

# Direct ethanol PEM fuel cells: The case of platinum based anodes

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## Abstract

PtSn/C catalysts were prepared by the direct decoration of Pt/C with Sn through a modified poly process. XRD results showed there existed obvious SnO<sub>2</sub> in this catalyst, different from the PtSn/C prepared by co-precipitation, Sn presenting in different valence. The techniques of cyclic voltammetry, anode polarization curve and single *direct ethanol fuel cell* (DEFC) tests were used to evaluate and compare the electrocatalytic activities to ethanol oxidation over PtSn/C prepared by different preparation procedure and over the commercial PtRu/C catalyst. The experimental results showed that PtSn/C presents higher electrocatalytic activity than PtRu/C. The results also showed that, compared to the PtSn/C prepared by co-precipitation, PtSn/C in this investigation exhibits a similar initial activity but a lower activity along with the current density increment, probably due to its poor electronic conductivity and part coverage of platinum active sites resulting from SnO<sub>2</sub>. It was found from the GC analysis results that PtSn/C can oxidize ethanol molecules to a deeper extent than PtRu/C, leading to both a higher fuel utilization coefficient and a higher fuel cell efficiency.

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## 1. Introduction

Direct ethanol fuel cells (DEFCs) have spurred more and more interest in recent years due to ethanol intrinsic advantages such as its low toxicity, renewability, and its easy production in great quantity by the fermentation from sugar-containing raw materials [1–3]. Furthermore, the high

theoretical mass energy density (about 8.00 kWh/kg) [4] provides it with a potential candidate fuel for polymer electrolyte membrane fuel cells. When ethanol is used as the fuel, its desired reaction in DEFCs is the complete oxidation to CO<sub>2</sub> and water. However, this process involves 12 electrons transfer per ethanol molecule, leading to many adsorbed intermediates and byproducts during the ethanol oxidation process. The main challenge is the cleavage of C–C bond, which does not easily take place at lower temperatures. Even if ethanol oxidation has been extensively investigated at Pt electrodes [5–7], many problems such as auto-inhibition or poisoning phenomena still exist when using a pure platinum electrode for direct ethanol electrooxidation. In order to improve the electrocatalytic activity of platinum to ethanol oxidation, platinum was often modified by adding a second metal like Ru [8,9], Pb [10], Sb [11],

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Rh [12], Mo [13], Os [14], Sn [15,16], thus promoting the electrocatalytic activity of pure platinum.

Our previous research results showed that Sn, Ru, Pd and W can enhance ethanol electro-oxidation activity over Pt in the following order: PtSn/C > PtRu/C > PtW/C > PtPd/C > Pt/C [17] and the Sn content plays an important role in the ethanol electrooxidation and consequently in the single DEFC performance [18]. From the practical point of view, the development of direct ethanol fuel cell depends on the progress in the electrocatalytic materials for ethanol electrooxidation to a great extent. Ethanol adsorption, dissociation and oxidation are mainly affected by the composition and structure of electrocatalysts and the catalyst preparation procedure plays a crucial role in electrocatalysts' composition and structure, especially in the interaction between different components. In the present work, a PtSn/C catalyst synthesized by the direct decoration of commercial Pt/C with Sn as anode electrocatalyst in direct ethanol fuel cell. The techniques of cyclic voltammetry, anode polarization curve and single DEFC tests were applied to compare the Pt-based electrocatalysts activity to ethanol oxidation. GC was used to analyze the product distribution of ethanol oxidation over PtSn/C and PtRu/C during constant cell voltage discharge process.

