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ELECTRO-OXIDATION OF ETHANOL AND ISOPROPANOL ONTO PT-SN AND PT-NI SURFACES

Abhik Chatterjee[1], Moitrayee Chatterjee[2], Susanta Ghosh[3],
I Basumallick[2]

[1]Department of Chemistry, Raiganj College (University College), Raiganj, W.B
[2]Electrochemical laboratory, Department of Chemistry, Visva-Bharati University, Santiniketan, W.B, INDIA
[3]ISERC, Visva-Bharati University,Santiniketan, W.B.

E-mail of Corresponding Author: abhikchatterjee07@gmail.com

ABSTRACT

A simple galvanostatic method is reported on the preparation of bimetallic Pt-Sn and Pt-Ni catalysts on graphite sheet electrode and studied their catalytic activity towards isopropanol (2-Propanol or 2-PrOH) and ethanol (EtOH) electro-oxidation. These catalysts have been characterized by SEM, EDX, Cyclic voltammetry (CV) and amperometry technique. The surface area of the deposited binary electro-catalysts has been estimated from Cu-UPD technique. A striking opposite catalytic behavior of $Pt_{86}Sn_{14}$ is observed for EtOH and 2-PrOH oxidation. Presence of Sn enhances catalytic activity of Pt for EtOH oxidation, while it deactivates the same for 2-PrOH oxidation. On the other hand, incorporation of small percentage of Ni in binary $Pt_{98}Ni_2$ enhances its catalytic activity for oxidation of both the alcohols. The results are explained in terms of bifunctional effect, electronic effect and strong adsorption of intermediate products.

Keywords: Electro-oxidation, Ethanol, Isopropanol, Binary electrocatalyst, Electronic effect, Bifunctional mechanism.

INTRODUCTION

Direct alcohol fuel cells (DAFCs) have drawn tremendous attention as power sources in numerous applications at low operating temperature. Among several alcohols, which can be used in a direct alcohol fuel cell (DAFC) are methanol (MeOH), EtOH and 2-PrOH [1]. Electro-oxidation of higher carbon atom alcohols involves more intermediates and products than that of methanol electro-oxidation and thus more efficient electro-catalysts are needed at lower temperature. Platinum is the best choice as an electro-catalyst, but its cost and surface poisoning phenomenon inhibit it from large scale applications. Thus, enhancement of catalytic activity of Pt in the presence of a second metal for electro-oxidation of simple alcohols is the field of research interest as it will reduce the cost of the catalyst without losing much efficiency. The longevity as well as efficient catalytic activity of bimetallic catalysts, such as Pt-Ru, Pt-Sn, Pt-Ni, can be explained in terms of bifunctional effect, electronic effect or combination of these two effects [2-4]. When the second metal is more oxophilic, like Ru, or Sn, it improves catalytic activity of Pt through bifunctional mechanism.

Thus the catalytic activity and its longevity may be enhanced by incorporating a second metal, like Ru or Sn. Pt-Sn has been reported as an effective electrocatalyst for methanol and ethanol oxidation, which is comparable with Pt-Ru catalyst having lower cost [5,6]. But very few reports are available in the literature on electro-oxidation of 2-propanol on bimetallic electrodes [7,8].

On the other hand, a second metal like Ni enhance the catalytic activity of Pt towards alcohol oxidation by altering the electronic states of the original catalytic metal, Pt [9,10]. But similar studies with 2-PrOH electro-oxidation are neither extensive nor conclusive.

Therefore the objective of the present study is to report the results of systematic studies on electro-oxidation of 2-PrOH in the presence of Pt-Sn and Pt-Ni catalysts, at their optimum compositions and compare the same with those of ethanol oxidation under similar conditions. It is expected that the present study will help in understanding the potentiality of Pt-Sn and Pt-Ni as electrocatalyst for 2-PrOH oxidation, which is a fuel of high theoretical power density.

MATERIAL AND METHODS

Materials: Sulfuric acid (Merck), Acetone (Merck), H_2PtCl_6 (Arrora Matthey Limited), $SnCl_2$ (Merck), $NiSO_4$ (E-Merck) were used as supplied. EtOH (Bengal chemicals) and 2-PrOH (Merck) were distilled before use.

Electrode preparation: Graphite sheet (Alfa-Aesar) was taken as substrate for metal deposition. Before each deposition, the graphite surface was electrochemically cleaned. Depositions were carried out galvanostatically (PAR VersaStat^{TM}II) with a current density of 2.5mA.cm^{-2} for 30 minutes.

