



Short communication

Direct borohydride fuel cell using Ni-based composite anodes

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ARTICLE INFO

Article history:

Received 4 December 2009
 Received in revised form 12 February 2010
 Accepted 12 February 2010
 Available online 20 February 2010

Keywords:

Fuel cell
 Direct borohydride fuel cell
 Nickel-based composite
 Oxygen
 Hydrogen peroxide
 Cell performance

ABSTRACT

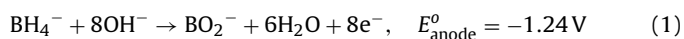
In this study, nickel-based composite anode catalysts consisting of Ni with either Pd on carbon or Pt on carbon (the ratio of Ni:Pd or Ni:Pt being 25:1) were prepared for use in direct borohydride fuel cells (DBFCs). Cathode catalysts used were 1 mg cm^{-2} Pt/C or Pd electrodeposited on activated carbon cloth. The oxidants were oxygen, oxygen in air, or acidified hydrogen peroxide. Alkaline solution of sodium borohydride was used as fuel in the cell. High power performance has been achieved by DBFC using non-precious metal, Ni-based composite anodes with relatively low anodic loading (e.g., 270 mW cm^{-2} for NaBH_4/O_2 fuel cell at 60°C , 665 mW cm^{-2} for $\text{NaBH}_4/\text{H}_2\text{O}_2$ fuel cell at 60°C). Effects of temperature, oxidant, and anode catalyst loading on the DBFC performance were investigated. The cell was operated for about 100 h and its performance stability was recorded.

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1. Introduction

A direct borohydride fuel cell (DBFC) is a device that converts chemical energy stored in a borohydride ion (BH_4^-) and an oxidant directly into electricity by redox processes. Usually, a DBFC employs an alkaline solution of sodium borohydride (NaBH_4) as fuel and oxygen or hydrogen peroxide as oxidant. DBFCs are considered attractive energy suppliers, especially for portable applications. DBFC supersedes direct methanol fuel cell (DMFC) in terms of capacity value, electrochemical activity, theoretical open circuit voltage, and power performance at ambient temperature. In addition, DBFCs use alkaline solution as the fuel which has relatively low corrosion activity, and therefore it is possible to apply readily available and low-cost non-precious metal anode catalysts. Besides oxygen, hydrogen peroxide can also be used as the oxidant in DBFCs. Thus, it becomes a very useful fuel cell for air deficient operations, such as in submarine or space applications. Another advantage of DBFC is that it is good for the environment as it does not involve carbon and its oxides in any reaction.

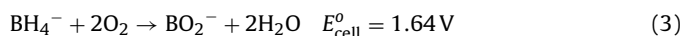
The anode reaction of the DBFC is the direct oxidation of borohydride in alkaline medium:



The cathode reaction with oxygen as the oxidant is written as:

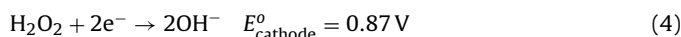


When oxygen is employed as the oxidant at the cathode, the overall fuel cell reaction is:

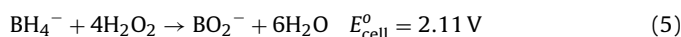


The theoretical cell voltage is 1.64 V.

Unlike DMFCs, H_2O_2 is a suitable oxidant in DBFCs [1]. The reduction reaction at the cathode with hydrogen peroxide is:



The overall cell reaction for DBFC using H_2O_2 as oxidant is expressed as Eq. (5)



The benefits of using hydrogen peroxide as an oxidant in DBFC in terms of theoretical and practical aspects have been discussed in the literature [2–4].

Pt is an extensively used electrocatalyst for oxygen reduction. For hydrogen peroxide reduction, Pt, Au, Pd, Ag, Pd/Ir, Pd–Ru, and Pd–Ag are studied as cathode catalyst materials in metal semi-fuel cells and direct borohydride fuel cells [5–10]. Both Au and Pd based cathode catalysts have shown to give good performance for direct borohydride hydrogen peroxide fuel cells [3,4].

