

# Effects of Treatment in Different Atmosphere on Pt<sub>3</sub>Sn/C Electrocatalysts for Ethanol Electro-oxidation

Luhua Jiang,<sup>†</sup> Zhenhua Zhou,<sup>†</sup> Wenzhen Li,<sup>†</sup> Weijiang Zhou,<sup>†</sup> Shuqin Song,<sup>†</sup>  
Huanqiao Li,<sup>†</sup> Gongquan Sun,<sup>†</sup> and Qin Xin<sup>\*,†,‡</sup>

Direct Methanol Fuel Cell Laboratory, and State Key Laboratory of Catalysis,  
Dalian Institute of Chemical Physics, CAS, China

Received October 22, 2003. Revised Manuscript Received March 17, 2004

Pt<sub>3</sub>Sn/C catalyst was prepared by a modified polyol process and treated in air, H<sub>2</sub>/Ar, and Ar atmosphere, respectively. XRD analyses indicate that all of these catalysts have face-centered cubic (fcc) crystal structure. Temperature-programmed reduction (TPR) experiments show that more Sn exists in zero-valence in the Ar-treated PtSn catalyst than in the others. Cyclic voltammetry (CV), chronoamperometry (CA) experiments, and the performance tests of direct ethanol fuel cell (DEFC) indicate that the catalytic activity of PtSn/C for ethanol oxidation was affected significantly by the chemical state of Sn in catalyst particles. The as-prepared PtSn/C gives the higher power density, while Ar-treated PtSn/C shows the lower cell performance. It seems that the multivalence Sn rather than the zero-valence Sn in the PtSn catalyst is the favorable form for ethanol oxidation. Energy dispersion X-ray analysis (EDX) of the PtSn/C-as prepared and PtSn/C (after stability test) shows the active species (platinum, tin, and oxygen) composition changed to a different extent. Further attempt to improve the catalyst stability is needed.

## Introduction

In recent decades, direct methanol fuel cells (DMFCs) are widely studied and considered as possible power sources for portable electronic apparatus and vehicles in the near future.<sup>1–8</sup> However, it is known that methanol is toxic, and its crossover from anode to cathode leads to the significant degradation of cell performance. As an alternative fuel, ethanol is safer and has higher energy density. In addition, as a green fuel, ethanol can be easily produced in great quantity by fermentation from sugar-containing raw materials. Therefore, ethanol is more attractive than methanol for direct alcohol fuel cells operating at lower temperatures.<sup>9,10</sup> However, the complete oxidation of ethanol to CO<sub>2</sub> involves 12 electrons per molecule. Thus many

adsorbed intermediates and byproducts are produced during the process of ethanol oxidation. Moreover, the cleavage of the C–C bond is difficult at low temperature. It is urgent to develop novel catalysts with high electrocatalytic activity for ethanol oxidation. Our previous research showed that PtSn catalysts prepared by a modified polyol process<sup>11</sup> presented higher activity for ethanol oxidation than PtRu catalysts,<sup>12</sup> but the mechanism of the promoting effect of Sn for ethanol oxidation is not well understood up to now. Particularly, the effects of surface-active species of PtSn/C catalyst prepared by the modified polyol process on ethanol oxidation reaction (EOR) need to be clarified.

In this paper, PtSn/C catalyst was prepared and treated in air, H<sub>2</sub>/Ar, and Ar atmosphere, respectively. XRD, TEM, CV, CA, TPR, EDX and direct ethanol fuel cell (single-cell) tests were used to characterize the treated catalysts in order to clarify the active phases for ethanol oxidation in PtSn/C catalysts. On the basis of these results, the possible factors affecting electrocatalytic activity for ethanol oxidation were analyzed.

## Experimental Section

### Preparation of Pt<sub>3</sub>Sn Catalysts Supported on Carbon.

H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O and SnCl<sub>2</sub>·2H<sub>2</sub>O were used as precursors of PtSn catalysts. XC-72R carbon black (Cabot Corp., *S*<sub>BET</sub> = 236.8 m<sup>2</sup> g<sup>-1</sup>) was used as a support for all samples. Ethylene glycol (EG) was used as a reducing agent. The detailed process has been described elsewhere.<sup>12</sup> Following is a brief description

\* Author to whom correspondence should be addressed. Tel. and Fax: 86-411-4379071. E-mail: Xinqin@dicp.ac.cn.

<sup>†</sup> Direct Methanol Fuel Cell Laboratory.

<sup>‡</sup> State Key Laboratory of Catalysis.

(1) Ren, X. M.; Zelenay, P.; Thomas, S.; Davey, J.; Gottesfeld, S. *J. Power Sources* **2000**, *86*, 111.

