

Platinum/Tin Oxide - Single Walled Carbon Nanotube Electrocatalysts for Direct Ethanol Fuel Cell

Ryan S. Hsu and Zhongwei Chen*

Department of Chemical Engineering, Waterloo Institute of Nanotechnology, Waterloo Institute for Sustainable Energy, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada,

A novel tin oxide (SnO_2) coated single-walled carbon nanotubes (SWCNT) supported platinum (Pt) electrocatalyst were developed for direct ethanol fuel cells (DEFCs). SnO_2 coated SWCNT were synthesized successfully with a simple method of hydrolysis-oxidation of SnCl_2 in water at room temperature, then SnO_2 -SWCNT supported Pt electrocatalyst (Pt/ SnO_2 -SWCNT) and SWCNT supported Pt electrocatalyst (Pt/SWCNT) were prepared by an ethylene glycol (EG) reduction method. The Pt/ SnO_2 -SWCNT catalyst demonstrated much higher catalytic activity for ethanol oxidation reaction (EOR) than that of the Pt/SWCNT.

Introduction

Ethanol offers many distinct advantages when considering alternative fuels for a direct energy fuel cell. Ethanol is energy dense (having an energy density approaching that of gasoline), readily available from biomass resources, easily stored and transported, and has the added benefit over methanol because it is non-toxic [1-3]. However, the kinetics of the ethanol oxidation reaction are slower compared to oxygen reduction reaction and the stability of the anodic electrocatalyst still needs to be greatly improved before direct ethanol fuel cells can be considered for commercialization [4].

The electrocatalysts utilized for ethanol oxidation face new and more difficult challenges than those used for the oxidation of methanol. Ethanol oxidation catalysts are required to break the C-C bond to produce carbon dioxide in order to realize the 12-electron pathway for complete combustion [5]. Standard platinum supported carbon catalysts yield unfavorable C-2 products such as acetaldehyde (two-electron pathway) and acetic acid (four-electron pathway), and thus generate low activity [6, 7]. Pt/C catalysts are also inadequate for ethanol oxidation because of reaction intermediates that may poison reaction sites by binding to the platinum surface. It is generally accepted that the catalysis of ethanol oxidation requires a multifunctional electrocatalyst for superior performance and durability [8].

The addition of tin oxide for direct ethanol fuel cell catalysts has been used with great success to enhance the catalytic activity of pure platinum [2, 9, 10]. Previous studies by Song et al. showed that significant increases occurred in the ethanol electro-oxidation over platinum through the addition of various metals – most notably Sn, Ru, W, and Pd. Of those binary-metallic electrocatalysts studied by Song et al., PtSn/C demonstrated superior performance and was able to oxidize ethanol to a deeper extent over PtRu/C [2]. A. Kowal et al. reports similar success using SnO_2 and attributes the increased ethanol oxidation activity in their catalyst to the surface interaction of SnO_2 and OH. This

interaction causes a shift in the surface oxidation of Pt to positive potentials, allowing greater Pt availability for catalytic reaction [10].

The novelty of this study stems from the use of single-walled carbon nanotubes (SWCNT) as a support material for the Pt and SnO₂ binary metallic catalyst in low temperature fuel cell applications. H.L. Pang et al. and C. Du et al. both report on the use of multi-walled carbon nanotubes (MWCNTs) in the creation of successful Pt based electrocatalysts. H.L. Pang et al. reports that Pt/SnO₂-CNT/graphite outperformed Pt/SnO₂/graphite electrodes and have higher electrocatalytic activity, better conductivity, and long-term stability [11]. The study conducted by C. Du et al. concludes that SnO₂-CNT composites are corrosion resistant and facilitate long-term durability of electrocatalysts due to the graphite-like properties of CNTs: high aspect ratio, high electronic conductivity, greater corrosion resistance, and enhanced mass transport capability [12, 13].

Single-walled carbon nanotubes have the inherent advantage of having higher surface area per mass ratios than multi-walled carbon nanotubes and exhibit enhanced electric conductive properties. Thus, in this study, it is proposed that the synthesis of a novel platinum based catalyst, with the addition of SnO₂ and single walled carbon nanotubes as support material, will create a multifunctional ethanol oxidation catalyst able to increase the performance and stability over traditional electrocatalysts. Figure 1 illustrates the basic steps utilized to treat and prepare the Pt/SnO₂-SWCNT electrocatalyst.

