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Preparation and characterization of PtSn/C anode electrocatalysts for direct ethanol fuel cell

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Abstract

Highly active PtSn/C catalyst was prepared by a polyol method. The catalyst was reduced in H_2/Ar atmosphere at 600 °C for 2 h in order to obtain different metallic phase. TEM images show uniform dispersion of spherical metal nanoparticles with average diameters of 1.8 and 3.9 nm for the as-prepared and treated catalysts, respectively. UV–vis spectrophotometry is employed to monitor the preparation process and the results indicate that Pt–Sn complex formed once the precursors of Pt and Sn were mixed together. The structure properties of the samples were characterized using X-ray diffraction. The results show that after reduction, the catalyst tends to form PtSn alloy. TPR experiment results show that Sn exists in multivalent state in the as-prepared sample while only zero-valence Sn was detected in the treated sample, while it could not be excluded that the multivalent tin existed in the treated sample. Cyclic voltammetry (CV) technique and single direct ethanol fuel cell (DEFC) tests indicate that the as-prepared catalyst possesses superior catalytic activity for ethanol oxidation to the treated sample. The results suggest that Pt and multivalent Sn are the active species for ethanol oxidation.

Keywords: Electrocatalyst; Direct ethanol fuel cell; Cyclic voltammetry

1. Introduction

In the past 20 years the direct methanol fuel cells (DMFCs) have been widely studied and considered as possible power sources for the portable electric apparatus and electric vehicles. DMFCs has a variety of benefits such as high energy density of methanol, availability and portability, but methanol ‘crossover’ from anode to cathode through polymer electrolyte membrane leads to low system efficiency and this liquid fuel is toxic. As an alternative fuel, ethanol is safer and exhibits higher energy density than methanol. As well known, ethanol is a complex molecule, so the complete oxidation of ethanol is more difficult than that of methanol. So far, it is difficult for the state of the art PtRu catalyst to oxidize ethanol completely, with many intermediates produced which lead to electrocatalyst poisoning [1–4]. Our previous study indicated that PtSn is more active than the commercial PtRu catalyst for ethanol electro-oxidation [5–8] though its activity for methanol is controversial [9–11]. However, the mechanism of the promoting effect of Sn for ethanol oxidation is not well understood up to now. Particularly, the effects of alloy extent and the active species of PtSn/C prepared by the modified polyol method on ethanol oxidation reaction (EOR) need to be clarified. In the present work, PtSn/C anode electrocatalyst (with 2:1 nominal atomic ratio) was prepared by the modified polyol method. The as-prepared sample was treated in H_2/Ar in order to obtain different metallic phases. UV–vis spectroscopy was employed to monitor the preparation process. XRD, TEM, TPR and CV techniques were used to characterize the electrocatalysts. On the basis of the characterization results from preparation to post-treatment, the possible active phases to ethanol oxidation in the PtSn/C catalyst were investigated.

2. Experimental

2.1. Preparation of Pt_2Sn catalysts supported on carbon

$H_2PtCl_6{\cdot}6H_2O$ and $SnCl_2{\cdot}2H_2O$ were used as precursors of PtSn catalysts. XC-72R carbon black (Cabot Corp., S_{BET}

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$= 236.8\,m^2\,g^{-1}$) and ethylene glycol (EG) was used as a support and reducing agent, respectively. The detailed process has been described elsewhere [12,13]. Following is a brief description of the preparation method: the required amounts of $H_2PtCl_6{\cdot}6H_2O$, $SnCl_2{\cdot}2H_2O$ and carbon were added to the mixture of EG and deionized water with stirring to form 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 sample was filtered, washed and dried at 80 °C for 10 h in a vacuum oven. The nominal loading of Pt in the catalysts was 20 wt.%. The as-prepared catalyst (denoted as PtSn/C-as pre) was treated at 600 °C in H_2/Ar (10 vol.% H_2) for 2 h, and denoted as PtSn/C–H_2.

2.2. Characterization of catalysts

UV–vis spectrophotometry was used to monitor the reaction process in the EG system. The experiment was carried out with a V-550 (made in Japan) spectrophotometer with a resolution of 0.1 nm. Before and after the reaction, 1 ml of the liquid was separated and diluted to be analyzed by UV–vis spectrophotometer.

