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International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.7, No.7, pp 3134-3140, 2015

ICEWEST-2015 [05th - 06th Feb 2015]
International Conference on Energy, Water and Environmental Science & Technology
PG and Research Department of Chemistry, Presidency College (Autonomous), Chennai-600 005, India

Electrooxidation of Hydrazine using H_2O_2 as An Oxidant in Membraneless Fuel Cells

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Abstract : This paper describes the continuous flow operation of membranelessfuel cell using acid/alkaline bipolar electrolyte. Here, hydrazine is used as a fuel and hydrogen peroxide is used as an oxidant under Alkaline-acid media configuration. In our operation, the laminar flow based microfluidic membranleless fuel cell achieved a maximum power density of 27 mW cm^{-2} when using alkaline hydrazine as the anolyte and acidic peroxide as the catholyte at room temperature with a fuel mixture flow rate of 0.3 mL min^{-1}. The simple planar structured membranelessfuel cell enables high design flexibility and easy integration of the microscale fuel cell into actual microfluidic systems and portable power applications.

Keywords: Alkaline-acid media, Hydrazine, Peroxide,Membranelessfuel cell, Portable power application.

Introduction

Fuel cell is a device that converts chemical energy intoelectrical energy, through electrochemical reactions.Of various fuel cell systems available, the microfluidicmembranelessfuel cells have been recognized as one of the most promising candidate for small-scale portable power applications[1-4]. A membraneless fuel cell is a well known electrochemical device that enables the conversion of chemical energy of fuels directly into electrical energy without a membrane as long as the fuel is supplied.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[5].

Hydrazine (N_2H_4) is a low cost material and its synthesis is relatively simple. Hydrazine is composed of only hydrogen and nitrogen; theoretically, the anode reaction produces only nitrogen. Therefore perfect zero emission equal to a pure hydrogen fuel can be realized[6]. The absence of carbon atom in hydrazine leads to zero production of species that may poison the electrocatalysts[7]. Compared with ethanol, methanol, hydrogen andV^{2+}, hydrazine has a higher overall theoretical open circuit potential and maximum efficiency as indicated in Table1. In addition, studies have shown that the hydrazine electro-oxidation process does not suffer from any poisoning effect[8,9]. In sum, hydrazine seems to be a promising fuel for fuel cells and thus has been explored by us as the fuel with the membraneless fuel cell in this paper.

Table 1

Fuel	$-\Delta G^{\circ}$(kJ/mol)	$-\Delta H^{\circ}$(kJ/mol)	E_{rev}° (V)	Energy Density (Wh/ L)	Maximum Efficiency (%)
Hydrazine	623.4	622.2	1.62	5400	100.2
Methanol	702.5	726.6	1.21	6400	96.68
Hydrogen	237.3	286	1.23	2600	82.97
Ethanol	174.9	277.7	1.15	7850	62.98

Theoretical open circuit potential and maximum efficiency of various fuels

In this study, membraneless fuel cell (MLFC) employs an alkaline solution of hydrazine as a fuel and hydrogen peroxide as an oxidant. All the aforementioned membrane-related issues can be avoided in the MLFC studied here. The performance implications of operating fuel cell under “alkaline-acid media”, i.e. one electrode is acidic and the other is alkaline is the focus of our study.The influence ofanolyte and catholyte on cell voltage and cell performance was studied. The effect of media (Alkaline-acid) flexibility and the electrode polarization were evaluated. This development was based on our previous results regarding the electro-oxidation of methanol in acid-alkaline media[10].

Experiments

Materials and reagents

All experiments were conducted at room temperature using hydrazine (98%, Merck) in de-ionized water as the fuel, and hydrogen peroxide (99%, Riedel) dissolved in 0.5 M sulfuricacid (98%, Merck) or 0.5 M Sodium hydroxide (98%, Merck) in de-ionized water as the oxidant.Pt/C (40-wt%, from E-TEK) was used as the anode and cathode catalyst.

Design of membraneless fuel cells (MLFC):

In the MLFC configuration, a laminar flow channel with catalyst-coated graphite plates of 1 mm thickness is used. Carbon supported platinum nanoparticles that act as anode and cathode and line the microfluidic channel. The microfluidic channel structure is moulded with polydimethylsiloxane(PDMS), typically 1–10 mm in thickness, and finally sealed with a solid substrate such as 2 mm thick pieces of polymethylmethacrylate (PMMA) 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.

