“Recent Developments and Trends in Direct Methanol Fuel Cell”

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Abstract— We give an overview about the recent trends and developments obtained in the performance of the direct methanol fuel cell. An effort has been made in this paper to highlight the studies of effect of methanol crossover on direct methanol fuel cell and the challenges in optimization of the performance of direct methanol fuel cell. Direct methanol fuel cell is being considered as an alternative of petroleum sources for energy transformations. It is also a very safe method of transforming energy from chemical to electricity and that the conversion is directly obtained. The construction, working, applications, and the problems associated with the performance of the DMFC have been exploited in this paper. The hard work of various people working on the optimization of performance of the direct methanol fuel cell has been incorporated in this paper.

Keywords— Direct Methanol Fuel Cell (DMFC), PEM (polymer electrolyte membrane), MEA (membrane electrode assembly), Methanol Crossover, Optimization, Catalysts, Bipolar plates.

I. INTRODUCTION

Direct-methanol fuel cells or DMFCs are a subcategory of proton-exchange membrane fuel cells. In DMFC, methanol is used as the fuel directly. The main advantage of direct methanol fuel cell is the ease of transport of methanol, an energy-dense yet reasonably stable liquid at all environmental condition. Efficiency is quite low for these type of fuel cells. The major applications of DMFC lie with small portable instruments such as laptops, mobiles, tablets, torch, etc. In contrast to indirect methanol fuel cells, DMFCs use a methanol solution (usually around 1M, i.e. about 3% in mass) to carry the reactant into the cell: common operating temperatures are in the range 50–120 °C, At high temperature operations DMFC is under pressurized conditions. DMFCs themselves are more efficient at high temperatures and pressures, but these conditions end up causing so many losses in the complete system that the advantage is lost therefore, atmospheric-pressure configurations are currently preferred [10]. Methanol is available in the liquid form in the temperature range of (-97.0 °C to 64.7 °C) at atmospheric pressure.

The energy density of methanol is much greater than that of pure or compressed hydrogen and also than that of lithium ion batteries. Moreover it is free from hydrogen storage and transportation problems as compared to PEMFC’s where hydrogen is used as a fuel, for which cryogenic storage and safety measures are to be ensured. It’s most important advantage is that the DMFC produces very less amount of carbon-dioxide as compared to other hydrocarbon sources and if various stacks are connected in series, DMFC can power bigger portable & stationary applications. Research work is going on in the reuse of carbon-dioxide generated at the anode in the DMFC. Major emphasis is on the reuse of carbon-dioxide to produce methanol or any other beneficial product.

II. CONSTRUCTION OF THE DMFC

A Direct Methanol Fuel Cell consists of a) Anode, b) Cathode, c) Polymer electrolyte Membrane, d) Bipolar Plates, e) Supportive plates for fuel cell stack, f) Source of oxygen, g) Methanol solution. The construction of the direct methanol fuel cell could be described in a simple manner as follows: It consists of an anode-catalyst layer generally platinum-ruthenium made, followed by the polymer electrolyte membrane (PEM) which acts as an electrolyte for the fuel cell. The PEM generally used in the direct methanol fuel cell is Nafion which is a perfluorosulfonic acid membrane [2]. This is then followed by cathode-catalyst layer which is generally platinum-carbon made. On the one side before anode-catalyst layer and on the other side after cathode-catalyst layer there exist bipolar plates which are made up of graphite usually. The function of these plates is to provide the fuel cell with the external electrical contact and as a directional element for the reactants to the direct methanol fuel cell on cathode and anode side. This complete arrangement is then fixed between two supportive plates generally made of aluminium. This complete infrastructure then makes a single direct methanol fuel cell stack assembly [2].
III. WORKING OF THE DMFC

In this type of fuel cell, methanol is fed as a reactant on the anode side and air or pure oxygen on the cathode side. Methanol concentration is restricted to up to 1M, it is because when the concentration exceeds 1M, methanol crossover increases to a larger extent causing high efficiency losses for the fuel cell. Also the methanol that has undergone crossover leads to undesirable and unwanted side reactions at the cathode side. Pure oxygen generally yields good results when used on the cathode side. At the anode side, oxidation of methanol takes place breaking it down into six protons, six electrons and along with that carbon dioxide evolution \([2]\). The six protons resulting from the oxidation of the methanol get transferred from the anode side to the cathode side through the PEM by migration. The six electrons flow out through the external electrical circuit provided in the fuel cell. The six protons when arrive at the cathode side combine with the oxygen provided from the air or in the form of pure oxygen to form water. The reason to choose methanol as feed for this fuel cell is that it is highly energy dense component then pure hydrogen and is free from storage and transportation problems. The products formed in this type of fuel cell are carbon-dioxide and water.

