



A High Output Voltage Direct Borohydride Fuel Cell

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A direct borohydride fuel cell (DBFC) employing hydrogen peroxide as oxidant with a power density of about 350 mW cm⁻² at the cell voltage of almost 1.2 V at 70°C is reported. The use of liquid reactants in DBFCs not only simplifies the engineering problems at the front end of the fuel cell, driving down complexity and hence cost, but operating a DBFC with an oxidant such as hydrogen peroxide also extends the operational environment for fuel cells to locations where free convection of air is limited, e.g., underwater applications.

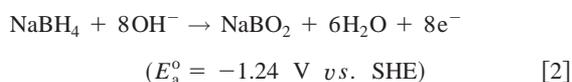
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Polymer electrolyte fuel cells (PEFCs) have advanced substantially but their successful commercialization is restricted owing to carbon monoxide poisoning of the anode while using a reformer with the PEFC, and hydrogen storage while using a directly-fueled PEFC.¹⁻⁵ Therefore, certain hydrogen-carrying organic liquid-fuels, such as methanol, ethanol, propanol, ethylene glycol, and diethyl ether, have been considered for fuelling PEFCs directly.⁶ Among these, methanol, with a capacity value of 5.06 Ah/g and a hydrogen content of 12.8 wt %, is undisputedly the most attractive organic-liquid fuel at present for directly-fueled PEFCs. Such fuel cells are referred to as direct methanol fuel cells (DMFCs).⁷⁻⁹ But DMFCs have limitations of low open-circuit-potential, low electrochemical-activity, and methanol crossover.^{4,10}

An obvious solution to the aforesaid scientific problems is to explore other promising hydrogen-carrying liquid fuels such as sodium borohydride,¹¹⁻¹⁸ which has a capacity value of 5.67 Ah/g and a hydrogen content of about 11 wt %. Amendola *et al.*^{14,15} were the first to propose an OH⁻-ion conducting anion exchange membrane-based borohydride-air fuel cell with a power density close to 60 mW cm⁻² at 70°C. However, the borohydride-air fuel cell due to Amendola *et al.*^{14,15} suffers from borohydride crossover as the BH₄⁻-ions can permeate through the anion exchange membrane. In addition, it would be mandatory to scrub CO₂ from air inlet of such a fuel cell to avoid carbonate fouling. Suda *et al.*¹⁶⁻¹⁹ mitigated the BH₄⁻ crossover problem by adopting a fuel cell structure using Nafion membrane as electrolyte to separate the fuel from the cathode and were able to achieve a power density as high as 160 mW cm⁻² at 70°C with such a fuel cell. But even in the borohydride-air fuel cell proposed by Suda *et al.*,¹⁶⁻¹⁹ it would be mandatory to scrub CO₂ from air both to avoid carbonate fouling as well as to prevent accumulation of alkali in the cathode pores to facilitate oxidant flux.

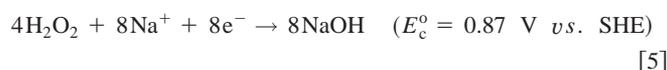
In this paper, we report a DBFC using hydrogen peroxide as oxidant with a power density of about 350 mW cm⁻² at a cell voltage of almost 1.2 V at 70°C.²⁰ In this fuel cell, sodium borohydride is oxidized at its anode according to



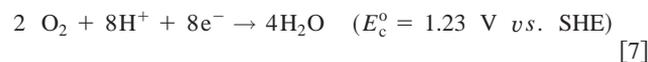
At the cathode of this DBFC, hydrogen peroxide is decomposed into oxygen and water at the catalyst/electrode interface²¹ according to



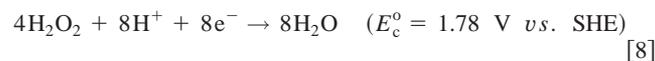
Electroreduction of hydrogen peroxide is also highly likely according to



As the pH of the H₂O₂ solution in the catholyte converges to 0, two reactions could take place: (a) decomposition of H₂O₂ to O₂ followed by its reduction as



and (b) electrochemical decomposition of H₂O₂ as



The variation in O₂ and H₂O₂ reduction potentials with pH is accordingly governed both by

$$E(\text{O}_2) = 1.23 - 0.059 \text{ pH} \quad [9]$$

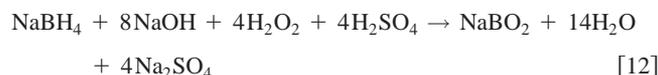
and

$$E(\text{H}_2\text{O}_2) = 1.78 - 0.059 \text{ pH} \quad [10]$$

The net cell reaction in such a DBFC shifts from



to



depending on the pH of H₂O₂ solution in the catholyte with the cell potential ranging between 1.64 and 3.02 V.

