Enhanced Performance Of Membraneless Fuel Cells

M. Gowdhamamoorthi[1], A. Arun[1], S. Kiruthika[2], B. Muthukumaran[1]*

[1]Department of Chemistry, Presidency College, Chennai – 600 005, India.
[2]Department of Chemical Engineering,SRM University, Chennai-603203, India.

*Corres.author: dr.muthukumaran@yahoo.com
Tel.: +91-44-28544894, Fax: +91-44-28510732

Abstract: This paper presents the development of membraneless fuel cell by using sodium perborate as fuel in acid/alkaline medium. In acid/alkaline bipolar electrolyte, perborate works both as an oxidant as well as reductant. Sodium perborate affords hydrogen peroxide in aqueous medium. The cell converts the energy released by H_2O_2 decomposition with H^+ and OH^- ions into electricity and produces water and oxygen. Such a novel design eliminates the need of a membrane, in which acid and alkaline electrolytes contact with each other. At room temperature, the laminar flow based microfluidic membraneless fuel cell can reach a maximum power density of 34 mW/cm^2 with the molar ratio of [Perborate]/[NaOH] = 1 as fuel and [Perborate]/[H$_2$SO$_4$] = 2 as oxidant for the first time. The developed sodium perborate fuel cell (MLSPBFC) emits no CO_2, features no proton exchange membrane, inexpensive catalysts, and simple planar structure, which enables high design flexibility and easy integration of the microscale fuel cell into actual microfluidic systems and portable power applications.

Keywords: Membraneless Microfluidic. Sodium perborate fuel cell (MLSPBFC). Portable power applications.

Introduction

The advancement of portable electronics and the continual integration of functionality into a single all encompassing device has created an increased demand on energy supply. It is a more and more accepted fact that fuel cells are one of the most fascinating and interesting aspects of today's technology. The interest in fuel cells has been intensified due to several requirements, such as environmental safety, simple fuel storage, good cost-efficiency, and, of course, sufficient electrical performance. No fuel cells have satisfied all these requirements, although various types of fuel cells have been competitively developed. For example, the direct methanol fuel cell *(DMFC)* emits carbon dioxide CO_2, which causes global warming. The hydrogen fuel cell *(HFC)* has difficulty in handling hydrogen gas, and leaking hydrogen could damage the ozone layer. Because these problems originate from the physical and chemical properties of methanol or hydrogen, they are not solved readily. Therefore, it is a pressing requirement and very important to search for another fuel that can overcome these inherent problems[1].

In general, among the existing types of fuel cells, proton exchange membrane fuel cell (PEMFC)[2,3] and direct methanol fuel cell (DMFC)[4,5] are considered to be suitable candidates for miniature fuel cells because of their low operating temperature, high power density, and feasibility for miniaturization. A novel design of miniature fuel cell based on microfluidic devices has emerged as another type of miniature fuel cells. This microfuel cell utilizes the nature of laminar flow in a microchannel at low Reynolds number[6].

A novel microfabrication method – fabrication inside capillaries using multistream laminar flow – provided the idea for a novel type of fuel cell, which eliminates several of the technical issues related to the use of PEMs. In multistream laminar flow, two or more liquid streams merge into a single microfluidic channel (Fig. 1), and continue to flow laminarly in parallel without turbulent mixing, if the system is characterized by a Reynolds number, $Re <\sim2100$[7,8] . This phenomenon can be utilized to create a membraneless micro fuel cell by merging two streams, one containing fuel and the other with oxidant, respectively, and allowing these streams to flow over the anode and cathode electrodes placed on opposing side walls within the microfluidic channel.
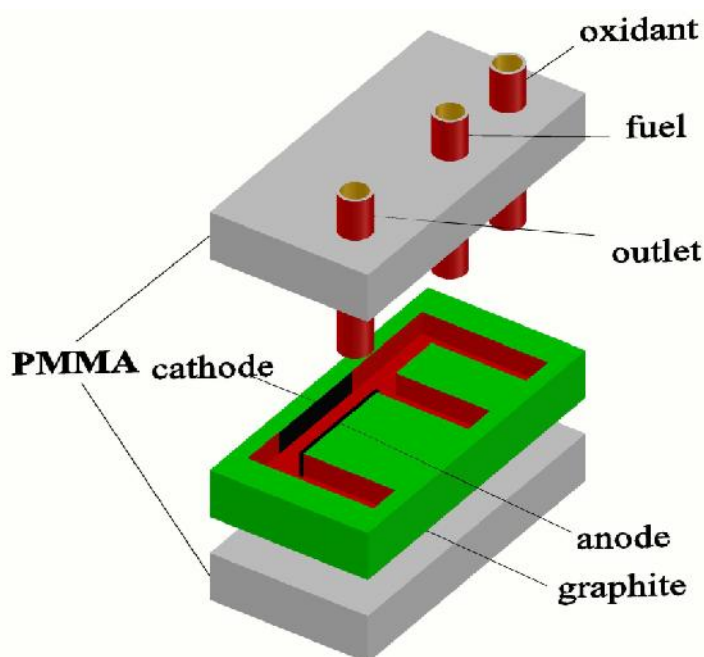