(2) Lamy, C.; Belgsir, E. M.; Leger, J.-M. *Appl. Electrochem.* **2001**, *31*, 799.

(3) Li, W. Z.; Liang, C. H.; Zhou, W. J.; Qiu, J. S.; Zhou, Z. H.; Sun, G. Q.; Xin, Q. *J. Phys. Chem.* **2003**, *107*, 6292.

(4) Wei, Z. B.; Wang, S. L.; Yi, B. L.; Liu, J. G.; Chen, L. K.; Zhou, W. J.; Li, W. Z.; Xin, Q. *J. Power Sources* **2002**, *106*, 364.

(5) Lim, C.; Wang, C. Y. *J. Power Sources* **2003**, *113*, 145.

(6) Arico, A. S.; Creti, P.; Antonucci, P. L.; Antonucci, V. *Electrochem. Solid-State Lett.* **1998**, *1*, 66.

(7) Song, S. Q.; Chen, L. K.; Liu, J. G.; Wei, W. Z.; Xin, Q. *J. Electrochem. (Chinese)* **2002**, *8*, 58.

(8) Delime, F.; Leger, J.-M.; Lamy, C. *J. Appl. Electrochem.* **1998**, *28*, 27.

(9) Ianniello, R.; Schmidt, V. M.; Rodriguez, J. L.; Pastor, E. *J. Electroanal. Chem.* **1999**, *471*, 167.

(10) Chen, G. L.; Chen, S. P.; Zhou, Z. Y.; Zhen, C. H.; Sun, S. G.; *J. Electrochem. (Chinese)* **2001**, *7*, 96.

(11) Zhou, Z. H.; Wang, S. L.; Zhou, W. J.; Wang, G. X.; Jiang, L. H.; Li, W. Z.; Song, S. Q.; Liu, J. G.; Sun, G. Q.; Xin, Q. *Chem. Commun.* **2003**, *3*, 394.

(12) Zhou, W. J.; Zhou, Z. H.; Song, S. Q.; Li, W. Z.; Sun, G. Q.; Tsiakaras, P.; Xin, Q. *Appl. Catal.* **2003**, *46*, 273.

of the preparation method: the required amounts of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O and SnCl<sub>2</sub>·2H<sub>2</sub>O and carbon were added to the mixture of EG and deionized water with stirring to form a homogeneous slurry. The slurry was heated to 130 °C and kept at this temperature in an oil bath for 3 h. Then the black solid samples were filtered, washed, and dried at 80 °C for 10 h in a vacuum oven. The Pt nominal loading of the catalysts was 20 wt % (the nominal atomic ratio of Pt to Sn is 3:1).

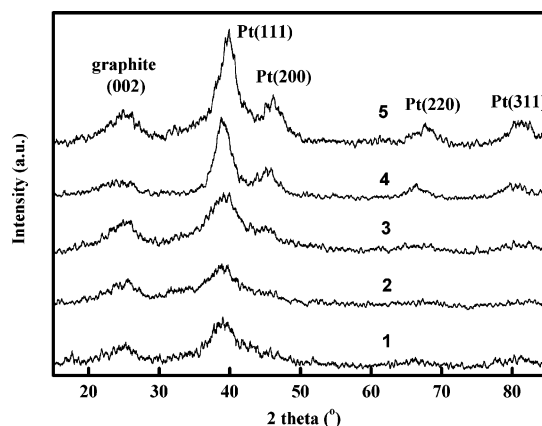
The as-prepared catalysts (denoted as PtSn/C-as pre) were treated at 200 °C in Ar, air, and H<sub>2</sub>/Ar(10 vol % H<sub>2</sub>) for 2 h, and denoted as PtSn/C–Ar, PtSn/C–O<sub>2</sub> and PtSn/C–H<sub>2</sub>, respectively. SnO<sub>2</sub>/C (4 wt % Sn) prepared using the above method and a commercially available Pt/C catalyst from Johnson Matthey (denoted as PtSn/C-JM) with a nominal Pt loading of 20 wt % were employed for comparison.

