Electrocatalysis of Oxygen Reduction on Carbon Supported Platinum Catalysts in Membraneless Fuel Cells

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Abstract: This paper presents the development of a novel liquid-based microscale fuel cell using Pt/C catalysts in an alkaline solution. The developed fuel cell is based on a membraneless structure. The operational complications of a proton exchange membrane lead the development of a fuel cell with the membraneless structure. In this fuel cell, glycerol is used as a fuel and sodium perborateis used as an oxidant in an alkaline medium. A maximum output power density of 24.4 mW cm^{-1} was achievedat room temperature. The simple planar structured Membraneless Glycerol Fuel Cell (MLGFC) enables high design flexibility and easy integration of the microscale fuel cell into actual microfluidic systems and portable power applications.

Keywords: Alkaline medium,Glycerol, Membraneless fuel cell, Sodium perborate.

Introduction

Rising power demands in portable electronics will require technical development of small and efficient power supplies in order to energize the next generation of portable devices. Microfluidic fuel cells are considered to be a technology with the potential to meet thesedemands[1-5]. Microfluidic fuel cells developed to date are fed by liquid fuels and oxidants under laminar flow regimen. These devices, also called laminar flow-based membraneless fuel cells, operate without a physical barrier to separate the anode and the cathode, which provides an opportunity to overcome the challenges associated with conventional PEM fuel cells. Such micro-structured fuel cells are able to provide longer duration with lighter weight without refuelling, and meet the growing demands of portable high energy density power sources[6].

Membraneless fuel cell has attracted wide attention due to their high energy density and continuous operation capability by refuelling[7]. Liquid fuels have a higher energy density than gaseous hydrogen[8-9]. Among the different possible alcohols, methanol is the most promising fuel because its use as a fuel has several advantages in aqueous electrolytes, liquid fuel available at low cost, easily handled, transported and stored, high theoretical density of energy comparable to that of gasoline[10]. However, the development of the DAFCs based on methanol fuel is facing serious difficulties: (i) slow electro-kinetic of methanol oxidation, (ii) high methanol crossover and (iii) high toxicity[11,12].

Therefore, other alcohols have been considered as alternative fuels. Polyhydric alcohols such as glycerol have also been investigated as the fuels for the fuel cell due to they have high boiling points and are less toxic than methanol. Glycerol is one of the most considerable compounds because of its versatile applications in the food and pharmaceutical industries[11]. Furthermore, glycerol has higher theoretical energy density than that of methanol and can be electrochemically oxidized[13-15]. Glycerol has been considered a promising fuel for membraneless fuel cells (MLFC), due to its relatively low price, simple purification and storage, and non-volatile and environment-friendly properties.

In our work, membranelessglycerol fuel cell (MLGFC) employs an alkaline solution of glycerol as a fuel and sodium perborate ($NaBO_3 . 4H_2O$), as an oxidant. Sodium perborate is an environmentally friendly, cheap, non-toxic, large scale industrial chemical used primarily in detergents and as a mild oxidant. Sodium perborate is a true peroxo salt and is a convenient source of hydrogen peroxide[16,17].

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

As mentioned in our earlier study, the sodium perborate fuel cell isunique from other fuel cells using H_2O_2, as it can be used not only as an oxidant but also as a reductant[18,19]. On the performance side, the membranelessglycerol fuel cell generates electric power comparable to a typical air breathing direct methanol fuel cell when operating in a microchemical channel at room temperature.

In this study, we have attempted to use sodium perborate as the oxidizer to develop a new type of glycerol-based membraneless fuel cell. The carbon supported pt catalysts was used as the catalyst for perborateelectroreduction reaction. The influence of anolyte and catholyte on cell voltage and cell performance was studied.Commercially available Pt/C (E-Tech) electrode was used as the anode and cathode in this study.

Experiments

Materials and reagents

All experiments were conducted at room temperature using glycerol (98%, Merck) in de-ionized water as the fuel, and sodium perborate (99%, Riedel) dissolved in 0.1 M potassium hydroxide (98%, Merck) in de-ionized water as the oxidant.

Catalyst deposition

For all the experiments of MLGFC, unsupported platinum black nanoparticles are used as a catalyst for 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^{-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 inner walls of the graphite plates that line the microfluidic channel, at a loading of 2 mg cm^{-2}. The solvent was then evaporated by using a heat lamp for uniform loading.