The XRD analyses of all samples were performed using a Rigaku diffractometer (D/max-2400 X) with a Cu Kα radiation source with a Ni filter 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 histogram of every PtSn/C catalyst sample.

TPR experiments were carried out on ChemBET 3000 (QuantaChrome Co.). All measurements were carried out with a heating rate of 10 °C/min to 120 °C and a H_2/Ar flow rate of 60 ml/min. Thirty milligrams of the as-prepared or treated catalyst was fixed in the bottom of a U-shape quartz reactor by packing quartz wool at both ends. Prior to the experiment, the samples were swept in an Ar flow (100 ml/min) at 120 °C for 30 min to clean the surface then cooled to room temperature. H_2/Ar was used to carry out TPR experiments. Electroactivities were measured by CV 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®-115-impregnated PtSn/C catalysts cast on a vitreous carbon disk electrode. A Pt gauze and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. The electrolyte was a solution of 0.5 M C_2H_5OH in 0.5 M H_2SO_4. The potential range was −0.2 to 1.0 V (versus SCE) and the scan rate was 50 mV s^{-1}.

2.3. Single direct ethanol cell tests

The membrane electrode assemblies (MEAs) were fabricated according to the method described in the literature [14]. PtSn/C (in-house) and Pt/C-JM were used as anode and cathode catalysts with Pt loadings of 1.5 mg cm^{-2} on the anode and 1.0 mg cm^{-2} 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.

3. Results and discussion

3.1. Characterization of the reaction process

UV–vis spectrophotometer was used to monitor the reaction process in order to clarify the reaction mechanism of H_2PtCl_6 and $SnCl_2$ in the EG system. UV–vis spectra of the reaction system were collected in Fig. 1. Fig. 1a and b are the UV absorption spectroscopy of $SnCl_2$/EG and H_2PtCl_6/EG, respectively. It can be seen that there is a prominent absorption peak at around 267 nm for H_2PtCl_6/EG and around 236 nm for $SnCl_2$/EG. In literature [12], the absorption peak at 267 nm assigned to Pt^{4+} was also observed. However, when H_2PtCl_6/EG and $SnCl_2$/EG were mixed, the absorption peaks that are found at about 325 and 267 nm disappeared. There appeared a novel peak at about 289 nm. Dai and coworkers [15] studied the interaction of Pt–Sn complexes in aqueous solution by UV reflectance spectroscopy and absorption spectroscopy and found that Pt–Sn interact with each other via Cl^- bridging. The absorption spectroscopy of H_2PtCl_6–$SnCl_2$, which varies depending on the Sn/Pt ratio, is extremely complex. The peaks of Pt–Sn complex may appear at any wavelength from 250 to 400 nm based on Sn/Pt ratio. Baronetti et al. [16] researched the H_2PtCl_6/$SnCl_2$ aqueous system and detected the existence of $(PtCl_2(SnCl_3)_2)^{2-}$ complex by diffuse reflectance spectroscopy. So it could be deduced that Pt ions reacted with Sn ions to form complex in EG system. According to the redox potential (step 3), Pt^{4+} is thermodynamically liable to be reduced to Pt^{2+}. $PtCl_4{}^{2-}$ produced by step (3) could form multi-nuclear complex with $SnCl_2$. Different complexes are

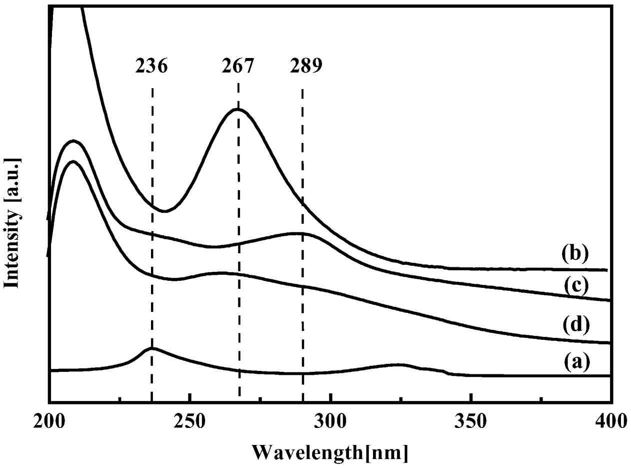

Fig. 1. UV–vis absorption spectroscopy of the reaction process of H_2PtCl_6 + $SnCl_2$/EG system: (a) $SnCl_2$/EG (b) H_2PtCl_6/EG (c) $SnCl_2$/EG + H_2PtCl_6/EG-initial (d) $SnCl_2$/EG + H_2PtCl_6/EG-final.

