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Electro-oxidation of Isopropanol in Membraneless Fuel Cells

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Abstract : This paper presents the development of membraneless sodium perborate fuel cell. Investigation of the cell operation is conducted by using isopropanol as a fuel and sodium perborate as an oxidant. The cell converts the energy released by H_2O_2 decomposition with H^+ and OH^- ions into electricity and produces water and oxygen. Such a novel design eliminates the need of a membrane, in which acid and alkaline electrolytes contact with each other. The effects of flow rates and the concentrations of various species at both the anode and cathode on the cell performance are also investigated. At room temperature, the laminar flow-based microfluidic membraneless fuel cell can reach a maximum power density of 23.8 mW/cm^2. The developed fuel cell emits no CO_2, features no proton exchange membrane, inexpensive catalysts, and simple planar structure, which enables high design flexibility and easy integration of the microscale fuel cell into actual microfluidic systems and portable power applications.

Keywords: Alkaline-acid media, Isopropanol, Membraneless fuel cell, Portable power applications.

Introduction

The decreasing availability of fossil fuels and the increasing impact of greenhouse gases on the environment lead to an extensive development of more efficient or renewable energy sources. Fuel cells are chemo electric device, which convert the chemical energy of a fuel directly into electricity. The process is an electrochemical reaction like a battery[1]. The key benefit of the membraneless laminar flow fuel cell technology is that it employs liquid fuels, which have high energy densities compare to gaseous fuels. Although, the initial idea was based on the use of methanol in membraneless laminar flow fuel cell, recent studies have also focused on the isopropanol.

In this work isopropanol used as a fuel and sodium perborate used as an oxidant. Isopropanol is the smallest secondary alcohol with less toxicity and higher electrochemical reactivity. Isopropanol is relatively inexpensive, has a low toxicity and is miscible with water. Qi et. al. reported that 2-propanol, an easily obtained fuel, can exhibit better performance compared to methanol, especially in the low current density range, which

was attributed to the combined effect of faster reaction kinetics of 2-propanol oxidation and its lower crossover rate.

In this communication, first time we introduce sodium perborate ($NaBO_3 . 4H_2O$) as an oxidant under "alkaline/acidic media", to demonstrate the performance of a membraneless sodium perborate fuel cell (MLSPBFC). Sodium perborate is a true peroxo salt and is a convenient source of hydrogen peroxide [4, 5].

$$[B(OH)_3(O_2H)]^- + H_2O \rightleftharpoons [B(OH)_4]^- + H_2O_2 \qquad\qquad (1)$$

The MLSPBFC has some advantages, such as Sodium perborate is a cheap, non-toxic, large scale industrial chemical used primarily in detergents and as a mild oxidant[6, 8]. The cell being more environmentally friendly than the other fuel cells and the sodium perborate can be handled more simply than hydrogen, as it is well known fact that sodium perborate solution is a widespread safe disinfectant.

Experimental

Materials and reagents

The materials and chemicals used during the tests are listed as follows: Isopropanol (≥99.5%, Aldrich), $NaBO_3 \cdot 4H_2O$ (99%, Riedel), KOH (98%, Merck) and H_2SO_4 (98%, Merck), PDMS poly(dimethylsiloxane) (99.9%, Chemsworth), and PMMA poly(methylmethacrylate) (92%, G. Khanna & Co), Graphite plates (Kriti Graphite), Silicon tubes (Shree Gaurav rubber products). All experiments were conducted at room temperature using isopropanol in deionised water as a fuel and sodium perborate in deionised water as an oxidant and 0.5M KOH and 0.5M H_2SO_4 in deionised water as electrolytes.

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 and anode that line the microfluidic channel. The catalyst suspensions for both anode and cathode were prepared by mixing at a concentration of 6.0 mg ml^{-1} 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^{-2}. Then solvent was evaporated by the use of a heat lamp for uniform loading.