## 2. Experimental

### 2.1. Electrocatalyst preparation and characterization

In the present investigation, different from the conventional preparation procedure—the precursors of Pt and Sn together supported on carbon (denoted as PtSn/C-b) [19], the PtSn/C catalyst with a Pt to Sn atomic ratio of 2 was prepared by using 20 wt% Pt/C (Johnson Matthey Corp.) as support and SnCl<sub>2</sub> as tin precursor (denoted as PtSn/C-a). An ethylene glycol solution containing the precursor of Sn was mixed with Pt/C slurry, and kept at 130 °C for 1 h after pH value was adjusted to 13. The reduced mixtures were then acidified again at room temperature. Then the slurry was filtered and washed with copious distilled water. The PtSn/C catalysts were obtained after the filter cake was dried in vacuum oven at 80 °C for 12 h. The catalysts were characterized by XRD on a Rigaku X-3000 X-ray powder diffractometer using Cu K $\alpha$  radiation with a Ni filter. The scanning range was from 15° to 90° and the scan rate was 5°/min. The fine Pt (220) plane was obtained by finely scanning from 60° to 75° at a rate of 0.5°/min to estimate the particle size by Scherrer formula [20].

### 2.2. Cyclic voltammetry experiments

The cyclic voltammetry experiments were carried out by employing a potentiostat/galvanostat (EG&G Model 273A) coupled to a personal computer and using the corresponding software provided by EG&G corporation. A known

amount of the catalysts was mixed with an appropriate amount of Nafion<sup>®</sup> solution (5 wt% Aldrich solution) in ethanol solution and transferred quantitatively with an injector to the clean glassy carbon disk electrode (with an area of 0.1256 cm<sup>2</sup>), which was then attached to the Model 616 RDE system. An aqueous solution containing 1.0 mol/l HClO<sub>4</sub> and 1.0 mol/l ethanol was used as the electrolyte, which was deaerated with highly pure nitrogen gas. A saturated calomel electrode (SCE) was used as reference electrode, and a platinum wire as counter electrode.

### 2.3. Anode polarization curve

The anode polarization curves were obtained by supplying the cathode with humidified H<sub>2</sub> instead of O<sub>2</sub>, which was used both as a *dynamic hydrogen reference electrode* (DHE) and as the counter electrode. The anode potential was controlled by a potentiostat/galvanostat (EG&G Model 273A) at a scan rate of 2.0 mV/s. The DHE was made by feeding humidified H<sub>2</sub> at atmospheric pressure and the hydrogen flow rate was 40 mL/min. The anode compartment was pumped by the preheated 1.0 mol/l ethanol aqueous solution at a flow rate of 1.0 ml/min, acting as the working electrode for the electrochemical measurements.

### 2.4. Membrane electrode assembly (MEA) preparation and single DEFC tests

The single DEFC tests were carried out using MEAs with a geometric active electrode area of 4 cm<sup>2</sup>. The MEAs preparation and operation conditions of single fuel cell have been previously described in detail [21]. The PtSn/C and PtRu/C with a Pt loading of 1.33 mg/cm<sup>2</sup> were made as the anode electrocatalysts while the cathode contained Pt/C (20 wt Pt%, Johnson Matthey Corp.) and the metal loading was 1.0 mg Pt/cm<sup>2</sup>. Prior to data collection, the MEAs were fully hydrated by feeding deionized water through the anode compartment at 75 °C for about 4 h by using a peristaltic pump. At the same time the cell was short-circuited several times to remove any low molecular weight organic impurity at the anode and to humidify the electrolyte membrane fully. At 90 °C, the polarization data were obtained by Arbin fuel cell test system with 1.0 mol/l ethanol aqueous solution supplied to the anode and at the same time 15 ml/min flux of oxygen with 2 atm pressure supplied to the cathode. The constant voltage discharge was fulfilled by Arbin fuel cell test station, with the same operating conditions as those described above for the single fuel cell test. The anode products were collected by a cold trap and analyzed by an FID gas chromatograph (HP 6890 series) equipped with a Porapak Q capillary column.

## 3. Results and discussion

The XRD patterns of PtSn/C catalyst are presented in Fig. 1. For comparison, the X-ray diffractograms for the

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