

Short Communication

Electro-reduction of hydrogen peroxide on iron tetramethoxy phenyl porphyrin and lead sulfate electrodes with application in direct borohydride fuel cells

R.K. RAMAN¹ and A.K. SHUKLA^{1,2,*}

¹Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, 560-012, India

²Central Electrochemical Research Institute, Karaikudi, 630 006, India

(*author for correspondence, tel.: +91-80-22932795, fax: +91-80-23601310, e-mail: shukla@sscu.iisc.ernet.in)

Received 28 February 2005; accepted in revised form 6 May 2005

Key words: direct borohydride fuel cell, hydrogen peroxide, iron tetramethoxy phenyl porphyrin, lead sulphate

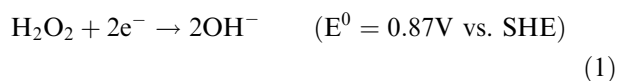
Abstract

Electroreduction of hydrogen peroxide in acidic medium is reported onto carbon-supported iron tetramethoxy phenyl porphyrin (FeTMPP/C) as well as carbon-supported lead sulphate (PbSO₄/C) electrodes. Both the catalytic electrodes can sustain electroreduction of hydrogen peroxide in direct borohydride fuel cells using hydrogen peroxide as oxidant but PbSO₄/C electrode shows catalytic activity.

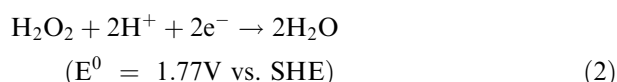
1. Introduction

Oxygen from air is commonly employed as oxidant in fuel cells [1], which restricts their operation to locations where free convection of air is absent, such as under water applications. To overcome this limitation, it becomes mandatory to use oxidants such as hydrogen peroxide in fuel cells [2]. There are two modes of using hydrogen peroxide as oxidant in fuel cells. One mode is to decompose hydrogen peroxide on a catalytic surface to oxygen and use the released oxygen for reduction in the fuel cell. The second is to use hydrogen peroxide as the oxidant directly in the fuel cell.

In an alkaline medium, hydrogen peroxide is reduced to OH⁻ ions as follows [3],



In the acidic medium, hydrogen peroxide is reduced to water according to the reaction [3],



In the literature, electro-reduction of hydrogen peroxide has been studied on platinum metal and palladium-iridium alloy, and has been employed in developing fuel cells for under water applications [2, 4, 5]. Platinoid-group catalysts are undoubtedly efficient for reducing hydrogen peroxide to water, but these cause partial decomposition of hydrogen peroxide to oxygen, which poses operational difficulties with the fuel cells. To mitigate this problem, it is imperative to find a catalyst

that is selective only to the electro-reduction of hydrogen peroxide [6]. Both direct methanol and direct borohydride polymer electrolyte membrane fuel cells operating on a solution of hydrogen peroxide as oxidant have been reported for ultra-portable applications [2, 4].

In this work, we have studied the electro-reduction of hydrogen peroxide separately onto iron tetramethoxy phenyl porphyrin (FeTMPP) and lead sulphate (PbSO₄) electrodes, and have examined their feasibility in realizing a direct borohydride fuel cell (DBFC). The study opens up a new possibility to develop low-cost direct borohydride fuel cells.

2. Experimental

About 60 mg of Vulcan XC-72R carbon was suspended in 20 ml of chloroform and 558 mg of FeTMPP was added to it while stirring the suspension. After 24 h of impregnation, chloroform was evaporated. Carbon-supported FeTMPP thus obtained was heat-treated in flowing hydrogen at 700 °C for 1 h. After heat treatment, 480 mg of carbon-supported FeTMPP catalyst was obtained [7].

In order to obtain PbSO₄, equimolar solutions of lead acetate and sulfuric acid were mixed in a beaker, filtered and washed copiously with hot distilled water. Resultant PbSO₄ precipitate was dried in an air oven at 80 °C for 12 h. PbSO₄ thus prepared was finely powdered and mixed with 10 wt% of Vulcan-XC-72R.