Fig. 1 Schematic of the E-shaped membraneless laminar flow-based fuel cell with graphite plates molded with PDMS poly(dimethylsiloxane) and sealed with PMMA poly(methyl methacrylate)

Recently, Da Mota N et al. reported a different membraneless, micro fuel cell concept at room-temperature that also lacks a PEM[9]. Both anode and cathode liquid streams flow in parallel through the microchannel without turbulent mixing appearing on the interface of both streams. Such a novel design removes the membrane used in conventional PEMFC and DMFC, and possesses many merits: the ohmic losses and fouling problems due to the membrane are eliminated, the fabrication and water management are simpler, the size of fuel cell can be greatly reduced, and the liquid fuel has higher energy density which is particularly important in the applications of portable power sources[10].

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. All the aforementioned membrane-related issues can be avoided in the MLSPBFCs studied here. The flexibility and the performance implications of operating MLSPBFCs under "mixed-media", i.e. 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 perborate, (Na$_2$BO$_3$. 4H$_2$O), and 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].

$$[B(OH)_3(O_2H)]^- + H_2O \rightleftharpoons [B(OH)_4]^- + H_2O_2 \qquad (1)$$
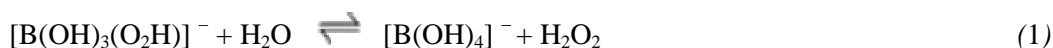
The sodium perborate fuel cell is unique from previous fuel cells using H_2O_2, the MLSPBFC uses perborate not only as an oxidant but also as a reductant. As for the use of Sodium perborate, the direct methanol hydrogen peroxide fuel cell[13] and the aluminum-hydrogen peroxide semi-fuel cell[14] have been reported. In these reports, H_2O_2 was used only as the oxidant, and methanol or aluminum was used as the reductant. In contrast, our MLSPBFC uses sodium perborate, both as the oxidant and as the reductant.

Many experimental studies had been performed in developing membraneless microfuel cells. A variety of fuels were used in these investigations such as formic acid, methanol, and hydrogen solutions. However, since they all used oxygen solution as the oxidant, the performance of these microfuel cells was found to be restricted severely by the low transport efficiency of oxygen in the cathode stream. An experimental study using hydrogen peroxide has been proposed for a Y-shaped microchannel fuel cell[15].

Table 1 Summary of thermodynamic data for different fuels

Fuel	Reaction	n (e)	$-H$ (kJ/ mol)	$-G$ (kJ/ mol)	E_{rev} (V)	Maximum Efficiency (%)
Hydrogen	$H_2 + 1/2\frac{1}{2}\,O_2 \quad H_2O\,(l)$	2	286	237.3	1.23	82.97
Methanol	$CH_3OH + 1/2\,O_2 \quad CO_2 + 2H_2O\,(l)$	6	726.6	702.5	1.21	96.68
Formic acid	$HCOOH + 1/2\,O_2 \quad CO_2 + H_2O\,(l)$	2	270.3	285.5	1.48	105.6
Hydrogen peroxide	$H_2O_2 + HO_2^- + 2H^+ + OH^- \quad O_2 + 3H_2O\,(l)$	2	138	176	1.83	127.54

Compared to hydrogen, methanol, and formic acid, hydrogen peroxide has a higher overall theoretical open circuit potential and maximum efficiency as indicated in Table 1. Furthermore, the hydrogen peroxide is used not only as a reductant but also as an oxidant. The decomposition of hydrogen peroxide in anode and cathode streams can generate electric power which is comparable to a typical air-breathing DMFC at room temperature, and produce no carbon dioxide emission and thus will be explored as the fuel with the membraneless fuel cell in this paper.