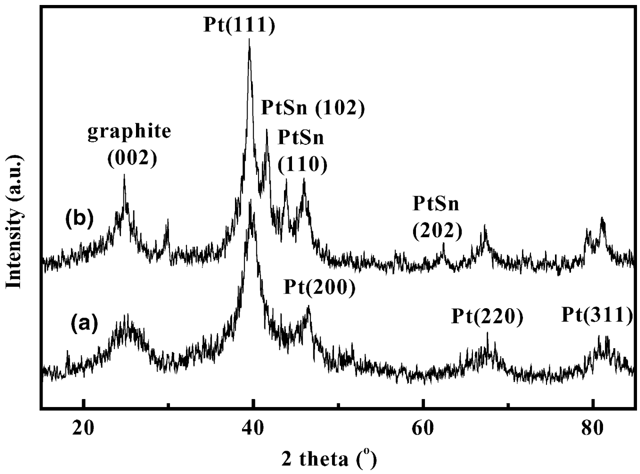

Fig. 2. XRD patterns of PtSn/C catalysts: (a) PtSn/C-as pre (b) PtSn/C–H_2.

formed depending on the Sn/Pt ratio. Larcher and Patrice [17] researched the possibility for the synthesis of alloys in the EG solution through simple thermodynamic consideration. It was suggested that the direct formation of an alloy is thermodynamically more favorable than the separate formation of the constituting metals. So it would be theoretically possible to prepare a bimetallic alloy starting from two precursors, one individually leading to metal and the other not. In our system, Pt^{4+} ions is liable to be reduced to Pt^0, while Sn^{2+} or Sn^{4+} is not, so according to Larcher's study, it is possible to reduce Pt^{4+} and Sn^{2+} (Sn^{4+}) to PtSn alloy. In Fig. 1d, the peak at about 289 nm before reaction attributed to some Pt–Sn complex ($PtSnCl_x$) [16] disappeared after the reaction. Therefore, it is indicated that Pt and Sn ions formed complex which could be reduced simultaneously at the conditions studied here, while part of Sn ions, which were not complex with Pt, could not be reduced and existed in multivalence.

$$PtCl_6{}^{2-} + 2e \rightarrow PtCl_4{}^{2-} + 2Cl^- \qquad E^o = 0.76\,V \qquad (1)$$

$$SnCl_6{}^{2-} + 2e \rightarrow SnCl_4{}^{2-} + 2Cl^- \qquad E^o = 0.14\,V \qquad (2)$$

$$PtCl_6{}^{2-} + SnCl_4{}^{2-} \rightarrow PtCl_4{}^{2-} + SnCl_6{}^{2-} \qquad E^o = 0.62\,V \qquad (3)$$

3.2. Characterization of structure properties of PtSn/C catalyst

XRD patterns of PtSn/C-as pre and PtSn/C–H_2 are shown in Fig. 2. The diffraction peaks at around 39°, 46°, 68° and 81° are attributed to Pt (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystalline plane, respectively, which represents the typical character of a crystalline Pt with face-centered cubic (fcc) structure. Pt (2 2 0) diffraction peak was selected to calculate the particle size and the crystalline lattice parameters of Pt in order to avoid the disturbance of carbon and tin, which have no peaks around this angle [18,19]. The crystalline lattice parameters of Pt in the two samples are 3.93 and 3.94 Å, respectively. Compared to the lattice parameter of bulk Pt (3.92 Å), Pt lattice parameter extended with the addition of Sn indicating that Pt and Sn alloy to some extent. This is well coincident with the above UV–vis spectra results to confirm part of PtSn alloy forms during the preparing process. After treatment, the XRD pattern of the as-prepared catalyst changed prominently. Besides the four strong lines of Pt, new peaks appear at around 41.5°, 43.7° and 62.3° attributed to PtSn (1 0 2), PtSn (1 1 0) and PtSn (2 0 2) according to the Joint Committee of Powder Diffraction Standard (JCPDF-250614). This result confirms that Pt alloy Sn to a great extent. The mean particle sizes calculated by Scherrer Formula [20] are 2.3 and 5.7 nm for the as-prepared and treated samples, respectively.

