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Enhanced Performance an Ethanol Membraneless Fuel Cell in Acidic Medium

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Abstract: The continuous flow operation of membranelesssodium perborate fuel cell using acidic media is presented in this paper. In this cell, ethanol is used as the fuel and sodium perborate is used as an oxidant for the first time in an acidic media. Sodium perborate generates hydrogen peroxide in aqueous medium. At room temperature, the laminar-flow-based microfluidic membraneless fuel cell can reach a maximum power density of with a fuel mixture flow rate of 0.3 mL min^{-1}. The developed fuel cell features no proton exchange membrane. The simple planar structured membranelessethanol fuel cell presents with high design flexibility and enables easy integration of the microscale fuel cell into actual microfluidic systems and portable power applications.

Keywords acidic media, Ethanol,Membranelesssodium perborate fuel cell, Portable power applications.

Introduction

A membraneless fuel cell is a novel device without a membrane that converts chemical energy generated from a fuel and an oxidant into electric energy by means of oxidoreduction reactions. In membraneless micro fuel cells, liquid reactants (fuel and oxidant) flow side by side in a laminar fashion in a single channel, not requiring a membrane for reactant flow. Anode and cathode electrodes are positioned on the channel walls opposite to each other and the mixing of fuel and oxidant in the channel occurs only by diffusion. Moreover, the chemical composition of the cathode and anode streams can be designed individually to optimise individual electrode kinetics as well as overall cell potential.

An additional advantage is that structures of membraneless micro fuel cells are very simple and easy to miniaturise[1],so that light and stackable fuel cells can be fabricated with simple microelectromechanical systems (MEMS) [2, 3]. The implications of flexibility and the performance of operating membraneless sodium perborate fuel cell (MLSPBFC)in alkaline-acidic media, in which one electrode is alkaline and the other acidic, is the focus of this study.

In the present work, ethanol is used as a fuel to study the performance of MLSPBFC. Ethanol is an accepted, more attractive and promising clean and energy-efficient cell[4]. Ethanol is a carbon-neutral, sustainable fuel that can be produced in great quantity through the fermentation of agricultural products or biomass. But, its many unique properties including low toxicity ease in handling and transportation make it a fuel of choice compared to other fuel cells.

A few studies were carried out that attempted to use oxygen solution as the oxidant. The performance of these micro fuel cells was found to be severely hampered by the low transport efficiency of oxygen in the cathode stream.

Membraneless sodium perborate fuel cell (MLSPBFC) is studied in this work using an acidic solution of sodium perborate (Na_2BO_3. $4H_2O$) as the oxidant. The impact of using acidic media (i.e., one electrode is acidic and the other one is alkaline condition) on the performance of the fuel cell is the focus of our study. Sodium perborate, the oxidant used in the study, is cost-effective, environmentally friendly, and nontoxic industrial chemical used on a large scale in detergents and as a mild oxidant. Sodium perborate, a true peroxo salt, proves to be a convenient source of hydrogen peroxide [5, 6].

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

Sodium perborate functions as both an oxidant and reductant, which makes this cell unique when compared with other fuel cells using H_2O_2[7, 8]. The performance of MLSPBFC in generating electric power is comparable to a typical air-breathing DMFC that operates in a microchemical channel at room temperature. The issues arising out of using a membrane cell, as explained before, can be avoided when a MLSPBFC is employed. Another advantage of using MLSPBFC is the simple structure of the cell in the absence of membrane electrode assemblies in addition to a reduction in the cost of materials.

In this study, new forms of simplified architectures, unique from those that have been reported in literature, have been developed by eliminating and integrating the key components of a conventional MEA. With these advantages, we believe membranelesssodium perborate fuel cells (MLSPBFC) can be used as an alternative for portable power applications.

Experimental

Materials and reagents

All experiments were conducted at room temperature using ethanol (98%, Merck) in de-ionized water as the fuel, and sodium perborate (99%, Riedel) dissolved in 1M sulfuric acid (98%, Merck) in de-ionized water as the oxidant.

