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## Performance of Pt-based Anode Catalyst for Urea Electro- Oxidation in Membraneless Fuel Cells

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**Abstract :** The electrocatalytic oxidation of urea on membraneless sodium perborate fuel cell using platinum is investigated. In this cell, urea is used as the fuel and sodium perborate is used as an oxidant. Sodium perborate generates hydrogen peroxide in aqueous medium. The effects of flow rates, distance between the electrodes 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 22.03 mW cm<sup>-2</sup> with a fuel mixture flow rate of 0.3 mLmin<sup>-1</sup>. The developed fuel cell features no proton exchange membrane. The simple planar structured membraneless ethanol 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:** Alkaline-acid media, Membraneless fuel cell, Portable power applications, Urea.

### Introduction

Fuel cell is an electrochemical cell that converts chemical energy from a fuel into electric energy through a clean and efficient electrochemical reaction. Small scale and microfluidic fuel cells have gained much interest over the past few years as power sources for portable electronic devices. The microfluidic fuel cell apparently demonstrates several advantages over proton exchange membrane fuel cells: it eliminates ohmic losses and fouling problems due to the membrane, the fabrication and water management are simpler, and the fuel cell size can be significantly reduced. Moreover, the liquid fuels have higher energy densities in comparison with gaseous fuels which is particular important for portable power source applications<sup>1</sup>.

In this paper, urea is fuel and sodium perborate is oxidant. Urea is a non-flammable, relatively non-toxic and colourless substance that is perhaps best known for its presence in urine. Urea is stable at room temperature and atmospheric pressure. The energy density of urea is higher than compressed or liquid hydrogen which makes it a potential energy carrier<sup>2</sup>. Unlike hydrogen, urea is a solid powder and is easily stored and transported. Urea effectively contains 10% hydrogen and is a potential indirect hydrogen storage material<sup>3</sup>. For

the hydrogen economy to be viable, new hydrogen delivery infrastructures are required while for urea delivery system is already in place.

In this communication, first time we introduce sodium perborate ( $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ ) as an oxidant under “alkaline media”, to demonstrate the performance of a membraneless sodium perborate fuel cell (MLSPBFC). Sodium perborate is a true peroxy salt and is a convenient source of hydrogen peroxide<sup>4,5</sup>.



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<sup>6-8</sup>. 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: Urea ( $\geq 99.5\%$ , Aldrich),  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$  (99%, Riedel), KOH (98%, Merck) and  $\text{H}_2\text{SO}_4$  (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 urea in deionised water as a fuel and sodium perborate in deionised water as an oxidant and 0.5M KOH and 0.5M  $\text{H}_2\text{SO}_4$  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  $6.0 \text{ mg ml}^{-1}$  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  $2 \text{ mg cm}^{-2}$ . 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  $0.3 \text{ mL min}^{-1}$  (total flow rate of  $0.6 \text{ mL min}^{-1}$ ). 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 laminarily 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.

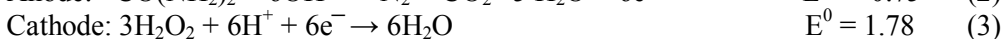
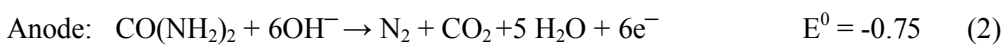
## Results and Discussion

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 urea oxidation/peroxide reduction reactions and from the acid/alkali electrochemical neutralization reactions, as evident from the overall cell reaction Eq. (4):

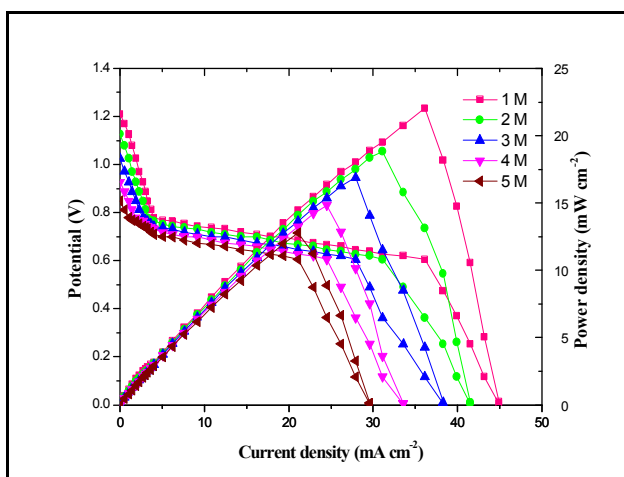
acid-alkaline media: alkaline anode, acidic cathode:



In this acid-alkaline media configuration, the combination of two galvanic reactions yields a desirable high theoretical OCP value of 2.53V. 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 urea oxidation, the open circuit potential is reduced to a measured value of 1.21 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 1.21V.

### Influence of fuel composition

The effect of fuel on the performance of MLSPBFC has been observed by varying the urea concentration between 1 M and 5 M (Fig. 1). The cell performance with different urea 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 urea concentration degrades the cell performance. Hence, there exists an optimum urea concentration of 1M that yields a maximum power density of  $22.03 \text{ mWcm}^{-2}$ , as shown in Fig. 1. As such, the increased urea concentration enhances the kinetics of UOR, which lowers the anode activation loss, so that the cell voltages are improved, as evidenced by OCV in Fig. 1. Therefore, the performance of the MLSPBFC upgrades with increase in urea concentration and further increase in urea concentration the fuel cell performance decreases.

