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Review Paper

Direct Methanol Fuel Cells – Clean Energy Source for Future?

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Abstract** - Fuel cells represent a clean alternative to current technologies for utilizing hydrocarbon fuel resources. Polymer electrolyte membrane fuel cells (PEMFCs) have acquired due importance as they are best suited for applications where a quick start up is required such as in automobiles. Direct methanol fuel cell (DMFC) is considered as a highly promising alternative power source. It is based on polymer electrolytes membrane (PEM) fuel cell technology. Direct methanol fuel cells are attractive for several applications, however, serious limitations still remain and need to be solved before developments of such devices and before they can become an alternative to internal combustion engines. It posses a number of advantages such as a liquid fuel, quick refueling, low cost of methanol and the compact cell design making it suitable for various potential applications including stationary and portable applications. DMFCs are also environmentally friendly. Although carbon dioxide is produced, there is no production of sulfur or nitrogen oxides. The development of commercial DMFCs has nevertheless been hindered by some important issues. The most important are the low power density caused by the slow electrochemical methanol oxidation at the anode and methanol crossover through PEM, which is responsible for inhibiting the activity of the cathode catalyst as well. At present, methanol crossover from the anode to the cathode appears to be the major limitation. This article reviews the development of direct methanol fuel cells, technical challenges and current status.

Keywords: Fuel cell, Direct methanol fuel cell, Alternative power, Clean energy, Methanol crossover.

Introduction

Throughout the world, the need of the hour is power generation with environmental protection. This has prompted research in various aspects of fuel cells. Savings in fossil fuels, due to high efficiency of energy conversion, low pollution level, low noise and low maintenance costs render fuel cells preferable over other energy conversion devices. Although fuel cells are not a recent development, the use of polymeric membranes as electrolytes has received a tremendous impetus in the recent past. It is because of this development that fuel cells are the premier candidates as portable source of power for light duty vehicles and buildings and as replacement for rechargeable batteries [1]. In addition to the development of materials for the fuel cell stack, PEMFC systems development has seen quite revolutionary advances. Modeling activities have enhanced both the efficiency as well as the reliability of the systems [2].

A fuel cell produces electricity directly from the electrochemical reaction of hydrogen, from a hydrogen-containing fuel, and oxygen from the air. Polymer electrolyte membrane (PEM) fuel cells, which convert the chemical energy stored in hydrogen fuel directly and efficiently to electrical energy with water as the only byproduct, have the potential to reduce our energy use, pollutant emissions, and dependence on fossil fuels. Great deal of efforts has been made in the past, particularly during the last couple of decades or so, to advance the PEM fuel cell technology and fundamental research [3]. H_2 is the ideal fuel for a fuel cell. Hydrogen is industrially produced by steam reformation of naphtha oil, methane, and methanol. High purity hydrogen has been mainly used as a fuel for low temperature fuel cells such as polymer or alkaline electrolyte fuel cells [4]. Fuel cells offer the possibility of zero-emissions electricity generation and increased energy security. In the last twenty years, the interest in fuel cells of all types has increased dramatically [5].

All fuel cells consist of a pair of electrodes, i.e. cathode and anode, and an electrolyte, plus an external circuit for electrical current and internal mechanism for allowing ion migration to complete the circuit. The output of electricity, which is always low-potential DC, is controlled by electrical potential or current regulators. A schematic view of a polymer electrolyte membrane fuel cell is shown in Figure 1.

A schematic view of a polymer electrolyte membrane fuel cell is shown in Figure 1. The H_2/O_2 fuel cell, commonly referred to as polymer electrolyte fuel cell (PEFC) and the direct methanol fuel cell (DMFC) are the two types of fuel cells which use polymer electrolytes [6]. DMFCs have higher energy density but exhibit shortcomings such as (a) slower oxidation kinetics than PEFC below 100 °C and (b) significant permeation of the fuel from the anode to the cathode resulting in a drop in efficiency of fuel utilization upto 50% [7].

