

# Enhanced Performance of ZnO/C Electrocatalysts for Membraneless Fuel Cell

M. Priya<sup>a</sup>, M. Elumalai<sup>a</sup>, S. Kiruthika<sup>b</sup> and B. Muthukumar<sup>a</sup>

<sup>a</sup>Department of Chemistry, Presidency College, Chennai – 600 005, India.

<sup>b</sup>Department of Chemical Engineering, SRM University, Chennai – 603 203, India.

\*E-Mail: [dr.muthukumar@yaho.com](mailto:dr.muthukumar@yaho.com); Tel.: +91-44-28544894; Fax: +91-44-28510732.

**Abstract**— This paper discusses a novel microfluidic fuel cell concept using alkaline/acidic media. In this study ethanol used as a fuel and sodium perborate used as a oxidant, ZnO/C act as a anode and Pt/C act as a cathode. This study analyzed various concentration of fuel, oxidant at room temperature. ZnO is a higher stability comparing to other oxide its gives maximum power density of 27.03 mW cm<sup>-2</sup> with 1M ethanol concentration in 1M KOH solution as fuel and 0.1M perborate in 1 M H<sub>2</sub>SO<sub>4</sub> solution as a oxidant. It is revealed that ZnO/C catalyst posses a high electrocatalytic activity and stability for the electro-oxidant of ethanol, and it provides a facile and eco-friendly. This membraneless fuel cell operate without membrane, fuel and oxidant flow continuously in a single channel and it is promise the sustainable power source for portable application.

**Keywords**- Alkaline-acidic media, Ethanol, Membraneless sodium perborate fuel cell, ZnO/C catalyst

## I. INTRODUCTION

In this paper represent for the fuel cell technology is amongst the most pursued topics in the effort to develop alternative energy generation methods. Microfluidic fuel cells are relatively new developments which take advantage of the characteristics of laminar flow to control the interaction between the fuel and oxidant entering the cell. Because the fuel and oxidant are able to flow concurrently and separately in a single microfluidic channel. It is possible for the cell to function without the need of a physical barrier such as a proton exchange membrane [1].

Ethanol fuel is more attractive and ethanol is the fermentation of agricultural product or biomass but, also possesses many unique properties, including higher energy density, low toxicity and ease in handling and transportation [2]. Further development of ethanol powered fuel cell is seriously hindered by slow kinetics and inefficient oxidation of ethanol to CO<sub>2</sub> on available electrocatalyst [3]. The implementation of the direct ethanol fuel cell technology has been hindered by sluggish ethanol oxidation reaction at the anode, due to the lack of an active anode catalyst.

Platinum and its alloys are the most common catalysts in both anode and cathode fuel cell reactions because of their excellent properties in the adsorption and dissociation of SOMS. The expense of Pt-based catalysts is a major impediment in the commercialization of fuel cell technology [4]. The addition of a co-catalyst to Pt or Pd including alloy formation between two metals or the introduction of metal oxide could potentially enhance the catalysts activity, and corrosion resistance [4].

Fundamental studies of the electronic and structural properties of such inverse catalyst systems revealed that the metal oxide interface plays a crucial role in enhancing catalytic activity. With large numbers of low-coordination and defect sites, small oxide nanoparticles are found to be more active than larger bulk-like metals. Therefore, introducing the metal oxide nanoparticles on metal surfaces could be an alternative approach for enhancing the activity of mixed metal/metal oxide catalysts [5]. In the mean time introducing some metal oxides into the catalyst such as CeO<sub>2</sub> [5], SnO<sub>2</sub> [6], RuO<sub>2</sub> [7], ZrO<sub>2</sub> [8], MgO [9], and V<sub>2</sub>O<sub>5</sub> [10] is another focus and many achievements have been obtained [6]. In our previous work, a microscale membraneless sodium perborate fuel cell (MLSPBFC) was fabricated on poly (dimethylsiloxane) (PDMS) and its performance was evaluated under different operating conditions [7-9]. Standard microfabrication techniques were used to develop the device. In this present work, ethanol is used as a fuel at ZnO/C anode and sodium perborate is used as an oxidant at Pt/C cathode under “alkaline anode and acidic cathode” conditions. ZnO is a high electron mobility, high thermal conductivity, wide and direct band gap and large excitation binding energy make ZnO suitable for a wide range of devices.