The types of anode catalysts examined in direct borohydride fuel cells include noble metals (Pd, Pt, Au, Os, Ag, and Ru), transition metals (Ni and Cu), and hydrogen storage alloys (AB_5 - and AB_2 -type). Electro-catalysts, such as Ni, Pt, and Pd have good catalytic activity towards both the electrochemical oxidation reaction and the hydrolysis reaction [11–13]. Therefore, DBFCs using these metals as anode catalysts give high power performance but have

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low fuel efficiencies, e.g., 50% for nickel [11] and 75% palladium [12]. Higher fuel efficiencies can be achieved on Pd and Pt electrodes at low BH_4^- concentrations and high anode currents [12]. Gold can catalyze the complete $8e^-$ oxidation of BH_4^- , but has relatively low electrochemical activity. Many researchers are engaged in developing anode made of composite materials, bimetallic and multimetallic materials to take advantage of the merits of each component of the catalyst material and thus hopefully show performance improvement. Among the non-precious metals, nickel has received a lot of attention as catalyst for electrooxidation of BH_4^- . High performance has been achieved by DBFCs using Ni-based composite catalysts loaded on nickel foam as the anode [14]. It has been pointed out that nickel foam may have non-negligible catalytic contributions in both borohydride electro-oxidation and hydrolysis [15].

In this present work, anodes are made by pasting a Ni-based composite catalyst on the commonly used carbon paper substrate. Different oxidants (oxygen, air, or hydrogen peroxide) are used in DBFCs using nickel based composite anode and different cathodes. Cell performance and performance stability of the DBFC are investigated.

2. Experimental

The anode catalysts were mixtures of nickel powder (INCO, Inc., type 210), carbon-supported palladium powders (10% Pd on Vulcan XC-72, BASF Fuel Cell, Inc.) or carbon supported platinum powders (10% Pt on Vulcan XC-72, BASF Fuel Cell, Inc.). The amount of Pd or Pt in the composite was relatively small, the ratio of Ni:Pt or Ni:Pt being 25:1. The anode catalyst was mixed with Nafion[®] solution (5 wt%, Ion Power, Inc.) and iso-propyl alcohol and was ultrasonicated to form anodic slurry which was then applied to a carbon paper (EC-TP1-060, Electrochem, Inc.) and dried in oven at 80 °C. The amount of Nafion[®] ionmer amounted to 15 wt% of the dry catalyst material.

Different cathodes were used in these experiments. The first was a simple commercially available cathode (ElectroChem, Inc.) with a catalyst loading of Pt 1 mg cm^{-2} (the catalyst was Pt 20 wt% on Vulcan XC-72). Nafion[®] solution (5 wt%, Ion Power, Inc.) was brushed on the Pt electrode surface which was then dried in oven at 80 °C. Cathodes were also prepared by electrodeposition methods. Palladium was electrodeposited on the Zorflex activated carbon cloth with surface area of 1000–2000 $\text{m}^2 \text{g}^{-1}$. The electrodeposition process was performed in a palladium electroplating bath (Pallaspeed VHS solution with 30 g/gallon, Technic, Inc.) by applying constant voltage with a Keithley sourcemeter at room temperature. Platinum wire was used as the counter electrode. After deposition, the carbon cloth was rinsed with deionized (DI) water and dried in air before Nafion[®] solution was applied.

Nafion[®] 212 membrane was used as the electrolyte membrane. It was boiled in aqueous solution of 3 wt% H_2O_2 and 3 wt% H_2SO_4 for 1 h and then boiled in DI water for 1 h. After the pretreatment, membrane was activated in 6N NaOH followed by another rinse by DI water before assembly. To prepare the membrane electrode assemblies (MEAs), the activated Nafion[®] membrane was held together between two electrodes by mechanical force. Fuel cell tests were performed using a single fuel cell. The flow plates of both anodes and cathodes were two 76.2 × 76.2 mm graphite blocks. Each graphite block had 5 cm^2 square flow area with rectangular channels of 0.8 mm width and 1 mm depth. The cell performance and stability data were obtained using Scribner Associates fuel cell test system (Series 890e, Scribner Associates, Inc., USA). The performance stability of the DBFC was evaluated by monitoring cell voltages as a function of time at a constant load current density.

