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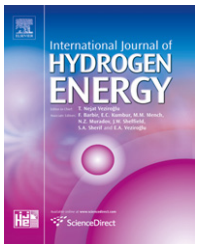

Synthesis and characterization of colloidal platinum nanoparticles for electrochemical applications

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ABSTRACT

Platinum colloidal nanoparticles were synthesized by chemical reduction of metallic salts in presence of poly (N-vinyl-2-pirrolidone) which served as a protecting agent. The preparation conditions for obtaining Pt nanoparticles were established by analyzing TEM and HRTEM images of the samples. Size of the synthesized Pt nanoparticles was in the range 2.5 to 8.5 nm depending on the molarity of $PtCl_4$ used to prepare the colloidal dispersion. The electrochemical characteristics of the Pt nanoparticles supported on carbon were investigated by analyzing their catalytic response to the oxygen reduction reaction (ORR). The reactivity of the prepared catalyst was comparable to that of the commercially available carbon supported Pt for the ORR. Catalytic parameters like charge transfer coefficient, Tafel constants and exchange current density were calculated for the prepared catalyst.

1. Introduction

The development of new nanostructured materials with optimal physicochemical characteristics for specific scientific and technological applications has necessarily promoted the use of chemical methods which can obtain materials with good control on particle size and distribution. Good quality colloidal nanoparticles are produced by thermal [1], photochemical [2], electrochemical [3] and chemical reduction methods [4–7].

The preparation of colloidal nanoparticles by chemical reduction has been recently investigated and this method has proved the feasibility to obtain well dispersed carbon supported catalyst [8,9]. The method is based on the reduction of the corresponding metallic ions in aqueous solution in presence of a stabilizer. Carbon supported nanostructured catalysts have recently been investigated in chemical and electrochemical systems to correlate their physicochemical properties like particle size, distribution, chemical composition, and the influence of structure on their catalytic performances [10–14]. There are many technical reports indicating the use and evaluation of metallic catalysts obtained by chemical methods in industrial applications due to their adequate catalytic activity and stable performance [15,16]. The growth of nanometric particles is achieved by the reduction of metallic ions in presence of different solvents

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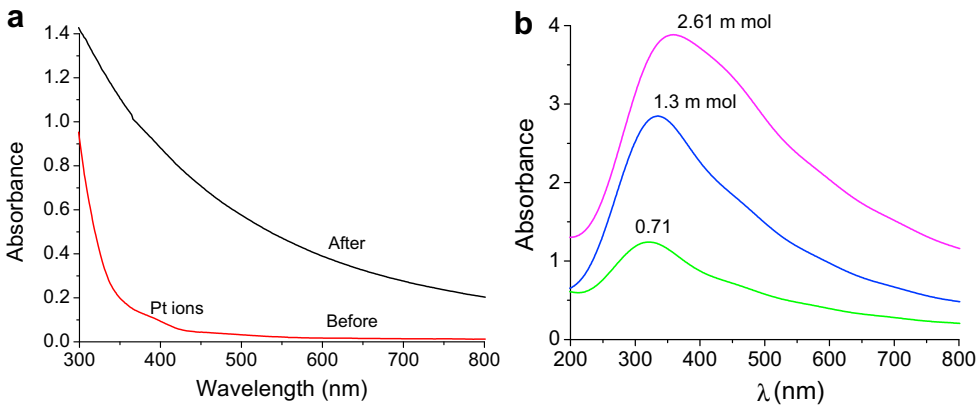

Fig. 1 – Optical absorption spectra of (a) colloidal dispersions of Pt before and after the reduction process; and (b) absorption spectra of the colloidal dispersions of Pt prepared at different precursor concentrations.