Despite the currently promising achievements and the plausible prospects of PEMFCs, there are many challenges remaining that need to be overcome before PEMFCs can successfully and economically substitute for the various traditional energy systems. The aim of this review is to provide an overview on DMFC, recent progress, research and development areas and current problems to be solved for the different applications [8].

The Fuel Cell Advantage

Fuels cells do not store electricity but produce it directly from fuel. They simply need to be fed with fuel and oxygen to work. That is why they have undeniable advantages over regular batteries such as increased operating time, reduced weight and ease of recharging. Besides, most of the world's energy comes from burning fossil fuels in low efficiency processes. The wide application range of fuel cells could also provide an alternative to these processes both for stationary and transportation applications [9].

The state of the art fuel cells are based on proton exchange membranes (PEM). The PEM fuel cells are the most promising fuel cells and show excellent performance when fed with hydrogen. The advantages of PEM cell are i) no corrosion problem, ii) CO_2 tolerance, iii) simple fabrication, iv) high power density and long life time, v) ability to operate on hydrogen and reformed fuels. However, production, storage and use of hydrogen are still a key limitation. Further, its performance is severely affected by poisoning species in hydrogen.

The performance of PEM fuel cells is known to be influenced by many parameters including operating temperature, pressure and relative humidity of the gas streams etc. In order to improve fuel cell performance, it is essential to understand the effect of operating parameters on fuel cell performance. Fuel cell manufacturers and research institutes working in these areas have studied the effect of operating conditions on fuel cell [10-13].

Direct Methanol Fuel Cell

Direct methanol fuel cells (DMFCs) are promising candidates for applications in portable power sources, electric vehicles and transport applications because they do not require any fuel processor and can be operated at room temperature[14,15].

DMFC Advantages

Methanol releases six protons and electrons per molecule during its oxidation. Its high energy density makes from methanol a suitable fuel for fuel cells [16]. DMFC works at low and intermediate temperatures (up to 150ºC) and are fed with a dilute aqueous solution of methanol in water. Cells operation in gas phase also gives good performance. Actually, the higher temperature enhances kinetics and methanol crossover is lowered with a gas phase feed. However, need for vaporization may be a limitation for some applications.

Mobility Advantage

In mobile applications, liquid fuels are usually preferable to gaseous ones, and often to solid ones as well. So, not surprisingly, researchers have long been on the lookout for a fluid that would also be a suitable fuel. Methanol was an obvious candidate early on, because it:

- ✓ can be readily made via a well known manufacturing process from plentiful raw materials,
- ✓ remains liquid under normal storage conditions (unlike, say, butane, which tends to evaporate much more easily),
- ✓ is compatible with the existing fuel distribution infrastructure,
- ✓ is relatively hydrogen-dense, *i.e.* four of the six atoms in methanol (CH_3OH) are hydrogen, and
- ✓ is environmentally acceptable[17].

Environmental Benefits of DMFC

Fuel Cells are considered as environmentally friendly as they do not produce toxic byproducts. However, they are not emission-free. They still produce carbon dioxide which is a green house gas. This is also true for hydrogen which produces CO_2 indirectly during reforming step in the water-gas shift reaction. Methanol and other alcohols also produce some other byproducts like aldehydes, ketones and carboxylic acids but in very low concentrations. If produced from biomass, the CO_2 formed during cell operation would nevertheless be balanced by CO_2 consumed in photosynthesis. Consequently, this form of energy would contribute no more to green house effect and will be renewable. Further, the higher efficiency of fuel cells makes that less CO_2 / kW is produced as compared to conventional processes.

DMFC Applications

There are essentially three main types of applications for fuel cells. Fuel cells are well known for being an alternative to the internal combustion engines but are also considered for portable and stationary applications.

