

Performance and stability of ethanol oxidation an alkaline-acid membraneless fuel cell

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The continuous flow operation of membraneless ethanol fuel cell using alkaline-acidic media is presented in this paper. In this cell, ethanol is used as the fuel and sodium perborate is used as an oxidant for the first time in an alkaline-acidic media. Sodium perborate generates hydrogen peroxide in aqueous medium. At room temperature, the laminar-flow-based microfluidic membraneless fuel cell can reach a maximum power density of 22.25 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 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-acidic media, ethanol, membraneless ethanol fuel cell, portable power applications.

Introduction

The portable multifunctional electronic devices with high-speed operations need better energy storage and supply options that are capable of delivering increased power and energy density. An important metric in the development of converged electronic devices is the operating time becoming limiting with conventional battery technology. The currently available battery technologies appear to be approaching a performance plateau, and seem insufficient to meet the needs of future devices. While portable fuel cells offer a better alternative as a battery possessing good potential to meet future needs, a number of technical challenges need to be resolved in them. As a result, several microfabrication techniques have been developed to increase the power density, because miniaturisation of fuel cell stacks and components are known to increase the electrochemically active surface-area-to-volume ratio, which is an important condition for improving performance.

A novel microfabrication method—fabrication inside capillaries using multistream laminar flow—is used to construct a new type of fuel cell, which eliminates several of the technical issues that crop up when using proton exchange membrane fuel cells (PEMFCs), such as fuel crossover¹, membrane degradation, a long startup time, ohmic losses, size,

fabrication, and water management^{2,3} limited durability of catalysts⁴. Furthermore, as MEAs are expensive components at present, the cell structure without the membrane provides two advantages: decrease of electrical resistivity in the cell and inexpensive material cost.

A membraneless fuel cell is a novel device without a membrane that converts chemical energy generated from a fuel and an oxidant into electric energy by means of oxidoreduction reactions. In membraneless micro fuel cells, liquid reactants (fuel and oxidant) flow side by side in a laminar fashion in a single channel, not requiring a membrane for reactant flow. Anode and cathode electrodes are positioned on the channel walls opposite to each other and the mixing of fuel and oxidant in the channel occurs only by diffusion. Moreover, the chemical composition of the cathode and anode streams can be designed individually to optimise individual electrode kinetics as well as overall cell potential.

An additional advantage is that structures of membraneless micro fuel cells are very simple and easy to miniaturise⁵, so that light and stackable fuel cells can be fabricated with simple microelectromechanical systems (MEMS)^{6,7}. The implications of flexibility and the performance of operating membraneless ethanol fuel cell (MLEFC) in alkaline-acidic media, in which one electrode is alkaline and

the other acidic, is the focus of this study.

In the present work, ethanol is used as a fuel to study the performance of MLEFC. Pure ethanol has an energy density of 8028 Wh/g⁸, as compared with the Li ion battery at 350–470 Wh.L⁻¹⁹. As well as Table 1 show the ethanol has higher energy density compared to methanol and formic acid fuel cell. Ethanol is an accepted, more attractive and promising clean and energy-efficient cell¹⁰. Ethanol is a carbon-neutral, sustainable fuel that can be produced in great quantity through the fermentation of agricultural products or biomass. But, its many unique properties including low toxicity, ease in handling and transportation make it a fuel of choice compared to other fuel cells¹¹.

Table 1. The summary of thermodynamic data and theoretical energy densities for various fuels

Fuel	N	–	–	Gravimetric	Volumetric energy
	(e)	ΔH°	ΔG°	energy	density
		(kJ/mol)	(kJ/mol)	density	(Wh./kg)
				(Wh./kg)	
Ethanol	12	277.7	174.9	6100	7850
Borohydride	8	1392	1267	2925	2840
Methanol	6	726.6	702.5	4690	6400
Formic acid	2	270.3	285.5	2086	1710

A few studies were carried out that attempted to use oxygen solution as the oxidant. The performance of these micro fuel cells was found to be severely hampered by the low transport efficiency of oxygen in the cathode stream.

