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Improving electrochemical activity of PtRu/SnO_2/C catalyst by reduction treatment and alkaline etching[☆]

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ABSTRACT

PtRu/SnO_2/C catalyst was prepared in a polyol process, followed by reduction treatment and alkaline etching. X-ray diffraction, transmission electron microscope with energy dispersive spectrometer and X-ray photoelectron spectroscopy were used to characterize the morphology, structure and composition of the catalysts. CO and methanol electro-oxidation activities of the catalysts were evaluated by CO stripping voltammetry, cyclic voltammetry and chronoamperometry measurements. Reduction treatment of the prepared PtRuSnO_2/C catalyst in a polyol process induced the enrichment of Sn on the surface, inhibiting methanol dissolution and CO adsorption on Pt. Alkaline etching removed Sn or SnO_x and thus exposed PtRu on the surface, resulting in enhanced activities for CO and methanol electro-oxidation due to the synergy effects of PtRu on the surface and Sn species beneath.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are attractive in energy conversion field due to their high efficiency and energy density with low/zero emission [1–3]. However, there are several challenges to overcome before their commercialization, including the development of highly CO-tolerant and durable catalysts [4–6]. The reformed gas contains hydrogen mixed with CO at ppm level, which can poison the anode catalyst of PEMFCs [7,8]. Moreover, the species of methanol dissociation include CO species, which adsorbs on the surface of catalyst to prevent further reaction, resulting in significant performance degradation in direct methanol fuel cells (DMFCs) [9,10]. So the development of CO-tolerant catalyst is critical to improve the performance of PEMFCs and DMFCs.

PtRu is currently considered as the most active bimetallic anode catalyst for CO and methanol electro-oxidation due to the bifunctional effect by Langmuir–Hinshelwood (L–H) mechanism, in which OH_{ads} is formed over Ru at low potentials and reacts with CO_{ads} over Pt to produce CO_2 [11–13]. But Pt and Ru are not abundant and expensive [13,14]. An alternative strategy is to introduce another cheap metal or metal oxide as substrate and PtRu distributed on the surface. When the particle size of the substrate is small enough, PtRu can surround on its surface. It is similar to a core-shell structure, which would increase PtRu utilization and improve aggregation resistance. In addition, PtSn catalysts show higher activities for ethanol electro-oxidation than Pt catalysts due to that the addition of Sn promotes the dissociative adsorption of ethanol molecules [15–17]. And SnO_x was shown to be the main existing form of Sn in the PtSn catalysts [15–19]. It is also reported that various metal oxides such as SnO_x, MoO_x, Ti_4O_7 and WO_x showed remarkably assisting electro-catalytic role for CO and methanol oxidation [20–24]. Synergy effect between Pt and metal oxides was usually considered as the dominant factor for greatly promoting the electro-catalytic activity [20–25].

Metal oxides have also been reported to promote the activities of PtRu towards CO and methanol electro-oxidation, however, the surface metal oxide blocked the PtRu and decreased the utilization of PtRu. Therefore, a novel preparation strategy is essential to expose more PtRu on the surface while maintaining the synergy effect of PtRu and metal oxide. In this work, PtRuSnO_2/C catalyst with uniform composition was prepared in a polyol process, and the interaction among different elements was strengthened by reduction treatment in H_2 at 300 °C. Finally, the exposed Sn or SnO_x was dissolved by NaOH etching and PtRu-enriched surface with SnO_2-riched core formed. The resulting catalyst showed improved activities for CO and methanol electro-oxidation.