The experiments described in this study show that membraneless sodium perborate fuel cells are media flexible; they can be operated in all-acidic, all-alkaline, alkaline anode and acidic cathode or vice versa. In this work we observed that the alkaline anode/acidic cathode configuration leads to a very high measured open circuit potentials (OCP) which is in good agreement with the OCP which is achieved in our previous work,

while other combinations were result in very low OCPs as a result of the pH dependence of standard electrode potentials. The flexibility of membraneless fuel cells to function with different media allowed the successful operation of mixed alkaline and acidic fuel cells. In addition, the development of ZnO/C catalysts to accelerate the efficiency of MLSPBFC will be the focus of this study. This fuel cell is a promising carbon-neutral and sustainable power source for portable, mobile, and stationary applications.

## II. EXPERIMENTAL

The materials and chemicals used during the tests are listed as follows: Zinc oxide powder (CAS No: 1314-13-2) <10 $\mu$ m, 98% Merck, India, Graphite plates (Kriti Graphite), 5% Platinum on Carbon type 5T18 paste from Johnson Matthey Catalysts, India. All other materials and chemicals used throughout the tests are listed as follows: C<sub>2</sub>H<sub>5</sub>OH (98%, Merck), NaBO<sub>3</sub>·4H<sub>2</sub>O (99%, Riedel), KOH (98%, Merck) and H<sub>2</sub>SO<sub>4</sub> (98%, Merck). All experiments were conducted at room temperature using ethanol in deionised water as a fuel and sodium perborate in deionised water as an oxidant and 1M KOH and 1M H<sub>2</sub>SO<sub>4</sub> in deionised water as electrolytes.

### A. Catalyst deposition

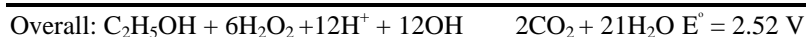
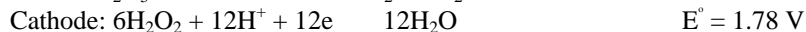
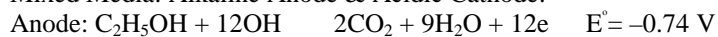
For all the experiments of MLSPBFC, unsupported platinum black nanoparticles are applied to the sides of the graphite plates to act as cathode that line the microfluidic channel. The catalyst suspension for cathode were prepared by mixing at a concentration of 6.0 mg ml<sup>-1</sup> Pt black nanoparticles (Alpha Aesar) in a 10 wt.% Nafion solution (Nafion stock solution: Dupont, 5% (w/w) solution). This mixture was sonicated and applied to the side faces of the graphite plates at a loading of 2 mg cm<sup>-2</sup>. Then solvent was evaporated by the use of a heat lamp for uniform loading. The catalyst suspension for anode were prepared by mixing at a concentration of 8.0 mg ml<sup>-1</sup> of Zinc oxide powder maintaining a total metal loading constant (each 4.0 mg ml<sup>-1</sup>) in a 10 wt.% Nafion solution. This mixture was sonicated and applied to the side faces of the graphite plates at a loading of 2 mg cm<sup>-2</sup>. Then solvent was evaporated by the use of a heat lamp for uniform loading.

## III. RESULT AND DISCUSSION

In this current exertion we consisted inside the suppleness and the performance implications of functioning MLSPBFC underside “alkaline-acidic media” using ZnO/C as an anode and Pt/C as cathode. In modern years, consequently alkaline-acidic media have an attractive high theoretical OCP of about 2.59 V [11]. Accordingly, we are inclined to use alkaline-acidic media to development for complementary enhancement in fuel cell performance as follows;

In alkaline-acidic media, the MLSPBFC functions using a fuel stream of an alkaline anode and an acidic cathode, which allows energy to be obtained both from the ethanol oxidation/peroxide reduction reactions and from the alkaline/acidic electrochemical neutralization reactions, as understandable from the overall cell reaction.

Mixed Media: Alkaline Anode & Acidic Cathode:



In this alkaline-acidic media, the combination of two galvanic reactions yields a agreeable high theoretical OCP of 2.52 V. Note that the fundamental value of the electromotive force of the MLSPBFC is higher than that of the HFC (1.23 V). However, because of the over potentials resulting from the slow kinetics of peroxide reduction and ethanol oxidation, the OCP gets reduced to a measured value of 1.810 V as shown in Fig.1 which was in good agreement with the preceding reported value of 1.53 V [12]. In alkaline-acidic media, together OH<sup>-</sup> and H<sup>+</sup> are inspired at the anode and cathode, respectively, at a rate of six ions for each molecule of ethanol.

