



## Investigation of isopropanol electrooxidation onto deposited Pt particles supported on different materials

Abhik Chatterjee

Department of Chemistry, Raiganj University, Raiganj, Uttardinajpur, 73134, India

**Abstract :** In this article, graphite and potassium expanded graphite acts as support material for Pt deposition. The graphite plate electrode had been expanded by doping with potassium (K) vapour using simple vapour incorporation method. After expansion, the expanded graphite and normal graphite electrodes were platinised by galvanostatic electro-deposition technique. In this paper catalytic properties of the electrodes towards isopropanol have been presented using cyclic voltammetry technique at different scan rates and amperometry studies. From the study it is found that anodic peak potentials as well as the corresponding peak currents vary with scan rate. It is also observed that oxidation current of the alcohol using the expanded graphite as the electrode material are higher. Amperometry studies shows that expanded supported electrocatalyst is more long-lasting than unexpanded support electrocatalyst. So Pt deposited on potassium expanded graphite acts as a better electrocatalyst.

**Keywords :** Electrocatalyst, electrooxidation, isopropanol, cyclic voltammetry, expanded graphite.

### Introduction:

Fuel cell is the cleansource of current. Different kinds of fuel cells are in different stages of development. Among the different kinds of fuel cells, direct alcohol fuel cells (DAFCs) draw significant attention as power sources in various applications at low temperature [1]. Aliphatic alcohols have been promoted as promising fuels for direct alcohol fuel cells (DAFCs) in particular ethanol and isopropanol[2]. The DAFCs using C3-alcohols as fuel show better performance than DMFCs and a much lower crossover current[3-4]and suggests a high energy barrier forthe cleavage of the C–C bond for the isopropanol. Also studies have focused on 2-PrOH as an alcohols fuel cell becauseit shows a lower overpotential and higher performance thanmethanol.Alcohols withmore than two carbon atoms have a number of isomers and special features of non-COadsorption. Different studies shows that acetone is the main electro-oxidation product of 2-PrOH. No dissociative adsorption of 2-PrOH was seen by in situ infrared spectra. Acetone plays both the role of product and intermediate, and that the formation of a further oxidized product, CO<sub>2</sub>, was also observed. Electrooxidation of alcohols widely studied onto different electrodes and in different environment [5-9].But in recent time, special attention is focused to support materials of the catalystsand innovations of the new support materials are challenging as well as demanding. Support materials for platinum (Pt) deposition in fuel cell are the vital components. Among supports, carbons such as activated carbon, carbon black, graphite and graphitized material are used. The use of expanded graphite as a catalyst support was also reported [10-12].Carbon supports possesses the following properties: a large surface area,high porosity and good electrical conductivity. Platinum catalysts deposited on carbon supports are widely used as electrode materials in proton exchange membrane fuel cells (PEMFC) [13].Due to the fine dispersion of metallic particles a much larger number of catalytic sites are accessible for reagents than in a corresponding bulk metal.

In this article systematic studies of isopropanol electrooxidations onto normal graphite(C) and potassium expanded graphite(K-C) decorated with Pt particles have been reported.

## Experimental:

### Materials

H<sub>2</sub>PtCl<sub>6</sub> (AuroraMatthey Limited), Sulfuric acid (Merck) were used as supplied. 2-PrOH (Merck) was distilled before use.

