

CHARACTERIZATION AND SYNTHESIS OF PLATINUM NANOPARTICLES FOR THE ELECTROCHEMICAL OXYGEN REDUCTION REACTION

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ABSTRACT

Pt metallic nanoparticles have been synthesized by the polyol method and stabilized with poly(vinylpyrrolidone) (PVP) at higher temperatures (130 °C). The structure of the particles has been determined using transmission electron microscopy and high-angle annular dark field (HAADF). The combination of these experimental techniques allowed the characterization of the structure and the determination of the distribution of the platinum nanoparticles. The electrochemical behavior of synthesized platinum nanoparticles (2-4 nm) was investigated toward oxygen reduction reaction by cyclic voltammetry in 0.5 M H₂SO₄. Experiments were carried out through synthesized solution and performed using a standard three-electrode cell configuration employing a gold wire counter electrode and an H⁺/H₂ reference electrode. The synthesized electrocatalyst, in comparison with polycrystalline Pt, showed a variation of the catalytic activity towards oxygen reduction.

Keywords: platinum metallic nanoparticles, polyol method, electrocatalyst, oxygen reduction reaction

INTRODUCTION

Metallic nanoparticles are of great interest because of the modification of properties observed due to size effects, modifying the catalytic, electronic, and optical properties of the monometallic nanoparticles. Metallic nanoparticles are of great interest because of the modification of properties observed due to size effects, modifying the catalytic, electronic, and optical properties of the monometallic nanoparticles. A colloidal method of synthesis has been proposed to obtain metallic nanoparticles in this work; the polyol method has been reported to produce small nanoparticles as the final product, easily changing composition and surface modifiers. This technique does not require an additional reducing agent since the solvent by itself reduces the metallic species. However, besides the

stoichiometry and order of addition of reagents in the synthesis process, one of the most important parameters in the preparation is the temperature. Modifications in temperature influence the reaction by changing the stabilization of the nanoparticles of Pt formed and the surface modifiers, e.g., PVP, and the nucleation rate of the reduced metallic atoms. A novel approach to characterize this kind of particles is based on the use of HAADF technique, in a high resolution transmission electron microscope (HRTEM), which allowed us the observation of the elements due to atomic number, densities, or the presence of strain fields due to differences in lattice parameters, structure, the presence of surfactants or any other surface modifier besides the size of the particle.

One of the most challenging problems in synthesis is the controlled generation of monodispersed nanoparticles with size variance so small. The realization of advanced, inexpensive catalyst materials is one of the most pressing priorities being pursued by fuel cells researchers. But in spite of intensive work on non-noble metal catalysts in recent years, platinum is still considered one of the best electrocatalyst for low temperature reactions in a H₂/O₂ fuel cell.

Oxygen reaction is one of the most important electrochemical reactions since it is the cathodic reaction in electrochemical energy conversions, as fuel cell systems and metal-air batteries. It is also frequently the cathodic reaction in the corrosion of metals, such as steel in the presence of the air, as well as reaction involved in water electrolysis and other industrial electrolytic processes such as chloralkali electrolysis. The particles dispersion of Pt and surface structure is fundamental aspect to consider when one or several intermediates might adsorb on the electrode surface. Effect of the metal particle size on the catalytic properties of supported metal catalysts electrodes have not yet been revealed clearly. The difficulty in such study must be caused mainly by the complexity of the structure of supported metal catalysts electrodes [11, 12].

In this work the electrochemical behavior of synthesized platinum monometallic nanoparticles was investigated toward oxygen reduction reaction by cyclic voltammetry.

EXPERIMENTAL SECTION

The basic polyol method was followed to obtain platinum metallic nanoparticles passivated with poly(vinylpyrrolidone) (PVP). Hexachloroplatinic (IV) acid (H_2PtCl_6) hydrate (99.99%), and poly (N-vinyl-2-pyrrolidone) (PVP-K30, MW = 40000) were purchased from Sigma Aldrich, and 1,2-ethylenediol (99.95%) was purchased from Fischer Chemicals; all the materials were used without any further treatment.

A 0.4 g sample of Poly (N-vinyl-2-pyrrolidone) (PVP) was dissolved in 50 mL of 1,2-ethylenediol (EG) under vigorous stirring, heating in reflux, until the desired temperature was reached (working temperatures ranged from 100 to 190 °C in increments of 10 °C). For the Pt metallic nanoparticles, a 0.1 mM EG-solution of the metal precursor was added to the EG-PVP solution, with continuous agitation for 3 h in reflux. When preparing the Pt metallic nanoparticles, the following criterion was used: after complete dissolution of PVP in EG, 2 mL of an EG solution of H_2PtCl_6 (0.05 M) was added to the EG-PVP solution in a period of 1 h. The reaction was carried out for 3 h at constant temperature. For this work the Pt nanoparticles presented the smaller average size for a synthesis performed at 130 °C.