Membraneless ethanol fuel cell (MLEFC) is studied in this work using an acidic solution of sodium perborate (Na₂BO₃·4H₂O) as the oxidant. The impact of using alkaline-acidic media (i.e. one electrode is acidic and the other one is alkaline condition) on the performance of the fuel cell is the focus of our study. Sodium perborate, the oxidant used in the study, is cost-effective, environmentally friendly, and nontoxic industrial chemical used on a large scale in detergents and as a mild oxidant. Sodium perborate, a true peroxy salt, proves to be a convenient source of hydrogen peroxide^{12,13}:



Sodium perborate functions as both an oxidant and reductant, which makes this cell unique when compared with other fuel cells using H₂O₂^{14,15}.

The performance of MLEFC in generating electric power

is comparable to a typical air-breathing DMFC that operates in a microchemical channel at room temperature. The issues arising out of using a membrane cell, as explained before, can be avoided when a MLEFC is employed. Another advantage of using MLEFC is the simple structure of the cell in the absence of membrane electrode assemblies in addition to a reduction in the cost of materials.

Using a bipolar electrolyte increases fuel utilization and produces a higher potential when compared to the acid and alkaline fuel cell, and also there has been a considerable focus on the alkaline-acidic fuel cell in the recent past¹⁶. This work also explains the bipolar electrolyte membraneless sodium perborate fuel cell as it operates at room temperature.

In this study, new forms of simplified architectures, unique from those that have been reported in literature, have been developed by eliminating and integrating the key components of a conventional MEA. With these advantages, we believe membraneless ethanol fuel cells (MLEFC) can be used as an alternative for portable power applications.

Experimental

Materials and reagents:

All experiments were conducted at room temperature using ethanol (98%, Merck) in de-ionized water as the fuel, and sodium perborate (99%, Riedel) dissolved in 1 M sulfuric acid (98%, Merck) or 1 M potassium hydroxide (98%, Merck) in de-ionized water as the oxidant.

Catalyst preparation:

For all the experiments involving MLEFC, unsupported platinum black nanoparticles (Alpha Aesar) are applied to the sides of the graphite plates (kiriti graphite), which act as the cathode and anode that line the microfluidic channel. The catalyst suspensions for both anode and cathode were prepared by mixing Pt black nanoparticles at a concentration of 6.0 mg m⁻¹ 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 the solvent was evaporated by the use of a heat lamp for uniform loading.

Design of membraneless ethanol fuel cell:

In MLEFC, an E-shaped laminar flow channel with catalyst-coated graphite plates of 1 mm thickness is used (Fig. 1). On subsequent deposition of catalyst to the cathode and

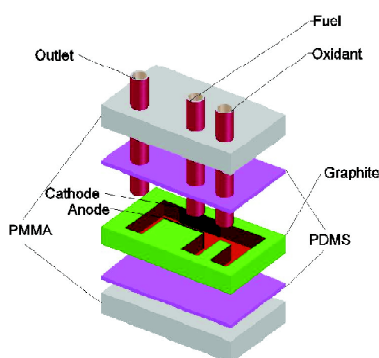


Fig. 1. Schematic of the E-shaped membraneless laminar flow based fuel cell with graphite plates molded with PDMS poly(dimethylsiloxane) and sealed with PMMA poly(methylmethacrylate).

anode, the E-shaped microfluidic channel structure is molded with poly(dimethylsiloxane) (PDMS; chemsworth), typically 1–10 mm in thickness, and finally sealed with a solid substrate, such as 2 mm thick pieces of poly(methylmethacrylate) (PMMA; 92% G. Khanna & Co.), to provide rigidity and supportive strength to the layered system. Silicon tubing (Shree Gaurav Rubber Products) is used to guide the fuel and oxidant into the E-shaped channel systems at the top and to let the waste stream out at the bottom of the channel.

Testing the fuel cell:

The fuel and oxidant solutions 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 work for an hour to enable the flow to reach a steady state. When injected through the inlets, the fuel and oxidant solutions merge at the E-junction and continue to exhibit a laminar flow in parallel without turbulent mixing, if the system is characterised by a Reynolds number, $Re < \sim 2100$ ¹⁷, over the anode and cathode where fuel and oxidant are allowed to be oxidised and reduced, respectively, as shown in Fig. 2.

Cell measurements were recorded 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 was found to keep these fluids stable without a separation membrane.

