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Synthesis of platinum nanoclusters and electrochemical investigation of their stability

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HIGHLIGHTS

- Investigated electrochemical coarsening in Pt nanoclusters.
- Studied the effect of the initial particle size distribution on growth kinetics.
- Narrow particle size distribution minimizes thermodynamic driving force for growth.
- Narrower the initial catalyst size distribution, the greater is their stability.

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ABSTRACT

Platinum nanoclusters were synthesized using two methods: (a) ascorbic acid reduction of K_2PtCl_4, (b) an H_2PtCl_6 polyol process. Both processes yield clusters of platinum consisting of nanoparticles with a narrow size distribution. Experiments were conducted using platinum nanoclusters as the working electrode and bulk platinum wire as the counter electrode, both supported on inert, electronically conducting substrates. The electrodes were immersed in a $PtCl_4$ + dimethyl sulfoxide electrolyte solution. The spacing between the electrodes was maintained at 1 mm or 6 mm. Electrical potential was measured across the two electrodes as a function of time. The samples (scraped off the nano-electrode) were examined using transmission electron microscopy (TEM). Experimental data show significantly lower kinetics of particle growth for the nanoclustered, uniformly sized particles as compared to commercially available carbon-supported platinum catalysts.

1. Introduction

The use of nanoparticles for catalytic applications has grown significantly over the last few decades, with particular emphasis on platinum. In many applications, however, the particles grow in size leading to a loss of catalytic activity. In several cases, the degradation kinetics are not fully understood. The principal objective of this work was to investigate the mechanism or mechanisms of the growth of nanoclustered platinum particles immersed in a liquid containing a dissolved Pt salt. Investigation of the growth of nanoparticles in a nanocluster also should allow elucidation of the role of coupled transport and the role of adjacent liquid on transport kinetics. One of the applications of Pt and Pt–alloy nanoparticles as a catalyst is in proton exchange membrane fuel cells (PEMFC). Some of the known modes of catalyst degradation in PEMFC are: (a) catalyst particle detachment from the support, (b) agglomeration/sintering, (c) Ostwald ripening, and (d) transport and precipitation into the membrane [1–12]. While many researchers have investigated these degradation mechanisms, few have addressed the effect of the initial particle size distribution on the kinetics of particle growth. An exception to this is a recent study by Popescu et al. who investigated the effect of initial particle size distribution of size-selected gold atomic clusters supported on carbon on the kinetics of growth when aged in air [13]. To the authors' knowledge, no such studies in any medium on platinum nanoparticles have been reported.

Many commercially available Pt or Pt alloy catalysts are ~1–6 nm in diameter and dispersed on a high surface area carbon support. In Ostwald ripening and agglomeration/sintering (Fig. 1), the driving force for growth is directly related to the reduction in surface energy accompanying particle growth. While many catalysts are metallic, such as platinum, in several electrochemical devices the medium in which the catalyst particles are submerged is almost always a nonmetallic liquid. Thus, the transport of Pt during growth involves the transport of ions (e.g. Pt^{2+} and/or Pt^{4+}) through the medium and a parallel (coupled) transport of electrons through the support which

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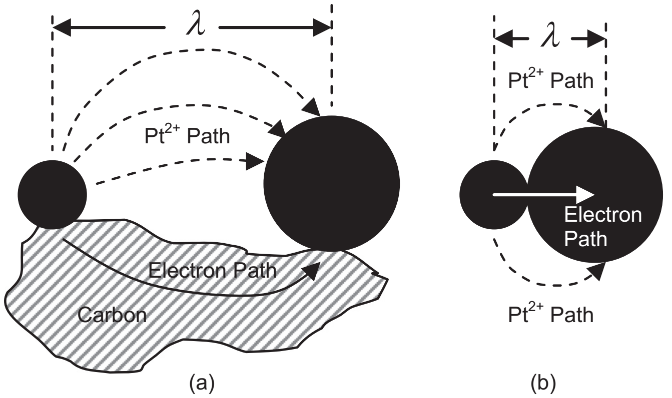

Fig. 1. Mechanism of particle growth in PEMFC by: (a) Ostwald ripening, (b) agglomeration/sintering. Both occur by a coupled transport of Pt^{2+} (and/or Pt^{4+}) ions through ionomer/aqueous media and electron transport through the electron conductor (or through direct contact). Net Pt transport occurs from smaller particles to larger particles.

is usually an electronic conductor such as carbon [14]. The net transport of Pt thus necessitates a coupled transport of Pt ions (Pt^{2+} and/or Pt^{4+}) through ionomer/aqueous medium and of electrons through the carbon support [14]. For particles that are immersed in a liquid medium and are also in physical contact, coupled transport involves the transport of Pt^{2+}/Pt^{4+} through the liquid and electron transfer through direct particle to particle contact. It is important to note that in most cases in which the temperature is low (e.g. room temperature), even for metallic nanoparticles in direct contact negligible transport occurs by a solid state mechanism (such as surface diffusion or bulk diffusion) due to the very low surface or bulk diffusion coefficients compared to ionic diffusion coefficients in liquids. For example, at room temperature the diffusion coefficient of Pt^{2+}/Pt^{4+} in liquid media is $\sim 10^{-6}$ cm^2 s^{-1}, while the solid state surface diffusion coefficient of Pt measured at room temperature is only on the order of 10^{-19} cm^2 s^{-1}, or some 13 orders of magnitude lower [15].