Catalyst preparation

For all the experiments involving MLSPBFC, unsupported platinum black nanoparticles (Alpha Aesar) are applied to the sides of the graphite plates (kiriti graphite), which act as the cathode and anode that line the microfluidic channel. The catalyst suspensions for both anode and cathode were prepared by mixing Pt black nanoparticles at a concentration of 6.0 mg m^{-1} 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 the solvent was evaporated by the use of a heat lamp for uniform loading.

Design ofmembraneless ethanol fuel cell

In MLSPBFC, an E-shaped laminar flow channel with catalyst-coated graphite plates of 1 mm thickness is used (Fig.1). On subsequent deposition of catalyst to the cathode and anode, the E-shaped microfluidic channel structure is molded with poly(dimethylsiloxane) (PDMS; chemsworth), typically 1–10 mm in thickness, and finally sealed with a solid substrate, such as 2 mm thick pieces of poly(methylmethacrylate) (PMMA; 92% G.khanna& Co), to provide rigidity and supportive strength to the layered system. Silicon tubing (Shree Gaurav Rubber Products) is used to guide the fuel and oxidant into the E-shaped channel systems at the top and to let the waste stream out at the bottom of the channel.

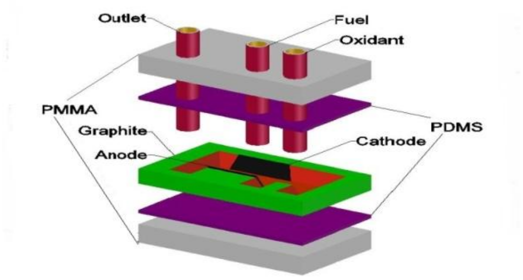

Fig. 1. Schematic of the E-shaped membraneless laminar flow based fuel cell with graphite plates molded with PDMS poly(dimethylsiloxane) and sealed with PMMA poly(methylmethacrylate).

Testing the fuel cell

The fuel and oxidant solutions 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 work for an hour to enable the flow to reach a steady state. over the anode and cathode where fuel and oxidant are allowed to be oxidised and reduced, respectively, as shown in Fig. 2.

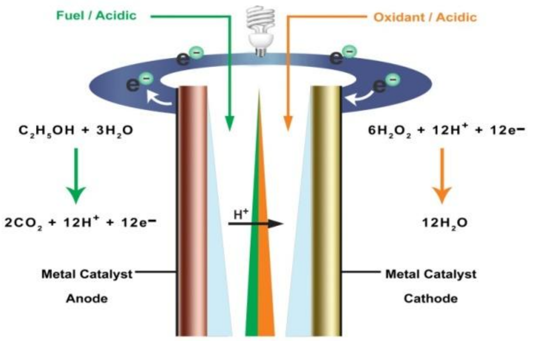

Fig. 2 A cross-section of channel showing depletion boundary layer over anode and cathode metal catalyst and interdiffusion zone at the liquid–liquid interface with vertical electrodes on side walls.

Cell measurements were recorded 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 was found to keep these fluids stable without a separation membrane.

Performance of MLSPBFC in all-acidic

The pH of the electrolyte influences reaction kinetics at the individual electrodes, as well as the electrode potential at which oxidation or reduction occurs[9-13]. Equations (2) and (3)represent the half-cell reactions and standard electrode potentials of ethanol oxidation and peroxide reduction in acidic media.Equations (4)represent the overall cell reaction, in all-acid media.Acidic direct ethanol fuel cell shows the high theoretical values. The most striking feature of acidic DEFCs is their quicker kinetics of the oxygen reduction reaction in acidic media, even with low-cost non-platinum metals as the electrocatalyst. Another important feature of acidic DEFCs is the use of a non-Ptelectrocatalyst on the cathode eliminates the oxidation of the fuel that may be transported from the anode, which makes the cathode potential higher in acid DEFCs [14]. The acidic–acidic media have a maximum theoretical open circuit potential (OCP) of 1.695 V below the equation shown.