### Electrode preparation

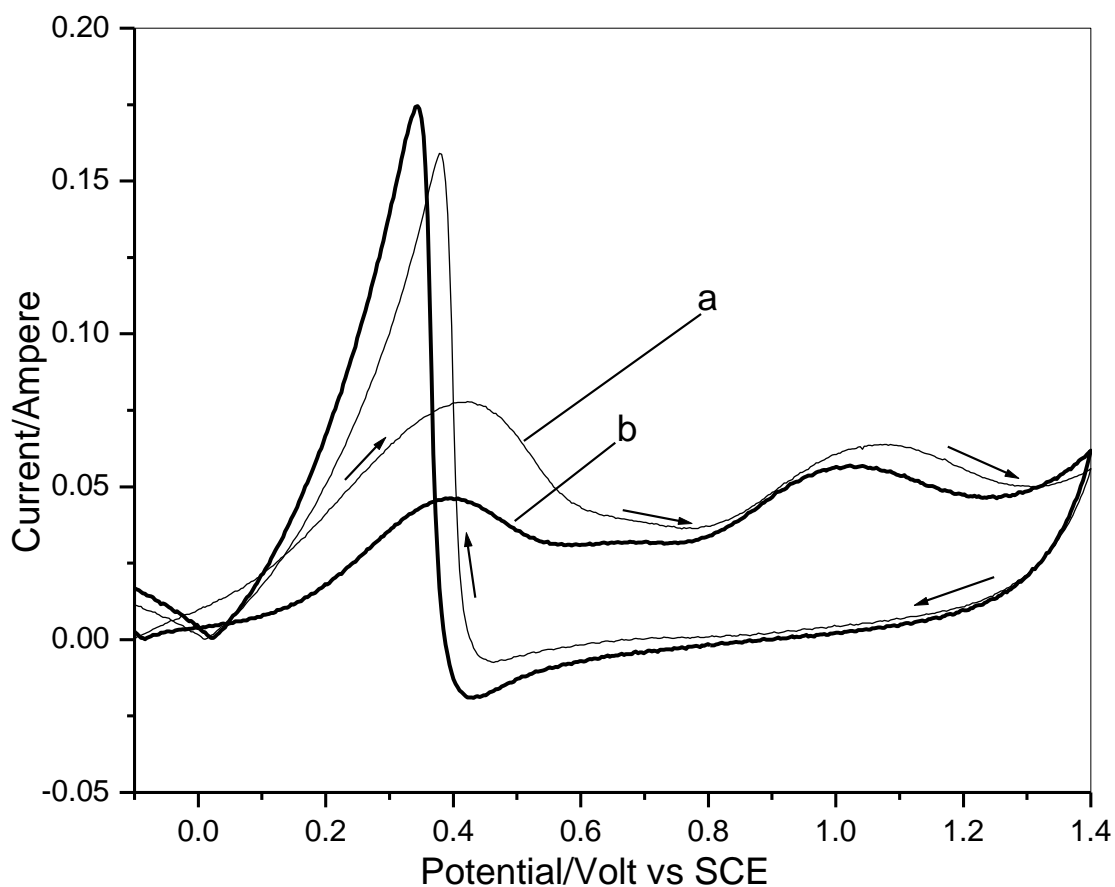
At first, graphite electrode was rubbed with sand paper and then boiled in distilled water for 15 minutes. The electrode surface was electrochemically cleaned by holding at 0.9 V vs. SCE for 30 seconds and then cycled in between -0.2 V to 1.1 V vs. SCE at a scan rate 30 mV s<sup>-1</sup>. Depositions were carried out galvanostatically (PAR VersaStat<sup>TM</sup> II) with a current density of 5 mA.cm<sup>-2</sup> for 30 minutes from chloroplatinic acid solution (0.01M) in 0.5M H<sub>2</sub>SO<sub>4</sub> deposition bath. Pt particles were deposited onto nonexpanded graphite the electrode hereafter referred as Pt/C electrode. Graphite plates were expanded using Potassium vapour [5,11]. Particles of Pt were deposited onto the potassium expanded graphite electrode under galvanostatic (PAR VersaStat<sup>TM</sup> II) condition using 5 mA.cm<sup>-2</sup> current for 30 minutes and the electrode hereafter referred as Pt/K-C.

### Electrochemical measurement

The catalytic property of all the deposited electrodes towards 2-PrOH oxidations was studied by cyclic voltammetry and amperometry technique. A three electrode arrangement was used for this electrochemical study, where supported electrodes were the working electrodes, the counter electrode was the Pt foil (1cm<sup>2</sup>), while a saturated calomel electrode (SCE) served as reference electrode. The electrolytes were 0.5 M sulfuric acid solution (blank), and 0.5 M sulphuric acid containing 2-PrOH (1.0M) solution. The electrooxidations were measured by cyclic voltammetry at different scan rates and durability was tested using amperometry technique. Electrochemical experiments were performed using a Potentiostat-galvanostat (VersaStat<sup>TM</sup> II, Princeton Applied Research). All the experiments were carried out at 25°C.

## Results and discussion:

Cyclic voltammograms of isopropanol electro oxidations in H<sub>2</sub>SO<sub>4</sub> medium at 30 mVs<sup>-1</sup> scan rate have been presented in figure 1. Initial kinetics of these electrodes is much slower followed by a sharp rise in current density. Cyclic voltammogram of isopropanol solution shows three oxidation peaks, at about 0.4V and at about 1.07V in the forward scan separated by a deep minimum and in the cathodic sweep i.e, the negative-going scan is characterized by an anodic peak at 0.3 V and this is attributed to renewed oxidation of the fuel.



