

Short communication

A direct borohydride fuel cell employing Prussian Blue as mediated electron-transfer hydrogen peroxide reduction catalyst

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Abstract

A direct borohydride-hydrogen peroxide fuel cell employing carbon-supported Prussian Blue (PB) as mediated electron-transfer cathode catalyst is reported. While operating at 30 °C, the direct borohydride-hydrogen peroxide fuel cell employing carbon-supported PB cathode catalyst shows superior performance with the maximum output power density of 68 mW cm⁻² at an operating voltage of 1.1 V compared to direct borohydride-hydrogen peroxide fuel cell employing the conventional gold-based cathode with the maximum output power density of 47 mW cm⁻² at an operating voltage of 0.7 V. X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray Analysis (EDAX) suggest that anchoring of Cetyl-Trimethyl Ammonium Bromide (CTAB) as a surfactant moiety on carbon-supported PB affects the catalyst morphology. Polarization studies on direct borohydride-hydrogen peroxide fuel cell with carbon-supported CTAB-anchored PB cathode exhibit better performance with the maximum output power density of 50 mW cm⁻² at an operating voltage of 1 V than the direct borohydride-hydrogen peroxide fuel cell with carbon-supported Prussian Blue without CTAB with the maximum output power density of 29 mW cm⁻² at an operating voltage of 1 V.

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1. Introduction

Over the years, hydrogen has come to be seen as the undisputed fuel for the future. It is also established that hydrogen as a fuel is most efficiently utilized in fuel cells. But hydrogen does not occur freely in nature and hence needs to be generated either from natural gas or other hydrogen containing compounds. Hydrogen thus generated contains carbon monoxide, which even at miniscule level can affect the performance of the fuel cell, besides requiring be stored and transported [1–3]. In the literature, efforts have also been expended to directly use organic fuels such as methanol, ethanol, propanol, formic acid, dimethylether, ethylene glycol, etc. in the fuel cells albeit a number of concerns associated with these organic fuels that include low activity, carbon monoxide poisoning, toxicity, and low oxidation efficiency,

compared to hydrogen [4,5]. An alternative is to use borohydride as a fuel in a Direct Borohydride Fuel Cell (DBFC), which exhibits a higher open circuit voltage and a higher power density than both hydrogen/oxygen and direct organic fuel cells [6,7].

There are two modes of using Hydrogen Peroxide (H₂O₂) as oxidant in fuel cells. One is to decompose H₂O₂ on a catalytic surface to oxygen and use the released oxygen for reduction in the fuel cell. The second is to use H₂O₂ as the oxidant directly in the fuel cell. DBFC employing H₂O₂ as direct oxidant also operate at higher output voltages as compared to the DBFC fed with oxygen from air as the oxidant. Besides, there is a need to mitigate carbonate fouling in DBFC while employing oxygen from air as oxidant [4,8–10]. Cheng et al. [9] have studied the materials aspects on the design and operation of direct borohydride fuel cells and found that the membrane electrode assembly, with the commercially available cathode from ElectrochemTechnic, UK, failed to sustain the cell even for half-an-hour, while conducting cathode stability test by monitoring changes in cell voltage during its galvanostatic operation. Cheng and Scott [9,10] have attributed this to the cathode flooding brought about by water

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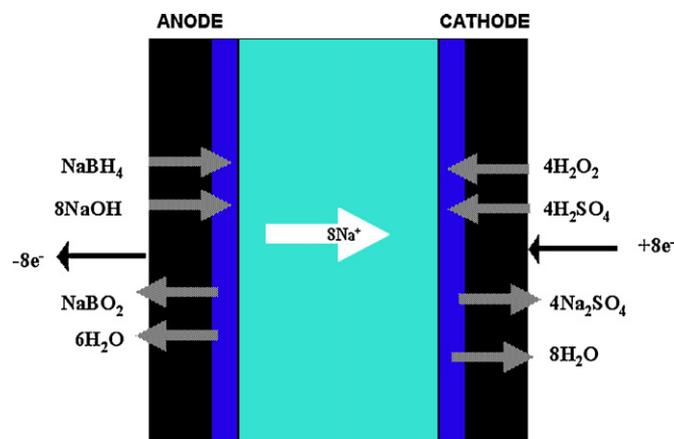
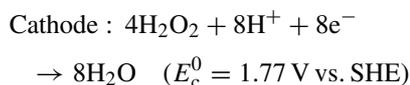
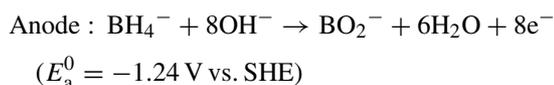


