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## Performance of sodium borohydride in membraneless fuel cells

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**Abstract:** This paper presents the membraneless sodium perborate fuel cell, constructed with three polymethyl methacrylate (PMMA) layers. A membraneless sodium perborate fuel cell converts chemical energy stored in borohydride ion and an oxidant directly into electricity by redox processes. Usually, an employs an alkaline solution of sodium borohydride (NaBH<sub>4</sub>) as fuel and acidic perborate as oxidant. The impact of different operating conditions such as fuel and oxidant concentration, on the performance of individual fuel cells is investigated. At room temperature, the laminar flow-based micro membraneless fuel cell can reach maximum power densities of 27.75 mWcm<sup>-2</sup> with 0.15 M NaBH<sub>4</sub> in 3 M NaOH solution as fuel and 0.15 M perborate in 1.5 M H<sub>2</sub>SO<sub>4</sub> solution as a oxidant.

**Keywords :** Alkaline-acidic media, Membraneless sodium carbonate fuel cell, Laminar flow Sodium borohydride.

### Introduction

As the production rate of nomad electronics devices increases, the demand for high energy portable generator becomes stringent. Of various fuel cell systems, the microfluidic fuel cells have been recognized as one of the most promising candidate for small-scale portable power applications<sup>1-5</sup>. A microfluidic fuel cell consists of a two electrodes which are typically positioned on the side walls along the channel. In such a system, the fuel and oxidant are introduced into the microchannel at a low flow rate which results in a laminar flow. The laminar flow in the microfluidic fuel cells plays a similar role to that of the solid membrane in proton exchange membrane fuel cells and maintains the separation of the fuel and oxidant.

Sodium borohydride (NaBH<sub>4</sub>) is gaining increasing interest for its possible applications in energy systems<sup>6</sup>. As a hydrogen storage material, it has attracted a lot of attention due to its higher gravimetric hydrogen capacity compared to metal hydrides and higher volumetric hydrogen capacity than compressed and liquefied hydrogen. In addition the poisoning and sluggish reaction rate associated with CO-contaminated H<sub>2</sub> and methanol respectively, these are all averted by employing the fuel borohydride. The fuel, also presents several advantages: it is non-toxic, easily stored and relatively stable in alkaline solution, while exhibits rather high energy density (9.3 Whg<sup>-1</sup> at 1.64 V) and also from the table.1 it has high hydrogen content (10.6 Wt.%) compared with formic acid (4.35 Wt.%). Besides, its oxidation product metaborate can be recycled to produce borohydride<sup>7,8</sup>.

Membraneless sodium carbonate fuel cell employs an alkaline solution of sodium borohydride as the fuel and acidic solution of sodium carbonate ( $\text{Na}_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$ ), as oxidant. All the aforementioned membrane-related issues can be avoided in the s studied here. The performance implications of operating fuel cell under “acid-alkaline media”, i.e. one electrode is acidic and the other one is alkaline condition will be the focus of this study. Among these, sodium carbonate does not produce any precipitate like permanganate and it does not undergo any decomposition like hydrogen peroxide and oxygen. Moreover, sodium perborate is an environmentally friendly, cheap, non-toxic, large scale industrial chemical used primarily in detergents and as a mild oxidant.

In this communication, first time we introduce sodium carbonate as an oxidant to demonstrate the performance of a membraneless sodium percarbonate fuel cell. Sodium percarbonate is a true peroxy salt and is a convenient source of hydrogen peroxide<sup>7,8</sup>.



The sodium per carbonate fuel cell is unique from other fuel cells using  $\text{H}_2\text{O}_2$ , as mentioned in our earlier study sodium percarbonate can be used as not only as an oxidant but also a reductant. 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

### Chemical and materials

The chemical used in the planar micro-fuel cell design was  $2\text{Na}_2\text{CO}_3$  (98%, Merck), NaOH (98%, Merck),  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$  (99%, Riedel),  $\text{H}_2\text{SO}_4$  (98%, Merck). All the solution prepared in deionised water. The materials used in fuel cells are PDMS poly(dimethylsiloxane) (99.9%, Chemsouth), and PMMA poly(methylmethacrylate) (92%, G. Khanna & Co), Graphite plates (Kriti Graphite), Silicon tubes (Shree Gaurav rubber products).