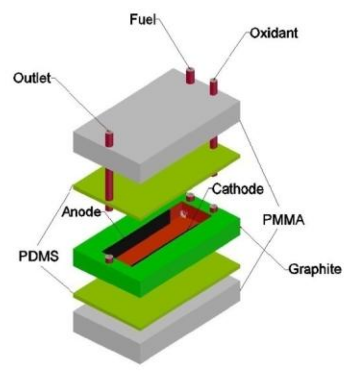

Figure 1. Schematic of the membraneless laminar flow based fuel cell with graphite plates molded with PDMS poly(dimethylsiloxane) and sealed with PMMA poly(methylmethacrylate).

Single celltest

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, $Re < \sim 2100$[11]. 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 (Hydrazine) and one oxidant (hydrogen peroxide), respectively, and allowing these streams to flow over the anode and cathode electrodes placed on opposing side walls within the microfluidic channel[12,13]. 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.

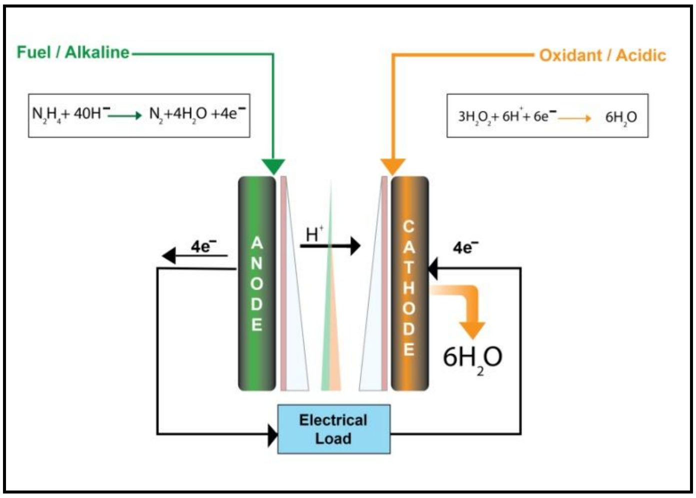

Figure 2.A cross section of channel showing depletion boundary layer over anode and cathode metal catalyst and inter diffusion zone at the liquid-liquid interface with verticalelectrodes on side walls

The current-voltage characteristics of MLEFC were measuredusing an electrochemical workstation (CH Instruments, model CHI6650, USA) and the data was verified using a multi-meter (MASTECH$^{®}$ MAS830L).

Alkaline-acid media flexibility of membraneless fuel cell

This membraneless micro fabrication method eliminates several of the technical issues related to the use of polymer electrolyte membrane fuel cells (PEMs)[14,15].In addition, lack of a membrane also allows for operation of MLFCs in more than one media. Moreover, the chemical composition of the cathode and anode streams can be designed individually to optimize individual electrode kinetics as well as overall cell potential. Furthermore, the MLFC has the flexibility to run in all-acidic, all-alkaline, or in an “Alkaline-acid media” mode in which the anode is exposed to acidic media while the cathode is exposed to alkaline media, or vice versa. The performance of MLFC in Alkaline-acid media configuration, using an alkaline anode and an acidic cathode was higher overall cell potential than what was obtained from all-acidic and all-alkaline fuel cell experiments.

Results and discussion

Performance of MLFC in all-acidic and all-alkaline media

The pH of the electrolyte has an effect on reaction kinetics at the individual electrodes, as well as the electrode potential at which oxidation or reduction occurs[16-20].Equations (2) and (3) represent the half-cell reactions and standard electrode potential of hydrazine oxidation and peroxide reduction in acidic media and Equations (5) and (6) represent the alkaline media. Equations (4) and (7) show the overall cell reaction, in all-acidic and all alkaline media. Both the acidic-acidic media and the alkaline-alkaline media have a maximum theoretical open circuit potential (OCP) of 1.56 V and 2.156 V respectively. On the other hand, we use the bipolar electrolyte to force reactions (3)and (5)to achieve further improvement in fuel cell performance.