### A. Influence of fuel variation

The effect of the fuel concentration on the product selectivity was studied by varying both ethanol and KOH concentrations. The effect of ethanol concentration was investigated by varying the

concentration of ethanol as 0.5, 1.0, 1.5, 2.0, 3.0, and 4.0 M while fixing the concentration of KOH at 1.0 M. similarly, the effect of KOH concentration was observed by varying the concentration of KOH as 0.5, 1.0, 1.5, to 2.0 M while fixing the concentration of ethanol at 1.0 M. among these several combinations of fuel and oxidant, the fuel solution containing 1.0 M ethanol and 1.0 M KOH gives the highest and most stable performance, and a decrease and fluctuation of cell voltage was observed as the ethanol and KOH concentrations are varied. The experimental results show that the fuel cell performance decrease as the ethanol concentration increases. The performance of the EOR (ethanol oxidation reaction) depends on not only the local concentrations of ethanol and OH<sup>-</sup> ions but also the balance of the competing adsorption between ethanol and the OH species. (13) This is because the high ethanol concentration causes more active sites to be covered by ethanol, which may block the adsorption of hydroxyl on the active sites (14).

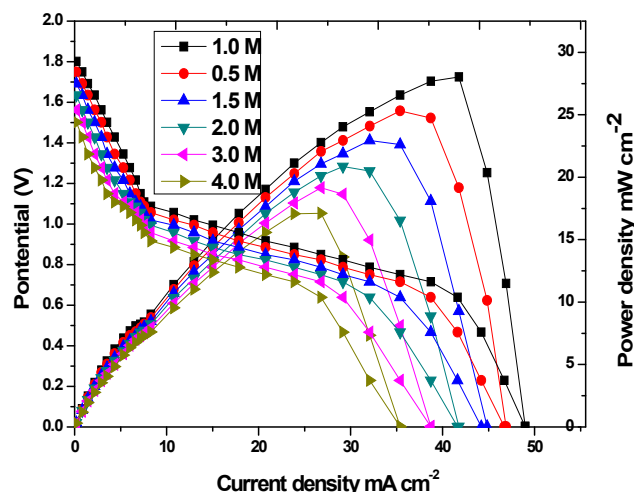
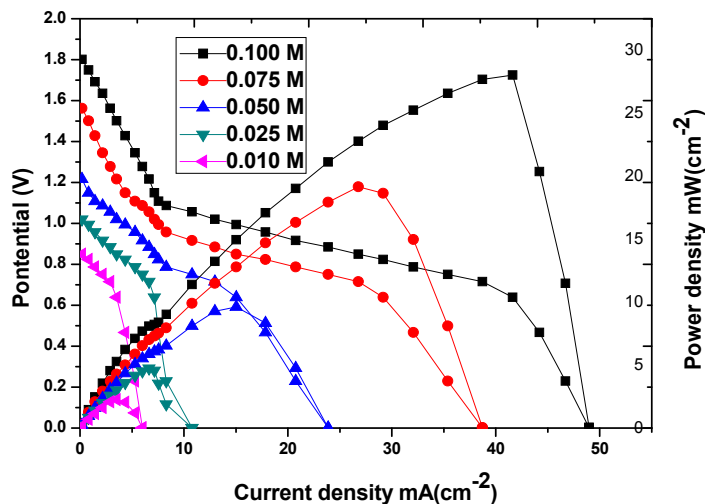


Fig1: Effect of ethanol concentration on the current and power density of the MLSPBFC at room temperature.  
 ([Fuel]: xM ethanol + 1 M KOH. [Oxidant]: 0.1 M perborate + 1 M H<sub>2</sub>SO<sub>4</sub>).

#### B. Influence of oxidant variation

Fig 2 Effect of perborate concentration on the current and power density of the MLSPBFC at room temperature. ([Fuel]: 1 M ethanol + 1 M KOH. [Oxidant]: x M perborate + 1 M H<sub>2</sub>SO<sub>4</sub>). The effects of perborate concentration on the cell performance were investigated at 0.01, 0.025, 0.05, 0.075 and 0.1M. the power density increased as sodium perborate concentration increases in the MLSPBFC system and reaches the maximum power density of (27.03 mW cm<sup>-2</sup>) was obtained at 1M KOH. Further increase in the concentration of KOH shows no improvement in the cell performance. Therefore, the value of 1 M has been fixed as the KOH concentration in the oxidant solution. Further increasing the electrolyte and oxidant concentration cell performance decreased, because concentration boundary layer formed near by the electrodes.