As for the acid/alkaline bipolar electrolyte, Ayato et al. used a polymer-electrolyte membrane consisting of acid and alkaline ion-exchange layers for a HFC[16]. 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 *(1)* and *(3)* to proceed. Thus, the use of perborate in the acid/alkaline bipolar electrolyte is characteristic of the MLSPBFC.

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. The cell being more environmentally friendly than the DMFC because there is no CO_2 emission and the sodium perborate fuel can be handled more simply than hydrogen, as it is well known fact that sodium perborate solution is a widespread safe disinfectant. On the performance side, the MLSPBFC generates electric power comparable to a typical air-breathing DMFC when operating in a microchemical channel at room temperature. In addition, the MLSPBFC requires no membrane-electrode assemblies *(MEAs)*. Thus the cost for the materials is low and the structure of the cell is simple. In this study a new branch of simplified architectures that is unique from those that have been reported in literature has been developed by eliminating and integrating the key components of a conventional MEA.

Experimental procedure

In the MLSPBFC configuration we used a microchemical channel in this study, a novel fuel cell consisting of a E-shaped laminar flow channel with electrodes on the inner sidewalls of the main channel was typically fabricated by using standard protocols[17]. In our microfluidic fuel cell fabrication, catalyst-coated graphite plates of 1mm *(Graphite India., poco grade EDM-3, 0.0001 in. particle size)* are employed to act as electrodes, current collectors, and channel structures as reported[17] . Since, the reduced diffusion interface inherent in the side-by-side design reduces the amount of reactant wasted to the mixing region, these graphite plates are placed side by side with a specific spacing and form the length of the channel where the fuel and oxidant streams flow next to each other[18].

The inlets to this channel are milled out of the graphite plates with a drill bit at desired dimensions, typically 0.250 mm. Before assembling the fuel cell, platinum black catalyst is applied on both the inner sidewalls of the graphite plates by electrodeposition method[19]. Subsequent electrodeposition 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(methyl methacrylate) to provide rigidity and supportive strength to the layered system
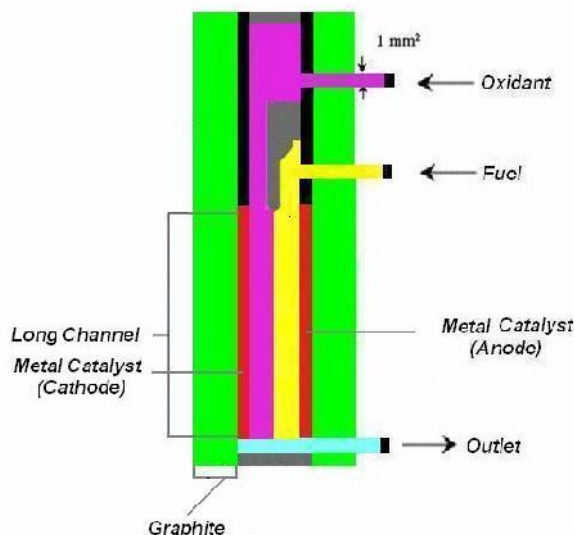

Fig. 2 The side view of the E - type planar membraneless microfuel cell

Silicon tubing (Instech Solomon *PE* = 205, I.D. 1.0 mm) 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. The tubing is inserted into holes that are punched exactly at the three ends of the E-shaped channel design and glued into place.

The fluid flow is regulated using a syringe pump with typical flow rates of ~17 *µL/s* per stream. Under the condition of low Reynolds number (~200), these fluids form a stable laminar flow without mixing with each other. Consequently, the microfluidic cell keeps these fluids stable without a separation membrane. A membrane, as used in MEAs, brings about a resistance to the transport of ions through the electrolytes. Furthermore, MEAs are expensive components at present. Therefore, the cell structure without the membrane has two merits, decrease of electrical resistivity in the cell and inexpensive material cost, apart from the problems associated with PEM-type fuel cells like fuel crossover[20], membrane degradation, a long startup time, ohmic losses, size, fabrication and water management limited durability of catalysts[21].