Stationary: Fuel cells are able to produce electricity directly from fuel with a good efficiency. For stationary applications, they would replace the combustion-based electric-generating methods where energy losses occur in the thermal engine as well as in the electric generator. They can be applied to residential, commercial and industrial sectors for electricity as well as for heat production. As DMFC do not need any reforming of methanol, there are no losses in the reformer. Besides the medium/low operating temperature make them suitable for residential-grade water heating.

Transportation: Although modern cars emit a lower amount of toxic gases than their predecessors, transportation is still a great source of pollution. Replacing a significant fraction by fuel cells would have a substantial effect on the environment. Reduced levels of transportation related pollution may be achieved by replacing a significant number of internal combustion engine vehicles with electric cars in the near future. In this regard, polymer electrolyte fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) have been envisaged as suitable power sources for electric cars. DMFCs which directly employ methanol as fuel [18]. Methanol fuel cells have been carefully investigated for transportation applications. The main advantage is that storage and tank refilling is easy for liquid methanol. Besides, they do not need any reformer or humidification system that would consume a lot of the available space in a car. Actually, their design is compact even if some water is needed to dilute methanol.

Portable Applications: Several organizations are actively engaged in the development of low power DMFCs for cellular phone, laptop computer, portable camera and electronic game applications [18]. The most important feature for a portable or micro fuel cell is a compact design. For a minimized size and weight, the cell has to work at ambient temperature. The low operating temperature of PEM fuel cell is a great advantage for portable applications. Actually, it is the only fuel cell able to work at ambient temperature [19]. For reasons similar to transportation application, it appears clearly that DMFC are more suitable than hydrogen fuel cells. Fuel cells are still a developing technology and need improvement in both technological performance and cost.

Direct Methanol Fuel Cell principle

Methanol is an attractive fuel because its energy density is much higher than that of hydrogen. It is inexpensive and easy to handle, store and transport. A thermodynamic reversible potential for a methanol oxygen fuel cell is 1.21 V at 25°C. This value is comparable to the value for a hydrogen oxygen fuel cell, which is 1.23 V [20].

Basically, the direct methanol fuel cell is a proton exchange membrane fuel cell that is fed with an aqueous solution of methanol. The two catalytic electrodes where the methanol oxidation (anode) and the oxygen reduction (cathode) occur are separated by a membrane which conducts protons from anode to cathode, while other compounds diffusion is blocked. The combination of electrodes and membranes is called membrane electrode assembly (MEA). Each electrode is made of a gas diffusion layer and a catalytic layer (Figure 2). The state of the art in membranes is Nafion. It was created by addition of sulfonic acid groups into the bulk polymer matrix of Teflon. These sites have strong ionic properties and act as proton exchange sites. Aqueous methanol is fed at the anode side. It diffuses through the diffusion layer to the catalytic layer where it is electrochemically oxidized into mainly carbon dioxide protons and electrons.

Protons formed during this reaction diffuse through the Nafion membrane to the cathode catalytic layer. They participate in oxygen reduction to form water at cathode side. Oxygen may be pure but can also come form air. Electrons are collected by graphite bipolar plates which are the two poles of the cell. The structure and working of the direct methanol fuel cell is described in Figure 2.

Reactions

Anode:

$CH_3OH\,(l) + H_2O\,(l) \quad Pt/Ru \longrightarrow CO_2\,(g) + 6\,H^+ + 6\,e^-$

Cathode:

$3/2\,O_2\,(g) + 6\,H^+ + 6\,e^- \quad Pt \longrightarrow 3\,H_2O\,(l)$

Overall:

$CH_3OH\,(l) + 3/2\,O_2\,(g) \longrightarrow CO_2\,(g) + 2\,H_2O(l)$

At anode, the methanol is oxidized into carbon dioxide and six protons plus six electrons. The six protons formed react at the cathode with oxygen to form water [21].

The overall reaction looks like a combustion reaction and is thus sometimes referred to as cold combustion. Actually the cell is a mean to control this reaction and use it to produce current directly. The standard cell voltage for a DMFC at 25ºC is 1.21V. However, this potential is never obtained in reality. The open circuit potential is usually about 0.6 to 0.8V in the best case.