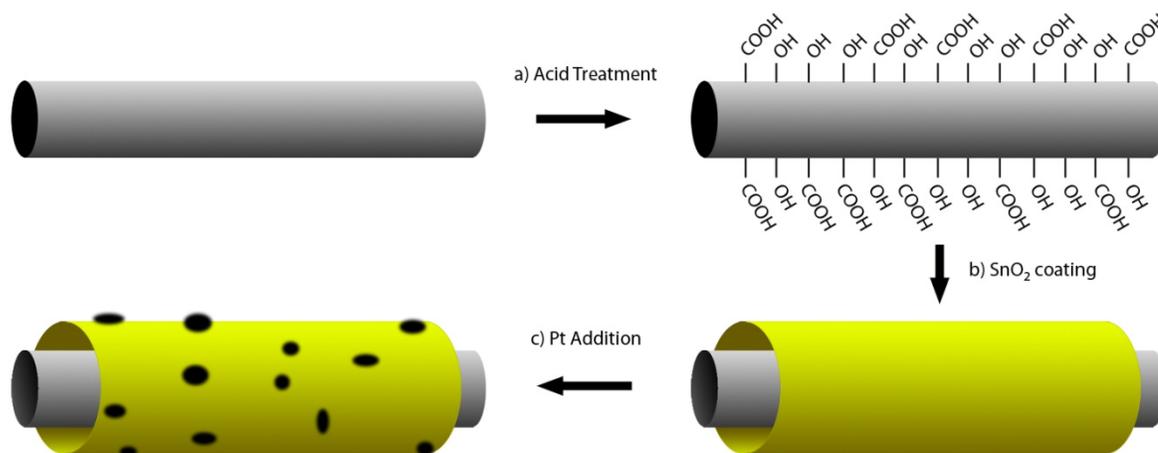


Figure 1: Electrocatalyst synthesis steps. a) Commercial SWCNTs are acid treated to produce functionalized SWCNT. b) SnO₂ is coated onto the surface of the functionalized SWCNTs by using SnCl₂ as a precursor. c) Pt addition to the SnO₂-SWCNT composite via a polyol method utilizing ethylene glycol as the reducing agent.

Experimental

Preparation of the SnO₂-SWCNT support

5.0 g of SnCl₂·2H₂O precursor was dissolved in 200 mL of H₂O and mixed with 7 mL of 38wt.% HCl. 100 mg of treated SWCNT was dissolved in another 200 mL of H₂O and mechanically stirred for 30 minutes. Both solutions were combined and ultrasonicated until proper dispersion was achieved. The resulting mixture was filtrated and washed

with de-ionized water and then heated in an oven at 70°C overnight. The dried precipitate was collected and weighed for use in the Pt/SnO₂-SWCNT electrocatalyst.

Preparation of the Pt/SnO₂-SWCNT and Pt/SWCNT electrocatalysts

To synthesize the platinum supported by single-walled carbon nanotubes electrocatalyst, a polyol process was used with ethylene glycol as the reducing agent. 160 mg of SWCNT was mixed with 80 mL of ethylene glycol and ultrasonicated for 20 minutes. A chloroplatinic acid solution was prepared by adding 106.2 mg of H₂PtCl₆·H₂O to 8.0 mL of ethylene glycol. The chloroplatinic acid solution was then added in a dropwise fashion to the carbon nanotube mixture and the resulting solution was mechanically stirred at room temperature for one hour. 2.5 M NaOH in ethylene glycol was added to ensure the pH of the Pt and SWCNT solution was greater than 13. The solution was continually mixed and heated to 130°C with reflux feeding back into the reaction chamber and flowing argon over the solution surface. This was carried out for 3 hours to ensure the platinum was completely reduced. The solution was then allowed to cool under stirring conditions before the pH was adjusted to 4-5 using 1.0 M HCl. The precipitate was filtrated and washed with 1 L of de-ionized water and allowed to dry at 70°C overnight. To synthesize the Pt/SnO₂-SWCNT electrocatalyst, the same polyol process was used replacing the synthesized SnO₂-SWCNT composite as the platinum support for the commercially obtained SWCNT.

Physical characterization of the Pt/SnO₂-SWCNT and Pt/SWCNT electrocatalysts

The crystalline structure and particle size of the SnO₂-SWCNT support and Pt particles attached onto the Pt/SWCNT and Pt/SnO₂-SWCNT electrocatalysts was determined by X-ray diffraction (XRD). An Inel XRG 3000 diffractometer using monochromatic CuK α radiation ($\lambda = 0.154$ nm) was used to perform broad range scans ($0.288^\circ \leq 2\theta \leq 113^\circ$) lasting 10 minutes for each catalyst sample. Transmission electron microscopy (TEM) was used to characterize dispersion as well as the particle size distribution of the Pt particles. Images were taken using a Philips CM 300 microscope at 300 kV.