**Figure 1. Cyclic Voltammograms of isopropanol solution onto (a) Pt deposited K-expanded graphite material and (b) Pt deposited graphite material Scan rate 30 mv/s.**

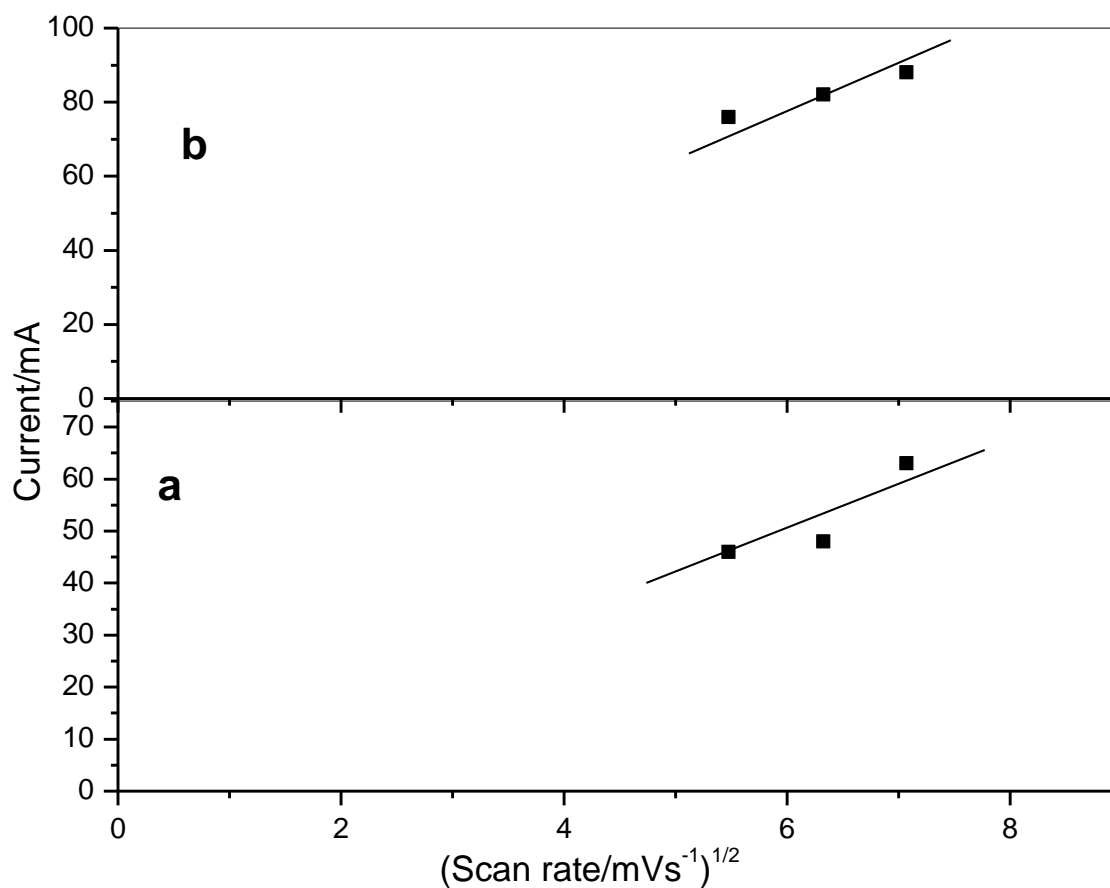
The first peak in the forward scan corresponding to the dehydrogenation of the alcohol and the second one associated with bulk oxidation of 2-propanol. It is undoubtedly seen from figure 1 that the onset potential for electro-oxidation of 2-PrOH is shifted to lower potential value on the expanded graphite surface (Pt/K-C). Two forward peak potentials onto (Pt/K-C) surface remarkably shifted to lower potential value compared to Pt/C surface. The anodic peak current of 2-PrOH electro-oxidation onto (Pt/K-C) surface is also higher than that of Pt (Pt/C). All these indicate significant enhancement of catalytic activity of Pt in presence of expanded support material. From the graphs it is clear, though patterns are the same, but the overall kinetics in expanded catalyst surface is superior to normal graphite support for isopropanol electro-oxidation. Actually chemical species (potassium) inserted into interlayer spacings of graphite. This improved catalytic activity may be due to some ion channel formation, which may be due to the higher surface area and some nanochannel formation [11].

The current  $I_p$  (considering the first oxidation peak) increases with the square root of scan rate. Plots of the anodic peak currents of isopropanol oxidation ( $I_p$ ) versus scan rates ( $V$ ) ranging from 30 to 50  $mVs^{-1}$  gave straight lines (figure 2) and thus obeys the following relationship.

$$I_p = 2.985 \times 10^5 n [(1-\alpha)n\alpha]^{-1/2} A D^{1/2} C V^{1/2} \quad (1)$$

Where  $I_p$  is the anodic peak current (mA),  $n$  is the number of electrons involved in the oxidation,  $A$  is the area of electrode ( $cm^2$ ),  $V$  is the scan rate ( $Vs^{-1}$ ),  $C$  is

The concentration of the electro active species in bulk solution ( $mol\ cm^{-3}$ ). Thus isopropanol electro-oxidation onto both electrodes show irreversibility.