Technical Barriers in DMFC

Slow Electro-Oxidation Kinetics

Various surface intermediates are formed during methanol electro-oxidation. Methanol is mainly decomposed to CO which is then further oxidized to CO_2. Other CO like species are also formed [22]. Principle by-products are formaldehyde and formic acid. Some of these intermediates are not readily oxidizable and remain strongly adsorbed to the catalyst surface. Consequently, they prevent fresh methanol molecules from adsorbing and undergoing further reaction. Thus electrooxidation of intermediates is the rate limiting step. This poisoning of the catalyst surface seriously slows down the oxidation reaction. Besides, a small percentage of the intermediates desorbs before being oxidized to CO_2 and hence reduce fuel efficiency but undergoing in complete oxidation. Thus, a very important challenge is to develop new electrocatalysts that inhibit the poisoning and increase the rate of the reaction. At the same time, they should have a better activity toward carbon dioxide formation.

Methanol Crossover

In PEM fuel cells, one of the objectives of the membrane is to stop fuel and oxygen to reach the electrode on the other side and undergo non-electrochemical oxidation. However, in DMFC, the fuel diffuses through Nafion membrane. Due to the hydroxyl group and its hydrophilic properties, methanol interacts with the ion exchange sites and is dragged by hydronium ions in addition to diffusion as a result of concentration gradient between anode and cathode. Methanol that crosses over reacts directly with oxygen at the cathode. Electrons are brought directly from the anode to the cathode along with methanol resulting in an internal short circuiting and consequently a loss of current). Besides, the cathode catalyst, which is pure platinum, is fouled by methanol oxidations intermediates similar to anode [23]. Therefore, methanol crossover not only losses of fuel but also decreases cell performance at the cathode [24, 25].

However, there still remain several critical issues to be resolved for commercialization of the DMFC. Among them, a working lifetime is one of the critical issues to be addressed. Nowadays, portable power sources for a note PC, portable multimedia player, 4G cellular phone, and so forth are requested to ensure working lifetime for thousands of hours, which is not satisfied by present DMFC systems. Thus, identifying the factors that affect the durability of DMFC and understanding the degradation mechanism are essential to improve the lifetime [26].

Solutions to Prevent Crossover: Two different pathways exist to solve this problem of methanol cross-over, the first being the development of ion-conductive membranes based on alternative polymers or polymer composites, the second being the modification of the existing Nafion membrane, in order to prevent cross-over.

Crossover is enhanced by the concentration and pressure gradient between anode and cathode. It can be easily limited by using a low methanol concentration in the anode feed solution and by increasing cathode pressure in a certain measure. A compromise should be found for the concentration. It should be small enough to reduce crossover as much as possible but also supply the anode catalytic layer with enough methanol to produce an acceptable current density. One of the reasons is that methanol can crossover through the proton exchange membrane PEM, such as Nafion 112, to reach the cathode side via physical diffusion and electro-osmotic drag by proton side. Such crossover not only results in a waste of fuel, but also lowers the cell performance. Most of the methanol crossover will be electrochemically oxidized at the cathode. Such an oxidation reaction lowers the cathode potential and also consumes some cathode reactant. If a reaction intermediate, such as carbon monoxide, adsorbs onto the catalyst surface, the cathode will be poisoned, too, which will further lower the cell performance. Lots of researchers made efforts to reduce methanol crossover by modifying the Nafion membranes via hybridizing Nafion with inorganic nano-particles, such as silicone oxide[27,30], tetraethoxysilane[31,32], diphenyl silicate[33], zirconium phosphate (ZrP)[34,36] and Nafion/PTFE and zirconium phosphate modified Nafion/PTFE[37], composite membranes phosphotungstic acid, etc. [38,40]. Methanol might crossover the Nafion membranes either via diffusion or via electro-osmosis through the ionic clusters of Nafion membranes. Mixing inorganic nano-particles into Nafion membranes and leading nano inorganic particles to locate inside the ionic clusters of Nafion membranes could reduce methanol crossover the membranes [27–40].

