

Rapid Communication

Bio-analogous electrode for oxygen reduction reaction

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A bio-analogous electrode consisting of a segment of single strand DNA-Zn porphyrin-Pt on carbon has been designed and fabricated. The system shows good oxygen reduction reaction activity even at as low as 1 wt.% Pt.

Keywords: Bioelectrodes Electrodes, Fuel cells, Oxygen reduction reaction

Fuel cells (PEMFC and DMFC) operate on a promising energy conversion technology. Typical advantages of fuel cells include high energy conversion and zero or low emission of pollutants. One of the technical barriers in the commercial viability of fuel cells is the high cost of Pt based electrodes. Research efforts have been focused on reducing the extent of Pt loading in the electrodes but retaining the electrochemical activity so as to enhance the reliability of fuel cells¹. The oxygen reduction reaction (ORR) activity at the cathode in fuel cells is a measure of the efficiency of these systems. Several attempts have been made to develop systems with enhanced ORR. Venkateswara Rao *et al.* have developed Pt-M/C (M=Fe, Co and Cr) alloy catalysts which exhibited ~ 1.5 times higher ORR activity and ~ 50 mV lower overpotential compared to the Pt/C (E-TEK) catalyst². Pt-M (V, Cr, Co, Ti, Ni) have been found to exhibit higher ORR activity compared to Pt alone in low temperature fuel cells³. Non-Pt electrodes like Pd-Fe/C (Pd₃-Fe/C) bimetallic alloys were found to exhibit ORR activity comparable to that of Pt/C⁴. Bezerra *et al.*⁵ have developed a non-noble metal based Fe-N/C ORR catalyst which exhibited a current density value of 0.23 A/cm² at a potential of 0.3 V. Charretier *et al.* have evaluated the effect of various carbon black supports on the ORR activity of Fe-N/C catalyst⁶. In addition, there have been attempts to use carbon supports with optimum characteristics⁶.

In one of the earliest attempts to develop a biological analogue for electrodes, we have fabricated a bioelectrode consisting of a segment of single strand (ss) DNA-Zn porphyrin-Pt on carbon. The system shows good ORR activity even at as low as 1 wt. % Pt.

Experimental

The requisite amount of ssDNA (Ocimum Biosolutions) [18.36 µg (200 µL, 10 µM in water)] was taken in 25 mL CCl₄ and stirred for 6 h. To this solution 2 µg of Zn porphyrin (2 mL of 1 µg/mL solution of Zn porphyrin in CCl₄) was added and allowed to interact with DNA by stirring for 24 h at 50 °C. To this system, 0.1 mL of H₂PtCl₆ solution, (Sisco Research Laboratory, India) (517.9 g/mol, 0.1058 M) in water (2 mg of Pt) was added. The contents were stirred for another 6 h. To this solution, 20 mg of NaBH₄ (Sisco Research Laboratory, India) (37.83 g/mol) in 5 mL water (mole ratio of H₂PtCl₆:NaBH₄ = 1:50) was added. The contents were again stirred for 12 h. To the resulting mixture of ssDNA-Zn porphyrin-Pt, 200 mg of graphite powder (Loba Chem) was added (1 wt. % of Pt w.r.t. graphite powder). The entire mixture was stirred for 24 h and subsequently the solvent was evaporated by rotary evaporation. The dried catalyst thus obtained was systematically characterized.

UV-vis spectra were recorded on a Jasco V – 530 UV/vis spectrophotometer. XRD pattern of the catalyst prepared was recorded using Rigaku miniflex II desktop X-ray diffractometer operated at 30 kV and 15 mA using Cu-K_α radiation (λ = 1.5418 Å) at a scan rate of 1°/min. The diffraction profiles were obtained in the scan range (2θ) of 5° – 90°

Cyclic voltammetric studies were carried out on a BAS Epsilon potentiostat using modified glassy carbon (Bioanalytic system, USA) as the working electrode, saturated Ag/AgCl as the reference electrode and a platinum wire as a counter (an auxiliary) electrode. The electrochemical measurements were carried out in a conventional three-electrode jacket glass cell. The oxygen reduction reaction was carried out in 0.5 M H₂SO₄ supporting electrolytic solution saturated with high pure N₂ followed by evaluating the ORR activity in the electrolyte solutions saturated with high pure oxygen. The working electrode was fabricated

as described by Venkateswara Rao *et al.*² Briefly, 10 mg of the catalyst was placed in 0.5 mL of isopropanol and ultrasonicated for 10 min. Then, 20 μ L of the dispersion was placed on 0.07 cm² of the glassy carbon electrode (57.41 μ g Pt/cm²) and the electrode was dried in an air oven at 363 K for a few minutes. The resulting catalyst coating was covered with 10 μ L of 5 wt. % Nafion solution followed by drying in air for a few minutes.