and organic materials as ligants or surfactants. Several factors like stabilizer, reducing agent and solvent have been modified to control the size of the particles. With the previously mentioned methods it is possible to control the size of the metallic particle but not the crystallographic orientation. Nevertheless, the synthesis of the nanoparticles with good dispersion is a first step followed by supporting these colloidal dispersions on carbon. Carbon supported Pt nanoparticles is one of the important components in the membrane electrode assembly (MEA) of proton exchange membrane (PEM) fuel cells. Pt is proven to be the best catalyst for both oxidation and reduction reactions, however high material cost is a major concern in the large scale production of MEAs. One way to overcome this is to use nano-sized catalyst, which can reduce the quantity of material due to the availability of large active surface area. We have prepared Pt nanoparticles by a wet chemical method and studied by TEM and optical absorption spectroscopy. In analytical chemistry, the color of the dispersed solution is important since it is related to the size of the particles which absorb the light [17,18]. TEM can provide indirect information of the atomic arrangements of the nanoparticles. The oxygen reduction rate of the prepared electrodes was studied by rotating disc electrochemical methods [19–22].

2. Synthesis and characterization of the monometallic Pt nanoparticles

For the preparation of colloidal dispersions of Pt nanoparticles, different amounts of platinum tetrachloride were dispersed in methanol (0.71, 1.3 and 2.61 m mol). 75 mg of poly (*N*-vinil-2-pirrolidone) (PVP) was added to 25 ml of the metal ion solution as the capping agent. A stable homogeneous dark brown colored colloidal dispersion was formed after adding $NaBH_4$ (1 ml of the 0.044 m mol solution).

A Shimadzu model UV1601 double beam spectrophotometer was used to measure the absorption spectra of the colloids in the range 300–800 nm. A typical absorption spectrum of a metal ion solution before and after the addition of reducing agent ($NaBH_4$) is presented in Fig. 1a. Absorption spectrum of the colloidal solutions prepared with different metal ion concentrations are presented in Fig. 1b. The absorption spectra prior to the addition of reducing agent show an absorption shoulder in the region 350–400 nm which is characteristic of the platinum ions [6,11].

3. Results and discussion

3.1. *UV–VIS absorption spectra*

The colloidal dispersions of platinum nanoparticles in presence of PVP after reduction do not exhibit any characteristic peak in their absorption spectrum (Fig. 1a), indicating the complete reduction of Pt ions to metallic atoms. The change in color of the solution from pale yellow to dark brown after the addition of reducing agent indicates the formation of nanometric particles. The changes in the absorption and in the color imply a change in the colloidal properties [23]. The increase in the absorbance towards shorter wavelengths (Fig. 1b) with the increase of metal ion concentration is in agreement with the previous reports [6,24].

3.2. *TEM analysis*

The size and shape of the platinum particles were determined from TEM analysis. For TEM study, a drop of colloidal sample was dispersed on a carbon coated microscopic grid and dried in vacuum. The average particle size was obtained by measuring the diameter of a sufficient number of particles and plotting their size distribution histogram. Typical TEM micrographs of the Pt nanoparticles with three different concentrations of the precursor solutions are shown in Fig. 2. Size distribution histograms of the corresponding nanoparticles are given beside their TEM micrographs (Fig. 2). From the histograms presented Fig. 2; the average size of the particles was estimated at 8.5, 4.5 and 2.7 nm for the precursor concentration of 2.61 m mol, 1.3 m mol and 0.71 m mol, respectively. The TEM images revealed the formation of Pt