Fig. 1. Conceptual diagram of direct borohydride-hydrogen peroxide fuel cell.

accumulation and carbonate fouling by carbonate formation due to the CO_2 present in the atmospheric air. It is reported [11–14] that the use of acidified H_2O_2 in aqueous sulfuric acid (H_2SO_4) as an oxidant increases the output voltage of DBFC. The conceptual diagram of the borohydride-peroxide fuel cell is given in Fig. 1. The half-cell reactions and standard equilibrium potentials are given below.



In the literature [15,16], electro-reduction of H_2O_2 has been studied on platinum, gold and palladium–iridium alloy. Platinoid group catalysts are undoubtedly efficient for reducing hydrogen peroxide to water, but these catalysts, besides being expensive, cause rampant partial decomposition of H_2O_2 to oxygen posing operational difficulties in the fuel cell. To mitigate this problem, it is imperative to find a catalyst that promotes electro-reduction of H_2O_2 without its chemical decomposition while operating in acidic medium.

Prussian Blue (PB) or Iron (III) hexacyanoferrate finds numerous electrochemical applications like electrochromism [17], ion selective electrodes [18,19], charge storage devices [20] and electrocatalysis [21–24]. Many researchers involved in the development of new hydrogen peroxide sensors have extensively studied the characteristics of PB [24–26]. Itaya et al. [27] first demonstrated that the reduced form of PB, also referred to as Prussian White, has a catalytic effect both towards the reduction of O_2 and H_2O_2 as the zeolitic nature of PB with a cubic unit cell of 10.2 \AA and channel diameter of about 3.2 \AA facilitates the diffusion of O_2 and H_2O_2 molecules through the crystal lattice. Due to this reason, PB is described as a three-dimensional catalyst. Indeed, molecules with molecular weights higher than H_2O_2 cannot diffuse through the PB lattice making it an electrochemically selective catalyst. It is also reported [28,29] that anchoring cetyl-trimethyl ammonium bromide (CTAB) onto PB promotes charge transfer by reducing the free energy barrier and increases

the stability of the PB matrix. Karyakin et al. [30] reported the catalytic activity of PB for H_2O_2 reduction to be about 100 times higher than that for O_2 . Further more, preparation of PB is simple, which, besides being cost effective, is highly stable in acidic media.

The present study describes electro-reduction of H_2O_2 on PB both with and without CTAB as anchored surfactant-moiety onto carbon as cathode catalyst in a DBFC. It has been possible to achieve a power density of 68 mW cm^{-2} while operating such a DBFC at 30°C , which is superior to that reported for the DBFC employing carbon-supported gold catalyst as cathode [11]. To our knowledge, this is the first ever study reporting the usage of PB as mediated electron-transfer cathode catalyst in direct borohydride-hydrogen peroxide fuel cells.

2. Experimental

2.1. Preparation of carbon-supported PB

A chemical route reported elsewhere [24] was adopted to prepare PB supported onto carbon. In brief, the required amount of Vulcan XC-72R (Cabot Corporation) was suspended in 0.1 M HCl and agitated in an ultrasonic water bath (Vibronics, 300 W , 250 kHz) to form slurry. The required amount of $0.5 \text{ M K}_3[\text{Fe}(\text{CN})_6]$ in 0.1 M HCl was added drop wise to the carbon slurry with constant stirring at room temperature followed by the addition of 0.5 M FeCl_3 in 0.1 M HCl . The solution was further stirred for 1 h . The resultant mass with adsorbed PB was collected by filtration and washed with 0.1 M HCl until the filtrate became colorless and then dried in an oven at 100°C for 3 h . The PB on carbon support was stored in dark in a desiccator at room temperature. The preparation procedure of PB on carbon support modified with CTAB was the same as above but while making carbon slurry 0.9 mM CTAB was added.

2.2. Preparation of membrane electrode assembly (MEA)

AB_5 -group $\text{M}_m\text{Ni}_{3.55}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.75}$ alloy, where M_m stands for Misch metal (La-30 wt.%, Ce-50 wt.%, Nd-15 wt.%, Pr-5 wt.%) was used as the anode material. It is noteworthy that both AB_2 and AB_5 -group alloys have been successfully employed as negative electrodes in nickel-metal hydride batteries by several researchers [31–34]. Although AB_2 -group alloys yield superior energy storage density, the AB_5 -group alloys have higher hydrogen retention capacity [31–33].