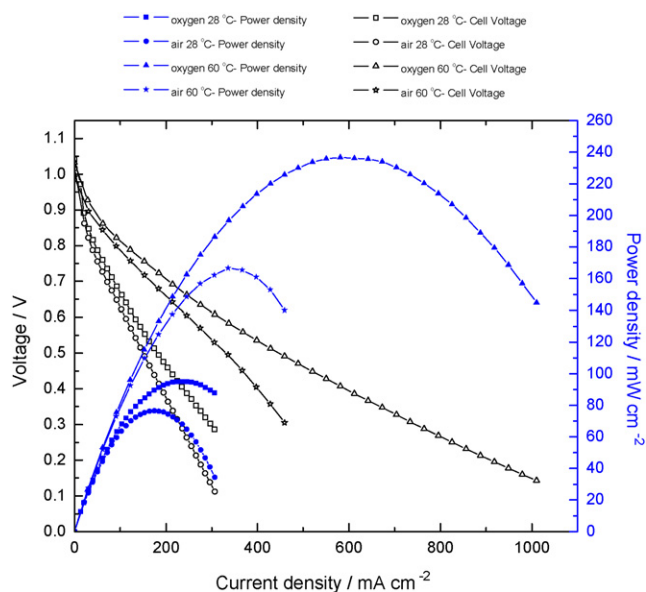


Fig. 1. Curves of cell polarization and power density of DBFC using oxygen and air at different temperatures. Anode: Ni + Pd/C, 1 mg metal cm^{-2} . Flow rate of the fuel: 5 mL min^{-1} . Fuel: 5% NaBH_4 + 10% NaOH. Cathode: 1 mg Pt cm^{-2} . Flow rate of the oxidant: 0.15 L min^{-1} .

The fuel was 5 wt% NaBH_4 and 10 wt% NaOH aqueous solution or 10 wt% NaBH_4 and 20 wt% NaOH aqueous solution. The fuel was recirculated through the anode chamber with a peristaltic pump. The anode flow rate was 5 mL min^{-1} . The oxidants used were oxygen, air, or acidified hydrogen peroxide (2.0 M H_2O_2 and 1.5 M H_2SO_4). The cathode gas flow rate was 0.15 L min^{-1} . The cathode gas was humidified by passing through a bubbler at room temperature. The hydrogen peroxide was recirculated through the cathode chamber with a peristaltic pump at a flow rate of 5 mL min^{-1} .

3. Results and discussion

3.1. DBFCs using Ni + Pd/C composite anode

3.1.1. Effect of temperature and oxidant conditions

A borohydride fuel cell, as described in the earlier section consisting of Nafion[®] 212 membrane electrolyte, Ni + Pd/C composite anode, and 1 mg cm^{-2} Pt/C cathode was assembled and tested. The fuel was 5 wt% NaBH_4 and 10 wt% NaOH aqueous solution, and its flow rate was 5 mL min^{-1} . The oxidant was humidified oxygen or oxygen in humidified air with flow rate of 0.15 L min^{-1} . Fig. 1 shows cell polarization and power density of the cell at 28 °C and 60 °C. As seen, the power densities increased by increasing the temperature. Peak power densities of 77 mW cm^{-2} and 167 mW cm^{-2} were achieved using humidified air at 28 °C and 60 °C, respectively. Major advantages of temperature elevation include: (1) improvement of diffusion and mass transfer of the reactants; (2) improvement of kinetics of both borohydride electrooxidation and oxidation reduction reaction; (3) enhancement of ionic conductivity of both anolyte and catholyte. All these factors result in increased power and sustained current density of DBFC. To the contrary, increase in temperature also results in an increase in the crossover rate and hydrolysis of BH_4^- , which results in a decrease of fuel utilization efficiency and affects the electro-catalytic activity of the cathode that is manifested in a decrease of OCV of the DBFC.