Electrode characterization: The surface morphologies of the anode materials were investigated with a scanning electron microscope (SEM), at an accelerating potential of 20kV. The elemental compositions of the electro-deposited catalysts were determined by energy dispersive X-ray (EDX) analysis.

Electrochemical measurement: The catalytic activity of all the deposited electrodes towards EtOH and 2-PrOH oxidation was studied by cyclic voltammetry technique and amperometry (at 25^{o}C). A three electrode setup was constructed for this study, where carbon supported electrodes (1cm x 1 cm) were the working electrodes, the counter electrode was the Pt foil (1cm^2), 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 EtOH/2-PrOH (1.0M) solution. Cyclic voltammograms of the blank solution and alcohol solutions were recorded between -0.2 to 1.1 V vs. SCE at a scan rate of 30 mV .s^{-1}. Amperometry measurements were done in 1.0 M EtOH and 2-PrOH in 0.5 M H_2SO_4 at 0.45 V for 1800s.

Surface area determination: The active surface area of the electrodes was determined by under-potential deposition of copper (Cu-UPD) and anodic stripping [6, 11]. To begin the surface area estimation, the linear sweep voltammogram (LSV) of a clean catalyst sample was recorded in 0.1M H_2SO_4 over a range of 0.059V to 0.8V vs. SCE at a sweep rate of 10mVs^{-1}. Afterwards, the working electrode was transferred into the solution containing 0.1M H_2SO_4 and 2 mM $CuSO_4$ solution for deposition of the Cu UPD monolayer. The electrode then polarized at 0.8V for 120s and then stepped to 0.059V for 300s. The anodic stripping was performed by carrying out a linear scan between 0.059V to 0.8V vs. SCE at 10mV.s^{-1}. The charge associated with this copper stripping was calculated by integration method after subtracting the charge associated for background process. The electro-active surface area was then calculated with the assumption of an adsorption ratio of a single Cu atom to each surface metal atom and a monolayer charge of 420 µC cm^{-2}.

RESULTS AND DISCUSSION

The literature report reveals that the optimum atomic percentage of Sn in Pt-Sn alloy for ethanol oxidation is 10-20 atom%, thus an intermediate composition, 14 atom % of Sn, has been selected [12,13]. For Pt-Ni alloy, a small atomic percentage, 2 atom% Ni, has been chosen in order to avoid leaching of Ni in acidic medium.

The loading of the electro-active metals onto graphite sheet has been calculated considering 100% coulombic efficiency. Calculated Pt loading is found to be 0.045 mg. cm^{-2}. The surface area of the electrodes is determined by Cu-UPD method . The effective surface area of Pt, Pt-Ni and Pt-Sn electrodes are 100, 97 and 88 cm^{2}, respectively.

The SEM images of the Pt, Pt-Sn, and Pt-Ni electrode surfaces have been presented in figure 1, 2 and 3, respectively. Though the SEM images do not provide much information on particle size and its growth kinetics, but a uniform growth of relatively smooth catalyst layer is reflected. Some elongated agglomerate was observed on Pt-Ni surface. On an average, the approximate particle size for those electro-catalysts range from 200 to 250 nm. The energy dispersion X-ray spectrums of the bimetallic catalysts show the composition of the catalysts (spectrums are not shown). Based on the composition of the catalysts, the electrodes may be designated as $Pt_{86}Sn_{14}$ and $Pt_{98}Ni_2$. Typical cyclic voltammograms of the blank and those of 1.0 M EtOH and 2-PrOH oxidation in 0.5M H_2SO_4 medium at 30 mV.s^{-1} scan rate within the potential limit –0.2 to 1.1V vs. SCE are shown in figure 4, 5 and 6, respectively. The CVs of the blank solutions (figure 4) exhibit typical hydrogen desorption/ adsorption for Pt and $Pt_{98}Ni_2$, but no such peaks are observed with $Pt_{86}Sn_{14}$ electrocatalyst. The characteristic features of alcohol oxidation on Pt surface, i.e. two well-defined oxidation peaks are found during the forward and the reverse scans. It is clearly seen from figure 5 and figure 6 that the onset potentials for electro-oxidation of EtOH are largely shifted to lower potential value on the bimetallic catalyst surface. The anodic peak current density of EtOH oxidation, normalized w.r.t. loading, on to $Pt_{86}Sn_{14}$ surface is also higher than that of Pt. All these indicate significant enhancement of catalytic activity of Pt in Pt-Sn bimetallic catalyst for EtOH oxidation. Contrary to this, a strong catalytic deactivation of Pt in Pt-Sn is observed (figure 5) for 2-PrOH oxidation. The opposite catalytic activity of $Pt_{86}Sn_{14}$ towards EtOH and 2-PrOH oxidation indicates that mechanism of electrooxidation of EtOH and 2-PrOH are different onto $Pt_{86}Sn_{14}$ surface. The observed catalytic deactivation on to $Pt_{86}Sn_{14}$ surface for 2-PrOH oxidation may be explained due to the adsorption of acetone, which is formed as an intermediate product during electro-oxidation of 2-PrOH on the electrode surface [13]. In order to confirm the finding, CVs of pure acetone on to $Pt_{86}Sn_{14}$ and $Pt_{98}Ni_2$ catalyst are recorded as shown in figure 7. It is interesting that no anodic peak is observed onto $Pt_{86}Sn_{14}$ surface. However, acetone oxidation starts at 0.5V and a maximum is appeared at 0.585 V vs. SCE onto $Pt_{98}Ni_2$ surface. Thus, the observed catalytic deactivation of $Pt_{86}Sn_{14}$ for 2-PrOH oxidation is attributed due to formation of acetone intermediate. Electro-oxidation of ethanol onto Pt-Sn surface seems to occur through bi-functional mechanism by water activation process as follows;