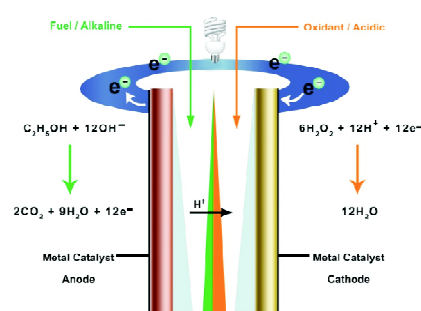


Fig. 2. A cross-section of channel showing depletion boundary layer over anode and cathode metal catalyst and interdiffusion zone at the liquid-liquid interface with vertical electrodes on side walls.

Results and discussion

We tested the cell for two objectives. The first step consisted in analysing the flexibility and the performance implications of operating membraneless ethanol fuel cell (MLEFC) in an alkaline-acidic media and the subsequent second step was intended to further improve the cell performance by characterising the main cell by changing several operational parameters, such as fuels compositions, oxidant compositions, electrolyte compositions, distance effect and flow rate, and to observe their influence on the polarisation behaviour of the cell.

Media flexibility of MLEFC:

In recent years, the effect of operating laminar flow based fuel cells in all-acidic, all-alkaline, and alkaline-acidic media has received considerable attention^{18,19}. Since certain hydrocarbons such as ethanol, methanol and formic acid can easily be stored in a liquid form under ambient conditions, they are known to generate high energy densities in a safe manner.

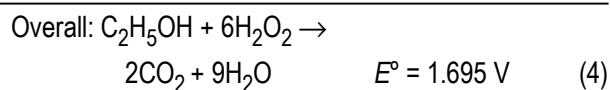
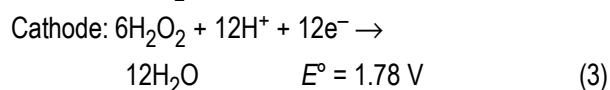
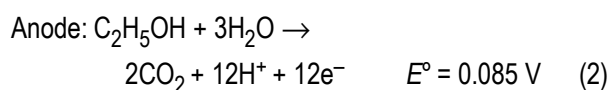
The MLEFC is flexible in the use of media such as all-acid, all-alkaline, or in an alkaline-acidic media, in which the anode is exposed to acidic media while the cathode is exposed to alkaline media, or vice versa. The performance of MLEFC in alkaline-acidic media, using an alkaline anode and an acidic cathode, has been found to result in a higher overall cell potential than that possible from all-acidic and all-alkaline fuel cell experiments.

Performance of MLEFC in all-acidic and all-alkaline media:

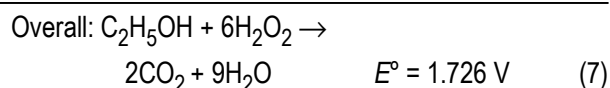
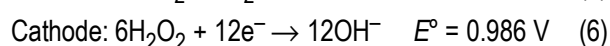
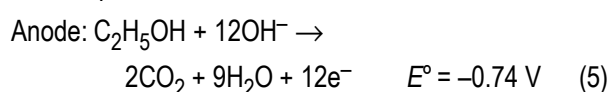
The pH of the electrolyte influences reaction kinetics at

the individual electrodes, as well as the electrode potential at which oxidation or reduction occurs^{20–24}. Eqs. (2) and (3) represent the half-cell reactions and standard electrode potentials of ethanol oxidation and peroxide reduction in acidic media and the eqs. (5) and (6) represent the alkaline media. Eqs. (4) and (7) represent the overall cell reaction, in all-acid or all-alkaline media. The alkaline-alkaline media and the acidic-acidic media have a maximum theoretical open circuit potential (OCP) of 1.726 V and 1.695 V. On the other hand, we use alkaline-acidic media to force reactions (3) and (6) to proceed with the aim of improving fuel cell performance.