Slurry of the alloy was obtained by agitating the required amount of alloy, $5 \text{ wt.}\%$ of Vulcan XC72 R carbon and $7 \text{ wt.}\%$ Nafion solution in isopropyl alcohol in an ultrasonic bath. The resultant slurry was spread onto the carbon cloth to fabricate the anode catalyst layer. The loading of the alloy catalyst was 5 mg cm^{-2} that was kept identical for all MEAs. To prepare cathode catalyst layer, the required amount of PB supported on carbon, both modified or unmodified, was suspended in isopropyl alcohol and agitated in an ultrasonic water bath. To this, $10 \text{ wt.}\%$ Nafion solution was added drop wise. The resultant slurry was spread onto a carbon cloth and dried in an air oven at 80°C for 1 h . The MEA was obtained by hot pressing the

cathode and anode on either side of a pre-treated Nafion 117 membrane (Dupont) at 60 kg cm^{-2} at 125°C for 3 min.

Both anode and cathode were contacted on their rear with flow-field plates machined from high-density graphite blocks in which holes connecting the main chamber were machined to achieve minimum mass polarization in DBFC. The free space between the holes makes electrical contact with the rear of the electrode and helps conducting current to the external circuit. The chamber supplies alkaline sodium borohydride solution to the anode and acidified hydrogen peroxide to the cathode. An aqueous alkaline sodium borohydride solution comprising 4 w/o NaBH_4 in 20 w/o aqueous NaOH was injected into the fuel chamber. A 2 M hydrogen peroxide solution in mixture of 1.5 M sulfuric acid and 0.5 M KCl is injected into the oxidant chamber. In all galvanostatic polarization studies 0.5 M KCl was used along with the oxidant. All studies were conducted at 30°C . The electrochemical activity of PB was supported in presence of K^+ -counter cation as the counter cation replaces the high spin iron during the transformation of insoluble PB to soluble PB (Prussian White) [28,35,36]. Graphite blocks were provided with electrical contacts. The active area of DBFC was 9 cm^2 .

3. Results and discussion

Powder X-ray diffraction (XRD) patterns both for modified and unmodified PB catalysts are shown in Fig. 2. The patterns show pronounced peaks at $2\theta = 17.4$ (2 0 0), $2\theta = 24.6$ (2 2 0), $2\theta = 35.2$ (4 0 0), $2\theta = 39.4$ (4 2 0) and $2\theta = 43.4$ (4 2 2) corresponding to $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$ [37,38]. The XRD peak positions for PB both with and without CTAB remain identical indicating the modification procedure to have little effect on the crystallinity of PB. An estimation of mean size of PB with and without CTAB is performed from the half width at full maximum (HWF) for the (2 0 0) Bragg reflection peak using the Debye–Scherrer equation. The mean particle sizes for PB with and without CTAB are $5 \mu\text{m}$ and $8 \mu\text{m}$, respectively. A decrease in particle size is observed in PB modified with CTAB suggesting that the surfactant moiety to influence the particle size of PB by preventing the agglomeration of PB particles.

The surface morphologies of both modified and unmodified PB are studied with the help of a JEOL JSM 5400 Scanning Elec-

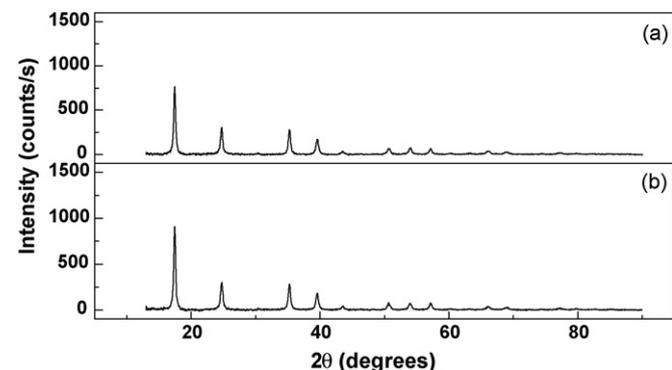


Fig. 2. Powder X-ray diffraction (XRD) patterns for (a) unmodified and (b) modified catalysts.

tron Microscope (SEM) coupled with Energy Dispersive X-ray Analysis (EDAX) facility. Fig. 3 shows the SEM micrographs for unmodified PB and CTAB modified PB at three different magnifications. The micrographs indicate that the presence of CTAB surfactant during PB preparation has a distinctive influence on the surface morphology and particle size. The particles of PB catalyst modified with CTAB are evenly distributed on the carbon surface while PB without CTAB contains larger particles with uneven distribution.