**Characterization of Catalysts.** The XRD analyses of all samples were performed using a Rigaku diffractometer (D/max-2400 X) with a Cu K $\alpha$  radiation source to characterize the crystalline structure change of Pt in all PtSn/C catalysts. Samples were examined using the JEOL JEM-2011 electron microscope operated at 100 kV. An amount of 300 metal particles were calculated to obtain the particle distribution diagram of every PtSn/C catalyst sample. TPR experiments were carried out on ChemBET 3000 (QuantaChrome Co.). The as-prepared catalysts were placed in a U-shape tube and were heated at 10 °C/min to 200 °C under Ar, air, or H<sub>2</sub>/Ar, respectively. Samples were held at that temperature for 2 h and then cooled to ambient conditions under Ar. H<sub>2</sub>/Ar was used to perform TPR experiments. Electroactivities were measured by CV and CA using an EG&G model 273 potentiostat/galvanostat and a three-electrode test cell at room temperature. The working electrode was a thin layer of Nafion-impregnated Pt/C composite cast on a vitreous carbon disk electrode. A 5.0 mg catalyst sample were suspended in 1.0 mL of ethanol, and 10.0 wt % Nafion was added as adhesive and proton conductor. The mixture were ultrasonically scattered for 10 min to form homogeneous ink. Then 25  $\mu$ L of ink were pipeted on a vitreous electrode with 4 mm diameter to act as the working electrode. A Pt gauze and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. EDX were carried out employing a Philips XL-30 Scan Electron Microscopy (SEM).

**Direct Ethanol Single-Cell Measurement.** The membrane electrode assemblies (MEAs) were fabricated according to the method described in the literature.<sup>13</sup> PtSn/C (in-house) and Pt/C (purchased from Johnson Matthey Inc., denoted as Pt/C-JM) were used as anode and cathode catalysts with Pt loadings of 1.5 mg cm<sup>-2</sup> on the anode and 1.0 mg cm<sup>-2</sup> on the cathode, respectively. The MEA was manufactured by pressing the electrodes onto either side of Nafion-115 membrane at 140 °C for 90 s.

## Results and Discussion

XRD patterns of Pt/C-JM and PtSn/C before and after treatment in different atmospheres are shown in Figure 1. The diffraction peak at 20–25° observed in all XRD patterns is attributed to the (002) plane of carbon. The diffraction peaks at around 39°, 46°, 68°, and 81° are attributed to Pt (111), (200), (220), and (311) crystalline plane, respectively, which represents the typical character of a crystalline Pt face-centered cubic (fcc) structure. It can also be seen from Figure 1 that all peak positions of Pt in PtSn/C catalysts, compared to Pt/C, shift to low angle more or less. Pt (220) peak positions of Pt/C and the PtSn/C-as pre are at around 67.61° and 66.99°, respectively. While after treatment, Pt (220)



**Figure 1.** XRD patterns of (1) PtSn/C-as pre, (2) PtSn/C–Ar, (3) PtSn/C–O<sub>2</sub>, (4) PtSn/C–H<sub>2</sub>, and (5) Pt/C-JM.

**Table 1. Data Calculated from XRD Patterns by Scherrer Formula**

samples	crystal lattice parameter (Å)	(220) diffraction peak position (2 $\theta$ )°
Pt/C (JM)	3.918	67.61
PtSn/C-as pre	3.946	66.99
PtSn/C–Ar	4.000	65.90
PtSn/C–O <sub>2</sub>	3.970	66.52
PtSn/C–H <sub>2</sub>	3.973	66.48
PtSn alloy <sup>†</sup>	4.001	65.97

peak shifts to 66.48° for PtSn/C–H<sub>2</sub> and 65.90° for PtSn/C–Ar. Pt (220) peak position of PtSn alloy is about 65.97° according to the Joint Committee of Powder Diffraction Standard (JCPDF-351360). It can be seen from XRD results that Pt and Sn interact more strongly after heat treatment.

Although XRD measurements cannot supply exact information of crystallite size when it is less than 3.0 nm, the results of XRD measurements qualitatively show that the size of Pt particles in the Pt/C-JM and PtSn/C–H<sub>2</sub> sample is larger than that in the other three samples. The broadening of diffraction peaks of PtSn/C–Ar catalyst may be explained by that the mild heat treatment could promote the interaction of Pt and Sn, which separates Pt particles.<sup>14</sup> While for the PtSn/C–O<sub>2</sub> sample, the broadening diffraction peak may be caused by the formation of tin oxide and platinum oxide microcrystals, which could not be detected by XRD.

