www.sphinxsai.com

ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.10 No.4, pp 097-102, 2017

# Effect of scan rate on isopropanol electrooxidation onto Pt-Sn electrode

**Abhik Chatterjee**

**Department of Chemistry, Raiganj University Raiganj-733134,India**

**Abstract :** This article presents the galvanostatic preparation of graphite supported Platinum-Tin (PtSn) electrode for electrooxidation study. The electrode was characterized by SEM and EDX. Investigation of electrooxidation of isopropanol onto Pt-Sn electrode was carried out by applying cyclicvoltammetry technique at different scan rates. A three electrode setup was used for this investigation. It is seen from the investigation that anodic peak potentials ($1^{st}$ and $2^{nd}$ oxidation peak) as well as the corresponding peak currents changed with scan rate.

**Keywords** : Isopropanol, elctrooxidation, cyclicvoltammetry.

## Introduction:

The kinetics of electrochemical oxidation of small organic molecules is of fundamental importance in electrocatalysis and is also a vital factor in the application in fuel cells. Now aliphatic alcohols have been promoted as promising fuels for direct alcohol fuel cells (DAFCs) in particular ethanol and propanol [1]. This is due to the better energy efficiency, easy handling during storing and transporting. Also the studies have concentrated on 2-propanol as an alcohol's fuel because it shows higher performance and a lower overpotential. Alcohols with more than two carbon atoms have many isomers and special characteristics of non-CO adsorption. Isopropanol is the smallest secondary alcohol molecule. It is of tremendous importance in fundamental studies. The mechanism of 2-PrOH electro-oxidation reaction has been investigated by means of electrochemical and spectroscopic techniques (in situ infrared spectroscopy),as well as online mass spectroscopy [2-4]. According to these investigations, it is observed that acetone is the main electro-oxidation product of 2-PrOH. No dissociative adsorption of 2-PrOH was found by in situ infrared spectra. Acetone acts both the role of product and intermediate, and that the formation of a further oxidized product, $CO_2$, was also observed. Although the mechanisms and kinetics of 2-propanol oxidation are comparatively well described using platinum electrodes, but there are very few reports on electrochemical oxidation of 2-PrOH on bimetallic electrodes. Some of the investigations showed that binary electrodes exhibit better electrocatalytic activity for isopropanol oxidation [5-7]. Gonza´lez et al. investigated the electro-oxidation of 2-PrOH onto PtSn surface at low potential. They observed that acetone is inert onto this surface [8]. Therefore, the objective of the present investigation is to report the results of systematic studies on electro-oxidation of 2-PrOH onto graphite supported Pt-Sn electrode.

## Experimental

Materials: Sulfuric acid (Merck), $H_2PtCl_6$ (Arrora Matthey Limited), $SnCl_2$ (Merck) were used as supplied. Isopropanol (Merck) was distilled before use.

Electrode preparation: Graphite sheet (Alfa-Aesar) was considered as substrate for metals (Pt and Sn) deposition. Before each deposition, the cleaning of graphite surface was done electrochemically. Depositions were carried out galvanostatically (PAR VersaStat$^{TM}$II) with a current density of 2.5mA.cm$^{-2}$ for 30 minutes from a mixed salt solution(Pt and Sn) bath.

Electrode characterization: The surface characterisation of the anode material was investigated with a SEM ,scanning electron microscope (SEM, Hitachi S-3000N), at an accelerating potential of 20kV. The elemental compositions of the electro-deposited catalyst was determined by EDX (energy dispersive X-ray) analysis. The EDX analysis was performed using an EXLII, oxford attached to the microscope.

Electrochemical measurement: The activity of the deposited electrodes towards 2-PrOH oxidation was studied by cyclic voltammetry technique (PAR VersaStat$^{TM}$II). For this study, a three electrode setup was constructed, where carbon supported electrodes (1cm x 1 cm) were the working electrodes, Pt foil (1cm$^2$) was the counter electrode, while a saturated calomel electrode (SCE) acted as reference electrode. The electrolytes were 0.5 M $H_2SO_4$ acid solution (blank), and 0.5 M $H_2SO_4$ containing 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. All the experiments were carried out at 25$^0$C.

