

# Decoration of carbon-supported Pt catalysts with Sn to promote electro-oxidation of ethanol

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## Abstract

Carbon-supported Pt/Sn catalysts were prepared by decorating carbon-supported Pt with Sn, by decorating carbon-supported Sn with Pt, and by co-deposition of Pt and Sn on carbon. All of the Pt/Sn catalysts exhibited greatly enhanced activities for ethanol oxidation relative to Pt alone, with the Sn decorated Pt catalyst showing the best performance. The latter catalyst was shown by XPS to contain no metallic Sn, emphasizing the importance of surface Sn oxide species in the activation of Pt for ethanol oxidation. Decoration of Sn with Pt is shown to be a feasible way to increase Pt utilization.

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**Keywords:** Pt/Sn catalyst; Ethanol oxidation

## 1. Introduction

In recent years, Pt/Sn catalysts have been found to be quite promising as anode catalysts for direct ethanol fuel cells [1–4]. There is therefore increasing interest in the study of Pt/Sn catalysts for electro-oxidation of ethanol, and in the factors that determine their activity.

To date, Pt has been shown to be the only active and stable single metal catalyst for electro-oxidation of ethanol in acidic media [5]. However, Pt is readily poisoned by reaction intermediates such as CO and becomes inactive for ethanol oxidation in the potential region of fuel cell interest. Fortunately, it has been found that addition of metals such as Sn and Ru to Pt catalysts can mitigate the poisoning effect of CO and enhance catalytic activities significantly [1,6–8]. Pt/Sn binary catalysts have generally been shown to be more active than Pt/Ru for ethanol oxidation [2,8]. The promoting effect of Sn has been explained by a bi-functional mechanism and electronic (ligand) effects [5,9]. In the bi-functional mechanism, Sn activates water at lower potentials than Pt and the activated water can oxidize the adsorbed CO and therefore liberate Pt active sites. The promoting effect

can also result, in part, from changes of the electronic properties of the Pt after addition of Sn. It has also been suggested that the longer lattice parameter of Pt/Sn favours C–C bond cleavage [8].

A variety of methods have been used to prepare Pt/Sn catalysts, including chemical reduction [2,3,7,8], mechanical ball milling [10], electrochemical reduction [5,11], and microfabrication techniques [12]. It has been found that the catalytic activity of Pt/Sn catalysts can depend strongly on the preparation method [13,14]. For example, Abruna and co-workers [15] reported that Pt/Sn intermetallic phase catalysts had no promoting effects on Pt for ethanol oxidation, while most other work [e.g. 1–5,7,8] has shown that addition of Sn to Pt catalysts has pronounced promoting effects.

Previous work has shown that underpotential deposition of Sn on Pt (decoration of Pt with Sn) can promote Pt for electro-oxidation of CO and small organic molecules in acidic media [16,17]. The decoration of Pt catalysts with adatoms has recently become an important tool in the development and study of new catalysts [18], but work with the Sn system has been limited relative to work with Ru.

In this work, we have investigated for the first time the use of Sn decorated Pt for ethanol oxidation, and have found that very large increases in catalytic activity can be obtained. Activities are shown to be comparable with those of the alloy catalysts prepared by co-deposition that are generally used, and this provides

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important insight into the factors that determine the activities of Pt/Sn catalysts for ethanol oxidation.

Another aim of the work reported here was to increase Pt utilization by decorating carbon-supported Sn with Pt, since Pt is a precious metal and there is a very limited resource. The advantage of this method is that Pt is on the surface of Sn so that not only is the bi-functional mechanism guaranteed but also blockage of Pt sites by Sn is minimized.

## 2. Experimental

### 2.1. Preparation of catalysts

Carbon-supported Pt/Sn catalysts were prepared by decorating carbon-supported Pt with Sn, by decorating carbon-supported Sn with Pt, and by co-deposition of Pt and Sn on carbon as follows.

#### 2.1.1. Decoration of carbon-supported Pt with Sn

Fifty milligrams of a 20 wt.% Pt on C catalyst (E-Tek) was dispersed in 30 ml of DI water by stirring. An appropriate amount of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (Anachemia) dissolved in 30 ml of DI water was then added dropwise and stirred for 0.5 h (the amount of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  was changed according to the targeted Pt/Sn atomic ratio. However, the volume of DI water was fixed at 30 ml. Taking the Pt/Sn atomic ratio of 4:1 for example, the concentration of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  solution was ca. 0.43 mM) followed by dropwise addition of a two times excess of  $\text{NaBH}_4$  (BDH) dissolved in 40 ml of DI water with further stirring for 0.5 h (the amount of  $\text{NaBH}_4$  was changed based on the amount of Sn. However, the volume of DI water was always fixed at 40 ml; for Pt/Sn atomic ratio of 4:1, the concentration of  $\text{NaBH}_4$  solution was ca. 0.64 mM). The product was collected by filtration and washed well with copious amounts of DI water, then dried at room temperature in a vacuum oven.

In addition to decorating commercial Pt catalysts, we have prepared carbon-supported Pt catalysts first, then decorated them with Sn. We also prepared Pt/Sn catalysts by decorating commercial Pt catalysts with Sn without a reduction step. However, it was found that Pt/Sn catalysts prepared by decorating commercial Pt catalysts with the reduction step had the highest activity for ethanol oxidation (see below). So our physical characterization of catalysts is focused on these catalysts.

#### 2.1.2. Decoration of carbon-supported Sn with Pt

Forty milligrams of Vulcan carbon (XC-72R, E-Tek) was dispersed in 30 ml of DI water by stirring, followed by dropwise addition of 50 ml of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (the amount of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  depends on the targeted loading of Sn on the carbon support. However, the volume of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  solution was fixed at 50 ml; for the 2 wt.% Sn on carbon, the concentration of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  solution was ca. 0.135 mM) and stirring for 0.5 h. A two times excess of  $\text{NaBH}_4$  in 40 ml of DI water was then added with further stirring for 0.5 h (the amount of  $\text{NaBH}_4$  was changed based on the amount of Sn and the volume of DI water was always fixed at 40 ml). The product was collected by filtration and washed well with copious amounts of DI water, then dried

at room temperature in a fume hood. The product was then re-dispersed in 30 ml of DI water by stirring, followed by dropwise addition of 50 ml of  $\text{K}_2\text{PtCl}_4(\text{aq})$  (PMO Ltd.) and stirring for 0.5 h (the amount of  $\text{K}_2\text{PtCl}_4$  depends on the targeted atomic ratio of Sn to Pt and the volume of  $\text{K}_2\text{PtCl}_4$  solution was fixed at 50 ml). A two times excess of  $\text{NaBH}_4$  in 40 ml of DI water was then added with further stirring for 0.5 h (the amount of  $\text{NaBH}_4$  depended on the amount of Sn and the volume of DI water was always fixed at 40 ml). The product was collected by filtration and washed well with copious amounts of DI water, then dried at room temperature in a vacuum oven.