Design of membranelessglycerol fuel cells (MLGFC):

In the MLGFC configuration, a laminar flow channel with catalyst-coated graphite plates of 1 mm thickness is used. Unsupported platinum black nanoparticles are electrodeposited to the sides of the graphite plates that act as anode and cathode and line the microfluidic channel. With the subsequent deposition of catalyst to the cathode and anode, the microfluidic channel structure is moulded 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 strength to the layered system. Silicon tubing is used to guide the fuel and oxidant into the microfluidic channel systems at the top and to guide the waste stream out at the bottom of the channel Figure 1.
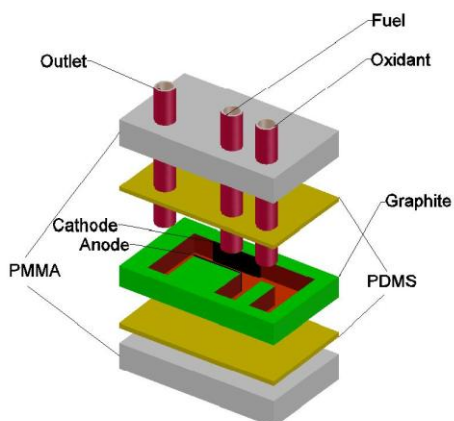
Figure 1. Schematic of the membraneless laminar flow based fuel cell with graphite plates molded with PDMS poly(dimethylsiloxane) and sealed with PMMA poly(methylmethacrylate).

Single Cell Test

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. In multistream laminar flow, two or more liquid streams merge into a single microfluidic channel (Fig. 2), and continue to flow laminarly in parallel without turbulent mixing, if the system is characterized by a Reynolds number, $Re < \sim 2100$[20]. In the previous work, we were able to show that this phenomenon can be utilized to create a membraneless micro fuel cellby merging two streams, one containing fuel(glycerol) and one oxidant (sodium perborate), respectively, and allowing these streams to flow over the anode and cathode electrodes placed on opposing side walls within the microfluidic channel[21,22]. Fuel and oxidant react at the electrodes while the two liquid streams and their common liquid–liquid interface provide the required ionic conductance to complete the fuel cell chemistries.
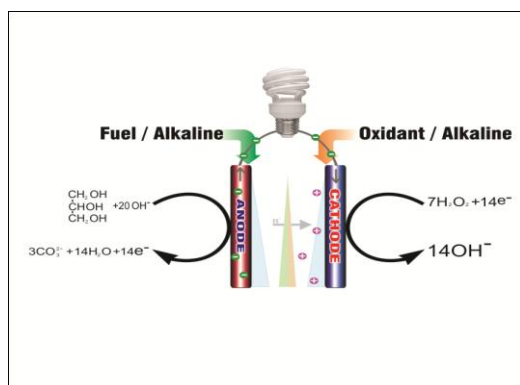

Figure 2.A cross section of channel showing depletion boundary layer over anode and cathode metal catalyst and inter diffusion zone at the liquid-liquid interface with vertical electrodes on side walls.

Cell measurements were conducted using a CS310 computer controlled potentiostat (Zhengzhou triangle instrument Co. Ltd.) with the associated Thales Z software package. For each analyzed 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

Fig. 3 shows a plot of both, cell voltage and power density *versus* current density for a mebranelessglycerol fuel cell operating 2M glycerol in 0.1 M KOH in the anolyte and 0.1M sodium perborate in 0.1M KOH in the catholyte at room temperature. The cell voltage curve shows an open circuit potential (OCP) value of 1.52 V.

