



The PtPdAg/C electrocatalyst with Pt-rich surfaces via electrochemical dealloying of Ag and Pd for ethanol oxidation



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ABSTRACT

In this work, the PtAg₂/C-D and PtPd₃Ag₅/C-D catalysts with Pt-rich surfaces were fabricated via chemical reduction following electrochemical dealloying. The as-prepared catalysts were characterized by X-ray diffraction (XRD), transmission electron spectroscopy (TEM), atomic adsorption spectroscopy (AAS), X-ray electron spectroscopy (XPS) and electrochemical methods. It is found that external Ag atoms are dealloyed by the cyclic voltammetry (CV) to expose more Pt active sites on the surface, which enhances the electrocatalytic performance greatly. The addition of Pd as another sacrificing element triggers higher activity due to the synergistic effect between Pd and Pt. The mass activity of as-prepared PtAg₂/C-D catalyst reaches 3.35 times as high as that of Pt/C. The PtPd₃Ag₅/C-D catalyst has the highest electrocatalytic activity of 4500 mA mg⁻¹, which is 6.22 and 1.87 times as high as those of mono-component Pt/C and Pd/C, respectively. Their high electrocatalytic activity is attributed to electronic effects, oxygen-containing species from Pd oxides and higher utilization of Pt.

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1. Introduction

In recent years, the direct ethanol fuel cells (DEFCs) have drawn great attention because ethanol fuel is a potentially clean and renewable energy [1,2]. However, the rareness and the high price of the commonly-used Pt metal hinder the commercialization of DEFCs [3]. The alloying of Pt with multi-elements is one of the most-investigated routes to enhance the catalytic performance and reduce the cost of the noble metals [4,5]. The intensive investigation on Pt-based catalysts, such as PtRu [6], PtSn [7,8], PtPd [9], PtPb [10], PtMo [11], etc., proves the existence of a bifunctional mechanism in which the foreign elements can provide oxygen-containing species to remove the CO-like poisoning species adsorbed to Pt sites [12]. And these alloy elements can also reduce Pt loading and modify Pt environment to boost the catalytic activity for ethanol oxidation.

Nowadays it has been increasingly common to alloy Pt with prone leaching elements, such as Al [13], Ni [14], Co [15], etc. After the treatment with H₂SO₄, these sacrificial elements are removed from the surface layer of the bimetallic or trimetallic alloying

nanocatalysts and the additional active sites of Pt are exposed. It indicates that these surface metal atoms with lower coordination numbers exhibit much higher catalytic activity than the original atoms [16]. Strasser et al. investigated the electrochemically dealloyed PtCu catalyst [17]. Since Cu dissolves drastically which creates a Pt-rich surface, lattice strain is shown with the modification of the d-band structure of the Pt atoms, which is more favorable for the oxygen-reduction reaction (ORR). Cu is one of the mostly-studied sacrificing metals in both chemical corrosion and electrochemically dealloying in anodic catalysts, such as Pt₁₀Au₁₀Cu₈₀/C, PtRuCu₆/C [18–21], but there is little research work on silver as the sacrificial element. Ag is the best electric conductor and helps the electronic coupling [22]. Bimetallic PtAg/C [23] or PdAg/C [24–27] catalysts have been investigated in the oxidation of alcohols. And as for the dealloyed Pt-based or Pd-based catalysts containing Ag, Cao et al. demonstrated that Ag could be selectively corroded in acid medium by chemical methods from PtAg alloy to form caves. Podlovchenko et al. [28] reported that voltammetric cycling of the deposited PdAg resulted in the preferential dissolution of both Ag and Pd components. Lu [29] converted the PdAg alloy nanoparticles into PdAg@Pd core-shell structured nanoparticles through a facile electrochemical treatment in acid media. Furthermore, chemical corrosion and electrochemical dealloying are the two most widely used methods on the

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carbon-supporting materials. In comparison with chemical dealloying, the electrochemical dealloying of carbon-supporting materials could be achieved in a typical three-electrode cell for testing or membrane-electrode-assemblies (MEAs) for the practical purpose [14], and it proved to be more facile and faster. However, little work is reported about the bulk phase compositions of the nanoparticles treated with electrochemical dealloying, such as atomic adsorption spectroscopy (AAS) analysis, for it is hard for the catalysts to be synthesized in large scale in three-electrode cells [20,21,29].

Inspired by the findings mentioned above, we successfully synthesized PtPd₃Ag₅/C catalysts with Pt-rich surfaces via the facile electrochemical dealloying. The structure and the catalytic activities for ethanol oxidation were studied in detail by the physical characterizations and electrochemical measurements. Its kinetics was also discussed. The as-synthesized catalyst achieved a prominent catalytic activity for ethanol oxidation, compared with mono-Pt and mono-Pd catalysts, demonstrating the promising application in DEFCs.

2. Experimental

2.1. Preparation of catalysts

The functionalization pretreatment of carbon black (Cabot Vulcan XC-72R) was performed in a 20% HNO₃ at 80 °C for 2 h, filtered, washed repeatedly with deionized water and then dried at 80 °C overnight in a vacuum oven. Each of the Pt/C, Pd/C, Ag/C, PtAg₂/C and PtPd₃Ag₅/C catalyst was synthesized using aqueous solution of H₂PtCl₆, H₂PdCl₄ and AgNO₃ as metal sources, NaBH₄ as the reduction agent and functionalized XC-72R as the support. All the reagents listed above were of analytical grade. 16 mg of pretreated Vulcan XC-72R carbon was dispersed in 20 mL of ethylene glycol in an ultrasonic bath. Then, the stoichiometric amount of metal sources and 2 mL sodium citrate (0.1 M) were added to the suspension and the mixture was ultrasonically stirred for 30 min. The total original loading of Pt plus Pd was maintained at 20 wt. % metals and 80 wt. % carbon in all catalysts, and Ag was added according to the molar ratio of each catalyst. After that, a fresh mixed solution of 15 mg NaBH₄ and 20 mL water was added dropwise to the mixture under stirring and the reaction lasted for 2 h. Finally, the black product was filtered, washed and dried in a vacuum oven at 80 °C overnight.