Better performance was obtained by using oxygen, compared to air under the same conditions. Peak power densities of 95 mW cm^{-2}

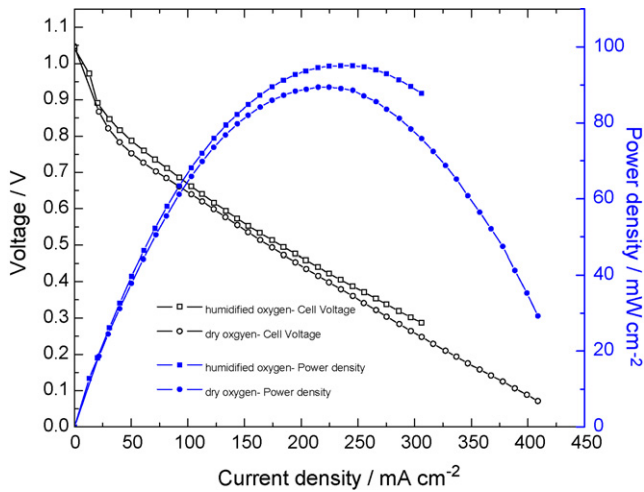


Fig. 2. Curves of cell polarization and power density of DBFC using dry oxygen and humidified oxygen at 28 °C. Anode: Ni + Pd/C, 1 mg metal cm⁻². Flow rate of the fuel: 5 mL min⁻¹. Fuel: 5% NaBH₄ + 10% NaOH. Cathode: 1 mg Pt cm⁻². Flow rate of the oxidant: 0.15 L min⁻¹.

and 237 mW cm⁻² were obtained using humidified oxygen at 28 °C and 60 °C, respectively. It has been explained that cathode kinetics are better when using oxygen instead of air [16]. Furthermore, it has been demonstrated that carbonate is formed due to the presence of CO₂ in air, which exerts a negative effect on electrode and electrolyte [16]. Also, it is shown that the increase in cell performance over this temperature range using oxygen is more than that using air due to the reduction of activation loss and concentration loss by the higher oxygen concentration. Although DBFCs using air do not yield as good a performance as those using oxygen, it is desirable to develop a DBFC with air as oxidant, simply because it is freely available in nature and may avoid the use of extra equipment and gas supply.

The effect of moisture in the oxidant was investigated by testing the cell performance with dry and humidified oxygen in DBFC. A maximum power density of 89 mW cm⁻² was obtained at 215 mA cm⁻² by using dry oxygen as oxidant while a maximum power density of 95 mW cm⁻² was obtained at 235 mA cm⁻² by using humidified oxygen as oxidant. The results, plotted in Fig. 2, show that the electrochemical performance is not significantly different by the oxidant humidification; only a small increase of power density is observed, since water is electro-osmotically dragged from the anode to the cathode which humidifies any incoming dry gas, oxygen or air.

3.1.2. Effect of anodic catalyst loading

Fig. 3 shows cell polarization and power density of DBFC at different anode catalyst loading, using humidified oxygen at 60 °C. An enhanced power density was found by increasing the loading of anodic catalyst. Peak power densities of 237 mW cm⁻², 243 mW cm⁻², and 261 mW cm⁻² were achieved by using catalyst loading of 1 mg cm⁻², 2 mg cm⁻², and 5 mg cm⁻², respectively. However, the increase in cell performance with the increase in anodic loading was not significant, possibly due to the negative effect of the thick catalyst layer on resistance and reduced mass transport of liquid and gaseous species. So the extra catalyst loading of 5 mg cm⁻² was not much advantageous for a small performance gain over 1 mg cm⁻² of anodic catalyst.

