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POLYANILINE COATED EXPANDED GRAPHITE ACTS AS A NEW ELECTRODE MATERIAL FOR ETHANOL FUEL CELL

Abhik Chatterjee¹, I Basumallick²

¹Department of Chemistry, Raiganj college (University college), Raiganj

²Electrochemical laboratory, Department of Chemistry, Visva-Bharati University, Santiniketan

E-mail of Corresponding Author: acpcju@yahoo.co.in

ABSTRACT

An expanded graphite electrode coated with a thin layer of polyaniline and loaded with platinum has been used to study electro-oxidation of ethanol. The graphite plate electrode was expanded by doping with potassium (K)-vapour using vapour incorporation technique developed at our laboratory. The expanded graphite was platinised by electro-deposition technique and its electrochemical behaviour was examined using a laboratory model fuel cell. The open-circuit potential (OCP) and shortcircuit current (SCC) values of laboratory model fuel cell in 1M H₂SO₄ comprising of normal and expanded graphite electrodes having same catalytic loading as working electrode were observed. The expanded graphite electrode was also coated with a thin film of polyaniline and then loaded with Pt catalyst as before. Cyclic voltammogram of polyaniline coated electrodes in H₂SO₄ solution was investigated. Electro-catalytic activity of the modified electrode is better than Pt deposited electrode due to the higher reaction area of Pt particles.

Keywords: Polyaniline, ethanol, electro-catalyst, expanded graphite

INTRODUCTION

Metal microparticles dispersed in polymer modified electrodes have been widely used as electro-catalyst. There are various polymeric films, such as polypyrrole (PPY), polyaniline (PANI), poly(3-methylethiophene) (PMT), poly(3,4-ethylenedioxythiophene) (PEDOT), and so forth, have been investigated as conducting catalyst supports^{1,2}. These polymers are usually used as matrix to incorporate noble metal catalysts in the application for electro-oxidation of small molecules such as hydrogen, methanol and formic acid, etc

^{3,4,5}. Among the various conducting polymers, polyaniline (PANI) is one of them most interesting material because of its moderately high conductivity, well behave electrochemistry, easy preparation and possible applications as electro-catalyst towards various electro-oxidation reactions. A thin film of a conducting polymer (CP) improves the interfacial properties between the electrode and the electrolyte. Conducting polymer can allow a facile flow of electronic charge during the electrochemical oxidation of alcohol on Pt. Generally, an electrochemically deposited conducting polymer develops three dimensionally on a substrate⁶. Therefore, it introduces a high porosity and roughness;

as a result it generates a large surface area for electrochemical reactions.

The major problems of fuel cells are poisoning of the electro-catalyst even with Pt as the catalyst and its crossover from anode to cathode compartment. Besides electro-catalyst, the carbon material used as catalytic support also plays an important role in dictating fuel cell efficiency. In the present research an attempt has been made to improve catalytic activity of ethanol (EtOH) fuel cell using polyaniline coated expanded graphite as catalytic support material.

MATERIAL AND METHODS

H₂SO₄ (Merck), H₂PtCl₆.6H₂O (Arora Matthey Limited) were used as supplied. Aniline (Merck) and EtOH (Bengal chemicals) were distilled before use. The distillate was collected rejecting head and tail fractions.

The anode was a 1cm² graphite plate of thickness 3.8 mm obtained from the R&D of BHEL, India. Graphite plates were expanded using a simple technique developed at our laboratory. The experimental arrangement for expansion is shown in figure 1⁷. The graphite plate was expanded to an extent of 20% by potassium vapour. Pt particles were deposited on the working electrode (2 cm²) under galvanostatic condition using +10 mA.cm⁻² current for 30 minutes from chloroplatinic acid solution (0.01M) in 0.5M H₂SO₄.

The air cathode was fabricated by loading a 1cm² graphite plate with Pt. For the sake of comparison a Pt loaded anode without expansion was used. All experiments were carried out at 30°C.

Polyaniline was prepared galvanostatically. Electrolyte solution was 0.5 M aniline in 1M H₂SO₄ solution. The solution was taken in a one compartment cell in which supporting material was used as working

electrode and counter and reference electrode merged to Pt wire. -1 mA.cm⁻² current under galvanostatic condition was passed for 100seconds to deposit a film of PANI. After polymerization the polymer coated electrodes were washed repeatedly with distilled water and used for electrochemical studies. Cyclic voltammogram of PANI coated electrodes in H₂SO₄ solution was investigated using a potentiostat-galvanostat (PAR VersastatTM II).

Laboratory model fuel cell

Laboratory model fuel cells were housed in two glass rectangular chambers (50ml capacity) connected by an inverted U-shaped bridge. Cathode and anode, as fabricated above, were inserted into the respective chambers through the openings of the lid. H₂SO₄(1M) were poured into cathode and anode chambers, respectively. Alcohol was added to the anode chamber to obtain the desired concentration. The U tube was plugged with foam, which had been soaked in the acid to avoid crossover of alcohol. Air was bubbled slowly through cathode chamber using an air pump.