A three-electrode glass cell was used for cyclic voltammetric experiments using an AutoLab PGSTAT-30. The working electrode was prepared by mixing FeTMPP/C or PbSO₄/C with 10 wt% PTFE suspension to

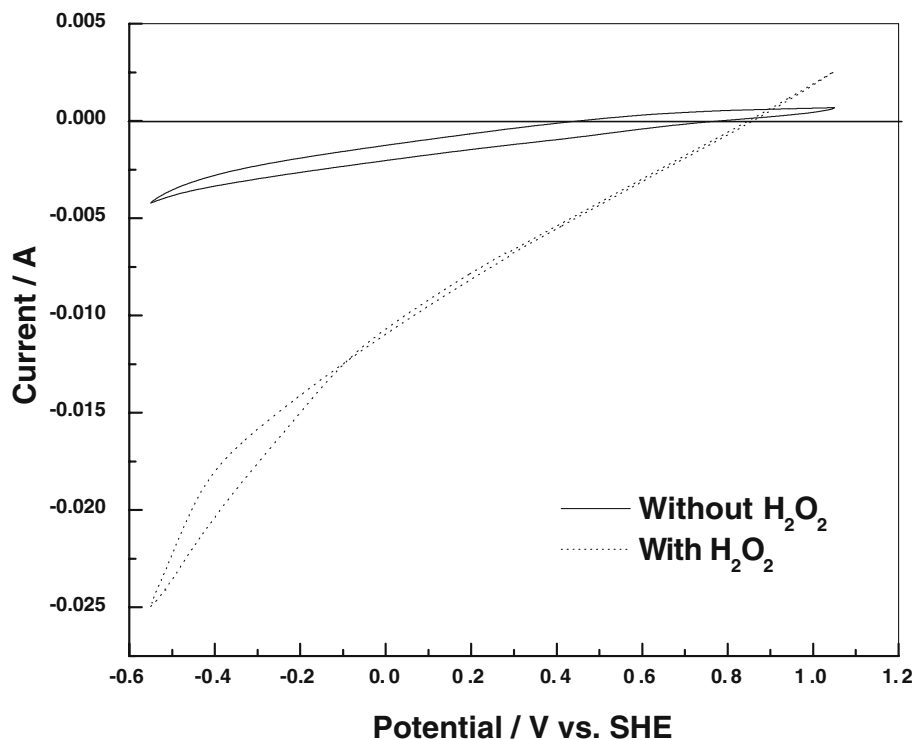


Fig. 1. Cyclic voltammograms for FeTMPP/C electrode in aqueous 0.5 M sulfuric acid with and without 0.5 M hydrogen peroxide.

obtain a thick paste, which was applied over stainless steel mesh, and compacted at 60 kg cm^{-2} to ensure its adhesion to stainless steel mesh; the electrode was subsequently heat-treated at $350 \text{ }^\circ\text{C}$ in N_2 atmosphere.

Membrane electrode assemblies were obtained by sandwiching the pre-treated Nafion[®]-117 polymer electrolyte membrane between the anode and cathode. To prepare the anode catalyst layer, a slurry of the AB₅-alloy (Mm Ni_{3.55} Al_{0.3} Mn_{0.4} Co_{0.75}), obtained by ultrasonically dispersing the required amount of alloy with 5 wt% Vulcan XC-72R carbon and 7 wt% of Nafion[®] solution in isopropyl alcohol, was pasted on carbon paper (Toray TGP-H-090) of 0.28 mm thickness. 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. In a similar manner, carbon paper (Toray TGP-H-090) of 0.28 mm thickness 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 carbon paper and dried in an air oven at $80 \text{ }^\circ\text{C}$ for 2 h. To prepare the reaction layer, the required amount of the catalyst (FeTMPP/C and PbSO₄/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 loading of cathode catalyst was 3 mg cm^{-2} for FeTMPP/C electrodes and 8 mg cm^{-2} for PbSO₄/C electrodes. A Nafion loading of 0.25 mg cm^{-2} was applied to the surface of each electrode. The membrane electrode assemblies (MEAs) with catalytic electrodes were obtained by hot pressing the cathode and anode on either side of a pre-treated Nafion[®]-117 membrane at 60 kg cm^{-2} at $125 \text{ }^\circ\text{C}$ for 3 min.

Liquid-feed DBFCs were assembled with various MEAs. The anode and cathode of the MEAs were contacted on their rear with gas/fluid flow field plates machined from high-density graphite blocks in which channels were designed to achieve minimum mass-polarization in the DBFCs. The ridges between the channels make electrical contact with the rear of the electrodes 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 blocks to heat the cell to the desired temperature. Aqueous sodium borohydride solution comprising 10 wt% NaBH₄ in 20 wt% aqueous NaOH was pumped to the anode chamber through a peristaltic pump. Optimized concentration of hydrogen peroxide (0.5 M) solution in 0.5 M H₂SO₄ 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. After installing single cells in the test station, performance evaluation studies were conducted.