The lattice parameters of these Pt-based catalysts obtained from XRD patterns<sup>15</sup> are listed in Table 1. In some literature,<sup>16,17</sup> change of crystal lattice parameter is used as measurement of the extent of alloying. According to the change of lattice parameter of Pt, as seen from Table 1, Pt interacts with Sn in PtSn/C-as pre sample. The lattice parameters are 4.000 Å for PtSn/C–Ar and 3.973 Å for PtSn/C–H<sub>2</sub>, close to lattice parameter of Pt<sub>3</sub>Sn alloy 4.001 Å (PDF-351360). This implies that Ar and H<sub>2</sub> treatment to PtSn/C is helpful to the interaction of Pt and Sn. According to the literature,<sup>18</sup> for PtSn/Al<sub>2</sub>O<sub>3</sub> catalysts, O<sub>2</sub> atmosphere is

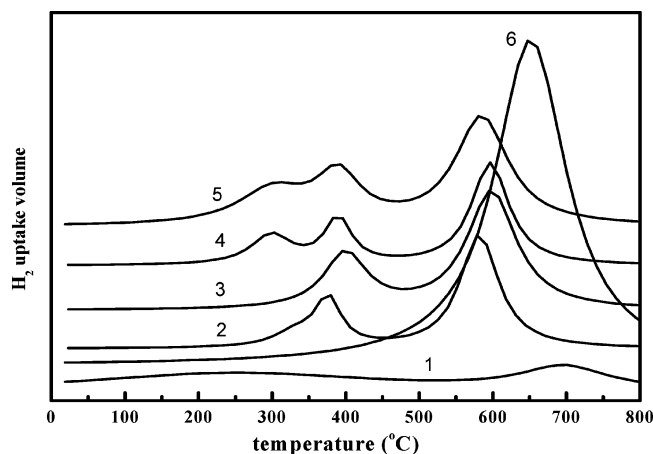
(14) Baronetti, G.; Miguel, S. de; Scelza, O.; Castro, A. *Appl. Catal.* **1986**, *24*, 109.

(15) Radmilović, V.; Gasteiger H. A.; Ross, P. N. *J. Catal.* **1995**, *154*, 98.

(16) Mukerjee, S.; Srinivasan, S. *J. Electroanal. Chem.* **1993**, *357*, 201.

(17) Mukerjee, S.; Srinivasan, S.; Soriaga, M. P.; McReen, J. J. *Electrochem. Soc.* **1995**, *142*, 1409.

(13) Li, W. Z.; Liang, C. H.; Qiu, J. S.; Zhou, W. J.; Han, H. M.; Wei, Z. B.; Sun, G. Q.; Xin, Q. *Carbon* **2002**, *1*, 791.



**Figure 2.** TPR profiles of (1) XC-Vulcan 72, (2) PtSn/C-Ar, (3) PtSn/C-H<sub>2</sub>, (4) PtSn-as pre, (5) PtSn/C-O<sub>2</sub>, and (6) SnO<sub>2</sub>/C.

**Table 2. The Percentage of Different Valence of Sn in Catalysts According to TPR Profiles**

sample	SnO <sub>2</sub> /C	PtSn/C-as pre	PtSn/C-Ar	PtSn/C-O <sub>2</sub>	PtSn/C-H <sub>2</sub>
Sn	0	52	73	58	55
Sn <sup>2+</sup>	0	22	10	18	20
Sn <sup>4+</sup>	100	26	17	24	25

in favor of the formation of SnO<sub>2</sub>, while Ar treatment favors the formation of Pt<sub>3</sub>Sn alloy. Our research confirms the result according to the change of lattice parameter.

To clarify the valence of Sn in the catalysts treated in different atmosphere, TPR experiments were carried out and the TPR profiles are shown in Figure 2. For comparison, blank experiment was also carried out using Vulcan XC-72R (sample 1). The sloping peak at about 650 °C should be attributed to the reaction between carbon and hydrogen. The peak at about 300 °C should be assigned to the reduction of PtO<sub>x</sub> to Pt, and the peak at about 400 °C and 600 °C should be attributed to the reduction of Sn<sup>2+</sup> and Sn<sup>4+</sup> to Sn, respectively.<sup>14</sup> It can be seen in Figure 2 that Sn exists in Sn<sup>4+</sup> exclusively in sample 6, while if Pt and Sn were carried on carbon simultaneously, the valence of tin is very different. Part of Sn exists in zero-valence, others in bivalence or quadrivalence. The peak at about 300 °C disappeared for sample 3 which can be explained that the platinum oxide on the surface of Pt particles was reduced to Pt during the H<sub>2</sub> pretreatment at 200 °C. The areas of every peak were calculated by using Origin software. The percentage of different Sn valence with the peak area of SnO<sub>2</sub>/C (sample 6) as benchmark, which stands for the corresponding amount of different valent tin, were calculated according to the corresponding peak area. The results were listed in Table 2. According to this table, most Sn possesses zero-valence in PtSn/C-Ar and PtSn/C-H<sub>2</sub>, while the other two samples give a lower percentage of zero-valence of Sn. These results are in good agreement with the above XRD experiments. In the literature,<sup>14</sup> PtSn/Al<sub>2</sub>O<sub>3</sub> prepared by wet impregnation method was treated in different atmospheres. It was also found that the use of neutral atmosphere favors an intimate Pt-Sn inter-

