

# Microwave Assisted Synthesis of Sn Promoted Pt Catalysts and Their Ethanol Electro-oxidation Activities

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**Abstract** In the present work, bi-metallic Pt-Sn electro catalysts were prepared by microwave assisted polyol method at 9:1, 7:3, and 5:5 Pt: Sn atomic ratios on carbon nanotube. The ethanol electro-oxidation activities of these catalysts were measured by cyclic voltammetry (CV). The effect of Sn addition to Pt for the improvement of ethanol electro-oxidation was also measured by CV measurements. Pt-Sn (07:03) catalyst exhibits the highest ethanol electro-oxidation activity. Furthermore, the rotating disk measurements were performed at 0-2000 rpm rotating rates on Pt-Sn (07:03) catalyst. The effect of ethanol concentration on ethanol electro-oxidation activity at varying ethanol concentrations (0.03 M-8.00 M) were measured on Pt-Sn (07:03) catalyst. CO stripping measurements were performed to determine the CO resistance of Pt-Sn electrocatalysts. As a result, CO oxidation onset potential decreases by the addition of Sn to Pt, revealing that Sn addition promotes the CO resistance of platinum.

**Keywords:** ethanol electro-oxidation, microwave assisted polyol method, DEFCs, Pt:Sn catalysts, cyclic voltammetry

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## 1. Introduction

Direct liquid ethanol fuel cells (DEFC) are promising energy sources for portable applications [1-6]. The employment of ethanol as fuel has much more advantage over methanol because ethanol has higher theoretical mass energy density than methanol and is relatively non-toxic. The complete ethanol electro-oxidation involves 12 electrons and breaking of C-C bond. However, methanol electro-oxidation reaction involves only 6 electrons. Following reaction scheme is proposed for ethanol electro-oxidation [7,8,9,10].

Anode reaction :  $C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$

Cathode reaction:  $3O_2 + 12H^+ + 12e^- \rightarrow 6H_2O$

Overall reaction:  $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

Carbon supported platinum is widely used as anode catalyst in acidic low temperature fuel cells but its activity for the oxidation of low molecular weight alcohols is poor. Pt-based multimetallic catalysts have been found to be more active than monometallic Pt for alcohol electro-oxidation reaction due to their resistance to CO poisoning. Bimetallic Pt-Sn carbon supported systems are known to exhibit high catalytic activity for ethanol oxidation in acid media. The presence of Sn alters the electronic structure of Pt, weakening CO adsorption on the Pt surface, thus reducing catalyst poisoning [8,11,12,13,14,15].

The microwave-assisted polyol method is fast and efficient for the preparation of nanoparticles. The uniform

heating of the solution leading to a more homogeneous nucleation and shorter crystallization time [16,17].

In the present study, a microwave assisted polyol method was employed for the synthesis of the carbon supported Pt-Sn catalysts. The electro-catalytic behavior of these catalysts towards electro oxidation of carbon monoxide and ethanol was evaluated using cyclic voltammetry.

## 2. Experimental

### 2.1. Preparation of Catalysts and Electrodes

Carbon supported Pt and Pt: Sn (10 wt% Pt) catalysts were prepared by microwave assisted polyol method. Appropriate amounts of Pt salt  $H_2PtCl_6 \cdot 6H_2O$  (Aldrich), Sn salt  $SnCl_2 \cdot 2H_2O$  (Aldrich) and carbon nanotube were dissolved in ethylene glycol mixture per gram support. As a result, carbon slurry was obtained. Then, the pH of this slurry was modified. Samples were inserted Anton Paar Monowave 300 reactor. Finally, the mixture was filtrated, washed, and dried. The details of the microwave assisted preparation method were reported previously [17]. Pt-Sn catalysts were prepared at 9:1, 7:3, and 5:5 Pt: Sn atomic ratios.

The 3 mg catalyst was suspended in 1ml Nafion® solution for about 1 h to obtain the catalyst ink for the preparation of the electrodes. Then, 3  $\mu$ l of the ink was spread on the surface of the glassy carbon electrode, using a micropipette and dried at room temperature to eliminate the solvent. The glassy carbon electrode was polished with alumina before formation of catalyst layer on its surface.

