyl)}\text{quinoloxaline})_3\text{-Cl}_2\text{BF}_4]_2\). The subsequent DMFC testing results indicated that the Pt75Ru25/C nanocatalyst had a higher open circuit voltage (OCV) and improved performance in comparison with a commercially produced, unsupported Pt50Ru50 catalyst.

In order to fully commercialize the DMFC, it is important to develop low-cost anode electrocatalysts with improved electrode kinetics for methanol oxidation compared to the presently used state-of-the-art Pt–Ru electrocatalyst.

3.2. Methanol crossover (MCO)

Under the operating conditions, the output voltage of DMFC (0.5 to 0.6 V) [12, 13] is much lower than its thermodynamic reversible voltage (1.21 V). This is due to two main problems. The first is the relatively slow kinetics of the methanol oxidation reaction at the anode as discussed in the previous section. Second is “methanol crossover” i.e. permeation of methanol through the membrane.
State of art membranes used in DMFC allows significant quantities of methanol to diffuse from anode to cathode. When methanol reaches the cathode it oxidized, leading to a “mixed potential” and an inevitable decrease in cell voltage. Moreover the oxidized methanol is unproductive loss. To overcome the methanol crossover, a large number of studies have been carried out. Possible ways to avoid this are:

- Developing a new proton-conducting membrane with low methanol permeability [14-17]. Nowofol GmbH manufactures an irradiated and sulfonated poly(ethylene-alt-tetrafluoroethylene (ETFE)) polymer known as ETFE-SA. The ETFE-SA membranes are prepared by irradiation followed by sulfonation without grafts of other polymers. For 1 and 2 M methanol solutions and at T =25 °C, the MCO (in mol min⁻¹ cm⁻² × 10⁸) are 0.3 and 0.6 for ETFE, respectively. Under the same conditions the MCO of Naﬁon® 115 are 6.7 and 12. ETFE-SA membranes (35 µm thick) are cheaper than Naﬁon® 115 (127 µm thick) [14].
- Modification of the existing membranes like Naﬁon® by making it a composite membrane [18, 19], surface modification by physical treatment [20], or by coating the surface with a thin film [21-23]. Ma et al. [21] prepare a modified composite electrolyte membrane coated with a thin Pd–Ag alloy layer on the Naﬁon membrane using the sputtering method. They found that this membrane is effective in reducing methanol crossover in the cell and gives a higher cell performance than that of a singular Naﬁon membrane. Among the modified Naﬁon 117 membranes with 0.1, 0.2, and 1 µm of sputtering Pd–Ag film, the 1 m thick film has given the highest performance. The experimental data also show that the performance of fuel cell with 1 µm sputtering Pd–Ag film is higher than that of cell with a Naﬁon membrane having catalyst loading twice as high. It illustrates that, in order to improve the performance of DMFCs, modifying the Naﬁon membrane to reduce methanol crossover is more important than increasing catalyst loadings.
- Reduction of methanol crossover by improving MEA and cell design [24, 25]. Eccarius et al. [25] used a phase separation membrane that was directly in contacted with concentrated methanol solution as the pervaporation film. In addition, a perforated plate was attached to the membrane so that the methanol delivery rate could be controlled by adjusting the open ratio of the perforated plate. They achieved relatively stable performance output with neat methanol at ambient temperature.
- Adopting high effective anode catalysts and methanol-tolerant cathode catalysts [26]
- Optimizing the feed concentration of methanol aqueous solutions [27, 28]

For the commercialization of DMFC, crossover problem is one of the main hurdles to overcome. Although past research efforts partly reduced the problem, a permanent solution must be sought.

3.3. Species management

3.3.1. Methanol management

It is important to maintain the appropriate methanol concentration in the anode catalyst layer. Increased concentration will increase the crossover problem, as it greatly depends on diffusion through membrane. On the other hand, too low methanol concentration in the anode CL, results in large mass-transport loss and thus a lowers the cell voltage.

Generally, a compromised methanol concentration, 3-5 M [29, 30] is used in the fuel reservoir of passive DMFC system. This diluted methanol makes specific energy of the stand-alone passive DMFC relatively low, which results in a short operation time for each fuel charge. Also when fuel cell starts working, there will be quick decrease in the reservoir’s concentration level, which creates insufficient level of methanol concentration in anode catalyst layer.

