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Significantly enhanced electrocatalytic activity for methanol electro-oxidation on Ag oxide-promoted PtAg/C catalysts in alkaline electrolyte

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ABSTRACT

Alloyed Pt_mAg nanostructures (m being the atomic Pt/Ag ratio, $m = 0.03–1.0$) supported on carbon black were prepared and comprehensively characterized by ultraviolet–visible spectroscopy, X-ray diffraction, and transmission electron microscopy techniques. Cyclic voltammetry (CV) and chronoamperometry studies of methanol electro-oxidation reaction (MOR) in alkaline electrolyte indicated that the catalytic activity and CO tolerance of Pt were improved remarkably by the co-presence of Ag. A volcano relationship between the activity and m was found for the Pt_mAg/C catalysts, and both the highest mass-specific activity and the highest intrinsic activity of Pt were reached at $m = 0.5$. Interestingly, we also found that the catalytic activity of the Pt_mAg/C catalysts strongly depended on the high-potential limit of CV. When the Pt_mAg/C catalysts were cycled up to 0.5 V (vs. saturated calomel electrode), which induced a significant redox process of Ag, they showed ca. 50 times higher catalytic activity than those not subjected to the Ag redox process (up to 0.1 V). Our study clearly demonstrated that the Ag oxide played a crucial role in promoting the catalytic role of Pt for MOR in alkaline electrolyte.

1. Introduction

The methanol electro-oxidation reaction (MOR) has attracted much attention in the past few decades due to its important application in direct methanol fuel cells (DMFCs) [1]. To date, Pt shows the highest electrocatalytic activity for MOR among monometallic catalysts [1,2]. However, monometallic Pt catalysts are easily poisoned by intermediate species such as CO_{ads} during the process of MOR, leading to the deactivation of the catalysts [3,4]. Over the past several years, a number of studies have been devoted to Pt–metal alloys, as the bifunctional mechanism or electronic effects enabled their enhanced electrocatalytic performance and CO tolerance in MOR compared to monometallic Pt [5–9]. The so-called bifunctional mechanism in the classic bimetallic PtRu catalysts, for instance, resulted in the most effective catalysts for MOR in acidic electrolytes and thus a big step forward in improving the anodic performance of DMFCs [9–12]. In addition, other bimetallic Pt-M catalysts, where M represents the promoter, e.g., a less noble metal (Au, Pd, Ag) or a base metal (Fe, Cu, Ni), have also been identified to show enhanced catalytic activity and/or anti-poisoning properties for MOR in acidic electrolyte [6,13–17]. Two kinds of effects, ligand and geometric effects, are proposed for the improved catalytic performance of Pt in alloys [6]. The ligand effects, relating to the electronic structure of surface Pt sites, are always induced by electronic charge transfer between individual components of an alloy. The geometric effects, including the effects of the Pt–M particle morphology (particle size or dispersion state) and interatomic distance, as well as co-ordination environment and lattice strain of Pt in the surface layers, are also important [18]. Recently, Cui and co-workers [17] and Xie and co-workers [19] reported that PtAg alloy catalyzed MOR in acidic electrolytes and found that the anti-poisoning properties of Pt in the PtAg alloy can be greatly improved by the presence of Ag. Sung and co-workers [6] and Fang and co-workers [14] reported that the catalytic activity of Pt in Pt–Ni and Pt–Cu alloy catalysts for MOR could be enhanced up to 2 and 5 times compared with that of monometallic Pt catalyst, respectively.

However, the commercial application of these bi-/multimetallic Pt-based catalysts has been hampered up to now, although these catalysts show more satisfactory catalytic performance than monometallic Pt catalysts. One important reason is that very few metal materials are stable in strong acidic electrolytes [20] and the dissolution of the promoters would cause the irreversible deactivation of the catalysts. It has been reported that the activity of PtRu catalyst for MOR could decrease by 50% due to the dissolution of Ru [7]. The advantages in using alkaline media as the electrolytes of fuel cells have been generally accepted [20–22]. The stability of the catalysts and electrodes can be improved markedly in alkaline electrolyte due to their less corrosive chemical nature; moreover, the reaction kinetics are more facile for both the anodic MOR and the cathodic oxygen reduction reaction (ORR) in alkaline than in acidic

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electrolytes [23,24]. However, the same problem of the poisoning of Pt by CO-like intermediate species still persists in alkaline electrolytes as in acidic electrolytes [25]. The adsorbed OH, which can be generated on the surfaces of some promoters at relatively lower potentials, is still necessary for the oxidative removal of the poisoning CO_{ads} species [26]. Besides the metallic promoters, some metal oxides (CeO_2, V_2O_5, NiO) have also been verified as effective promoters for Pt for MOR in alkaline electrolytes due to synergistic effects or bifunctional mechanisms [27–29].

In this work, a series of alloyed Pt_mAg samples (m being the atomic Pt/Ag ratio, m = 0.03–1.0) supported on carbon black were carefully prepared according to methods reported previously [30,31] and used as anodic catalysts for MOR in alkaline electrolytes. Electrochemical characterizations of these catalysts showed that the series of Pt_mAg/C catalysts exhibited enhanced electrocatalytic activity for MOR in comparison with monometallic Pt catalyst. And interestingly, the activities strongly depended on the high-potential limit of CV measurements. When the catalysts were subjected to a potential range of −1.0 to 0.5 V, the redox process of Ag happened and the catalytic activities exhibited a dramatic increase compared with those subjected to a narrow potential range of −1.0 to 0.1 V. These in situ CV results suggested that the Ag oxide formed in the redox process of Ag played an important role in promoting the catalytic performance of Pt for MOR. These findings are of fundamental importance to the in-depth understanding of the MOR mechanism in alkaline electrolyte and also advantageous for developing more effective bi-/multimetallic MOR catalysts via modification of the nanostructures.

