CHEMICAL TECHNOLOGY

An Indian Journal

Full Paper

Trade Science Inc.

Electro-oxidation of ethanol and isopropanol onto ternary Pt-Sn-Ni surface

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ABSTRACT

A simple galvanostatic method is reported on the preparation of bimetallic Pt-Sn and trimetallic Pt-Sn-Ni catalysts onto graphite sheet electrode and studied their catalytic activity towards isopropanol (2-Propanol/2-PrOH) and ethanol (EtOH) electro-oxidation. These catalysts have been characterized by SEM, EDX, CV and amperometry. The results indicate that the Pt-Sn-Ni catalyst performs better than the binary Pt-Sn catalyst for both the alcohols. The results are explained in terms of bifunctional effect, electronic effect and strong adsorption of intermediate products.
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KEYWORDS

INTRODUCTION

Direct alcohol fuel cells (DAFCs) have drawn tremendous attention as power sources in stationary and mobile applications at low operating temperature[1]. Electro-oxidation of EtOH and 2-PrOH involve 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 for DAFC, but its cost and surface poisoning phenomenon inhibit it from large scale applications. It is well established 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, is reported to play a crucial role for enhance the electro-catalytic activity

of Pt as a co-metal[2]. On the other hand, a decrease of Pt loading in the construction of electrodes of a DAFC is always beneficiary for the reduction of the cost of the fuel cells. Thus without compromising of adding small percentage of bi-functional metals like Sn, introduction of a third metal in place of costly Pt is a convenient way to modify the Pt electro-catalytic properties in order to increase the catalytic activity and weaken or even overcome poisoning by the alcohol electro-oxidation intermediates especially the adsorbed CO-like species. The different research groups investigated the ethanol electro-oxidation on carbon supported Pt–Sn catalysts[3-8]. Again, many research groups examined the electro-oxidation of ethanol on a ternary Pt–Sn–Ni electro-catalyst (50:40:10) and they showed the superiority of Pt-Sn-Ni over Pt-Sn[9-10].

But very few reports are available in the literature on electro-oxidation of 2-propanol on bimetallic elec-

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trodes[11-13].

Thus, it is found that there are many reports available on ethanol electro-oxidation using ternary electro-catalyst, but there is hardly report on 2-PrOH electro-oxidation onto ternary electro-catalyst. Secondly, the ternary electro-catalyst was prepared mainly using chemical routes. In the present study, we would like to prepare ternary Pt-Sn-Ni catalysts galvanostatically, since it is one of the promising systems and would like to study their electro-catalytic behaviour towards ethanol and 2-PrOH electro-oxidation and compared with pure Pt and Pt-Sn data.

EXPERIMENTAL

Sulphuric acid (Merck), $H_2PtCl_6,6H_2O$(Arora Matthey Limited), $SnCl_2$ (Merck), $NiSO_4,7H_2O$ (E-Merck) were used as supplied. The concentrations of all the salt solutions were 0.005M using 0.5 M HCl (Merck). EtOH (Bengal chemicals) and 2-PrOH (Merck) were distilled before use. Graphite foil, 0.5 mm thick (Alfa-Aesar) was taken as substrate for metal deposition. Before deposition, the graphite surface was electrochemically cleaned. Depositions were carried out galvanostatically (PAR VersaStat™II) with 2.5 mA.cm^{-2} for 30 minutes using a two electrode configuration. The catalytic activity of all the deposited electrodes towards EtOH and 2-PrOH oxidation was studied by cyclic voltammetry and amperometry techniques. A three electrode setup was constructed for this study, where graphite supported electrodes (1cm^2) were the working electrode, 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 sulphuric acid solution (blank), or 0.5 M sulphuric acid containing EtOH/2-PrOH (1.0M) solution. 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. All the experiments were carried out at 25^{0}C.