#### IV. CONCLUSION

In this membraneless fuel cell, ethanol is engaged as a fuel at ZnO/C anode and sodium perborate is used as an oxidant at Pt/C cathode for the first time under “alkaline-acidic media”. In this work, we tend to determine that the alkaline anode/acidic cathode media ends up in a high measured OCP of 1.810 V, while other combinations results in very low OCPs as a result of the pH dependence of standard electrode potentials. At room temperature, the laminar flow-based microfluidic fuel cell produced a maximum power density of 27.03 mW cm<sup>-2</sup> under alkaline anode/ acidic cathode media. We concluded that alkaline-acidic media of MLSPBFC seems to outperform the all-acidic and all-alkaline MLSPBFCs. The MLSPBFC has the advantages of a miniature size, simplicity of fabrication, use of aqueous fuel, and good cost efficiency. Furthermore, perborate is a cheap, nontoxic, stable, easily handled, environment-friendly, large-scale industrial chemical, and is a convenient source of hydrogen peroxide. We expect that the MLSPBFC may be a promising candidate for practical fuel cells to generate clean and sustainable energy in the future.

#### References

1. Richarged Anger, “Development of advanced carbon electrodes for use in microfluidic vanadium redox fuel cells”.
2. L. An, T. S. Zhao, “Performance of an alkaline-acid direct ethanol fuel cell”, International journal of hydrogen energy 36 (2011) 9994e 9999.
3. Wei-Ping Zhou, Stephanus Axanada, G. Michael White, Radoslav R. Adzic, and Jan Hrbek, “Enhancement in the Ethanol/Electrooxidation by SnOx Nanoislands Grown on Pt (111):Effect of metal oxide –Metal interface sites”, J.Phys.Chem.C2011,115, 16467-16473.
4. Du. Wenxin, Qi. Wang, David Saxner, N. Aaron Deskins, Su. Dong, E. Krzanowski, I. Anatoly, Frenkel, and Xiaowei Teng, “Highly active Iridium/Iridium Tin/Tin oxide heterogeneous nanoparticles as slternative electrocatalysts for the ethanol oxidation reaction”, J. Am. Chem.Soc. 2011, 133,15172-15183.
5. Wei-Ping Zhou, Stephanus Axanada, G. Michael White, Radoslav R. Adzic, and Jan Hrbek “Enhancement in the Ethanol/Electrooxidation by SnOx Nanoislands Grown on Pt (111): Effect of metal oxide –Metal interface sites”,
6. Yu Lihong, Xi Jingyu, “CeO<sub>2</sub> nanoparticles improved Pt-based catalysts for direct alcohol fuel cells”, International Journal of Hydrogen Energy 37 (2012) 15938-1594.
7. M. Gowdhamamoorthi, A. Arun, S. Kiruthika, B. Muthukumar, “Enhanced performance of membraneless fuel cell”, Int. J. of ChemTech Research., 2013, 5, 1143-1151.
8. M. Gowdhamamoorthi, A. Arun, S. Kiruhtika, B. Muthukumar, “Enhanced performance of membraneless sodium percarbonate fuel cell”, J. of Materials., Article ID 548026, 2013, and 2013, 1-7.
9. A. Arun, M. Gowdhamamoorthi, S. Kiruhtika, B. Muthukumar, “Electrocatalyzed oxidation of methanol on carbon supported Pt electrode in membraneless sodium percarbonate fuel cell (MLSPCFC)”, Int. J. Of ChemTech Research., 2013, 5, 1152-1161.
10. Yen T, Fang N, Zhanga X, Lu GQ, Wang CY, “A micro methanol fuel cell operating at near room temperature”, *Appl. Phys. Lett.* 2003, vol.83: pp.4056.
11. An, T.S. Zhao, J.B. Xu, “A bi-functional cathode structure for alkaline-acid direct ethanol fuel cells”, International journal of hydrogen energy 36 (2011) 13089-13095.
12. M. Priya, A. Arun, M. Elumalai, S. Kiruthika and B. Muthukumar, “ A development of ethanol/percarbonate membraneless fuel cell” Advances in Physical chemistry Volume 2014, Article ID 862691.
13. S.Y.Shen, T.S. Zhao, Q.X. Wu, “Product analysis of the ethanol oxidation reaction palladium-based catalysts in an anion- exchange membrane fuel cell environment”. International Journal of Hydrogen Energy 37(2012) 575-582.
14. An L, Zhao TS, “Performance of alkaline electrolyte – membrane-based direct ethanol fuel cells, International journal of hydrogen energy”, 2011, 36: 9994-9999.