## Results and Discussion

SEM image of the PtSn electrode surface is presented in figure 1. It is seen that the bimetallic electrode is covered with a uniform, relatively smooth catalyst layer. Here the SEM images do not give much information on particle size and its growth kinetics, but a uniform growth of relatively smooth catalyst layer is observed.

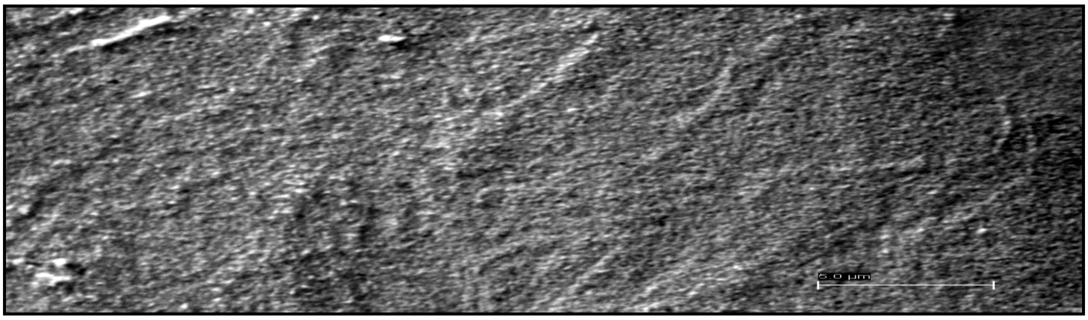

**Figure.1 SEM image of PtSn electrode.**

The energy dispersion X-ray (EDX) spectrums of the electrode is given in figure 2. It is seen from the spectrum that peaks at about 1.6, 2.2, 8.3, 9.4, 10, 11 and 13keV with a strong intensity peak at 2.2 keV are observed for metallic Pt which matches with the literature values. Tin peaks come at about 3.0 and 3.5 keV. Table 1 shows the bath composition and EDX composition.

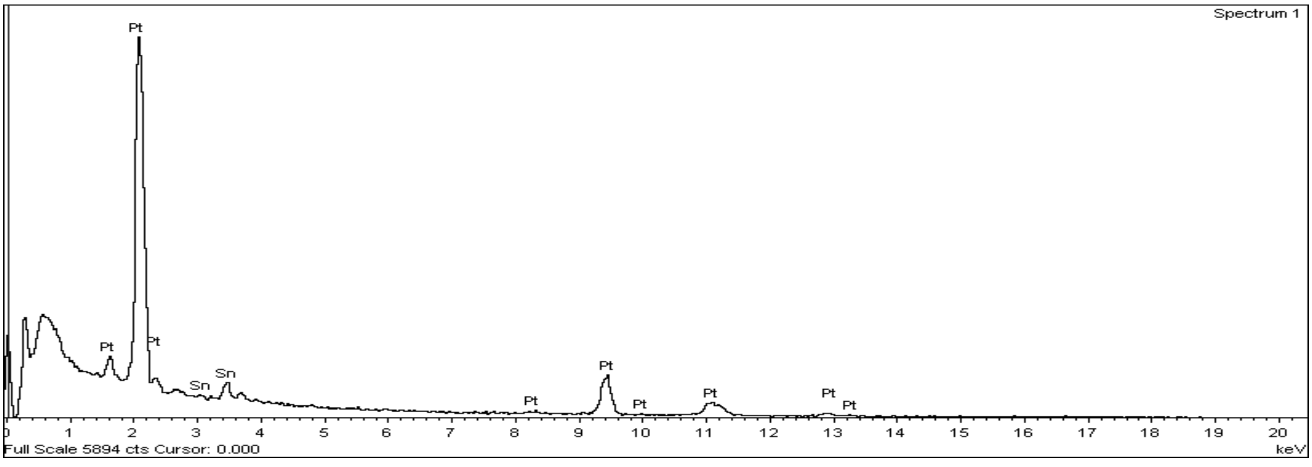

**Figure.2 EDX spectrum of PtSn electrode**

**Table:1**

| | **Bath composition [ Pt: Sn salt]** | **Atomic composition (%) [ From EDX spectrum]** |
|---|---|---|
| Pt-Sn | 3:1 | 85.78:14.22 |

The standard reduction potential (SHE) of the species involved in the electro-deposition of Pt, Sn are as follows;

$[PtCl_6]^{2-}$ / $[PtCl_4]^{2-}$ = 0.68 V,$[PtCl_4]^{2-}$ /Pt = 0.76 V, $Sn^{2+}$/Sn = -0.14 V.