$$Sn + H_2O \longrightarrow Sn-(OH) + H^+ + e^-$$

The adsorbed aldehyde species formed during EtOH oxidation then react with adsorbed -OH to produce acetic acid as follow;

$$Pt + CH_3CH_2OH \longrightarrow Pt\text{-}CH_3CHOH_{ads} + H^+ + e$$

$$Pt\text{-}(COCH_3) + Sn\text{-}(OH) \longrightarrow Pt + Sn + CH_3COOH$$ and so on.

Anodic peak current onto $Pt_{98}Ni_2$ catalyst surface for electro-oxidation of these alcohols are higher than that of pure Pt and onset potentials are largely shifted to lower potential values. Thus, shift of onset potential and higher anodic peak current values are indicative of better electro-catalytic activity of $Pt_{98}Ni_2$ for both the alcohols. As Ni-O bond energy is about 200 $kJ.mol^{-1}$ lower than that of Pt-C bond, bi-functional mechanism does not operate here for EtOH or 2-PrOH oxidation, but the observed enhancement of catalytic activity of Pt in presence of trace amount of Ni may be due to its electronic effect.

Amperometry studies (figure 8 and figure 9) also corroborate these findings, showing better catalytic activities of $Pt_{98}Ni_2$ for EtOH and 2-PrOH, but poor catalytic activity of $Pt_{86}Sn_{14}$ towards 2-PrOH oxidation.

CONCLUSION

In the present paper, electro-oxidation of EtOH and 2-PrOH has been studied on to $Pt_{86}Sn_{14}$ and $Pt_{98}Ni_2$ surfaces. In case of EtOH, improved catalytic activities of Pt are observed in the presence of Ni and Sn. This is explained in terms of electronic effect of Ni and bi-functional effect of Sn. However, for 2-PrOH oxidation catalytic activity of Pt inhibited in the presence of Sn. This is due to the formation of acetone during 2-PrOH oxidation and its strong adsorption onto Sn surface. This was confirmed by cyclic voltammogram of acetone onto $Pt_{86}Sn_{14}$ surface that indicates inactiveness of this catalyst towards acetone oxidation. Thus, present study does not recommend $Pt_{86}Sn_{14}$ as a catalyst for 2-PrOH electro-oxidation, but it recommends the same as potential catalyst for ethanol oxidation with a caution that ethanol should be free of contamination of secondary alcohols like 2-PrOH and ketones like acetone.

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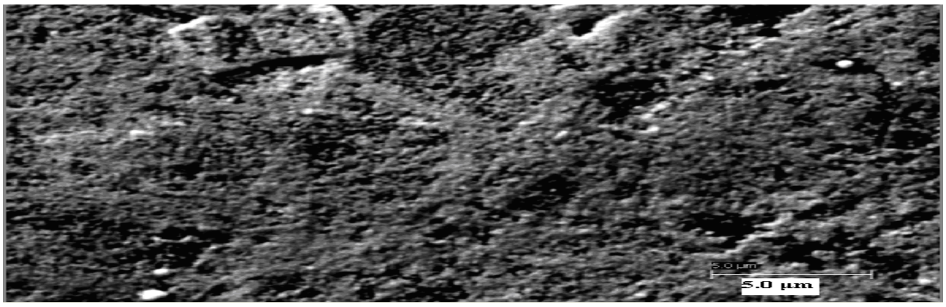

Figure-1: SEM image of carbon supported Pt electrode.