Experimental

Similar to Suda *et al.*,¹⁶⁻¹⁹ we have also used a Nafion membrane to separate anode and cathode compartments of the fuel cell while employing an AB₅-group MmNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75} alloy, where Mm stands for Misch metal comprising La-30 wt %, Ce-50 wt %, Nd-15 wt %, Pr-5 wt %, as the anode material. In the literature,²²⁻²⁷ both AB₂ and AB₅-group alloys have been successfully employed as negative electrodes in nickel-metal hydride batteries. Although AB₂-group alloys yield superior energy storage density,²⁶ the AB₅-group alloys have higher hydrogen retention capacity.²²⁻²⁵

MmNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75} alloy was prepared by arc melting stoichiometric amounts of the constituent metals in a water-cooled copper crucible under argon atmosphere.²²⁻²⁵ The alloy ingot was mechanically pulverized to a fine powder, which was characterized by

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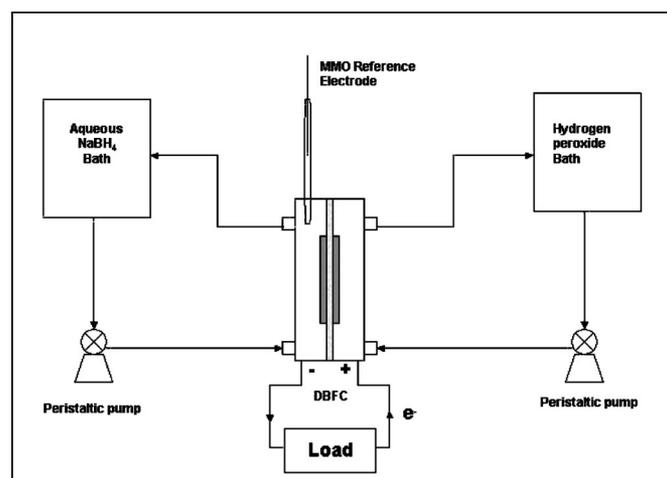


Figure 1. Schematic representation of the DBFC.

recording its powder X-ray diffraction (XRD) pattern on a Siemens D-5005 X-ray Diffractometer using $\text{Cu K}\alpha$ radiation. The alloy was also subjected to energy dispersive analysis by X-ray (EDAX) employing a JEOL JSM-840A scanning electron microscope (SEM) to determine the composition of its constituent elements.

The sulfite-complex route²⁸⁻³¹ was adopted to prepare 60 wt % platinized carbon. In brief, the required amount of Vulcan-XC 72R carbon was suspended in distilled water and agitated in an ultrasonic water bath at about 80°C to form a slurry. Subsequently, the required amount of $\text{Na}_6\text{Pt}(\text{SO}_3)_4$ was dissolved in 1 M H_2SO_4 and diluted with distilled water, and the solution was added dropwise to the carbon slurry with constant stirring at 80°C. This was followed by the addition of 30% w/v H_2O_2 with the temperature maintained at 80°C, which resulted in vigorous gas evolution. The solution was further stirred for 1 h, and platinized carbon was obtained by adding 1 wt % formic acid solution. Then the platinized carbon was filtered, washed copiously with hot distilled water, and dried in an air oven at 80°C for 2 h.

For the electrochemical characterization of the direct borohydride fuel cell, membrane electrode assemblies (MEAs) were obtained by sandwiching the pretreated Nafion 117 polymer electrolyte

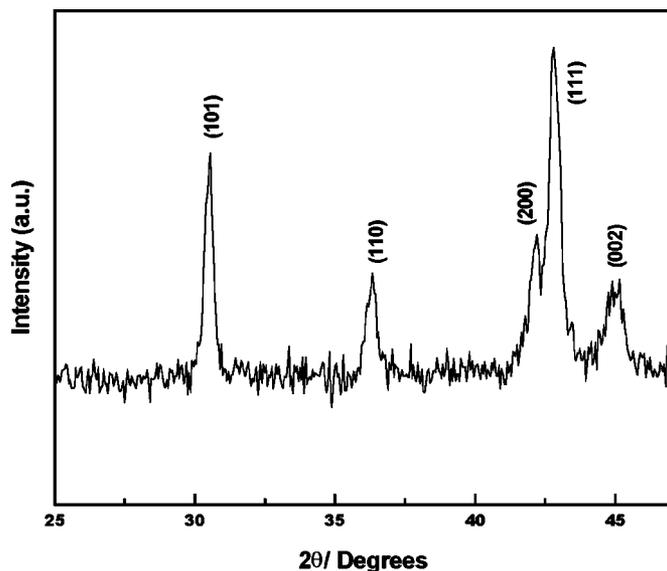


Figure 2. Powder XRD patterns for AB_5 -group $\text{MmNi}_{3.55}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.75}$ alloy.