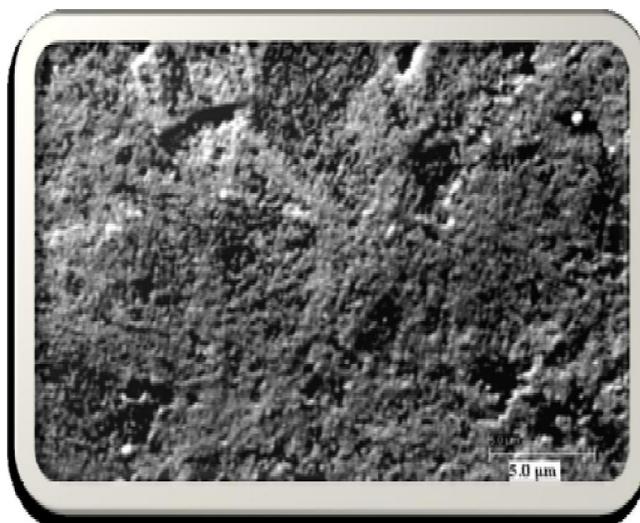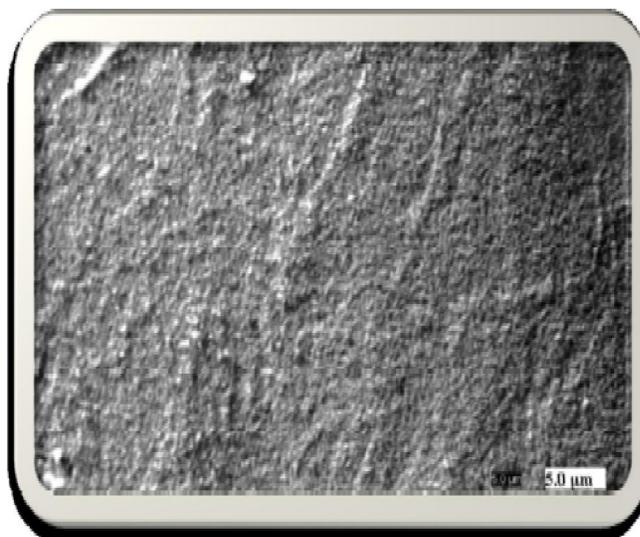**Figure 1 : SEM image of Pt electrode.**
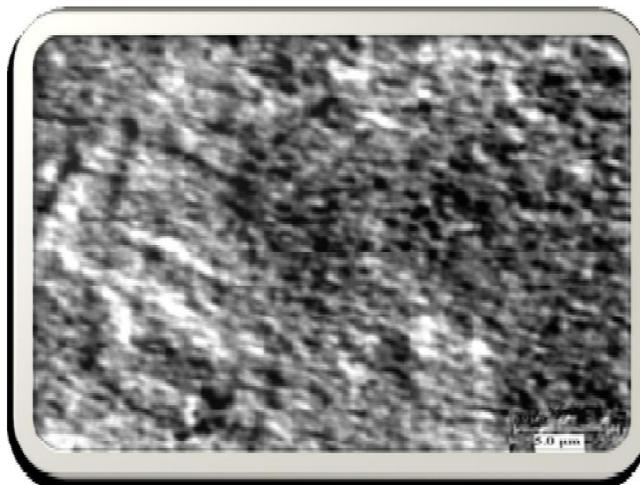

Figure 2 : SEM image of Pt-Sn electrode.

Figure 3 : SEM image of Pt-Sn-Ni electrode

RESULTS AND DISCUSSION

SEM images of the Pt, Pt-Sn, and Pt-Sn-Ni electrode surfaces are shown in Figure 1, 2 and 3, respectively. It is seen that these electrodes are covered with a uniform, relatively smooth catalyst layer. The average particle size in all these surfaces range from 200 to 250 nm.

Based on the composition of the catalysts, obtained from the EDX analysis, the electrodes may be designated as $Pt_{86}Sn_{14}$ and $Pt_{85}Sn_{13}Ni_2$ [Atomic percentage, Pt:Sn = 86:14, Pt:Sn:Ni = 85:13:2].

Typical cyclic voltammograms of the blank and those of 1.0 M EtOH and 2-PrOH solution 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.

Cyclic voltammogram of the Pt electrode shows the features of hydrogen desorption, double layer charging, oxide formation, oxide reduction and hydrogen adsorption. The double layer region for the Pt electrode, followed by hydrogen region, is featureless. The current slowly increases from 0.575 V vs. SCE indicating the formation of surface oxide. But for Pt-Sn electrode, there is no sign of hydrogen desorption and adsorption. The current slowly increases from 0.280 V and a peak appears at about 0.51 V.
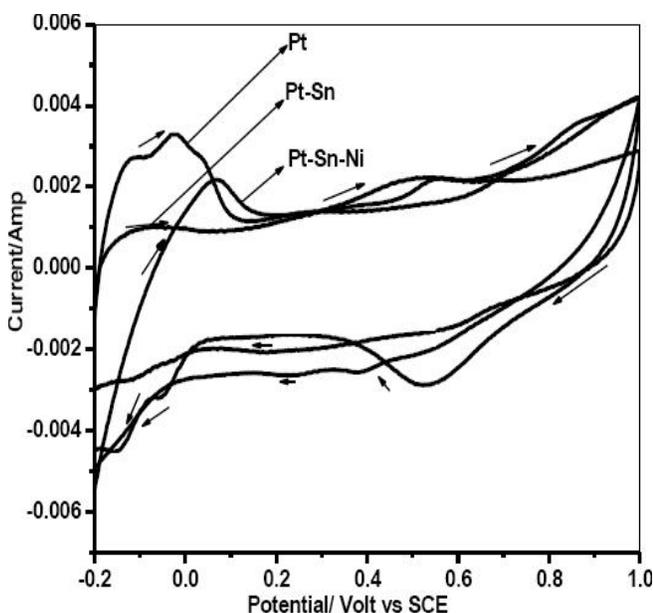

