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Development of Novel anode catalysts for Membraneless Sodium Perborate Fuel cells

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Abstract : This Study reports the media flexibility of membraneless sodium perborate fuel cell (MLSPBFC). Investigation of the cell operation is conducted by using glucose as a fuel and sodium perborate as an oxidant for the first time under "acid-alkaline media" configurations. The MLSPBFC architecture enables interchangeable operation with different media combinations. The experimental results indicate that operating under "acid-alkaline media" conditions significantly improves the fuel cell performance compared with all-acidic and all-alkaline conditions. The effect of flow rates, distance effect and the concentrations of various species at both the anode and cathode on the cell performance are also investigated. It has been demonstrated that the laminar flow based microfluidic membraneless fuel cell can reach a maximum power density of 26 mW cm^{-2} with a fuel mixture flow rate of 0.3 mL min^{-1} at room temperature.
Keywords: Alkaline-acid media, Glucose, Membraneless fuel cell, Portable power applications.

Introduction

With an increasing world population and advances in civilization, the energy consumption in the 20th century was marked with an unprecedented high[1]. This trend of increasing energy consumption is likely to continue in the 21st century. Coupled with rapidly diminishing conventional energy sources, predominately based on fossil fuels, this increasing demand on energy has prompted various efforts around the world to explore alternative methods in harvesting energy. Electrochemical power generation is one of the alternative energy-harvesting technologies that are attracting considerable interest due to its sustainability and environmental friendliness [2].

Micro fuel cells are emerging as promising high energy density power sources for portable applications. Although the energy density of the miniaturized fuel cells such as proton exchange membrane fuel cells (PEMFCs) increases as their size continues to shrink, several technological and mechanical challenges including efficiency issues related to water and heat management, the ohmic overpotential caused by the membrane, and fabrication difficulties still remain [3,4]. Because of these limitations, novel designs are required to make a miniaturized fuel cell commercially viable. The microfluidic fuel cell is an innovative design with a

great potential to overcome the current drawbacks of the miniaturized fuel cells, and become an inexpensive and reliable compact power source for practical applications[5]. The flexibility and the performance implications of operating membraneless sodium perborate fuel cell (MLSPBFC) in "alkaline media", that is, both the electrode in alkaline condition, will be the focus of this study.

Glucose is a promising fuel for miniature fuel cells. It has high energy content (if it can be completely oxidized), abundant in nature, easy to extract or produce, simple to store due to is nonflammable, nontoxic and nonvolatile nature, renewable, and environmentally friendly[6]. Glucose is a renewable and abundant energy as it can be derived from a large amount of waste biomass that is generated by agricultural activities and from dedicated energy crops, such as corn and other grains [7, 8]. Potential approaches for deriving energy from glucose include production of ethanol and conversion to hydrogen, but these approaches are hindered by technical and economic problems [9, 10]. An alternative approach to deriving energy from glucose is to feed it to a fuel cell that directly oxidizes the fuel to generate electricity.

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 [11, 12].

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

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 [13-15]. 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: Glucose (≥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 glucose 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 (Fig. 1.).

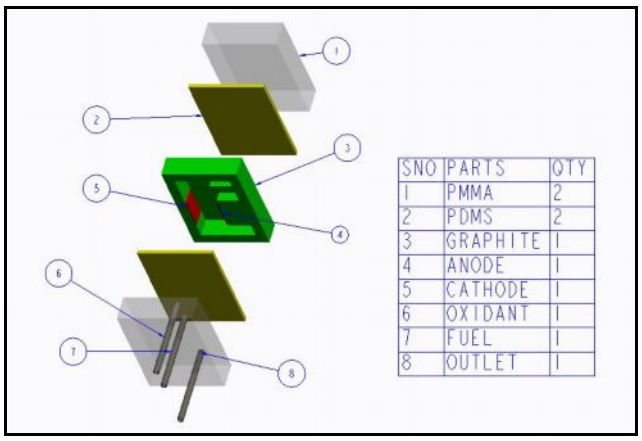

Fig. 1 Schematic of the E-shaped membraneless laminar flow based fuel cell with graphite plates molded with PDMS poly(dimethylsiloxane) and sealed with PMMA poly(methylmethacrylate).