Influence of fuel composition

The effect of fuel on the performance of MLGFC has been observed by varying the glycerol concentration between 2 M and 0.5 M as shown in Fig.3. When fuel concentration is high, the limiting current density and the maximum power density are 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. Thus the current density did not increases ignificantly, while increasing the fuel concentrations beyond2M, 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 glycerol as low as0.5M did not result in a reduction of the cell performance, which indicates that the cell is cathode limited. In the present study, experimental results show that the fuel cell performance is maximum at 2M and further increase in the glycerol concentration has no significant effect on the fuel cell.
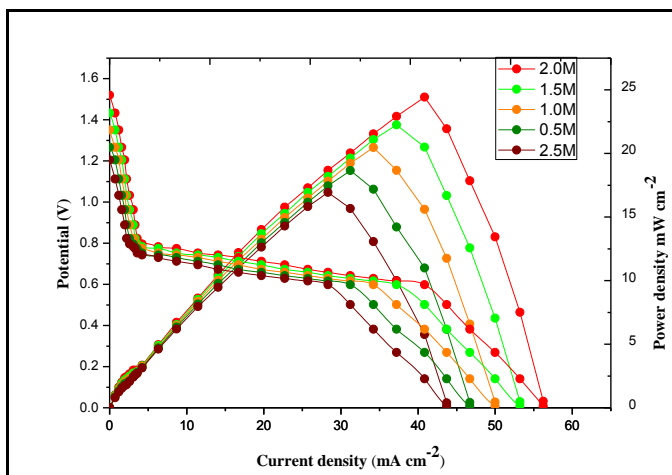

Figure 3.Effect of glycerol concentration on the current and power density of the MLGFC at room temperature.

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 the MLGFC system and reached the maximum of 1.52 V at 0.1 M sodium perborate. Peak power densities of 4.37, 8.41, 13.57, 18.66, 24.42 mW cm^{-2} were obtained at 0.01, 0.025, 0.05 0.075 and 0.1 M respectively as shown in Fig. 4. 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.
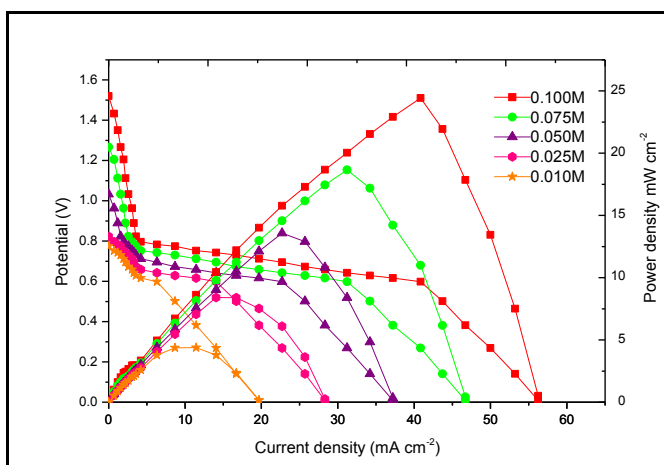

Figure 4.Effect of perborate concentration on the current and power density of the MLGFC at room temperature.

Influence of distance effect on the performance of MLGFC

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 to find between 1 to 100 mm. When the distance between the anode and cathode decreased, the maximum power density increased as shown in Fig 8. Considered 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 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[23].
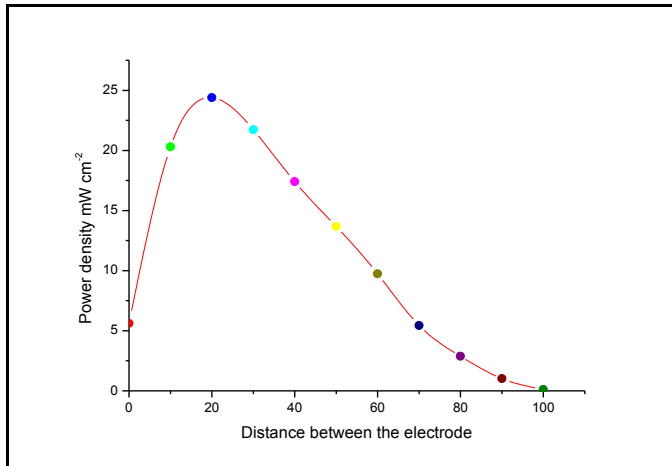

Figure 5.Effect of distance between anode and cathode on the maximum power density of the MLGFC at room temperature.