Typical EDAX spectra for the PB modified with and without CTAB are shown in Fig. 4 and analysis of the data suggests the presence of carbon, nitrogen, oxygen, potassium and iron. Notably, the potassium peak indicates formation of the reduced form of PB, namely Prussian White. If potassium ions were not an integral part of PB then their presence would be highly unlikely as the catalyst was copiously washed. The presence of potassium ions accounts for the charge balance in the reduced form of PB. It is note worthy that chemical method for preparation of PB reportedly yields only its reduced form [39].

The galvanostatic polarization data were obtained for various DBFCs described in Table 1. The polarization data for DBFC 1 and DBFC 2 are shown in Fig. 5. Although the open-circuit voltages for both the systems are similar, the performance for DBFC 2 is superior to DBFC 1 over the entire polarization range. A maximum power density of 50 mW cm^{-2} at 1 V is obtained for DBFC 2 as against 29 mW cm^{-2} for DBFC 1. Senthil Kumar et al. [29] have shown that the permeability of CTAB-modified iron (III) hexacyano ferrate film is greater than the unmodified film which accounts for facile entry and exit of charge compensating K^+ -ions; it is also reported that peak-to-peak separation potential ($\Delta E_p = E_{pA1} - E_{pC1}$) is much less for the CTAB-modified iron(III) hexacyano ferrate composite film signifying that the surface electron transfer process is relatively faster for CTAB-modified composite film electrode. In the present study, the superior performance obtained with CTAB-modified PB could be accounted only for enhanced charge transfer mechanism, since all the other experimental conditions, such as composition of anolyte and catholyte, membrane electrolyte, operating conditions and cell configuration, are similar. It is reported [28] that the negatively charged PB film absorbs cationic CTAB micelles due to electrostatic attraction. The presence of CTAB favors charge transfer by reducing the free energy barrier. Besides, it imparts highly porous structure to PB matrix [29] resulting in increased oxidant diffusivity.

The performance data for DBFC 3, DBFC 4, DBFC 5 and DBFC 6 in relation to DBFC 2 are compared in Fig. 6. The data suggest DBFC 2 to be superior in performance in relation to DBFC 3, DBFC 4, DBFC 5 and DBFC 6. A maximum power density of 50 mW cm^{-2} is achieved at 1 V for DBFC 2. A higher amount of PB on carbon is expected to increase the performance as more PB catalyst becomes available near the interface. However, the decrease in performance for DBFC 6 could be due to reduced electronic conductivity. Accordingly, DBFC 2 gives the optimum performance.

The effect of PB, while keeping the ratio of PB and carbon modified with CTAB constant at 4:1 loading per square centimeter, on the performance of DBFC is conducted through