#### 2.1.3. Co-deposition of Pt and Sn on carbon

Forty milligrams of Vulcan carbon (XC-72R, E-Tek) was dispersed in 30 ml of DI water by stirring, followed by dropwise addition of 50 ml of an aqueous metal precursor solution containing 21.3 mg  $\text{K}_2\text{PtCl}_4$  (giving a nominal 20 wt.% Pt on C) and an appropriate amount of  $\text{SnCl}_4$  (Aldrich) (the amount of  $\text{SnCl}_4$  was changed according to targeted Pt/Sn atomic ratio and the volume of the solution was always fixed at 50 ml). The suspension was then stirred for 0.5 h, followed by dropwise addition of two times excess of  $\text{NaBH}_4$  in 40 ml of DI water and further stirring for 0.5 h (the amount of  $\text{NaBH}_4$  depended on the amount of Pt and Sn and the volume of DI water was always fixed at 40 ml). The product was collected by filtration and washed well with copious DI water, then dried at room temperature in a vacuum oven.

### 2.2. Characterization of catalysts

#### 2.2.1. X-ray photoelectron spectroscopy (XPS)

XPS analysis of one catalyst was obtained with a VG ESCALAB 3 Mark II at Ecole Polytechnique de Montreal.

#### 2.2.2. X-ray diffraction (XRD)

XRD patterns of the catalysts were obtained on an X-ray diffractometer (Rigaku D/Max-2200V-PC) using a Cu K $\alpha$  source ( $\lambda = 1.5418 \text{ \AA}$ ) at a scan rate of  $1.5^\circ \text{ min}^{-1}$ . The scan range was from  $20^\circ$  to  $120^\circ$ .

### 2.3. Electrochemistry

#### 2.3.1. Preparation of electrodes

Two milligrams of the catalyst was dispersed in 500  $\mu\text{l}$  of 5% Nafion solution (DuPont) by sonication for 50 min. Two microlitres of the resulting ink was then deposited onto a  $0.071 \text{ cm}^2$  glassy carbon electrode with a micropipet and dried at room temperature, giving a catalyst loading of ca.  $0.11 \text{ mg cm}^{-2}$ . The glassy carbon electrode was polished with  $0.3 \mu\text{m}$  alumina before deposition.

For long-term electrolysis, the electrode was prepared as follows: 5 mg of the catalyst was mixed with 20 mg of 5% Teflon suspension by sonication for 0.5 h. The resulting paste was then applied onto  $1 \text{ cm}^2$  of carbon fiber paper (CFP) and dried at room temperature.

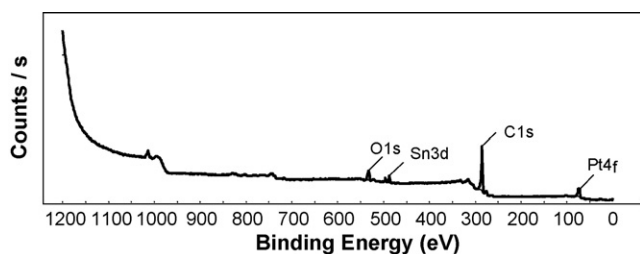


Fig. 1. A XPS survey spectrum of a carbon-supported Pt/Sn (4:1) catalyst prepared by decorating an E-Tek 20% Pt on C catalyst with Sn.

### 2.3.2. Electrochemical measurements

Electrochemical measurements were carried out in a conventional three-compartment cell at room temperature with an EG&G PAR 273A potentiostat/galvanostat or a Solartron 1286 electrochemical interface. A Pt wire was used as the counter electrode. The reference electrode was a SCE (0.24 V versus SHE). However, all potentials are reported with respect to the SHE. Before measurements the electrolyte solution was purged with pure N<sub>2</sub> to expel oxygen, and then protected with N<sub>2</sub> during measurements.

## 3. Results and discussion

### 3.1. XPS

Fig. 1 shows a XPS survey spectrum of a carbon-supported Pt/Sn (4:1) catalyst prepared by decorating a commercial Pt catalyst with Sn (note that the atomic ratio of 4:1 is nominal, and that all of the other molar ratios of Pt to Sn used in this paper are nominal except for the molar ratios obtained by XPS). It can be seen that the catalyst contained C, Pt, and Sn as expected. It also contained oxygen, indicating that some elements were in an oxide form. The atomic % of O in the catalyst was 10.5 as listed in Table 1. No residue Cl was detected, indicating that washing of the catalyst was effective.

It was found that the atomic ratio of Pt to Sn was ca. 2:1 (Table 1), much lower than the nominal ratio of 4:1. This is consistent with the results reported by Crabb et al. [14], who also found that experimental atomic ratios of Pt/Sn determined with XPS were ca. half of nominal atomic ratios for their Pt/Sn catalysts prepared from organometallic precursors using surface organometallic chemistry. The high apparent Sn ratio is presumably due to the deposition of Sn on the surface of the Pt particles, which would decrease the XPS signal from the underlying Pt.