2. Experimental

2.1. Catalyst preparation

$H_2PtCl_6{\bullet}6H_2O$, $SnCl_2{\bullet}2H_2O$ and $RuCl_3{\bullet}xH_2O$ were used as the precursors of PtRu/SnO_2/C catalyst and Vulcan XC-72R as the support material. The nominal mass loading of SnO_2 was 30% and PtRu was 20% with Pt/Ru ratio of 1. The detailed preparation process

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was described as follows. The precursors was calculated, weighed and dissolved into ethylene glycol in a three-necked flask. Then the pH value of the solution was increased to about 13 with 1 mol/L NaOH solution under stirring. The solution was heated to 170 °C at a rate of 10 °C/min and kept at that temperature for 4 h, and then the solution was cooled down to 90 °C. The carbon black was dispersed into ethylene glycol and added into the flask. HCl solution was then added into the flask to adjust the pH value to about 2 and the solution was kept at 90 °C for 24 h. Finally, the obtained catalyst was filtered, washed, and dried at 80 °C for 10 h in a vacuum oven. The obtained catalyst was denoted as $PtRuSnO_2/C$. Then the solid was reduced at 300 °C in 5% H_2/Ar atmosphere for 2 h and the resultant catalyst was denoted as $PtRuSnO_2/C–H_2$. Finally, $PtRuSnO_2/C–H_2$was immersed in 2 mol/L NaOH solution for 3 h. Finally, the sample was filtered and washed with de-ionized water thoroughly, and the catalyst was dried and denoted as $PtRu/SnO_2/C$.

2.2. Physicochemical characterization

Catalyst morphology was investigated using a JSM 2100F transmission electron microscope (TEM) and JEM-ARM200F high-angle annular dark-field scanning TEM (HAADF-STEM). More than 200 particles were measured to obtain the average particle size and particle size distribution of the catalysts. X-ray energy dispersive spectrometer (EDS) analysis was also applied to analyze element composition of the catalysts. X-ray diffraction (XRD) patterns of all the samples were obtained with an Empyrean X-ray diffractometer using Cu$K\alpha$ radiation. The 2θ angular scan was measured from 10° to 90° with a scan rate of 0.2 °/s. The tube current was 40 mA with a tube voltage of 40 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Thermo Scientific spectrometer with an Escalab 250 Xi X-ray as excitation source. The Pt 4*f*, Ru 3*p* and Sn 3*d* signals were collected. The position of the C 1 *s* peak, that is, 284.6 eV was used to correct the binding energies of the catalysts.

2.3. Electrochemical measurements

Electrochemical measurements were carried out in a home-made three-electrode cell at room temperature. A glassy carbon (GC) electrode ($\Phi = 6$ mm, where Φ is defined as the diameter of the GC) covered by the prepared catalyst with Nafion ionomer as a binder was used as a working electrode. Pt sheet and saturated calomel electrode (SCE) was used as a counter electrode and a reference electrode, respectively. The potential of the working electrode was controlled by a PARSTAT2273 working station (Princeton). 5 mg of the catalyst was dispersed in a mixture of 1 mL water, 1 mL ethanol and 50 µL Nafion solution (5 wt%, Aldrich) with ultrasonic stirring to form a homogeneous ink [26]. The catalyst layer was prepared by dropping 25 µL of the ink onto the GC disk electrode by a microsyringe and drying at room temperature. All potential values in this paper are referred to RHE. For CO stripping voltammetry measurements, pure CO was supplied into the electrolyte solution (0.1 mol/L $HClO_4$) for 20 min at a fixed potential of 0.09 V, and then high-purity Ar was bubbled for 30 min to remove the CO dissolved in the electrolyte solution. The current-potential cycles were obtained from 0 to 1.0 V at a scan rate of 20 mV/s. Cyclic voltammetry (CV) of methanol electro-oxidation experiments were performed in a potential range between 0 and 1.0 V in 0.1 mol/L $HClO_4$ + 0.5 mol/L CH_3OH solution saturated with high-purity Ar gas, and the scan rate was set as 20 mV/s. Linear sweep voltammetry (LSV) of methanol electro-oxidation were recorded from 0 to 0.55 V at a scan rate of 1 mV/s. The chronoamperometry (CA) curves were obtained by polarizing the electrode at 0.50 V for 3600 s in the above-mentioned electrolyte solution.