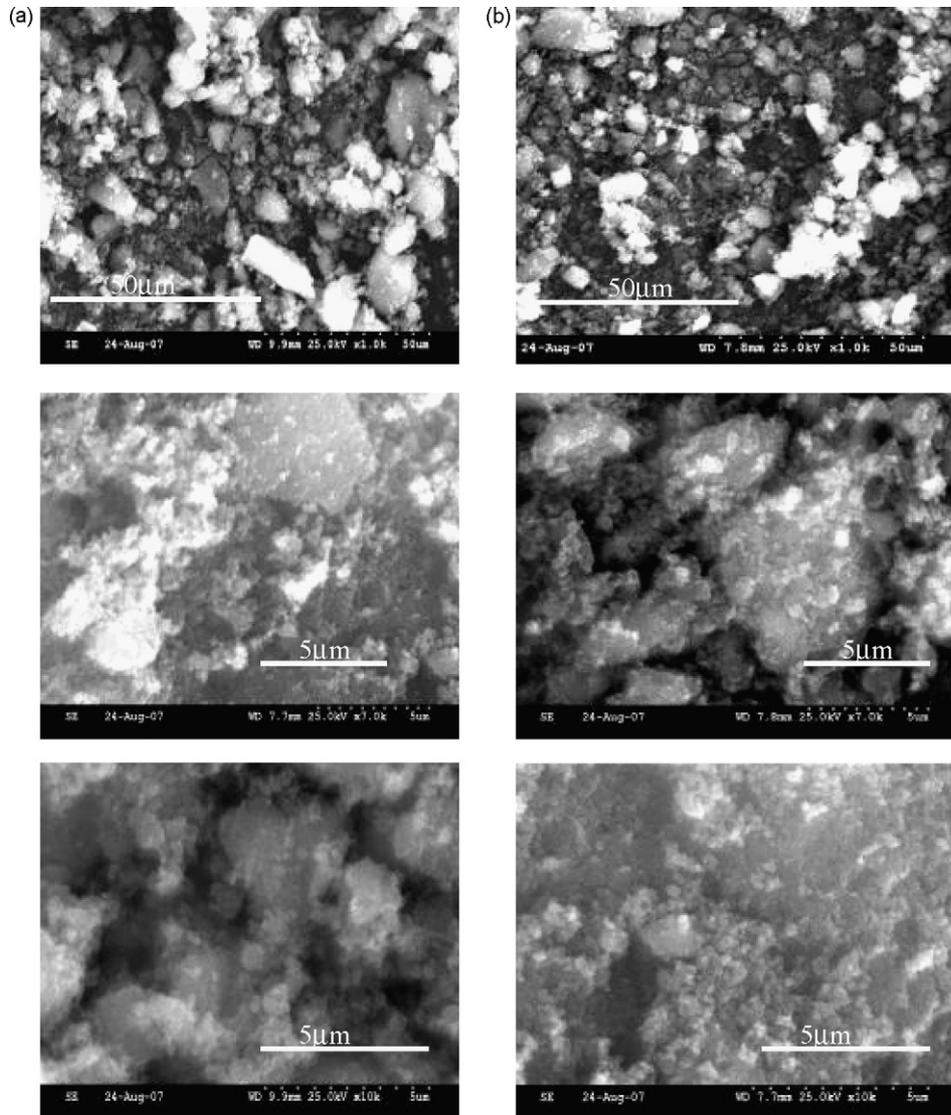


Fig. 3. SEM micrographs for DBFC catalysts (a) with CTAB and (b) without CTAB modification.

Table 1
Performance data for various DBFCs investigated during the study

S. No.	Cathode catalyst	Loading of PB (mg cm^{-2})	Peak power density (mW cm^{-2})	Cell voltage at peak power density (V)
Effect of CTAB				
DBFC 1	PB without CTAB (weight ratio of PB:C as 4:1)	30	29	0.991
DBFC 2	PB with CTAB (weight ratio of PB:C as 4:1)	30	50	1.059
Effect of amount of PB with respect to C				
DBFC 3	PB with CTAB (weight ratio of PB:C as 1:1)	30	14	1.024
DBFC 4	PB with CTAB (weight ratio of PB:C as 2:1)	30	28	0.986
DBFC 5	PB with CTAB (weight ratio of PB:C as 3:1)	30	39	0.975
DBFC 2	PB with CTAB (weight ratio of PB:C as 4:1)	30	50	1.059
DBFC 6	PB with CTAB (weight ratio of PB:C as 5:1)	30	44	1.19
Effect of PB loading				
DBFC 2	PB with CTAB (weight ratio of PB:C as 4:1)	30	14	1.024
DBFC 7	PB with CTAB (weight ratio of PB:C as 4:1)	40	68	1.107
DBFC 8	PB with CTAB (weight ratio of PB:C as 4:1)	50	59	1.05
Comparative performance of PB with commercial catalyst				
DBFC 7	PB with CTAB (weight ratio of PB:C as 4:1)	40	68	1.107
DBFC 9	Au supported on carbon (40 w/o Au/C)	2	47	0.705

