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Review Article

Direct Methanol Fuel Cell: A Review

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Abstract

Direct methanol fuel cell (DMFC) is considered as a highly promising power source. It is based on polymer electrolytes membrane (PEM) fuel cell technology. It poses 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 environmental friendly. Although carbon dioxide is produced, there is no production of sulphur or nitrogen oxides. 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. With the eventual goal of improving the overall performance of the DMFC, this study has been concerned with an investigation of the issues and effect of various parameters on its performance.

Keywords: *DMFC, power source, environment friendly, PEM, Catalyst, issues*

1. Introduction

Fuel cells are conversion devices, which are used to convert chemical energy into electrical energy. Hydrocarbon or a substance obtained from hydrocarbon or based on hydrocarbon such as hydrogen or alcohol, are mostly used as fuel in DMFC's. Fuel cells are classified according to the electrolyte used and the temperature conditions in which they are supposed to operate. They are as follows

1.1 Low Temperature

1) Alkaline Fuel Cell (AFC)
2) Phosphoric Acid Fuel Cell (PAFC)
3) Polymer Electrolyte Fuel Cell (PEFC)

1.2 High Temperature

1) Solid Oxide Fuel Cell (SOFC)
2) Molten Carbonate Fuel Cell (MCFC)

Direct methanol fuel cell (DMFC) is derived from polymer electrolyte fuel cell (PEFC) by the anode reactant. In PEFC's gaseous hydrogen is replaced by methanol and water to obtain DMFC's. In today's world there are many limitations to the capacity of batteries thus DMFC's can be alternative power source replacing present power sources. However the maximum power densities which can be achieved by DMFC at the moment are still very low for commercial applications. Thus various methods are studied to increase the capacity of power density and lower the initial and operating cost of DMFC's. Application of DMFC's in portable power source and in hybrid electric vehicles has been investigated. (Nirmal Ramakrishna Joshi, 2014). Under the influence of methanol crossover and water management high performance can be achieved and the passive structure is simpler the active DMFC (F.A. Halim *et al*, 2012). A critical analysis was performed about fundamental aspects regarding DMFC technology. They focused mainly on the proton exchange membrane and proton exchange membrane development chain, performing an overview of research progress regarding the DMFC component. A detail study was done related to membrane preparation, characterization, DMFC tests and modeling (Vasco S. Silva *et al*, 2005).

2. Direct Methanol Fuel Cell

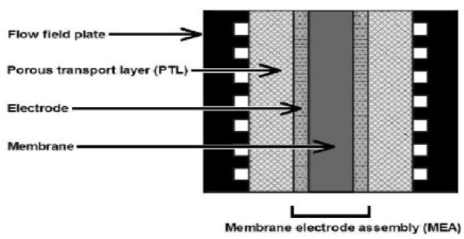

Fig. 1 Direct methanol fuel cell

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3. Components for DMFC

3.1 Proton conducting membrane

The DMFC consists of a proton conducting membrane at the centre, the solid polymer electrolyte which is used to provide ionic conductivity and avoid the flow of electrons thus acting as a barrier between the reactants to maintain mechanical and chemical stability. The thickness of membrane is in the range of 30-200m.

3.2 Electrodes

Electrodes generally consist of expensive noble metal catalyst used to achieve sufficient rate of reaction at low temperature. Normally Platinum is used as cathode and Platinum-Ruthenium alloy at anode for DMFC. In DMFC to obtain useful current densities, the electrodes should have high surface area with respect to geometric area.

3.3 Membrane electrode assembly

The membranes and electrodes together form an assembly which is called as membrane electrode assembly. This assembly is sandwiched between the porous transport layers (PTL's) in DMFC's.

3.4 Porous transport layers(PTL's)

The purpose of PTL's is to form a thermal and electronic contact between the electrodes and flow field plates which are used as transport path for the reactants. They have high electrical and thermal conductivity, good chemical and mechanical properties with high porosity. Generally PTL's material is carbon based papers which have macro porous backing layer and a micro diffusion layer on one or both sides of backing layers. The thickness of PTL is in the range of 300-400ˡm.

4. Working

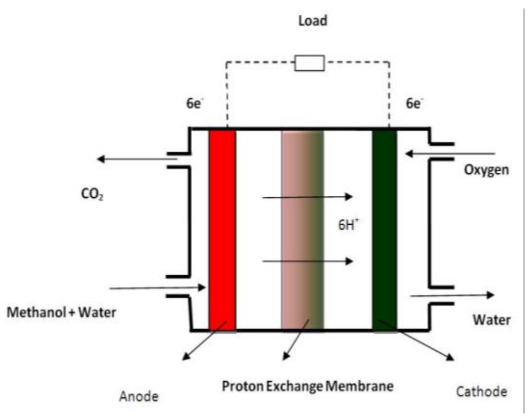

Fig. 2 Working of DMFC

Electrochemical reactions involved in DMFC

Anodic Reaction (Oxidation): 0.03 V
$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ 6e^-$

Cathodic reaction (Reduction): 1.22 V
$3/2\ O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$

Overall reaction: 1.19 V
$CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2H_2O$

The DMFC consists of two electrodes anode and cathode along with catalyst Pt/Ru and pt respectively. There is a solid electrolyte between these electrodes. As DMFC is derived from PEFC it contains a polymer electrolyte membrane between the electrodes which enables the flow of protons between them. Six electrons are transferred to the electrode for complete oxidation to form carbon dioxide from methanol. Thus make the methanol electro-oxidation process slow. The above figure shows the basic operation of DMFC. Methanol and water are supplied and converted to carbon dioxide, protons and electrons at the anode. Methanol can be fed as aqueous solution or in the form of vapour to the anode. The produced electrons from the anode reaction are subsequently transferred via the external circuit (protons and electrons reduce oxygen (from air) to form water at the cathode (Nirmal Ramkrishna joshi, 2014).

