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Chemical Engineering



Elixir Chem. Engg. 73 (2014) 26330-26332

Experimental studies on catalysts in direct methanol fuel cell R. Govindarasu^{1,*}, R. Parthiban¹ and P.K. Bhaba²

ABSTRACT

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ARTICLE INFO

Article history: Received: 12 June 2014; Received in revised form: 25 July 2014; Accepted: 9 August 2014;

Keywords

DMFC, Catalyst, Electro chemical reaction, Crossover. Characterization.

Introduction

In the present energy crisis, it has become inevitable to find out alternatives for the largely exploited fossil fuels. Recent developments in the field of fuel cells have given encouraging results suggesting their possible use of replacing the conventional highly polluting, less efficient internal combustion engines. In this context Direct Alcohol Fuel Cell (DAFC) appears to be the most promising source for powering cellular phones, laptop computers and other portable electronics[3]. DAFC generate power through the direct oxidation of alcohol in conjunction with the reduction of oxygen/air. In this type of fuel cell, either methyl alcohol or ethyl alcohol is not reformed into hydrogen gas but it is fed directly to the fuel cell [1].

Direct Methanol Fuel Cell (DMFC) is limited in the power that it can produce, but can still store high energy in a small space. This means that they can produce a small amount of power over a long period of time. Methanol is attractive as a fuel because it is inexpensive, widely available and can be handled and distributed easily [11]. With growing interests in the development and use of DMFC, much research work has been undertaken to eliminate the drawbacks and to promote its application in everyday. The role of catalyst in DMFC performance is vital as it enables the breakdown of methanol into proton and electron.

The efficiency of catalyst depends on the degree to which it can decompose as well as unite the proton in both the anode and cathode compartments respectively [2]. Methanol is one of the most electro active liquid organic fuels in the low temperature range. This is because of its low carbon content, high solubility in aqueous electrolytes and possesses a readily oxidisable hydroxyl group. In the early stages platinum is used as a catalyst for both half-reactions. This contributes to the loss of cell voltage potential, as any methanol that is present in the cathode chamber will oxidize. Furthermore, platinum is very expensive and contributes to the high cost per kilowatt of these cells.

Carbon Monoxide is formed during the methanol oxidation, which is strongly adsorbed onto the platinum catalyst, reducing the surface area and thus the performance of the cell [4].

DMFC has tremendous potential in serving as a source of clean and renewable energy. Different catalyst combinations are prepared and characterized in DMFC at various operating conditions. The characteristic curves are plotted. Effect of prepared catalyst in DMFC performance is analyzed at load and no load conditions. Demerits of Platinum catalyst is minimized to a great extent by the specially designed catalyst combinations. Based on the DMFC performance, the best catalyst combination (Pt-Ru/C) is identified and analysed in different operating conditions.

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The catalyst requirement is such that if another catalyst could be found for the reduction of oxygen, the problem of methanol crossover would be significantly reduced. It has been observed that, though platinum is being used as a conventional catalyst, modifications like alloying or impregnations of other elements on it enables a better and cost effective catalyst. However, their dependence on expensive Pt-based catalysts for both anode and cathode make them unsuitable for large-scale commercialization without modifications. Nowadays much research efforts are being made to develop a suitable high performance catalyst for the direct electrochemical oxidation of methanol. The key to success of a direct methanol fuel cell, however, remains in the development of highly efficient [5] fuel and air electrode catalysts.

The objective of the present investigation is to prepare and study the activity of pure Pt catalyst and non-novel catalyst combinations. Their performances are compared to select the best optimum catalyst. The effect of Cathode reagent, Cell temperature and pressure on the performance of DMFC with the best optimised catalyst combination is also analysed.

Experimental Methods

It is necessary to identify an appropriate and optimized catalyst to carry out the operation of DMFC, since catalysts are playing vital role for the conversion of reactants into product in electrochemical reaction. To enable that various non-noble catalyst combinations namely Pt-Ru, Pt-W, Pt-Sn and pure Pt supported on carbon [6,7] are prepared and tested in a standard DMFC setup (Figure 1). DMFC 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.