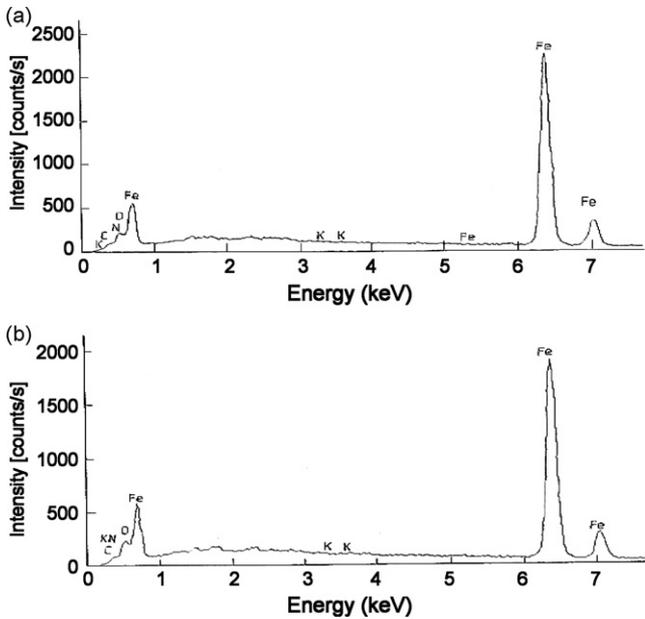


Fig. 4. EDAX spectra for (a) unmodified and (b) modified catalysts.

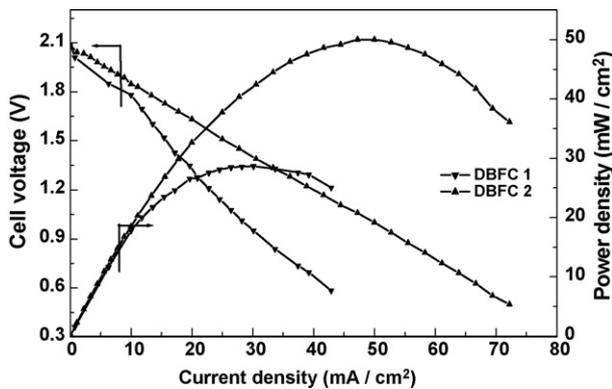


Fig. 5. Polarization data for DBFC 1 and DBFC 2.

galvanostatic polarization studies and the polarization data are shown in Fig. 7. It can be seen that DBFC 7 shows superior performance in relation to DBFC 2 and DBFC 8. One would expect that the higher amount of PB loading would give higher performance but a reduced performance with increased loading could

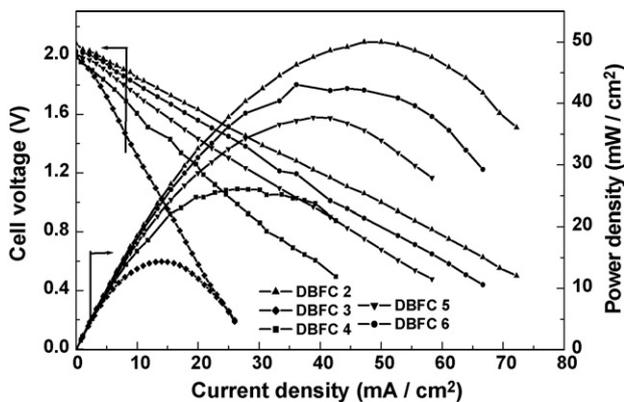


Fig. 6. Polarization data for DBFC 2, DBFC 3, DBFC 4, DBFC 5 and DBFC 6.

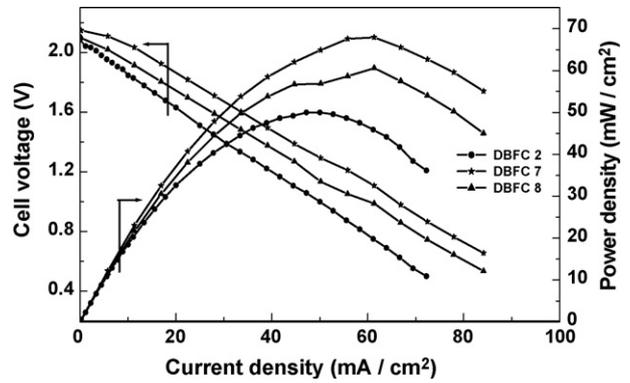


Fig. 7. Polarization data for DBFC 2, DBFC 7 and DBFC 8.

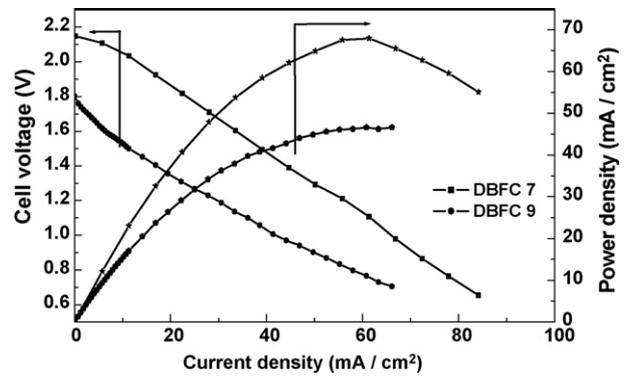


Fig. 8. Polarization data for DBFC 7 and DBFC 9.