2.2. Physical characterization

The XRD patterns were detected by X-ray diffractometer (Rigaku Ultimate IV) with the Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at the scan rate of 2° min^{-1} with a step of 0.02° . Atomic adsorption spectroscopy (AAS, TAS-986) was used to analyze the compositions of the as-prepared catalysts. X-ray photoelectron spectroscopy (XPS, VG ESCALAB 250) measurements were obtained using an Al K α X-ray source of 1486.6 eV. The electron binding energy was corrected by referencing the C 1s peak at 284.6 eV. The microstructure and morphology of the catalysts were examined by a transmission electron microscope (TEM, FEI Tecnai G2 F20).

2.3. Electrochemical measurement

The electrochemical characterizations were carried out in a typical three-electrode cell connected to a CHI660E electrochemical working station (CH Instrument Inc.). The glassy carbon electrode (GCE) and a piece of platinum foil were used as the working and counter electrodes, respectively. The mercuric oxide electrode (Hg/HgO/1 M KOH) or the mercurous sulfate electrode (Hg/Hg₂SO₄/0.5 M H₂SO₄) was used as the reference electrode depending on the alkaline or acidic electrolyte.

The characterizations of the catalysts were performed on the working electrode. Firstly, 5 mg as-prepared catalyst was ultrasonically mixed with 1 mL isopropyl alcohol and 15 μL Nafion solution (15 wt. %, DuPont) to produce a well-dispersed slurry. Then, 4 μL of the catalyst slurry was pipetted and covered on the pre-polished GCE using a micropipette. Finally, the ink on the working electrode was dried under an infrared lamp. The dealloying of the as-synthesized catalysts on the thin-film electrode was carried out in a 0.5 M H₂SO₄ solution if needed. The dealloyed PtAg₂/C and PtPd₃Ag₅/C catalysts are denoted as PtAg₂/C-D and PtPd₃Ag₅/C-D, respectively. All the electrochemical dealloying processes and measurements were operated at $30 \pm 0.1^\circ \text{C}$ and de-oxygenated with high-purity N₂. Cyclic voltammetry (CV) was performed in a range of -0.7 to 0.5 V in 1 M KOH + 1 M C₂H₅OH solution at a scan rate of 50 mV s^{-1} . Chronoamperometry (CA) was performed at -0.3 V for 1800 s right after 10 cycles in the alkaline ethanol solution above. The adsorption of CO on the film-coated GCE was going on for 15 min before tests and then the CO stripping tests were conducted in a pre-N₂-saturated KOH solution. Electrochemical impedance spectroscopies (EIS) were obtained in the range of 10 kHz and 0.1 Hz.

3. Results and discussion

XRD patterns of the carbon-supported mono-Pt, Pd, Ag metals and their alloys are shown in Fig. 1. The vertical solid and dashed lines refer to the peak positions of Pt/C and Ag/C, respectively. The broad peak at about 25° in all diffractograms is attributed to graphite (002) facet of XC-72R. The profile of Pt/C reveals four main symmetrical diffraction peaks located at 39.8° , 46.2° , 67.6° and 81.3° , which are the corresponding (111), (200), (220) and (311) facets of the face centered cubic (fcc) Pt crystal (JCPDS Card No. 04-0802), while the peaks of homological facets of Ag crystal (JCPDS Card No. 04-0783) are located at 38.0° , 44.3° , 64.4° , 77.3° . The peak positions of Pd/C are very close to those of Pt/C, while the peak positions of Ag/C are much lower, which is in agreement with the obvious expansion of the lattice parameter due to the bigger unit cell parameter of Ag [24,30]. For the binary and ternary catalysts, all the corresponding peak positions of PtAg₂/C, PtPd₃Ag₅/C are located between those of Ag/C and Pt/C, and their peaks are

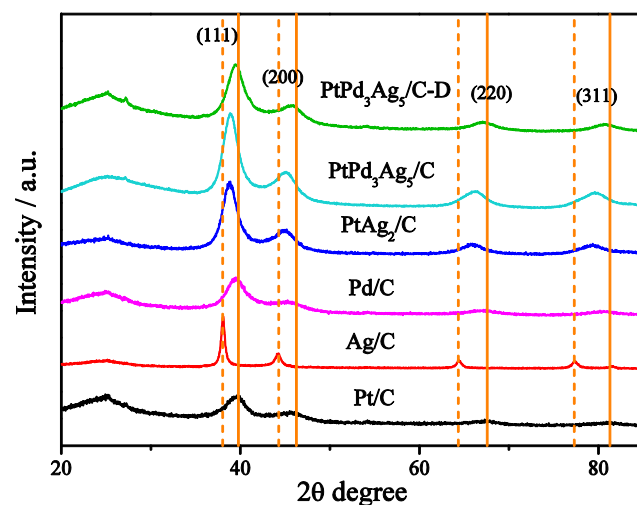


Fig. 1. XRD spectra of Pt/C, Ag/C, Pd/C, PtAg₂/C, PtPd₃Ag₅/C and PtPd₃Ag₅/C-D catalysts.

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