Figure 4 : Cyclic voltammograms recorded in sulphuric acid solution onto Pt, Pt-Sn and Pt-Sn-Ni catalyst. Scan rate 30 mV.s⁻¹.

This may be due to tin oxide formation. Interesting features are observed for Pt-Sn-Ni electrode. The hydrogen desorption profile is characterized by large single peaks at about 0.03 V. But the current-potential response in the hydrogen adsorption region becomes broader and not defined at all.
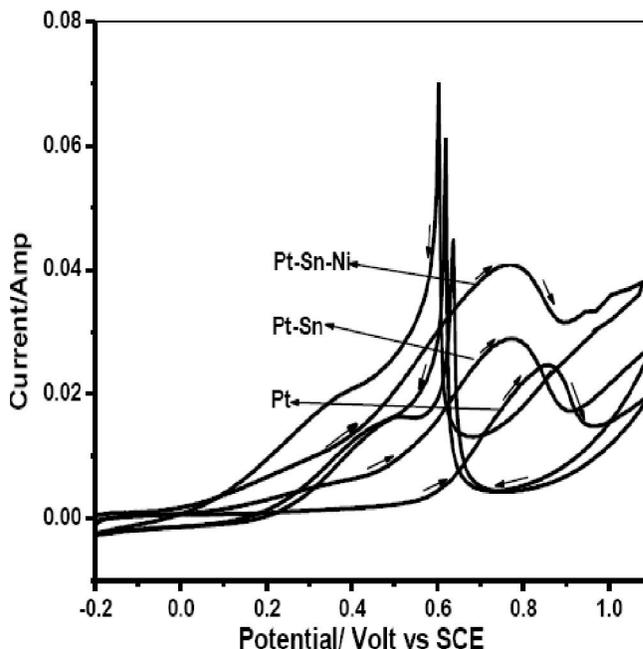

Figure 5 : Cyclic voltammograms of ethanol (1M) in H_2SO_4 solution onto different electrodes Pt, Pt-Sn and Pt-Sn-Ni catalyst, Scanrate 30 mV.s⁻¹.

The characteristic features of alcohol electro-oxidation on Pt, i.e. two well-defined oxidation peaks are found during the forward and the reverse scans. It is clearly seen from Figure 5 that the onset potential for electro-oxidation of EtOH is shifted to lower potential value on the bimetallic catalyst surface. The anodic peak current of EtOH electro-oxidation onto Pt-Sn surface is also higher than that of pure Pt. All these indicate significant enhancement of catalytic activity of Pt in presence of Sn for EtOH electro-oxidation. In the cathodic sweep only one anodic peak is observed and this is attributed to renewed oxidation of the fuel. The cyclic voltammogram of EtOH oxidation, as shown in Figure 5, shows two distinct oxidation regions. Initial kinetics of these electrodes is much slower followed by a sharp rise in current density. From the graph it is clear, though patterns are the same, that the overall kinetics in Pt-Sn-Ni catalyst surface is superior to Pt-Sn and pure Pt for ethanol electro-oxidation. It is also cleared that the on-

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set potential for ethanol electro-oxidation is shifted to lower potential for Pt-Sn-Ni electrode compared to Pt-Sn and pure Pt. Thus, a negative shift of the onset potential and higher anodic peak current values are indicative of better electro catalytic activity of Pt-Sn-Ni for EtOH electro-oxidation compared to Pt-Sn and pure Pt. The improved catalytic effect of ternary electrode is due to the bi-functional effect of Sn and electronic effect of Ni i.e. synergistic effect.