Hydrazine / Peroxide in Acidic Medium:

Anode: $N_2H_4 + H^+ \rightarrow N_2 + 5H^+ + 4e-$ $E^0 = 0.22$ V (2)
Cathode: $3H_2O_2 + 6H^+ + 6e^- \rightarrow 6H_2O$ $E^0 = 1.78$ V (3)

Overall: $N_2H_4 + 3H_2O_2 + 2H^+ + 6e^- \rightarrow N_2 + 6H_2O$ $\Delta E = 1.56$ V (4)

Hydrazine / Peroxide in Alkaline Medium:

Anode: $N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^-$ $E^0 = -1.17$V (5)
Cathode: $3H_2O_2 + 6e^- \rightarrow 6OH^-$ $E^0 = 0.986$ V (6)

Overall: $N_2H_4 + 3H_2O_2 + 2e^- \rightarrow N_2 + 4H_2O + 2OH^-$ $\Delta E = 2.156$ V (7)

A comparison of the performance of an MLFC in all-acidic and all alkaline media is exhibited in Figs. 3a and 3b respectively. Initially at low current densities both the polarization curves are identical, and thus the performance of MLFC is independent of the medium. The mass transport limitation region is around 6 mA cm^{-2} in the MLFCrunning for both acidic and alkaline media was in agreement with the previous researcher[21].The MLFC were run over several days without any drop in performance under a variety of test conditions.

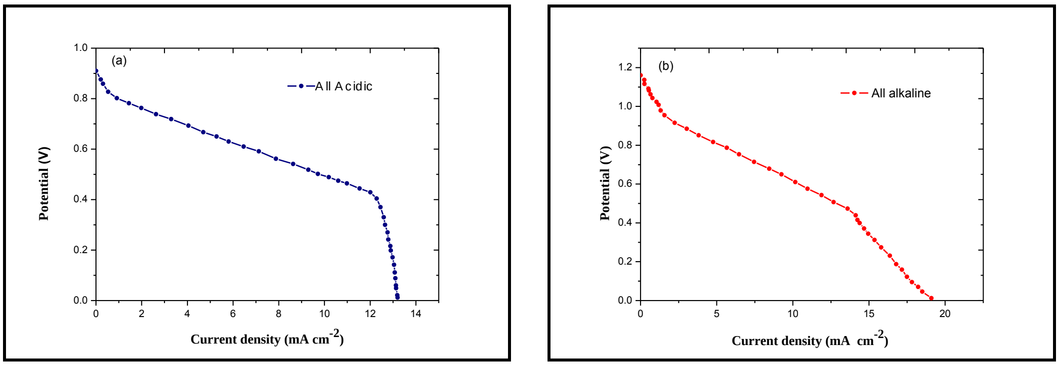

Figure 3. Polarisation curves for overall cell performance of MLFC operating in: (a) all acidic and (b) all alkaline media at room temperature.

Performance of MLFC in Alkaline-acid media 1: acidic anode, alkaline cathode:

The performance of MLFC using a fuel stream of 0.075 M Hydrazine in 0.5M H_2SO_4 and an oxidant stream of 0.1 M Peroxide in 0.5 M NaOH was investigated. The measurements were taken at room temperature for two configurations: Alkaline-acid media 1: acidic anode, alkaline cathode and alkaline-acid media 2: alkaline anode, acidic cathode. In these Alkaline-acid media configurations the neutralization reaction of OH^- and H^+ to water occurs at the liquid-liquid interface between the fuel and oxidant stream. In the first configuration, the overall cell reaction, Eq. (8), can be obtained from Eqs. (2) and (6):

Alkaline-acid media 1: Acidic Anode & Alkaline Cathode:

Anode: $N_2H_4 + H^+ \rightarrow N_2 + 5H^+ + 4e-$ $E^0 = 0.22$ V (2)
Cathode: $6H_2O_2 + 6e^- \rightarrow 12OH^-$ $E^0 = 0.986$ V (6)

Overall: $N_2H_4 + 3H_2O_2 + H^+ + 2e^- \rightarrow N_2 + 5H^+ + 6OH^-$ $\Delta E = 0.766$ V (8)

In this Alkaline-acid media configuration 1, the maximum theoretical OCP is 0.766 V. The energy liberated in the hydrazine oxidation and peroxide reduction reactions is mostly consumed by the water ionization reaction. In this configuration, coexistence of the galvanic and hydrazine electrolytic reactions has been found to be the reason why useful amounts of energy could not be yielded, and why it was not studied any further.