Design of membraneless sodium perborate fuel cells (MLSPBFC)

In the MLSPBFC configuration, an E-shaped laminar flow channel with catalyst-coated graphite plates of 1 mm thickness is used. Subsequent deposition of catalyst to the cathode and anode, the E-shaped microfluidic channel structure is molded with PDMS poly(dimethylsiloxane), typically 1–10 mm in thickness, and finally sealed with a solid substrate such as 2 mm thick pieces of PMMA poly(methylmethacrylate) to provide rigidity and supportive strength to the layered system. Silicon tubing is placed to guide the fuel and oxidant into the E-shaped channel systems at the top and to guide the waste stream out at the bottom of the channel.

Test of the fuel cell

The solutions of fuel and oxidant were pumped through the device using a syringe pump (Schiller India). The flow rate of each of the streams was 0.3 mL min^{-1} (total flow rate of 0.6 mL min^{-1}). Also, the cell was allowed to run for an hour for the flow to reach a steady state. When injected through the inlets, fuel and oxidant solutions will merge at the E-junction and continue to flow laminarly in parallel over the anode and cathode where fuel and oxidant are allowed to be oxidized and reduced, respectively.

Cell measurements were conducted using a CS310 computer controlled potentiostat (Zhengzhou triangle instrument co. ltd.) with the associated Thales Z software package. For each analysed factor, the performance of the fuel cell was evaluated by recording the cell polarisation and obtaining the corresponding power density curves. Consequently, the microfluidic cell keeps these fluids stable without a separation membrane.

Results and Discussion

Two different approaches have been pursued: the first step consisted in the flexibility and the performance implications of operating membraneless sodium perborate fuel cell (MLSPBFC) under "acid-alkaline media" configuration; the second step was intended to further improve the cell performance by

characterising the main cell by changing several operational parameters, namely the fuels' compositions, oxidants' compositions, electrolytes' compositions, distance effect and flow rate, and to observe their influence on the polarisation behaviour of the cell.

Performance of MLSPBFC in acid-alkaline media: alkaline anode, acidic cathode

In acid-alkaline media configuration, the MLSPBFC using a fuel stream of an alkaline anode and an acidic cathode allows energy to be obtained both from the isopropanol oxidation/peroxide reduction reactions and from the acid/alkali electrochemical neutralization reactions, as evident from the overall cell reaction Eq. (4):

acid-alkaline media: alkaline anode, acidic cathode:

Anode: $CH_3CHOHCH_3 + 2OH^- \rightarrow CH_3COCH_3 + 2\,H_2O + 2e^-$	$E^0 = -0.67$	(2)
Cathode: $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	$E^0 = 1.78$	(3)
Overall: $CH_3CHOHCH_3 + H_2O_2 + 2H^+ + 2OH^- \rightarrow CH_3COCH_3 + 4H_2O$	$\Delta E = 2.45$	(4)
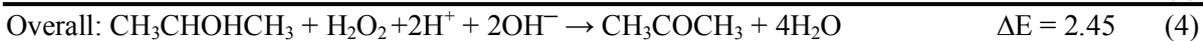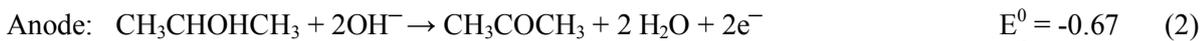
In this acid-alkaline media configuration, the combination of two galvanic reactions yields a desirable high theoretical OCP value of 2.45V. Note that the inherent value of the electromotive force of the MLSPBFC is higher than that of the HFC (1.23 V) and the PEMFC or DMFC (1.21 V). However, because of the overpotentials resulting from the slow kinetics of peroxide reduction and isopropanol oxidation, the open circuit potential is reduced to a measured value of 1.36 V (Fig. 3). Operating in this acid-alkaline media configuration, with an alkaline anode and an acidic cathode, resulted in a higher overall cell potential of 1.36V.