Table 2 lists high-resolution XPS data of the catalyst. Peak assignments were based on reference data from references

Table 1  
XPS survey data for a carbon-supported Pt/Sn (4:1) catalyst prepared by decorating an E-Tek 20% Pt on C catalyst with Sn

| Element | Center (eV) | at. % |
|---------|-------------|-------|
| O 1s    | 533.0       | 10.5  |
| Sn 3d   | 487.0       | 0.7   |
| C 1s    | 285.0       | 97.3  |
| Pt 4f   | 72.0        | 1.5   |

Table 2

High-resolution XPS data of the carbon-supported Pt/Sn (4:1) catalyst

| Name | B.E. (eV)   | Identification            | at. % |
|------|-------------|---------------------------|-------|
| C1   | 285.0       | C—C                       | 51.4  |
| C2   | 286.3       | C—O                       | 15.7  |
| C3   | 287.7       | C=O                       | 7.1   |
| C4   | 289.1       | O—C=O                     | 5.9   |
| C5   | 291.2       | Shake-up $\pi$ — $\pi^*$  | 3.6   |
| O1   | 531.3       | O—metal                   | 2.6   |
| O2   | 532.7       | C=O                       | 3.3   |
| O3   | 534.0       | C—O                       | 3.3   |
| O4   | 535.3       | ?                         | 1.2   |
| O5   | 536.7       | ?                         | 0.5   |
| Pt1  | 71.9–75.2   | Pt <sup>0</sup> and Pt—Sn | 1.8   |
| Pt2  | 73.0–76.3   | Pt (II)                   | 1.3   |
| Pt3  | 75.4–78.7   | Pt (IV)                   | 0.4   |
| Sn1  | 487.4–495.9 | Sn (II) and Sn (IV)       | 2.0   |

[19–21]. It was found that there were three different oxidation states for Pt. They are Pt (0), Pt (II), and Pt (IV). The atomic ratios of Pt (0)/Pt (II)/Pt (IV) were 1.8/1.3/0.4, indicating that only ca. 50% of the Pt was in the metallic state on the catalyst surface, although the catalyst had been reduced with NaBH<sub>4</sub>. The higher oxidation states of Pt are assumed to be due to the formation of Pt—O<sub>ads</sub> and surface PtO and PtO<sub>2</sub> [21]. It is generally believed that Pt metal is effective for ethanol oxidation [2–4]. The effects of platinum oxides on ethanol oxidation are not clear yet. Therefore, further studies are needed.

Fig. 2 shows a high-resolution XPS spectrum of Sn in the catalyst. There are two peaks corresponding to Sn (II) and/or Sn (IV) as shown in the figure. No peaks for metallic Sn were found. This indicates that Sn existed in an oxidized form on the catalyst surface, although NaBH<sub>4</sub> was added as a reducing agent. Other researchers also found that most tin atoms existed as oxides in Pt/Sn catalysts prepared by different methods [14,21,22]. In addition, it is impossible to distinguish between Sn (II) and Sn (IV) by XPS, since their binding energies are very close [22,23]. The Sn/Sn (II) formal potential of ca. 0.2 V versus SHE reported for Sn on Pt (1 1 1) [24] indicates that any metallic Sn on the surface of the catalysts prepared in this work would be oxidize by air to Sn (II).

In conclusion, only ca. 50% of the Pt was in the metallic state on the catalyst surface and no evidence of metallic Sn was found on the catalyst surface.

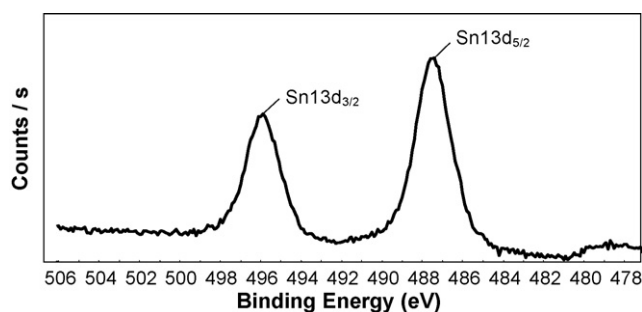


Fig. 2. A high-resolution XPS spectrum of the Sn region in Fig. 1.

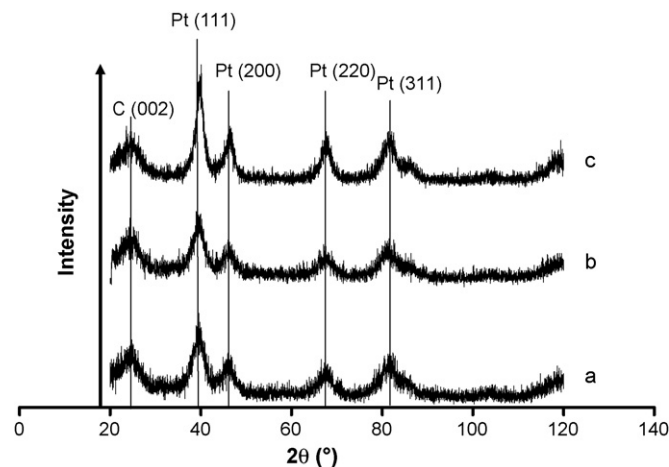


Fig. 3. XRD patterns of an E-Tek 20% Pt on C catalyst (a), a Pt/Sn catalyst (4:1) prepared by decorating an E-Tek 20% Pt on C catalyst with Sn (b), and a Pt/Sn (4:1) catalyst prepared by decorating a home-made 20% Pt on C catalyst with Sn (c).

### 3.2. XRD

Fig. 3 presents XRD patterns of Pt/Sn catalysts, along with the commercial 20% Pt on C catalyst. The diffraction peak at ca.  $25^\circ$  is due to the C (002) plane, while the peaks at ca.  $40^\circ$ ,  $46^\circ$ ,  $67.5^\circ$ , and  $81.5^\circ$  represent the Pt (111), Pt (200), Pt (220), and Pt (311) planes, respectively. No peaks for Sn or Pt/Sn alloys were observed, suggesting that Sn was either highly dispersed or in an amorphous state. XPS data clearly show that Sn was in an oxidized state. Therefore, Sn was more likely in an amorphous state in the Pt/Sn catalysts.

The mean particle sizes were estimated from the (220) peak width according to the Scherrer equation [23]:

$$D = \frac{0.9\lambda}{B \cos \theta} \quad (1)$$

where  $D$  is the mean particle diameter,  $\lambda$  the X-ray wavelength,  $B$  the peak width at half height in radians, and  $\theta$  is the diffraction angle. The results are listed in Table 3. It was found that decoration of the commercial catalyst with Sn did not significantly change the particle size, which is consistent with the deposition of Sn oxide on the Pt surface. The home-made catalysts (Sn on Pt or co-deposited Pt + Sn) both had significantly larger particle sizes than the commercial catalyst.