TEM images and the corresponding metal particle size distribution histograms of the catalyst before and after treatment are shown in Fig. 3. It indicates that the PtSn/C–H_2 catalyst consists of uniform nanosized metal particles, although its metal particles are slightly larger than its as-prepared counterpart. The mean particle sizes of the catalyst before and after treatment are 1.8 and 3.9 nm obtained from TEM results, which are a little smaller than that from XRD patterns. It is mainly because only large particles were picked up in XRD patterns, while all particles whether large or small were counted in TEM images.

TPR experiments were carried out to clarify the chemical state of Pt and Sn in catalysts. It can be seen from Fig. 4. There are four peaks for the as-prepared catalyst at 270, 410, 530 and 720 °C, which are attributed to the reduction of surface platinum oxide, SnO, SnO_2 and the reaction of C and H_2, respectively [16]. Yang et al. [21] studied the low loading $PtSn/Al_2O_3$ catalyst and also found that the bivalent and quadrivalent tin could be reduced to zero-valent tin. Furthermore, the energy dispersion X-ray (EDX) analyses of the as-prepared sample also confirmed the existence of multivalent tin [8]. For the treated sample, there appeared two peaks. The one of around 270 °C should be assigned to the reduction of the surface platinum oxide formed during the operation and the other occurred at about 760 °C should be attributed to the reaction of C and H_2. Although tin is more liable to be oxidized than platinum in the same condition, no peak assigned to the reduction of Sn(2+) or Sn(4+) was detected in the treated sample. This phenomenon may imply that tin alloy platinum which could not be oxidized easily. From the above discussion, it could be deduced that most Sn in the as-prepared catalyst exists in multivalence, while after reductive treatment Sn exists in zero-valence. Considering the XRD results, it is believed that PtSn alloy formed after treatment. In the as-prepared sample it is confirmed that part of Sn exists in multivalence, while the existence of alloy state of Sn could not be excluded for there is no direct proof. It could be deduced only from the dilatation of Pt crystal lattice parameter that PtSn alloy and Sn coexist in the as-prepared sample.

