



Size control of carbon-supported platinum nanoparticles made using polyol method for low temperature fuel cells



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HIGHLIGHTS

- The sizes of the Pt nanoparticles in the catalysts mainly depend on precursor initial concentration.
- The concentration of nanoparticles is fixed and independent of the precursor initial concentration.
- Between XRD and TEM a good correlation of crystallite sizes and mean diameter is observed.

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ABSTRACT

The aim of this work is to present the results of the synthesis of Pt nanoparticles using the modified polyol method, using carbon black powder Vulcan XC-72R as a support. Two different techniques were used to synthesize the catalysts: (a) fixing the initial concentration of the precursor (2 mM in H_2PtCl_6) while adding the required amount of support to obtain different nominal loads of platinum; (b) changing the initial concentration of the precursor to obtain altogether 10 wt% nominal load of platinum. Catalysts were characterized using X-ray diffraction, transmission electron microscopy and cyclic voltammetry. The particles obtained ranged in sizes between 2.2 and 6.2 nm. These sizes were controlled by the initial concentration of the precursor. It has been found that the concentration of nanoparticles formed during synthesis was the same regardless of (a) the initial concentration of the precursor and (b) the amount of carbon support. In order to explain experimental results a new and simple statistical and geometrical treatment is used.

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1. Introduction

Catalysts used in gas diffusion electrodes have become key materials in low temperature fuel cells. Catalysts based on platinum are used because of their high activity and stability (Adzic et al., 2007; Bagotsky, 2009; Zhang et al., 2005; Zhao et al., 2011). Synthesis of dispersed Pt supported catalysts has been widely used in electrodes developed for fuel cells (Oh et al., 2007; Senthil Kumar et al., 2010; Vengatesan et al., 2008). Black carbon materials have been used to improve electrical conductivity and dispersion of active material. Because of the requirements of electrical conductivity, the carbons used need to have a certain degree of graphitizing to lower its ohmic resistance. Fuel cell electrodes are to be economical and efficient, so the Pt load must

be minimized while maximizing the specific area. Different ways are typically used to achieve a reduction in the metal load: one of them is the control of the size of the nanoparticles used (Kinoshita, 1990; Shao et al., 2011) and the other is the formation of alloys, either skin or core-shell structure, by combination with other metals (Yano et al., 2007; Zhao et al., 2011).

The limiting step in low temperature fuel cells is the oxygen reduction reaction (ORR), one of the most important reactions in electrochemistry. ORR seems to depend on the size of the Pt nanoparticles (Bagotsky, 2009; Leontyev et al., 2011) but this is under debate (Nesselberger et al., 2011). Nevertheless, monodispersions of nanoparticles is required when we wish to study the effects of their diameters on the physical properties of catalysts.

Among the many methods of synthesis of catalysts (Bock et al., 2004; Liu et al., 2006; Oh et al., 2008; Yano et al., 2007), the method most widely used to generate colloidal suspensions of metals is the reduction of transition-metal salts in solution. In fact, this method is quite simple to implement. A wide range of reducing agents have been used to obtain colloidal materials:

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gases such as hydrogen or carbon monoxide, hydrides or salts such as sodium boron hydride or sodium citrate, or even oxidative solvents such as alcohols. The different reduction methods of the Pt precursors, which differ in the reduction agent used, are described in the literature. These include the formic acid method (Liu et al., 2006; Prabhuram et al., 2003, 2004; Zhou et al., 2003), impregnation method followed by reduction with hydrogen at high temperature (Liu et al., 2006) and microwave-assisted polyol (Chu et al., 2010) or polyol method (Chen and Xing, 2005).

In a series of papers Finke and co-workers, (Watzky and Finke, 1997; Besson et al., 2005; Watzky et al., 2008) present the first examples of nanoparticles that are suitable for in-depth mechanistic studies and show a way of monitoring the formation of nanoparticles in real time. According to these authors, the acting mechanism consists of four steps (double autocatalytic step mechanism):



As Finke et al. claim, one of the conditions for the synthesis of “near” mono-dispersed nanoparticles is the separation in time of the nucleation and growth steps. If all nuclei are initially formed with similar sizes and are uniformly distributed, they will statistically grow at the same rate since they are indistinguishable and surrounded by the same chemical environment. The term “near” is applied considering that the thermal fluctuations in the concentration of the precursor define the final diameter distribution. In this sense, materials that are “near” mono-dispersed are the ones that present higher specific areas: the ratio area/volume is inversely proportional to the diameter.

