

Short communication

Effects of preparation conditions on performance of carbon-supported nanosize Pt-Co catalysts for methanol electro-oxidation under acidic conditions

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Abstract

Carbon-supported Pt-Co and Pt catalysts are prepared by NaBH_4 reduction of metal precursors. The particles size of Pt-Co varies with the pH used in the preparation, it is largest (12 nm) in alkaline solution and smallest (3.7 nm) in un-buffered solution. For the latter, X-ray photoelectron spectroscopy shows that Pt exists principally in the metallic state, whereas cobalt is mostly oxidized. The performance of the catalysts for methanol electro-oxidation in acidic media at room temperature is evaluated and compared with that of a Pt/C catalyst. Electrochemical measurements by cyclic voltammetry and chronoamperometry demonstrate consistently high catalytic activities and improved resistance to carbon monoxide for the Pt-Co catalysts, particularly for that prepared in un-buffered solution.

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1. Introduction

Among the different types of fuel cell technologies, direct methanol fuel cells (DMFCs) are the most suitable for mobile and portable electronic applications because of their high volumetric energy density, relatively low operating temperature, and the convenience of a liquid fuel that, thereby, enables a greatly simplified system design [1]. One of the major problems of DMFCs is sluggish methanol oxidation kinetics at the anode, which is made worse by the progressive loss of catalytically active sites by CO-like reaction intermediates that are generated during the stepwise dehydrogenation of methanol [2]. It is commonly acknowledged that Pt, as the most common oxidation catalyst for organic molecules including methanol, is highly active for the dehydrogenation

reaction, but it is also highly susceptible to CO poisoning [3].

To address the issue of CO poisoning, alloys of Pt with oxophilic metals have been investigated as replacement methanol electro-oxidation catalysts [4]. The increased resistance to CO poisoning is generally explained by a bifunctional mechanism in which the CO-like intermediates on Pt are oxidized by the OH species on the oxophilic metal [5]. Among the binary Pt alloys developed with enhanced catalytic activity and improved CO tolerance in mind, the Pt–Ru [6,7] and Pt–Sn systems [8,9] have been the most extensively investigated. While the effectiveness of the Pt–Sn catalysts is still an ongoing debate [2,10], the Pt–Ru catalysts are generally recognized as the most active methanol electro-oxidation catalyst currently available [6]. The efficiency of DMFCs operating on Pt–Ru is, however, still insufficient for most practical purposes. Furthermore, the supply of Ru [11] and the toxicological effect of Ru remain questionable. Therefore,

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investigations on alternative Ru-free DMFC anode catalysts continue to be undertaken.

Pt-Co has been used primarily as a magnetic material [12], and an oxygen reduction catalyst [13], and its suitability as a DMFC anode catalyst has not been explored in detail. There has, however, been a report about its performance as a methanol oxidation catalyst under alkaline conditions [14]. Its performance under the more commonly used acidic conditions was only recently assessed using organometallics-derived Pt-Co catalysts [15]. As cobalt is more electropositive than platinum, Pt could withdraw electrons from the neighbouring cobalt atoms and bring about an oxide-cleansing action that places Pt in a more reduced state than in the absence of Co [16]. In this study, carbon-supported Pt-Co catalysts with nanometer particle size and a narrow size distribution are prepared under relatively gentle conditions. The particles size is found to be a function of the pH used in the synthesis. The activity and CO-tolerance of the catalysts in methanol electro-oxidation are evaluated by cyclic voltammetry (CV) and chronoamperometry (CA) in half-cell experiments. The performance is compared with that of a carbon-supported Pt catalyst with the same Pt loading prepared under similar experimental conditions.

2. Experimental

Chloroplatinic acid (H_2PtCl_6) from Aldrich, sodium citrate ($\text{Na}_3\text{Cit}\cdot 2\text{H}_2\text{O}$), sodium boron hydride (NaBH_4), cobalt chloride (CoCl_2), sulfuric acid (95–97%) and methanol were supplied by Merck. The carbon support was Vulcan XC-72 (BET surface area of $250\text{ m}^2\text{ g}^{-1}$ and average particle size of 40–50 nm) from Cabot. All chemicals were used as received without further purification. De-ionized water was used throughout the study.