The particles were determined to be Pt monometallic from energy-dispersive spectroscopy (EDS) analysis.

Samples for the electron microscopy analysis were prepared over carbon coated copper TEM grids. HAADF images were taken with a JEOL 2010F microscope in the STEM mode, with the use of a HAADF detector with collection angles from 50 mrad to 110 mrad. The Pt monometallic system synthesized at 130 °C was analyzed.

For the electrochemical measurements, the inks were prepared from aqueous dispersions of electrocatalysts (20 wt % Pt/C and Pt_{NP}) using ultrapure water (Milli-Q water) using a concentration of 2 g L^{-1} in unsupported electrocatalysts [13]. Each sample was ultrasonically homogenized for 30 min. A 6.5 μL aliquot of this aqueous dispersion was deposited onto polished glassy carbon plates (GC of 1 mm thick, 50 – 50 mm^2) from Alfa Aesar. One drop of this dispersion was deposited and centered on the GC, after it was dried in the oven at 60 °C for 30 min. Finally 1 μL of a mixture of Nafion solution (5% Aldrich) and water (50:50%) were added onto the electrocatalyst film and dried at 60 °C for 15 min. The solvent was then evaporated.

For electrochemical cell, electrochemical experiments were carried out with a CHI-900 electrochemical workstation (CH Instruments, Austin, TX), employing a three-electrode cell with a glassy carbon plate working electrode where the material was supported, a gold wire

counter electrode and H^+/H reference electrode. Mainly, cyclic voltammetry was used in electrochemical measurements of the catalysts based on powders.

The solutions were prepared from concentrated H_2SO_4 (Fisher Scientific). The electrochemical experiments were carried out at 25° C in either Ar-purged or O_2 saturated with a scan rate of 100 mV/ s.

RESULTS AND DISCUSSION

Following the polyol method with ethylene glycol as solvent-reductor, it was possible to obtain monometallic platinum nanoparticles with narrow size distributions in systems with small particles (2-4 nm) and different structures depending on the temperature of reaction. The structure of a platinum nanoparticle is cubic, face centered has can be seen from Figure 1. The monometallic synthesis of Pt nanoparticles by itself showed a distinctive morphology, which does not depend on the temperature of reaction in this case.

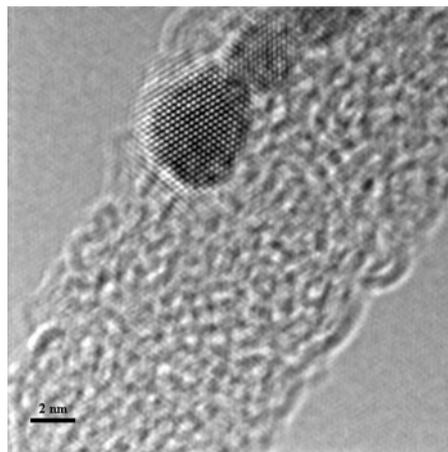
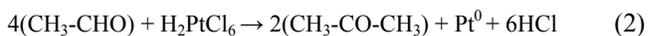


Figure 1. A microscopy image by HRTEM, shows a platinum nanoparticle synthesized at 130 °C.

Reaction proceeds in general as an oxidation of the ethylene glycol reducing the metallic precursor to its zero-valence state [14, 15]



This is the reaction involved in the reduction of Pt^{4+} to Pt^0 .

In the presence of a surface modifier, the reaction changes depending on the ability of the metal to coordinate with it, as in the case of PVP where the metallic precursor could coordinate with the oxygen of the pyrrolidone group,

when the particles are in the nanometer size range, while when they are in the micrometer size range the coordination is mainly with the nitrogen, as reported by F. Bonet et al. [15, 16]

The synthesis of monometallic platinum nanoparticles yielded narrow size distributions centered at 3.06 nm. The temperature in the synthesis of these nanoparticles seemed to not have an important effect on neither the size nor the morphology, as observed by Bonet et al. [17] The Pt particles showed a tendency toward spherical shapes. Figure 2a shows a HAADF image of the particle distribution, and 2b presents the size distribution typical from one sample of this system. It is seen in these images that Pt nanoparticles are very small and have a narrow size distribution, and they remain attached to PVP even after purification of the system, as indicated by the dimensional stability observed by TEM.