Electrochemical characterization of the Pt/SnO₂-SWCNT and Pt/SWCNT electrocatalysts

Cyclic voltammetry (CV) and rotating disc electrode (RDE) techniques were used for both Pt/SWCNT and Pt/SnO₂-SWCNT catalysts using a PINE Instrument Bipotentiostat (Model AFCBP1). CV experiments were conducted using the following conditions: 0.1 M HClO₄ in H₂O electrolyte, scan rate of 50 mV/s, bubbling N₂ gas, Pt loading of 40 $\mu\text{g}/\text{cm}^2$ at room temperature. Simple linear sweeps were also done to test the catalytic performance in ethanol oxidation reaction (EOR) conditions utilizing a similar setup however in 0.1 M HClO₄ + 1.0 M CH₃CH₂OH in H₂O electrolyte.

Results and discussion

Structural characterization of SnO₂-SWCNT, Pt/SnO₂-SWCNT and Pt/SWCNT powders were investigated through XRD and the corresponding results are shown in Figure 2. The diffraction peaks at ca. 27°, 32° and 52° correspond to the (110), (101) and (211) faces of SnO₂, respectively. Similarly, the diffraction peaks at ca. 40°, 47°, 68° and 81° correspond to the (111), (200), (220) and (311) faces of platinum, respectively. It should be noted that ca. 27° on the XRD diffraction pattern, graphitic carbon also has a peak

representing the (002) plane of carbon - not to be misrepresented for the (110) face of SnO₂.

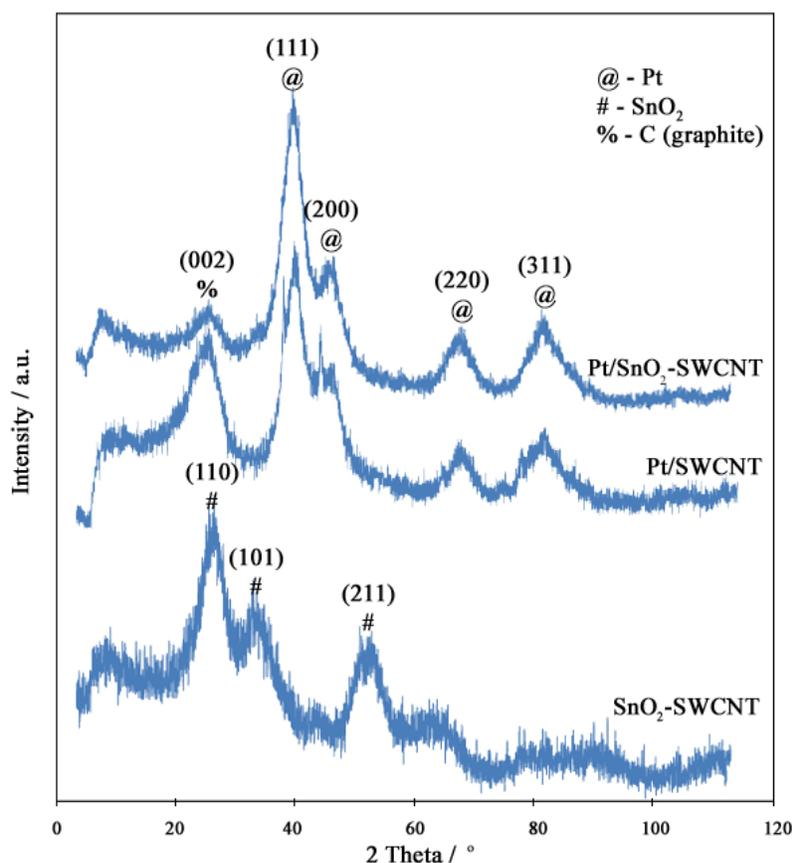


Figure 2: XRD diffraction patterns of Pt/SnO₂-SWCNT, Pt/SWCNT and SnO₂-SWCNT are shown with the Pt, SnO₂ and C (graphite) diffraction peaks labeled.