Results and discussion

The UV-vis spectra of Zn porphyrin alone and Zn porphyrin-ssDNA mixture in CCl₄ were recorded (Figs 1 (a) & (b)). Five characteristic absorption peaks at 476, 506, 546, 584 and 652 nm were observed in the case of Zn porphyrin. Upon addition of ssDNA, the first two peaks located at 476 and 506 in the original

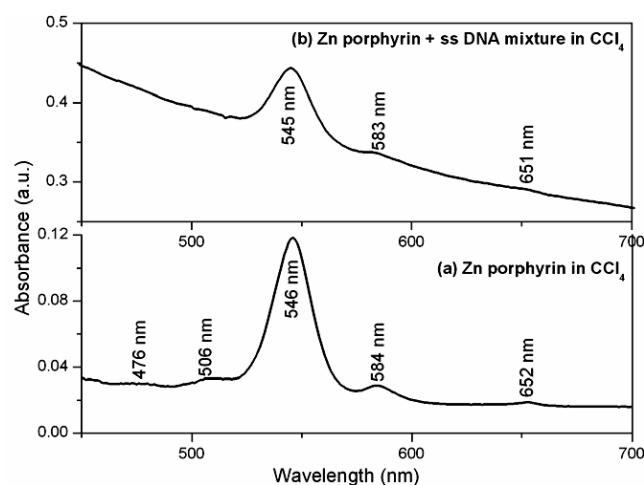


Fig. 1—UV-vis spectra of Zn porphyrin (a), and, Zn porphyrin and ssDNA mixture in CCl₄ (immediately after addition of ssDNA to zinc porphyrin solution) (b).

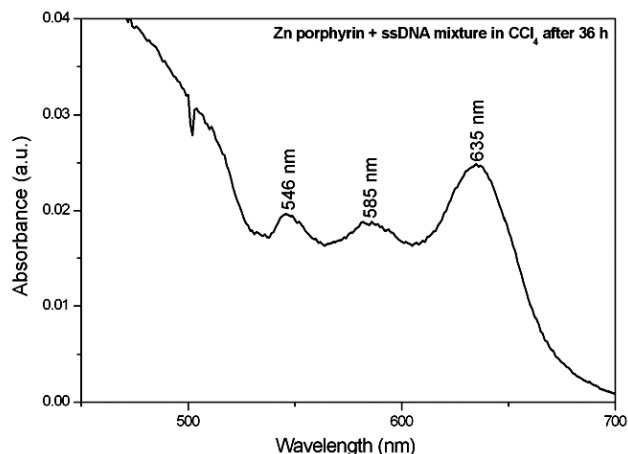


Fig. 2—UV-vis of porphyrin and ssDNA mixture in CCl₄ on standing for 36 h after addition of ssDNA to porphyrin solution.

Zn porphyrin absorption spectrum disappeared completely. Not only the addition of ssDNA but also the time of interaction between Zn porphyrin and ssDNA in CCl₄ has a noteworthy effect on the absorption spectrum of Zn porphyrin. The absorption spectrum of Zn porphyrin-ssDNA mixture in CCl₄, recorded after 36 h (Fig. 2), showed the reappearance of the first two bands located at 476 and 506 nm. Moreover, with time, the first three bands of the porphyrin, initially located at 476, 506 and 546 nm have respectively shifted to 547, 584 and 636 nm. These observations indicate the presence of interaction between the ssDNA and the Zn porphyrin moiety.