## 2.2. Electrochemical Measurements

All electrochemical measurements were performed using CHI 660 potentiostat. A conventional three-electrode system was employed including a glassy carbon electrode (diameter, 3 mm) as the working electrode, a platinum wire as the auxiliary electrode, and an Ag/AgCl (saturated KCl (3 M)) electrode as the reference electrode. All the experiments were carried out at room temperature. CV measurements were taken on 10% Pt/C, 10% Pt-Sn (9:1)/C, 10%Pt-Sn (7:3)/C, 10%Pt-Sn (5:5)/C catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M C<sub>2</sub>H<sub>5</sub>OH solution. First of all, CV measurements were taken on 10% Pt/C in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M C<sub>2</sub>H<sub>5</sub>OH solution via rotating disc electrode by changing the rotating speed 0-4000 rpm. Then, CV measurements were performed on 10%Pt-Sn/C catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M C<sub>2</sub>H<sub>5</sub>OH solution to observe the effect of Sn addition on ethanol electro-oxidation reaction. As a result of these measurements, the optimum Pt-Sn ratio was defined as 7:3. Following these measurements, ethanol concentration was varied from 0.03 M-8.00 M to observe the effect of ethanol concentration on the ethanol electrooxidation reaction on Pt-Sn (07:03) catalyst.

CO stripping voltammograms were obtained on 10% Pt/C, 10% Pt-Sn (9:1)/C, 10%Pt-Sn (7:3)/C, 10%Pt-Sn (5:5)/C catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution after bubbling CO gas in the cell for 20min at 0.0V, followed by electrolyte exchange and argon purging to remove the excess of CO.

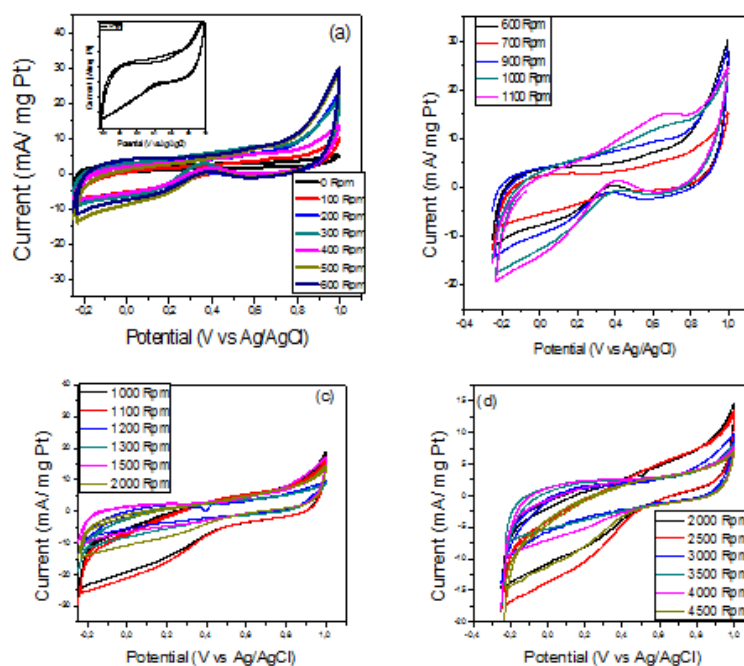
## 3. Results and Discussion

The ethanol electro-oxidation activity was measured on the 10% Pt/C, 10% Pt-Sn (9:1)/C, 10%Pt-Sn (7:3)/C, 10%Pt-Sn (5:5)/C catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M C<sub>2</sub>H<sub>5</sub>OH at 25°C to investigate the effect of tin addition on ethanol electro-oxidation reaction. First of all, the ethanol electro oxidation measurements on 10% Pt/C catalyst was performed at different rotation rates (0-4500 rpm). Our