All experiments were conducted using sodium perborate, $NaBO_3.4H_2O$ (Riedel) with sodium hydroxide (Merck AR Grade) in deionized water as the fuel, and sodium perborate with sulphuric acid (Merck AR Grade) in deionized water as the oxidant, keeping the molar ratio of [Perborate]/[NaOH] = 1 and [Perborate]/[H_2SO_4] = 2. The experiments were conducted at room temperature with electrodeposited platinum black on both the electrodes as the catalyst. For fuel cell characterization the current and potential were measured at different loads using a variable resistor.

Performance of the membraneless sodium perborate fuel cell (MLSPBFC)

The performance of MLSPBFC using a fuel stream of 0.75 M Perborate + 0.375 M NaOH and an oxidant stream of 0.75 M Perborate + 0.75 M H_2SO_4 was investigated. Figures (4) and (5) illustrate the typical polarization and power density curves obtained with the MLSPBFC using [Perborate]/[NaOH] as the fuel and [Perborate]/[H_2SO_4] as the oxidant.

H$_2$O$_2$ is usually known as an oxidant. In an acid electrolyte, the electron-gaining reaction of the oxidant proceeds as follows[22]-

$$H_2O_2 \,(aq) + 2H^+ + 2e^- \quad 2H_2O \quad E^\circ = 1.763 \text{ V} \qquad (2)$$
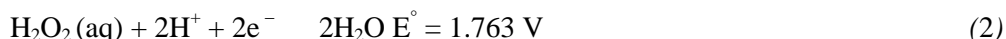
where *(aq)* means the molecule is dissolved in water and E° is the standard reduction potential. On the other hand, H$_2$O$_2$ can act as a reductant, depending on reaction conditions such as pH and content of strong oxidants. In an alkaline electrolyte, the electron-losing reaction of H$_2$O$_2$ proceeds in two steps, the first being

$$H_2O_2 \,(aq) + OH^- \,(aq) \quad HO_2^- \,(aq) + H_2O \qquad (3)$$
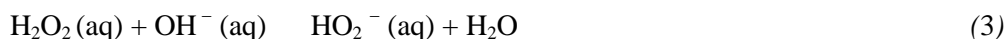
which is the acid-base reaction between the weak acid, H$_2$O$_2$, and the alkaline electrolyte. The second is

$$HO_2^- \,(aq) + OH^- \,(aq) \quad O_2 + H_2O + 2e^- \qquad E^\circ = 0.0649 \text{ V} \qquad (4)$$
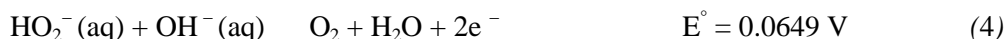
Here, we use the acid and alkaline electrolytes contacting one another *(acid/alkaline bipolar electrolyte)* as shown in *(Fig.3)*. This is the principal novel point for the MLSPBFC, because reactions *(2)* and *(4)* can proceed to generate electricity in the respective electrolytes. Then the overall electrochemical reaction of the MLSPBFC is

$$H_2O_2 \,(aq) + HO_2^- \,(aq) + 2H^+ \,(aq) + OH^- \,(aq) \quad O_2 + 3H_2O \qquad (5)$$
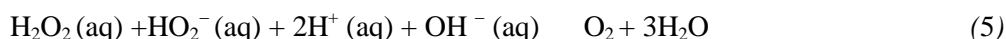
and involves the disproportionation reaction of H$_2$O$_2$ together with the combination of H$^+$ and OH$^-$ ions. The calculated electromotive force *(emf)* of Eq. *(5)* is 1.828 V *(=1.763 + 0.0649 V)*. The inherent value of the electromotive force of the MLSPBFC is higher than that of the HFC *(1.23 V)* and the PEMFC or DMFC *(1.21 V)*. However, the open circuit potential *(OCP)* of the MLSPBFC becomes much lower than the EMF. Thus the OCP does not significantly contribute to the observed phenomena.

