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A direct borohydride–peroxide fuel cell using a Pd/Ir alloy coated microfibrinous carbon cathode

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ABSTRACT

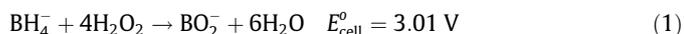
A direct borohydride fuel cell with a Pd/Ir catalysed microfibrinous carbon cathode and a gold-catalysed microporous carbon cloth anode is reported. The fuel and oxidant were NaBH₄ and H₂O₂, at concentrations within the range of 0.1–2.0 mol dm⁻³ and 0.05–0.45 mol dm⁻³, respectively. Different combinations of these reactants were examined at 10, 25 and 42 °C. At constant current density between 0 and 113 mA cm⁻², the Pd/Ir coated microfibrinous carbon electrode proved more active for the reduction of peroxide ion than a platinised-carbon one. The maximum power density achieved was 78 mW cm⁻² at a current density of 71 mA cm⁻² and a cell voltage of 1.09 V.

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1. Introduction

Precious metal nanoparticles supported on carbon have led to a reduction in catalyst loadings for proton exchange membrane fuel cells (PEMFCs) by a factor of 10–100-fold [1]. The morphology of the particles and the support material can also have a profound effect on the catalytic output of the electrode structure [2,3]. For example, Zheng et al. [4] showed that a 5 wt% Pt-coated platelet micro-carbon fibre structure was more active for oxygen reduction than a 5 wt% Pt-coated fish-bone carbon one. Other support materials such as microfibrinous carbon electrodes coated with Pd/Ir, designed for the reduction of H₂O₂, have been used in a semi-fuel cells for underwater applications [5].

The oxidation of the BH₄⁻ ion in alkaline electrolyte coupled with the reduction of H₂O₂ in acid electrolyte at 298 K:



can provide a high energy density direct borohydride fuel cell (DBFC). Several anode materials have been proposed to extract the 8 electrons from the BH₄⁻ ion [6–9] but gold is considered to

be amongst the most effective [10]. The oxidation of BH₄⁻ ions at 100 nm sized gold nanoparticles on a gold-plated nickel grid (<0.8 mg cm⁻²) and on a commercial Au electrode (1.8–2.0 mg cm⁻²) was compared [11,12]. The Au nanoparticles on the Ni-supported electrode showed a higher activity than the commercial gold electrode.

Although most research on the DBFC has focused on the anode, benefits are also achievable via improved engineering of the cathode materials. In this paper, a DBFC with a H₂O₂ catholyte using a recently introduced Pd/Ir coated microfibrinous cathode and a commercial Au-coated carbon cloth anode is considered. The performance of the Pd/Ir cathode is compared with carbon-supported Pt.

2. Experimental details

Fig. 1 shows an electrochemical filter-press cell (FM01-LC) [13] adapted as a DBFC. The electrodes were separated by a Nafion[®] 117 membrane. Two pumps (March May model TE-3K-MD) were used to circulate the electrolytes at $\approx 85 \pm 5 \text{ dm}^3 \text{ h}^{-1}$ flow rate (12 cm s⁻¹) at 10 ± 2 , 25 ± 2 and 42 ± 2 °C temperature, controlled with a thermostatic bath (Grant, model LTD6G). The anolyte was 0.1, 1 or 2 mol dm⁻³ NaBH₄ in 6 mol dm⁻³ NaOH and the catholyte, 0.05, 0.15 or 0.45 mol dm⁻³ H₂O₂ in 1 mol dm⁻³ HCl.

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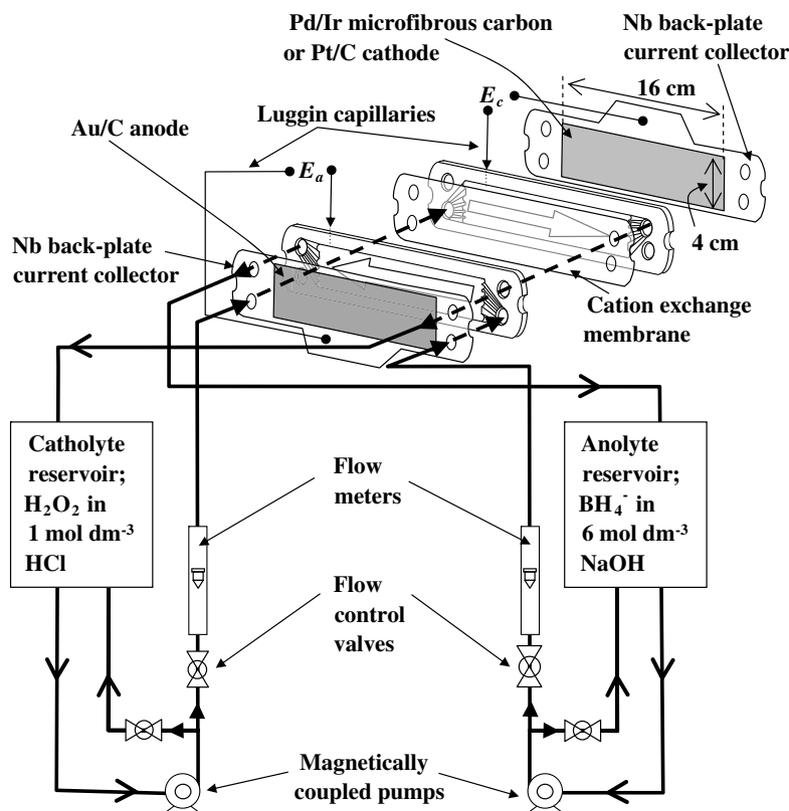