TEM (not shown) confirmed that modification of the commercial catalyst did not significantly change the particle size, or the distribution of Pt particles on the carbon support. In both

Table 3  
Particle sizes of Pt/Sn catalysts and a carbon-supported Pt catalyst (based on the 220 plane)

| Name <sup>#</sup>           | Mean particle size (nm) |
|-----------------------------|-------------------------|
| 20% Pt on C (E-Tek)         | 2.5                     |
| Sn on home-made C/Pt (4:1)  | 4.2                     |
| Sn on commercial C/Pt (4:1) | 2.8                     |
| Pt + Sn on C (5:1)          | 5.4                     |

<sup>#</sup> Pt:Sn atomic ratios are indicated.

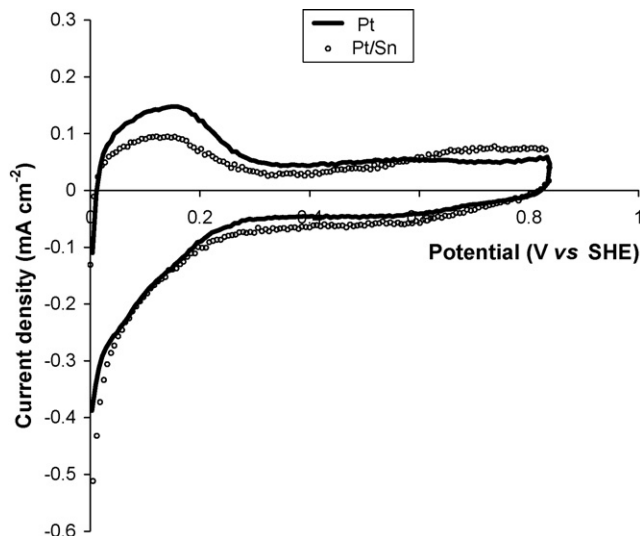


Fig. 4. Cyclic voltammetry in 1 M H<sub>2</sub>SO<sub>4</sub>(aq) of an E-Tek 20% Pt on C catalyst and a Pt/Sn (4:1) catalyst prepared by decorating it with Sn. Scan rate: 10 mV s<sup>-1</sup>.

cases, the average particle size appeared to be somewhat higher than indicated by XRD, suggesting some agglomeration of the Pt crystallites.

### 3.3. Cyclic voltammetry

The electrochemically active areas of the catalysts were investigated by cyclic voltammetry (CV) in 1 M H<sub>2</sub>SO<sub>4</sub>(aq). Fig. 4 compares CVs of the commercial C/Pt catalyst and a Pt/Sn (4:1) catalyst prepared by decorating it with Sn. It is seen that the hydrogen adsorption waves on the Pt/Sn catalyst were significantly smaller than those on the Pt catalyst. Similar results were also reported by Crabb et al. [14], who found that hydrogen adsorption on Pt decreased by a factor of 3 with addition of 1 monolayer equivalent of Sn to a Pt catalyst. The significant decrease of the hydrogen adsorption waves after addition of Sn indicates that some of the Pt active sites for hydrogen adsorption were blocked by Sn or that the electronic properties of Pt were changed significantly by addition of Sn. Frelink et al. [25] had prepared Pt/Sn catalysts for methanol oxidation by deposition of Sn onto Pt catalysts and found that Sn was preferentially deposited onto Pt active sites for hydrogen adsorption. Considering the fact that the Pt/Sn catalyst used here was also prepared by deposition of Sn onto Pt, the drop of hydrogen adsorption on the Pt/Sn catalyst is more likely due to the blockage of Pt active sites by Sn (obviously, it is also very likely that some of Sn deposited on the carbon support).

The significant drop of the Pt/Sn catalyst for hydrogen adsorption suggests that Sn has been incorporated into the Pt catalyst and the Pt catalyst surface has been decorated by Sn successfully.

Fig. 5 compares CVs (second cycle) of a Pt/Sn catalyst in 1 M H<sub>2</sub>SO<sub>4</sub>(aq) before and after electrolysis of 1 M ethanol(aq) for 1 h at a potential of 0.5 V versus SHE. It is seen that the hydrogen adsorption peaks did not change significantly. This suggests that dissolution of Sn into the acidic ethanol aqueous solution

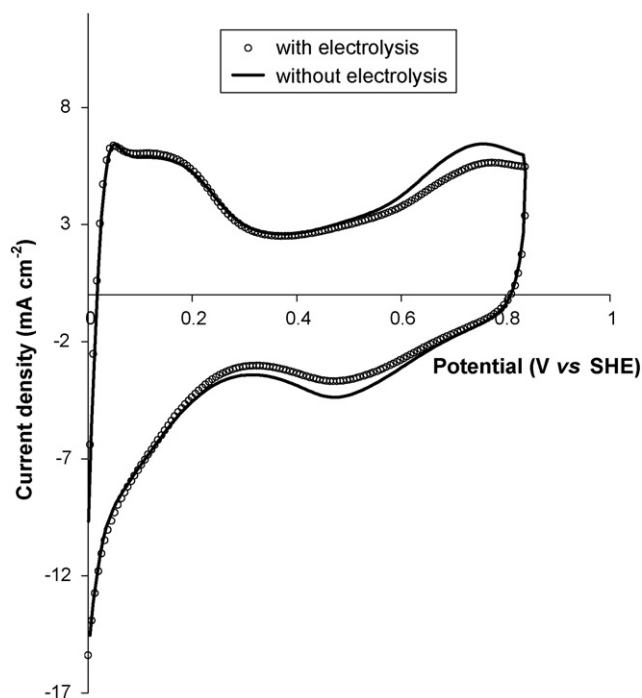


Fig. 5. Cyclic voltammetry in 1 M  $\text{H}_2\text{SO}_4(\text{aq})$  of a carbon-supported Pt/Sn (4:1) catalyst before and after electrolysis of 1 M ethanol(aq) for 1 h at 0.5 V vs. SHE. The catalyst was prepared by decorating an E-Tek 20% Pt on C catalyst with Sn. Scan rate:  $10 \text{ mV s}^{-1}$ .

was insignificant. Otherwise, the hydrogen adsorption peaks on the catalyst should increase significantly after long-term electrolysis. It should be noted that the catalyst loading ( $5 \text{ mg cm}^{-2}$ ) used in the electrolysis experiments (Fig. 5) was much higher than that used in the linear sweep experiments ( $0.11 \text{ mg cm}^{-2}$ ), including Fig. 4.