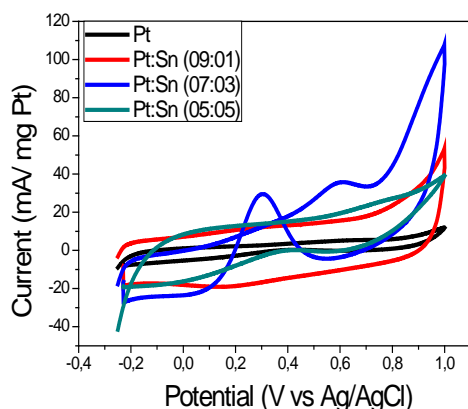
aim to conduct ethanol electrooxidation measurements at different rotation rates on Pt to reveal CO poisoning effect could be decreased by increasing rotation rate. The steady state cyclic voltammograms of these catalysts are presented in Figure 1. In Figure 1a, insert shows the ethanol electrooxidation measurement at 0 rpm rotation rate. The forward ethanol electrooxidation peak was observed at 0.5 V, but it not strong peak. However, the reverse ethanol electrooxidation peak observed at 0.4 V is clear. The increase in the rotation rate results in an increase in the ethanol electrooxidation peak currents. The magnitude of current for 0 rpm experiment is small as compared to higher rotation rates. By increasing rotation rate, CO-like species leading to poisoning on the Pt surface could not be adsorbed on the Pt surface.

At 1100 rpm rotation speed, the maximum current density was obtained for 10% Pt/C catalyst. On the other hand, one could note that rotation speed variation does not significantly influence ethanol electro oxidation activity of 10% Pt/C catalyst. Surface chemisorbed ethanol is oxidized at around 0.7 V potential and Pt surface is oxidized at 1.0 V. Furthermore, bulk ethanol was oxidized via surface Pt oxide at around 0.4 V upon reversing the potential [18]. This reverse peak corresponds to ethanol electro-oxidation. During anodic scan Pt surface was regenerated after reduction of PtO [19].

The ethanol electro-oxidation activity was evaluated on the 10%Pt: Sn/C catalysts in the 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at 25°C to investigate the effect of Sn addition in ethanol electro-oxidation activity. The cyclic voltammograms which were taken at 0.02 V/s scan rate of 10%Pt: Sn/C catalysts prepared at 09:01, 07:03, and 05:05 Pt-Sn atomic ratios in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M C<sub>2</sub>H<sub>5</sub>OH solution. These voltammograms are presented in Figure 2. Ethanol electro-oxidation current values increased when Sn amount increased significantly. The optimum current density is obtained for Pt-Sn (07:03) catalyst. When Pt: Sn atomic ratio decreased 05:05 value, a decrease in oxidation current value is observed.



**Figure 1.** Cyclic voltammograms of carbon supported 10 % Pt catalysts prepared in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M C<sub>2</sub>H<sub>5</sub>OH solution at 0.02 V/s scan rate at (a) 0-600 rpm : insert shows the 0 rpm measurements (b) 600-1100 rpm, (c) 1000-2000 rpm, (d) 2000-4500 rpm rotation rates

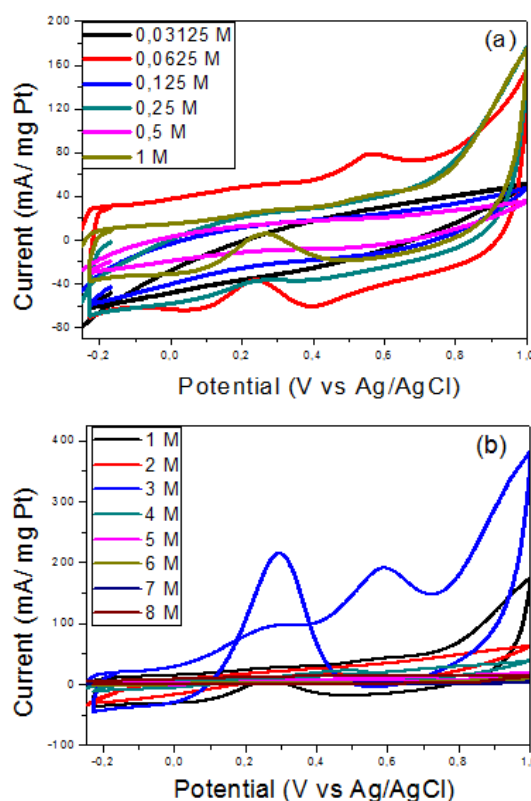


**Figure 2.** Cyclic voltammograms of carbon supported 10 % Pt-Sn catalysts in 0.5 M  $\text{H}_2\text{SO}_4$  + 1 M  $\text{C}_2\text{H}_5\text{OH}$  solution at 0.02 V/s scan rate

In order to observe the effect of ethanol concentration on ethanol electro oxidation activity, ethanol electro oxidation measurements at varying ethanol concentration (0.03 M-8.00 M) in 0.5 M  $\text{H}_2\text{SO}_4$  solution was performed at 0.02 V/s scan rate. Results of these measurements are presented in Figure 3. These results indicate that the current value increase by increasing the ethanol concentration until 3.00 M ethanol concentration. Maximum current value was observed at 3.00 M ethanol concentration. Above, 3.00 M ethanol concentration, the ethanol electro-oxidation current values decreases.