Fig. 1. Electrolyte circuit and electrochemical cell. E_a and E_c refer to the anode and cathode potentials, respectively.

The microfibrous carbon cathode support was fabricated by a direct charging electrostatic flocking (DCEF) applying technique. A 30–100 kV pulse was applied between a carbon plate containing the carbon microfibers (Mitsubishi Chemicals K63712) and a titanium foil substrate plate containing a conducting carbon adhesive film [14]. The density of the carbon fibres was 125,000 fibres per cm^2 , 11 μm in diameter and 500 μm length (Mitsubishi Chemical, K63712).

The electrode containing the carbon microfibres was linearly cycled between -0.15 and -0.30 V vs. Ag/AgCl at a linear potential sweep rate of 1 mV s^{-1} in $2 \times 10^{-3} \text{ mol dm}^{-3}$ PdCl₂ and $2 \times 10^{-3} \text{ mol dm}^{-3}$ Na₂IrCl₆H₂O in 0.2 mol dm^{-3} KCl and 0.1 mol dm^{-3} HCl solutions at 70 °C. Fig. 2 shows a typical SEM

micrograph of the microfibrous carbon coated with Pd/Ir. The catalyst loading was 12.3 mg cm^{-2} and consisted of nodules 5–10 mm in height which showed cauliflower features (inset) of 1:1 Pd:Ir composition. The anode was a carbon cloth electrode with 10 wt% Au on a Vulcan XC-72 carbon support ($0.5 \text{ mg Au cm}^{-2}$) from E-TEK Inc.

An electronic load (Kikusui model PLZ334 W) was used and the electrode potentials were monitored using 1 mm internal diameter tubing inserted in the anolyte and catholyte compartments.

3. Results and discussion

3.1. Pd/Ir coated microfibrous carbon and Pt/C cathodes

The current in the DBFC was increased in small steps of 0.2 A. Each current step was applied for a minute until 7.3 A (113 mA cm^{-2}). Fig. 3 compares the cell voltage and power density vs. current density of the Pd/Ir coated microfibrous carbon and nanoparticulate Pt/carbon black cathodes (4 mg Pt cm^{-2} Johnson Matthey Inc.) [3,15]. The anode in both systems was Au/C as described above.

The open-circuit potential (OCP) of the cell in the microfibrous cathode-based DBFC was 1.85 V. This is ≈ 1.15 V lower than the standard cell potential expected for a DBFC operating on acidified H₂O₂ [16]. The low value was probably caused by a mixed potential at the anode and cathode from the simultaneous oxidation of BH₄⁻ ions and hydrogen at the anode and reduction of H₂O₂ and O₂ at the cathode. The polarisation characteristics of the Pd/Ir microfibrous carbon cathode in Fig. 3 show a near linear E_{cell} vs. I response, indicating a strong dependence on the ohmic resistance. The power density for the Pd/Ir microfibrous carbon electrode showed a maximum of 71 mW cm^{-2} at a current density of 66 mA cm^{-2} and a cell voltage of 1.09 V. In comparison, a cobalt phthalocyanine cat-

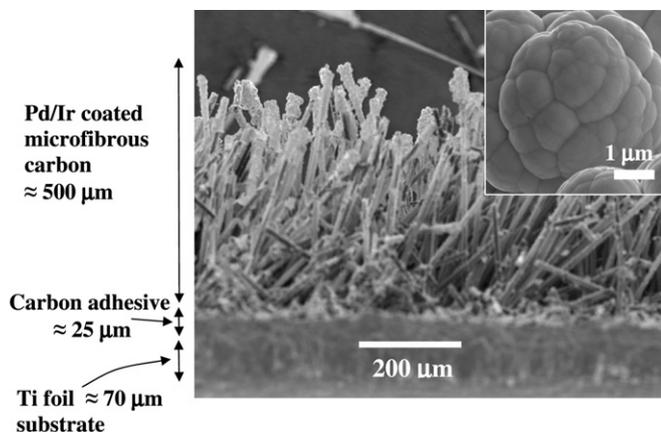


Fig. 2. SEM image of the Pd/Ir coated microfibrous carbon cathode. The inset shows a magnified view of the Pd/Ir catalyst.