The X-ray diffraction pattern of the designed catalyst is shown in Fig. 3. The intense sharp peak located at a 2 θ value of 27° is indexed to the (002) diffraction plane of hexagonal graphitic carbon. Since the amount of Pt relative to graphite is very low (only 1 wt. % Pt with respect to graphite), the peaks characteristic of Pt metal are not visible. However, the diffraction peaks with low intensities (Inset of Fig. 3) at 2 θ values of 40.39, 47.0, 68.4, 82.4 and 87 are respectively indexed to the (111), (200), (220), (311) and (222) diffraction planes typical of Pt metal with a face centered cubic lattice (JCPDS file No. 87-0647). The characteristic bands observed in the FT IR spectrum of Zn-porphyrin at 1090, 1192, 1352, 1417, 1635, 2353 and 3450 cm⁻¹ have been retained in the case of the catalyst system, indicating that the structure of the Zn-porphyrin is unimpaired in presence of ssDNA, Pt and graphite. Thus, from the UV-vis and FT-IR results it is probable that weak interactions (probably hydrogen bonding) are present between the ssDNA and porphyrin, which needs further study.

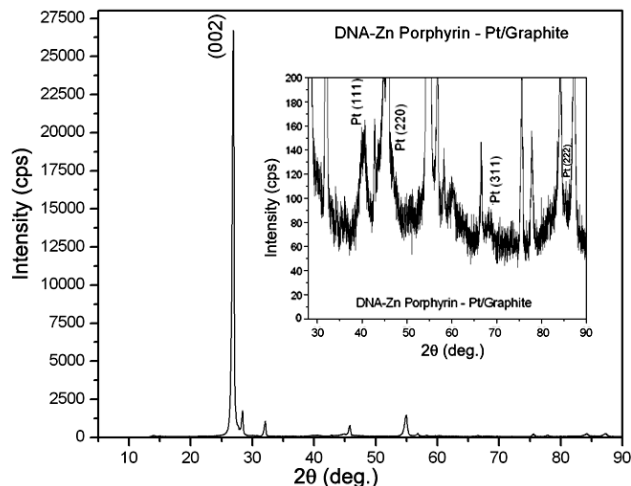


Fig. 3—XRD pattern of ssDNA-Zn porphyrin-Pt/graphite. [Inset: Peaks at low intensity].

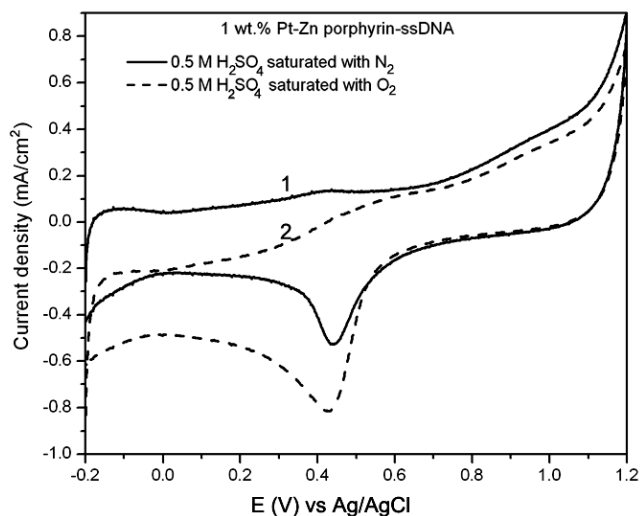


Fig. 4—Cyclic voltammetric response of GC/graphite – ssDNA Zn porphyrin Pt (1 wt.%)– Nafion electrode in 0.5 M H₂SO₄ saturated with nitrogen (1), and, oxygen (2) at a scan rate of 5 mV/s between -0.2 and 1.2 V vs Ag/AgCl.

The cyclic voltammograms recorded in both N₂ and O₂ saturated 0.5 M H₂SO₄ between -0.2 and 1.2 V vs Ag/AgCl are shown in Fig. 4. The electrocatalyst exhibited an ORR activity of 0.32 mA cm⁻² (at 0.7 V vs NHE) with an onset potential value of 910 mV vs NHE for ORR at a very modest loading of Pt with the Zn porphyrin facilitating the easy transport of the reduced species. It is deduced that Pt sites thus generated on the catalyst are in a favourable configuration for oxygen reduction reaction. This configuration may be arising out of the electronic environment around Pt or the geometry of the Pt site

with molecular entities similar to those in living systems.

Mediated electron transfer appears to be another pathway for designing electrodes for electrochemical devices. The present multiple component electrode system designed with ssDNA, Zn porphyrin, Pt and carbon shows good ORR activity. Further studies may provide appropriate clues for designing efficient electrodes for electrochemical devices based on the behaviour of living systems.

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