5. Advantages

5.1 Advantage of methanol

Methanol releases six protons and electrons per molecule during its oxidation. Its high energy density makes methanol a suitable fuel for fuel cells (Vasco S Silva *et al* 2005).

Table 1 Energy density of fuels for direct polymer electrolyte fuel cells

Fuel	Fuel cell reaction	Energy density $WHCM^{-3}$
Hydrogen(Liquid -273°C)	$H_2+0.5O_2 \rightarrow H_2O$	2.7
Hydrogen (Gas at 20MPA)	$H_2+0.5O_2 \rightarrow H_2O$	0.5
Methanol (LIQ.)	$CH_2OH+1.5O_2 \rightarrow CO_2+2H_2O$	4.8

5.2 Environmental concerns

Fuel Cells are considered as environmental 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.

5.3 Potential 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.

5.4 Stationary applications

Fuel cells can be efficiently used for stationary applications replacing the combustion based method where there are more losses in thermal engine as well as in generator.

5.5 Transportation

Fuel cells can be efficiently used for stationary applications replacing the traditional batteries for power source in vehicles.

5.6 Portable applications and micro-fuel cells

The design of DMFC fuel cells is comparatively compact making the size small and reducing the weight. Thus, they can be easily ported from one place to another.

6 Disadvantages (Issues In DMFC)

6.1 Slow electro-oxidation kinetics

During methanol electro oxidation process various surface intermediates are formed. Methanol is mainly decomposed to CO which is then further oxidized to CO2. Other CO likes species are also formed: COH, HCO, HCOO. Principle by-products are formaldehyde and formic acid. Some of these intermediates are not readily oxidized and remain strongly adsorbed to the catalyst surface. Consequently, they prevent fresh methanol molecules from adsorbing and undergoing further reaction. Thus electro oxidation 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 CO2 and hence reduce fuel efficiency but undergoing in complete oxidation. Thus, a very important challenge is to develop new electro catalysts 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 (Alexendre Hacquard, 2005).

6.2 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 (Figure 3).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 (Figure 3). Besides, the cathode catalyst, which is pure platinum, is fouled by methanol oxidations intermediates similar to anode (Alexendre Hacquard, 2005).

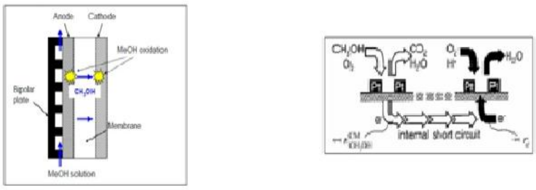

Fig. 3 Internal short circuit created by crossover (Alexandre Hacquard, 2005)

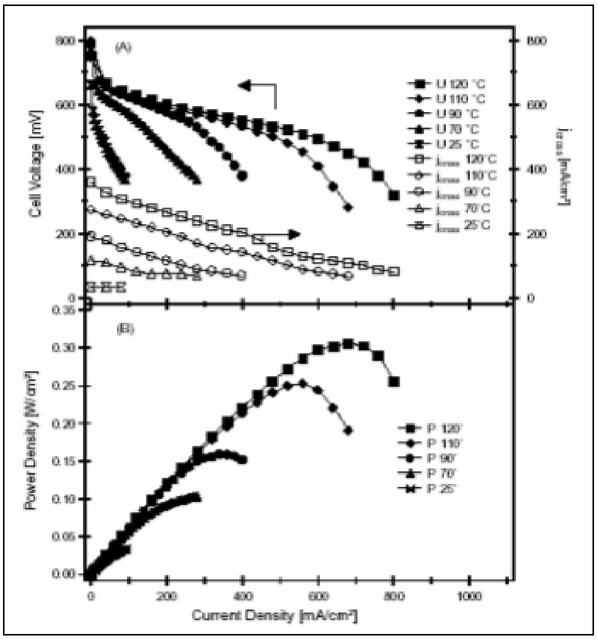

Fig. 4 Performance of DMFC under crossover (Alexandre Hacquard, 2005)

Conclusions

1) Methanol can be a better alternative to other fuel cells.
2) A passive vapour feed DMFC has simpler structure compared to active DMFC and high performance can be achieved.
3) Use of bi-metallic catalyst on anode helps in reducing the crossovers.
4) High power can be achieved at low voltage, which is a merit for portable device applications.
5) DMFC has proven a better competitor for recent times as alternative for conventional power supplies. It has a great future scope and a detail research subject for its betterment in the field of low power supply and clean energy resource.

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