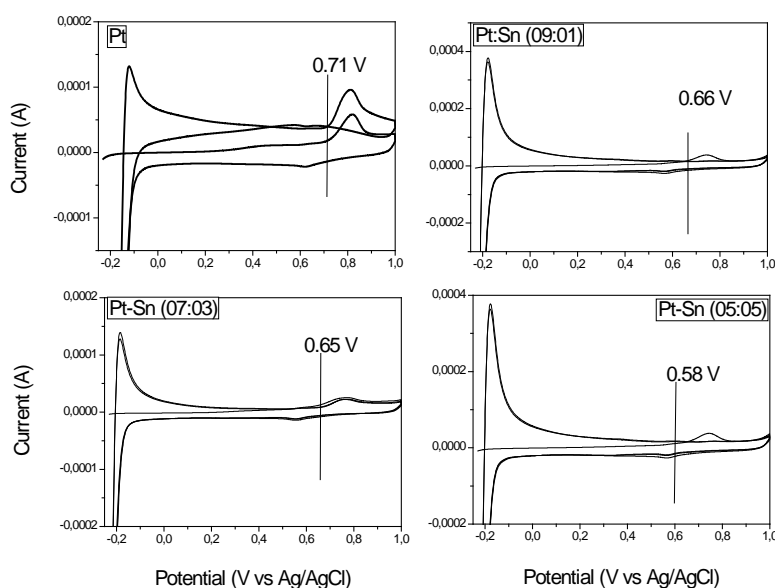
The carbon monoxide electro oxidation reaction at platinum-based electrodes is an important model reaction and practical reaction in fuel cell catalysis. The development of catalytic materials tolerant to the presence of small amounts of CO is extremely important. Figure 4 shows the CO stripping measurements on 10% Pt/C, 10% Pt-Sn (9:1)/C, 10%Pt-Sn (7:3)/C, 10%Pt-Sn (5:5)/C catalysts. Results of these measurements are given in Figure 4. The CO oxidation onset potential of Pt/C catalyst is 0.71 V. On the other hand we observed that Sn enhances CO oxidation reaction. In fact, the onset potential for the CO oxidation reaction is close to 0.66 V for 10% Pt-Sn (9:1)/C catalyst. The CO oxidation onset potential is 0.65 V for 10%Pt-Sn (7:3)/C catalyst and 0.58 V for 10%Pt-Sn (5:5)/C catalyst. The catalyst surface

composition, alloy degree and surface structure play an important role.



**Figure 3.** Cyclic voltammograms of carbon supported 10 % Pt-Sn (07:03) catalyst at different ethanol concentrations

Hence, Sn produce electrochemically active OH on their surface for the oxidative removal of CO adsorbed on adjacent Pt sites. Accordingly, the CO tolerance increases in the subsequent way: 10% Pt/C < 10% Pt-Sn (9:1)/C < 10%Pt-Sn (7:3)/C < 10%Pt-Sn (5:5)/C. As a result, 10%Pt-Sn (7:3)/C catalyst has low onset potential for CO oxidation and the highest anodic current during the ethanol oxidation reaction. Despite the high CO tolerance delivered by 10%Pt-Sn (5:5)/C catalyst, ethanol electro oxidation current of this catalyst lower than 10%Pt-Sn (7:3)/C catalyst.



**Figure 4.** CO stripping measurements of carbon supported 10 % Pt-Sn catalysts in 0.5 M  $\text{H}_2\text{SO}_4$  at 0.02 V/s scan rate

## 4. Conclusions

Ethanol electro oxidation and CO stripping measurements were performed on 10% Pt/C, 10% Pt-Sn (9:1)/C, 10%Pt-Sn (7:3)/C, 10%Pt-Sn (5:5)/C catalysts prepared by microwave assisted polyol method. As a result, one could note that these catalysts were prepared successfully by microwave assisted polyol method. Furthermore, Sn promotes ethanol electro oxidation reaction and increases the CO resistance of the Pt.

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