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Full Paper

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## Cyclicvoltammetry study of isopropanol electrooxidations onto PtNi electrode

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### ABSTRACT

This article presents the electrooxidation of isopropanol on to Pt and Pt-Ni electrodes applying cyclicvoltammetry technique at different scan rates. The effect of scan rate on the electrooxidations was studied using a three electrode cell. Anodic peak potentials as well as the corresponding peak currents changed with scan rate. In cyclicvoltammetric experiments a gradual increase of the oxidation peaks with the increasing scan rate has been observed and shifts the peak potential in the positive direction. It is also seen that the isopropanol (2-PrOH) electrooxidation onto Pt and PtNi electrode is irreversible in nature.

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### KEYWORDS

Isopropanol;  
Electrooxidation;  
Electrocatalyst;  
Cyclicvoltammetry;  
Electronic effect.

### INTRODUCTION

Direct alcohol fuel cells (DAFCs) draw tremendous attention as power sources in numerous applications at low operating temperature<sup>[1]</sup>. Recently aliphatic alcohols have been promoted as promising fuels for direct alcohol fuel cells (DAFCs) in particular ethanol and propanol<sup>[2]</sup>. This is due to the better energy efficiency, easy handling during storing and transporting. Also the recent studies have focused on 2-propanol as an alcohol's fuel because it shows a lower overpotential and higher performance than methanol. Alcohols with more than two carbon atoms have several isomers and special features of non-CO adsorption. Electro-oxidation of 2-PrOH 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 most active electro-catalyst for DAFC, but its cost and surface poisoning phenomenon inhibit it from large scale applications. It is well known fact that the incorporation of small percentage of Ru or Mo with Pt moiety enhances the life-time of the catalyst by removing CO via bi-metallic function, but they are highly expensive metals. Thus, search for an alternate cheaper bi-functional metal is urgently needed. Recently, transitional metals like Sn, Ni is reported to play a crucial role for enhance the electro-catalytic activity of Pt as a co-metal<sup>[3]</sup>.

During the last decade, several researchers have reported the operation of a direct 2-propanol (2-

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PrOH) fuel cell<sup>[4-6]</sup>, and recently it has been reported that the performance of a cell operating on 2-PrOH is substantially higher than when it is operating on methanol. The reaction mechanism of 2-PrOH electro-oxidation<sup>[4,7-11]</sup> has also been investigated by means of electrochemical and spectroscopic techniques (in situ infrared spectroscopy), on line mass spectroscopy<sup>[11]</sup>. According to these studies, it is found that acetone is the main electro-oxidation product of 2-PrOH. No dissociative adsorption of 2-PrOH was observed 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. Although the mechanisms and kinetics of 2-propanol oxidation are relatively well described using platinum electrodes, but there are very few reports on electrochemical oxidation of 2-PrOH on bimetallic electrodes.

Rodrigues et al.<sup>[12-13]</sup> studied the electro-oxidation of isopropanol onto binary electrodes. Binary electrodes show better electrocatalytic activity for isopropanol oxidation. Since 2-PrOH is a secondary alcohol, only acetone and CO<sub>2</sub> are generated. The total yield of CO<sub>2</sub> and acetone has been determined from the DEMS measurements. Gonza'lez et al. studied the electro-oxidation of 2-PrOH onto PtSn surface at low potential. They found that acetone is inert onto this surface<sup>[14]</sup>. Lee et al.<sup>[15]</sup> studied the effect of temperature on methanol, ethanol, 2-PrOH and 2-butanol oxidation on to Pt/C and PtRu/C microporous electrode. The addition of Ru reduces the poisoning effect, although it is ineffective for secondary alcohols. Since the secondary alcohols follow different path for their electro-oxidation. Thus from the literature review it is seen that little attention was given to the 2-PrOH electro-oxidation on to binary electrodes.

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 graphite supported Pt-Ni catalyst, at their optimum composition. It is expected that the present study will help to understand the potentiality of Pt-Ni as electro-catalyst for 2-PrOH electro-oxidation, which is a fuel of high theoretical power density.

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## EXPERIMENTAL

### Materials

Sulfuric acid (Merck), H<sub>2</sub>PtCl<sub>6</sub> (Arrora Matthey Limited), NiSO<sub>4</sub> (E-Merck) were used as supplied. 2-PrOH (Merck) was 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™II) with a current density of 2.5mA.cm<sup>-2</sup> for 30 minutes.

### Electrode characterization

The surface morphologies of the anode materials were investigated with a scanning electron microscope (SEM, Hitachi S-3000N), at an accelerating potential of 20kV. The elemental compositions of the electro-deposited catalysts were determined by energy dispersive X-ray (EDX) analysis. The EDX analysis was performed using an EXLII, Oxford attached to the microscope.