From the above potential values, it is seen that in the course of co-deposition, the possibility of reduction of tin precursors to metallic Sn is lower as compared to that of Pt. EDX results support the above supposition. Thus based on the composition obtained from EDX analysis of the electrode, the electrode may be designated as $Pt_{86}Sn_{14}$.

Cyclic voltammogram(CV) of the blank solution presented in figure 3. This CV does not exhibit any typical hydrogen desorption/ adsorption peaks. The current slowly increases from 0.280 V and a peak appears at about 0.51 V. This may be due to tin oxide formation.

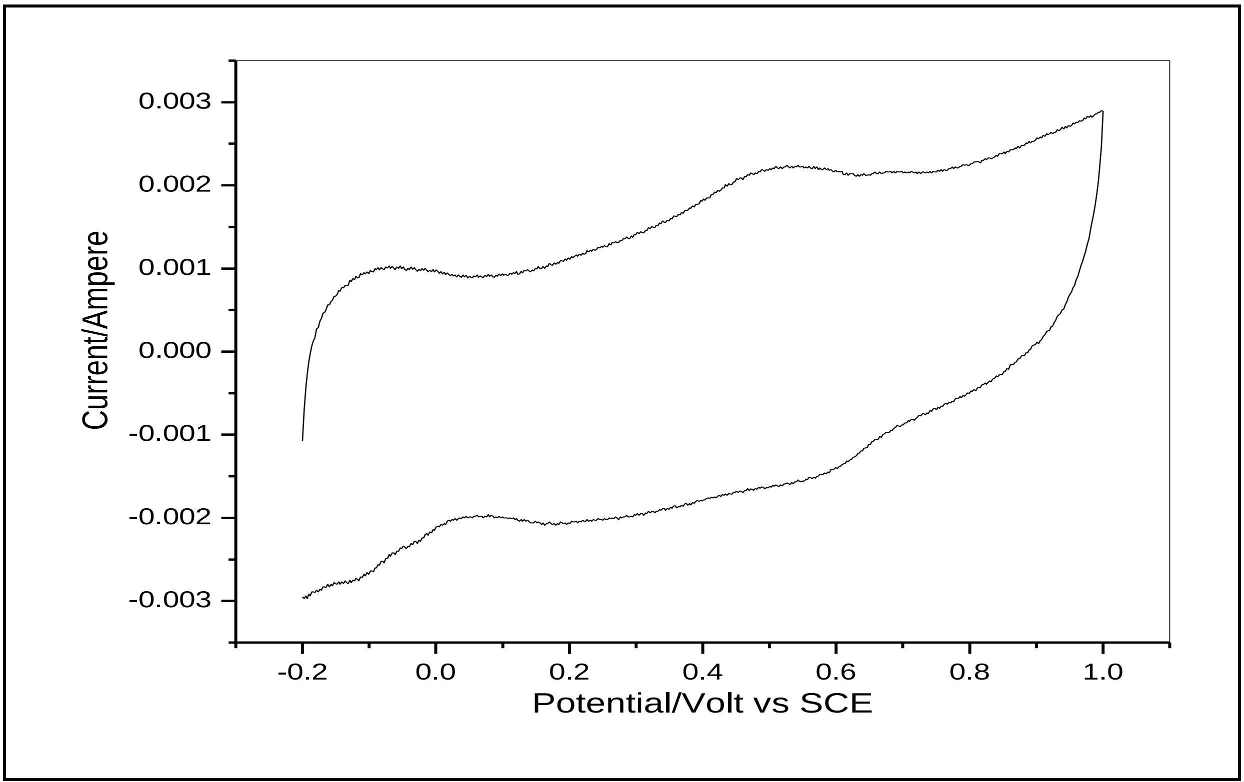

**Figure 3. Cyclic Voltammogram of $H_2SO_4$ solution (blank) on to $Pt_{86}Sn_{14}$. Scan rate 30 $mVs^{-1}$.**

The figure 4 illustrates the cyclic voltammogram profiles of isopropanol electrooxidation onto $Pt_{86}Sn_{14}$working electrode at different scan rates within the potential limit –0.2 to 1.1V vs. SCE. Two anodic oxidation peaks are observed during the potential sweep towards higher potential and one oxidation peak appears during reverse scan. In case of, $Pt_{86}Sn_{14}$ current increases from 0.12 V and the first peak appears at 0.3V followed by a 2nd peak appears at about 0.7 V.The appearance of two oxidation peaks on the forward scan can be described to the oxidation of the fuel by two kinds of chemisorbed oxygen species. It is also observed that anodic peak potential as well as the corresponding anodic peak currents has been changed with scan rate. An increase in scan rate increases the peak current and shifts the peak potential in the positive direction.

