Electrochimica Acta 129 (2014) 152–159

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Effect of Current Density on Electrochemical Shape Control of Pt Nanoparticles

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ARTICLE INFO

Article history:
Received 9 January 2014
Received in revised form 17 February 2014
Accepted 17 February 2014
Available online 3 March 2014

Keywords:
Galvanostatic electrolysis
Shape control
Pt nanoparticles
Catalyst
Polymer electrolyte fuel cell

ABSTRACT

Shape-controlled Pt nanoparticles were electrochemically prepared on a graphite plate by galvanostatic electrolysis using an electrolytic cell containing a graphite plate cathode and a Pt sheet anode. The galvanostatic electrolysis was performed in a 0.5 M HNO_3 solution at 50 °C, and cubic nanoparticles were obtained by appropriately controlling cathodic and anodic current densities only. An extremely small amount of Pt ions produced by oxidative dissolution of the Pt anode diffused to the graphite cathode through the electrolyte solution and were reduced to form Pt nanoparticles having a cubic structure. Balancing the reduction rate of Pt ions at the graphite cathode and the dissolution rate of the Pt anode significantly influenced the shape of deposited Pt nanoparticles.

1. Introduction

Pt-based nanoparticles are known to be highly active anode and cathode catalysts for polymer electrolyte fuel cells but face serious problems, such as scarce Pt reserves and high prices. The consumption of Pt is increasing, and reducing that consumption has become an urgent issue that has been extensively researched [1–21]. The preparation of Pt nanoparticles of higher dispersions and smaller sizes [1–6], which increases the specific surface area, and alloying of Pt with foreign metals, which causes electronic modification [7–21], has been investigated for improving the catalytic activity.

Shape control of Pt nanoparticles is another attractive method for realizing high catalytic activity. The surfaces of shape-controlled nanoparticles are often limited to specific planes. For example, Pt nanoparticles with cubic and tetrahedral structures are enclosed by (100) and (111) planes, respectively. It has been reported that catalytic activity depends strongly upon the crystal plane [22–27]. Markovic et al. found that the exchange current density for hydrogen evolution reaction and hydrogen oxidation reaction on Pt single crystals in sulfuric acid solution increases in the order $(111) < (100) < (110)$ [25]. In contrast, Housmans et al. reported that the maximum reactivity of methanol oxidation reaction on Pt single crystals in sulfuric and perchloric acid solutions increases in the order $(111) < (110) < (100)$ [27]. The catalytic activity of Pt nanoparticles can thus be enhanced by appropriately controlling the crystal plane or shape.

Recently, many studies on the preparation of shape-controlled Pt nanoparticles have been reported [28–37]. Chemical reduction methods employing stabilizers that adsorb to a specific plane to suppress crystal growth are often used for this purpose. For example, poly(*N*-vinyl-2-pyrrolidone) (PVP) preferentially adsorbs onto the Pt (111) plane to form tetrahedral nanoparticles, while sodium polyacrylate adsorbs onto the Pt (100) plane to form cubic nanoparticles [29]. Long et al. synthesized cubic, octahedral, tetrahedral, and polyhedral Pt nanoparticles by using PVP as a stabilizer, ethylene glycol as a reductant, and $AgNO_3$ as an additive [37]. However, these methods always require a reductant and a stabilizer, and the deposition rate cannot be controlled easily. In addition, it is hard to remove the stabilizers because of their strong adsorption, leading to degradation of catalytic activity [38]. Meanwhile, the unique electrochemical shape-control method without any stabilizers has been proposed by Zheng et al. [39]. They found that Pt nanospheres which were prepared on a glassy carbon by potential cycling in a 0.2 M H_2SO_4 solution containing 2 mM H_2PtCl_6 were converted to cubic nanoparticles by square-wave potential step treatment in a 0.1 M H_2SO_4 solution containing 30 mM ascorbic acid.

We have previously developed a new method for preparing Pt-based nanoparticles by using an electrochemical technique or double potential step electrodeposition in which no reductant

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http://dx.doi.org/10.1016/j.electacta.2014.02.105
0013-4686/

is used [21,40]. In this study, we report a new electrochemical preparation technique for cubic Pt nanoparticles on graphite electrode. Galvanostatic electrolysis using an electrolytic cell containing a graphite cathode and Pt anode in an acidic solution is the most appropriate way of achieving this. During the electrolysis, Pt ions are produced by oxidative dissolution of the Pt anode and are then reduced onto the graphite cathode to form shape-controlled Pt nanoparticles. The concentration of Pt ions in the acidic solution is low enough that the deposition of Pt is extremely slow, leading to the formation of cubic nanoparticles. In this system, both a stabilizer and a Pt precursor were not added in advance, and a shape control could be done in just one process. So this system seems to be more effective way than other previous methods. Here, we examined the growth process of cubic Pt nanoparticles during galvanostatic electrolysis in detail and determined the conditions for the formation of cubic nanoparticles.

2. Experimental

Pt nanoparticles were prepared on a graphite plate (10 mm × 30 mm × 3 mm) cathode by galvanostatic electrolysis using a Pt sheet (20 mm × 30 mm × 0.1 mm) or a graphite plate (20 mm × 30 mm × 3 mm) electrode as the anode. The distance between the cathode and anode was kept at 2 cm. An Ag/AgCl electrode was used as the reference electrode in all experiments. The Pt nanoparticles were prepared using a one-compartment cell (Fig. 1(a)) or a two-compartment cell (Fig. 1(b)) separated by an anion-exchange membrane (Selemion (AHO), AGC Engineering). In the two-compartment cell, graphite, Pt, and Ag/AgCl electrodes were placed in one compartment (compartment A) and a Pt electrode acting as a counter electrode to both the graphite and Pt electrodes was placed in the other compartment (compartment B). Two galvanostats were used for separately controlling both cathodic and anodic current densities. The cathodic current was applied between the graphite electrode in the compartment A and the Pt electrode in the compartment B, while the anodic current was applied between the Pt electrode in the compartment A and the same Pt electrode in the compartment B.