It is found in the previous literature that high methanol concentration in the reservoir can be achieved by adding any methanol transport barrier before the MEA [31-35]. Tsujiguchi et al. [34] developed a vertical passive DMFC for high methanol concentration. They used porous carbon plate (PCP) to increase the mass transfer resistance of methanol. PCP was placed between the anode current collector and the methanol reservoir. It was found that the PCP used in this study could strictly control the methanol transport resulting in the use of a high concentration of methanol up to 100%. Based on the single cell structure with PCP, they also developed an octagonal shaped passive DMFC stack of with 8 cells. The maximum power output of 1.8 W was obtained with 100% methanol.

So, in passive DMFC is how to maximizing the system specific energy and simultaneously maintaining adequate methanol concentration in the anode CL is a challenging task and more work is needed in this direction.

3.3.2. Water management

Proper water management is of vital importance to ensure stable, reliable and high performance of passive
DMFCs [36, 37]. The water management comprises of following three tasks:

- Water needs to be supplied as a reactant at the anode in sufficient quantity (stoichiometry = 1:1, needed much more than this). Insufficient water causes formation of intermediate compounds e.g. formaldehyde, formic acid etc. due to incomplete oxidation of methanol.
- Water needs to be removed efficiently as a product at the cathode. Otherwise, it will accumulate in the cathode porous layers, resulting in a water flooding problem, which increases the mass transfer resistance of oxygen and thus lowers the cell performance.
- Polymer Membrane must be well hydrated as it will conduct protons only when it is wet.

Moreover, a significant amount of water in the anode permeates the polymer membrane and reaches the cathode (electro-osmotic drag), which not only exaggerates cathode flooding problem but also, causes anode water loss. Thus a water make-up system is required, which makes the overall system more complex and bulky. Therefore, recovering the excess water from the cathode to the anode is a good option in this regard, as it also reduces cathode water flooding. This provision also facilitates possibility of feeding concentrated methanol solutions or neat methanol at the anode. [38, 39]

Jewett et al. [40] developed a water management system for a passive DMFC. Water was recovered from the cathode of the cell by adding water management layers to the cathode of the cell which had a micro-porous layer of 50 wt% PTFE on a carbon cloth. The micro-porous layer increased the hydraulic pressure at the cathode and forced water to pass back through the membrane to the anode. Two water management layers were found to be adequate to maintain a water balance coefficient greater than zero for all current loadings.

Xu et al. [36] developed a numerical model to investigate the effect of various parameters including effect of cathode hydrophobic air filter layer (AFL) on water crossover flux in a passive DMFC (Fig.2). It is clear from the graph that water crossover flux for the cathode without an AFL is positive, indicating that the water crossover is from the anode to the cathode, and increases with the current density. On the contrary, the water crossover flux for the cathode with an AFL is negative, meaning the water crossover is from the cathode to the anode, and the flux of water crossover from the cathode to the anode is increased with current density. This negative water crossover results from the reduction of water flux by diffusion from the anode to the cathode, and the significant increase in the water flux by convection from the cathode to the anode caused by the AFL. This result also clearly indicates that the water loss from the cathode to the environment without an AFL is much larger than that with an AFL.

![Fig. 2. variation in the flux of water crossover through the membrane with different cathode structure [36]](image)

The commercialization of DMFCs is still hindered by several technological problems, among which water management is one of the key issues. Tremendous studies in this area are still continuing for achieving better performance.
3.3.3. Carbon dioxide management

Carbon dioxide (CO\textsubscript{2}) gas management is an important issue in the development of the passive direct methanol fuel cell. CO\textsubscript{2} is an anode reaction product that should be removed from the electrode structure and cell as efficiently as possible to maintain effective reaction. Its accumulation at anode resists mass transport of methanol and thus increasing the mass transport loss which reduces the cell voltage [41]. How to remove this quickly and passively is a major concern.

One mole of CO\textsubscript{2} is produced for each mole of methanol oxidized. Since CO\textsubscript{2} has limited solubility in methanol, CO\textsubscript{2} bubbles are formed at the anode and reduce the effective anode area, as studied by Yang et al. [42] CO\textsubscript{2} build-up also increases pressure inside the DMFC fuel tank which increases the methanol crossover problem and finally may lead to tank or seal rupture. This is a critical issue for all passive fuel cells that strive for volumetric efficiency and have no pressure relief mechanism.

On the other hand, CO\textsubscript{2} accumulation in anode electrode increases mass transport resistance of methanol so facilitates the use of highly concentrated methanol fuel in the reservoir [43].