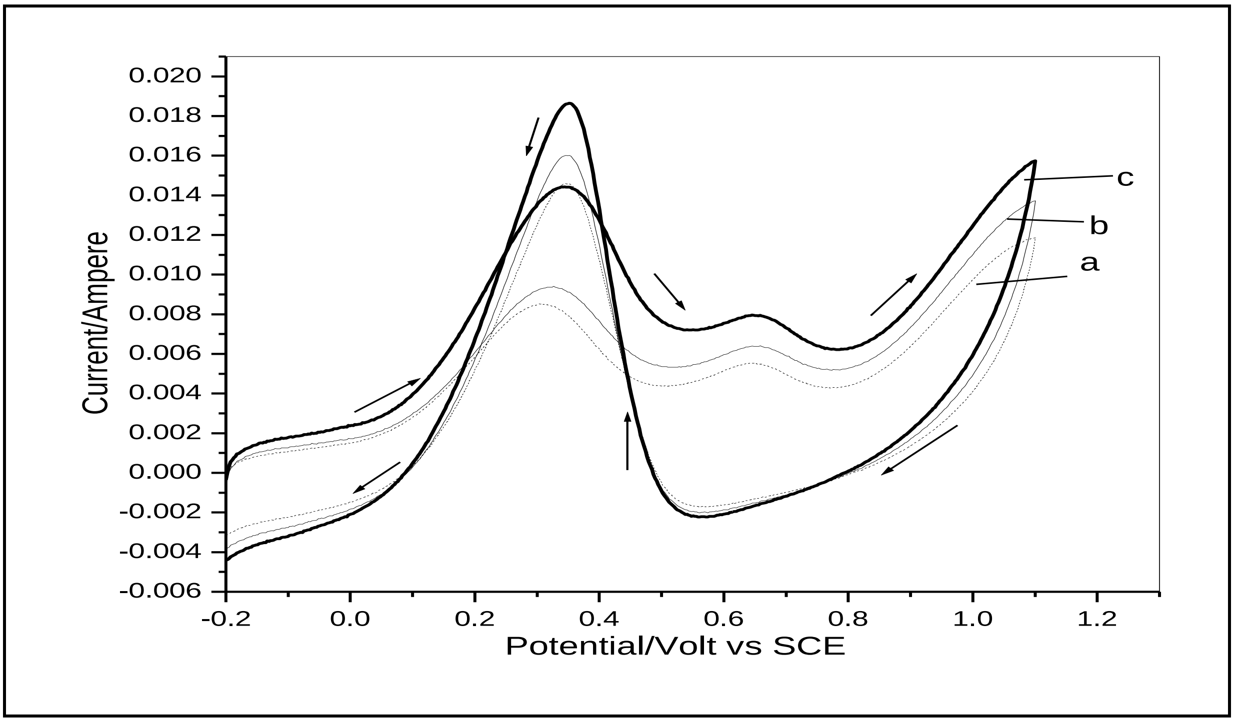

**Figure.4 Cyclic voltammograms recorded in 1M isopropanol solution onto PtSn-catalyst at (a) 30 (b) 40 (c) 50 mV.s$^{-1}$ scan rates.**