RESULTS

Figure 2 shows the galvanostatic polymerization curve of aniline on support material surface from a deposition bath of 0.5M aniline in 1M H₂SO₄. From the figure, it is clear that the polymerization starts at about potential of 0.95 volts and continues in the potential range of 0.9 to 1.0 V for a period of 100 seconds. Figure 3 shows the cyclic voltammogram of expanded graphite-PANI electrode in H₂SO₄ solution (blank) at a scan rate of 50 mV.s⁻¹.

It is found that within the potential limits – 0.2 to 1.3 V vs. SCE, the response changed on cycling⁸. After about the five cycles, the PANI film shows a steady response and

then it was used as an anode material for deposition of Pt. The open-circuit potential (OCP) and shortcircuit current (SCC) values of laboratory model fuel cell in 1M H₂SO₄ comprising of normal and expanded graphite electrodes having same catalytic loading as working electrode are shown in table1. Steady open-circuit potentials (OCP) were reached within 30 minutes. The potential remained undisturbed for an appreciable duration which indicates that these electrodes are stable in acidic medium. The shortcircuit current (SCC) values were measured after attainment of a steady OCP value. These data demonstrates the role of support material on the activity of catalyst.

To compare the performances of laboratory model fuel cells with different anodes, cells were discharged under 0.20 mA current for 180 minutes and profiles are presented in figure 4. The observed discharge profiles indicate that the cell with expanded graphite electrode exhibits better performances.

DISCUSSION

The CV of PANI coated electrode shows two peaks (figure 3). In the anodic scan, the peaks at about 0.57 V is due to SO₄²⁻ anion up taking. In the reverse scan, the peaks at about 0.23 V is due to SO₄²⁻ anion expulsion⁸.

Generally, graphite electrodes are utilised for providing support only, no electro-catalytic activity has been observed for alcohol fuel cell. Pt deposited on support material is known as an efficient electro-catalyst for alcohol oxidation. But the catalytic activity of the electrode can be enhanced if the support material is modified. It is seen from the table that OCP value is higher for Pt loaded expanded graphite material electrode. This indicates better catalytic effect of expanded graphite.

Electro-oxidation of EtOH takes place via an initial absorption onto the anode surface followed by deprotonation. For expanded graphite the nanographite channels act as better absorption sites⁷ and the electro-catalytic activity of Pt within these channels is also enhanced as is reflected in their SCC values (table1). Basically, potassium metal as dopant changes the interlayer distance between graphite layers. Table1 also indicates the relative improvement of catalytic effect of normal and expanded graphite when loaded with Polyaniline and Pt. It is very interesting that when Pt particles were deposited onto PANI coated electrode, catalytic effect is further improved. This is due to high dispersion of Pt particles. As a result the specific reaction area of these electrodes is increased and thus improves catalytic efficiency.

The observed discharge profiles (figure 4) indicate that the cell with expanded graphite electrode exhibits better performance. The reason is the higher tolerance of the platinum particles to poisoning effect, in comparison with the serious problem of poisoning effect on bulk platinum electrodes. PANI may adsorb some of the poisonous intermediates and thus the adsorption prevents the dispersed Pt particles from becoming deactivated⁹. Thus this research introduces the use of polyaniline modified expanded graphite as an efficient electrode material in fuel cell.

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Table-1: Electrochemical parameters for a laboratory model cell comprising of normal/expanded graphite as anode material in 1 M ethanol in 1M H₂SO₄ vs Air electrode (fabricated cathode)

Anode	OCP(Volt)	SCC(mA)
Graphite plate + Pt	0.710	0.230
Graphite plate + PANI + Pt	0.740	0.360
Expanded Graphite plate + Pt	0.728	0.320
Expanded Graphite plate + PANI+ Pt	0.754	0.470

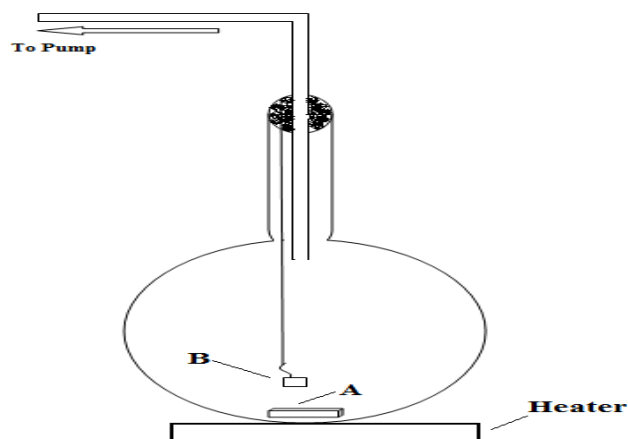


Figure-1: Expansion of graphite plate Using K-vapour, (A) solid block of potassium; (B) graphite electrode.