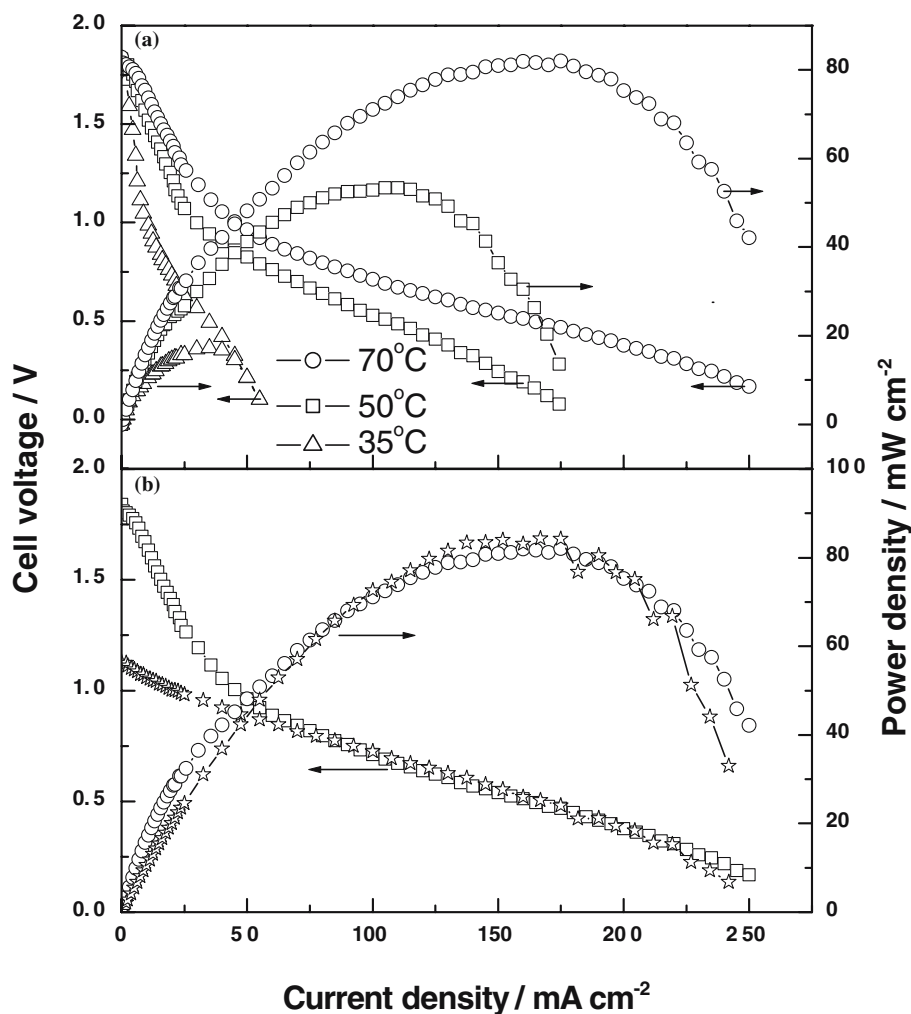


Fig. 2. (a) Cell polarization data for the DBFC operating at temperatures between 30 °C and 70 °C with alkaline aq. NaBH_4 feed at its anode and 0.5 M H_2O_2 in 0.5 M sulfuric acid solution feed at FeTMPP/C cathode, and (b) a comparison of DBFC polarization data with acidic hydrogen peroxide feed at FeTMPP/C cathode at 70 °C and alkaline hydrogen peroxide feed at FeTMPP/C cathode at 70 °C.

3. Results and discussion

Cyclic voltammograms for heat-treated FeTMPP/C catalyst in aqueous 0.5 M sulfuric acid, with and without 0.5 M hydrogen peroxide, are shown in Figure 1. These data indicate the onset potential for hydrogen peroxide reduction on FeTMPP/C electrode to be at 0.8 V. The galvanostatic polarization data for the DBFC with FeTMPP/C cathode between 30 °C and 70 °C are shown in Figure 2(a). Although an open-circuit voltage of 1.8 V is observed initially, it drops steeply to about 1.2 V subsequent to which the cell polarization with increasing current density is relatively low. Indeed, the cell polarization curve beyond 1.2 V matches well with the polarization data obtained for the cell operating with alkaline hydrogen peroxide solution shown in Figure 2(b). This observation is in conformity with Gojković et al. [7] who have shown FeTMPP/C to exhibit better catalytic activity in alkaline medium. We observe a maximum power density of 82 mW cm^{-2} , 53 mW cm^{-2} and 18 mW cm^{-2} at respective cell potentials of 0.5 V, 0.53 V and 0.5 V at 70 °C, 50 °C and 30 °C,