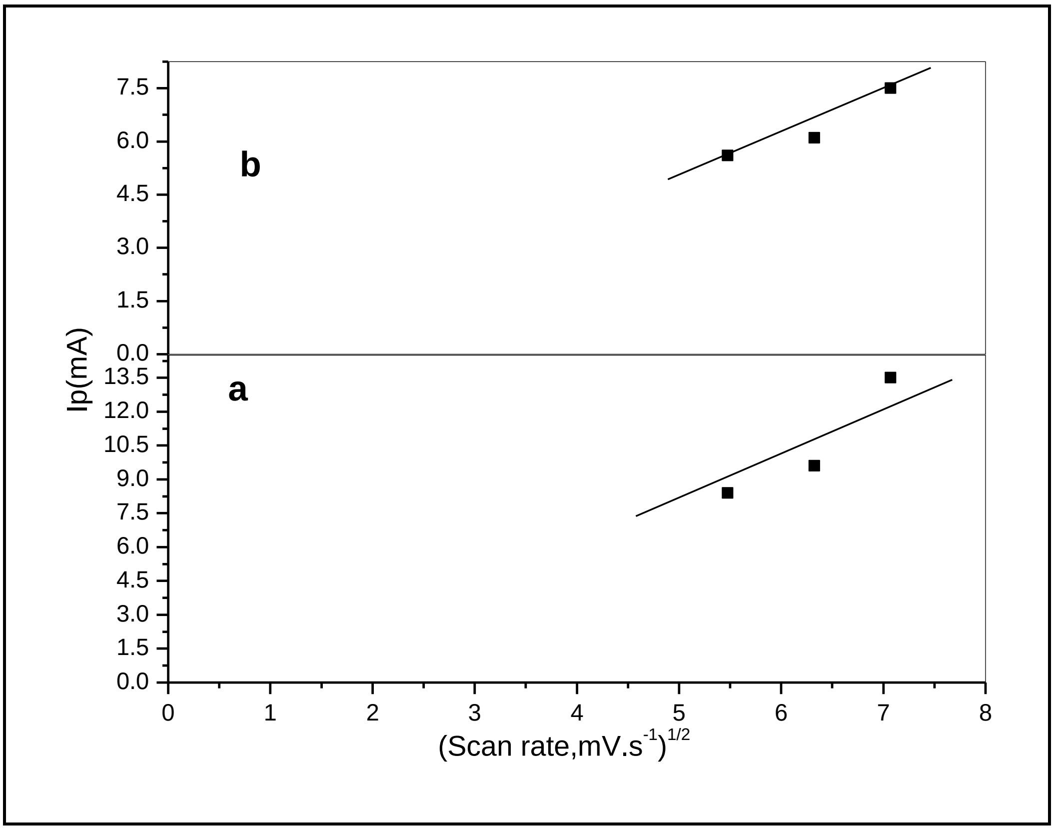

**Figure 5. Plot of $I_p$ vs square root of scan rate on PtSn electrode (a) 1st Oxidation peak current (b) 2nd Oxidation peak current.**

The relationship between the peak currents (Ip) of isopropanol electrooxidation on the electrode surface and the square root of scan rate is shown in figure 5 and thus obey the following relationship.

$$Ip = 2.985 * 10^5\, n\, [(1-\alpha)n_\alpha]^{-1/2}\, A\, D^{1/2}\, C\, V^{1/2} \qquad (1).$$

Where $Ip_a$ 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 $cm^{-3}$). Actually Figure 5 represents the oxidation current associated with both peaks 1st and 2nd (Ip) for forward oxidation is plotted as a function of (scan rate)$^{1/2}$ . The variation is linear in both cases and lines pass through the origin. The linearity is expected for a process that occurs under diffusion control.

The dependence of the peak potential on the scan rate provides kinetic information. A peak potential which is independent of the scan rate indicates a reversible charge-transport process, whereas an irreversible charge transfer process causes the peak potential to vary with scan rate. Both peak potentials (Ep) increase with the increase of scan rate, indicating that isopropanol oxidation on the Pt electrode is an irreversible charge-transport process. Figure 6 present the dependence of peak potentials (Ep) on the logarithm of the scan rate. Peak potential for the 1st oxidation peak changes more with scan rate compared to 2nd oxidation peak. An increase of scan rate potential increases the peak current density and shifts the peak potential in the positive direction as is typical of completely irreversible system.