Performance of MLFC in Alkaline-acid media 2: alkaline anode, acidic cathode:

In contrast, in Alkaline-acid media configuration 2, the MLFC using a fuel stream of an alkaline anode and an acidic cathode allows energy to be obtained both from the Hydrazine oxidation/peroxide reduction reactions and from the acid/alkaline electrochemical neutralization reactions, as evident from the overall cell reaction Eq.(9):

Mixed Media 2: Alkaline Anode and Acidic Cathode:

Anode: $N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^-$ $E^0 = -1.17$ V (5)
Cathode: $3H_2O_2 + 6H^+ + 6e^- \rightarrow 6H_2O$ $E^0 = 1.78$ V (3)

Overall: $N_2H_4 + 3H_2O_2 + 6H^+ + 4OH^- + 2e^- \rightarrow N_2 + 10H_2O$ $\Delta E = 2.95$ V (9)

In this Alkaline-acid media 2 configuration, the combination of two galvanic reactions yields a desirable high theoretical OCP of 2.95 V. Note that the inherent value of the electromotive force of the MLFC is higher than that of the HFC (1.23 V) and the PEMFC or DMFC (1.21 V). However, because of the over potential resulting from the slow kinetics of peroxide reduction and hydrazine oxidation, the open circuit potential is reduced to a measured value of 1.72 V as shown in Fig.4. In the Alkaline-acid media configuration both OH^- and H^+ are consumed at the anode and cathode, respectively, at a rate of four for each molecule of hydrazine.

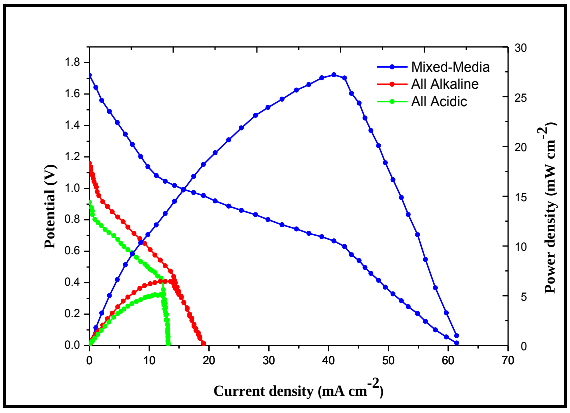

Figure4. Performance of media flexibility on current and power density of MLFC at room temperature.

Operating in this Alkaline-acid media configuration, with an alkaline anode and an acidic cathode, resulted in a higher overall cell potential than those obtained for the all acidic and all- alkaline MLFC experiments. In MLFC, the all-acidic and all-alkaline experiments have maximum power densities of 5.2 and 6.4 mW cm^{-2} respectively, both at a cell potential of about 0.91 V, 1.16 V whereas the Alkaline-acid media experiment results in a power density maximum of 27 mW cm^{-2} at a cell potential of about 1.72 V. Within this condition, the Alkaline-acid media fuel cell clearly outperforms both the all acidic and all-alkaline fuel cell. The higher power densities in the Alkaline-acid media MLFC are a direct result of higher overall cell potentials due to the unprecedented ability to operate the cathode and anode at different p^H in an MLFC.

Influence of fuel composition

The effect of fuel on the performance of MLFC has been observed by varying the Hydrazine concentration between 0.025 M and 0.125 M as shown in Fig.5.

The experiment results show that the fuel cell performance decreases as the Hydrazine concentration increases. This decreasing trend in cell performance at higher hydrazine concentrations is due to four reasons i) creation of mixed potential at the cathode due to fuel crossover ii) kinetic decrease in anode iii) transport resistance increase at the anode iv) ohmic resistance increase.

In a fluidic system, fuel crossover can create mixed potential, decrease cell efficiency, and even deactivate the catalyst. Fortunately, the device design and operating parameters can be controlled so that fuel crossover can be prevented[22,23] in any membraneless fuel cell. Therefore higher hydrazine 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 hydrazine on Pt has a positive reaction order between 0.025 M and 0.075 M. The activity at the anode increases as the concentration of fuel increases. Therefore, the anode is not limited by kinetic performance with higher hydrazine concentration.