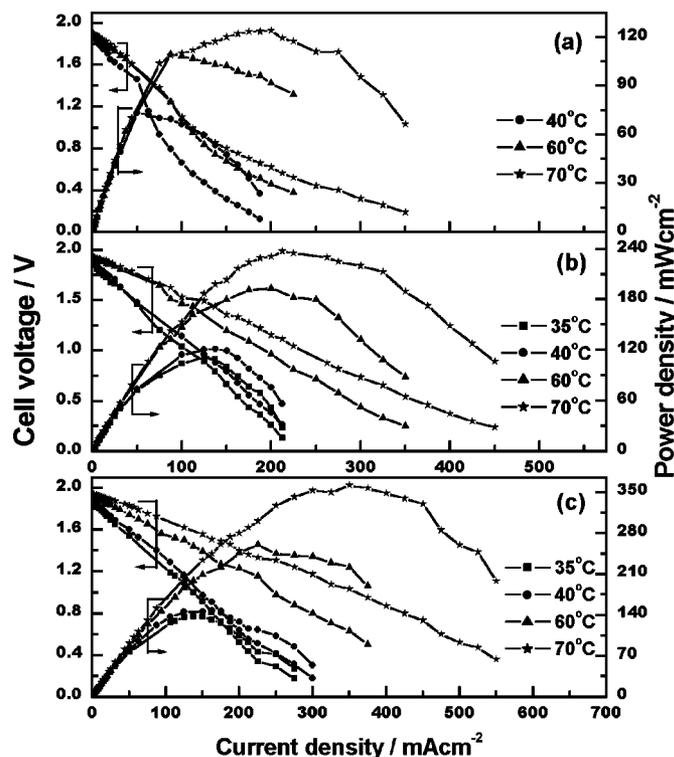


Figure 3. Cell polarization data for the DBFC operating at temperatures between 35 and 70°C with optimized solution of aq. NaBH_4 at anode and 15% w/v H_2O_2 solution of (a) pH \sim 1, (b) pH \sim 0.5, and (c) pH \sim 0 at cathode.

membrane between the anode and cathode. To prepare the anode catalyst layer, a slurry of the alloy obtained by ultrasonication the required amount of alloy with 5 wt % Vulcan XC-72R carbon and 7 wt % of Nafion solution in isopropyl alcohol was pasted on 0.28 mm thick carbon paper (Toray TGP-H-090). The loading of the alloy catalyst was 5 mg cm^{-2} , which was kept identical for all the MEAs. The cathode comprises a backing layer, a gas-diffusion layer, and a reaction layer. A 0.28 mm thick carbon paper (Toray TGP-H-090) was employed as the backing layer for the cathode. To prepare the gas-diffusion layer, Vulcan-XC 72R carbon was suspended in water and agitated in an ultrasonic water bath. To this, 10 wt % Nafion solution obtained from Aldrich was added with continuous agitation. The required amount of cyclohexane was then added to it dropwise. The resultant slurry was spread onto a Teflonized carbon paper and dried in an air oven at 80°C for 2 h. To prepare the reaction layer, the required amount of the catalyst (60 wt % Pt/C) was suspended in isopropyl alcohol. The mixture was agitated in an ultrasonic water bath, and 7 wt % of Nafion solution was added to it with continuing agitation for 1 h. The catalyst ink thus obtained was coated onto the gas-diffusion layer of the electrode. The cathode contained 60 wt % Pt/C catalyst with platinum loading of 1 mg cm^{-2} . A Nafion loading of 0.25 mg cm^{-2} was applied to the surface of each electrode. The membrane electrode assembly was obtained by hot pressing the cathode and anode on either side of a pretreated Nafion 117 membrane at 60 kg cm^{-2} at 125°C for 3 min.