Ethanol / perborate in acidic media:

Anode: $C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^- E^\circ = 0.085$ V (2)

Cathode: $6H_2O_2 + 12H^+ + 12e^- \rightarrow 12H_2O$ $E^\circ = 1.78$ V (3)

Overall: $C_2H_5OH + 6H_2O_2 \rightarrow 2CO_2 + 9H_2O$ $E^\circ = 1.695$ V (4)

Influence of fuel composition

The effect of fuel on the performance of MLSPBFC was analysed by varying the concentration of ethanol between 0.5 and 3 M (Fig. 3).

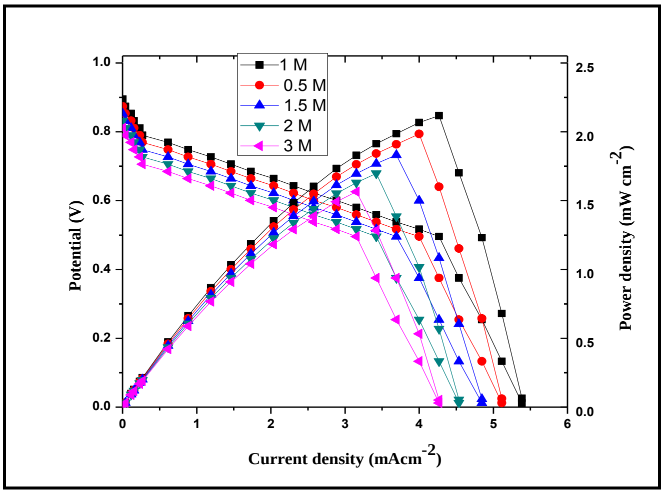

Fig. 3Effect of ethanol concentration on the current and power density of the MLSPBFC at room temperature. ([Fuel]: xMethanol + 0.5 M H_2SO_4. [Oxidant]: 0.1 M perborate + 0.5 M H_2SO_4).

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, to 3.0 while fixing the concentration of H_2SO_4 at 0.5M, the effect of H_2SO_4concentration was observed by varying the concentration of H_2SO_4 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 0.5 M H_2SO_4 gives the highest and most stable performance, and a decrease and fluctuation of cell voltage was observed as the ethanol and H_2SO_4concentrations are varied.The experimental results show that the fuel cell performance decreases as the ethanol concentration increases. This decreasing trend in cell performance at higher ethanol concentrations can be explained as resulting from (a) creation of mixed potential at the cathode due to fuel crossover; (b) kinetic decrease in anode; (c) transport resistance increase at the anode; and (d) ohmic resistance increase.

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 as sodium perborate concentration increases in the MLSPBFC system and reaches the maximum of 0.916 V at 0.1 M sodium perborate. Peak power density obtained at 0.01, 0.025, 0.05, 0.075 and 0.1 M of sodium perborate, respectively (Fig. 4). A further increase in the oxidant concentration shows no improvement in the cell performance. Therefore, the value of 0.1 M has been fixed as theperborate concentration in the oxidant solution.

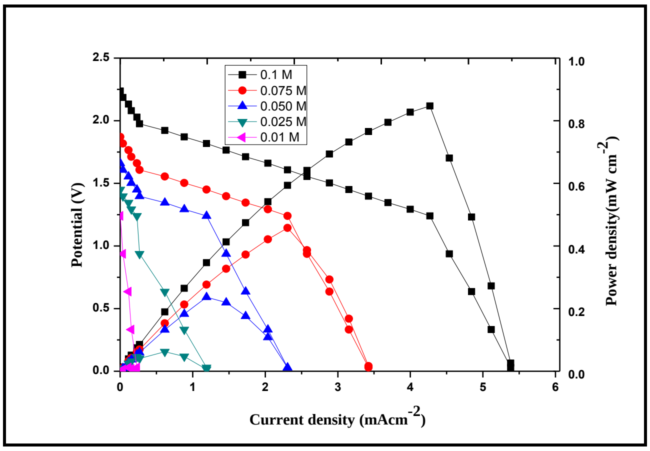

Fig. 4Effect of perborate concentration on the current and power density of the MLSPBFC at room temperature. ([Fuel]: 1 M ethanol + 0.5 M MH_2SO_4. [Oxidant]: x M perborate + 0.5 M H_2SO_4).