The acid/alkaline bipolar electrolyte illustrated in Fig.3 consists of sulfuric acid, and sodium hydroxide, solutions. For the reaction of Eq. *(5)* to proceed continuously, SO$_4^{2-}$ ion neutralizes Na$^+$ ion electrically at the acid/alkaline bipolar electrolyte interface. Consequently, the MLSPBFC produces water and oxygen but no CO$_2$. In this regard, the MLSPBFC is more environmental friendly than the DMFC.
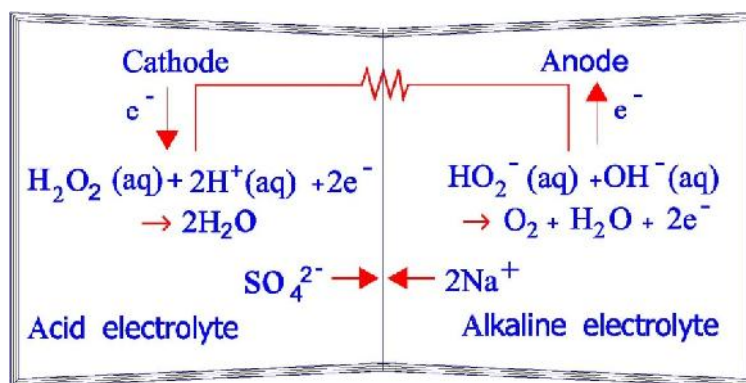

Fig. 3 Operating principle of membraneless sodium perborate fuel cell *(MLSPBFC)* using acid/alkaline bipolar electrolyte

Since the diffusion process at the liquid/liquid interface determines the performance of the membraneless fuel cell, the two key parameters are the Reynolds number: $Re = \dfrac{U\,H}{v}$ and the peclet number: $Pe = U\,H\,/\,D_{H+}$. Where *U* is the mean flow velocity in the reaction channel, *H* is the channel height, *v is* the kinematic viscosity of the fuel/oxidant liquids. For simplification, we assume for an operation temperature of 25 °C a kinematic viscosity of water $v = 0.871 \times 10^{-6}$ m^{2}s^{-1} for both fuel and oxidant liquids and a diffusion coefficient of proton $D_{H+} = 9.31 \times 10^{-9}$ m^{2}s^{-1}. With the known volumetric flow rate and channel cross section of 1 mm^2, the Reynolds numbers and the peclet numbers can be estimated with the above properties.

Figures 4*(a)* & 5*(a)* shows the measured cell potentials as a function of the current density at room temperature. The measurements were carried out with external resistances and PC-controlled digital multimeter keeping the molar ratio of [Perborate]/[H_2SO_4] = 2, we prepared the acid [Perborate] solutions. We also prepared the alkaline [Perborate] solutions with the molar ratio of [Perborate]/[NaOH] = 1. The [Perborate] concentration was varied from 0.075 to 0.75 mol/L, a range which is lower than the concentration of normal [Perborate] disinfectant. These acid and alkaline solutions with the same [Perborate] concentration flowed over the cathode and the anode, respectively. The open circuit voltage, V_{oc}, increases slightly with increasing [Perborate] concentration. This is attributed to the activity of the reactant as expressed in the Nernst equation[1].

The maximum value of V_{oc} was measured as 0.8 V at 0.75 mol/L [Perborate]. Supposing that the cathode reaction of the MLSPBFC proceeds through the hydroxyl radical intermediate adsorbed on the Pt surface[23], the value of V_{oc} is expected to be ~0.9 V. The difference between the measured and the expected V_{oc} may come from the spontaneous decomposition of H_2O_2 on the electrodes. In this study, the maximum power density is nearly proportional to the concentration. At 0.75 mol/L [Perborate], a value of 34 mW/cm^2 was obtained which is comparable to 20-35 mW/cm^2 obtained for an air breathing DMFC[24,25]. The DMFC uses MEAs with an activated carbon catalyst loaded with Pt/Ru. In contrast, the present MLSPBFC uses no such an expensive catalyst. This means that the power density of the MLSPBFC will further increase with improving activity and specific surface area of the electrode.

Table 2 Efficiency of the membraneless sodium perborate fuel cell *(MLSPBFC)*

Cathode	Anode	Catalyst	Max cell potential (V)	Max current density (mA/cm^2)	Max power density (mW/cm^2)	Voltage efficiency %
[Perborate] /[H_2SO_4]	[Perborate]/[NaOH	Pt-black	0.8	153.85	34	44

Polarization curves of the membraneless fuel cell were obtained using [Perborate]/[NaOH as the fuel and [Perborate]/[H_2SO_4] as the oxidant. The polarization curves recorded from these membraneless fuel cells have the same characteristic shape of typical fuel cells with the kinetically limited, ohmic, and mass transport limited regions *(Figs. 4 & 5)*. Using the corresponding power density curves optimal operation parameters can be deduced: 34 mW/cm^2 at the potential of 0.46 V. In this experiment, the maximum cell potential obtained is 0.8 V and the maximum current density is 153.85 mA/cm^2 *(Table 2)*. Accordingly, the cell performance will be enhanced intensely if the concentration of oxidant in cathodic stream can be increased to raise the exchange current density at the cathode can be made as high as possible.