Influence of fuel composition

The effect of fuel on the performance of MLSPBFC has been observed by varying the isopropanol concentration between 1 M and 5 M (Fig. 1). The cell performance with different isopropanol concentrations at a KOH concentration of 1 M is shown in Fig. 1. When fuel concentration is high, the limiting current density and the maximum power density is larger. Further increase in isopropanol concentration degrades the cell performance. Hence, there exists an optimum isopropanol concentration of 1M that yields a maximum power density of 23.8 mWcm^{-2}, as shown in Fig. 1. As such, the increased isopropanol concentration enhances the kinetics of IOR, which lowers the anode activation loss, so that the cell voltages are improved, as evidenced by OCV in Fig. 1. When fuel concentration is high, the limiting current density and the maximum power density is larger. As more reactants enter the cell, the mass transport to the electrodes increases. Accordingly, the current density and power density increases. However, the transport rate is limited by the depletion region [9]. Thus the current density did not increase significantly, while increasing the fuel concentrations beyond 1 M, which also suggests that the performance of the membraneless fuel cells is limited by slow anode/cathode kinetics or slow diffusion of reagents to the electrode surface due to the formation of a concentration boundary layer. From this we conclude that the concentration of isopropanol as low as 0.5 M did not result in a reduction of the cell performance, which indicates that the cell is cathode limited [10]. In the present study, experimental results show that the fuel cell performance is maximum at 1 M and further increase in the isopropanol concentration has no significant effect on the fuel cell.
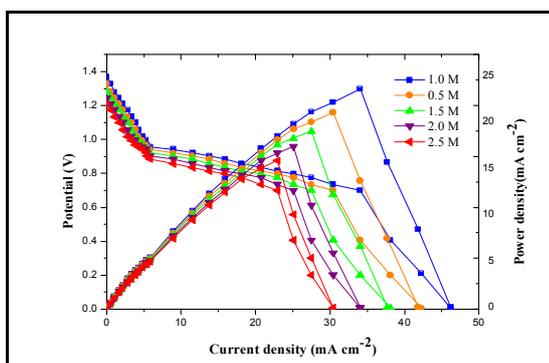
Fig.1. Effect of isopropanol concentration on the current and power density of the MLSPBFC at room temperature. [Fuel]: x M isopropanol + 1 M KOH. [Oxidant]: 0.1 M perborate + 0.5 M H$_2$SO$_4$. Stream flow rates: 0.3 mL min^{-1}.

When the isopropanol concentration is raised further to 1.5 M, the cell performance is lowered. The cell performance decreases with further increase in isopropanol concentration from 1.5 M to 2.5 M, due to the lowered electrochemical kinetics and the increased ohmic loss.

Influence of oxidant composition

The effects of perborate concentration on the cell performance were investigated at 0.01, 0.025, 0.05, 0.075 and 0.1 M. The power density increased in correlation to increased sodium perborate concentration in MLSPBFC and reaches the maximum of 1.36 V at 0.1 M sodium perborate. Peak power densities of 1.95, 3.70, 8.05, 16.04, 23.80, mW cm^{-2} were obtained at 0.01, 0.025, 0.05, 0.075 and 0.1 M respectively (Fig. 2). Further increase in the oxidant concentration shows no improvement in the cell performance. Therefore the value of 0.1 M has been fixed for the perborate concentration in the oxidant solution.
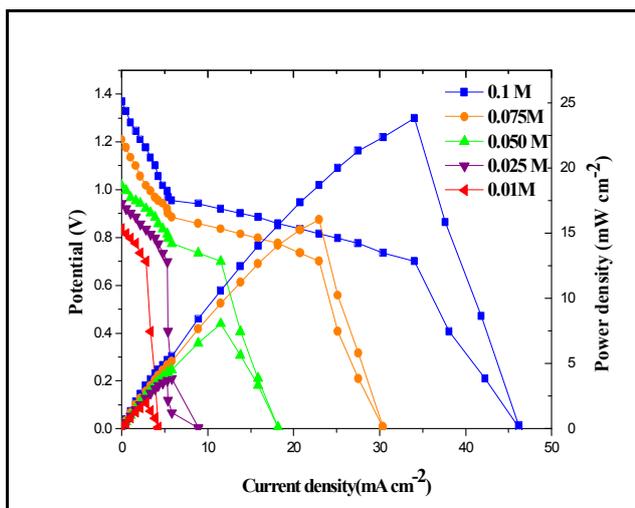
Fig.2. Effect of perborate concentration on the current and power density of the MLSPBFC at room temperature. [Fuel]: 1 M Isopropanol + 1 M KOH. [Oxidant]: x M perborate + 0.5 M H₂SO₄. Stream flow rates: 0.3 mL min⁻¹.