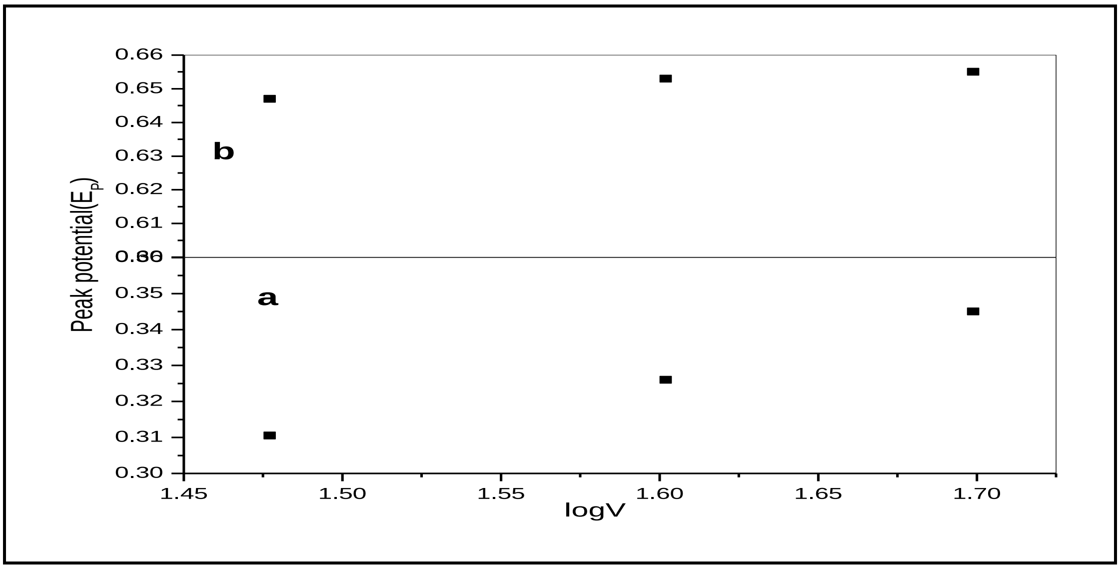

**Figure 6. Plot of $E_p$ vs logV(a) 1st Oxidation peak potential (b) 2nd Oxidation peak potential.**

## Conclusion:

In the present article, electro-oxidation of 2-PrOH has been investigated on to PtSn surface. It is observed that anodic peak potentials as well as the corresponding peak currents have been changed with scan ate. An increase in scan rate increases the peak current and shifts the peak potential in the positive direction. The peak potential (Ep) increases with the increase of scan rate, indicating that isopropanol oxidation on to the electrodes is an irreversible process. The relationship between the peak current density of isopropanol oxidation on to the electrodes and the square root of sweep rate indicates that isopropanol oxidations on the electrodes are controlled by a diffusion process.

## Acknowledgement:

Author is thankful to Prof I Basumallick and Dr S Ghosh of Visvabharati for providing the lab facility.

## References:

1. Lamy C, Belgsir EM, L´eger J-M. Electrocatalytic oxidation of aliphatic alcohols: Application to the direct alcohol fuel cell (DAFC). J Appl Electrochem 2001, 31(7),799-809.

2. Sun S, Lin Y., Kinetics of isopropanol oxidation on Pt(111), Pt(110), Pt(100), Pt(610) and Pt(211) single crystal electrodes -Studies of in situ time-resolved FTIR spectroscopy. Electrochim Acta, 1998, 44 ,1153-1162.
3. Sun S, Lin Y., In situ FTIR spectroscopic investigations of reaction mechanism of isopropanol oxidation on platinum single crystal electrodes. Electrochim Acta, 1996,41(5), 693-700.
4. Pastor E, Gonzalez S, Ariva AJ.,Electroreactivity of isopropanol on platinum in acids studied by DEMS and FTIRS, J Electroanal Chem, 1995, 395, 233-242.
5. Rodrigues IA, Nart FC. 2-Propanol oxidation on platinum and platinum–rhodium electrodeposits. J Electroanal Chem., 2006, 590(2), 145-151.
6. Rodrigues I A, de Souza J P I, Pastor E, Nart F C. Cleavage of the C−C bond during the electrooxidation of 1-Propanol and 2-Propanol: effect of the Pt morphology and of codeposited Ru. Langmuir 1997, 13(25), 6829-6835.
7. Chatterhee A, Chatterjee M, Ghosh S, Basumallick I., Electro-oxidation of ethanol and isopropanol onto pt-sn and pt-ni surfaces. IJCRR,2012, 4, 13-20.
8. Gonzalez MJ, Hable CT, Wrighton MS, Electrocatalytic oxidation of small carbohydrate fuels at Pt−Sn modified electrodes. J Phys Chem B 1998, 102(49), 9881-9890.

*****