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Electrochemical Oxidation of Platinum Based Anode Catalysts for Membraneless Fuel Cells

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Abstract: This paper presents the continuous flow operation of membraneless sodium percarbonate fuel cell using acid/alkaline bipolar electrolyte. In this membraneless fuel cell, ethylene glycol is used as a fuel and sodium perborate is used as an oxidant for the first time under "multi-media" configuration. Sodium perborate affords hydrogen peroxide in aqueous medium. 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 23.5 mW cm^{-2} 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 membraneless sodium percarbonate fuel cell enables high design flexibility and easy integration of the microscale fuel cell into actual microfluidic systems and portable power applications.

Keywords: Ethylene glycol, Membraneless sodium percarbonate fuel cell (MLSPCFC), Multi-media, Portable power applications.

Introduction

The portable multifunctional electronic devices with high speed operations necessitate better energy storage and supply options that deliver increased power and energy density. Current battery technologies appear to be approaching a performance plateau, insufficient to meet the needs of future devices. Portable fuel cells while a battery alternative that shows good potential to meet future needs, have yet to resolve a number of technical challenges. As a result, several microfabrication techniques are developed to increase the power density, because miniaturization of fuel cells stacks and components increases the electrochemically active surface area to volume ratio, which is an important consideration to improve performance.

A novel microfabrication method—fabrication inside capillaries using multistream laminar flow provided the idea for a new type of fuel cell, which eliminates several of the technical issues related to the use of proton exchange membrane fuel cells (PEMFCs), such as fuel crossover,[1] membrane degradation, a long startup time, ohmic losses, size, fabrication and water management limited durability of catalysts[2].

A membraneless fuel cell is a device that does not contain membrane, converts chemical energy from a fuel and an oxidant into electric energy, by means of oxidoreduction reactions. It eliminates the above problems of PEMFCs associated with membranes. Membraneless micro fuel cells use liquid reactants (fuel and oxidant) that flow side by side in a laminar fashion in a single channel without a membrane. Anode and cathode electrodes are positioned on the opposing channel walls and the mixing of fuel and oxidant in the channel occurs only by diffusion[3.6].The flexibility and the performance implications of operating membraneless sodium percarbonate fuel cell (MLSPCFC) under "multi-media", that is, one electrode is acidic and the other one is alkaline condition, will be the focus of this study.

In this communication, first time we introduce sodium percarbonate ($2Na_2CO_3 \cdot 3H_2O_2$) as an oxidant under "multi-media", to demonstrate the performance of a membraneless sodium percarbonate fuel cell (MLSPCFC). Sodium percarbonate is a true peroxo salt and is a convenient source of hydrogen peroxide [7, 8].

$$2Na_2CO_3.3H_2O_2 \rightarrow 2Na_2CO_3 + 3H_2O_2 \qquad (1)$$

The sodium percarbonate fuel cell (MLSPCFC) is unique from previous fuel cells using H_2O_2, as mentioned in our earlier study sodium percarbonate can be used as not only as an oxidant but also as a reductant. [9,10]

The MLSPCFC has some advantages, such as sodium percarbonate is a cheap, non-toxic, large scale industrial chemical used primarily in detergents and as a mild oxidant.[11] The cell being more environmentally friendly than the other fuel cells and the sodium percarbonate can be handled more simply than hydrogen, as it is well known fact that sodium percarbonate solution is a widespread safe disinfectant

In this work, we use ethylene glycol as a fuel to study the performance of MLSPCFC. The function of their bipolar membrane was mainly to keep the power stable by modifying water management. On the other hand, we use the bipolar electrolyte to force reactions (3) and (4) to proceed. Thus, the use of percarbonate in the acid/alkaline bipolar electrolyte is characteristics of the MLSPCFC.

Experimental

Materials and reagents.

The materials and chemicals used during the tests are listed as follows: Ethylene glycol (98%, Merck), $2Na_2CO_3.3H_2O_2$ (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 ethylene glycol in deionised water as a fuel and sodium percarbonate in deionised water as an oxidant and 1M KOH and 1M H_2SO_4 in deionised water as electrolytes.

Catalyst deposition.

For all the experiments of MLSPCFC, 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.