3.3.3. Air/oxygen management

In passive DMFC air/oxygen is transported to the cathode by diffusion and natural convection. The main issue for the efficient air management is to reduce oxygen mass transport resistance between current collector and cathode catalyst layer. However in the passive DMFC frequently occurring cathode flooding increase the mass-transport resistance of oxygen, which leads to mass transport loss and low cell voltage. Not much literature been found on this problem and must be necessarily resolved for commercialization.

3.4. Heat management

In passive DMFC heat is generated at electrodes due to electrochemical reactions (shown in article 2). This heat is mainly dissipated to the anode fuel reservoir and the cathode ambient air. For facilitating maximum oxygen transport, cathode is completely exposed to ambient air which can lead to a higher heat dissipation rate from the cell to ambient. As a result, the operating temperature of passive DMFCs is usually low (below 35 °C) which, in turn, causes slower kinetics of the electrochemical reactions and thus lower cell performance. Therefore, how to reduce the heat loss such that the cell can operate at a sufficiently high temperature is important in the design of passive DMFCs.

The passive DMFC facilitates maximum oxygen transport by fully exposing the cathode to ambient air. But this results in a high heat dissipation rate. Thus the operating temperature of DMFC becomes low, which may leads to slower electrochemical reaction rate and lowers the cell performance. So, for improving the temperature and thus, cell performance, it is important to decrease the heat transfer rate [44, 45].
In the Chen et al. work, a passive DMFC with its cathode current collector made of porous metal foam was investigated experimentally. They found that the porous current collector showed a higher cell operating temperature, which can be attributed to the following factors. First, the higher oxygen transfer rate using the porous current collector yields a higher rate of the exothermic reaction between the permeated methanol and oxygen on the cathode. Second, the lower effective thermal conductivity of the porous current collector reduces the heat loss to the ambient.

But this operating temperature must not be very high as it may increase methanol crossover due to swelling of membrane. Optimizing this operating temperature is a critical task of heat management. Also, much work remains to be done to analyze heat management in a passive DMFC and to understand how heat flow affects water management. It is expected that heat management will become a major technological challenge in development of portable DMFC power systems.

3.5. Cost

At the present moment the major factor preventing passive DMFC from successful commercialization is their high price. Making step from prototypes to mass production, it is possible to reduce manufacture expenses, but it will not affect on materials costs. DMFC uses costly platinum and platinum alloy as electrode catalyst material, which significantly increases total price of fuel cell system. Two approaches were found in the literature to overcome this:

- Reduction in the catalyst loading of passive DMFC, which is around ten times higher than that of the hydrogen polymer membrane fuel cells.
- Development of new and non platinum catalyst. Metal alloys of noble metals (Pt, Pd, Ru, Os etc) with base metals (Fe, Co, Ni etc) are well investigated in reaction of oxygen reduction. Electrodeposited PdNi alloy, exotic electrocatalyst based on dispersed gold nanoparticles onto a polyaniline (PANI) grafted multiwall carbon nanotube (MWNT-g-PANI) matrix, Metal-free carbon nitride nanotubes were used as catalysts for methanol electrooxidation. The authors show that Au nanoparticles dispersed into PANI-grafted MWNT exhibit the essential characteristics, including enhanced electrocatalytic activities for methanol oxidation, restricted poisoning influence from adsorbed carbon monoxide, better oxidation kinetics, and performance at elevated temperatures, for use in DMFC applications.

Also Nafion® polymer membranes, which has a major contribution in DMFC cost, account for 20% of the total cost of Nafion® based membrane electrode assemblies (MEAs). So, a cheaper alternative to the costly Nafion® membrane is required. In recent years, significant progress has been made in the development of polymer electrolyte membranes for DMFCs in terms of cost reduction and improvement of functionality, together with other associated technology advancements. The hydrocarbon membranes e.g. sulfonated poly(ether ether ketone) (sPEEK), sulfonated poly(sulfonated polysulfones) (sPSU), polybenzimidazole (PBI), sulfonated polyphosphazene (sPPZ), are found cheaper and more technically effective for DMFC than Nafion® membranes. They have lower methanol crossover and higher conductivity and stability.

3.6. Conclusive remark

Primary barriers to the world-wide commercialization of DMFC were explained in this paper. The research efforts, made so far, have lead to significant progress on many scientific and technological problems. Bringing the passive DMFC technology close to the era of commercialization, there are still some major challenges like poor anode reaction rate, methanol crossover, efficient management of reactant and product, heat management and the cost. The achievement of the above mentioned goals is vital in order to speed up the process of manufacturing and commercializing passive DMFCs.

References