Another probable explanation for the better catalytic behavior of Pt-Sn-Ni is considered which is in agreement with the electro-negativity series, an electron transfer from Ni and Sn to Pt can be possible. As a result, it could be inferred that these electron transfers can also contribute to weakening the bond of Pt-CO like species, assisting the conversion to CO_2. Low onset potential for Pt-Sn-Ni indicates that the dissociative adsorption of ethanol is also favored by the presence of co-metals.

Cyclic voltammograms of 2-PrOH electro-oxidation, shown in Figure 6, reveals very interesting features onto Pt-Sn and Pt-Sn-Ni electrode. In the anodic sweep, two peaks appear and in the cathodic scan only one anodic peak appears. But for Pt-Sn-Ni electrode, a current increment occurs from 0.07 V with the 1st peak appears at 0.42V followed by the 2nd peak at 0.7
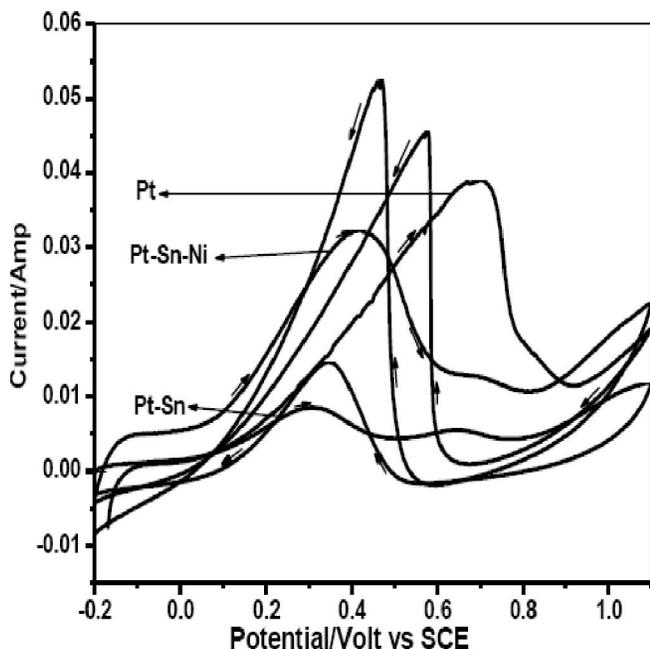
V. On the other hand, Pt-Sn-Ni electrode exhibit high current values in between 0.128 V to 0.43 V regions, where Pt-Sn activity is almost negligible. Thus, high current value indicates the better catalytic activity of the Pt-Sn-Ni electrode in the low potential region. In case of 2-PrOH electro-oxidation onto Pt-Sn-Ni electrode the oxidation current is increased compared to Pt-Sn electrode but still it is inferior to that of Pt electrode. A catalytic deactivation of Pt in Pt-Sn is observed (Figure 6) for 2-PrOH electro-oxidation due to the formation of acetone[13].

Figure 7 shows the amperograms of EtOH electro-oxidation for Pt, Pt-Sn and Pt-Sn-Ni at 450 mV *vs*. SCE for 1800 seconds. Initial sudden drop in current within first 6 minutes is observed for both Pt-Sn and Pt-Sn-Ni, followed by a slower decay. From the i-t plot, it is cleared that the current values, obtained for Pt-Sn-Ni, were always higher than those obtained for Pt-Sn. These results confirm that Pt-Sn-Ni is the best catalyst compared to Pt-Sn and pure Pt for EtOH electro-oxidation. The bi-functional mechanism suggests, in this specific case, that oxygenated species on Sn assisted by Ni allows the removal of the reaction intermediates such as CHx and CO at lower potentials and thus better catalytic activity towards ethanol electro-oxidation is explained.

