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Pulsed electrodeposition of Pt particles on indium tin oxide substrates and their electrocatalytic properties for methanol oxidation

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ABSTRACT

The platinum (Pt) particle electrocatalysts supported on the indium tin oxide (ITO) substrate were prepared by the pulsed electrodeposition for the methanol oxidation. The effect of the lower potential pulse duration (t_l) of the electrodeposition on the surface morphology and structure of the Pt particles was investigated by the X-ray diffraction and scanning electron microscopy. The amount of the Pt loading was determined by an inductively coupled plasma method, and the electrocatalytic activity of the prepared Pt electrocatalysts on the ITO for the methanol oxidation was characterized by cyclic voltammetry. The results showed that the t_l has a significant influence on the surface morphology of the Pt particles on the ITO substrate. As the t_l decreases from 1 to 0.01 s, the deposited Pt particles on the ITO exhibit flower-, nanosheet-, prickly and smooth spherical-like morphology in turn. Furthermore, there is a remarkable effect of the surface morphology of the Pt particles on the electrocatalytic activity for the methanol oxidation. Among all these morphologies, the flower- and nanosheet-like Pt particles on the ITO have a much higher mass specific activity (MA) for the methanol oxidation, and the Pt particles with prickly surface followed while the smooth spherical Pt particles have the lowest MA. In particular, the dispersed Pt nanosheets prepared at t_l of 0.5 s has the highest MA. The much improved MA of the dispersed Pt nanosheets is attributed not only to the large electrochemically active surface area (ECSA) achieved, but also to the high electrocatalytic activity per unit ECSA related to its special morphology.

1. Introduction

Noble metal micro- and nanoparticles have attracted considerable and increasing attention in a variety of important applications such as catalysis, biological labeling, optics and electronics [1,2]. For particular applications such as electrocatalysis and electrochemical sensors, it is essential to support the noble metal particles on an appropriate conductive substrate [3–5]. Typical support materials include carbon-based materials (e.g., carbon black, glassy carbon, carbon fiber and carbon nanotubes) [6–8], metallic materials (e.g., Au, Ni and Ti) [9,10] and metal oxides (e.g., TiO_2) [11]. Recently, the application of indium tin oxide (ITO) as the support has received increasing interest due to its low cost and prominent characteristics including high electrical conductivity, excellent optical transparency, wide electrochemical working window, and stable electrochemical and physical properties [3–5,12–15]. For example, Oyama et al. [16–18] prepared Au, Ag particles on the ITO surface using seed-mediated growth method and Pt particles on the ITO by chemical reductive growth method. The fabricated Au, Ag and Pt/ITO electrodes exhibit high electrocatalytic activity for the electro-oxidation of nitric oxide [16], the reduction of the methyl viologen [17] and the oxygen reduction and methanol oxidation respectively [18]. It was found that the oxidation peak current of the Pt nanoparticles on the ITO increased over three times compared with the bulk Pt electrode for methanol oxidation [18]. Ballarin et al. [13,19] prepared Au–Pt and Au nanoparticles on the ITO electrodes by electrosynthesis and sputtering respectively, which showed promising results for methanol oxidation. In the authors' previous work, it has also been demonstrated that the Pt/ITO electrodes can be successfully used for ammonia oxidation [20,21].

Up to date, a number of preparation methods, such as the seed mediated growth [16,17,22–25], sputtering [13,26], chemical reduction [18,27] and electrodeposition [12,19,20,28–31], have been developed to prepare the noble metal particles on the ITO. Among these methods, electrodeposition technique is of particular interest due to its unique advantages including high purity of deposits, low cost of implementation and easy-to-control procedure [32–34]. Various electrodeposition methods, including galvanostatic electrodeposition [21,28,29], potentiostatic electrodeposition [30,31] and electrodeposition in a cyclic

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voltammetric mode [20,35,36], have been successfully utilized to prepare Pt, Au and Au–Pt particles on the ITO. Furthermore, since the deposits are strongly dependent on the electrodepositing conditions, it is expected that there are essential effects of the electrodeposition methods and parameters on the electrocatalytic activity of the prepared noble metal particles on the ITO [7,19,29]. Previous studies concerning the pulsed electrodeposition on other substrates found that the pulsed electrodeposition favors the formation of nucleation sites and thus contributes to a high dispersion of the deposits compared with other electrodeposition methods [37–40], which has a potential advantage on improving the catalytic activity of the prepared electrocatalysts. However, there has been no report focusing on the pulsed electrodeposition of noble metal electrocatalysts on the ITO substrates. Furthermore, the parametric influence of the pulsed electrodeposition (e.g., lower potential pulse duration t_l) on the formed noble metal particles on the ITO and the corresponding electrocatalytic activities have remained unclear.

In the present work, the pulsed electrodeposition was used to prepare the Pt particles on the ITO substrate for the methanol oxidation. The effect of the t_l of the pulsed electrodeposition on the surface morphology and structure of the deposited Pt particles were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The exact amount of the deposited Pt was determined by an inductively coupled plasma (ICP) method. Furthermore, the relationship between the surface morphology of the Pt deposits and the electrocatalytic activity for the methanol oxidation were investigated by cyclic voltammetry (CV).