Ethanol/perborate in acidic media:



Ethanol/perborate in alkaline media:



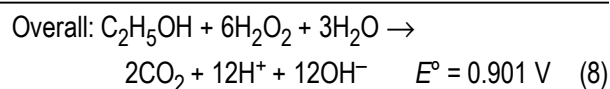
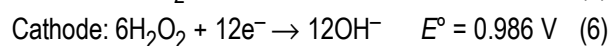
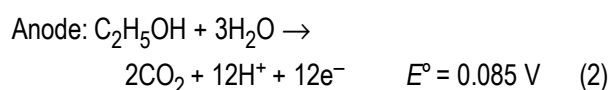
A comparison of the performance of an MLEFC in all-alkaline and all-acidic media is shown in Fig. 3. Initially at low current densities, both the polarisation curves are identical and thus it is clear that the performance of MLEFC is independent of the medium. The mass transport limitation region is around 6 mA cm⁻² in the MLEFC in both alkaline and acidic media and was in good agreement with the previous study²⁵. The MLEFC worked for several days without any drop in its performance in a vast array of test conditions. No issues with carbonate formation were encountered in this MLEFC at room temperature, as any carbonate that does form is immediately removed from the system by the flowing streams.

Performance of MLEFC in acidic-alkaline media: acidic anode, alkaline cathode:

The performance of MLEFC using a fuel stream of 1 M

ethanol in 1 M H₂SO₄ and an oxidant stream of 0.1 M perborate in 1 M KOH was investigated. The measurements were carried out at room temperature for two configurations: (i) acidic-alkaline media: acidic anode, alkaline cathode and (ii) alkaline-acidic media: alkaline anode, acidic cathode. In alkaline-acidic media of this kind, the neutralisation reaction of OH⁻ and H⁺ to form water occurs at the liquid-liquid interface between the fuel and the oxidant streams. In the first configuration, the overall cell reaction, eq. (8), can be obtained from eqs. (2) and (6):

Mixed media 1: Acidic anode and alkaline cathode:

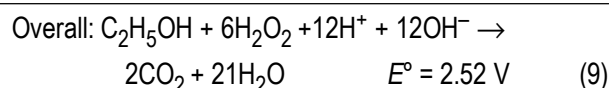
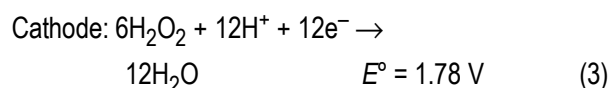
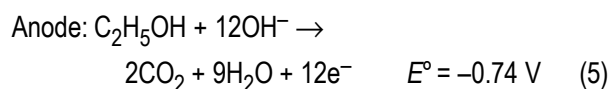


In this alkaline-acidic media, the maximum theoretical OCP that can be obtained is 0.901 V. The energy liberated in ethanol oxidation and peroxide reduction reactions is mostly consumed for ionisation of water. In this configuration, the coexistence of the galvanic and ethanol electrolytic reactions has been found to be the reason for a very low yield of energy, and therefore they were not studied any further.

Performance of MLEFC in alkaline-acidic media: alkaline anode, acidic cathode:

In alkaline-acidic media, the MLEFC functions using a fuel stream of an alkaline anode and an acidic cathode, which allows energy to be obtained both from the ethanol oxidation/peroxide reduction reactions and from the acid/alkali electrochemical neutralisation reactions, as evident from the overall cell reaction eq. (9):

Mixed media 2: Alkaline anode and acidic cathode:



In this alkaline-acidic media, the combination of two galvanic reactions yields a desirable high theoretical OCP of

2.52 V. Note that the inherent value of the electromotive force of the MLEFC 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 ethanol oxidation, the OCP gets reduced to a measured value of 1.56 V as shown in Fig. 3, which was in good agreement with the previous reported value of 1.4 V²⁵. In alkaline-acidic media, both OH⁻ and H⁺ are consumed at the anode and cathode, respectively, at a rate of six ions for each molecule of ethanol.

In alkaline-acidic media, in which an alkaline anode and an acidic cathode are used, a higher overall cell potential was realised compared to that obtained for the all-acidic and all-alkaline MLEFC experiments. Fig. 3 shows the power density curves of the MLEFC experiments performed using different media combinations at the anode and cathode.