3.1.3. Stability test

Besides power density, cell performance stability is another important aspect that should be examined in DBFC development. Short-term stability of DBFC using Ni + Pd/C composite anode was

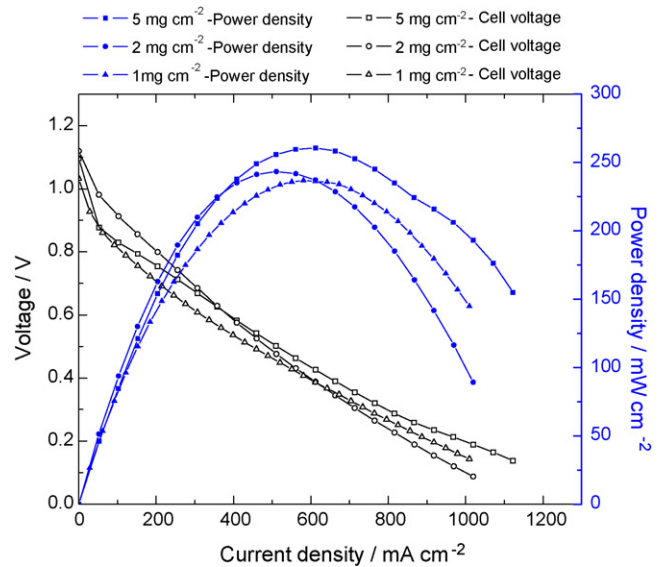


Fig. 3. Curves of cell polarization and power density of DBFC at different anode loading, using humidified oxygen at 60 °C. Anode: Ni + Pd/C. Fuel: 5% NaBH₄ + 10% NaOH. Flow rate of the fuel: 5 mL min⁻¹. Cathode: 1 mg Pt cm⁻². Flow rate of the oxidant: 0.15 L min⁻¹.

tested by monitoring the cell voltage change during the galvanostatic discharge of 50 mA cm⁻² of the DBFC in a period of about 100 h at room temperature (Fig. 4). The DBFC 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 possible reasons for the gradual decline in cell performance with time may be due to dissolution or agglomeration of anode catalyst, poisoning of catalyst surface, deactivation of cathode and membrane by NaOH and Na₂CO₃.

3.2. Borohydride–oxygen fuel cell using Ni + Pt/C composite anode

A borohydride–oxygen fuel cell was later assembled with a different composite anode consisting of Ni + Pt/C (a ratio of Ni:Pt being 25:1) with 1 mg cm⁻² metal loading and was tested for power

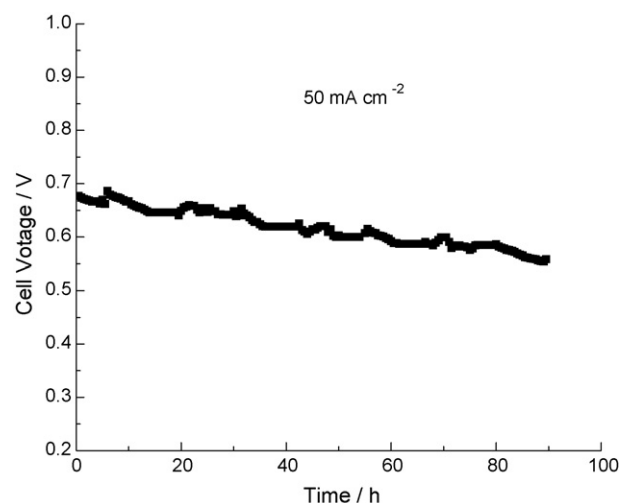


Fig. 4. Performance stability of the DBFC operating at current density of 50 mA cm⁻² at room temperature. Anode: Ni + Pd/C, 1 mg metal cm⁻². Flow rate of the fuel: 5 mL min⁻¹. Fuel: 5% NaBH₄ + 10% NaOH. Cathode: 1 mg Pt cm⁻². Flow rate of the humidified oxygen: 0.15 L min⁻¹.