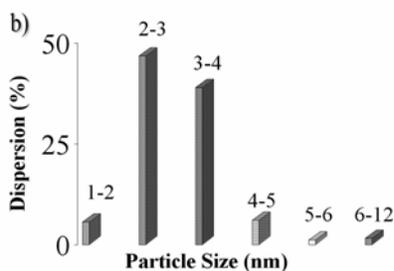
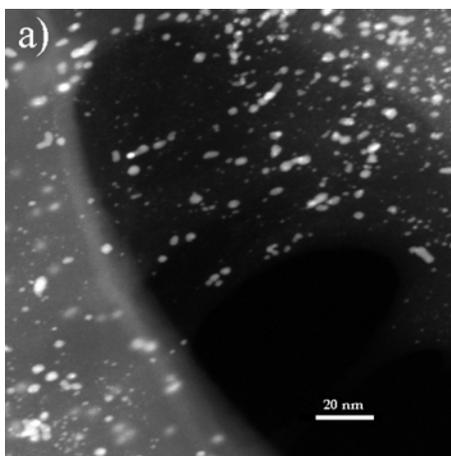


Figure 2 (a) HAADF image of Pt nanoparticles synthesized at 130 °C. Here we can observe a well dispersed sample with a narrow size distribution. (b) Particle size distribution. The average size observed is 3.06 nm.

As can be seen in Figure 2, there is a marked tendency to form well-separated monometallic nanoparticles at the temperatures of this regime. The analysis of HAADF images of these samples show only particles with

homogeneous contrasts. There were no identifiable changes in intensity that would indicate the presence of more than one type of element forming the particles. This hypothesis was supported with the results obtained with EDS.

With respect to Pt monometallic nanoparticles, Pt did not show important variations as the temperature was increased, during the synthesis process, neither in size nor in structure.

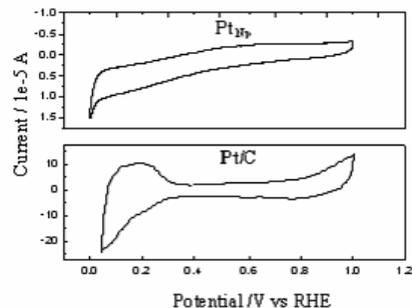


Figure 3. Cyclic voltammetric curves (100 mVs^{-1}) for Pt_{Np} and Pt/C electrodes, respectively as a function of the applied electrode potential in Ar-purged 0.5 M H_2SO_4 electrolyte.

For the electrochemical measurements, Figure 3 shows representative cyclic voltammetric curves of current-potential in the acid electrolyte in Ar-purged 0.5 M H_2SO_4 electrolyte, recorded on Platinum Nanoparticles (Pt_{Np}) and Pt/C electrocatalyst from 0.05 V to 1.0 Potential V versus RHE. The potential interval between 0.05 and 1.0 V shows the well-known electrochemical finger print of platinum Pt/C. In comparison to this typical response, the surface reactions on Pt_{Np} are strongly attenuated at both potential ends the corresponding electrochemical reactions (proton reduction and water oxidation). It suggests a surface modification since the synthesis method. Therefore, the use of the hydrogen zone to quantify the free platinum surface sites is difficult.

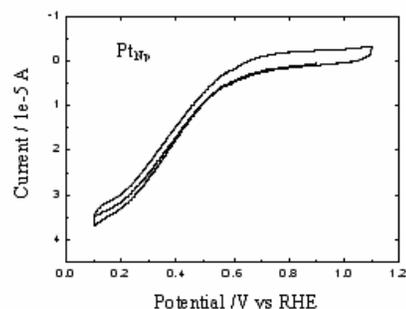


Figure 4. Current-potential curves of Pt_{Np} in O_2 saturated 0.5 M H_2SO_4 (Scan rate = 0.5 mV/s).

Figure 4 presents cathodic potential scans (5mV s^{-1}) starting at 1.1 V in the oxygen-saturated 0.5M H_2SO_4 solution. The cathodic current due to O_2 reduction for Pt_{NP} electrocatalyst is considerable. This polarization curve presents the potential shift on the kinetic zone due to slow electron transference. Furthermore, the generated cathodic current with the synthesized catalyst was from $3.7 \text{ e}^{-5} \text{ A}$.

CONCLUSION

The synthesized Pt_{NP} electrocatalyst, in comparison with polycrystalline Pt, shows a variation in its electrosorption properties and by consequence in the catalytic activity towards oxygen reduction that is evident through the change of electrochemically active surface area and in the oxygen reduction activity expressed through the specific current densities.

Comparison of the change in electrosorption properties with the amount of metal dissolve and TEM observations leads to the conclusion that the surface involved in chemisorption reactions consisted of a part of the atomic layers in all the Pt metallic nanoparticles used as electrocatalyst.

The target, in the near future, is to develop materials based essentially on non-noble metals; however this work was illustrative to explore.

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