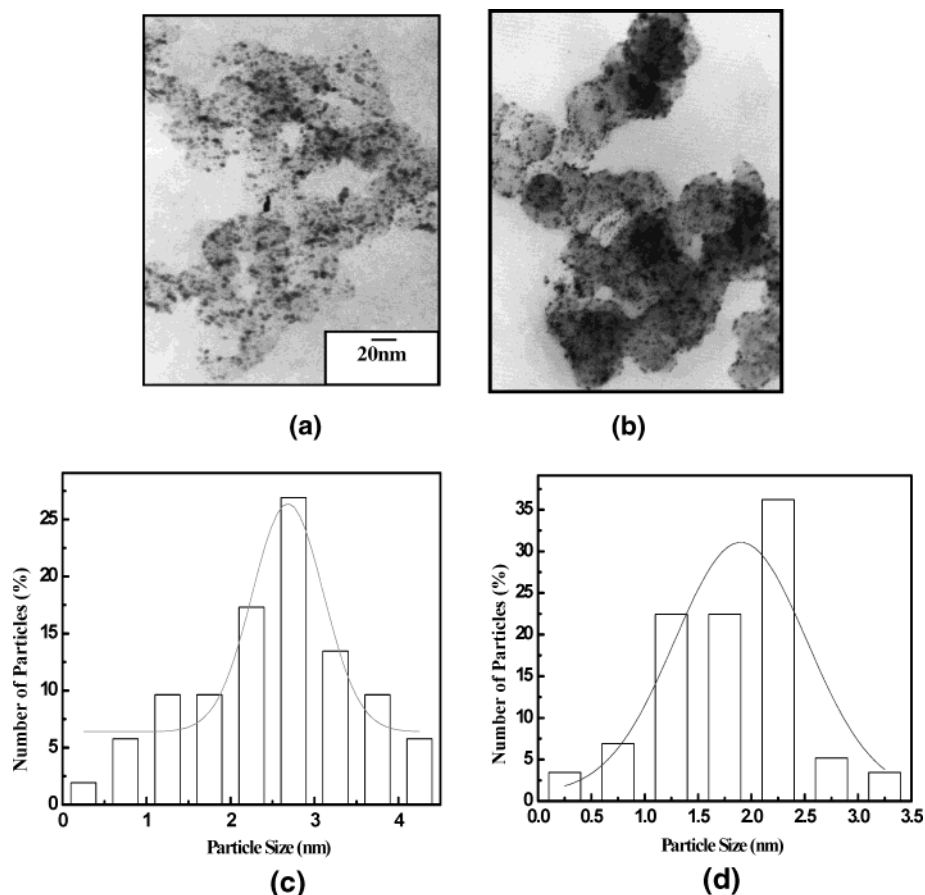
action (formation of the PtSn alloy), while the use of an oxidative atmosphere results in demixion (formation of two distinct phases, Pt<sup>0</sup> and SnO<sub>2</sub>).

Figure 3 is the TEM images of PtSn/C-as pre and PtSn/C-Ar catalysts and their metal particle size distribution diagrams. It can be seen that the metal particles are homogeneously spherical in the two samples. The mean particle sizes of PtSn/C-as pre and PtSn/C-Ar are about 2.6 and 1.8 nm, respectively. This result confirms that the treatment in Ar separates Pt particles into smaller ones.