### Electrochemical measurement

The catalytic activity of all the deposited electrodes towards 2-PrOH oxidation was studied by cyclic voltammetry technique. 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<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. 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°C.

## RESULTS AND DISCUSSION

SEM images of the Pt and Pt-Ni electrode surfaces are shown in Figure 1 and 2, respectively. It is found that these electrodes are covered with a uni-

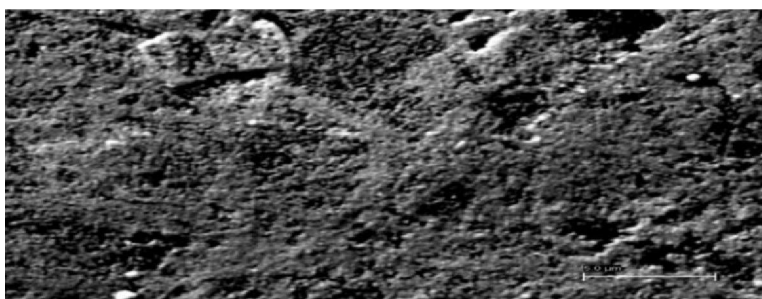


Figure 1 : SEM image of Pt electrode

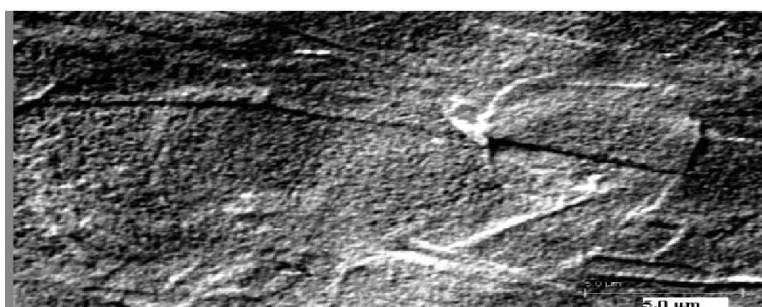


Figure 2 : SEM image of PtNi electrode

form, relatively smooth catalyst layer. The presence of Ni with Pt changes the morphology of the electrode surface as shown in SEM images, Figure 2. 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 observed.

The loading of the deposited metals onto graphite sheet has been calculated considering 100% coulombic efficiency. Calculated Pt loading is 0.045 mg. cm<sup>-2</sup>. EDX analysis has been carried out to determine the average composition ratio of Pt and Pt-Ni electrodeposits on graphite substrates. The energy dispersion X-ray spectrums of the bimetallic catalysts are shown in Figure 3. From the spectrum it is seen that peaks at about 1.6, 2.2, 8.3, 9.4, 10, 11 and 13keV with a strong peak at 2.2 keV are found for metallic platinum which matches with the literature values. Ni Peaks appear at about 0.5, 7.4 and 8.4 keV and also matches with the literature values. TABLE 1 shows the bath composition and EDX composition.

For Pt-Ni alloy, a small atomic percentage of

Ni, has been chosen in order to avoid leaching of Ni in acidic medium. Again it is also reported that below 10 atom% Ni enhance the electro-catalytic activity of Pt-Ni electrode towards the alcohol oxidation<sup>[17-18]</sup>. From the table, it is seen that atomic percent of Ni is very low i.e., Ni has been deposited as a trace metal. The standard reduction potential (SHE) of the elements involved in the electro-deposition of Pt and Ni are given below;



From the above, it is clear that in the course of co-deposition, the possibility of reduction of nickel precursors to metallic nickel is lower as compared to that of platinum. EDX result corroborates the above supposition.

The characteristic features of alcohol oxidation on Pt surface, i.e. two well-defined oxidation peaks are seen during the forward and the reverse scans (Figure 4 and 5). It is clearly found from Figure 5 that the onset potentials for electro-oxidation of 2-PrOH are largely moved to lower potential value

TABLE 1 : Composition of the electrodes

	Bath composition[V/V]	Atomic composition (%) [From EDX]
Pt	1:0	100
Pt-Ni	8:2	97.87:2.13