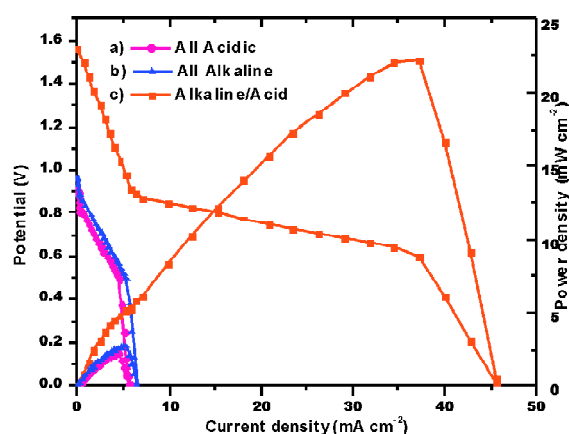


Fig. 3. Performance of media flexibility on current and power density of MLEFC at room temperature. (a) All alkaline media ([Fuel]: 1 M ethanol + 1 M KOH. [Oxidant]: 0.1 M perborate + 1 M KOH), (b) All acidic media ([Fuel]: 1 M ethanol + 1 M H₂SO₄. [Oxidant]: 0.1 M perborate + 1 M H₂SO₄), (c) Alkaline-acidic media ([Fuel]: 1 M ethanol + 1 M KOH. [Oxidant]: 0.1 M perborate + 1 M H₂SO₄).

When all-acidic and all-alkaline are used, the maximum power densities generated by the MLEFC are 2.25 and 2.67 mW cm⁻², respectively, both at a cell potential of about 0.5 V, whereas when an alkaline-acidic media is used, it results in a power density maximum of 22.25 mW cm⁻² at a cell potential of about 0.5 V. The alkaline-acidic media fuel cell clearly outperforms both the all-acidic and all-alkaline fuel cell (Table 2). The higher power densities in the MLEFC using alkaline-acidic media result from higher overall cell po-

Table 2. Effect of medium on the performance of the MLEFC

	All-alkaline	All-acidic	Alkaline-acidic
Open circuit voltage (V)	0.96	0.916	1.56
Short-circuit current density (mA cm ⁻²)	6.53	5.69	45.53
Peak power density (mW cm ⁻²)	2.67	2.25	22.25
Cell voltage at peak power density (V)	0.49	0.48	0.59
Current density at peak power density (mA cm ⁻²)	5.38	4.53	37.26

tentials due to the unprecedented ability to operate the cathode and anode at different pH values in an MLEFC.

Influence of fuel composition:

The effect of fuel on the performance of MLEFC was analysed by varying the concentration of ethanol between 0.5 and 4 M (Fig. 4).

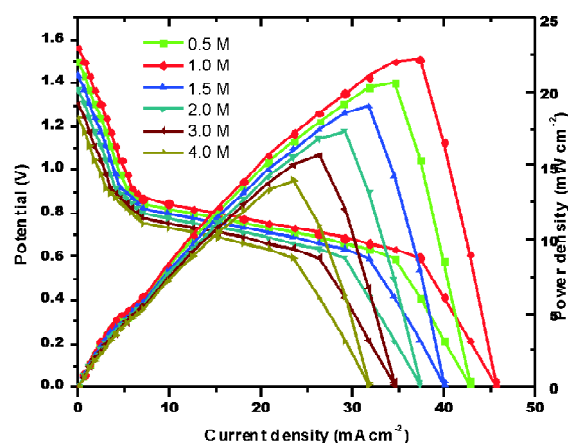


Fig. 4. Effect of ethanol concentration on the current and power density of the MLEFC at room temperature. ([Fuel]: xM ethanol + 1 M KOH. [Oxidant]: 0.1 M perborate + 1 M H₂SO₄).

The effect of the fuel concentration on the product selectivity was studied by varying both ethanol and KOH concentrations. The effect of ethanol concentration was investigated by varying the concentration of ethanol as 0.5, 1.0, 1.5, 2.0, 3.0 to 4.0 M while fixing the concentration of KOH at 1.0 M. Similarly, the effect of KOH concentration was observed by varying the concentration of KOH as 0.5, 1.0, 1.5 to 2.0 M while fixing the concentration of ethanol at 1.0 M. Among these several combinations of fuel and oxidant, the fuel so-

lution containing 1.0 M ethanol and 1.0 M KOH gives the highest and most stable performance, and a decrease and fluctuation of cell voltage was observed as the ethanol and KOH concentrations are varied.