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 glucose 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: $C_6H_{12}O_6 + 2OH^- \rightarrow C_6H_{12}O_7 + H_2O + 2e^-$	$E^0 = -0.85$	(2)
Cathode: $3H_2O_2 + 6H^+ + 6e^- \rightarrow 6H_2O$	$E^0 = 1.78$	(3)
Overall: $C_6H_{12}O_6 + 3H_2O_2 + 6H^+ + 4e^- + 2OH^- \rightarrow C_6H_{12}O_7 + 7H_2O$	$\Delta E = 2.63$	(4)

In this acid-alkaline media configuration, the combination of two galvanic reactions yields a desirable high theoretical OCP value of 2.63V. 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 glucose oxidation, the open circuit potential is reduced to a measured value of 1.41 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 1.41V.

Influence of fuel composition

The effect of fuel on the performance of MLSPBFC has been observed by varying the glucose concentration between 0.25 M and 1.25 M (Fig. 2). The cell performance with different glucose concentrations at a KOH concentration of 0.5 M is shown in Fig. 3. When fuel concentration is high, the limiting current density and the maximum power density is larger. Further increase in glucose concentration degrades the cell performance. Hence, there exists an optimum glucose concentration of 0.5M that yields a maximum power density of 26 $mWcm^{-2}$, as shown in Fig. 2. As such, the increased glucose concentration enhances the kinetics of GOR, which lowers the anode activation loss, so that the cell voltages are improved, as evidenced by OCV in Fig. 2. Therefore, the performance of the MLSPBFC upgrades with increase in glucose concentration from 0.25 to 0.5 M.

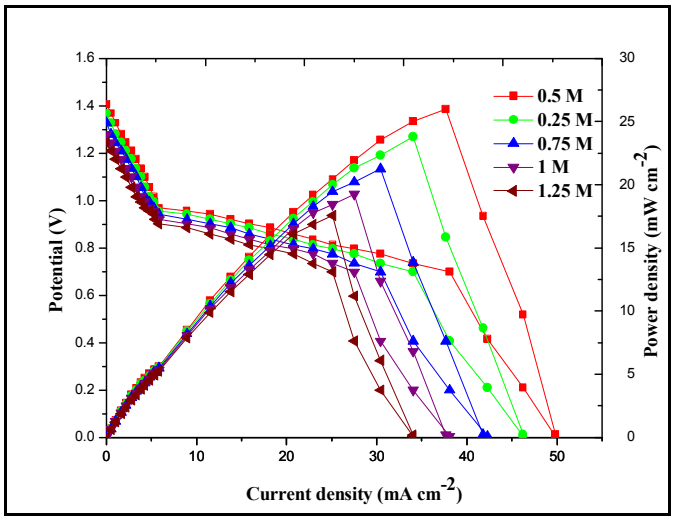

Fig.2. Effect of glucose concentration on the current and power density of the MLSPBFC at room temperature. [Fuel]: x M glucose + 0.5 M KOH. [Oxidant]: 0.1 M perborate + 0.5 M H_2SO_4. Stream flow rates: 0.3 mL min^{-1}.

When the glucose concentration is raised further to 1.25 M, however, the cell performance is lowered. This is because the glucose concentration will be too high at the active surfaces corresponding to the hydroxyl ions concentration rendered by 0.5 M KOH, and thereby lead to difficulty in the adsorption of hydroxyl on the active site. Hence the electrochemical kinetics is lowered, as shown in Fig. 2, and the cell performance is reduced [16]. As a result, the cell performance decreases with further increase in glucose concentration from 0.5 to 1.25 M, due to the lowered electrochemical kinetics and the increased ohmic loss. From this we conclude that the concentration of glucose as low as 0.25 M did not result in a reduction of the cell performance, which indicates that the cell is cathode limited [17].