### Catalyst deposition

In the s, graphite plates served as current collectors and catalyst structures. For all the experiments of fuel cells, unsupported platinum black nanoparticles are applied to the sides of the graphite plates to act as cathode and anode that line the microfluidic channel. For both electrodes the catalyst suspensions were prepared by mixing at a concentration of  $6.0 \text{ mg ml}^{-1}$  Pt black nanoparticles (Alpha Aesar) in a 10 wt.% Nafion solution (Nafion stock solution: Dupont, 5% (w/w) solution). This mixture was sonicated and hand-painted into the side faces of the graphite plates at a loading of  $2 \text{ mg cm}^{-2}$ . Then solvent was evaporated by the use of a heat lamp for uniform loading<sup>9</sup>.

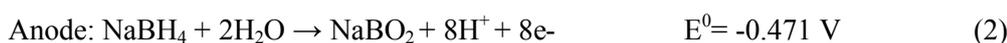
## Result and Discussion

### Scheme of the various cell reactions

In these paper, we treated the in all acidic, all alkaline, acidic-alkaline media 1 (acidic fuel-alkaline oxidant) and alkaline acidic media 2 (alkaline fuel-acidic oxidant). Their cell reactions and theoretical potential are illustrated below. For s, the anode stream was 0.15M sodium borohydride ( $\text{NaBH}_4$ ) in 3.0M sodium hydroxide (NaOH) and the cathode stream was 0.15M per carbonate in 1.5M  $\text{H}_2\text{SO}_4$ .

### Performance of in all acidic media

Eqs. (2)-(3) show the half-cell reactions and standard electrode potentials of sodium borohydride oxidation and percarbonate reduction in acidic media. Eqs. (4) represents the overall cell reaction<sup>10</sup>. The acidic-acidic case have a maximum theoretical open circuit potential (OCP) of 2.251 V. But we achieved the maximum potential 0.94 V at the current density  $32.49 \text{ mA cm}^{-2}$  in the running in all acidic media.



### Performance of in all alkaline media

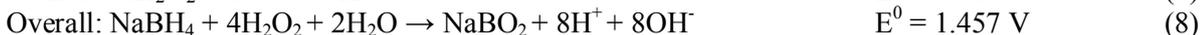
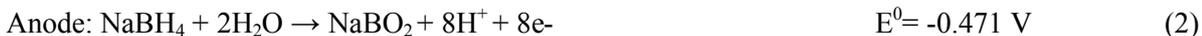
Anode and cathode in alkaline media eqs. (5), (6) show the redox reactions and standard electrode potentials of  $\text{BH}_4^-$  oxidation and perborate reduction in alkaline media. Eq. (7) represents the net cell reaction. In this case has a maximum theoretical open circuit potential of 2.226 V<sup>11</sup>.



The mass transport limitations region, however, is reached at 1.29 V around 40.9 mA cm<sup>-2</sup> of current density achieved in the running in all alkaline media.

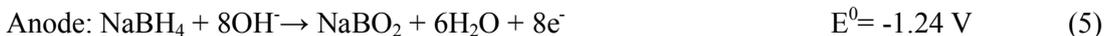
### Performance of in mixed media-1: (acidic anode, alkaline cathode)

In Mixed media-1 system where one stream is acidic while the other stream is alkaline. In this configuration, the overall cell reaction, Eq. (8), can be obtained from Eqs. (2) and (6): the maximum theoretical OCP is 1.457 V in mixed media configuration-1. An open circuit potential of 0.49 V is observed due to the over potentials on the cathode and anode<sup>7</sup>. This run in the acidic anode, alkaline cathode configuration is still limited by borohydride hydrolysis in the presence of acidic condition causes the anode potential to drop<sup>12,13</sup>.



### Performance of in mixed media-2: (alkaline anode, acidic cathode)

In contrast, in mixed media configuration-2, use of an alkaline anode stream (Eq. (5)) and an acidic cathode stream (Eq. (3)) allows energy to be obtained both from the borohydride oxidation/percarbonate reduction reactions as evident from the overall cell reaction (Eq. (9)). The coupling of two galvanic reactions in this configuration yields a desirable high theoretical OCP of 3.02 V than  $\text{H}_2/\text{O}_2$  and  $\text{CH}_3\text{OH}/\text{O}_2$  fuel cells that have equilibrium voltages 1.24 and 1.21 V respectively<sup>14</sup>.