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

In a fluidic system, fuel crossover can create mixed potentials, decrease in cell efficiency, and could even deactivate the catalyst. Fortunately, the device design and operating parameters can both be controlled to prevent fuel crossover^{26,27} in any membraneless fuel cell; therefore the higher ethanol concentration is not the cause for decrease of performance in a fuel cell. The kinetic decrease in the anode also cannot be a factor because the electro-oxidation of ethanol 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 at higher ethanol concentrations. Taking into account these factors, the ethanol concentration of 1 M seems to be the best composition for the fuel, and so this value was fixed for the remaining experiments.

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 as sodium perborate concentration increases in the MLEFC system and reaches the maximum of 1.56 V at 0.1 M sodium perborate. Peak power densities of 1.03, 2.77, 5.83, 14.03, 22.25 mW cm⁻² were obtained at 0.01, 0.025, 0.05, 0.075 and 0.1 M of sodium perborate, respectively (Fig. 5). A further increase in the oxidant concentration shows no improvement in the cell performance. Therefore, the value of 0.1 M has been fixed as the perborate concentration in the oxidant solution.

Likewise, the effect of H₂SO₄ concentration in the oxidant solution has also been analysed. The concentration of H₂SO₄ was varied between 0.1 and 1.0 M. The maximum

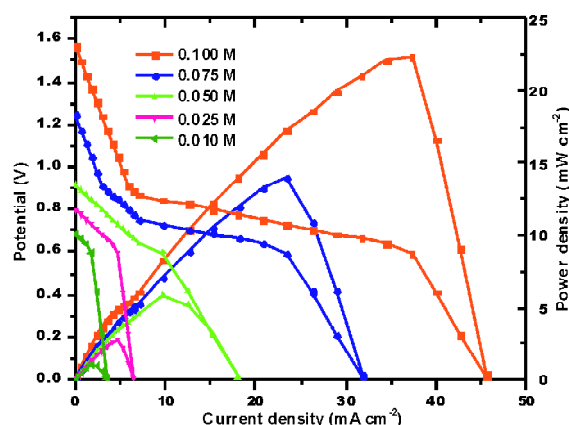


Fig. 5. Effect of perborate concentration on the current and power density of the MLEFC at room temperature. ([Fuel]: 1 M ethanol + 1 M KOH. [Oxidant]: xM perborate + 1 M H₂SO₄).

power density (22.25 mW cm⁻²) was obtained at 1 M H₂SO₄ (Fig. 6). A further increase in the concentration of H₂SO₄ shows no improvement in the cell performance. Therefore, the value of 1 M has been fixed as the H₂SO₄ concentration in the oxidant solution.

Influence of distance effect on the performance of MLEFC:

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

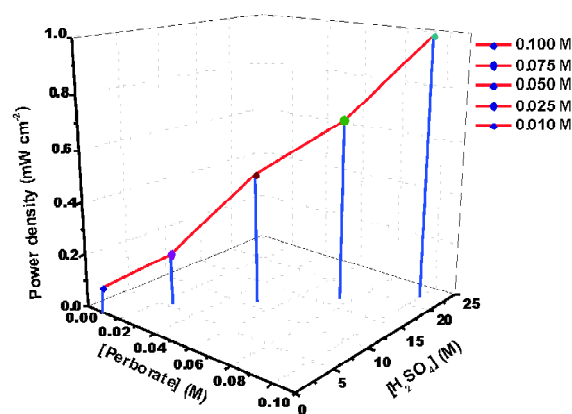


Fig. 6. Effect of various combinations of perborate and sulphuric acid concentrations on the maximum power density (22.25 mW cm⁻²) of the MLEFC at room temperature. The fuel mixture for variation of oxidant is ([Fuel]: 1 M ethanol + 1 M KOH, [Oxidant]: xM perborate + 1 M H₂SO₄) and the fuel mixture for variation of sulphuric acid is ([Fuel]: 1 M ethanol + 1 M KOH, [Oxidant]: 0.1 M perborate + xM H₂SO₄).

anode and cathode decreased, the maximum power density was observed, as shown in Fig. 7. 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 cell²⁸.