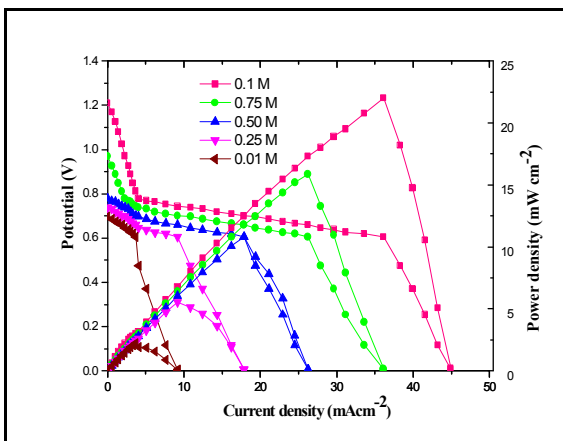


**Fig. 1.** Effect of urea concentration on the current and power density of the MLSPBFC at room temperature. [Fuel]: x M urea + 1 M KOH. [Oxidant]: 0.1 M perborate + 0.5 M H<sub>2</sub>SO<sub>4</sub>. Stream flow rates: 0.3 mL min<sup>-1</sup>.

When the urea concentration is raised further to 2 M, however, the cell performance is lowered. The cell performance decreases with further increase in urea concentration from 2 M to 5 M, due to the lowered electrochemical kinetics and the increased ohmic loss.

### Influence of oxidant composition

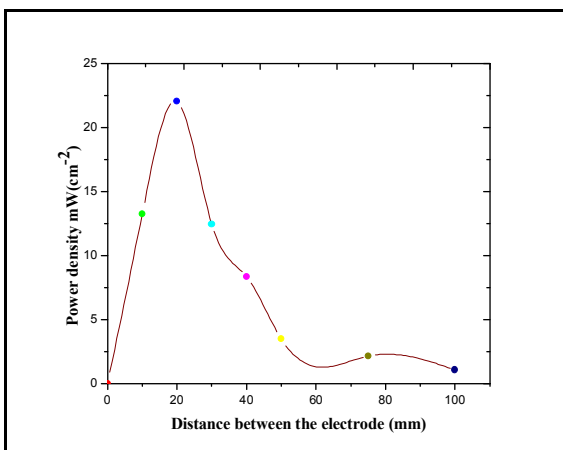
The effects of perborate concentration on the cell performance were investigated at 0.01, 0.025, 0.05, 0.075 and 0.1 M. The power density increased in correlation to increased sodium perborate concentration in MLSPBFC and reaches the maximum of 1.21 V at 0.1 M sodium perborate. Peak power densities of 1.95, 3.70, 8.05, 16.04, 26.00,  $\text{mW cm}^{-2}$  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 Urea + 1 M KOH. [Oxidant]: x M perborate + 0.5 M  $\text{H}_2\text{SO}_4$ . Stream flow rates:  $0.3 \text{ mL min}^{-1}$ .

### Influence of distance effect on the performance of MLSPBFC

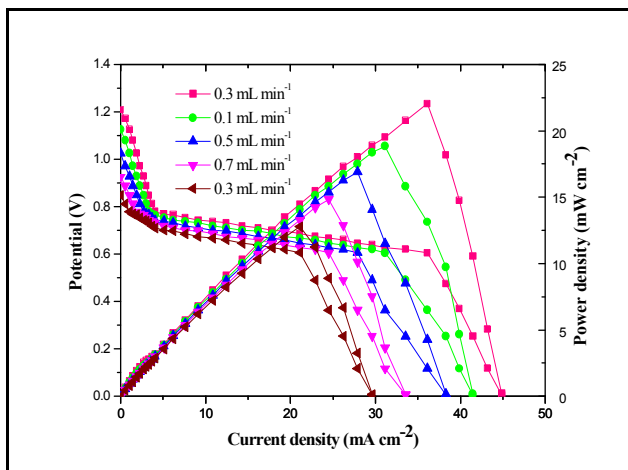
In order to analyse the potential benefit arising from a reduced diffusion length of the reacting species moving between the anode and cathode, the distances were varied between 1 and 100 mm. When the distance between the anode and cathode decreased, the maximum power density was observed, as shown in 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<sup>9</sup>.



**Fig. 3.** Effect of distance between anode and cathode on the maximum power density of the MLSPBFC at room temperature. ([Fuel]: 1 M urea + 0.1 M KOH. [Oxidant]: 0.1 M perborate + 0.5 M  $\text{H}_2\text{SO}_4$ ).

### 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<sup>-1</sup> 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<sup>-1</sup>, 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 urea + 0.1 M KOH. [Oxidant]: 0.1 M perborate + 0.5 M H<sub>2</sub>SO<sub>4</sub>).

### 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. Urea 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 1.21 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 1.21 V is in good agreement with the theoretical OCP of 2.53 V. At room temperature, the laminar flow-based microfluidic fuel cell produced a maximum power density of 22.03 mW cm<sup>-2</sup> under alkaline anode/ acidic cathode acid-alkaline media configurations. The effects of flow rates of the fuel and oxidant, variation of concentrations of urea, 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 urea 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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