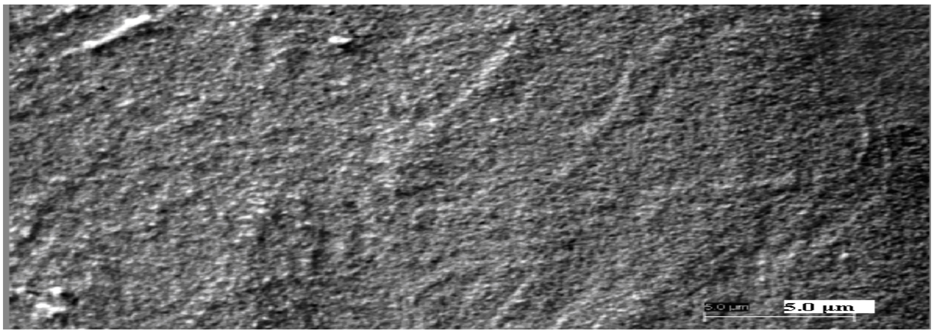

Figure-2: SEM image of carbon supported $Pt_{86}Sn_{14}$ electrode.

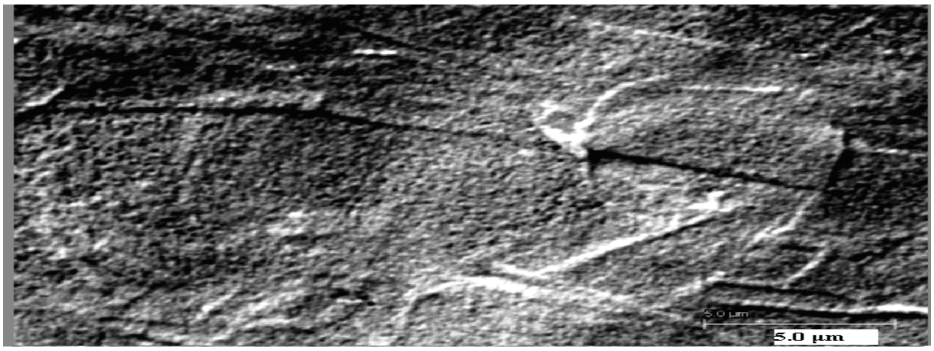

Figure-3: SEM image of carbon supported $Pt_{98}Ni_2$ electrode.

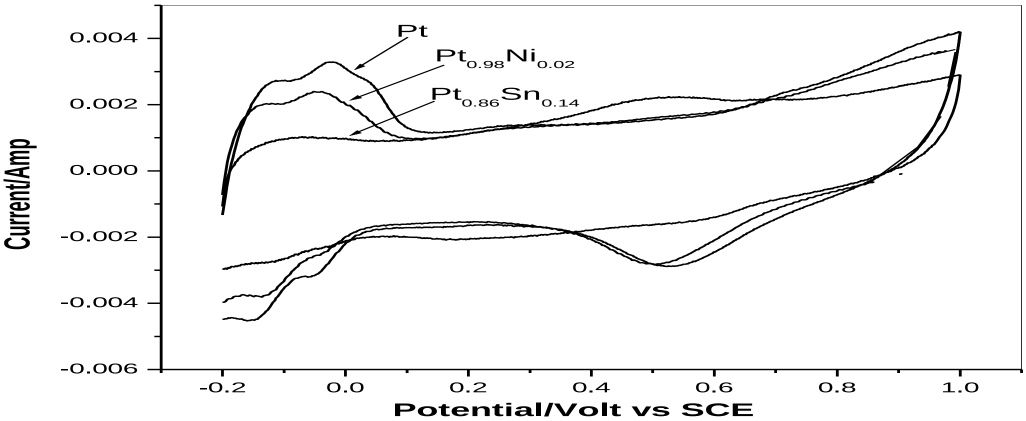

Figure-4: Cyclic Voltammograms in H_2SO_4 solution (blank).