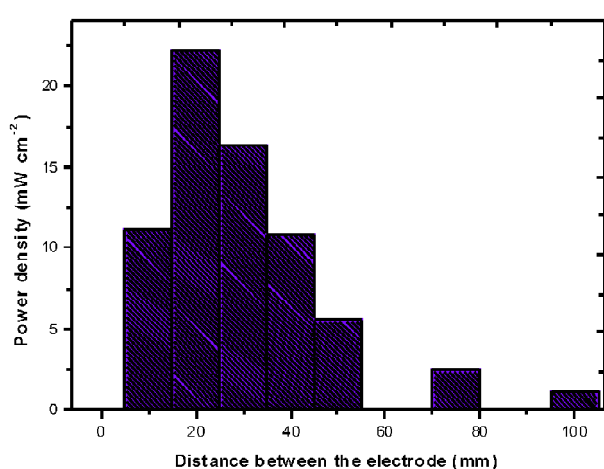


Fig. 7. Effect of distance between anode and cathode on the maximum power density of the MLEFC at room temperature. ([Fuel]: 1 M ethanol + 1 M KOH. [Oxidant]: 0.1 M perborate + 1 M H₂SO₄).

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⁻¹ 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⁻¹, after which the maximum power density decreases with an increase in the flow rate as shown in Fig. 8. It is believed that more electrochemical reactions would take place at a given time and a greater output current could develop in the end.

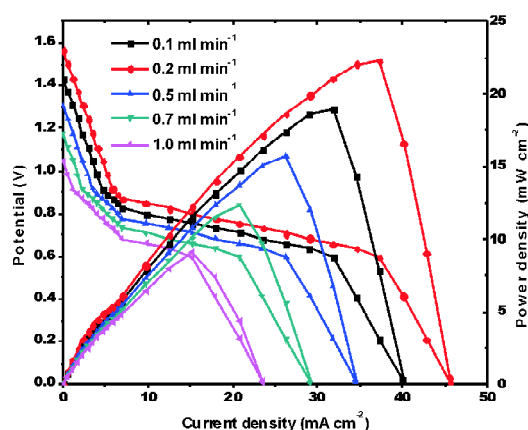


Fig. 8. Effect of flow rate of fuel mixture on the current and power density of the MLSEFC at room temperature. ([Fuel]: 1 M ethanol + 1 M KOH. [Oxidant]: 0.1 M perborate + 1 M H₂SO₄).

Conclusions

A microscale membraneless ethanol fuel cell (MLEFC) was fabricated on PDMS and its performance was evaluated under different operating conditions. Standard microfabrication techniques were used to develop this device. Ethanol 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 all-acidic, all-alkaline, or even alkaline-acidic media.

In this work, we observed that the alkaline anode/acidic cathode alkaline-acidic media leads to a very high measured OCP of 1.56 V, while other combinations result in very low OCPs as a result of the pH dependence of standard electrode potentials. For the MLEFC operating in the alkaline anode/acidic cathode alkaline-acidic media, the measured OCP of 1.56 V was found to be in a reasonable agreement with the theoretical OCP of 2.52 V.

At room temperature, the laminar flow-based microfluidic fuel cell produced a maximum power density of 22.25 mW cm⁻² in the alkaline anode/acidic cathode alkaline-acidic media. We conclude that alkaline-acidic media MLEFC outperforms the all-acidic and all-alkaline MLEFCs. The effects of flow rates of the fuel and the oxidant, variation of concentrations of ethanol, perborate, and electrolytes were analysed in alkaline-acidic media. The performance was characterised by V-I curves and anode polarization plots.

The results demonstrated that the performance of the developed membraneless fuel cell is significantly enhanced if the concentration of the oxidant in the cathodic stream is 10 times larger, and the current density is also increased approximately 10 times, whereas in the case of variation of ethanol concentration at the anode, fuel cell performance decreases as the ethanol concentration increases, due to the increase of ohmic resistance.

Thus, the present experimental findings have confirmed that the membraneless microfuel cell designed in our study is cathode limited and suggest that a crucial factor in improving cell performance is increasing the concentration of the oxidant in the cathodic stream. The flexibility of membraneless fuel cells to function with different media allowed for the successful working of mixed alkaline and acidic fuel cells. 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.

In addition, the development of metal catalysts to accelerate the efficiency of MLEFC is in progress. Some further experimental studies focused on the microchannel design and the flow rate of MLEFC with various fuels will be beneficial to verify the predictions in this study and enable the practical utilisation of the cell in portable power sources.

The MLEFC 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 MLEFC may be a promising candidate for practical fuel cells to generate clean and sustainable energy in the future.

Acknowledgements

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