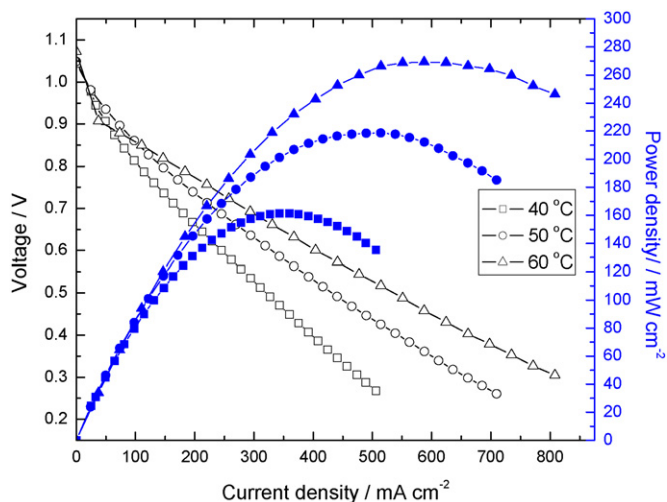


Fig. 5. Curves of cell polarization and power density of DBFC using oxygen at different temperatures. Anode: Ni+Pt/C, 1 mg metal cm^{-2} . Flow rate of the fuel: 5 mL min^{-1} . Fuel: 5% NaBH_4 + 10% NaOH. Cathode: 1 mg Pt cm^{-2} . Flow rate of the oxidant: 0.15 L min^{-1} .

performance at elevated temperatures. As shown in Fig. 5, peak power densities of 161 mW cm^{-2} , 219 mW cm^{-2} , 270 mW cm^{-2} were achieved at 40 °C, 50 °C and 60 °C. DBFCs with Ni+Pt/C composite anode gave approximately 33 mW cm^{-2} higher power density than using Ni+Pd/C at 60 °C under similar conditions. It has been demonstrated that Pt could be an effective catalyst for borohydride oxidation [17]. Electrochemical studies have shown that alloying Au with Pt improves borohydride oxidation activity more than alloying of Au with Pd (both Au–Pt and Au–Pd had 1:1 atomic ratio) [18,19]. It has been suggested [13] that Ni–Pt alloy has even higher activity than Au–Pt alloy (Pt–Au and Pt–Ni had 1:1 atomic ratio). In the present research, Nafion[®] was added to the Ni composite material in making the anode catalyst. In a previous study [14], addition of Nafion[®] was found to reduce BH_4^- concentration on the catalyst surface. At low borohydride concentration (<1 M), the columbic number of Pd anode is between 6e and 8e while a quasi-8e-reaction occurs at Pt anode as the result of extra catalytic sites for H_2 electrooxidation [12]. Given that Pt is the best catalyst for hydrogen reduction, it is possi-

ble that Ni–Pt catalyst may be able to achieve a good balance between borohydride oxidation and hydrolysis reactions, as H_2 released by hydrolysis may be oxidized effectively. Further studies are being made to investigate in detail the mechanism and reaction process of borohydride electro-oxidation on Ni-based composite anodes and the co-catalytic effects of two metals in the composite catalyst.

Geng et al. [20] reported a maximum power density of 221 mW cm^{-2} achieved by a DBFC employing carbon supported platinum nickel alloy ($\text{Ni}_{37}\text{-Pt}_3/\text{C}$) catalyst at the anode at 60 °C. The present research suggests that the DBFC performance can be improved simply by mixing Ni and Pt metals to get a composite catalyst and it may not be necessary to alloy them. Table 1 summarizes some representative power performance data of DBFCs in recent years. Comparing with the data shown in the table with the results obtained in the present study, one can conclude that it is possible to achieve high power performance using non-precious anode catalysts at relatively low catalyst loading.