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 1.41 V at 0.1 M sodium perborate. Peak power densities of 1.95, 3.70, 8.05, 16.04, 26.00, mW cm^{-2} were obtained at 0.01, 0.025, 0.05, 0.075 and 0.1 M respectively (Fig. 3). 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.

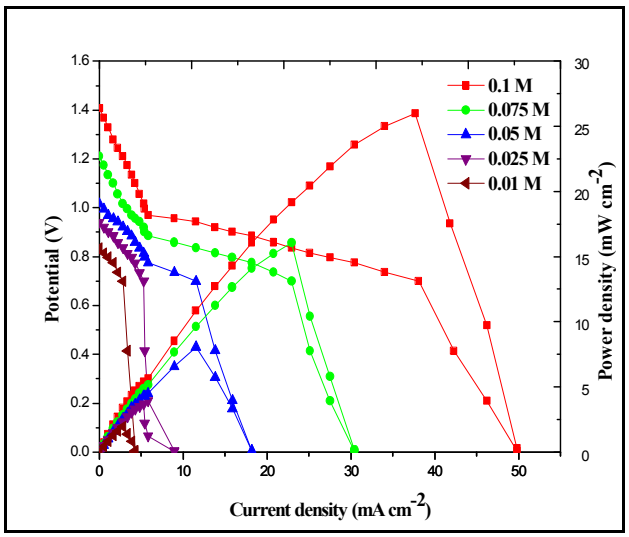

Fig.3. Effect of perborate concentration on the current and power density of the MLSPBFC at room temperature. [Fuel]: 0.5 M glucose + 0.5 M KOH. [Oxidant]: x M perborate + 0.5 M H_2SO_4. Stream flow rates: 0.3 mL min^{-1}.

Likewise, the effect of H_2SO_4 compositions in the oxidant solution has also been analysed. The H_2SO_4 concentration was varied between 0.01 M and 0.5 M. The maximum power density (26 mW cm^{-2}) was obtained at 0.5 M H_2SO_4 (Fig. 4). Further increase in the H_2SO_4 concentration shows no improvement in the cell performance. Therefore the value of 0.5 M has been fixed for the H_2SO_4 concentration in the oxidant solution.

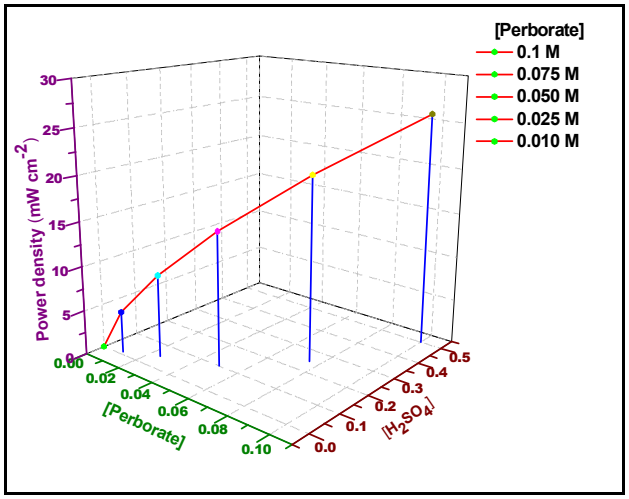

Fig.4. Effect of various combinations of perborate and sulphuric acid concentrations on the maximum power density (26 mW cm^{-2}) of the MLSPBFC at room temperature. The fuel mixture for variation of oxidant is ([fuel]: 0.5 M glucose + 0.5 M KOH, [oxidant]: x M perborate + 0.5 M H_2SO_4) and the fuel mixture for variation of sulphuric acid is ([fuel]: 0.5 M glucose + 0.5 M KOH, [oxidant]: 0.1 M perborate + x M H_2SO_4). Stream flow rates: 0.3 mL min^{-1}.

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. Glucose 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 1.41 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 1.41 V is in good agreement with the theoretical OCP of 2.95 V. At room temperature, the laminar flow-based microfluidic fuel cell produced a maximum power density of 26 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 glucose, 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 glucose 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.

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