2. Experimental

2.1. Preparation of Pt/ITO electrode

The ITO glasses (Southern Glass Co., Ltd., Shenzhen, China) were used after being washed in acetone and ultrapure water by sonication and drying with a nitrogen steam. Pt particles were prepared on an ITO substrate by the pulsed electrodeposition in 5 mmol L^{-1} H_2PtCl_6 and 0.5 mol L^{-1} H_2SO_4 solution. The electrodeposition was performed in a classical three electrode cell, using a sheet of ITO with an exposed geometry area of 1 cm^2 as the working electrode, a mercury sulfate electrode (MSE) as the reference electrode, and a Pt plate as the counter electrode. All solutions were prepared with ultrapure water obtained from a water purification system (Millipore, 18.2 MΩ cm). Fig. 1 shows the schematic diagram of the pulsed electrodeposition. The upper potential limit (E_u), lower potential limit (E_l) and the upper potential pulse duration t_u were 0.1 V (MSE), −1 V (MSE) and 1 s, respectively. The lower potential pulse duration t_l was changed between 0.01 and 1 s. The total time of t_l under different electrodeposition conditions are all set as 20 s. When only E_u is applied, i.e., t_l = 0 s, there are no Pt particles formed on the substrate. While only E_l is applied, i.e., t_u = 0 s, the formed Pt particles are quite similar to those formed at t_l = 1 s and t_u = 1 s.

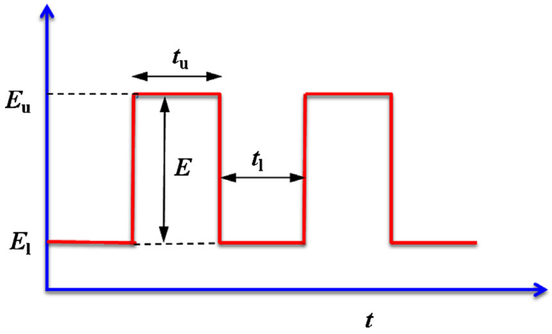

Fig. 1. Schematic diagram of the potentiostatic pulsed electrodeposition.

2.2. Characterizations of surface morphology, structure and amount of the deposited Pt on ITO

The surface morphology of the deposited Pt particles on the ITO substrate was obtained using a field-emission SEM (FEI Sirion 250). The crystalline structure of the Pt particles was characterized by an XRD (BRUKER-AXS) using Cu Kα radiation (λ = 0.15406 nm) at a scan rate of 0.5° min^{-1}. The exact amount of the Pt deposits, i.e., Pt loading, on an ITO substrate was determined by an ICP (Thermo Scientific, iCAP 6000) method after dissolving Pt from the substrate. The Pt loading (μg cm^{-2}) is normalized by the geometric area of the working electrode.

2.3. Electrochemical characterizations

The electrocatalytic activity of the prepared Pt/ITO electrode for the methanol oxidation was characterized by CV measurements in the solution containing 0.5 mol L^{-1} H_2SO_4 and 1 mol L^{-1} CH_3OH at a scan rate of 0.05 V s^{-1}. The electrochemically active surface area (ECSA, cm^2 cm^{-2}) of the Pt deposited on the ITO was evaluated from the steady-state CVs recorded at 0.05 V s^{-1} in 0.5 mol L^{-1} H_2SO_4 solution, and its value was normalized by the geometric area of the working electrode. The solution was deaerated by purging a high-purity N_2 gas (99.999%) throughout the test. All tests were carried out at 25 ± 1 °C. Each test was repeated five times and the standard deviation of the obtained results was calculated and shown as error bar in the figures.

3. Results and discussion

Fig. 2 shows the SEM images of the surface morphologies of the Pt particles prepared by pulsed electrodeposition under various t_l ranging from 1 to 0.01 s. The bright dots in the images refer to the deposited Pt particles. It is clear that the surface morphology of the deposited Pt particles on the ITO substrate is strongly dependent on the t_l. When the t_l is 1 s, the Pt particles on the ITO surface are featured with a flower-like morphology (Fig. 2a). The magnified image indicates that such flower-like Pt particle actually consists of a large number of nanosheets (Fig. 2b). When the t_l decreases to 0.5 s, dispersed Pt nanosheets are formed on the surface of ITO (Fig. 2c and d). As the t_l further reduces to 0.1 and 0.05 s, Pt particles with prickly surface are formed on the ITO substrate (Fig. 2e–h). When the t_l is 0.01 s, Pt particles are characterized by a spherical-like morphology with a smooth surface (Fig. 2i and j).

During the electrodeposition process, the mass transfer of Pt ions from the bulk solution through the diffusive layer toward the electrode (diffusion process) and the reduction reaction on the electrode (activation process) coexist [32]. For the pulsed electrodeposition in the present work, the reduction of Pt ions and the following nucleation and growth of Pt nuclei occur during the cathodic half-cycle of the pulsed electrodeposition when a low cathode potential of −1 V(MSE) is applied. Lower potential pulse duration t_l plays a key role in determining the competitive effects between the diffusion and activation processes, leading to different surface morphologies of the Pt deposits. During the cathodic half-cycle of the electrodeposition, Pt ions are consumed due to the reduction process while diffusion of Pt ions to the electrode compensates the depletion. When the Pt ion consumption rate is higher than the diffusion rate, a Pt ion depletion layer is formed, affecting the growth of Pt nuclei [20]. During the anodic half-cycle, the consumed Pt ions at the electrode surface are replenished. Thus, the anodic half-cycle would decrease the thickness or even eliminate the Pt depletion layer. This strongly facilitates the Pt ion transport,