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.5. 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 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 [15].

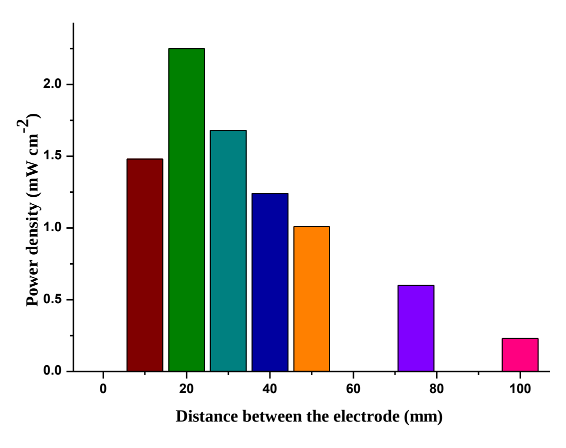

Fig. 5Effect of distance between anode and cathode on the maximum power density of the MLSPBFC at room temperature. ([Fuel]: 1 M ethanol + 0.5 M H_2SO_4. [Oxidant]: 0.1 M perborate + 0.5 M H_2SO_4).

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.8). It is believed that more electrochemical reactions would take place at a given time and a greater output current could develop in the end.

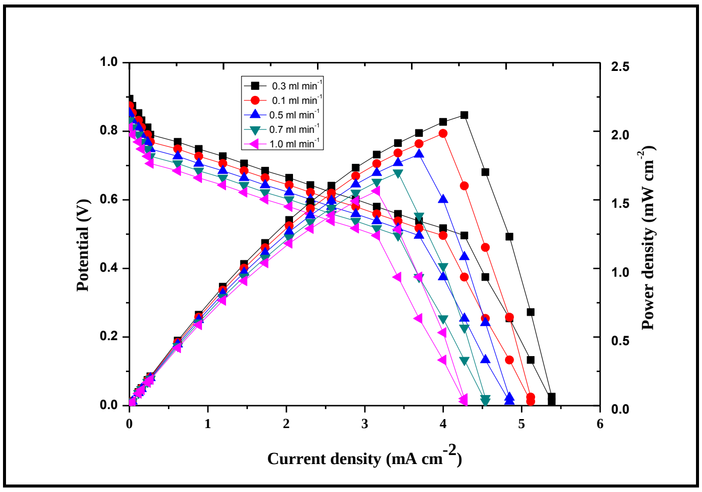

Fig. 6Effect of flow rate of fuel mixture on the current and power density of the MLSPBFC at room temperature. ([Fuel]: 1 M ethanol + 0.5 MH_2SO_4. [Oxidant]: 0.1 M perborate + 0.5 M H_2SO_4).

Conclusion

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. Ethanol 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 acidic media.

In this work, we observed that the acidic anode/acidic cathode acidic media leads to a very high measured OCP of 0.916 V, while other combinations result in very low OCPs as a result of the pH dependence of standard electrode potentials. For the MLSPBFC operating in the acidic anode/acidic cathode acidic media, the measured OCP of 0.916V was found to be in a reasonable agreement with the theoretical OCP of 1.695V.The effects of flow rates of the fuel and the oxidant, variation of concentrations of ethanol, perborate, and electrolytes were analysed in acidic media. The performance was characterized by *V–I* curves and anode polarisation plots.

Thus, the present experimental findings have confirmed that the membraneless microfuel cell designed in our study is cathode limited and suggest that a crucial factor in improving cell performance is increasing the concentration of the oxidant in the cathodic stream. 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.

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