Influence of distance effect on the performance of MLSPBFC

In order to analyse the potential benefit arising from a reduced diffusion length of the reacting species moving between the anode and cathode, the distances were varied between 1 and 100 mm. When the distance between the anode and cathode decreased, the maximum power density was observed, as shown in Fig. 3. Considering the role of a charge carrier, a shorter diffusion length is believed to result in a faster electrochemical reaction because the diffusion time of reacting species would be shorter. This leads to more reactions taking place at a given time, which increases the total number of charges involving the electrochemical reactions at the anode and cathode. This finding provides a good evidence for the presence of a charge carrier moving between the anode and cathode in the fuel mixture to complete redox reactions of the fuel cell [11].
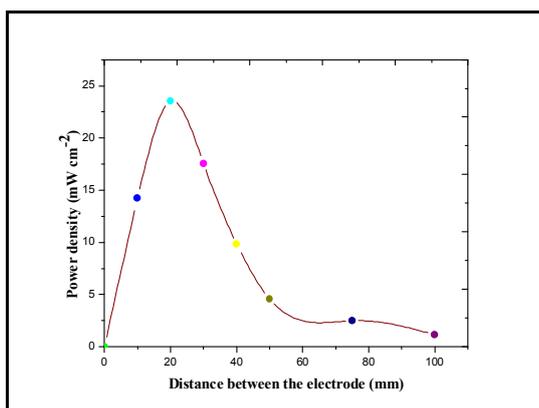
Fig. 3. Effect of distance between anode and cathode on the maximum power density of the MLSPBFC at room temperature. ([Fuel]: 1 M isopropanol + 0.1 M KOH. [Oxidant]: 0.1 M perborate + 0.5 M H₂SO₄).

Influence of fuel mixture flow rate

     Since maximum power density is dependent on the transport time of the reacting species, it can be controlled by the flow rate. In this experiment, flow rates of 0.1, 0.3, 0.5, 0.7 and 1.0 mL min^{-1} were tested. The cell potential and current were measured with different external loads as a function of the flow velocity of the fuel mixture. Using the flow rate applied and the cross-sectional area of the channel, a flow velocity can be calculated. In our experiments, the maximum power density was obtained at a flow rate of 0.3 mL min^{-1}, after which the maximum power density decreases with an increase in the flow rate as shown in (Fig. 4). It is believed that more electrochemical reactions would take place at a given time and a greater output current could develop in the end.
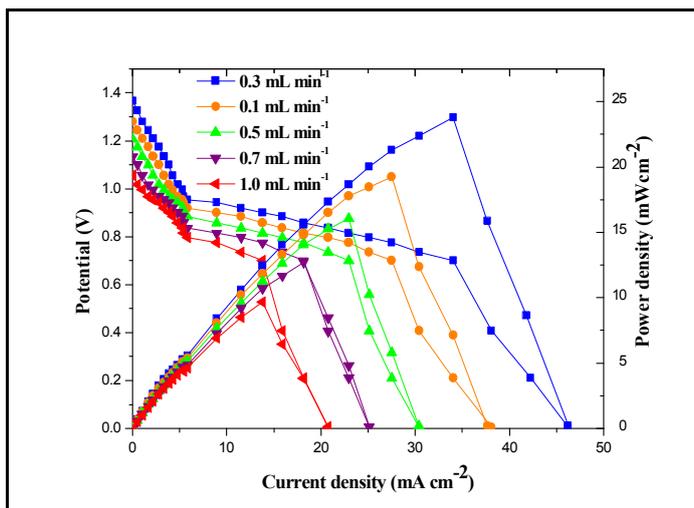
Fig. 4. Effect of flow rate of fuel mixture on the current and power density of the MLSPBFC at room temperature. ([Fuel]: 1 M isopropanol + 0.1 M KOH. [Oxidant]: 0.1 M perborate + 0.5 M H$_2$SO$_4$).