respectively. Anode potential in the cells measured against a standard hydrogen electrode (SHE) reference electrode was found closer to its thermodynamic value of -1.2 V for the entire load current density range [2]. By contrast, the cathode exhibited substantial polarization loss suggesting the cell to be cathode limited. As reported in the literature, either Fe(II)/Fe(III) redox couple [8] or graphitic carbon coated FeN_4 moiety generated during heat-treatment [9] in FeTMPP/C could be the possible active catalytic sites. In cyclic voltammogram shown in Figure 1, we do not see redox couple responsible for two oxidation states of Fe. Accordingly, we tend to believe that the FeN_4 moiety is the active catalytic site as reported in the literature [10].

Figure 3 shows the cyclic voltammogram for hydrogen peroxide reduction on PbSO_4/C electrode. Electro-reduction of hydrogen peroxide starts at 0.75 V (reaction 2) in acidic medium. The inset to Figure 3 shows that hydrogen peroxide reduction takes place in the potential range where the cathodic peak develops in absence of hydrogen peroxide, akin to that observed by Mocchi et al. [11] for oxygen reduction reaction on pyrolysed CoTMPP

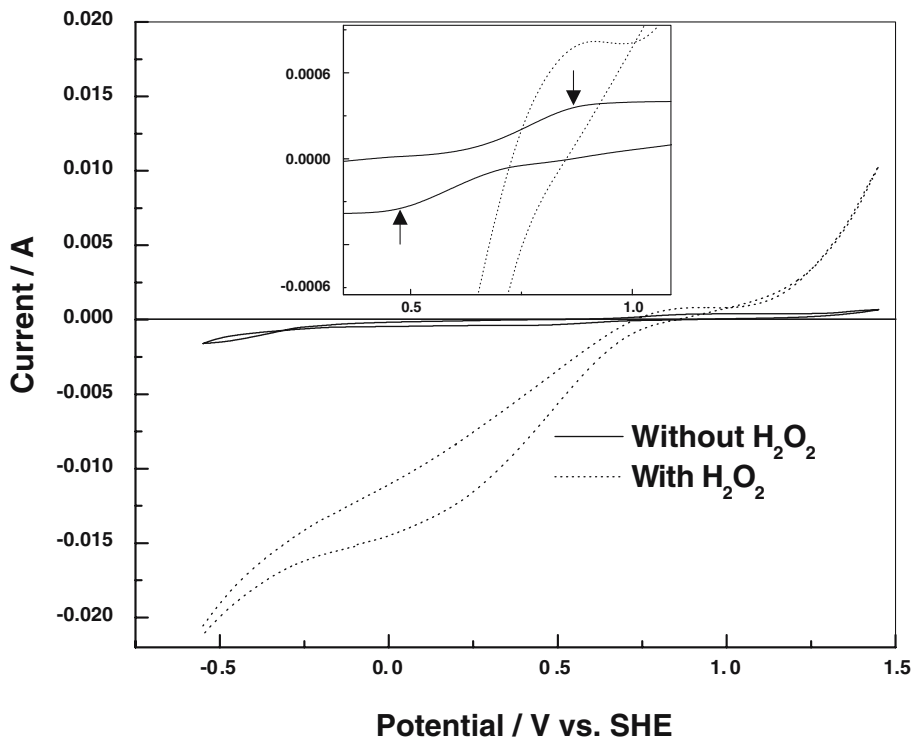


Fig. 3. Cyclic voltammograms for PbSO₄/C electrode in aqueous 0.5 M sulfuric acid with and without 0.5 M hydrogen peroxide. The inset shows the presence of Pb(II)/Pb(II+x) redox couple.

catalyst. Therefore, we believe that a Pb(II)/Pb(II+x) surface redox couple is responsible for the activity of PbSO₄ towards hydrogen peroxide reduction. Figure 4 shows the galvanostatic polarization curve for the DBFC with PbSO₄ cathode at varying load current densities

while operating it at 30 °C, 50 °C and 70 °C. We observe a maximum power density of 120 mW cm⁻², 65 mW cm⁻² and 32 mW cm⁻² at respective cell potentials of 1.1 V, 0.82 V and 0.67 V at 70 °C, 50 °C and 30 °C, respectively.