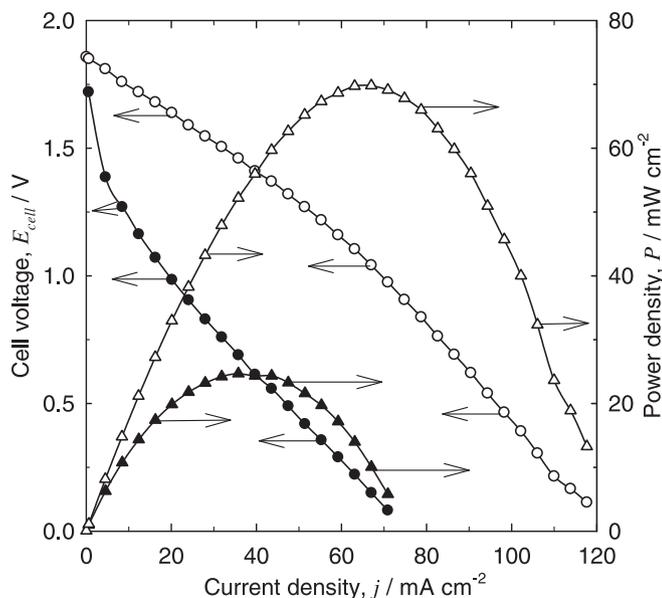


Fig. 3. Cell voltage and power density vs. current density for DBFCs with different cathodes: (○) E_{cell} and (△) P for a Pd/Ir coated microfibrillar carbon cathode, 12.3 mg cm^{-2} . (●) E_{cell} and (▲) P for Pt/C-black bound with a cationic, Nafion[®]-based ink on carbon paper (4.0 mg cm^{-2} loading). Anode for both systems: Au/C with $0.5 \text{ mg of Au cm}^{-2}$. Catholyte: 0.15 mol dm^{-3} of H_2O_2 in 1 mol dm^{-3} HCl. Anolyte: 2 mol dm^{-3} of NaBH_4 in a 6 mol dm^{-3} NaOH. Mean linear flow velocity of 12 cm s^{-1} at 25°C .

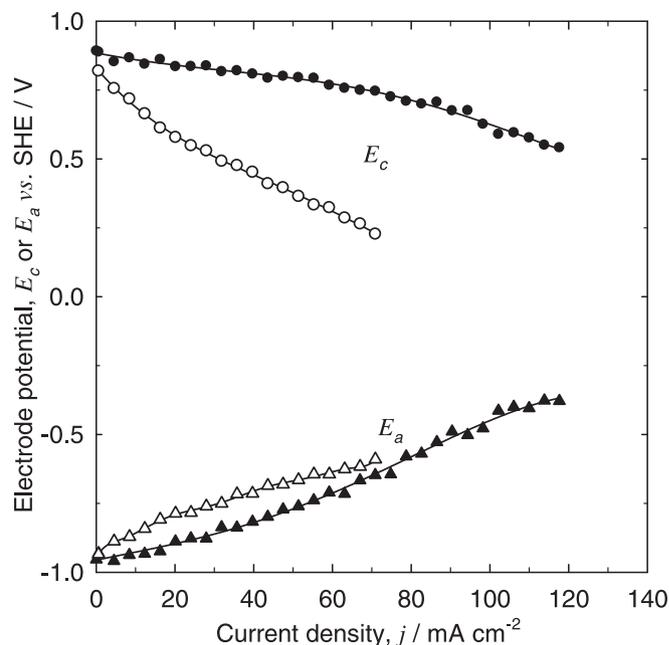


Fig. 4. Cathode and anode potentials vs. current density, for the fuel cell in Fig. 3. (●) E_c and (▲) E_a for a Pd/Ir coated microfibrillar carbon cathode. (○) E_c and (△) E_a for a Pt/C.

alysed cathode and H_2 storage alloy (HSA) catalysed anode ($\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_{0.3}$) reported in the literature, showed a maximum power density of 90 mW cm^{-2} at 175 mA cm^{-2} and 0.5 V [17]. Although the current density in Ref. [17] was larger, the cell voltage was half of the value obtained with the Pd/Ir coated microfibrillar carbon cathode.

The cell voltage vs. current density behaviour obtained with the Pt/C cathode showed an OCP value of 1.72 V and a similar linear behaviour experienced with a Pd/Ir coated microfibrillar cathode. In this case, however, the cell voltage dropped more rapidly as the current density increased. At 25°C , the maximum power density was 25 mW cm^{-2} at 36 mA cm^{-2} and 0.7 V . Although this system was operated under the same conditions as the Pd/Ir alloy coated microfibrillar carbon cathode-based DBFC, it produced only

35% of the power density. This is attributable in part to the different cathode catalyst materials and loadings.