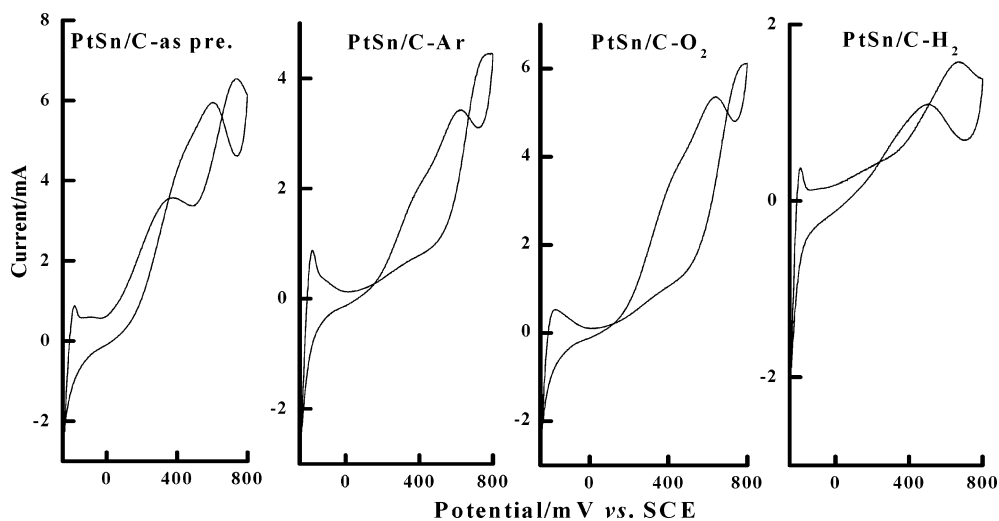
Figure 4 shows the cyclic voltammograms of ethanol oxidation under acidic conditions (0.5 M CH<sub>3</sub>CH<sub>2</sub>OH/0.1 M HClO<sub>4</sub>) catalyzed by the PtSn/C catalyst. The potential range was -0.24-0.8 V (vs SCE) and the scan rate was 50 mV s<sup>-1</sup>. The onset of oxidative current peak and the maximum oxidative current are index to the ethanol electro-oxidation activity of catalysts. The voltammetric features are in good agreement with our published work.<sup>12</sup> The current peak at about 730 mV (vs SCE) in the forward scan is attributed to ethanol electro-oxidation on the PtSn/C catalysts.<sup>12</sup> Figure 4 clearly shows that this peak is significantly higher in the PtSn/C-as pre catalyst than in the others. Two oxidative current peaks (at about 365 mV and 730 mV) appear in the forward scan for PtSn/C-as pre catalyst, which exhibits the highest oxidative current (about 6.6 mA) for ethanol at around 730 mV. The peak oxidative current is 6.1 mA at about 800 mV (vs SCE) for PtSn/C-O<sub>2</sub>, while PtSn/C-Ar and PtSn/C-H<sub>2</sub> give lower activities for ethanol oxidation according to the peak oxidation currents (4.4 mA at 800 mV and 1.6 mA at 668 mV, respectively).

From a practical point of view, data obtained by CA methods are more useful. Figure 5 presents examples of the CA curves obtained in 0.5 M ethanol solution in 0.1 M HClO<sub>4</sub> at an anodic potential of 0.7 V vs SCE. This potential was chosen because it was close to the potential of the anodic peak in the CVs (see Figure 4). In all of the CA curves there is a sharp initial current drop in the first 5 min, followed by a slower decay. The sharp decrease might rise from the Pt surface auto-poisoning in the ethanol solution. In longer runs it was found that the current (*j* after 30 min polarization at 0.7 V vs SCE) obtained on PtSn/C-as pre electrodes is higher than the other electrodes. The steady-state current density stabilized for all of the catalysts within half hour at the potential hold. The final current densities after holding the cell potential at 0.7 V vs SCE were the following: PtSn/C-as pre 4.1 mA cm<sup>-2</sup>; PtSn/C-O<sub>2</sub> 3.6 mA cm<sup>-2</sup>; PtSn/C-Ar 2.5 mA cm<sup>-2</sup>; and PtSn/C-H<sub>2</sub> 1.1 mA cm<sup>-2</sup>. This result is consistent with the above CV results.

The performance curves of DEFC using PtSn/C as anode catalysts are displayed in Figure 6. Each experimental point was measured after stabilization for 5 min. It can be seen that PtSn/C-as pre gives a better performance than any other catalysts. The performance of the single cell with PtSn/C-O<sub>2</sub> as anode is similar to but a little better than that with PtSn/C-H<sub>2</sub>. PtSn/C-Ar catalyst possesses the higher open circuit potential (OCP) of about 0.821 V. Its performance is better than PtSn/C-O<sub>2</sub> catalysts at lower current density (<20 mA cm<sup>-2</sup>), which may be attributed to the stronger Pt-Sn



**Figure 3.** TEM analysis of PtSn/C-as pre and PtSn/C-Ar catalysts TEM image of (a) PtSn/C-as pre and (b) PtSn/C-Ar; corresponding particle size distribution of (c) PtSn/C-as pre and (d) PtSn/C-Ar.

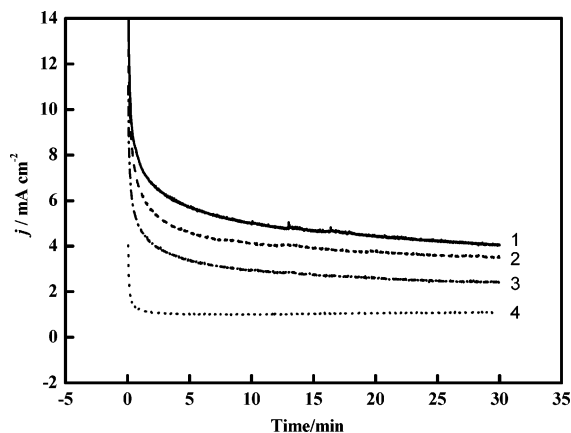


**Figure 4.** Cyclic voltammograms of PtSn/C electrode in 0.5 M CH<sub>3</sub>CH<sub>2</sub>OH/0.1 M HClO<sub>4</sub> electrolyte at 50 mV s<sup>-1</sup> at room temperature.