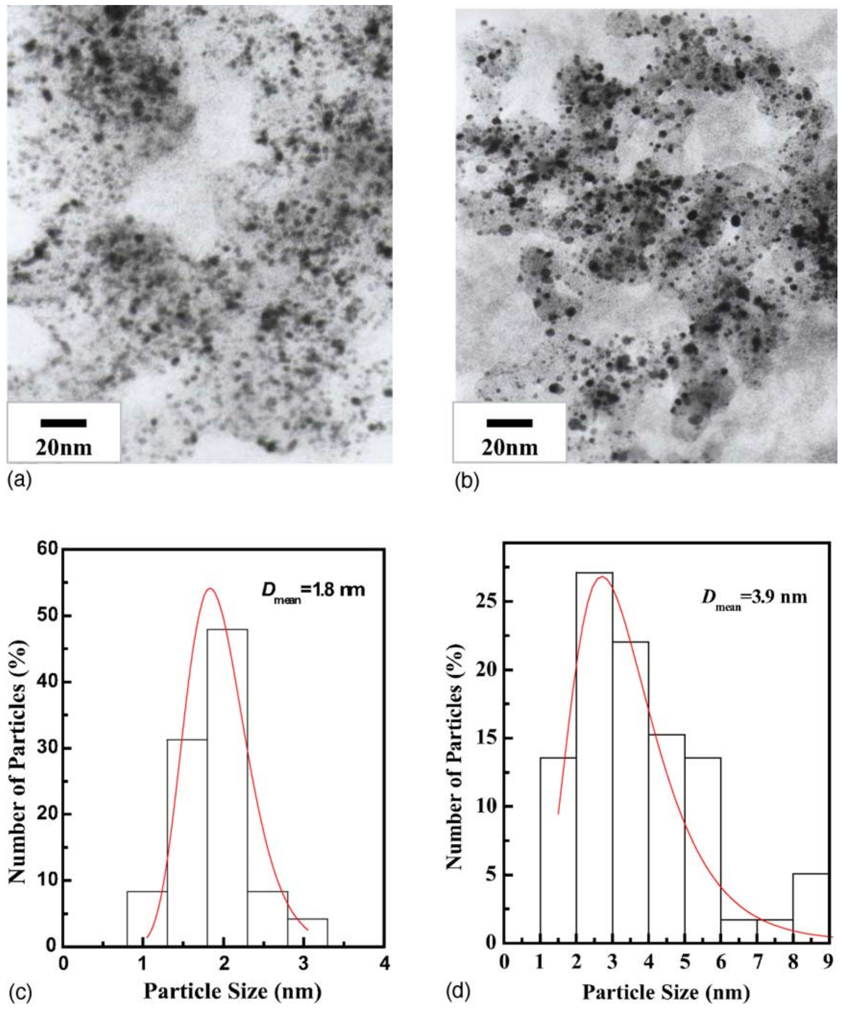

Fig. 3. TEM images of (a) PtSn/C-as pre and (b) PtSn/C–H_2, corresponding particle size distributions of (c) PtSn/C-as pre and (d) PtSn/C–H_2.

3.3. *Electrochemical activities of PtSn/C catalysts*

Fig. 5 shows the cyclic voltammograms of ethanol oxidization under acidic conditions (0.5 M C_2H_5OH/0.5 M H_2SO_4) catalyzed by the PtSn/C catalysts. It can be seen in this figure that the onset potentials of ethanol electro-oxidation on PtSn/C-as pre and PtSn/C–H_2 are both at about 0.2 V (versus SCE) while the positive sweep peak currents of ethanol on PtSn/C-as pre and PtSn/C–H_2 are 5.1 and 4.3 mA at 0.74 V (versus SCE), respectively. This indicates that PtSn/C-as pre shows the higher catalytic activity for ethanol electro-oxidation than PtSn/C–H_2.

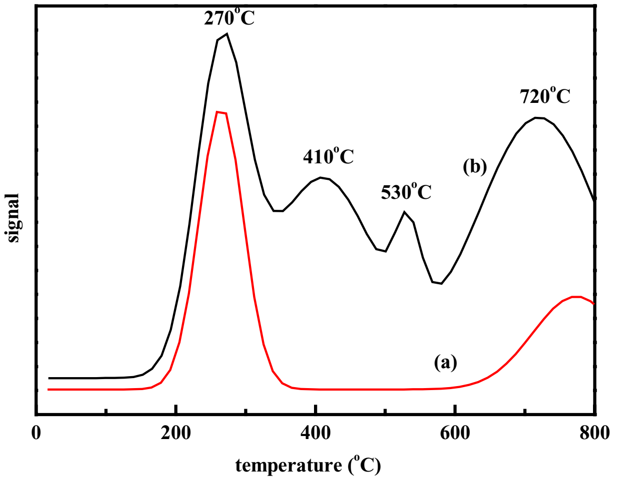

Fig. 4. TPR profiles of (a) PtSn/C–H_2 (b) PtSn/C-as pre.

3.4. *Single direct ethanol fuel cell tests*

The performance (*I*–*V* curves) of DEFC using PtSn/C as anode catalysts are displayed in Fig. 6. As can be seen from this figure, the PtSn/C-as pre gives better performance than the PtSn/C–H_2. The open circuit potentials (OCP) for PtSn/C-as pre and PtSn/C–H_2 are 0.797 and 0.774 V, respectively. In the whole performance tests PtSn/C-as pre showed better performance for ethanol electro-oxidation than PtSn/C–H_2. This is well agreement with the above CV results.