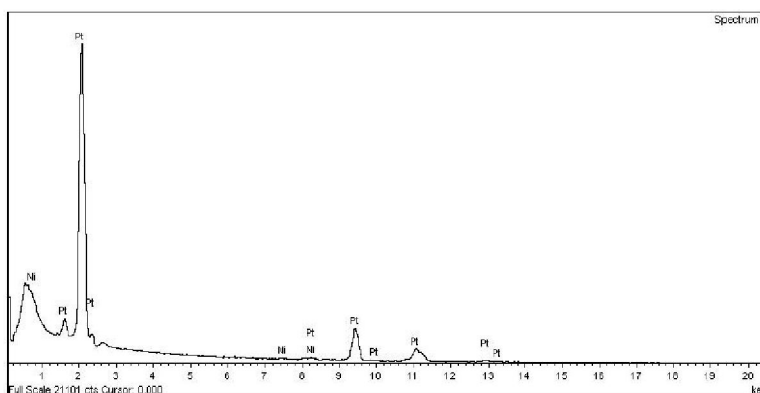


Figure 3 : EDX spectrum of PtNi electrode

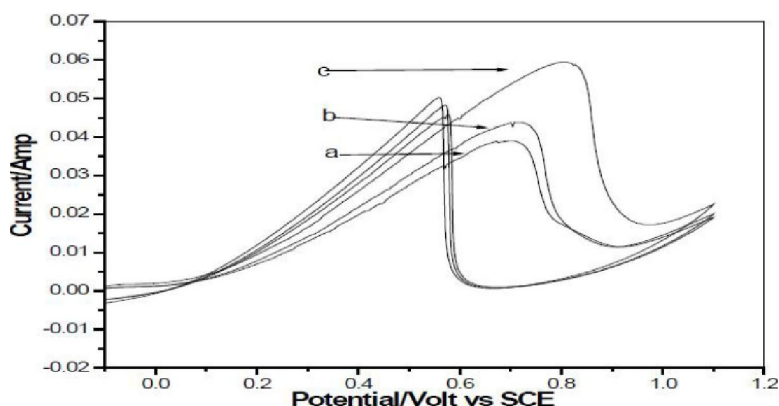


Figure 4 : Cyclic voltammograms recorded in 1M isopropanol solution onto Pt-catalyst at (a) 20 (b) 30 (c) 50 mV.s<sup>-1</sup> scan rates

on the bimetallic, Pt-Ni catalyst surface. Anodic peak currents onto PtNi catalyst surface for electro-oxidation of isopropanol 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 PtNi for the isopropanol. As Ni-O bond energy is about 200 kJ.mol<sup>-1</sup> lower than that of Pt-C bond, bi-functional mechanism does not work here for 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<sup>[16,19]</sup>.

Figure 4 shows the CVs of isopropanol as a function of scan rate recorded at Pt working electrode. It is observed that anodic peak potential as well as the corresponding anodic peak currents has been changed. An increase in scan rate increases the peak current and shifts the peak potential in the positive direction. 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. The peak potential ( $E_p$ ) increases with the increase of scan rate, indicating that isopropanol oxidation on the Pt electrode is an irreversible charge-transport process.

Figure 5 shows the CVs of isopropanol as a function of scan rate recorded at Pt-Ni working electrode. It is also seen that anodic peak potential as well as the corresponding peak currents has been changed. This figure shows that the oxidation current increases with the increase of scan rate and peak potential shifts to positive direction. The peak potential increases with the increase of sweep rate, indicating that isopropanol oxidation on the Pt-Ni electrode is an irreversible charge-transport process.

The relationship between the peak current ( $I_p$ ) of isopropanol oxidation on the electrodes and the square root of scan rate is shown in Figure 6 and thus obey the following relationship.

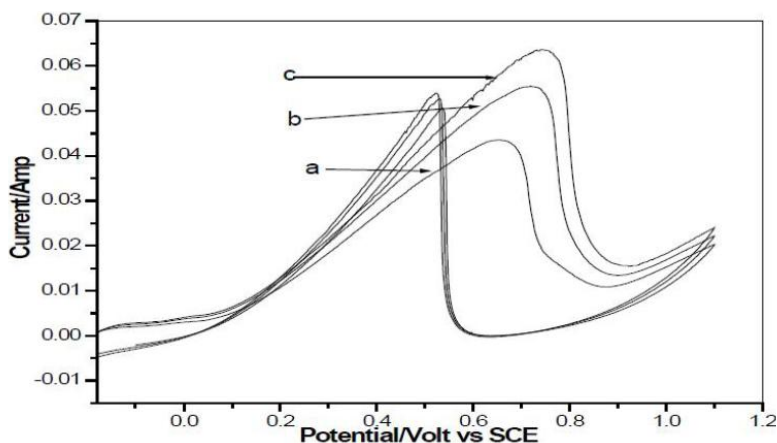


Figure 5 : Cyclic voltammograms recorded in 1M isopropanol solution onto PtNi-catalyst at (a)20 (b)30 (c)50  $\text{mVs}^{-1}$  scan rates