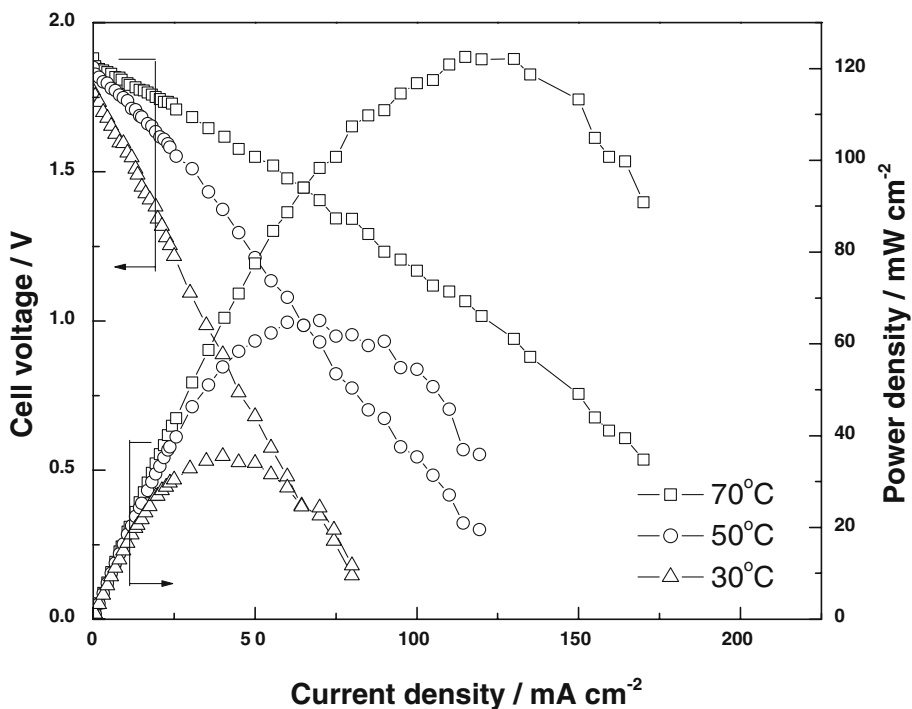


Fig. 4. Cell polarization data for the DBFC operating at temperatures between 30 °C and 70 °C with alkaline aq. NaBH₄ feed at its anode and 0.5 M H₂O₂ in 0.5 M sulfuric acid solution feed at PbSO₄/C cathode.

4. Conclusions

FeTMPP and PbSO₄ are shown to be possible catalysts for electro-reduction of hydrogen peroxide. As observed from cyclic voltammograms, the origin of the activity towards hydrogen peroxide reduction is due to a Pb(II)/Pb(II+x) redox couple on a PbSO₄/C electrode, while the presence of FeN₄ moiety is responsible for facilitating electro-reduction of hydrogen peroxide on FeTMPP electrode. The study demonstrates a DBFC with the aforesaid platinum-free catalysts and opens up a newer possibility to develop cost-effective fuel cells.

Acknowledgements

Financial assistance from the Council of Scientific and Industrial Research, New Delhi is gratefully acknowledged. We thank Dr. R. A. Mashelkar, F R S for his keen interest and encouragement.

References

1. A.K. Shukla, C.L. Jackson, K. Scott and R.K. Raman, *Electrochim. Acta* **47** (2002) 3401.
2. R.K. Raman, N.A. Choudhury and A.K. Shukla, *Electrochem. Solid State Lett.* **7** (2004) A488.
3. A.K. Shukla and R.K. Raman, *Annu. Rev. Mater. Res.* **33** (2003) 155.
4. T.I. Valdez, S.R. Narayanan, C. Lewis, and W. Chun in S. R. Narayanan, S. Gottesfeld and T. Zawodzinski (Eds), *Direct Methanol Fuel Cells*, Proceedings Volume 2001–04, The Electrochemical Soc. Inc. (2001) 265.
5. R.R. Bessette, J.M. Cichon, D.W. Dischert and E.G. Dow, *J. Power Sources* **80** (1999) 248.
6. A.A. Karyakin, E.E. Karyakina and L. Gorton, *J. Electroanal. Chem.* **456** (1998) 97.
7. S.L. Gojković, S. Gupta and R.F. Savinell, *J. Electroanal. Chem.* **462** (1999) 63.
8. D. Chu and R. Jiang, US Patent 6 245 707 (2001).
9. G.Q. Sun, J.T. Wang, S. Gupta and R.F. Savinell, *J. Appl. Electrochem.* **31** (2001) 1025.
10. G. Faubert, R. Côté, D. Guay, J.P. Dodelet, G. Dénès and P. Bertrand, *Electrochim. Acta* **43** (1998) 341.
11. C. Mocchi and S. Trasatti, *J. Molecular Catalysis A: Chemical* **204–205** (2003) 713.