Fig. 4 shows the half-cell potentials for the two fuel cells shown in Fig. 3. The large variation in the cathode potentials is noteworthy and confirms that the variation in cathode activity is responsible for the different power densities seen in Fig. 3. The OCP for the Pd/Ir and Pt/C cathodes are 0.90 V vs. SHE and 0.80 V vs. SHE , respectively. These values are lower than the standard value for the reduction of hydrogen peroxide (1.77 V vs. SHE) due to the mixed potential involved. When the current density increased to 70 mA cm^{-2} , the electrode potential of the Pd/Ir coated electrode dropped only 16% from the OCP value to 0.75 V vs. SHE while the electrode potential of the Pt/C cathode dropped 72% to 0.22 V vs. SHE from the OCP value.

The OCP values of the two anodes were -0.95 and -0.92 V vs. SHE for the cells operating with Pd/Ir and Pt/C cathodes,

Table 1

Comparison of the highest power densities obtained from nine combinations of H_2O_2 and NaBH_4 concentrations at three temperatures

[NaBH ₄] (mol dm ⁻³)	T (°C)	Concentration of H ₂ O ₂ (mol dm ⁻³)								
		0.05			0.15			0.45		
		Power density, P (W cm ⁻²)	Current density, j (mA cm ⁻²)	Cell voltage, E _{cell} (V)	Power density, P (W cm ⁻²)	Current density, j (mA cm ⁻²)	Cell voltage, E _{cell} (V)	Power density, P (W cm ⁻²)	Current density, j (mA cm ⁻²)	Cell voltage, E _{cell} (V)
0.1	10	13	18	0.72	10	13	0.74	9	13	0.66
	25	15	20	0.77	13	18	0.75	10	15	0.68
	42	18	24	0.75	17	26	0.70	11	18	0.65
1	10	13	12	1.05	29	32	0.90	33	38	0.87
	25	20	16	1.16	42	47	0.88	59	60	0.97
	42	30	28	1.08	64	63	1.01	75	75	1.00
2	10	19	20	0.94	50	47	1.06	38	40	0.95
	25	35	36	0.97	70	67	1.04	53	55	0.95
	42	41	44	0.93	78	71	1.09	66	71	0.93

The anolyte contained 6 mol dm^{-3} NaOH and the catholyte contained 1 mol dm^{-3} HCl. Anode: Au/Vulcan XC-72 on C felt (0.5 mg cm^{-2} loading Au) and cathode: microfibrillar carbon with $12.3 \text{ mg of Pd/Ir cm}^{-2}$ on Ti foil. The geometrical area of the electrodes was 64 cm^2 with a mean linear electrolyte flow velocity of 12 cm s^{-1} .

respectively. Both anode potentials increased with the current density and remained relatively close throughout the polarisation region.

3.2. Pd/Ir alloy coated microfibrinous cathode at different H_2O_2 and $NaBH_4$ concentrations

Nine combinations of $NaBH_4$ and H_2O_2 concentration were investigated at 10, 25 and 42 °C. The maximum power densities obtained at each combination and temperature are shown in Table 1. The data in Table 1 shows the power density at a fixed H_2O_2 concentration of 0.05 mol dm^{-3} to increase with $NaBH_4$ concentration and temperature. A similar trend was observed with the intermediate 0.15 mol dm^{-3} peroxide concentration. When the peroxide concentration was increased to 0.45 mol dm^{-3} , however, there was a change in behaviour and the maximum power density was obtained at a borohydride concentration of 1 mol dm^{-3} . Further studies are required in order to better understand these concentration effects in order to optimise DBFC operation, including pH monitoring of the anolyte and catholyte.

4. Conclusions

1. A 3-dimensional, microfibrinous carbon substrate with high surface area support for the electrodeposition of Pd/Ir electrocatalyst ($12.3 \text{ mg Pd/Ir cm}^{-2}$) targeting H_2O_2 reduction in a DBFC has been demonstrated. Further improvements in the utilisation of the cathode should be achievable by improved catalysts deposition techniques.
2. The maximum power density of the DBFC using Pd/Ir coated microfibrinous carbon electrode was 78 mW cm^{-2} at 42 °C compared to 25 mW cm^{-2} obtained with Pt/C-black (4 mg Pt cm^{-2}) electrocatalysts.
3. The electrode potential of the Pd/Ir coated microfibrinous and Pt/C cathodes dropped 16% and 72%, from the OCP value, respectively, at a current density of 70 mA cm^{-2} .

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