(a)

(b)
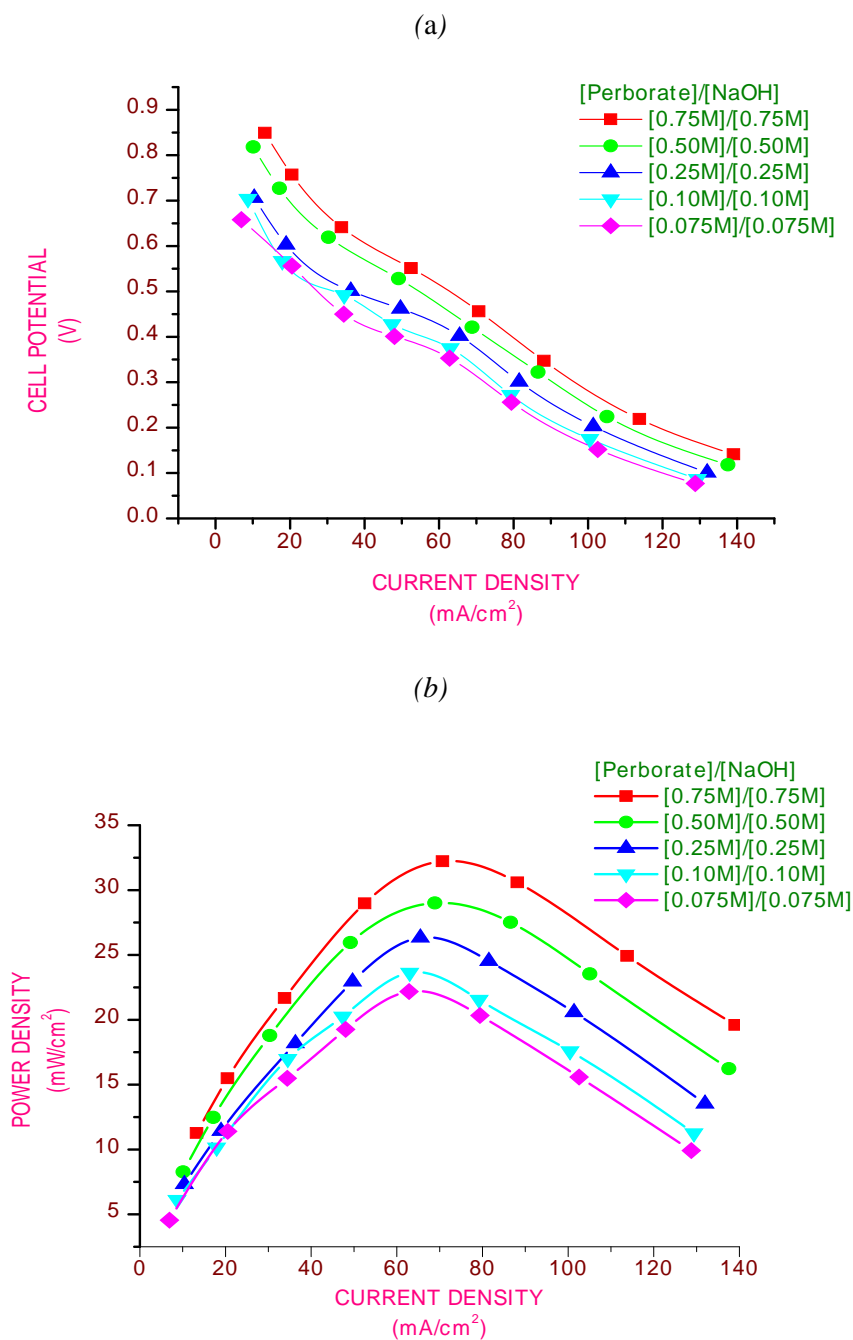
Fig. 4 Variations of cell performance with five assigned concentrations of [Perborate]/[NaOH]:
(a) **the polarisation curves;** *(b)* **the corresponding power density curves**

(a)

(b)

Fig. 5 Variations of cell performance with five assigned concentrations of oxidant:
(a) **the polarisation curves;** *(b)* **the corresponding power density curves**