Reaction at the Anode side

\[
\text{CH}_3\text{OH(l)} + \text{H}_2\text{O(l)} \rightarrow \text{CO}_2(g) + 6 \text{H}^+ + 6 \text{e}^-
\]

Reaction at the Cathode side

\[
\frac{3}{2} \text{O}_2(g) + 6 \text{H}^+ + 6 \text{e}^- \rightarrow 3\text{H}_2\text{O(l)}
\]

Overall Reaction

\[
\text{CH}_3\text{OH(l)} + \frac{3}{2} \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O(l)}
\]

IV. APPLICATIONS OF DMFC

The current direct methanol fuel cells are limited in the power they can produce, but can still store high energy content in a small space. This means that, they can produce a small amount of power over a long period of time. This makes them unavailable for powering large vehicles (at least directly), but ideal for smaller vehicles such as forklifts and tuggers and consumer goods such as mobile phones, digital cameras or laptops. Direct methanol fuel cells are finding their applications largely in military since they have low noise and thermal operations and no toxic effluent. These applications include power for man-portable tactical equipment, battery chargers, and autonomous power for test and training instrumentation. Direct Methanol fuel cells are available with power outputs between 25 watts and 5 kilowatts with durations up to 100 hours. This includes the time for refueling of the fuel cell also.

V. CHALLENGES IN DMFC PERFORMANCE

When air flow rate is small: Under this condition it is observed that the direct methanol fuel cell exhibits an unusual behavior. It is observed that the active area of the fuel cell splits into two regions when the air flow rate is small \([5]\). The region close to the inlet of oxygen channel operates in the normal fuel cell mode (Galvanic mode) and the region close to the outlet of the oxygen channel works in the electrolysis mode. The electrolysis of the methanol at the cathode side takes place due to consumption of current in galvanic mode to form hydrogen \([5]\). Thus the cell operates in a bifunctional regime due to permeated methanol at the cathode side due to crossover \([5]\). This causes a great loss in the cell output.

Membrane preparation and selection: Majority of the polymer electrolyte membrane fuel cells (PEMFC’s) are technically relevant on perfluoro sulfonic acid membranes called as ‘Nafion’ \([2]\). These are generally obtained by polymerization of TFE (tetrafluoroethylene) in sulfonyl fluoride form followed by hydrolization and acid treatment. The proton conductivity of these membranes is highest in the complete state of hydration of membrane. But as the degree of hydration is reduced the proton conductivity is decreased and the crossover is increased. Membranes with high proton conductivity and low solution transfer are an exclusive area of research \([2]\). Membranes withstand high temperatures are also an area of research in this field.
The current trends followed for the same reason are 1) make use of shorter side groups to strengthen the interchain macromolecular attractions to increase the sulfonic acid groups density, 2) incorporation of water retaining additives such as nanoscale oxides, 3) production of composite membrane materials. For very high temperature operations, membranes manufactured with phosphoric acid treatment with polybenzimidazole polymer are under test\textsuperscript{[2]}.

**Catalysts used in DMFC, selection and preparation:** Selection of methanol catalyst is done on the basis of the methanol oxidation kinetics \textsuperscript{[6]}. Most widely used is platinum-ruthenium bimetallic catalyst. During methanol oxidation process, it splits up in six protons, six electrons, carbon-dioxide, formaldehyde, and formic acid. Thus except the first two species all other act as poisons for the platinum catalyst. Thus to counter the effect of poisons work on different compositions of the catalyst is under research. It has also been observed that the catalyst structure plays an important role in the oxidation process. Alloy structure is not necessary but ruthenium sites closer to platinum sites are more beneficial for the process (In case of Pt/Ru bimetallic catalyst). Different methods of preparation used and under the study are soft chemistry method of nanoparticle impregnation, electro deposition, micro emulsion, impregnation by annealing, etc \textsuperscript{[6]}. Selection of oxygen catalyst is also an area of research as the reduction of air at the cathode side is a complex phenomenon. This is because the crossover methanol at the cathode side leads to non deserving side reactions thereby decreasing the life of the cathode catalyst. Most widely used is Platinum-Carbon catalyst. Major emphasis is on development of platinum catalyst retaining its electro activity and resisting the effect of crossover methanol and the study of electrocatalysts completely inert to the crossover methanol at the cathode side. The problem of hydrogen peroxide formation has to be tackled during the process\textsuperscript{[6]}.