3.3. Use of hydrogen peroxide as the oxidant

In addition to oxygen and air, H_2O_2 was also used as an oxidant in this study. The fuel concentration was optimized as 10 wt% NaBH_4 and 20 wt% NaOH, and the oxidant concentration was optimized as 2.0 M H_2O_2 and 1.5 M H_2SO_4 . It has been reported that among noble metals, palladium-based catalysts show both good results in activity and selectivity to electro-reduction of hydrogen peroxide [21]. So Pd was electrodeposited on the Zorflex activated carbon cloth with surface area of 1000–2000 $\text{m}^2 \text{g}^{-1}$ for use as cathode catalyst. A borohydride– H_2O_2 fuel cell with Ni+Pt/C composite anode and Pd cathode was assembled and tested. With H_2O_2 , the OCV of the cell was about 1.7 V compared to about 1.05 V with oxygen. The peak power densities are also much higher compared to the use of oxygen or air. As can be seen in Fig. 6, this fuel cell achieved very high peak power densities of 327 mW cm^{-2} and 665 mW cm^{-2} at 28 °C and 60 °C, respectively. To the authors' best knowledge, this is the first investigation using Ni based composite anode catalyst in borohydride– H_2O_2 fuel cell, and this is the highest reported power density achieved with a non-precious metal anode catalyst. Table 2 summarizes some representative power performance data of borohydride–hydrogen peroxide fuel cells. The present results with non-precious metal anode compare very favorable with the

Table 1
Representative power performance data of DBFCs.

Anode electrocatalyst	Cathode electrocatalyst	Membrane	Oxidant	Fuel	Temperature (°C)	Power density (mW cm^{-2})	Ref.
Ni+Pd/C+ surface-treated Zr–Ni alloy (10 mg metal cm^{-2})	Pt/C (1 mg cm^{-2})	Nafion [®] 117	O_2 150 ml min^{-1}	5 wt% NaBH_4 10 wt% NaOH 10 ml min^{-1}	Room temperature	65	[22]
Ni+Pd/C (20 mg metal cm^{-2})	Pt/C (1 mg Pt cm^{-2})	Nafion [®] 112	Air 5 L min^{-1}	10 wt% NaBH_4 20 wt% NaOH L min^{-1}	60	250	[14]
$\text{Ni}_{37}\text{-Pt}_3/\text{C}$ (1 mg metal cm^{-2})	Pt/C (15 L min^{-1} mg Pt cm^{-2})	Nafion [®] 212	O_2 L min^{-1}	5 wt% NaBH_4 10 wt% NaOH 1 ml min^{-1}	60	221	[20]
Zr–Ni Laves phase alloy AB_2 + Pd/C	Pt/C	Nafion [®] 211	Air 5 L min^{-1}	10 wt% NaBH_4 20 wt% NaOH L min^{-1}	60	290	[23]
Pt–Ni/C (mole, 1:1) (5 mg metal cm^{-2})	Pt (4 mg Pt cm^{-2})	Nafion [®] 117	O_2 L min^{-1}	2 M NaBH_4 1 M NaOH 50 ml min^{-1}	60	53	[13]
Pt–Ni/C (mole, 1:1) (0.8 mg metal cm^{-2})	Pt/C (1.3 mg Pt cm^{-2})	Anion-exchange membrane (Morgane [®] ADP)	Ambient air	2 M NaBH_4 1 M NaOH	Room temperature	120	[24]

Table 2
DBFC performance data obtained with hydrogen peroxide as the oxidant.