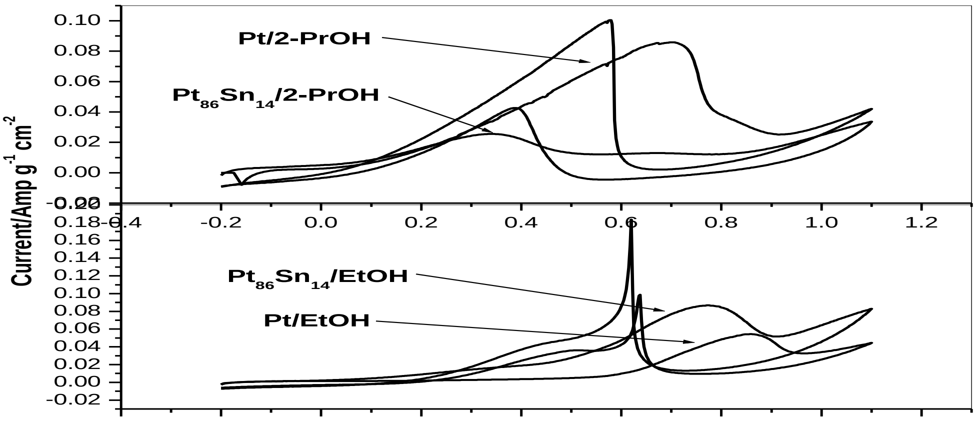

Figure-5: Cyclic Voltammograms of 1.0M EtOH and 2-PrOH in H_2SO_4 solution onto Pt and $Pt_{86}Sn_{14}$ catalyst.

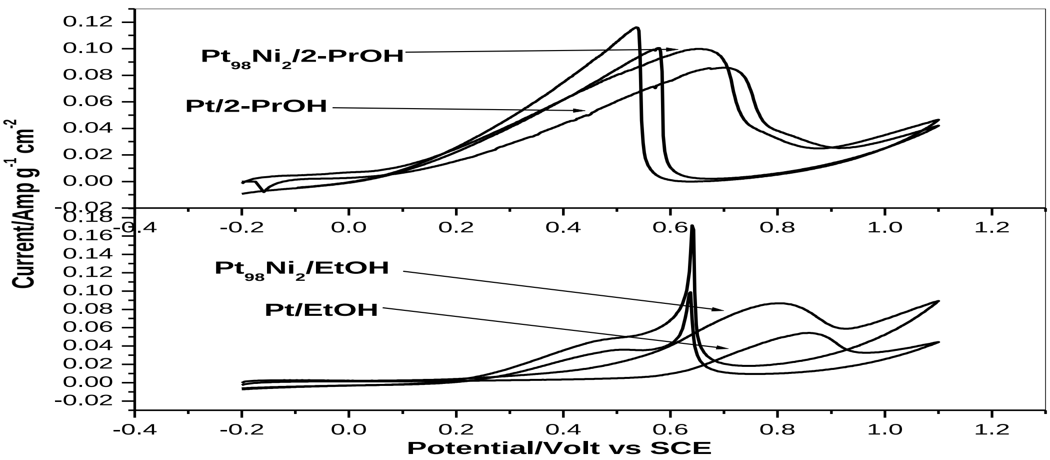

Figure-6: Cyclic Voltammograms of 1.0M EtOH and 2-PrOH in H_2SO_4 solution onto Pt and $Pt_{98}Ni_2$ catalyst.

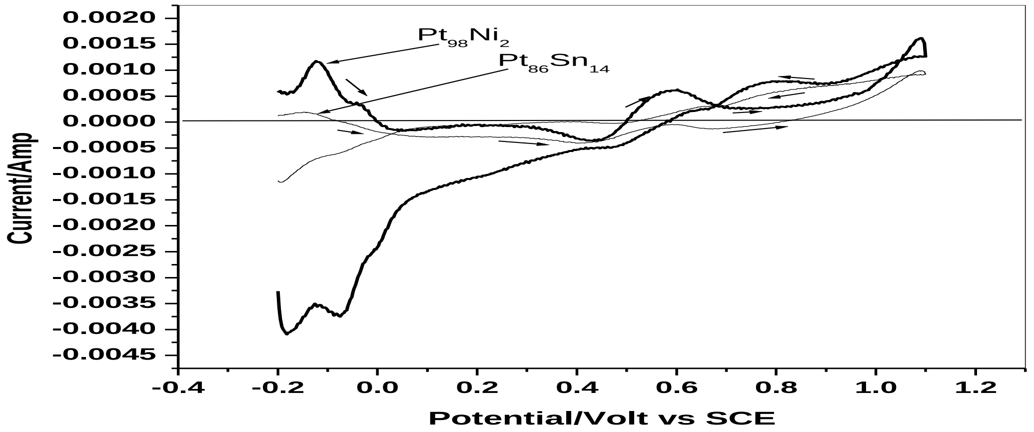

Figure-7: Cyclic Voltammograms of acetone onto $Pt_{86}Sn_{14}$ and $Pt_{98}Ni_2$ surface.