Influence of fuel mixture flow rate

Since maximum power density is dependent on the transport time of reacting species it can be controlled by its flow rates. 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 fuel mixture. Using the flow rate applied and the cross sectional area of the channel, a flow velocity can be calculated. In this work, the maximum power density was obtained at about 0.3 mL min^{-1}. After that the maximum power density decreased with increase in flow rate as shown in Fig 9. It is believed that more electrochemical reactions will take place in a given time and a greater output current can develop in the end.
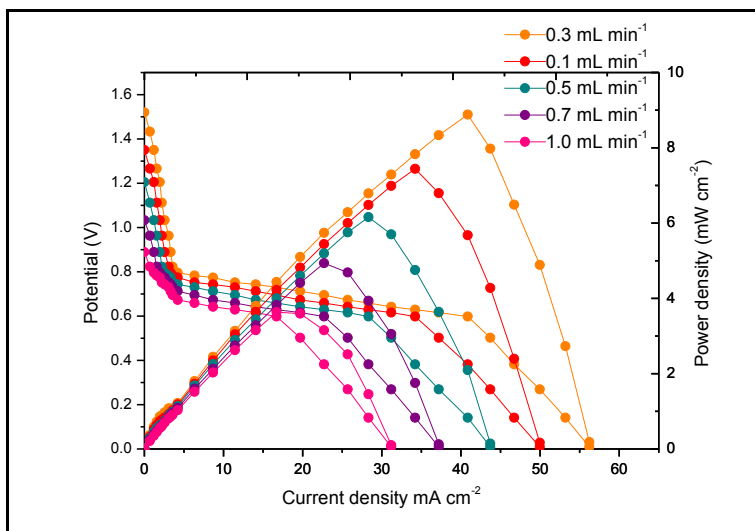

Figure 6.Effect of flow rate of fuel mixture on the current and power density of the MLGFC at room temperature

Stability test

Durability of the MLGFC was examined Short-term stability of MLGFCunder alkaline media was tested by monitoring the cell voltage change during the galvanostatic discharge of 56.4mA cm^{-2}of the MLGFC in a period of about 100 h (Fig. 10).The MLGFC maintained a relatively stable performance with a little decay of cell voltage over the test period. The fluctuation in the cell voltage was due to addition of the new fuel solution, restarting the experiments, or small variation in cell temperature. The result of the durability test showed that the MLGFC in our research has good stability at room temperature which is able to satisfy the necessary conditions as portable power sources.
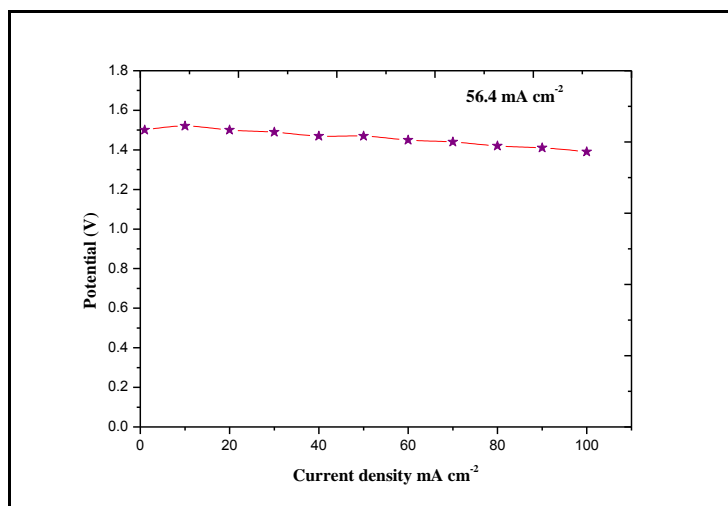

Figure 7.Performance stability of the MLGFC operating at current density of 56.4mA cm^{-2}at room temperature.

Conclusion

A microscale membraneless glycerol fuel cell (MLGFC) was fabricated on PDMS and its performance was evaluated under different operating conditions. Standard microfabrication techniques were used to develop this device. Glycerol is used as a fuel at the anode and sodium perborate is used as an oxidant at the cathode in this membraneless fuel cell under alkaline media. At room temperature, the laminar flow-based microfluidic fuel cell produced a maximum power density of 24.4 mW cm^{-2} in the alkaline media. The membraneless microfuel cell system investigated in this study seems to be a good candidate having many potential applications because its performance is comparable to an air-breathing DMFC. The MLGFC 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 MLGFC may be a promising candidate for practical fuel cells to generate clean and sustainable energy in the future.