### 3.4. Catalytic activities

The catalytic activities of the catalysts for electro-oxidation of ethanol were investigated at ambient temperature in a conventional cell by linear sweep voltammetry (LSV) and chronoamperometry (CA). It was found that there was an optimum Pt to Sn ratio for the best catalyst performance. Addition of too much Sn resulted in a decrease in catalytic activity, since too much Sn can block Pt active sites for ethanol adsorption. The optimum atomic ratio of Pt to Sn was 4:1 for the Pt/Sn catalysts prepared by decorating the commercial C/Pt catalyst, as shown in Fig. 6. Lamy and coworkers [5] also reported that the optimum atomic ratio for their Pt/Sn catalysts was 4:1. Their Pt/Sn catalysts were prepared by electrochemical deposition of Sn on Pt electrodes.

Fig. 7 shows LSV for oxidation of 1 M ethanol in 0.1 M  $\text{H}_2\text{SO}_4(\text{aq})$  on carbon-supported Pt/Sn catalysts prepared by four different methods. It is seen that, in the low potential region of fuel cell interest, all of the Pt/Sn catalysts exhibited significantly enhanced catalytic activities for ethanol oxidation relative to Pt alone. Also, the onset potentials for oxidation of 1 M ethanol(aq) on all of the Pt/Sn catalysts were significantly lower than that on the Pt catalyst. The Pt/Sn catalyst prepared by dec-

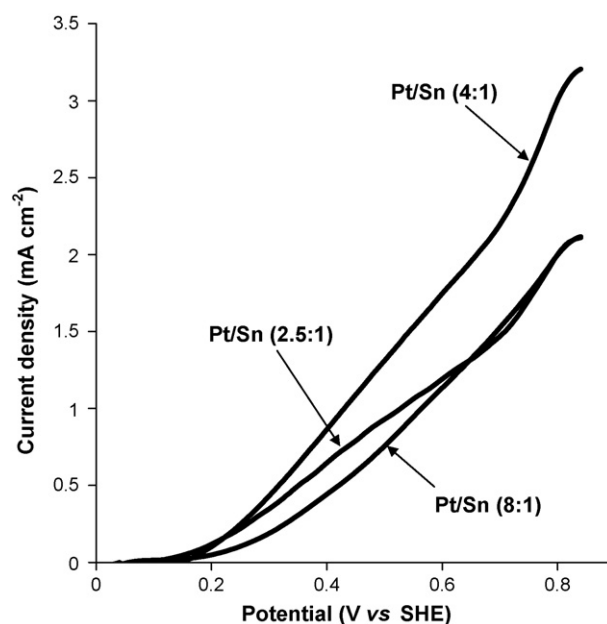


Fig. 6. Linear sweep voltammograms for oxidation of 1 M ethanol in 0.1 M  $\text{H}_2\text{SO}_4(\text{aq})$  on Pt/Sn catalysts of different ratios of Pt to Sn. The catalysts were prepared by decorating an E-Tek 20% Pt on C catalyst with Sn. Scan rate:  $10 \text{ mV s}^{-1}$ .

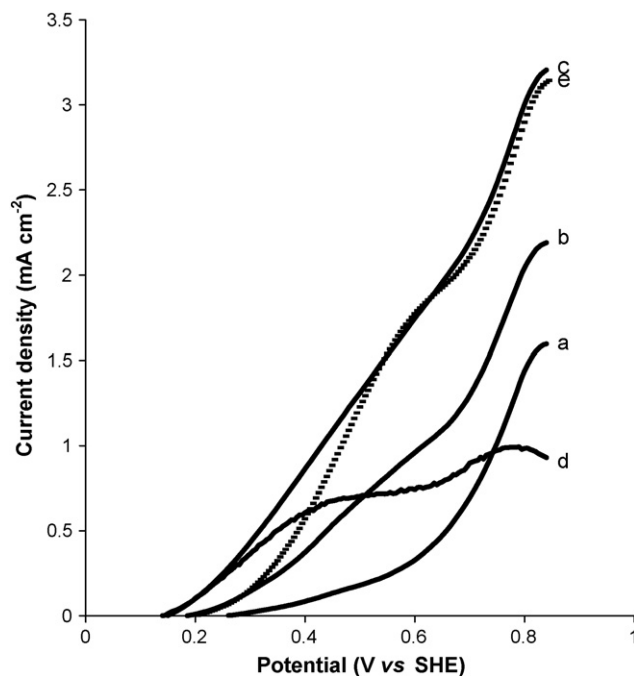


Fig. 7. Linear sweep voltammograms for oxidation of 1 M ethanol in 0.1 M  $\text{H}_2\text{SO}_4(\text{aq})$  on an E-Tek 20% Pt on C catalyst (a), a Pt/Sn (4:1) catalyst prepared by decorating a home-made 20% Pt on C with Sn (b), a Pt/Sn (4:1) catalyst prepared by decorating an E-Tek 20% Pt on C catalyst with Sn (c), a Pt/Sn (4:1) catalyst prepared by decorating an E-Tek 20% Pt on C catalyst with Sn without the reduction step (d), and a Pt/Sn (5:1) catalyst prepared by co-deposition of Pt and Sn on C (e). Scan rate:  $10 \text{ mV s}^{-1}$ . All the catalysts had the same Pt mass loadings.

orating the commercial C/Pt catalyst gave the best performance with an onset potential 0.11 V lower than for Pt alone, and a peak current density over two times higher. The much higher activity of this Pt/Sn catalyst for ethanol oxidation relative to Pt alone can be attributed to Sn oxides, rather than Sn metal, since XPS data clearly show that Sn existed as Sn oxides in the catalyst.

The lower onset potentials and enhanced catalytic activities of the Pt/Sn catalysts can be explained, in part, as being due to the oxidation of adsorbed CO by tin oxides [2,3]. However, Lamy and coworkers [2] have shown that CO<sub>2</sub> formation on Pt/Sn is partially disconnected from the CO coverage, and that there is oxidation of ethanol via a pathway that does not produce adsorbed CO. Incomplete oxidation to acetaldehyde and acetic acid occurs at the onset potential, and this is promoted by Sn [26].

Interestingly, deposition of Sn on the Pt catalyst resulted in a decrease in Pt active sites as discussed above, and this seems contradictory to the fact that the catalytic activity of the Pt/Sn for ethanol oxidation was significantly higher than that of the Pt catalyst. This contradiction indicates that the surface concentration of Pt sites is not the limiting factor in ethanol oxidation. Thus, although the Sn deposit physically blocks Pt sites, it must also free-up additional Pt sites by facilitating the removal of adsorbed intermediates, which increases the turnover rate of each site.