The formation mechanism of nanoparticles in this process is complex since it takes place in a heterogeneous phase and depends on both; the rate of reaction and the transport properties. The latter can vary with the degree of completion of the reaction. In addition, when a clear separation between nucleation and growth steps is not achieved, the grown particles may present a large diameter-dispersion and a low specific area.

In order to avoid agglomeration of nanoparticles (reactions iii and iv), protective agents of steric or electrostatic nature are used. Macromolecules such as polymers or oligomers are used to stabilize the colloid, (i.e. PVP in the case of polyol methods). The resulting adsorption of macromolecules onto the surfaces of the nanoparticles provides a protective layer against agglomeration by restricting the motion of the colloid in the space between the particles. This causes both a decrease in entropy and an increase in free energy (Roucoux et al., 2002). Nevertheless, the addition of macromolecules also influences the rates of reaction for nucleation and growth, e.g. viscosity of the environment is changed, and the diffusion coefficients of the involved species also change.

Electrostatic stabilization can be achieved using ionic solutions of compounds such as halides, polyoxoanions or carboxylates (Watzky and Finke, 1997; Watzky et al., 2008). The adsorption of these compounds and their related counter-ions onto the metallic surface create an electric double-layer around the particles generating electrostatic repulsion between them.

In the present paper the results obtained on the synthesis of Pt nanoparticles by the modified polyol method are discussed. The characterization of the catalysts is carried out by correlating the XRD, TEM and CV measurements. The results show that the

nanoparticle diameters were near-monodisperse with a Gaussian distribution. Their sizes were controlled by the initial concentration of the precursor, regardless of the Pt loading within certain limits. One of the conclusions of this work is that in the case of the synthesis of Pt nanoparticles through the polyol method, the concentration of nanoparticles in the solution after synthesis was constant independently of the initial concentration of the precursor. A new and simple statistical and geometrical treatment is presented in Appendix A which is used to explain the experimental results.

2. Experimental

2.1. Pt/C synthesis

The nanoparticles of Pt were prepared using the modified polyol method (Chen and Xing, 2005). The solvent and reducing agent was an ethylene glycol/water (volume ratio 3:1) solution. The catalysts were prepared with a protecting agent PVP to prevent the subsequent agglomeration of nanoparticles (reactions iii and iv). The support material in all cases was carbon black powder (Vulcan XC-72R, Cabot international) with area BET 250 m² g⁻¹. The platinum precursor was H₂PtCl₆.

The typical catalyst preparation involves dissolving the precursor in ethylene glycol/water solution and adding a predetermined amount of black carbon. The amount of precursor used was determined by the desired Pt mass loading in the catalyst, which is defined as the weight percentage of Pt in the catalyst consisting of Pt and carbon. The amount of PVP added to the solution was measured in relation to the mass of Pt using a molar ratio of PVP/Pt equal to 0.1 (referred to monomer unit of PVP). This proportion was calculated considering Chen and Xing's work (Chen and Xing, 2005) in which the authors demonstrate that the catalyst active surface area is high and can be maintained at a high level, even if the Pt loading reaches 35 wt%.

Reduction of the precursor was achieved through heating at a 2 °C min⁻¹ rate and keeping the polyol solution on reflux for an hour under continuous magnetic stirring. After the polyol solution was cooled-down to room temperature, the catalysts were filtered, washed with Milli-Q (Milipore) water 18.2 MΩ cm and dried in vacuum at 80 °C for 3 h. The synthesis of final catalysts (Pt+carbon) was done by two different ways:

- Taking c_p^i fixed at 2 mM and adding the required amount of support to obtain different Pt nominal loads, wt%, defined as:

$$\text{wt}\% = 100 \, m_{\text{Pt}} / (m_{\text{Pt}} + m_{\text{S}}).$$
- Changing the initial concentration of the precursor to obtain a total 10 wt% nominal Pt load. Measurements of wt% were done in duplicates by gravimetric method, approx. 0.1 g of sample, previously washed in distilled water and dried in a ceramic melting pot, tared with an analytical scale (± 0.01 mg). Samples were dried in an oven with high purity N₂ at 100 °C, cooled down and weighed again using the same scale. Samples were then calcinated in the same oven circulating clean air at 600 °C for 3 h (enough time to guarantee the total oxidation of the Carbon). Cooling was done turning off the oven and passing a current of pure N₂ until room temperature was attained. The melting pot containing the metal Pt was once again weighed. The wt% was calculated by difference.

2.2. Physical characterization

All samples were analyzed with an X-3000 Philips powder X-ray diffractometer using Co K α radiation. The crystallite sizes

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