2.1. Preparation of electrocatalysts

Thirty milligrams of sodium citrate was added to a mixture of 1 ml of 50 mM of H_2PtCl_6 and 1 ml of 50 mM CoCl_2 , and then diluted with water to 40 ml. The pH of the as-prepared mix was 5.5. Thirty-six milligrams of Vulcan XC-72 was then introduced followed by 30 min of sonication in an ultrasonic bath. Twenty-two milliliters of solution containing 30 mg NaBH_4 was added dropwise to the carbon suspension with stirring at room temperature. Stirring was continued for 6 h before the suspension was filtered to recover the solid product and was washed copiously with water. The recovered solid was then dried in a vacuum oven at $80\text{ }^\circ\text{C}$ for 2 h. The catalyst obtained as such is termed as ‘Pt-Co/C’. Pt-Co-acidic/C and Pt-Co-basic/C catalysts were prepared following nearly the same procedures except that acids and bases were introduced during the syntheses to adjust the pH to 1.0 and 11.0, respectively. A Pt/C catalyst was also prepared likewise and the Pt loading was kept the same at 20 wt.% for all catalysts.

2.2. Characterization of electrocatalysts

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max-3B diffractometer, using $\text{CuK}\alpha$ radiation. The X-ray photoelectron spectroscopic (XPS) analysis of samples was conducted on a VG ESCALAB MKII spectrometer using the supplied XPSPEAK software to deconvolute the narrow scan spectra of C, Pt and Co. The elemental compositions of the catalysts were measured by an energy dispersive X-ray (EDX) analyzer attached to a JEOL MP5600LV scanning electron microscope (SEM) that operated at 15 kV. A JOEL JEM2010 transmission electron microscope (TEM) operating at 200 kV was used to examine the particles.

2.3. Electrochemical measurements

The activities of the catalysts were measured by cyclic voltammetry and chronoamperometry by means of an EG&G 273 potentiostat/galvanostat. The working electrode was fabricated by casting Nafion-impregnated catalyst ink on to a 4-mm diameter vitreous glassy carbon disk electrode. A Pt gauze and a saturated calomel electrode (SCE) were used as the counter and the reference electrode, respectively, while the electrolyte was 2 M CH_3OH in 1 M H_2SO_4 . All reported potentials were referenced to the SCE. The catalysts were cycled between 0 and 1 V at 50 mV s^{-1} until a stable response was obtained before the cyclic voltammograms and chronoamperograms were recorded.

3. Results and discussion

TEM images of the Pt nanoparticles are shown in Fig. 1, together with those of Pt-Co nanoparticles synthesized under acidic (pH = 1.0), un-buffered (pH = 5.5) and alkaline (pH = 11.0) conditions, respectively. The mean and the standard deviation (σ) of the diameters for the Pt-only nanoparticles are 4.0 and 1.0 nm, respectively. The particle size of the Pt-Co catalysts is strongly dependent on the pH of the solution in which they are formed, with mean diameters of 3.7 (± 0.9), 7.0 (± 3.0) and 12 nm (± 2.3 nm) for Pt-Co/C, Pt-Co-acidic/C and Pt-Co-basic/C, respectively. Hence, Pt-Co nanoparticles synthesized without any pH adjustment have the smallest particle size and a narrow size distribution compared with those of Pt-only nanoparticles.

The size-dependence of the Pt-Co particles on the pH of preparation can be understood as follows. Citric acid is a triprotic acid with $\text{p}K_{\text{a}1} = 2.8$, $\text{p}K_{\text{a}2} = 4.2$ and $\text{p}K_{\text{a}3} = 5.4$, respectively [17]. Citric acid therefore exists as Cit^{3-} in alkaline solutions and as un-dissociated H_3Cit in acidic solutions. At the unadjusted pH of the as-prepared solution (pH = 5.5), H_3Cit , $[\text{H}_2\text{Cit}]^-$, $[\text{HCit}]^{2-}$ and Cit^{3-} coexist, with $[\text{HCit}]^{2-}$ and Cit^{3-} as the majority species. The most stable Co^{2+} complex with citrate known to exist in the solution, $[\text{Co}(\text{HCit})_2]^{2-}$ [18], cannot therefore be formed under highly acidic or alka-

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