In this work, platinum nanoclusters were synthesized to study the kinetics of particle growth in an ion-conducting medium involving a coupled transport. The driving force for growth is related to differences in the chemical potentials of adjacent particles and can be given by the Gibbs–Thomson equation, according to which the smaller the particle size the higher is the chemical potential [16]. Typically, the size variation among the individual Pt particles provides a sufficient chemical potential difference and is the driving force for Ostwald ripening/particle coarsening. In the case of nanoclustered platinum catalyst particles, the size variation in the nanoparticles residing on the surface of the nanoclusters is expected to provide the driving force for their growth. If the particle size distribution is narrow, the driving force will be small, and this should lead to a lowering of the kinetics of particle growth.

Two processes were used for the synthesis of nanoclustered platinum particles; an ascorbic acid reduction process and a polyol process [17,18]. Both processes are fairly simple to use and lead to platinum nanoclusters composed of nanoparticles roughly 3–5 nm in diameter. However, the polyol process produces a very noticeable layer of platinum on the substrate (many nanoclusters form chains), while the ascorbic acid reduction process tends to yield individual nanoclusters that are evenly distributed. Two different types of substrates were used upon which platinum nanoclusters were deposited. These substrates with platinum nanoclusters served as the working electrode. A platinum wire wrapped around another identical substrate served as the counter electrode. The experimental procedure, results, and discussion are presented in what follows.

2. Experimental procedure

2.1. Materials

K_2PtCl_4 (99.9%), $PtCl_4$ (99.99%), and dimethyl sulfoxide (DMSO) (99.9%) were obtained from Alfa Aesar. L-ascorbic acid and H_2PtCl_6 were obtained from Sigma Aldrich. Indium tin oxide (ITO) coated glass slides (surface resistance 70–100 Ω sq^{-1}, 25 mm × 25 mm) and glassy carbon plates (100 mm × 100 mm × 1 mm) were purchased from Sigma Aldrich and Alfa Aesar, respectively. Ethylene glycol was purchased from Fisher Scientific. The ITO-coated glass was cut into 6 mm × 6 mm pieces and the glassy carbon plates were cut into sizes of 50 mm × 10 mm, 50 mm × 2 mm, and 10 mm × 10 mm. Prior to use, the substrates were cleaned in acetone, ethanol, pure water and dried in N_2 gas. Bulk platinum wires used in the counter electrode were purchased from Alfa Aesar (0.5 mm diameter, annealed, 99.95% and 0.025 mm diameter, 99.95%). De-ionized water was used in all processing.

2.2. Ascorbic acid reduction process

A similar synthesis procedure as reported by Chang et al. was used in the present work [17]. All substrates were cleaned using the procedure described earlier. Pt nanoclusters were deposited using aqueous solutions of K_2PtCl_4 of various concentrations. Also, the time of deposition was varied over a wide range. The concentrations of K_2PtCl_4 in the solutions used were 10 mM, 15 mM, 20 mM, 40 mM, 60 mM, 80 mM, and 500 mM. The deposition process was conducted for 1 min, 5 min, 15 min, 30 min, 60 min, 90 min, and 120 min. While many conditions were used for synthesis, mainly to identify optimum conditions, most of the experiments were conducted only on a few selected samples. The procedure used for the synthesis was as follows: First 1 ml of the solution of the desired concentration of K_2PtCl_4 was added to 36 ml of de-ionized water. Then the cleaned substrate was submerged into the solution. Next 2.0 ml of 100 mM ascorbic acid was added to the solution containing the substrate and maintained in the solution for the various times mentioned above. All depositions were carried out at room temperature. The samples were removed and rinsed in pure water several times and dried in N_2 gas. Characterization by FEI-SEM (FEI NanoNova), TEM (Tecnai F20 TEM/STEM/AFM), and electrochemical measurements were conducted on some of the prepared samples.

2.3. Polyol process

A similar synthesis procedure as reported by Sun et al. was used [18]. All substrates were cleaned using the procedure described earlier. A solution was prepared by dissolving 33 mg of H_2PtCl_6 in 4 ml of ethylene glycol ($\sim$20 mM) while stirring for 5 min. The substrates were placed on a hotplate at 180 °C. Once the substrates reached 180 °C, the ethylene glycol solution was added drop-wise to the substrate until covered and was maintained for 5 min. After 5 min, a platinum nanocluster film had formed and all other products had evaporated. The samples were cooled to room temperature, rinsed with water, and dried in N_2 gas. Characterization by FEI–SEM (FEI NanoNova), TEM (Tecnai F20 TEM/STEM/AFM), and electrochemical measurements were conducted on some of the prepared samples.

2.4. Electrochemical measurements

A schematic of the cell used for electrochemical measurements is shown in Fig. 2. A 0.1 M $PtCl_4$ in DMSO electrolyte solution was used in all experiments. The working electrode was the deposited nanoclustered platinum on a substrate (glassy carbon or ITO-coated