From Figure 2, the particle diameter, d , can be estimated by the Sherrer equation as follows:

$$d = \frac{0.89 \lambda}{\beta \cos \theta}$$

Where λ (nm) is the X-ray wavelength, β (rad) is the full width at half-maximum of the diffraction peak and θ ($^{\circ}$) is known as the Bragg diffraction peak [14]. The average particle diameter of SnO₂ was calculated to be 1.91 nm using the (211) plane of SnO₂. The particle diameter of the platinum species of the Pt/SnO₂-SWCNT and Pt/SWCNT was calculated using the (220) face of platinum which was determined to be 2.14 nm and 2.15 nm respectively. The platinum particle sizes of both Pt/SWCNT and Pt/SnO₂-SWCNT were compared to that of commercial Pt/C (2.5 nm) produced by E-TEK and found to be slightly smaller.

The pure SWCNT morphology and Pt size distribution on the Pt/SnO₂-SWCNT catalyst can be seen in the TEM image shown in Figure 3. From the figure 3A and 3B, it is evident that the SWCNT bundles are coated with a thin tin oxide layer. The image also shows good dispersion of Pt particles over the SnO₂-SWCNT support.

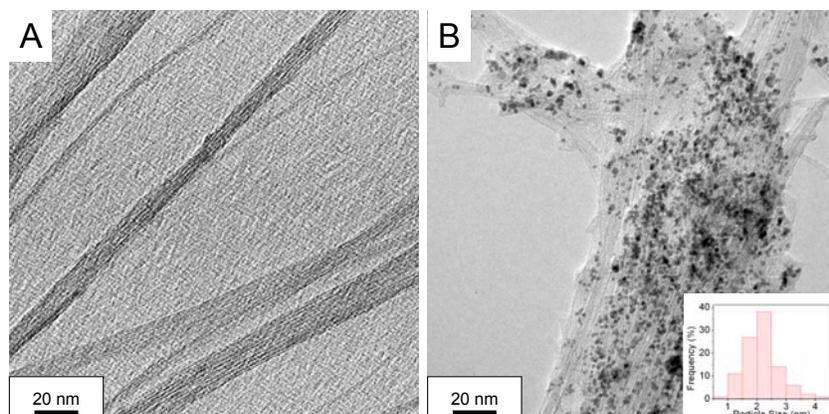


Figure 3: Representative transmission electron microscope image of (A) SWCNT, and (B) Pt/SnO₂-SWCNT bundle. Insert is the particle size distribution for the Pt particle size on Pt/SnO₂-SWCNT catalyst

The diameter of 100 nanosized platinum particles was measured from the Pt/SnO₂-SWCNT catalyst to obtain a histogram of the particle size distribution. This graph is shown in Figure 3b. The mean diameter was measured to be 2.16 nm which is in good accordance to the XRD data.

Figure 4 shows the resulting CV curves for the Pt/SWCNT and Pt/SnO₂-SWCNT catalyst. The base shape of the voltammograms shows clear hydrogen adsorption/desorption regions. This indicates that Pt and SnO₂ are separate species within the electrocatalyst without alloying. XRD data confirms this result as SnO₂ and Pt peaks can be seen in the diffraction patterns. Pt supported by SnO₂-SWCNT showed high current densities in the hydrogen region (-0.15 to 0.2 V vs. Ag/AgCl) indicating a greater electrochemically active surface area for Pt. The hydrogen adsorption/desorption peaks of cyclic voltammetry graphs are commonly used to estimate the ECSA by the following equation:

$$ECAS = \frac{Q_H}{m \cdot c}$$

Where Q_H (mC cm⁻²) is the charge for hydrogen adsorption or desorption, m (mg cm⁻²) is the Pt loading and c (0.21 mC cm⁻² for Pt) is the amount of charge required to oxidize one monolayer of hydrogen on the catalyst surface [15]. The ECAS for Pt/SWCNT and Pt/SnO₂-SWCNT were found to be similar, which are 45.5 and 47.4 m² g⁻¹ respectively.