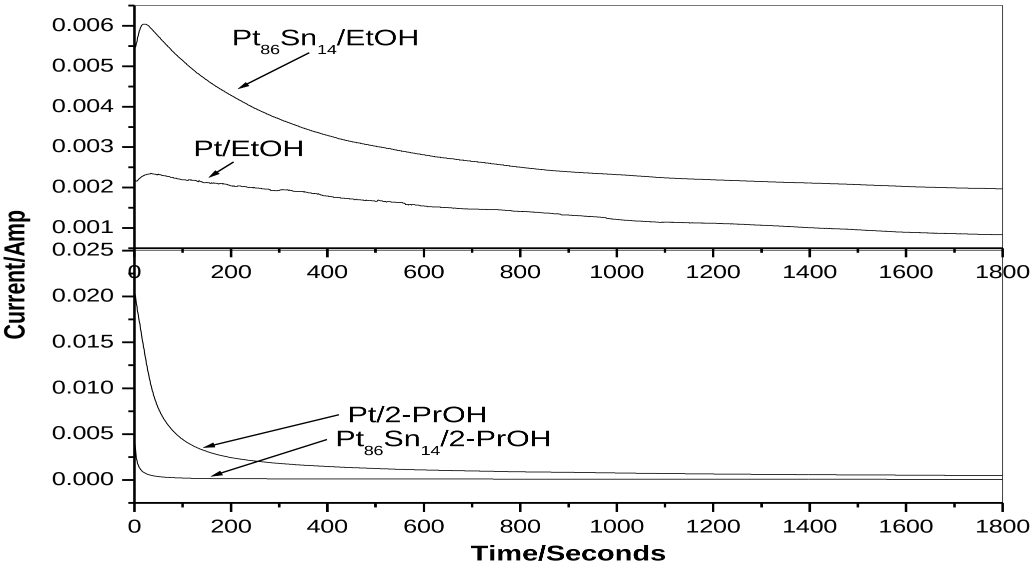

Figure-8: Amperometric i-t curves of EtOH and 2-PrOH electro-oxidation at 0.45 volt onto Pt and $Pt_{86}Sn_{14}$ catalyst.

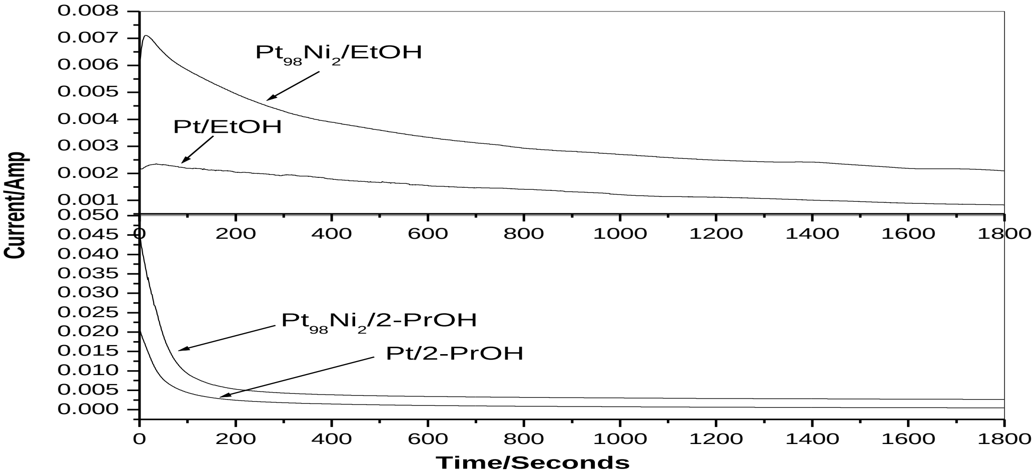

Figure-9: Amperometric i-t curves of EtOH and 2-PrOH electro-oxidation at 0.45 volt onto Pt and $Pt_{98}Ni_2$ catalyst.