Liquid-feed DBFCs were assembled with various MEAs. The anode and cathode of the MEA were contacted on their rear with gas/fluid flow field plates machined from high-density graphite blocks in which channels were machined to achieve minimum mass-polarization in the DBFCs. The ridges between the channels make electrical contact with the back of the electrode and conduct the current to the external circuit. The channels supply alkaline sodium borohydride solution to the anode and hydrogen peroxide to the cathode. Electrical heaters were placed behind each of the graphite

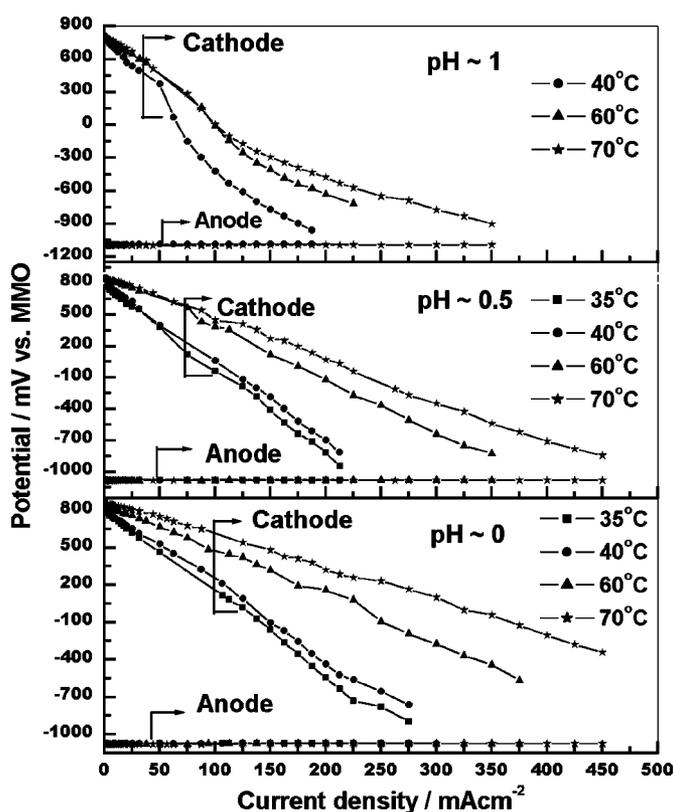


Figure 4. Anode and cathode polarization data for the DBFC operating with optimized aq. NaBH_4 and H_2O_2 solution at different pH values at temperatures between 35 and 70°C .

blocks to heat the cell to the desired temperature. Aqueous sodium borohydride solution comprising 10 wt % NaBH_4 in 20 wt % aqueous NaOH was pumped to the anode chamber through a peristaltic pump. Hydrogen peroxide 15% w/v solution with varying pH was introduced into the cathode chamber through another peristaltic pump. The graphite blocks were also provided with electrical contacts and tiny holes to accommodate thermocouples. The DBFC is shown schematically in Fig. 1. After installing single cells in the test station, performance evaluation studies were initiated.

Galvanostatic-polarization data for the DBFC in the temperature range between 35 and 70°C were recorded by circulating aqueous sodium borohydride solution in the anode chamber, and 15% w/v hydrogen peroxide solution acidified with aq. H_2SO_4 to pH values ranging between 1 and 0 in the cathode chamber. Anode polarization data for the DBFC at various temperatures were also obtained employing an Hg/HgO , OH^- (MMO) reference electrode. Cathode polarization data were derived by subtracting anode polarization values from the respective cell polarization data at various load current-densities;³² in-cell cathode polarization data have also been obtained to ascertain the technique of anode polarization subtraction. Cyclic voltammograms (CVs) for the cathode at varying pH values of the catholyte were also obtained at 35°C .

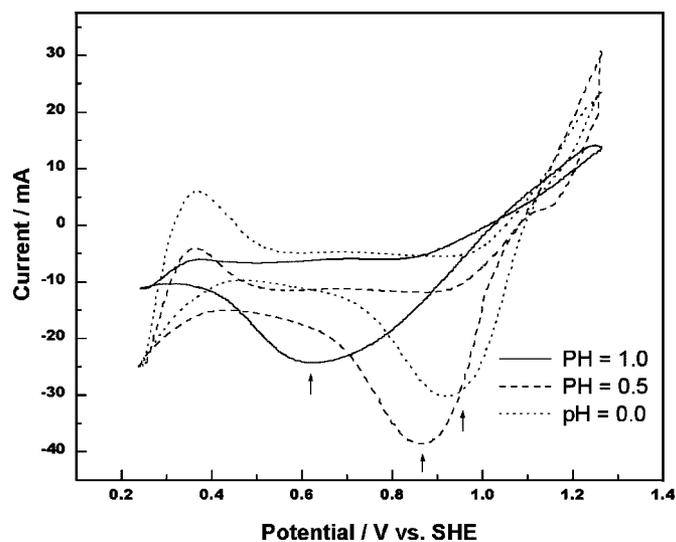


Figure 5. CVs for peroxide reduction at 35°C . The positive shift in reduction peak with decreasing pH is indicated by arrow.