The exchange current density for anode and cathode also indicates that the activation losses are primarily due to the lower chemical activity at cathode[26]. Accordingly, we may conclude that the cell performance will be enhanced intensely if the concentration of oxidant in cathodic stream can be increased to raise the exchange

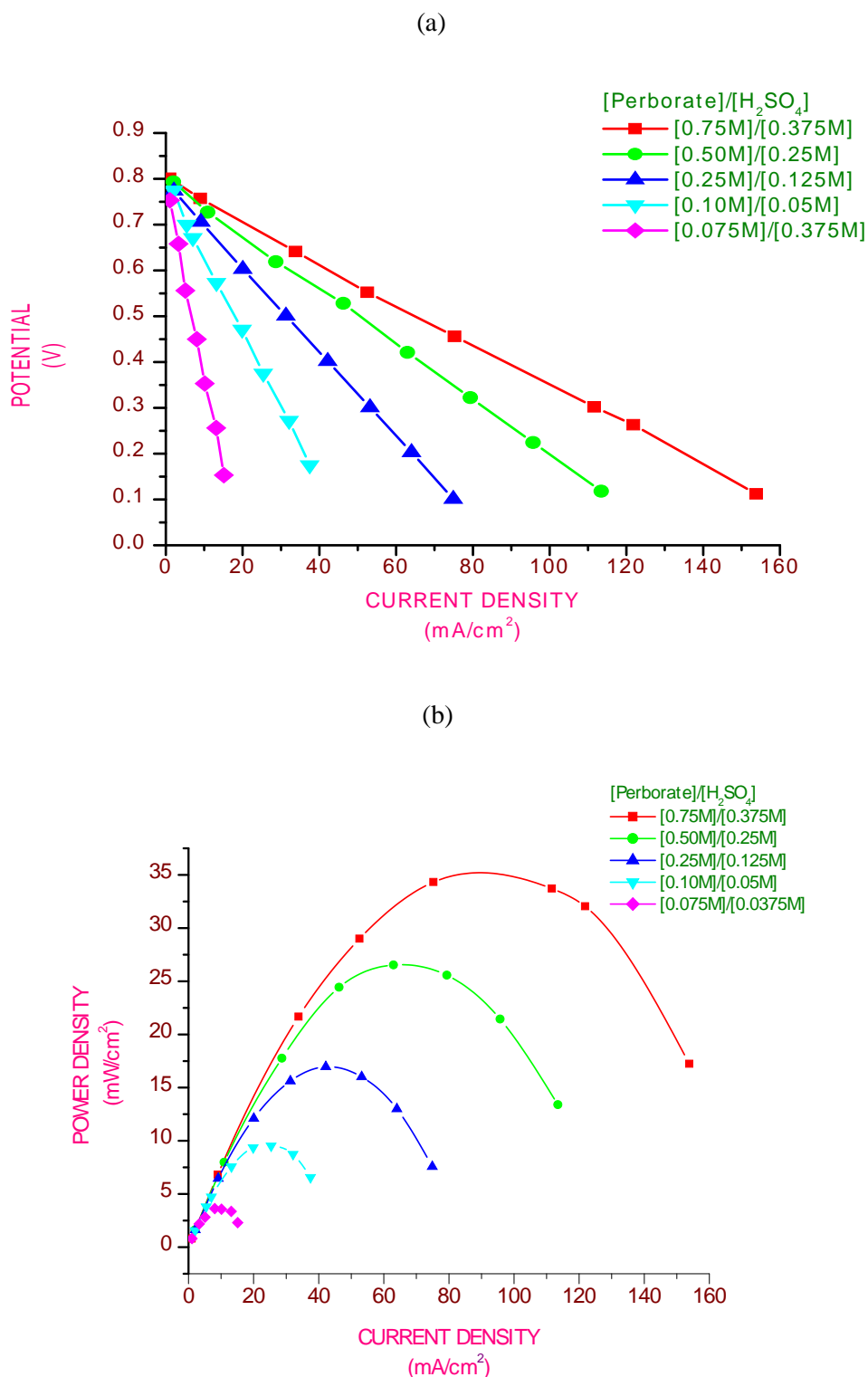current density at the cathode can be made as high as possible. While a variation of concentration for [Perborate]/[NaOH] will produce small influence on cell performance only. These inferences are examined in *(*Figs. 4 and 5*)* by changing the concentrations of reactants in anodic and cathodic streams, respectively.