2. Experimental

2.1. Preparation of the carbon-supported Pt_mAg/C samples

Vulcan XC-72 carbon black (Cabot, BET surface area 250 m^2/g) was pretreated in flowing CO_2 at 500 °C for 2 h before use. The typical procedure for preparation of the carbon-supported Pt_mAg/C samples is as follows: 5 mL K_2PtCl_6 solution (1×10^{-3} M), 5 mL $AgNO_3$ solution (1×10^{-2} M), and 5 mL sodium citrate solution (6×10^{-2} M) were mixed and diluted to 100 mL with deionized water. After they were stirred for 30 min, 3 mL $NaBH_4$ solution (0.1 M) was added dropwise under vigorous stirring to produce colloidal $Pt_{0.1}Ag$ nanoparticles. Then, 95 mg Vulcan XC-72 carbon black was added in the as-prepared colloidal solution. The mixture was kept under stirring for 4 h. After filtration, the precipitate was extensively washed with deionized water and dried overnight under vacuum at 323 K to give a $Pt_{0.1}Ag$/C sample. The other Pt_mAg/C samples (m = 0.03, 0.05, 0.5, 1.0) were prepared with the identical procedure. The amount of $AgNO_3$ was kept constant in all the syntheses, while the amount of K_2PtCl_6 was changed according to the desired atomic Pt/Ag ratio (m) in the alloy products. The metal loadings of Ag were ca. 5 wt.% in these samples. For comparison, monometallic Pt/C catalyst was also prepared according to the above procedure without adding Ag precursor.

2.2. Characterization

UV–vis spectra were recorded on a Cary 300 Bio UV–visible spectrophotometer (Varian) with a resolution of 0.5 nm. The morphology of the Pt_mAg/C nanostructures was investigated using a JEM-2010 transmission electron microscope (TEM) operating at 120 kV. X-ray diffraction (XRD) patterns were measured with a D8-Advance Bruker diffractometer at a scan rate of 4°/min ($30° < 2\theta < 85°$); the wavelength of the incident radiation was 1.5406 Å (Cu Kα). X-ray photoelectron spectroscopy (XPS) measurements were taken on a Thermo ESCALAB 250 instrument with Al Kα radiation ($h\nu$ = 1486.6 eV). The actual loading amount and composition of Pt and Ag in the as-prepared carbon-supported catalysts were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Perkin Elmer Optima-4300DV spectrometer).

2.3. Preparation of the working electrodes

A glassy carbon (GC) electrode (d = 3 mm) was polished with 0.5- and 0.05-μm alumina suspensions prior to each use, followed by ultrasonic washing with HNO_3 (1:1), ethanol, acetone, and deionized water, sequentially. The catalyst ink was prepared by sonicating a suspension of the carbon-supported catalyst (5.0 mg) in isopropanol (1.0 mL). A sample of 10 μL of the suspension was first transferred onto the disk electrode; after solvent evaporation at room temperature, 10 μL 0.05 wt.% Nafion solution (Dupont) was pipetted onto the catalyst layer and then air-dried.

2.4. Electrochemical measurement of the Pt_mAg/C catalysts

Cyclic voltammetry (CV) and chronoamperometry (CA) were carried out in a conventional three-electrode cell using a potentiostat/galvanostat model 273 controlled by PowerSuite software (Princeton Applied Research) at room temperature. A Pt foil (1.0 × 1.0 cm) and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrodes, respectively. All potentials mentioned in this work are given with respect to the SCE. Cyclic voltammetry (CV) and chronoamperometry (CA) tests of MOR were performed in 0.5 M KOH + 2.0 M CH_3OH solution. The stable CV curves were recorded with a scanning rate of 20 mV s^{-1}, and the linear polarization curves were recorded between −0.55 and −0.15 V with a scanning rate of 10 mV s^{-1}. The CA curves were tested under a constant potential of −0.40 V vs. SCE.

3. Results and discussion

3.1. Characterization of the Pt_mAg nanostructures

It has been reported that the surface functional groups of the carbon support play a crucial role in determining the extent and strength of its interaction with the supported metal particles [32]. The carbonyl and hydroxyl groups formed on the carbon support surface in the pretreatment (flowing CO_2 at 500 °C) could act as the anchoring sites for the negatively charged PtAg colloidal particles through electrostatic interaction [33,34]. A representative TEM image of the $Pt_{0.5}Ag$/C sample is shown as Fig. 1A. The metal particles, roughly spherical with a mean metal particle size of 5.4 ± 0.7 nm, were fairly dispersed on the support without significant aggregation. The metal particle size distribution is shown by the bar graph in the inset. Fig. 1B presents a HRTEM image of the metal particles. No significant fringes corresponding to Pt (2.24 Å) and Ag (2.36 Å) were found in the $Pt_{0.5}Ag$/C sample; instead, the fringes of 2.30 Å corresponding to the (1 1 1) lattice spacing of PtAg alloy [35] could easily be detected by electron diffraction (the corresponding Fourier transform pattern is shown in the inset of Fig. 1B). For the other Pt_mAg/C samples, the mean particle sizes were in the range of 5–6 nm and the same patterns corresponding to PtAg alloy were also obtained. Further investigation on the PtAg alloy using XRD will be presented later.

For the discrepancy between surface plasmon resonance (SPR) behavior of Pt and Ag, UV–vis can be used as a surface-sensitive tool for the characterization of Pt_mAg nanoparticles. Fig. 2 shows the UV–vis spectrum of the series of Pt_mAg nanoparticles with different m. Since there is no significant plasmon absorption for