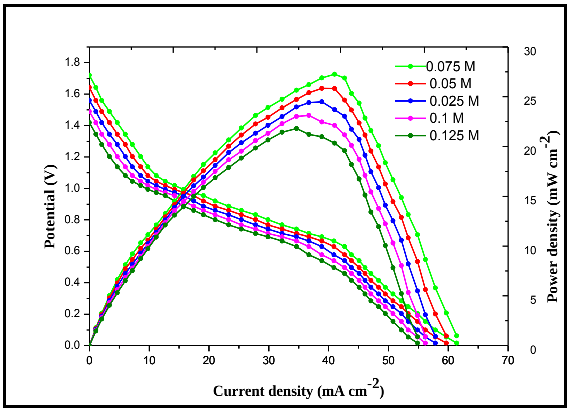

Figure 5. Effect of hydrazine concentration on the current and power density of the MLFC at room temperature.

Influence of oxidant composition

The effects of peroxide 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 hydrogen peroxide concentration in the MLFC system and reached the maximum of 1.72 V at 0.1 M hydrogen peroxide. Peak power densities of 1.77, 5.28, 9.66, 20.30, 27 mW cm^{-2} were obtained at 0.01, 0.025, 0.05 0.075 and 0.1 M respectively as shown in Fig. 6. 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 peroxide concentration in the oxidant solution..

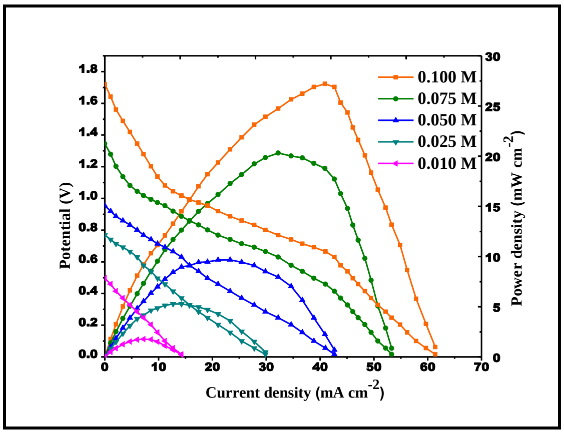

Figure 6. Effect of peroxide concentration on the current and power density of the MLFC at room temperature.

The effects of peroxide and H_2SO_4 composition in the oxidant solution have also been analyzed. The H_2SO_4 concentration was varied between 0.01 M and 0.5 M. The maximum power density 27 mW cm^{-2} was obtained at 0.5 M H_2SO_4. Further increase in the H_2SO_4 concentration shows no improvement in the cell performance. Therefore, the value of 0.5 M has been fixed for the H_2SO_4 concentration in the oxidant solution.

Stability test

Durability of the MLFC was examinedShort-term stability of MLFCunder alkaline-acid media configurations was tested by monitoring the cell voltage change during the galvanostatic discharge of 61.4mA cm^{-2}of the MLFC in a period of about 100 h (Fig. 10).The MLFC 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 MLFC in our research has good stability at room temperature which is able to satisfy the necessary conditions as portable power sources.

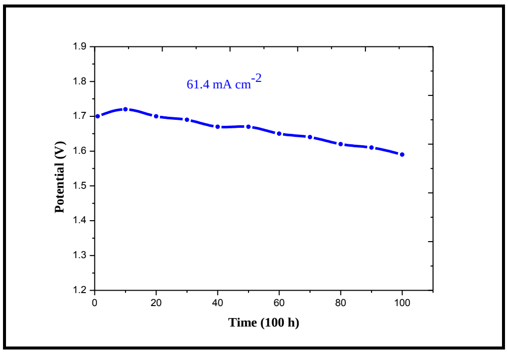

Figure 7. Performance stability of the MLFC operating at current density of 61.4mA cm^{-2}at room temperature.

Conclusions

A small scale membraneless fuel cell (MLFC) was fabricated on PDMS and its operating behaviour were evaluated under different conditions. Hydrazine is used as a fuel at the anode and hydrogen peroxide is used as an oxidant at the cathode in this membraneless fuel cell under alkaline-acidic media. The experiments described in this study clearly indicate that membraneless fuel cells are media flexible and they can be operated in all-acidic, all-alkaline, or even combined alkaline-acidic media.At room temperature, the laminar flow-based microfluidic fuel cell produced a maximum power density of 27 mW cm^{-2}.The MLFC has the advantages of a miniature size, simplicity of fabrication, use of aqueous fuel, and good cost efficiency. We expect that the MLFC promises to be the environmentally friendly power source of the future for portable power applications.

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