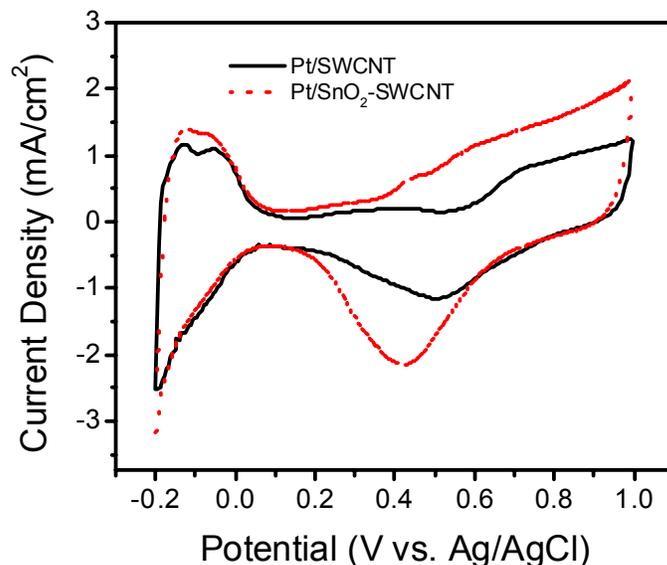


Figure 4: Cyclic voltammetry curve for a thin film of Pt/SWCNT and Pt/SnO₂-SWCNT on a glassy carbon electrode. CV was conducted in 0.1 M HClO₄ with bubbling N₂ and sweep rate was set at 50 mV/s.

Pt/SnO₂-SWCNT and Pt/SWCNT's catalytic performance were studied for the ethanol oxidation reaction. Cyclic voltammograms were used to determine the impact of each catalyst over the range of -0.2 V to 1.0 V vs. Ag/AgCl at room temperature. From Figure 5, it can clearly be seen that the current density of the SnO₂-SWCNT support is higher than that of the SWCNT support and that this difference becomes more pronounced as the potential increases. This improved catalytic activity is mainly due to the promoting effect of the SnO₂ that is found in the Pt/SnO₂-SWCNT catalyst. A comparison of the height of the forward peaks produced by both catalyst shows that Pt/SnO₂-SWCNT is better for ethanol oxidation because of its greater ability to catalyze the ethanol oxidation.

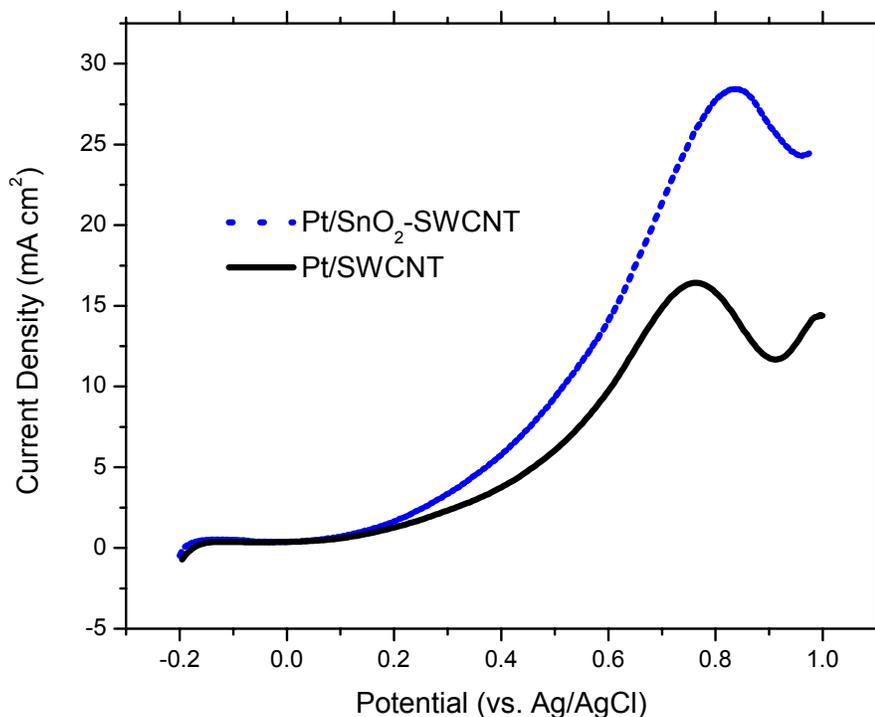


Figure 5: Ethanol oxidation reaction with Pt on different supports in 0.1 M HClO₄ + 1.0 M CH₃CH₂OH.

Conclusions

Pt/SnO₂-SWCNT and Pt/SWCNT electrocatalysts were prepared and investigated for use as electrocatalysts for ethanol oxidation reaction. Pt particles were well distributed onto the supports and sized at roughly 2.1 nm. The Pt/SnO₂-SWCNT catalyst demonstrated much higher ethanol oxidation reaction (EOR) catalytic activity than the Pt/SWCNT. The SnO₂-SWCNT could be a promising candidate as catalyst support for electrocatalysts in ethanol fuel cell applications.

References

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