Galvanostatic electrolysis to deposit Pt nanoparticles on the graphite plate cathode was performed in a 0.5 M HNO_3 solution at 50 °C. Before the electrolysis, the Pt anode was electrochemically polished by repeatedly sweeping the potential between -0.21 and 0.94 V versus Ag/AgCl.

The surface structure of Pt nanoparticles deposited on the graphite cathodes was characterized by cyclic voltammetry and Cu-stripping voltammetry. Cyclic voltammograms (CVs) were recorded in the potential range of between -0.21 and 0.64 V in an N_2-saturated 0.1 M H_2SO_4 solution at 30 °C using a sweep rate of 100 mV s^{-1}. Before recording a Cu-stripping voltammogram, underpotential deposition (UPD) was performed on the Pt nanoparticle surface to form Cu adatoms by holding the cathode potential at 0.06 V for 2 min in an N_2-saturated 0.1 M H_2SO_4 solution containing 0.2 mM $CuSO_4$ at 30 °C and then sweeping the cathode potential from 0.06 to 0.64 V at a sweep rate of 100 mV s^{-1}. For reference, Cu-stripping voltammetry for polycrystalline Pt was also examined in the above condition.

The surface morphology of deposited Pt nanoparticles was observed using a field-emission scanning electron microscope (FE-SEM, Hitachi S-4800). Elemental analysis of the Pt nanoparticles was conducted by energy dispersive X-ray spectroscopy (EDX, AMETEK GENESISXM2). The concentration of Pt ions anodically dissolved in the electrolyte solution was analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Thermo Scientific X series II)

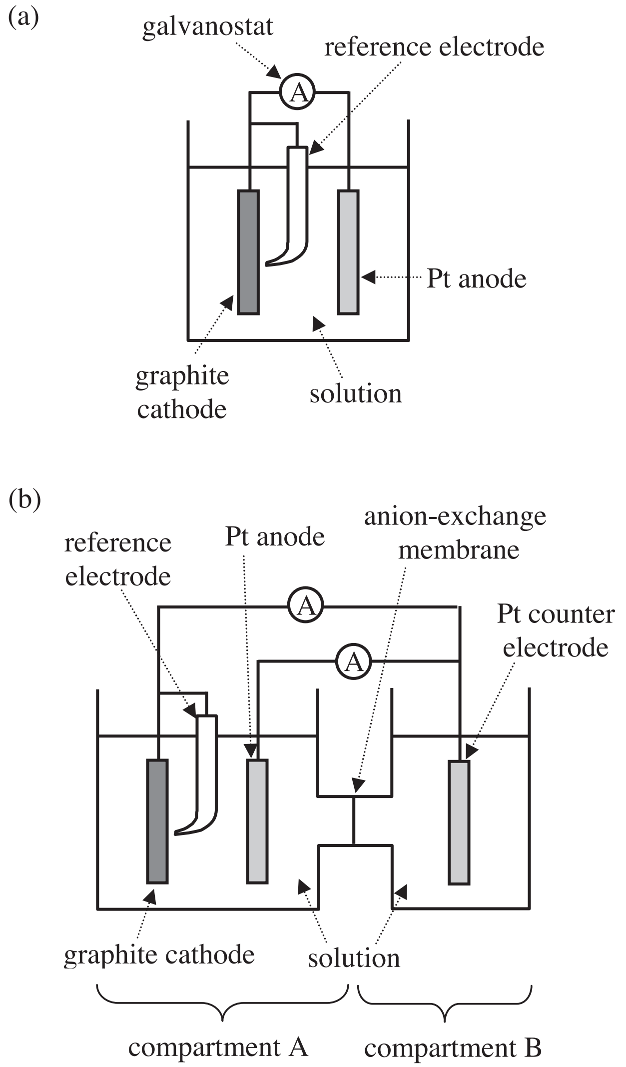

Fig. 1. Schematic drawings of (a) one-compartment and (b) two-compartment cells.

3. Results and discussion

3.1. Preparation of the cubic Pt nanoparticles by galvanostatic electrolysis

The cathode potential can be influenced by the kind of anode and electrolyte because reduction reactions such as Pt deposition, hydrogen evolution and/or nitrate reduction occur at the cathode. The reduction reactions were qualitatively related to the cathode potential. Fig. 2 shows the time series of the potential of the graphite cathode during galvanostatic electrolysis at a cathodic current density of 100 mA cm^{-2} and anodic current density of 50 mA cm^{-2} when using a one-compartment cell containing a 0.5 M HNO_3 or 0.5 M H_2SO_4 solution (50 °C) for 12 h with the Pt sheet or graphite plate used as the anode. In each case, the cathode potential was around -1.0 V at the beginning of the electrolysis and hydrogen evolved on the graphite cathode surface. The cathodic potential then shifted in the positive direction as time elapsed, finally reaching a constant value. When the graphite anode was used, the steady potential of the graphite cathode was around -0.65 V in nitric acid and around -0.75 V in sulfuric acid. In the nitric acid solution, the electroreduction of NO_3^- can occur with hydrogen evolution because the electrode potential is negative enough to reduce NO_3^- to NH_3 and N_2. The gas generated