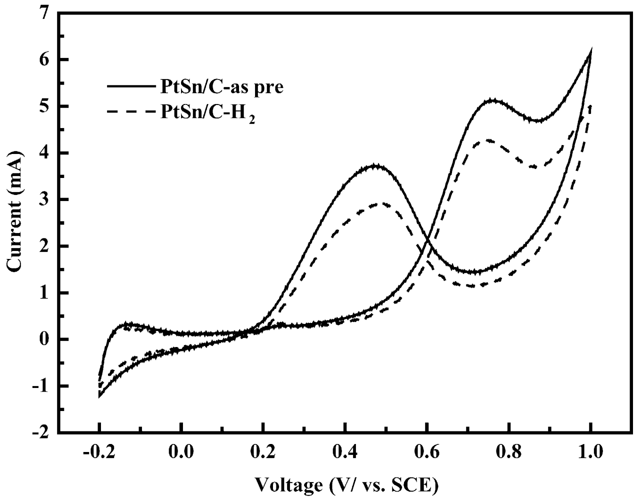

Fig. 5. Cyclic voltammograms of PtSn/C electrodes in 0.5 M C_2H_5OH/0.5 M H_2SO_4 electrolyte at 50 mV s^{-1} at room temperature.

Though the promoting effect of Sn on Pt for methanol oxidation is controversial, our research in the present paper shows clearly that Sn plays an important role for ethanol oxidation in PtSn catalysts [6]. It is noteworthy that the promoting effect taken by Sn strongly depends on its chemical state. As stated above, multivalence Sn was found in the as-prepared sample, which showed a better performance. However, the treated sample, in which only zero-valence Sn was found, showed an inferior cell performance. In the literature [6] it was depicted the probable mechanism of the promoting effect of Sn on Pt for ethanol oxidation. It was deemed that the dilatation of Pt crystal cell parameter by addition of Sn favors for the adsorption of ethanol molecules and that the CO_{ads} removal is mainly via the weakening of the CO_{ads} adsorption on PtSn/C catalyst although there are surface oxygen-containing species taking part in the oxidative removal of intermediates. According to the results here and the possible promoting mechanism [6], it is deduced that the coexistence of the alloy state of Pt and multivalence Sn in the as-prepared catalyst favors the ethanol electro-oxidation, and consequently this catalyst demonstrated the enhanced cell performance. Further work about the stability and other properties of the PtSn/C catalysts for ethanol electro-oxidation is being conducted in our lab.

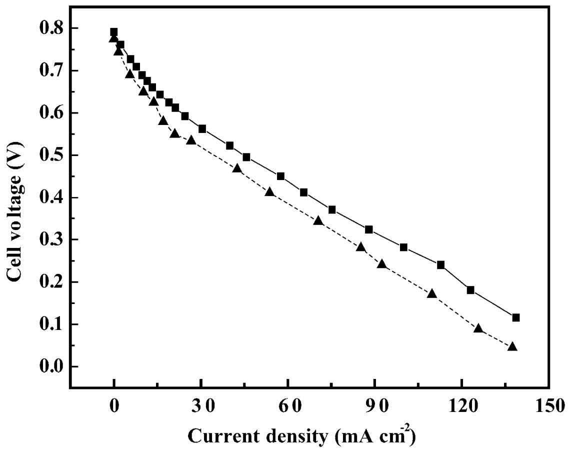

Fig. 6. Comparison of the fuel cell performance of a direct ethanol fuel cell with PtSn/C and PtRu/C catalysts operated at 90 °C anode catalyst and metal loading: (■) PtSn/C-as pre, 1.5 mg cm^{-2} Pt; (▲) PtSn/C–H_2, 1.5 mg cm^{-2} Pt; cathode catalyst and metal loading: 1.0 mg cm^{-2} Pt (20% Pt, Johnson Matthey Inc.), Nafion®-115 was used as electrolyte; ethanol concentration and flow rate: 1 M and 1.0 ml/min.

4. Conclusion

In the present paper PtSn/C was prepared by a modified polyol method. In the reaction process a small part of Pt ions formed complex with Sn ions. The complex was liable to be reduced to form PtSn alloy, which is confirmed by the dilatation of Pt crystal lattice parameter. While most of Sn ions could not be reduced to zero-valence and partially existed in multivalence according to TPR profiles. After reductive treatment, the metal particle size of the as-prepared is similar to that of the treated sample, both of which have sharp size distribution. However, most of tin exists in alloy state in the latter. CV and single DEFC tests showed that PtSn/C-as pre has higher activity for ethanol electro-oxidation than PtSn/C–H_2, which implies that it is coexistence of PtSn alloy and multivalence Sn that play an important role for ethanol electro-oxidation.

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