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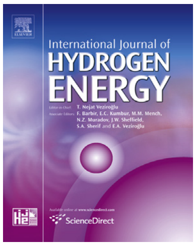

Electrochemical surface modification on CuPdAu/C with extraordinary behavior toward formic acid/formate oxidation

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ABSTRACT

In this article we innovatively propose a new surface modification strategy which applies a chronoamperometry on CuPdAu/C to get the surface copper removed CuAuPd/C (SCR-CuAuPd/C). Moreover, the chronoamperometric process can also modify the surface constitution with oxides such as PdO_2 and Au_2O_3. The removal of surface Cu will diminish the drawbacks brought by the instability of surface Cu in alkaline media, and the oxides like PdO_2 will help oxidize CO_{ad} and thus reduce catalyst poisoning. The electrochemical measurements confirm the positive effect of chronoamperometric treatment, the SCR-CuPdAu/C achieve objective progress after chronoamperometric treatment, with highest activity and anti-poisoning properties toward formic acid/formate oxidation in both acidic and alkaline media.

Introduction

Direct formic acid fuel cell (DFAFC) has some unique features such as high open circuit voltage (1.45 V), allowable of high concentration, and less crossover through membranes, making it an ideal alternative for portable power sources [1,2]. The formic acid oxidation mainly determined by oxidization of reaction intermediates such as formate group ($HCOO^-$) and rapid removal of poisoning species (such as CO) from the catalyst surface [3]. Compared to formic acid (HCOOH), formate ($HCOO^-$) is also an attractive candidate for alkaline fuel cells, as the oxidation of formate species attributes to the majority of the current density, and formate does not poison palladium in alkaline solutions [4–6]. As for the catalyst design, Pd-based catalysts exhibit remarkable electrocatalytic activity toward formic acid/formate oxidation in both alkaline and acidic media [7,8]. One of the most successful strategies to improve the electrocatalytic performance is to alloy Pd with transition metals, which should be oxophilic or provide oxygen-containing species at low potentials to help oxidize adsorbed CO, thereby decreasing catalytic poisoning [9–12].

In this article, we first synthesized the surface Au modified CuPdAu/C catalyst. Density functional theory predicts that Cu will induce significant strain and charge transfer on palladium, resulting more efficient oxidization on small organic molecules [13]. On this account, we first synthesized the

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alloyed CuPd nanoparticles, both for the purpose of lowering Pd load and improving electron structure on Pd [14]. Then we modified the CuPd surface with Au to get the CuPdAu nanoparticles, as the surface Au may help reduce adsorption energy of CO [15]. We found that the surface Cu in alkaline media would result in some drawbacks in electrocatalysis [16], on this account the chronoamperometry was firstly applied on the obtained CuPdAu/C to get the surface copper removed CuPdAu/C (SCR-CuPdAu). To conduct a chronoamperometry on the CuPdAu/C electrode in the sulfuric acid solution, it can make the surface Cu continuously leached out in to the solution, while the Pd and Au will stay and be partially oxidized to PdO_2 and Au_2O_3, etc. During this process surface Cu was removal, consequently enhance the surface roughness and electrochemical surface active area. The removal of surface Cu will also diminish the drawbacks brought by the instability of surface Cu in alkaline media. Moreover, certain amounts of PdO_2 and Au_2O_3 were formed after the dealloying treatment, the oxygen-containing oxides can help oxidize CO_{ad} and thus reduce catalyst poisoning [17]. To evaluate the performance of the as-prepared catalysts, electrochemical measurements toward HCOOH/$HCOO^-$ oxidation were conducted. The HCOOH oxidation in acidic solution is widely researched, while the alkaline formate oxidation is less reported. Compared to HCOOH, potassium formate (HCOOK) is easily handled in solutions, stable and less toxic. Moreover, Pd-based catalysts won't be poisoned during oxidation process in alkaline media. These properties indicate that the alkaline fuel cell would also be a potential high performance, low cost and environmentally friendly fuel cell technology. On this account, we evaluated the HCOOH oxidation in acidic solution, as well as the HCOOK oxidation in alkaline solution to compare the performance of the obtained catalysts.