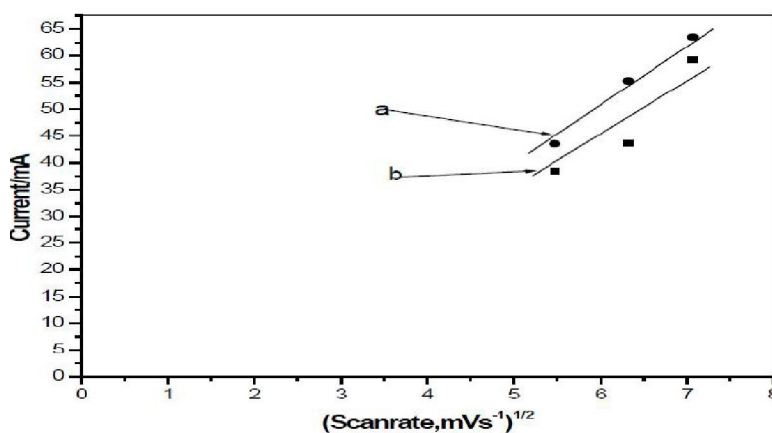


Figure 6 : Plot of  $I_p$  vs square root of scan rate on (a) PtNi (b) Pt electrode

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

Where  $I_{p_a}$  is the anodic peak current (mA),  $n$  is the number of electrons involved in the oxidation,  $A$  is the area of electrode ( $\text{cm}^2$ ),  $V$  is the scan rate ( $\text{Vs}^{-1}$ ),  $C$  is the concentration of the electro active species in bulk solution ( $\text{mol cm}^{-3}$ ). Thus 2-PrOH electro-oxidation onto Pt and PtNi electrode show irreversibility and isopropanol oxidation on both the electrodes is controlled by a diffusion process.

## CONCLUSION

In the present article, electro-oxidation of 2-PrOH has been studied on to Pt and PtNi surface. It is found that anodic peak potential as well as the corresponding peak currents has been changed. An increase in scan rate increases the peak current and shifts the peak potential in the positive direction. The peak potential ( $E_p$ ) increases with the increase

of scan rate, indicating that isopropanol oxidation on to the electrodes is an irreversible charge-transport 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.

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## REFERENCES

- [1] C.Lamy, E.M.Belgsir, J.M.Leger; J.Appl. Electrochem., **31**, 799 (2001).
- [2] F.Vigier, C.Coutanceau, F.Hahn, E.M.Belgsir, C.Lamy; J.Electroanal.Chem., **563**, 81 (2004).

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- [3] W.J.Zhou, W.Z.Li, S.Q.Song, Z.H.Zhou, L.H.Jiang, G.Q.Sun, Q.Xin, K.Poulianitis, S.Kontou, P. Tsiakaras; *J.Power Sources.*, **131**, 217 (2004).
- [4] J.Wang, S.Wasmus, R.F.Savinell; *J.Electrochem. Soc.*, **142**, 4218 (1995).
- [5] Z.Qi, A.Kaufman; *J.Power.Sources.*, **112**, 121 (2002).
- [6] M.Umeda, H.Sugii, M.Mohamedi, I.Uchida; *Electrochemistry.*, **70**, 961 (2002).
- [7] S.N.Raicheva, M.V.Christov, E.I.Sokolova; *Electrochim.Acta.*, **26**, 1669 (1981).
- [8] E.I.Sokolova, M.V.Christov; *J.Electroanal.Chem.*, **175**, 195 (1984).
- [9] L.W.H.Leung, S.C.Chang, M.J.Weaver; *J. Electroanal.Chem.*, **266**, 317 (1989).
- [10] S.G.Sun, D.F.Yang, Z.W.Tian; *J.Electroanal.Chem.*, **289**, 177 (1990).
- [11] E.Pastor, S.Gonzalez, A.J.Arvia; *J.Electroanal. Chem.*, **395**, 233 (1995).
- [12] I.A.Rodrigues, J.P.I.De Souza, E.Pastor, F.C.Nart; *Langmuir.*, **13**, 6829 (1997).
- [13] I.A.Rodrigues, F.C.Nart; *J.Electroanal.Chem.*, **590**, 145 (2006).
- [14] M.J.Gonzalez, C.T.Hable, M.S.Wrighton; *J.Phys.Chem.B.*, **102**, 9881 (1998).
- [15] C.G.Lee, M.Umeda, I.Uchida; *J.Power.Sources.*, **160**, 78 (2006).
- [16] A.Chatterjee, M.Chatterjee, S.Ghosh, I.Basumallick; *IJCRR.*, **4**, 13 (2012).
- [17] J.Mathiyarasu, A.M.Remona, A.Mani, K.L.N.Phani, V.Yegnaraman; *J.solid state electrochem*, **8**, 968 (2004).
- [18] M.A.Abdel Rahim, H.B.Hassan, R.M.Abdel Hameed; *Fuel cells.*, **7**, 298 (2001).
- [19] K.Park, J.Choi, B.Kwon, S.Lee, Y.Sung, H.Ha, S.Hong, H.Kim, A.Wieckowski; *J.Phys.Chem.B.*, **106**, 1869 (2002).