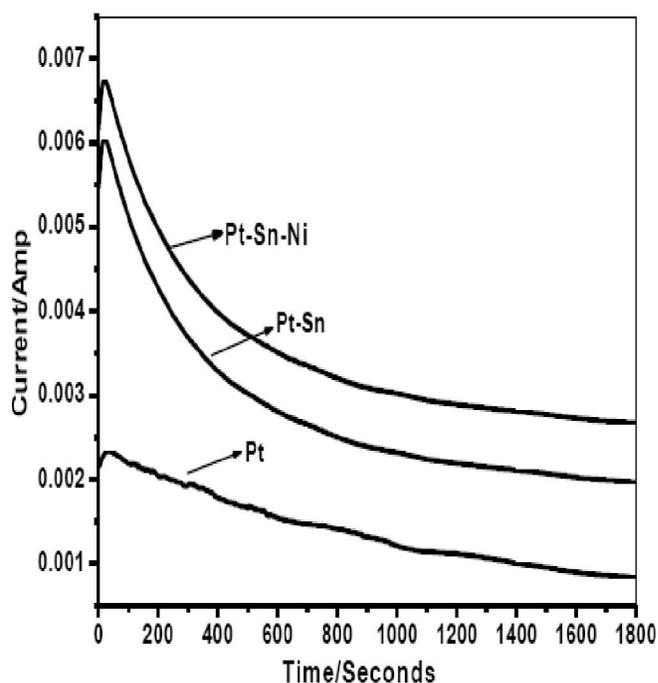**Figure 6 : Cyclic voltammograms of 2-PrOH(1M) in H_2SO_4 solution onto Pt, Pt-Sn and Pt-Sn-Ni catalyst. Scan rate 30 mV.s⁻¹.**

Figure 7 : Amperometric i-t curves of EtOH (1M) in H_2SO_4 solution at 0.45 volt onto Pt, Pt-Sn and Pt-Sn-Ni catalyst.

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But the amperometry study of 2-PrOH electro-oxidation (Figure 8) shows that both Pt-Sn and pure Pt are not so efficient catalyst compared to Pt-Sn-Ni. From the Figure it is seen that the current for Pt-Sn-Ni system is always higher. Bi-functional mechanism does not operate for 2-PrOH electro-oxidation, but the observed enhancement of catalytic activity of Pt-Sn-Ni in presence of Ni may be due to its electronic effect[14].
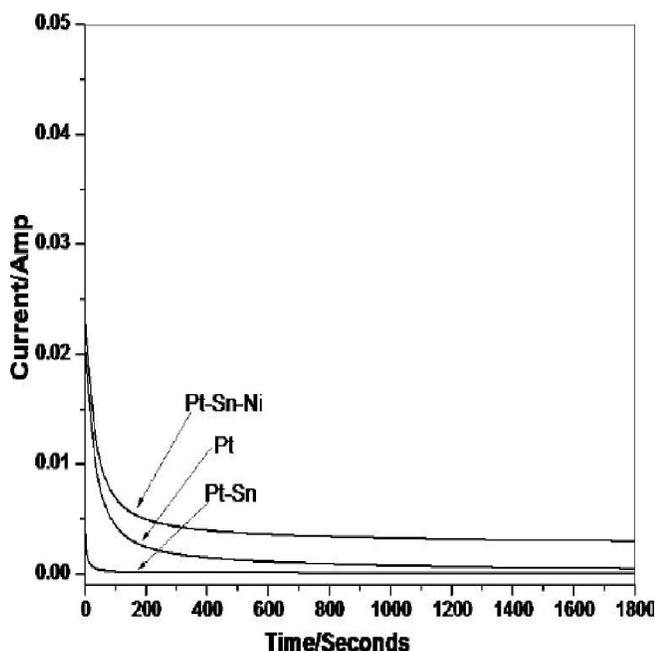

Figure 8 : Amperometric i-t curves of 2-PrOH (1M) in H_2SO_4 solution at 0.45 volt onto Pt, Pt-Sn and Pt-Sn-Ni catalyst.

CONCLUSION

In this study, electro-oxidation of EtOH and 2-PrOH has been studied onto ternary Pt-Sn-Ni surfaces and compared the results with pure Pt and Pt-Sn surfaces. In case of EtOH, improved catalytic activities of Pt are observed in the presence of Sn and in presence of two co-metals Sn and Ni. The results indicate that the Pt-Sn-Ni catalyst performs better than the binary Pt-Sn catalyst due to the promoting effect of Ni. This is explained in terms of electronic effect of Ni and bi-functional effect of Sn. However, for 2-PrOH electro-oxidation catalytic activity of Pt is inhibited in the presence of Sn. This is due to the formation of acetone during 2-PrOH electro-oxidation and its strong adsorp-

tion onto Sn surface. In case of 2-PrOH on to Pt-Sn-Ni electrode the oxidation current is increased compared to Pt-Sn and pure Pt electrode. The marginal improvement in the catalytic activity of the Pt-Sn-Ni electrode towards 2-propanol electro-oxidation might be due to the resultant effect of Sn and Ni. Though Sn has negative impact on 2-PrOH electro-oxidation, but introduction of Ni enhances the electronic effect, which overcome the negative impact of Sn and thus has better catalytic activity compared to Pt-Sn and Pt alone.

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