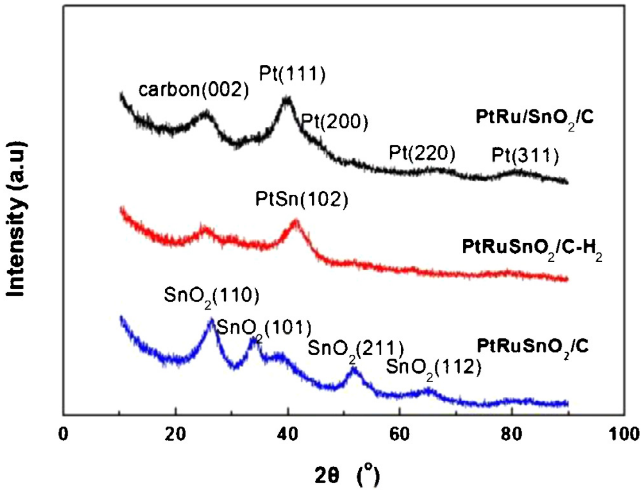

Fig. 1. XRD patterns of $PtRuSnO_2/C$, $PtRuSnO_2/C–H_2$ and $PtRu/SnO_2/C$ catalysts.

3. Results and discussion

3.1. Structure, morphology and composition characterization

The structure and phase analysis of different catalysts were conducted by XRD measurements. As shown in Fig. 1, the diffraction peaks of SnO_2 can be observed in $PtRuSnO_2/C$ catalyst with 2θ angular near 26.2°, 33.9°, 51.6° and 65.2° according to XRD peak analysis software of X'Pert High score (Reference code: 00-001-0625). The weak peak of about 38.9° may be attributed to the diffraction peak of Pt(111), which indicates that the particle size of Pt or PtRu alloy is too small to be visible or the crystallinity is poor. When $PtRuSnO_2/C$ catalyst was reduced by H_2 at 300 °C for 2 h, XRD diffraction peaks changes significantly. The peak at about 41.2° can be attributed to the diffraction peak of PtSn(102) (Reference code: 03-065-0959). While after the catalyst was immersed in 2 mol/L NaOH solution for 3 h, it is interesting to observe that the XRD peaks changes again. PtRu diffraction peaks appear at about 40.0°, 67.8° and 81.8° for Pt(111), Pt(220) and Pt(311), respectively. In addition, there is a weak peak at about 34° for SnO_2. It indicates that the surface Sn would be dissolved into NaOH solution and PtRu alloy formed at the same time.

The catalyst morphology was characterized by TEM and HAADF-STEM as shown in Fig. 2. It can be seen that the particles in $PtRuSnO_2/C$ catalyst are more uniformly distributed on the carbon support compared with $PtRuSnO_2/C–H_2$ and $PtRu/SnO_2/C$ catalysts. The mean particle size of $PtRuSnO_2/C$ catalyst is calculated to be 3.3 nm. After reduction by H_2 at 300 °C, the particle aggregation occurred with an increase of particle size in $PtRuSnO_2/C–H_2$ catalyst. The mean particle size is 4.2 nm for $PtRuSnO_2/C–H_2$ and 4.4 nm for $PtRu/SnO_2/C$, respectively. HAADF-STEM image of $PtRu/SnO_2/C$ catalyst is shown in Fig. 2(d), giving the fine structure of a particle. The spacing lattice planes are assigned to Pt(220) of 0.139 nm and SnO_2(210) of 0.210 nm. The XRD peak for SnO_2(210) often locates at about 42° of 2θ, while the corresponding peak in the Fig. 1 might be overlapped with the diffraction peak of Pt (111). It can be seen that the PtRu alloy and SnO_2 co-exist in a crystalline particle and PtRu disperses on the surface of the particle. The results of EDS analysis are listed in Table 1. The atomic ratio of Pt, Ru and Sn changes little before and after H_2 treatment. Assuming that the content of Pt in the catalyst does not change, the composition of Sn decreases a lot from 66.9% to 27.6% due to the dissolution of Sn in NaOH solution. The Ru/Pt ratio is decreased slightly from 0.6 to 0.4, indicating a small amount of Ru was also dissolved in the alkaline solution.

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