**Methanol Crossover, its effects, and the solutions to overcome the problem:** It is defined as the phenomenon by virtue of which methanol diffuses through the polymer electrolyte membrane (PEM) of the direct methanol fuel cell. The reason behind this factor is differences in the concentration of the feed (concentration gradient) and the electro osmotic drag present between the solution and the PEM material of construction. Another reason responsible for the methanol crossover is ion clustering with the PEM; also the direct methanol fuel cell design and the reactant supply formats contribute to this major factor in some or the other way.

Methanol crossover is responsible as a major factor causing a great loss to the efficiency of the fuel cell. It causes depolarization losses at the cathode, conversion losses in terms of lost fuel, leading to secondary reactions (crossover methanol at the cathode side), decrease energy and power densities, excess thermal load, reduced electrochemical potential and overall voltage.

**Solution to above defined problems can be described as follows:** Methanol cross-over and/or its effects can be alleviated by (a) developing alternative membranes\textsuperscript{[2]}, (b) improving the electro-oxidation process in the catalyst layer and improving the structure of the catalyst and gas diffusion layers\textsuperscript{[3]}, and (c) optimizing the design of the flow field and the membrane electrode assembly (MEA) which can be achieved by studying the current density distributions\textsuperscript{[4]}. Other issues include the management of carbon dioxide created at the anode, the sluggish dynamic behavior, and the ability to maintain the solution water.

**Inorganic membrane preparation and selection:** New inorganic membranes with complete reduction of methanol crossover and highest proton conductivity are the area of strong research. Major emphasis is on the work of development of sulfonated polyetherketone (SPEK) membranes and the sulfonated polyetheretherketone (SPEEK) membranes\textsuperscript{[7]}. The major elements used for the membrane modification are SiO\textsubscript{2}, TiO\textsubscript{2}, and ZrO\textsubscript{2}\textsuperscript{[7]}. With ZrO\textsubscript{2} 60% reduction in the methanol flux was observed with 13 fold decrease in proton conductivity as per the literature survey. Silane is another element under observation for organic modification of the membrane. A combination of zirconium oxide and zirconium phosphate is an area of research and also a proven option for optimum results regarding the methanol crossover and proton conductivity\textsuperscript{[7]}.

**Fuel modification in direct methanol fuel cell:** The investigation of methanol crossover through the fuel modification represents an interesting and an alternative approach to the reduction of methanol crossover. Major emphasis is on the two systems which have proven to reduce the methanol crossover and increase the proton conductivity. The two systems under consideration on the basis of literature survey are 1) Acetic acid/water/methanol solution and 2) Propionic acid/water/methanol solution\textsuperscript{[8]}. The use of sulphuric acid, phosphoric acid, trifluoromethane sulfonic acid is an area of research but the trials used have led to the conclusion of cell material corrosion and catalyst poisoning which limited their use\textsuperscript{[8]}.
The above described two systems are proven but the kinetics and the dynamics of the systems are yet to be fully concluded and validated.

**Flow Field Design and selection:** Two types of flow field designs are compared for the performance of the direct methanol fuel cell namely single serpentine flow field design (SSFF) and parallel flow field design (PFF) [9]. The experimental and literature survey showed that the single serpentine flow field design is superior to that of the parallel flow field design. As per the literature survey it was reported that PFF was found with the channel blocking phenomenon at lower and higher flow rates of methanol while in contrast to that SSFF shows greater open ratio enhancement of the fuel cell. These two design patterns are continuously being innovated and tested under different set of conditions which again forms a major research area with evolution of the new flow field design possibility [9]. The optimized flow field design will thereby help to reduce the methanol crossover to a greater extent and will even allow optimum use of both the reactants on the cathode and anode side respectively.

**VI. CONCLUSION**

Complete overview of the direct methanol fuel cell along with its applications, construction and working procedures have been discussed in the paper. Methods to reduce the crossover of methanol have been given a major importance along with the performance optimization of the direct methanol fuel cell. The challenges occurring in the performance of the direct methanol fuel cell has also been discussed in detail in this paper. How DMFC is more advantageous over the other sources of electricity production and can be a source of power for various portable applications is concluded. The hard work of various people working on these challenges and finding a solution to the above defined problems has been incorporated in this paper.

**REFERENCES**