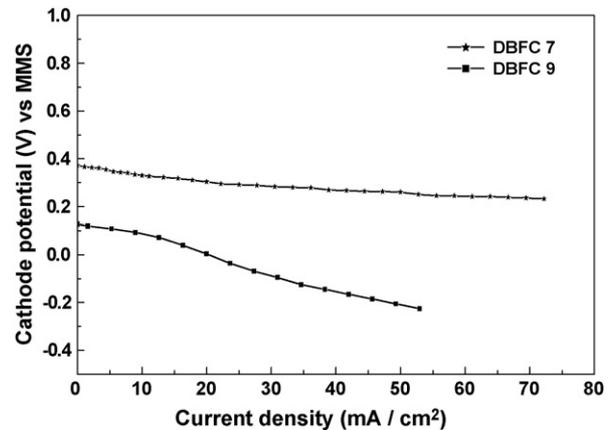


Fig. 9. Cathode polarization data for DBFC 7 and DBFC 9.

arise due to the increased diffusion path length for the reactants. Accordingly, DBFC 7 yields the best performance.

Comparisons of galvanostatic polarization data for DBFC 7 and DBFC 9 with carbon-suuported gold as cathode catalyst are shown in Fig. 8. It is seen that DBFC 7 performs better than DBFC 9. DBFC 7 yields a power density of 68 mW cm^{-2} at operational voltage of 1.1 V while DBFC 9 is limited to a maximum power density of only 47 mW cm^{-2} at 0.71 V. To understand the comparative electrocatalytic activity of gold and PB, the cathodic polarization data obtained against $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{SO}_4^{2-}$ (MMS) reference electrode placed in the oxidant chamber are shown in Fig. 9. It is clearly seen that the PB catalyst shows lesser

cathodic polarization in relation to gold. Accordingly, this study clearly establishes PB as a better and cost-effective alternative cathode catalyst for DBFC-H₂O₂ fuel cell in relation to gold.

4. Conclusions

Prussian Blue is shown to be an effective catalyst for the electro-reduction of hydrogen peroxide. XRD, SEM, and EDAX studies confirm that CTAB addition to Prussian Blue matrix affects the catalyst morphology. The performance of the direct borohydride-hydrogen peroxide fuel cell with carbon-supported CTAB anchored PB cathode is found to be superior to direct borohydride-hydrogen peroxide fuel cell with bare carbon-supported PB cathode.