Conclusions

     A microscale membraneless sodium perborate fuel cell (MLSPBFC) was fabricated on PDMS and its performance was evaluated under different operating conditions. Standard microfabrication techniques were used to develop this device. Isopropanol is used as a fuel at the anode and sodium perborate is used as an oxidant at the cathode in this membraneless fuel cell for the first time in an alkaline-acidic media. The experiments described in this study show that membraneless sodium perborate fuel cells are media flexible and they can be operated in alkaline-acidic media.

     In this work, we observed that the alkaline anode/ acidic cathode acid-alkaline media configuration leads to a very high measured OCP of 1.36 V, while other combinations will result in very low OCPs as a result of the pH dependence of standard electrode potentials. The MLSPBFC operated in the alkaline anode/ acidic cathode acid-alkaline media configuration, the measured OCP of 1.36 V is in good agreement with the theoretical OCP of 2.45 V. At room temperature, the laminar flow-based microfluidic fuel cell produced a maximum power density of 23.8 mW cm^{-2} under alkaline anode/ acidic cathode acid-alkaline media configurations. The effects of flow rates of the fuel and oxidant, variation of concentrations of isopropanol, perborate, and electrolytes were evaluated under acid-alkaline media configurations. The performance was characterized by *V*–*I* curves and anode polarization plots.

     The results demonstrated that the performance of the developed membraneless fuel cell enhanced profoundly if the concentration of oxidant in cathodic stream is 10 times larger, and the current density is also increased approximately ten times, and the current density is also increased approximately 10 times, whereas in the case of variation of isopropanol concentration at the anode, fuel cell performance decreases as the ethanol concentration increases, due to the increase of ohmic resistance.

     The MLSPBFC has the advantages of their miniature sizes, simplicity of fabrication, use of aqueous fuel, and good cost efficiency. Furthermore, perborate is a cheap, nontoxic, stable, easily handled, environmental 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 establish a clean and sustainable energy future.

References

1. Thomas C.E. Fuel cells and battery electric vehicles compared. International Journal of Hydroen energy., 2009, 34: 6005-6020.
2. Jie Yang, Sasan Ghobadian, Payton, J.Goodrich, Reza Montazami, Nastaran Hashemi. Miniaturized biological and electrochemical fuel cells: challenges and applications. Phys.Chem. phys., 2013, 15: 14147.
3. Lu G.Q, Crown A,Wieckowski A Formic acid decompositionon polycrystalline platinum and palladized platinum electrodes. JPhys Chem., 1990, 103:9700–9711.
4. Cotton F.A, Wilkinson G. Advanced inorganic chemistry.Wiley Interscience, New York, 1990, p 812.
5. Karunakaran C, Kamalam R Structure−reactivity correlationof anilines in acetic   acid. J Org Chem., 2002, 67:1118–1124.
6. Gowdhamamoorthi M, Arun A, Kiruthika S, Muthukumaran B., Enhanced Performance Of Membraneless Fuel Cells, International Journal of ChemTech Research, 2013, 5:3: 1143-1151.
7. Enhanced Performance of Membraneless Sodium Percarbonate Fuel Cells. Journal of Materials., 2013, 548026: 7.
8. Arun A, Gowdhamamoorthi M, Kiruthika S, Muthukumaran B., Electrocatalyzed Oxidation of Methanol on Carbon Supported Platinum Electrode in Membraneless Sodium Percarbonate Fuel Cells (MLSPCFC). International Journal of ChemTech Research., 2013, 5:3:1152-1161.
9. Lu GQ, Wang CY, Yen TJ, Zhang X., Development and characterization of a silicon-based micro direct methanol fuel cell. Electrochim. Acta. 2004, 49:821–828.
10. Park HB, Lee KH, Sung HJ., Performance of H-shaped membraneless micro fuel cells. J Power Sources. 2013, 226:266–271.
11. Kundu., Micro-fuel cells – Current development and applications, Journal of Power Sources, 2007, 170: 67–78.

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