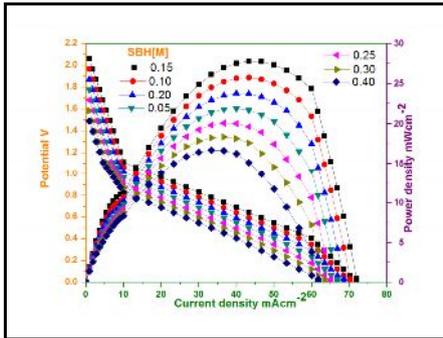
Operating in this mixed media configuration, with an alkaline anode, acidic cathode, resulted in higher overall cell potential than those obtained for the all-alkaline, all acidic and mixed media-1 experiments. For example, the mixed-media configuration-2 provides a potential of 2.06 V, whereas both the all-acidic, mixed media configuration-1 cells already start from a lower OCP, and thus have current density that are significantly lower than those of the mixed media configuration-2

On first sight, the higher power densities of the mixed media configuration-2 fuel cells may look very promising. Due to the higher power densities and higher cell potential of the mixed media-2 are taken to investigate the further tests namely, effect of fuel and oxidant concentration, flow rate variation, electrode distance effect and cell stability.

### Influence of fuel concentration

Increasing  $\text{NaBH}_4$  concentration, the fuel diffusion and the oxidation kinetics would be improved, which leads to higher power density, however, borohydride hydrolysis will also increase and results in open circuit voltage decrease in turn. So there will be optimized  $\text{NaBH}_4$  concentration for better cell performance. The effect of the used sodium borohydride amount on the performance of the assembled laboratory has been observed by varying the  $\text{NaBH}_4$  concentration between 0.05 and 0.4 M in 3 M NaOH.

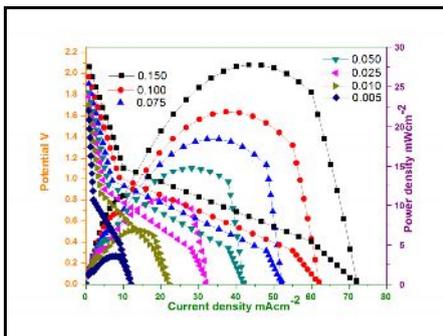
The cell polarization and power density curves in fig. 3 indicate the corresponding X and Y axes. When the  $\text{NaBH}_4$  concentration changes, the cell OCP keeps practically in the range of 2.06-1.49 V, the current density acquires in the 72.04-61.74 mAcm<sup>-2</sup> for 0.15 M  $\text{NaBH}_4$ . From a cost-effective perspective, the 0.15 M  $\text{NaBH}_4$  concentration seems the best composition for the fuel.



**Fig. 3.**Curves of cell polarization and power density for at different fuel Concentration: Fuel: X M in 3 M NaOH. Oxidant: 0.15 M percarbonate in 1.5 M H<sub>2</sub>SO<sub>4</sub> solutions. Flow rate of the reactants: 0.3ml min<sup>-1</sup>.

**Effect of oxidant composition**

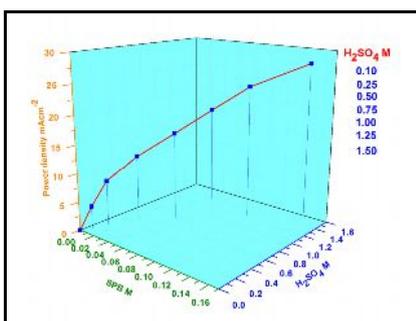
For the liquid cathode reactant, increasing percarbonate concentration, potential will increase according to the electrode reaction. Fig. 4 shows the influence of percarbonate concentration on the cell performance. The cell voltage-current density polarization are completely differ from fig.3, i.e. nearly linear decreasing of cell potential with the increasing of current density. The cell performance is improved with increasing percarbonate concentration from 0.010 to 0.15 M in 1.5 M H<sub>2</sub>SO<sub>4</sub>.However, further increase in perborate concentration no change in cell performance. The peak power density is high as 27.75 mWcm<sup>-2</sup>, at 0.64 V and 43.37 mAcm<sup>-2</sup> for 0.15 M percarbonate.



**Fig. 4.**Curves of cell polarization and power density for at different oxidant Concentration: Oxidant: X M Percarbonate in 1.5 M H<sub>2</sub>SO<sub>4</sub>. Fuel: 0.15 M NaBH<sub>4</sub> in 3 M NaOH solutions. Flow rate of the reactants: 0.3ml min<sup>-1</sup>.