The combination of electrodes and membranes is called the Membrane Electrode Assembly (MEA). Each electrode is made up of a gas diffusion layer and a catalytic layer. Aqueous methanol is fed at the anode side. It diffuses through the diffusion layer to the catalytic layer where it is electrochemically oxidized into 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 or in the form of air. Electrons are collected by graphite bipolar plates which are the two poles of the cell [8].

The electrochemical reactions [9] involved in the cell are Anode reaction:



Figure 1. Schematic diagram of direct methanol fuel cell

The performance evaluation of the prepared non-novel catalyst combinations are carried out at different operating conditions namely at various temperature and pressure, with and without load conditions. The experiment is repeated with the cathode reagent oxygen instead of air to evaluate the impact of cathode

reagent in DMFC performance. Characterization curves of DMFC operation are plotted and analysed [10].

Results and Discussion

Non-novel catalyst combinations Pt-Ru, Pt-W, Pt-Sn and pure Pt supported on carbon are prepared and the characteristic study of these catalysts are carried out in a DMFC. Their performances are evaluated and reported in Table 2. From the table it is noticed that the Pt-Ru/C catalyst combination performs better than others and at the same time Pt/C catalyst shows poor performance.

This poor performance of pure Pt/C catalyst is due to the rapid deactivation of Pt catalyst by CO and hence reduction in potential and a steep fall of voltage to zero at the load of 200mA occurs. But it is reverse in the case of Pt-Ru/C catalyst combination (Voltage of 0.25V is recorded at the maximum current load of 1000 mA). Pt-Ru/C catalyst combination in DMFC with the cathode reagent of oxygen is also tested in this work.

The characteristic study of Pt-Ru/C catalyst combination in DMFC with cathode reagents of air and oxygen are plotted in Figure 2. It is noted from Figure 2, DMFC output is higher for oxygen. Experimental results on Pt-Ru/C catalyst combination at no load current condition with different pressures (Constant temperature of 60° C), at load current conditions with different pressures (Constant temperature of 60° C) and various temperatures (Constant pressure of 5 psi) are given in Figure 3 to 5. At no load current operation (Figure 3) no impact of pressure on fuel cell voltage is observed at constant temperature of 60° C. Since there are no significant variations in DMFC

performance at different pressures (Figure 4), minimum pressure (5 psi) is considered for further studies.

Table 2. Performance of DMFC with different catalyst combinations

Load	Voltage(V)			
(mA)	Pt-Ru/C	Pt-Sn/C	Pt-W/C	Pt / C
100	0.5	0.48	0.36	0.21
200	0.47	0.45	0.35	0
300	0.46	0.42	0.31	-
400	0.45	0.4	0.29	-
500	0.43	0.36	0.25	-
600	0.41	0.3	0.2	-
700	0.38	0.28	0	-
800	0.35	0.2	-	-
900	0.31	0.11	-	-
1000	0.25	0	-	-
1100	0	-	-	-

Higher performance of DMFC is obtained (Figure 5) at temperature of 60° C and 5 psi pressure.



Figure 2. Characterization with Pt-Ru/C for different cathode reagent



Figure 3. Characterization with Pt-Ru/C at different pressures with no load



Figure 4. Characterization with Pt-Ru/C at different pressures and $T = 60^{\circ}C$



Figure 5. Characterization with Pt-Ru/C at different temperatures and P = 5 psi

Conclusion

In this work different non-novel catalyst combinations (Pt-Ru, Pt-W, Pt-Sn and pure Pt supported on carbon) are prepared and analyzed in a standard Direct Methanol Fuel Cell. It is concluded from the characteristic curves that Pt-Ru/C catalyst gives better performance than others. It is found that the electrochemical reactions are accelerated higher with the cathode reagent of oxygen than air. In this study, it is observed that higher temperature and lower pressure gives maximum voltage output.

Acknowledgements

Financial support from AICTE, New Delhi under Research Promotion Scheme(RPS) is gratefully acknowledged.

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