The effect of methanol crossover has attracted attention worldwide. Many factors, such as membrane material and modification, membrane thickness, methanol concentration, cell temperature and the pressure of cathode reactant, have been investigated [15,41,45]. Generally speaking, methanol crossover can be reduced by increasing membrane thickness and equivalent weight, by increasing the cathode reactant pressure, and by decreasing cell temperature and methanol concentration. In order to overcome the methanol crossover, most reports [22, 46] utilized commercial Nafion 117 as starting material for lower methanol crossover rate in order to get better DMFC performance. Reports utilizing Nafion 112 as starting material also exist, but about one order lower than that of Nafion 117 due to its higher methanol crossover rate. However, in addition to the cell temperature, methanol concentration, and membrane thickness not only suppressed the crossover of methanol, but also proton [47,48]. The proton-conducting membrane as “heart of the fuel cell” has to fulfill several demanding requirements at the same time. The most important of these are: high proton conductivity while being electrically isolating, high chemical stability under oxidizing and reducing conditions and very low permeability for the reactants such as hydrogen, methanol and air [49].

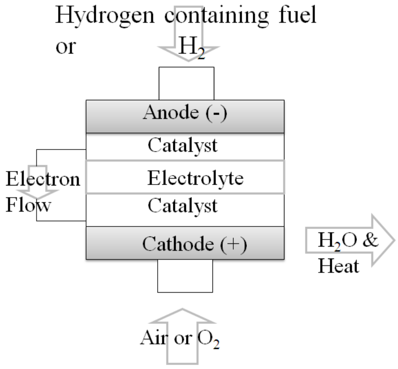

Figure 1: Schematic view of a polymer electrolyte membrane fuel cell

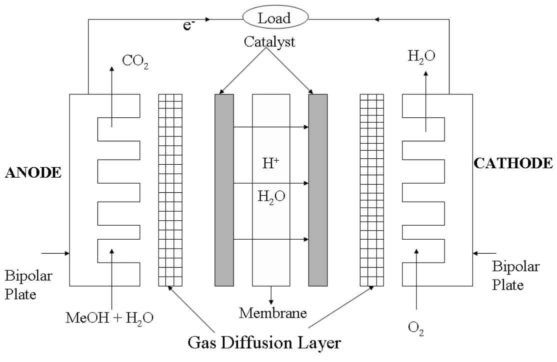

Figure 2: Generalized structure of Direct Methanol Fuel Cell

Conclusion

The direct methanol fuel cell is an attractive option for numerous applications. However its use is hindered by limitation of high methanol permeation through the membrane. Two primary barriers to the world-wide commercialization of PEM fuel cell technology are needed to be overcome namely durability and cost. Phenomena of methanol crossover play an important role in the DMFC performance. This will not only decrease the efficiency of DMFC, lower the open circuit voltage, and degrade the cathode performance, but also the overall fuel utilization will be much lower. In addition to finding a new membrane to inhibit the methanol crossover, we found that choosing thicker membrane, decreasing cell temperature and decreasing methanol concentration all have a negative effect on the methanol crossover. In addition to the effect of methanol crossover, the concentration of methanol and the operating temperature also affect the DMFC performance markedly. For lower cell temperature, the performance will be limited to the concentration polarization for lower methanol solution concentration. For higher cell temperature, optimal methanol concentration is better for DMFC performance because lower concentration will lead to concentration polarization and higher concentration will lead to serious methanol crossover.

In order to improve the performance of the DMFC, it is necessary to eliminate or, at least, to reduce the loss of fuel across the cell, usually termed ‘‘methanol crossover’’. In this sense, the membrane technology is one of the alternatives for trying to solve this problem.

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