**Variation of electrolyte concentrations**

The performance of the oxidant is dependent on electrolyte concentration. Fig. 5 shows that the power density of the fuel cell increase when the H<sub>2</sub>SO<sub>4</sub> concentration increases from 0.10-1.5 M and in further increase sulphuric acid concentration the cell performance decreased. Therefore, 1.5 M sulphuric acid fixed for the oxidant solution.



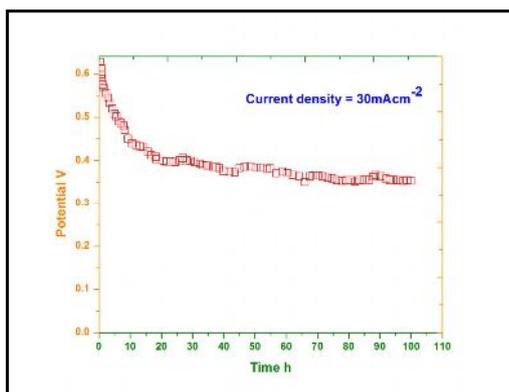
**Fig. 5.**Effect of various combinations of perborate and sulphuric acid concentrations on the maximum power density (27.75 mW cm<sup>-2</sup>) of the at room temperature. The fuel mixture for variation of oxidant is ([fuel]: 0.15M sodium borohydride + 3 M NaOH, [oxidant]: X M percarbonate + 1.5 M H<sub>2</sub>SO<sub>4</sub>) and the

**fuel mixture for variation of sulphuric acid is ([fuel]: 0.15 M sodium percarbonate + 3 M NaOH, [oxidant]: 0.15 M percarbonate + x M H<sub>2</sub>SO<sub>4</sub>). Stream flow rates: 0.3 mL min<sup>-1</sup>.**

Alkali concentration in anolyte also affects the fuel cell performance. Increasing NaOH concentration up to 3 M has been found to be beneficial for performance in terms of enhanced OCP, power density, and sustained current density beyond which a negative effect is observed. Increasing NaOH concentration has negative effects of improving anode reaction, increasing the conductivity of the sodium hydroxide solution and reducing possible borohydride hydrolysis<sup>15, 16</sup>. Yet, increased NaOH concentration has negative effect to cathode reaction and also leads to an increase in solution viscosity which decreases the movability of borohydride ions and sodium ions in the catalyst layer<sup>17-19</sup>. Increase in NaOH concentration also results in the formation of sodium carbonate in the presence of atmospheric CO<sub>2</sub>

### Cell stability study

Performance stability of the fuel cell was tested by applying constant current densities and in the absence of current flow. Short-term stability of was tested by monitoring the cell voltage change during the galvanostatic discharge of the in a period of about 100 h. an example is shown in fig. 8, where the fluctuation in the cell voltage was due to addition of the solutions or restarting the experiments after an overnight break. The maintained a relatively stable performance with a little decay of cell voltage over the test period. The reasons for the deterioration were presumably due to changes in the catalyst surface area, supplies of the fuel and the oxidant as well as the removal of the product etc.



**Fig. 8. Performance stability of the operating at current density of 30 mA cm<sup>-2</sup> at room temperature. [Fuel]: 0.15 M sodium borohydride + 3 M NaOH. [Oxidant]: 0.15 M percarbonate + 1.5 M H<sub>2</sub>SO<sub>4</sub>. Stream flow rates: 0.3 mL min<sup>-1</sup>.**

### Conclusion

In this work, we observed that the alkaline anode/ acidic cathode alkaline-acidic media leads to a very high measured OCP of 2.06 V, while other combinations will result in very low OCPs as a result of the pH dependence of standard electrode potentials. The operated in the alkaline anode/ acidic cathode alkaline-acidic media 2, the measured OCP of 2.06 V is in good agreement with the theoretical OCP of 3.02 V.

This work demonstrated the performance of an alkaline sodium borohydride anode coupled with an acidic perborate cathode in a microfluidic fuel cell. At room temperature, the laminar flow based microfluidic fuel cell produced a maximum power density of 27.75 mW cm<sup>-2</sup>. In the fuel cell power density increased with increase of per carbonate concentration at 0.15 M above this concentration decrease the cell performance. While a variation of concentration for sodium borohydride at the anode produced only a small influence on the cell performance.