Results and discussion

Two different approaches have been pursued: the first step consisted in the flexibility and the performance implications of operating membraneless sodium percarbonate fuel cell (MLSPCFC) under "multi-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 MLSPCFC in multi-media : alkaline anode, acidic cathode.— In contrast, in multi-media configuration, the MLSPCFC using a fuel stream of an alkaline anode and an acidic cathode allows energy to be obtained both from the ethylene glycol oxidation/peroxide reduction reactions and from the acid/alkali electrochemical neutralization reactions, as evident from the overall cell reaction Eq. (8):

multi-media : alkaline anode, acidic cathode:

Anode: $C_2H_6O_2 + 10OH^- \rightarrow 2CO_2 + 8H_2O + 10e^-$ $E^o = -0.81$ V (4)
Cathode: $5H_2O_2 + 10H^+ + 10e^- \rightarrow 10H_2O$ $E^o = 1.78$ V (3)
Overall: $C_2H_6O_2 + 5H_2O_2 + 10H^+ + 10OH^- \rightarrow 2CO_2 + 18H_2O$ $\Delta E = 2.59$ V (8)

In this multi-media configuration, the combination of two galvanic reactions yields a desirable high theoretical OCP of 2.59 V. Note that the inherent value of the electromotive force of the MLSPCFC is higher than that of the HFC (1.23 V) and the PEMFC or DMFC (1.21 V). However, because of the over potentials resulting from the slow kinetics of peroxide reduction and ethylene glycol oxidation, the open circuit potential is reduced to a measured value of 1.57 V. In the alkaline anode/acidic cathode multi-media configuration both OH^- and H^+ are consumed at the anode and cathode, respectively, at a rate of eight for each molecule of ethylene glycol.

Influence of fuel composition

The effect of fuel on the performance of MLSPCFC has been observed by varying the ethylene glycol concentration between 0.5 M and 1.25 M Figure **4**.

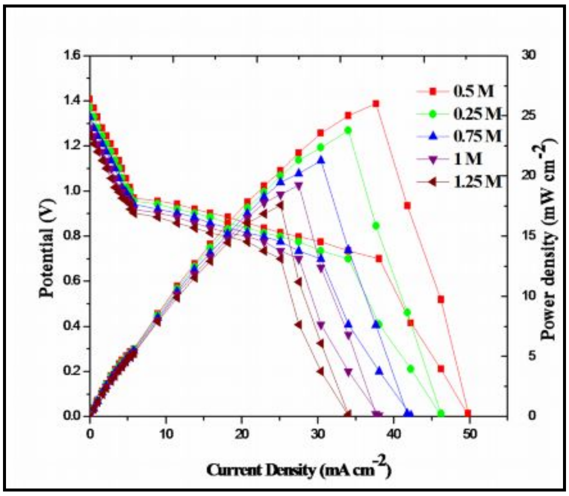

Figure 4. Effect of ethylene glycol concentration on the current and power density of the MLSPCFC at room temperature. [Fuel]: x M ethylene glycol + 1 M KOH. [Oxidant]: 0.1 M percarbonate + 1 M H_2SO_4. Stream flow rates: 0.3 mL min^{-1}.

The experimental results show that the fuel cell performance decreases as the ethylene glycol concentration increases. This decreasing trend in cell performance at higher ethylene glycol concentrations can be explained in four capable reasons: a) creation of mixed potential at the cathode due to fuel crossover; b) kinetic decrease in anode; c) transport resistance increase at the anode; d) ohmic resistance increase.

As mentioned above, fuel crossover will not be present in any membraneless fuel cell; therefore higher ethylene glycol concentration is not the cause for decrease of performance in fuel cell. The kinetic decrease in anode also cannot be the reason because the electro-oxidation of ethylene glycol on Pt has a positive reaction order between 0.5 and 1 M. Thus, the activity at the anode increases initially as the concentration of fuel increases. Therefore, the anode is not limited by kinetic performance with higher ethylene glycol concentrations.

Also, mass transport resistance should actually decrease with increased ethylene glycol concentration. This is because of a higher concentration would create a higher driving force for the ethylene glycol to diffuse across the depletion boundary layer to the electrode. This leaves an increase in ohmic resistance, hence, the protons cannot be transported efficiently and this leads to a poor cell performance, is the only explanation for having decreased cell performance with the higher ethylene glycol concentrations. From these reasons, the 0.5 M ethylene glycol concentration seems to be the best composition for the fuel, this value being fixed for the remaining experiments.

Influence of oxidant composition — The effects of percarbonate 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 percarbonate concentration in the MLSPCFC system and reaches the maximum of 1.42 V at 0.1 M sodium percarbonate. Peak power densities of 9.12, 12.40, 15.68, 18.97, 22.25 mW cm^{-2} were obtained at 0.01, 0.025, 0.05, 0.075 and 0.1 M respectively Figure 5. 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 percarbonate concentration in the oxidant solution.