Fig. 7 also demonstrates that the Pt/Sn catalyst prepared by simply impregnating the C/Pt catalyst with SnCl<sub>2</sub>·2H<sub>2</sub>O solution without a reduction step exhibited significant enhancement for ethanol oxidation compared with Pt alone. This further supports the conclusion that the promoting effect is due to Sn oxide(s) rather than Sn (0).

Fig. 8A presents CA for oxidation of ethanol on different carbon-supported Pt/Sn catalysts, together with that on the commercial C/Pt catalyst. It is seen that all of the Pt/Sn catalysts exhibited significant enhancements in catalytic activities for electro-oxidation of ethanol relative to the Pt catalyst alone at 0.5 V versus SHE. The best catalyst for electro-oxidation of ethanol at 0.5 V versus SHE was carbon-supported Pt/Sn (4:1) prepared by decorating the commercial C/Pt catalyst. This is consistent with the LSV results. The catalytic activity of this catalyst was ca. 23-fold higher than that of the Pt catalyst at 0.5 V versus SHE, when the current attained a relatively steady state. It was also found that for ethanol oxidation on these catalysts, the current dropped quickly at first, then dropped slowly and finally became relatively stable after ca. 300 s. The drop of current at later times is presumably due to slow poisoning of the catalyst by adsorbed intermediates, since the data in Fig. 5 show that the Sn deposit remains on the electrode. However, Goetz and Wendt [27] reported that using a single electrode and CA to test the stability of catalysts was of limited significance. They found that stability data obtained by CA were much lower than that gained in fuel cell testing.

The differences between the performance of the different Pt/Sn catalysts seen in Fig. 8A are in part due to differences in mean particle size, which changes the total surface area of the catalyst for the fixed masses used here. To correct for this, Fig. 8B shows current densities that have been normalized with respect to the specific area (cm<sup>2</sup> g<sup>-1</sup>) of each catalyst.

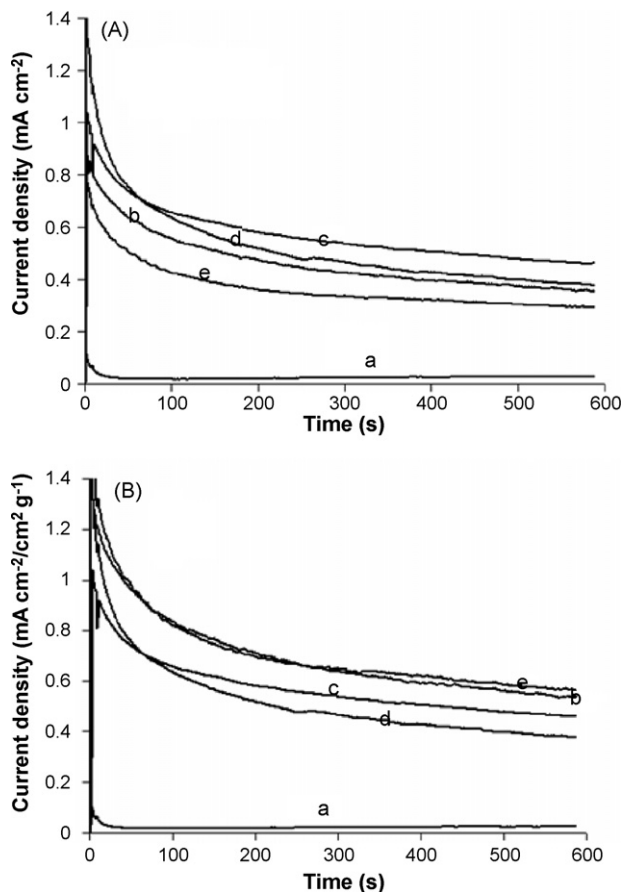


Fig. 8. (A) Chronoamperometry for oxidation of 1 M ethanol in 0.1 M H<sub>2</sub>SO<sub>4</sub>(aq) at 0.5 V vs. SHE on an E-Tek 20% Pt on C catalyst (a), a Pt/Sn (4:1) catalyst prepared by decorating a home-made 20% Pt on C with Sn (b), a Pt/Sn (4:1) catalyst prepared by decorating an E-Tek 20% Pt on C catalyst with Sn (c), a Pt/Sn (4:1) catalyst prepared by decorating an E-Tek 20% Pt on C catalyst with Sn without the reduction step (d), and a Pt/Sn (5:1) catalyst prepared by co-deposition of Pt and Sn on C (e). Initial potential: 0.24 V vs. SHE. All the catalysts had the same Pt mass loadings. (B) Current normalized to surface areas of Pt particles calculated from the XRD results.

Interestingly, this shows that the bigger (home made) particles produce more current per square centimetre of catalyst. Importantly, the co-deposited and decorated catalysts with similar particle sizes (i.e. b and e) give the same performance per square centimetre. This clearly shows that it is not necessary to form a PtSn alloy to obtain the maximum promoting effect of Sn.

Fig. 9 compares LSV of ethanol oxidation on a carbon-supported Pt/Sn (4:1) catalyst prepared by decorating the commercial C/Pt catalyst with that on a commercial 20% Pt/Ru (1:1) on C catalyst (E-Tek). It can be seen that the onset potential for ethanol oxidation on the Pt/Ru catalyst was 0.14 V versus SHE, 0.01 V lower than that on the Pt/Sn catalyst. However, the Pt/Sn catalyst provided significantly larger currents than the Pt/Ru catalyst when the potential was above ca. 0.25 V versus SHE. It was also found that currents decreased with increasing potential above ca. 0.7 V versus SHE for ethanol oxidation on the Pt/Ru catalyst, while on the Pt/Sn catalyst currents continued to increase. This indicates that the reaction mechanisms for