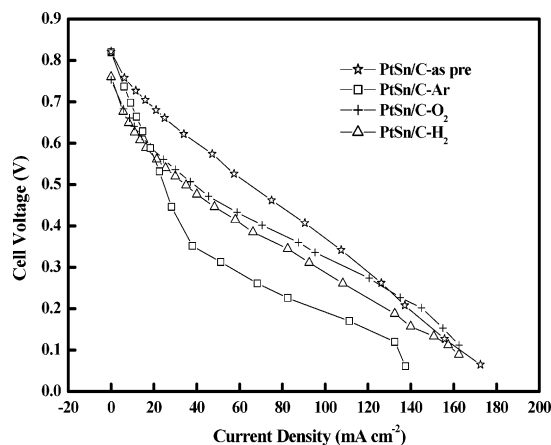
interaction. In contrast, though the OCP of the single cell with PtSn/C-O<sub>2</sub> as anode is about 70 mV lower than that with PtSn/C-Ar, the performance curve of the former dropped tardily. These results may imply that multivalence Sn play a much more important role for ethanol electro-oxidation than the zero-valent Sn at higher current density.

To evaluate the stability of the PtSn/C electrocatalysts, EDX measurements for the PtSn/C-as pre and PtSn/C-after stability test (40 h) were carried out. The results were listed in Table 3. It is noteworthy that the

oxygen content decreased greatly after the stability test, which implies that the oxygen species takes part in the reaction and was consumed. The Sn content was dropped a little compared to the PtSn/C-as pre sample. Unexpectedly, the Pt content was decreased prominently after a 40-h stability test. Generally speaking, the noble metal is stable under the anode operating condition. Gülzow et al. also observed the platinum concentration on the anode is reduced significantly during the polymer electrolyte membrane fuel cell (PEMFC) operation via X-ray photoelectron spectroscopy (XPS).<sup>19</sup> Two possible



**Figure 5.** Current density–time dependence measured by the CA method in 0.5 M EtOH + 0.1 M HClO<sub>4</sub> solution for (1) PtSn/C-as pre, (2) PtSn/C–O<sub>2</sub>, (3) PtSn/C–Ar, (4) PtSn/C–H<sub>2</sub>,  $E_a = 0.7$  V vs SCE.



**Figure 6.** Performances of DEFCs with PtSn/C as the anode catalysts operated at 90 °C. Anode catalyst and metal loading: PtSn/C, 1.5 mg Pt/cm<sup>2</sup>; cathode catalyst and metal loading: 20% Pt-JM, 1.0 mgPt/cm<sup>2</sup>. Nafion-115 was used as electrolyte. Ethanol concentration and flow rate: 1 M & 1.0 mL min<sup>-1</sup>, respectively

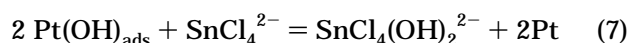
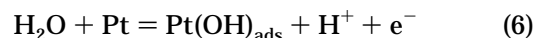
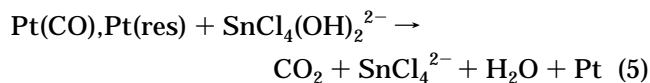
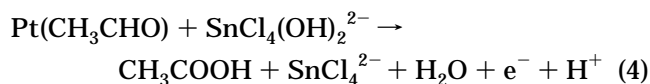
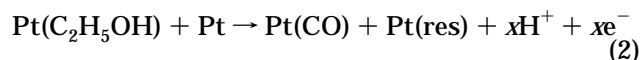
**Table 3. EDX Results (mass %)**

sample	C	O	Sn	Pt
as-prepared	66.0	6.9	2.8	24.2
after stability test (40 h)	79.0	3.0	2.6	15.4

explanations were given out, one of which is the change in the platinum distribution and the other is that the platinum has moved to the interface between membrane and electrode and has adhered to the membrane when separating the electrode from the MEA. In our experiments, the EDX analysis gave the bulk composition of the catalyst, so the former deduction could be ruled out. The only explanation for the decreased platinum concentration could be the move of platinum in the interface between the PtSn electrode and the membrane under the electric fields. However, the direct experiment proof was not obtained at present.