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References

- [1] J. Larminie, A. Dicks, *Fuel Cell System Explained*, second ed., John Wiley & Sons Ltd., England, 2003, pp. 67–118.
- [2] S.C. Amendola, S.L. Sharp-Goldman, M.S. Janjua, N.C. Spencer, M.T. Kelly, P.J. Petillo, M. Binder, *Int. J. Hydrogen Energy* 25 (2000) 969–975.
- [3] C. Wu, H. Zhang, B. Yi, *Catal. Today* 93–95 (2004) 477–483.
- [4] H. Cheng, K. Scott, *J. Power Sources* 160 (2006) 407–412.
- [5] A.K. Shukla, A.S. Aricò, V. Antonucci, *Renew. Sustain. Energy Rev.* 5 (2001) 137–142.
- [6] S.C. Amendola, US Patent 5,804,329.
- [7] Z.P. Li, B.H. Liu, K. Arai, K. Asaba, S. Suda, *J. Power Sources* 126 (2004) 28–33.
- [8] N.A. Choudhury, R.K. Raman, S. Sampath, A.K. Shukla, *J. Power Sources* 143 (2005) 1–6.
- [9] H. Cheng, K. Scott, K. Lovell, *Fuel Cells* 6 (2006) 367–375.
- [10] G. Kosher, K. Kordes, *J. Power Sources* 136 (2004) 215–219.
- [11] R.K. Raman, N.A. Choudhury, A.K. Shukla, *Electrochem. Solid State Lett.* 7 (2004) A488–A491.
- [12] C. Ponce de Leon, F.C. Walsh, A. Rose, J.B. Lakeman, D.J. Browning, R.W. Reeve, *J. Power Sources* 164 (2007) 441–448.
- [13] G.H. Miley, N. Luo, J. Mather, R. Burton, G. Hawkins, L. Gu, E. Byrd, R. Gimlin, P.J. Shrestha, G. Benavides, J. Laystrom, D. Carroll, *J. Power Sources* 165 (2007) 509–516.
- [14] C.A. Sequeira, T.C. Pardo, D.M. Santos, J.A. Condeco, M.W. Franco, M.C. Goncalves, *ECS Trans.* 3 (2007) 19–23.
- [15] R.K. Raman, A.K. Shukla, *J. Appl. Electrochem.* 35 (2005) 1157–1161.
- [16] L. Gu, N. Luo, H. Miley, *J. Power Sources* 173 (2007) 77–85.
- [17] D.M. DeLongchamp, P.T. Hammond, *Chem. Mater.* 16 (2004) 4799–4805.
- [18] C. Gabrielli, P. Hémerly, P. Liatsi, M. Masure, H. Perrota, *J. Electrochem. Soc.* 152 (2005) H219–H224.
- [19] M. Pyrasch, A. Toutianoush, W. Jin, J. Schnepf, B. Tiede, *Chem. Mater.* 15 (2003) 245–254.
- [20] K. Honda, H. Hayashi, *J. Electrochem. Soc.* 134 (1987) 1330–1334.
- [21] F. Ricci, D. Moscone, C.S. Tuta, G. Palleschi, A. Amine, A. Poscia, F. Valgimigli, D. Messeri, *Biosens. Bioelectron.* 20 (2005) 1993–2000.
- [22] I.B. Rejeb, F. Arduini, A. Amine, M. Gargouri, G. Palleschi, *Anal. Chim. Acta* 594 (2007) 1–8.
- [23] A. Radoi, D. Compagnone, E. Devic, G. Palleschi, *Sens. Actuators B* 121 (2007) 501–506.
- [24] F. Ricci, A. Amine, C.S. Tuta, A.C. Ciucu, F. Lucarelli, G. Palleschi, D. Moscone, *Anal. Chim. Acta* 485 (2003) 111–120.
- [25] E.A. Puganova, A.A. Karyakin, *Sens. Actuators B* 109 (2005) 167–170.
- [26] R. Garjonyte, A. Malinauskas, *Sens. Actuators B* 46 (1998) 236–241.
- [27] K. Itaya, N. Shoji, I. Uchida, *J. Am. Chem. Soc.* 106 (1984) 3423–3429.
- [28] R. Vittal, M. Jayalakshmi, H. Gomathi, G. Prabhakara Rao, *J. Electrochem. Soc.* 146 (1999) 786–793.
- [29] S.M. Setnil Kumar, K. Chandrasekara Pillai, *J. Electroanal. Chem.* 589 (2006) 167–175.
- [30] A.A. Karyakin, O.V. Gitelmacher, E.E. Karakina, *Anal. Chem.* 67 (1995) 2419–2423.
- [31] V.G. Kumar, K.M. Shaju, N. Munichandraiah, A.K. Shukla, *J. Power Sources* 76 (1998) 106–111.
- [32] K.M. Shaju, V.G. Kumar, S. Rodrigues, N. Munichandraiah, A.K. Shukla, *J. Appl. Electrochem.* 30 (2000) 347–357.
- [33] K.M. Shaju, V.G. Kumar, S. Rodrigues, N. Munichandraiah, A.K. Shukla, *J. Solid State Electrochem.* 3 (1999) 464–467.
- [34] B. Hariprakash, S.K. Martha, A.K. Shukla, *J. Appl. Electrochem.* 33 (2003) 497–504.
- [35] J.J. Garcia-Jareno, A. Sanmatias, D. Benito, J. Navarro-Laboulasis, F. Vicente, *Int. J. Inorg. Mater.* 1 (1999) 343–349.
- [36] J.J. Garcia-Jareno, A. Sanmatias, J. Navarro-Laboulasis, F. Vicente, *Electrochim. Acta* 44 (1998) 395–405.
- [37] H.J. Buser, D. Schwarzenbach, W. Petter, A. Ludi, *Inorg. Chem.* 16 (1977) 2704–2710.
- [38] X. Zhang, C. Sui, J. Gong, R. Yang, Y. Luo, L. Qu, *Appl. Surf. Sci.* 253 (2007) 9030–9037.
- [39] V.D. Neff, *J. Electrochem. Soc.* 125 (1978) 886–887.