The results demonstrated that the performance of the developed membraneless fuel cell enhanced profoundly if the concentration of oxidant in cathodic stream is 10 times larger, and the current density is also increased approximately ten times.

The has the advantages of their miniature sizes, simplicity of fabrication, use of aqueous fuel, and good cost efficiency. Furthermore, percarbonate is a cheap, nontoxic, stable, easily handled, environmental friendly,

large-scale industrial chemical and is a convenient source of hydrogen peroxide. We expect that the may be a promising candidate for practical fuel cells to establish a clean and sustainable energy future.

## References

1. de Jong J, Lammertink R.G.H, Wessling M, Membraneless and microfluidic: a review, Lab on a chip., 2006, 6: 1125-1139.
2. Kjeang E, Djilali N, Sinton D., Microfluidic fuel cells; A review, J. Power Sources., 2009, 186 :353-369.
3. Mousavi Shaegh S.A, Nguyen N.-T, Chan S.H., Air-breathing membraneless laminar flow-based fuel cell with flow-through anode, Int. J. Hydrogen Energy., 37 3466-3476.
4. S.F.J. Flipsen, Power sources compared; The ultimate truth?, J. Power Sources, 162 (2006) 927-934.
5. C.K. Dyer, Fuel cell for portable applications, J. Power Sources, 106, (2002) 31-34. [6] J.C. McDonald, D.C. Duffy, J.R. Anderson, D.T. Chiu, H.K. Wu, O.J.A. Schueller, G.M. Whitesides," Fabrication of microfluidic systems in poly(dimethyl siloxane), Electrophoresis, 21, 2000,27-40.
6. Demerci U.B., Direct liquid-feed fuel cells: Thermodynamics and environmental concerns, J. Power Sources., 2007, 169: 239-246.
7. Santos D.M.F, Sequeira C.A.C., On the electrosynthesis of sodium borohydride, Int. J. Hydrogen energy., 2010, 35 :9851-9861.
8. Gowdhamamoorthi M, Arun A, Kiruthika S, Muthukumar B., Enhanced performance of membraneless fuel cells, Int.J.ChemTech Res., 2013, 5:1143-1151.
9. You S. J, Zhao Q.L, Zhang J.N, Jiang J.Q, Zhao S.Q., A microbial fuel cell using permanganate as the cathodic electron acceptor, J. Power Sources., 2006, 16 :1409-1415.
10. Cotton F.A, Wilkison G., Advanced Inorganic Chemistry. Wiley Interscience, New York. 1988, 812.
11. Karunakaran C, Muthukumar B., Molybdenum(VI) catalysis of perborate or hydrogen peroxide oxidation of iodide ion, Transition Met Chem., 1995, 20 460-462.
12. Kabalka G.W, Shaup T.M, Goudgaon N.M., Sodium perborate: a mild and convenient reagent for efficiently oxidizing organoboranes, J.org. chem., 1989, 54:5930-5933.
13. Gowdhamamoorthi M, Arun A, Kiruthika S, Muthukumar B., Enhanced performance of membraneless fuel cells, J. Materials., 2013, 7.
14. Lifengu Gu, Nie Luo, George H. Miley., Cathode electrocatalyst selection and deposition for a direct borohydride/hydrogen peroxide fuel cell, J. Power Sources., 2007, 173 :77-85.
15. Jia Ma, Yogeshwar Sahai, Rudolph Buchheit G., Direct borohydride fuel cell using Ni-based composite anodes, J. Power Sources., 2010, 195: 4709-4713.
16. de Leon C.P, Walsh F.C, Pletcher D, Browning D.J, Lakeman J.B., Direct borohydride fuel cells, J. Power sources., 2006, 155:172-181.
17. Wee J.H., Which type of fuel cell is more competitive for pportable application: direct methanol fuel cells or direct borohydride fuel cells, J. Power Sources., 2006, 161:1-10.
18. Cheng H, Scott K., influence of operating conditions on direct borohydride fuel cell performance, J. Power Sources., 2006, 160:407-412.
19. Duteanu N, Vlachogiannopoulos G, Shivhare M.R, Yu E.H, Scott K., A parametric study of a platinum ruthenium anode in a direct borohydride fuel cell, J. Appl. Electrochem., 2007, 37:1085-1091.

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