As shown in Figs. 4*(*a*)* and *(*b*)*,five typical concentrations of [Perborate]/[NaOH], 0.75 M, 0.5 M, 0.25 M, 0.1 M and 0.075 M are considered. It is found that if the fuel concentration reduces to 0.25 M or even smaller 0.075 M, the performance still does not drop significantly. These results are consistent with the experimental findings[8]. While if we can raise the concentration of oxidant in cathodic stream, the cell performance appears to be improved significantly as shown in Fig. 5*(*a*)* and *(*b*)*, in which five assigned values of oxidant concentration 0.75 M, 0.5 M, 0.25 M, 0.1 M and 0.075 M are investigated. One can see that if the concentration of oxidant is 10 times larger, the current density is also increased approximately ten times. Thus, the present analyses confirm the experimental results 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. In this experiment, we examined the thermodynamic properties for the overall reaction of the MLSPBFC by using chemical thermodynamic data[27]. We additionally used the following data: the enthalpy change ΔH = -55.9 kJ/mol and the entropy change ΔS = 80.5 J/Kmol for the reaction of $H^+ + OH^-$ H_2O, the ΔH = -30.8 kJ/mol and the ΔS = 120 J/Kmol for $H^+ + HO_2^-$ *(*aq*)* H_2O_2 *(*aq*)*. The Gibbs free energy change ΔG *(*= ΔH - TΔS*)*, the ΔH, and the ΔS of Eq. *(*4*)* are estimated as -176, -138, and 128 J/Kmol, respectively. Note that the ΔS is positive value. As a result, the energy term of TΔS *(*=38.1 kJ/mol at 298 K*)* additionally contributions to the ΔG. If all of the ΔG were converted into electrical energy, the maximum efficiency, $\Delta G/\Delta H$, would be 128%. This means that the MLSPBFC has the potential to convert the TΔS as heat. This energy conversion may appear in the MLSPBFC, when we reduce some irreversible energy losses, such as activation losses of electrochemical reactions, resistance to the transport of electrons through the electrodes and interconnections, resistance to the transport of ions through the electrolytes, concentration losses of reactants near the electrode surfaces, and the loss due to the intermediate formation[23].

Using the ΔG value, we estimated the energy density of perborate fuel. When we make an acid and an alkaline solution from perborate, conc.H_2SO_4 and NaOH *(*the molar ratio of [Perborate]/[H_2SO_4] = 2 and [Perborate]/[NaOH] = 1*)*, the energy density is 436 Wh/L. This value is comparable to that of hydrogen as a compressed gas: 459 Wh/L estimated at 200 kgf/cm^2 and 25°C with neglect of container volume. Note that our perborate fuel was an aqueous solution. Therefore, we can handle the fuel more simply than gaseous hydrogen.

In addition to the experiment with a single cell, we have been carrying out series and parallel integrations of the cell on a microchemical chip. This simple structure can allow an easier integration process than a micro-DMFC[28,29]and a micro-HFC[30]. Because the integration allows the MLSPBFC to increase the power, it could be utilized for various portable power applications.

Conclusions

A microscale membraneless sodium perborate fuel cell *(*MLSPBFC*)* was fabricated and its operating behaviour characterized for the first time. Standard microfabrication techniques were used to create the device. The novel microfuel cell utilized a membraneless dual-electrolyte design with sodium perborate as both reductant and oxidant. At room temperature, the laminar flow based microfluidic fuel cell produced a maximum power density of 34 mW/cm^2. The electrochemical performance of the membraneless fuel cell was examined in detail with respect to several critical system parameters.

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, the current density is also increased approximately ten times. While a variation of concentration for [Perborate]/[NaOH] at the anode produced only a small influence on the cell performance. Thus, the present experimental results 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. In this experiment, we also examined the thermodynamic properties for the overall reaction of the MLSPBFC.

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 without CO_2 emission. In addition, the development of metal catalysts to accelerate the efficiency of MLSPBFC

are in progress. Some further experimental works towards the micro channel and the flow rate of MLSPBFC will be beneficial to verify the present predictions and fulfill the practical utilization in portable power sources.

The MLSPBFC has the advantages of no CO_2 emission, use of aqueous fuel, and good cost-efficiency. Furthermore, perborate is a cheap, non-toxic, 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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