Experiments

Catalyst preparation

The preparation procedure of CuPdAu/C catalyst is under a moderate wet chemistry method. First, 55 mg (0.21 mmol) $Cu(acac)_2$, 45.6 mg (0.15 mmol) $Pd(acac)_2$ and 30 mg PVP_{K30} were dissolved in 40 mL ethylene glycol (EG) in the nitrogen atmosphere, then the mixture was heated to 80 °C under stirring for 1.5 h to get the CuPd nanoparticles. After that 6.2 mg (0.015 mmol) $AuCl_3 \cdot 4H_2O$ was added into the obtained solution and maintained for 0.5 h to get the CuPdAu nanoparticles. The obtained CuPdAu solution was first centrifuged at 12,000 rpm and then the precipitates were washed with the mixture of ethanol and acetone under sonication. After centrifugation the obtained nanoparticles were dispersed in ethanol, then we got ethanol dispersion of CuPdAu nanoparticles. 60 mg Vulcan XC-72 was added into the dispersion and dried under vigorous stirring at 75 °C, after the ethanol was evaporated, the resulting catalyst was subjected to N_2 at 250 °C for 3 h to get the CuPdAu/C catalyst. The Pd/C catalyst was prepared in the same way using only $Pd(acac)_2$ as metal source. The precise composition of the catalysts are determined by the Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). The metallic atomic constitution of CuPdAu/C is $Cu_{0.5}Pd_{0.45}Au_{0.05}$.

Electrochemical measurement and catalyst preparation

The working electrodes for electrochemical experiments were prepared by thin film electrode method. A polished glassy carbon (GC, Φ 5 mm) was used as the substrate. The Pd loading is controlled at the same level, 8 ug Pd on each electrode. Certain amount of sample was dispersed in 2 mL ethanol under sonication for 20 min, and then 50 μL suspension was pipetted onto a GC substrate. After ethanol evaporation, the deposited catalysts were covered by 5 μL Nafion solution (0.5 wt%, Dupont). All electrochemical measurements were carried out on a CHI 660A electrochemical workstation (Shanghai Chenhua apparatus corporation, China) using a conventional three-electrode cell with a platinum sheet as the counter electrode. The reference electrode is an Hg/Hg_2SO_4, K_2SO_4 electrode (mercurous sulfate electrode, MSE, 0.615 V vs. NHE) in acidic solution, or an $Hg/HgO/OH^-$ electrode (mercuric oxide electrode, 0.098 V vs. NHE) in alkaline solution.

The surface copper removed catalyst SCR-CuPdAu is prepared by a chronoamperometric progress with CuPdAu/C electrode in a solution of 0.5 M H_2SO_4. The original potential is set at −0.6 V and high potential is set at 0 V(vs. MSE), the pulse length is 2000 s. During this period, the Cu will be continuously diffusing into the solution while Pd and Au will stay.

Results and discussion

Fig. 1 shows the typical TEM images of the as-prepared CuPdAu/C and SCR-CuPdAu. From the TEM images we can find the particle sizes of CuPdAu and SCR-CuPdAu haven't changed much after the electrochemical dealloying treatment, the average size of CuPdAu and SCR-CuPdAu nanoparticles is ca. 15.0 nm and 15.7 nm, respectively. The fast fourier transform is applied to calculate the d-spacing values of the nanoparticles. From Fig. 1B and D we can observe lattice of the nanoparticles. The CuPdAu nanoparticles expose complicated facets. As the atomic proportion of Au is only 5% in CuPdAu, the lattice is mainly determined by Cu and Pd. From the calculated d-spacing of the CuPdAu nanoparticles, we can infer the exposed facet of CuPdAu is complex, most of them can be ascribed to CuPd alloy phases with different Cu/Pd ratios, which means CuPdAu is heterogeneous alloy. The exposed facets are mainly (200), with a small proportion of (111). After the electrochemical surface Cu removal, there seems to be no obvious changes on the TEM images of SCR-CuPdAu, the crystal facet of SCR-CuPdAu remains the same, and the particles sizes enlarge a little, which may result from the loosened structure after the dealloying treatment.

XPS was employed to substantiate the surface composition and the surface oxidation states of the prepared CuPdAu/C and SCR-CuPdAu. Fig. 2 shows the deconvolution spectra of Cu, Pd and Au elements before and after the chronoamperometric progress. For the CuPdAu/C catalyst (Fig. 2A–C), the $3d_{5/2}$ peak of Pd(0) is located at 335.36 eV, shifting positively by 0.4 eV compared to Pd substance, which indicates a downshift of the d-band center of Pd due to the electron