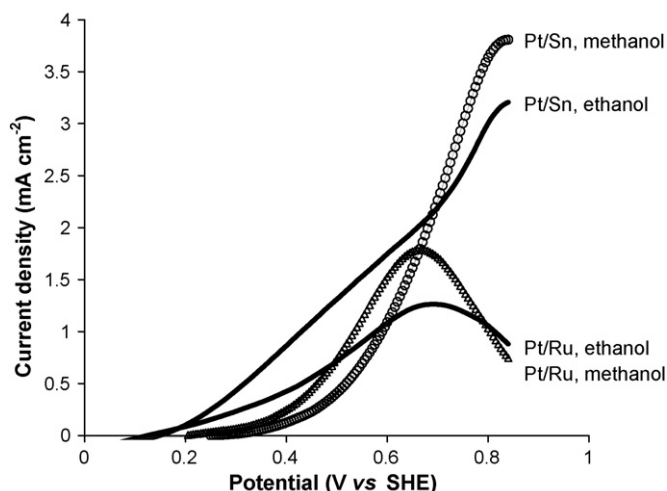


Fig. 9. Linear sweep voltammograms for oxidation of 1 M ethanol in 0.1 M H<sub>2</sub>SO<sub>4</sub>(aq) on a carbon-supported Pt/Sn (4:1) catalyst prepared by decorating an E-Tek 20% Pt on C catalyst with Sn and on an E-Tek 20% Pt/Ru (1:1) on C catalyst, together with oxidation of 1 M methanol in 0.1 M H<sub>2</sub>SO<sub>4</sub>(aq) on these catalysts. Scan rate: 10 mV s<sup>-1</sup>.

ethanol oxidation on the Pt/Sn catalyst were different from those on the Pt/Ru catalyst.

For comparison, oxidation of methanol on these two catalysts was also investigated. As shown in Fig. 9, the Pt/Sn catalyst was much more active for ethanol oxidation than for methanol oxidation in the potential region of fuel cell interest, while the Pt/Ru was more active for ethanol oxidation than for methanol oxidation at potentials below ca. 0.5 V versus SHE, but more active for methanol oxidation at higher potentials.

Fig. 10 presents CA for ethanol oxidation and methanol oxidation on these two catalysts at 0.5 V versus SHE. As expected, it was found that for ethanol oxidation, the Pt/Sn catalyst exhib-

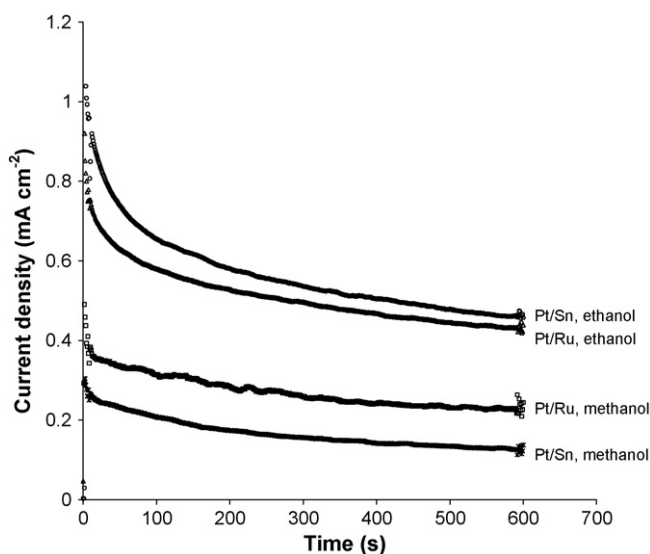


Fig. 10. Chronoamperometry for oxidation of 1 M ethanol in 0.1 M H<sub>2</sub>SO<sub>4</sub>(aq) at 0.5 V vs. SHE on a carbon-supported Pt/Sn (4:1) catalyst prepared by decorating an E-Tek 20% Pt on C catalyst with Sn and on an E-Tek 20% Pt/Ru (1:1) on C catalyst, together with that for oxidation of 1 M methanol in 0.1 M H<sub>2</sub>SO<sub>4</sub>(aq) on these catalysts. Initial potential: 0.24 V vs. SHE.

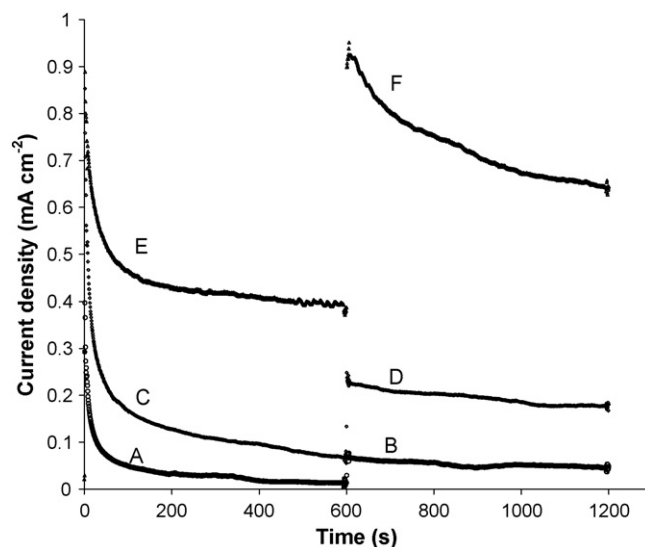


Fig. 11. Chronoamperometry for oxidation of 1 M ethanol in 0.1 M H<sub>2</sub>SO<sub>4</sub>(aq) on a carbon-supported Pt/Sn (4:1) catalyst prepared by decorating an E-Tek 20% Pt on C catalyst with Sn as a function of potential vs. SHE. A: 0.25 V; B: 0.3 V; C: 0.35 V; D: 0.4 V; E: 0.5 V; F: 0.6 V. Note: During measurements, two different potentials were set at each run. Initial potential: 0.24 V vs. SHE.

ited higher catalytic activity than the Pt/Ru catalyst, while for methanol oxidation, the Pt/Ru catalyst was more active.

Fig. 11 shows CA of ethanol oxidation at different potentials on a carbon-supported Pt/Sn (4:1) catalyst prepared by decorating the commercial C/Pt catalyst. It is seen that the current increased significantly with increasing potential as expected. This is consistent with the results of LSV.

### 3.5. Carbon-supported Sn/Pt catalysts

In order to increase the utilization of precious Pt, some Pt/Sn catalysts were prepared by decorating carbon-supported Sn with Pt, rather than by decorating Pt with Sn. The obvious benefit of this approach is that precious Pt atoms are on the surface of the catalyst, not covered by Sn atoms. Therefore, the utilization of Pt should be greatly increased. However, it was found that it was very difficult to filter high loading Sn on C products prepared by using NaBH<sub>4</sub> as the reducing agent, and even difficult with 10% Sn on C. Using formaldehyde as the reducing agent, 20% Sn on C was successfully prepared. However, LSV showed that Sn/Pt catalysts based on this 20% Sn on C exhibited no catalytic activity for ethanol oxidation. A possible reason for this is that Sn existed as oxides on the carbon support, resulting in very low electronic conductivity to the Pt sites.