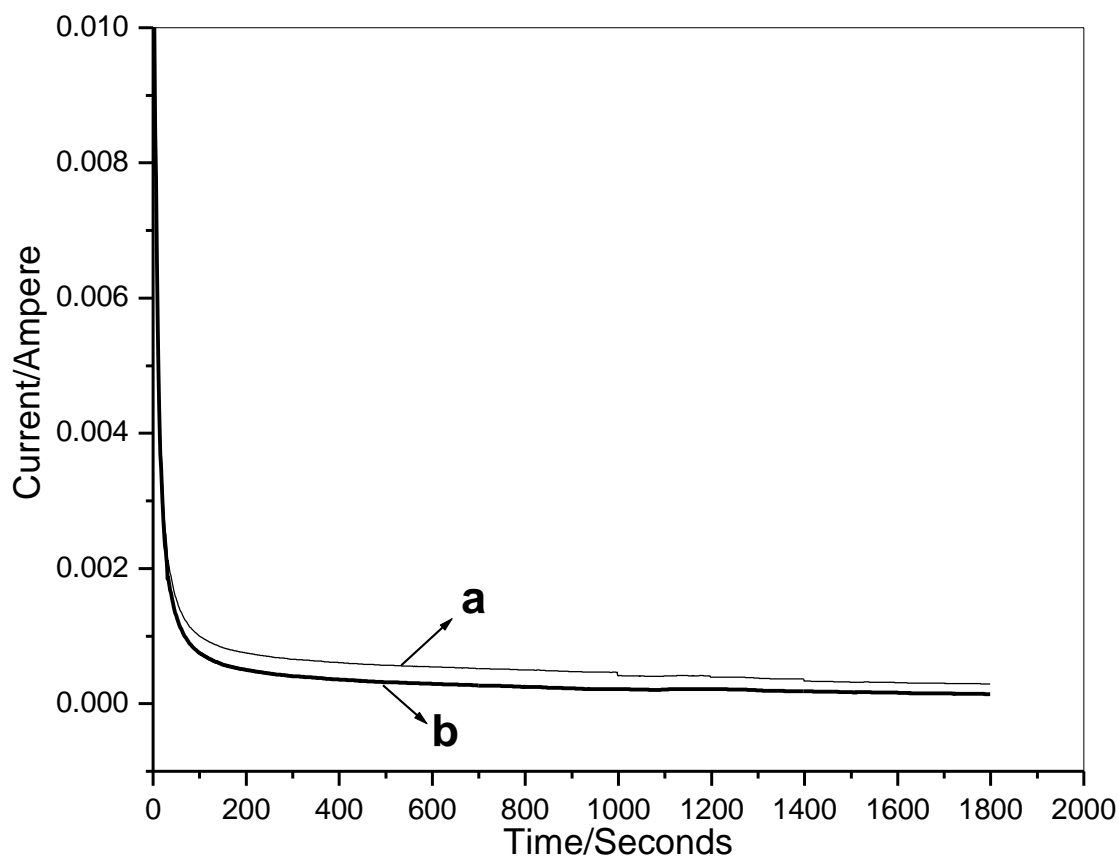


**Figure-2. Peak current versus square root of scan rate (a) Pt deposited graphite material and (b) Pt deposited K-expanded graphite material.**

The forward peak current (first peak consideration) in the anodic sweep and the reversed peak current in the cathodic sweep are compared in table 1, and a significant increase in both the current densities are observed with the expanded supported catalyst compared with the non expanded supported catalyst. However peak current of Pt/C-K was 1.6orders of magnitude higher than those obtained incase of Pt/C. It is also seen from the table that the tolerance power of expanded material is also higher.

**Table 1. Peak currents and tolerance power**

Catalyst	$I_f$	$I_b$	Tolerance power ( $I_f/I_b$ )
Pt/CK	0.077	0.158	0.48
Pt/C	0.046	0.173	0.27



**Figure-3:Amperometric i-t curves of 2-PrOH electro-oxidation at 0.45 volt onto Pt and expanded catalyst.**

The stability of the electrocatalysts in the reaction condition for alcohol oxidations is one of the major factor in DAFCs. This can be roughly estimated by amperometric studies ( $i-t$  curves). Figure 3 shows Amperometry curves of (a) Pt deposited K-expanded graphite material and (b) Pt deposited graphite material for isopropanol oxidation at 0.45 V. Expanded graphite based electrode shows better life time towards isopropanol oxidation.

## Conclusion

In this work, a comparative study has been performed on the electro-oxidation of 2-propanol onto graphite supported Pt particles and expanded graphite supported Pt particles. Cyclic voltammogram (CV), onset potential ( $E_s$ ), peak potential ( $E_p$ ), peak current ( $I_p$ ) and amperometry studies have been used to compare the electrocatalytic activity of the electrodes towards alcohol electrooxidations. On the basis of these parameters and studies it is concluded that deposited Pt particles onto potassium expanded graphite act as a better electrode. The improved catalytic effect of expanded electrode is due to enhanced surface area and nanochannel formation.

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