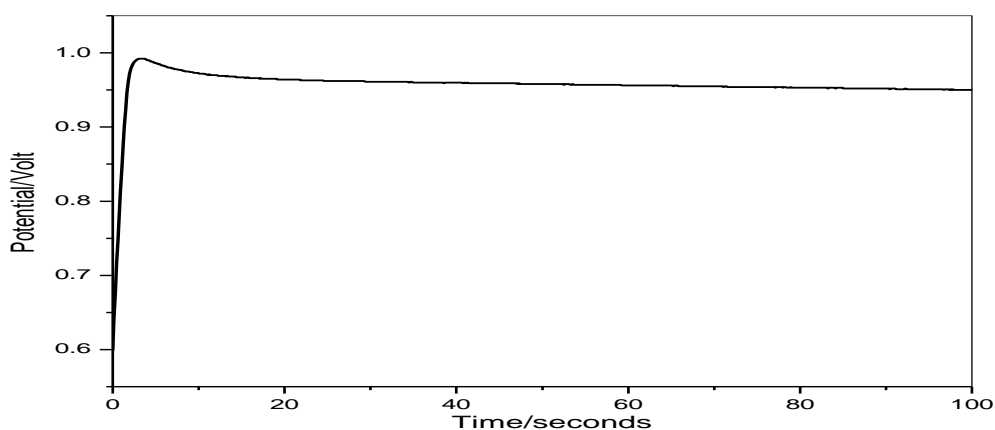


Figure- 2: Plot of potential vs. time for PANI deposition onto expanded graphite electrode.

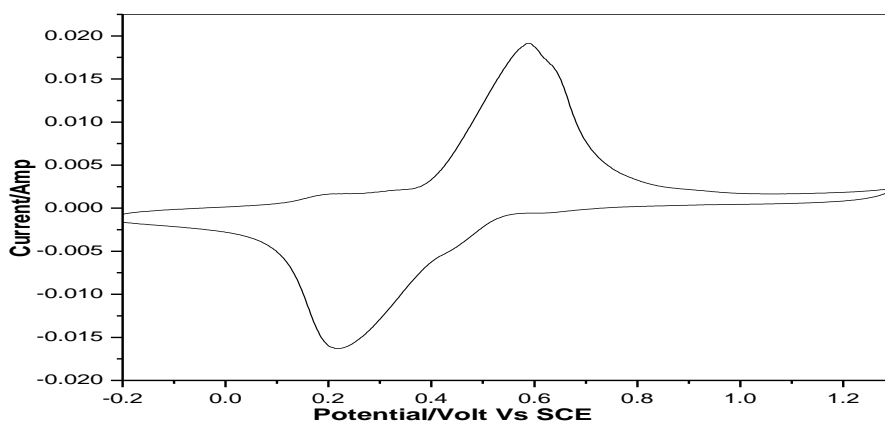


Figure-3: Cyclic Voltammogram (6th CV) of expanded graphite-PANI electrode in H₂SO₄ solution (blank). Scan rate 50 mV.s⁻¹.

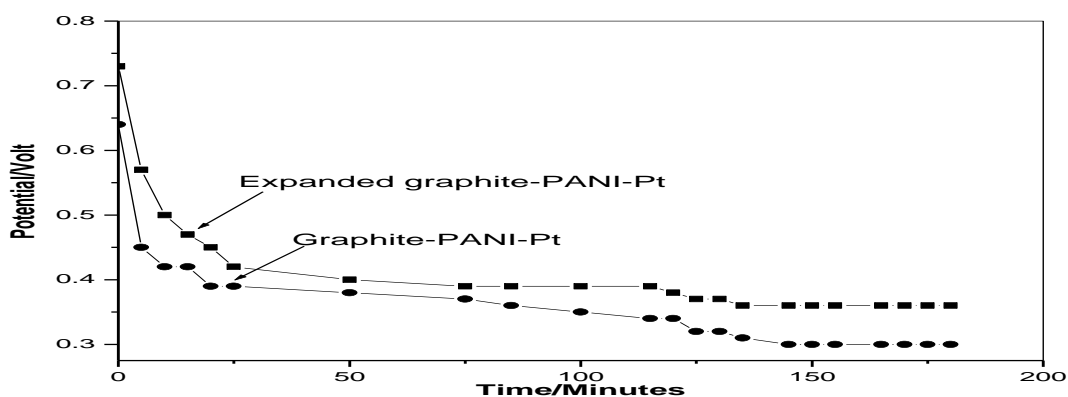


Figure-4: Discharge study of laboratory model direct ethanol fuel cell with normal and expanded graphite electrodes under a steady current drain of 0.20 mA.