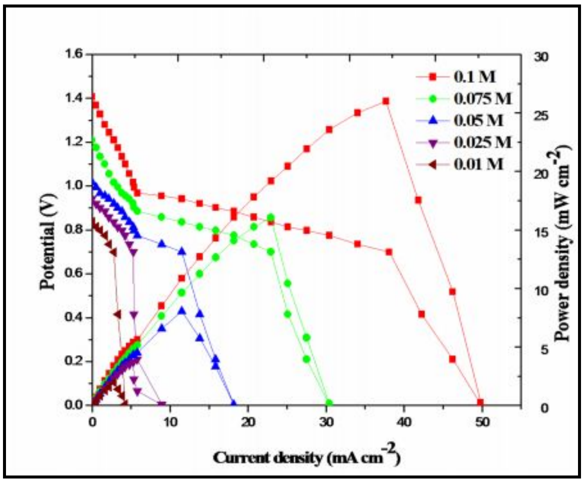

Figure 5. Effect of percarbonate concentration on the current and power density of the MLSPCFC at room temperature. [Fuel]: 0.5 M ethylene glycol + 1 M KOH. [Oxidant]: x M percarbonate + 1 M H_2SO_4. Stream flow rates: 0.3 mL min^{-1}.

Influence of distance effect on the performance of MLSPCFC.— In order to find the potential benefit from a reduced diffusion length of reacting species moving between the anode and cathode the fuel cell test was conducted for different distances between 1 to 100 mm. When the distance between the anode and cathode decreased, the maximum power density increased as shown in Figure 6. Considering the role of a charge carrier, a shorter diffusion length is believed to give a faster electrochemical reaction because the diffusion time of reacting species would be shorter. Therefore, more reactions can take 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 of the presence of a charge carrier moving between the anode and cathode in the fuel mixture to complete redox reactions of the fuel cell.[21]

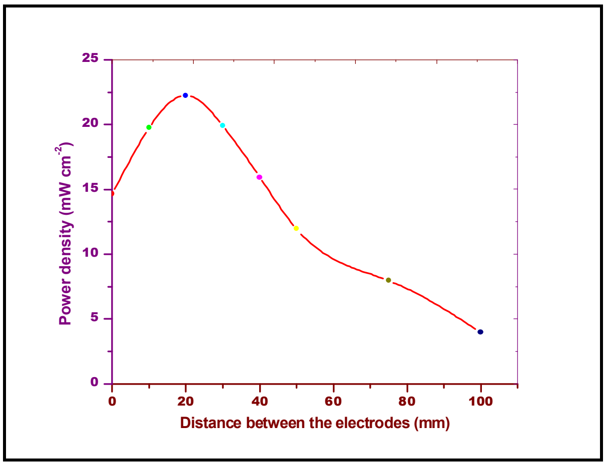

Figure 6. Effect of distance between anode and cathode on the maximum power density of the MLSPCFC at room temperature. [Fuel]: 0.5 M ethylene glycol + 1 M KOH. [Oxidant]: 0.1 M percarbonate + 1 M H_2SO_4. Stream flow rates: 0.3 mL min^{-1}.

Conclusions

A microscale membraneless sodium percarbonate fuel cell (MLSPCFC) was fabricated on PDMS and its performance was evaluated under different operating conditions. Standard microfabrication techniques were used to develop the device. In this membraneless fuel cell, ethylene glycol is used as a fuel at the anode and sodium percarbonate is used as an oxidant at the cathode for the first time under “multi-media”. The experiments described in this study show that membraneless sodium percarbonate fuel cells are media flexible; they can be operated in all-acidic, all-alkaline, or even multi-media configurations.

In this work, we observed that the alkaline anode/ acidic cathode multi-media configuration leads to a very high measured OCP of 1.42 V, while other combinations will result in very low OCPs as a result of the pH dependence of standard electrode potentials. The MLSPCFC operated in the alkaline anode/ acidic cathode multi-media configuration, the measured OCP of 1.42 V is in good agreement with the theoretical OCP of 2.59 V.

At room temperature, the laminar flow-based microfluidic fuel cell produced a maximum power density of 23.5 mW cm^{-2} under alkaline anode/ acidic cathode multi-media configurations. We concluded that multi-media MLSPCFC seems to outperform the all-acidic and all-alkaline MLSPCFCs. The effects of flow rates of the fuel and oxidant, variation of concentrations of ethylene glycol, percarbonate, and electrolytes were evaluated under multi-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, whereas in the case of variation of concentration for ethylene glycol at the anode, fuel cell performance decreases as the ethylene glycol concentration increases due to the increase of ohmic resistance.

Thus, the present experimental findings have confirmed that this membraneless microfuel cell is cathodic limited and suggest that it is a crucial factor in improving cell performance to increase the concentration of oxidant in the cathodic stream. The flexibility of membraneless fuel cells to function with different media allowed the successful operation of mixed alkaline and acidic fuel cells. The membraneless microfuel cell system investigated in this study seems to be a good candidate for feasible application because its performance is comparable to an air-breathing DMFC.

The MLSPCFC has the advantages of their miniature sizes, simplicity of fabrication, use of aqueous fuel and good cost efficiency. Furthermore, percarbonate 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 MLSPCFC may be a promising candidate for practical fuel cells to establish a clean and sustainable energy future.

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