Anode electrocatalyst	Cathode electrocatalyst	Membrane	Oxidant	Fuel	Temperature (°C)	Power density (mW cm ⁻²)	Ref.
Au/C (0.5 mg cm ⁻²)	Pd/Ir (12.3 mg cm ⁻²)	Nafion® 117	0.15 mol dm ⁻³ H ₂ O ₂ 1 mol dm ⁻³ HCl 12 cm s ⁻¹	2 mol dm ⁻³ NaBH ₄ 6 mol dm ⁻³ NaOH 12 cm s ⁻¹	25	71	[25]
Pt–Ru	Pd–Ir	Nafion® 115	0.4 mol dm ⁻³ H ₂ O ₂ 3 mol dm ⁻³ NaOH 40 cm ³ min ⁻¹	0.2 mol dm ⁻³ NaBH ₄ 3 mol dm ⁻³ NaOH 40 cm ³ min ⁻¹	65	350	[26]
Pd	Au (0.5 mg cm ⁻²)	Nafion® membrane	10 wt% NaBH ₄ 5 wt% NaOH 5 wt% ammonium hydroxide	10 wt% H ₂ O ₂ 5 wt% phosphoric acid	60	680	[9]

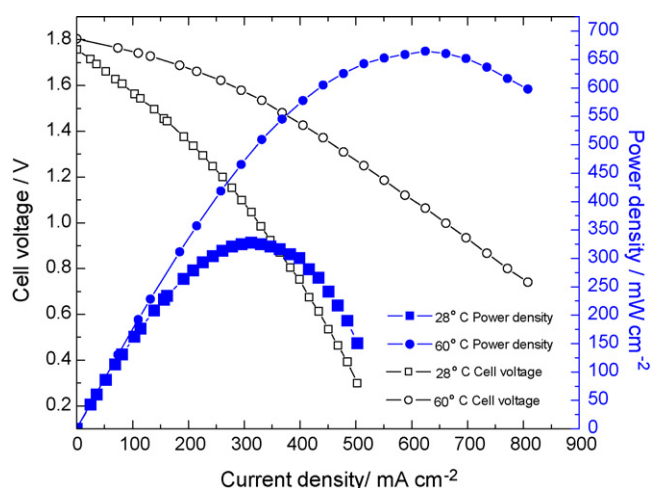


Fig. 6. Curves of cell polarization and power density of DBFC using hydrogen peroxide at different temperatures using Ni + Pt/C composite anode and electrodeposited Pd cathode. Flow rate of the fuel: 5 mL min⁻¹. Fuel: 5% NaBH₄ + 10% NaOH. Flow rate of hydrogen peroxide: 5 mL min⁻¹.

reported results. The results are very promising and will help in making a less expensive fuel cell.

4. Conclusions

Anodes made by pasting a composite Ni catalyst with either carbon supported Pd or with carbon supported Pt on carbon paper were used in a direct borohydride fuel cell (DBFC) using oxygen, air, or hydrogen peroxide as oxidant. Cell performance at various anodic loading and performance stability of the DBFC were investigated. With Ni + Pd/C anodic catalyst (1 mg metal cm⁻² loading), peak power densities of 95 mW cm⁻² and 237 mW cm⁻² were obtained using humidified oxygen at 28 °C and 60 °C, respectively while peak power densities of 77 mW cm⁻² and 167 mW cm⁻² were achieved using humidified air at 28 °C and 60 °C, respectively. Dry oxygen as oxidant gave a little less but comparable cell performance in term of power density as compared to the humidified oxygen. A slightly enhanced power density was found by increasing the loading of anodic catalyst. The borohydride–oxygen fuel cell maintained a relatively stable performance with little decay for up to about 100 h. DBFCs with Ni + Pt/C composite anode gave approximately 33 mW cm⁻² higher power density than using Ni + Pd/C at 60 °C under similar conditions. Peak power densities of 327 mW cm⁻² and 665 mW cm⁻² were achieved at 28 °C and 60 °C,

respectively using nickel based composites as the anode catalyst and hydrogen peroxide as the oxidant. This study suggests that Ni based composite anode catalysts are suitable for use in DBFC. It was also found that H₂O₂ is a good oxidant for air deficient applications, such as for power in submarine or power in space. With electrodeposited Pd as cathode and Ni composite anode very high power density can be achieved.

Acknowledgements

Financial support for this work was provided by the Third Frontier Fuel Cell Program of State of Ohio and from ITN Energy Systems of Littleton Colorado.

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