Some low loading Sn on C products were also prepared by using NaBH<sub>4</sub> as the reducing agent, followed by decoration with Pt to prepare Sn/Pt catalysts. It was found that these Sn/Pt catalysts exhibited significantly enhanced catalytic activity for ethanol oxidation in the potential region of fuel cell interest relative to a same loading E-Tek Pt catalyst. The preliminary results are presented here.

Fig. 12 shows LSVs for ethanol oxidation on a 2% Sn on C-based Sn/Pt (1:7.5) catalyst, a 5% Sn on C-based Sn/Pt (1:3) catalyst, and a commercial E-Tek 20% Pt on C catalyst, respec-

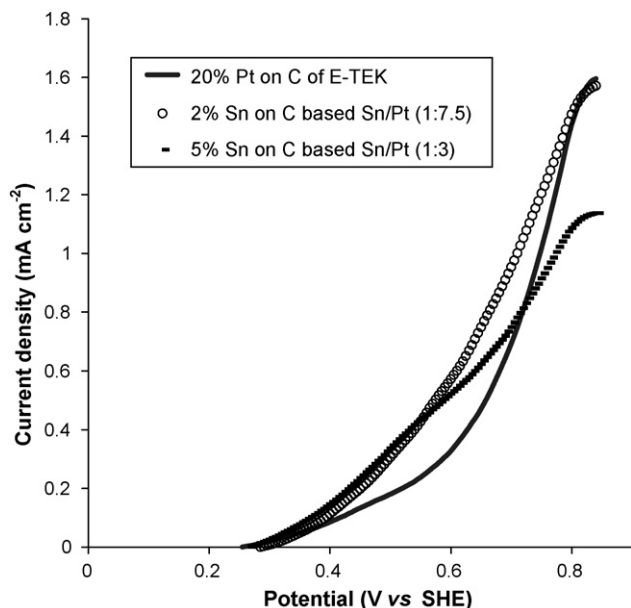


Fig. 12. Linear sweep voltammograms for oxidation of 1 M ethanol in 0.1 M  $\text{H}_2\text{SO}_4(\text{aq})$  on Sn on C-based Sn/Pt catalysts, together with that on an E-Tek 20% Pt on C catalyst. Scan rate:  $10 \text{ mV s}^{-1}$ .

tively (these three catalysts all contained a nominal 20% Pt on C). It is seen that both of the Sn/Pt catalysts exhibited enhanced catalytic activities for ethanol oxidation over Pt alone in the potential region of 0.3–0.72 V versus SHE. However, at potentials above 0.72 V versus SHE, the 5% Sn on C-based Sn/Pt (1:3) catalyst showed lower activity for ethanol oxidation compared with Pt alone. This may be due to low electronic conductivity of the Sn/Pt catalyst.

Fig. 13 compares CA for oxidation of ethanol on these three catalysts at 0.5 V versus SHE. It was found that the currents for ethanol oxidation on both Sn/Pt catalysts were significantly higher than those on Pt alone and that the 2% Sn on C-based

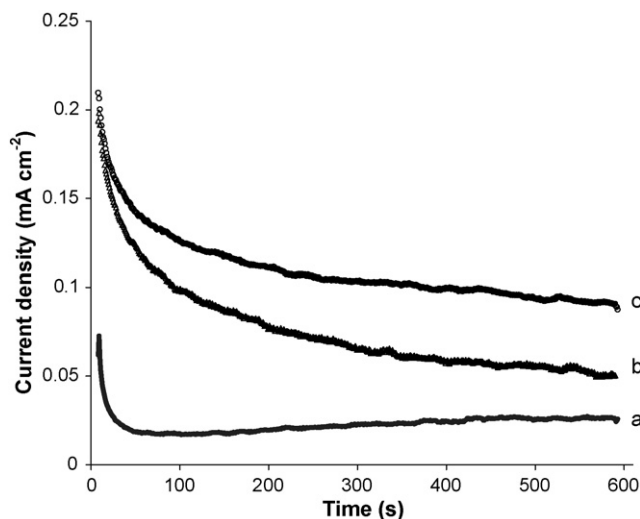


Fig. 13. Chronoamperometry for oxidation of 1 M ethanol in 0.1 M  $\text{H}_2\text{SO}_4(\text{aq})$  at 0.5 V vs. SHE on an E-Tek 20% Pt on C catalyst (a), a 5% Sn on C-based Sn/Pt (1:3) catalyst (b), and a 2% Sn on C-based Sn/Pt (1:7.5) catalyst (c). Initial potential: 0.24 V vs. SHE.

Sn/Pt (1:7.5) catalyst gave the highest currents. Furthermore, the 2% Sn on C-based Sn/Pt (1:7.5) catalyst provided more stable currents than the 5% Sn on C-based Sn/Pt (1:3) catalyst.

The above results clearly show that the 2% Sn on C-based Sn/Pt (1:7.5) catalyst and 5% Sn on C-based Sn/Pt (1:3) catalyst are much more active than the E-Tek 20% Pt on C catalyst for ethanol oxidation. This means that Pt utilization is increased significantly on these two Sn/Pt catalysts relative to the E-Tek Pt catalyst, if we define Pt utilization as the ratio of current to mass of Pt.

#### 4. Conclusions

A number of carbon-supported Pt/Sn catalysts have been prepared by decoration methods, and all exhibited significantly enhanced catalytic activities for ethanol oxidation compared with Pt alone. Among these catalysts, a carbon-supported Pt/Sn (4:1) catalyst prepared by reductive decoration of a commercial Pt on C catalyst showed the highest catalytic activity for ethanol oxidation. This catalyst has also shown excellent activity in direct ethanol fuel cells [28].

XPS data show that Sn existed as Sn oxides in the Pt/Sn catalysts. Therefore, the promoting effect appears to be due to the oxide species, rather than Sn metal or a Pt/Sn alloy. The data clearly show that it is not necessary to form a Pt/Sn alloy to obtain the maximum promoting effect of Sn.

Preliminary data show that decoration of Sn with Pt is a feasible strategy to increase Pt utilization, although further work is needed to optimize this system.

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