To determine the faradaic efficiency of oxidation, an alkaline solution containing 1.26×10^{-3} mol of sodium borohydride was injected into the anode chamber of the fuel cell. Subsequently, the cell was operated for 60 min at a load current density of 50 mA cm^{-2} at 70°C . The amount of hydrogen liberated during this experiment was obtained by collecting it at the anode outlet by downward displacement of water in a graduated tube. The amount of sodium borohydride left in the anolyte was determined by collecting hydrogen gas evolved upon acidification to ascertain mass balance of the reaction.³³

Results and Discussion

The powder XRD pattern (Fig. 2) for the AB₅-group alloy of composition $\text{MmNi}_{3.55}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.75}$ suggests that it crystallizes in hexagonal $P6/mmm$ space group with lattice parameters $a = 4.99 \text{ \AA}$ and $c = 4 \text{ \AA}$.^{19,21-24} The average particle size of the alloy sample was $\sim 60 \mu\text{m}$. The composition of the alloy $\text{MmNi}_{3.55}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.75}$ as determined employing EDAX was $\text{Mm}_{0.76}\text{Ni}_{3.71}\text{Al}_{0.34}\text{Mn}_{0.32}\text{Co}_{0.71}$.

The anode was fed with aqueous NaBH_4 solution at a feed rate of 3 mL/min, and the cathode was fed with 15% w/v H_2O_2 solution with pH values close to 1, 0.5, and 0 at a feed rate of 5.5 mL/min to the cathode. Notably, the borohydride-crossover concentrations in DBFCs are much lower as compared to methanol-crossover concentrations reported for DMFCs.^{34,35} The cell performance data at various temperatures with varying pH values of H_2O_2 solution are shown in Fig. 3a-c. Single-electrode polarization curves at various temperatures for catholyte with varying pH values are shown in Fig. 4. From the CV of the cathode obtained at varying pH values of the catholyte shown in Fig. 5, it is evident that the oxygen reduction reaction is more facile at pH 1 but shifts toward peroxide reduction as the catholyte pH is decreased to 0. While the anode potentials are

Table I. Electrical performance data for the DBFC.

Catholyte PH	Peak power density (mW cm^{-2}) at different temperatures				Cell voltage (V) at peak power density at different temperatures			
	35°C	40°C	60°C	70°C	35°C	40°C	60°C	70°C
~1	-	70	110	130	-	1.5	1.2	0.7
~0.5	112	122	194	236	0.90	0.89	0.98	1.1
~0	136	146	260	352	1.0	0.98	1.2	1.2

close to its thermodynamic value, the cathode shows substantial polarization losses rendering the DBFC cathode limited.

A summary of the performance data for the DBFCs studied is presented in Table I. It has been possible to attain a maximum power density of about 120 and 350 mW cm⁻² while operating such a DBFC employing hydrogen peroxide solution as oxidant with near zero pH at 35 and 70°C, respectively. The faradaic efficiency of oxidation in the DBFC at 70°C was estimated to be 83%, and the rate of hydrogen evolved at the anode was measured to be 2×10^{-7} mol s⁻¹. By contrast, the rate of oxygen evolution was dependent on the pH of the catholyte as also the temperature of the cell. For example, while keeping catholyte pH 0.5 and cell temperature at 70°C, the rate of the oxygen evolution was 5.9×10^{-6} mol s⁻¹. The operational conditions for the DBFC, however, are not yet fully optimized, and a further enhancement in its performance is highly likely.

Conclusions

In the future, as it becomes possible to realize an effective cathode catalyst for H₂O₂ reduction, it would be feasible to produce DBFCs with voltages near 3 V, which is close to the voltages achieved with any of the advanced lithium cells. The specific energy of such a fuel cell will be as high as about 17 kWh/kg. Accordingly, such a fuel cell with its high output voltage would provide a pragmatic gateway to solve the most challenging problem associated with the currently available batteries, namely, their limited energy density.

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