References:

1. Dunn-Rankin D, Leal EM, Walther DC.Advanced energy technologies to power human autonomy. Progress in Energy and Combustion Science., 2005, 31 (5–6): 422–465.
2. Dyer CK. Fuel cells for portable applications. Journal of Power Sources., 2002, 106 (1–2) : 31–34.
3. Morse JD.Micro- fuel cell power sources.International Journal of Energy Research., 2007, 31 (6–7) :576–602.
4. Jan CT, Albert Van Den Berg. Energy conversion in Microsystems: Is there a role for micro/nanofluidics. Lab on a Chip 7 (10) (2007) 1234–1237.
5. Lee JW, Kjeang E.A plate-frame flow-through microfluidic fuel cell stack.Biomicrofluidics 2010, 4 (4):041301–041312.
6. Ferrigno R, Stroock AD,Clark TD, Mayer M, Whitesides GM. Membraneless vanadium redox fuel cell using laminar flow. J. Am. Chem. Soc. 124 (2002) 12930–12931.
7. Moeller DW. Environmental Health third edition.Science 296 (2002) 1222–1224.
8. Larminie J, Dicks A, Fuel Cell Systems Explained, 2nd ed., John Wiley & Sons Ltd., Chichester, 2003.

9. H.L. Maynard, J.P. Meyers. Transport phenomena in a reformer with micro-power applications. J. Vac. Sci. Technol. B 2002,20 : 1287–1297.

10. JianHua San, Jie Yi Yu, Man Zhi Zhang, Ying Jung Liang, Chang Wei Xu, Glycerol electrooxidation on Au/NiCore /shell three dimensional structure catalyst. Int. J. Electrochemical Science., 2012, 7: 4362-4368.

11. Etesami M, Mohamed N. Catalytic Application of Gold Nanoparticles Electrodeposited by Fast Scan Cyclic Voltammetry to Glycerol Electrooxidation in Alkaline Electrolyte. Int. J. Electrochem. Sci., 2011, 6 : 4676

12. Dasari MA, Kiatsimkul PP, Sutterlin WR Suppes GJ.Low pressure hydrogenolysis of glycerol to propylene glycol.Appl. Catal. A., 2005, 281: 225

13. Falase A, Garcia K, LauC Atanassov P. Electrochemical and in situ IR characterization of PtRu catalysts for complete oxidation of ethylene glycol and glycerol.Electrochem.Commun., 2011, 13: 1488-1491

14. Falase A, Main M, Garcia K, Serov A, Lau C, Atanassov P.Electrooxidation of ethylene glycol and glycerol by platinum-based binary and ternary nano-structured catalysts. Electrochim.Acta., 2012, 66: 295-301.

15. Matsuoka K, Inaba M, Iriyama Y, Abe T, Ogumi Z, Matsuoka M.Alkaline direct alcohol fuel cells using anion exchange membrane. J. Power sources.,2005, 4: 27-31.

16. Cotton FA, Wilkilson G.Advanced Inorganic Chemistry. Wiley Interscience. New York (1988).

17. KarunakaranC, Muthukumaran B. Molybdenum(VI) catalysis of perborate or hydrogen peroxide oxidation of iodide ion Transition Metal Chemistry.Transition Met Chem.,1995, 20 : 460-462.

18. Gowdhamamoorthi M, Arun A, Kiruthika S, Muthukumaran B.Int. Journal of ChemTech Research., 2013, 5 :1143.

19. Durga S, Ponmani K, Kiruthika S, Muthukumaran B. Electrochemical oxidation of hydrazine in membraneless fuel cell. J. Electrochem. Sci. Technol., 2014, 5(3) : 1-9.

20. Kenis PJA, Ismagilov RF, Whitesides GM. Microfluidic reactors for polymer particles.Science.,1999, 83 : 285.

21. Durga S, Ponmani K, Kiruthika S, Muthukumaran B. A development of membranelessper carbonate/hydrazine fuel cell. J. Mater. Environ. Sci., 2014, 5(5) : 1611-1621.

22. Ponmani K, Durga S, Gowdhamamoorthi M, Kiruthika S, Muthukumaran B. Influence of fuel and media on membraneless sodium percarbonate fuel cell.Ionics.,DOI 10.1007/s11581-014-1118-z.

23. Sung W, Choi JW.Microfluidic fuel cells and batteries.J. Power Sources.,2007, 172 : 198.

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