According to a hypothesis suggested by Kubota<sup>20</sup> and Fujiwara,<sup>21</sup> and later by Haner and Ross,<sup>22</sup> in the presence of Sn the alcohol oxidation process proceeds as a homogeneous catalytic reaction with the participa-

tion of complexed Sn<sup>4+</sup> ions. It can be illustrated by the following reactions: (i) ethanol molecules in solution exchange with H<sub>2</sub>O molecules adsorbed on Pt active sites (step 1); (ii) exchanged ethanol molecules dehydrogenate on Pt sites to form acetaldehyde, acetic acid, or CO-like species (steps 2,3); (iii) acetaldehyde reacts with OH species further to form acetic acid, and CO to form CO<sub>2</sub> (steps 4,5); (iv) water is dehydrogenated at Pt active site to form hydroxide, which reacts with SnCl<sub>4</sub><sup>2-</sup> to produce SnCl<sub>4</sub>(OH)<sub>2</sub><sup>2-</sup> (steps 6,7). It suggests that oxygen-containing species is indispensable in order to facilitate the reaction, while PtSn/C–Ar could not offer sufficiently such oxygen species because more tin species exist in zero-valence. In contrast, PtSn/C-as pre and PtSn/C–O<sub>2</sub> could meet this requirement because a pronounced portion of tin exists in oxide. Moreover, the appropriate dilatation of Pt lattice parameter caused by the interaction of Pt and Sn would favor the adsorption of ethanol.<sup>12</sup> Compared with the adsorption of ethanol molecules and the desorption of residues on Pt sites, ethanol molecule oxidation seems to be the rate-determining step (RDS) for the slow reaction rate at lower current density; while at higher current density, ethanol oxidation rate rises to produce more intermediates so that more OH species were needed to take part in the reaction. According to the TPR results, there exists more Sn oxide in PtSn/C-as pre and PtSn/C–O<sub>2</sub>, which would provide enough oxygen-containing species to react with these intermediates, leading to a smooth reaction pathway. So PtSn/C-as pre and PtSn/C–O<sub>2</sub> showed higher activity for ethanol oxidation than PtSn/C–Ar. The EDX results also confirm that the oxygen species was consumed during the reaction. By analyzing the anode effluent solution, CO<sub>2</sub> and acetic acid are the main products of DEFCs and acetaldehyde was also detected in the products. This implies that the following deduced mechanism is possible. Moreover, note that this mechanism does not activate water at a lower potential than pure Pt, in agreement with our observation that tin did not change the potential of onset for ethanol oxidation on platinum.<sup>12</sup>



(20) Kubota, M. *Inorg. Chem.* **1990**, *29*, 574.

(21) Fujiwara, N.; Friedrich, K. A.; Stimming, U. *J. Electroanal. Chem.* **1999**, *472*, 120.

(22) Haner, A. N.; Ross, P. N. *J. Phys. Chem.* **1991**, *95*, 3740.

(19) Gülzow, E.; Sander, H.; Wagner, N.; Lorenz, M.; Schneider, A.; Schulze, M. *The 1st Sino-Germany Workshop on Fuel Cells*, Oct. **2002**, 156, Dalian, China.

### Conclusions

In this paper, PtSn/C catalyst has been treated in different atmospheres to clarify the active phases for ethanol oxidation in PtSn/C catalyst. The catalysts, which were treated at the same temperature and in different atmospheres, have fcc crystal structure but different Pt–Sn interaction degree. TPR experiments indicate that Sn exists in different valences in PtSn/C catalysts. Among these treated catalysts, more zero-valence of Sn appeared in PtSn/C–Ar catalyst, while more multivalence Sn exist in the other catalysts. Single fuel-cell tests showed the stronger Pt–Sn interaction favors ethanol electro-oxidation at lower current density; while at higher current density multivalence Sn and Pt active sites are believed to play more important roles for ethanol oxidation. The catalytic activity of PtSn/C for ethanol electro-oxidation was determined by

both PtSn interaction degree and multivalence Sn and Pt active sites. The 40-h stability test showed that the composition of the catalyst was changed, especially the oxygen content. Besides, the contents of platinum and tin also decreased to different extents, which implies that the stability of this catalyst still needs to be improved.

**Acknowledgment.** The authors are thankful for the financial support of National Natural Science Foundation of China (Grant No.: 20173060) and Innovation Foundation of Dalian Institute of Chemical Physics. The authors also thank Dr. Bing Zhou (from Headwaters Nanokinatix Inc., USA) for the valuable discussion and revision.

EF034073Q