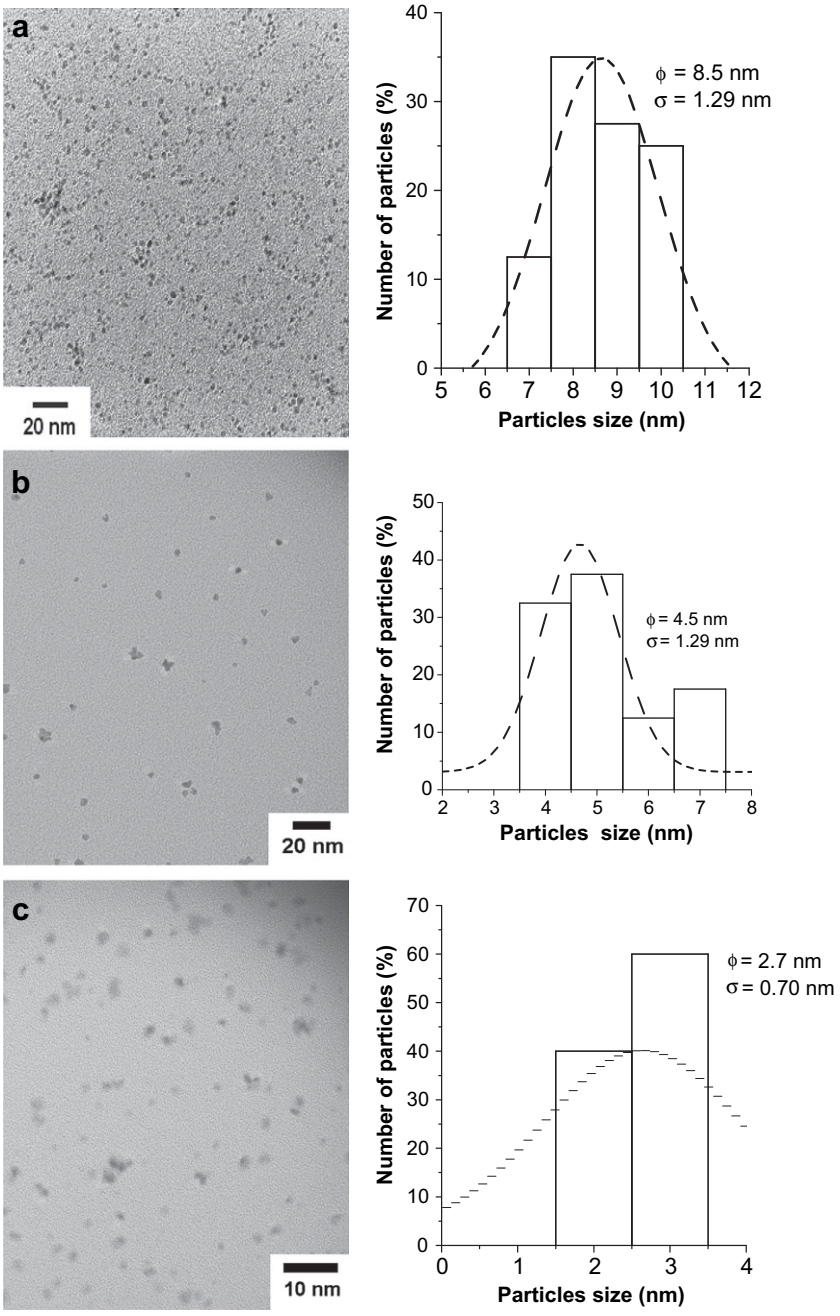

Fig. 2 – TEM micrograph of platinum particles with (a) 2.61 m mol of $PtCl_4$, (b) 1.3 m mol of $PtCl_4$, (c) 0.71 m mol of $PtCl_4$ in the reaction mixture. Corresponding particle size distribution histograms are presented alongside.

particles of spherical shape with increasing size on increasing the concentration of the precursor as reported in literature [25]. As can be seen from Fig. 2, the Pt nanoparticles prepared with higher concentrations of the metal precursor are partially agglomerated. This indicates that the amount of PVP should be increased with the increase of metal precursor in the reaction solution to obtain well dispersed particles. In order to determine the form and structure of the obtained nanoparticles, HREM analysis was carried out. Fig. 3 shows typical HREM image of the particles of about 2.5 nm sizes with almost perfect lattice planes of cubic fcc structure.

4. Electrochemical characterization

4.1. *Synthesis and preparation of electrodes*

The carbon supported Pt catalyst was prepared by mixing 2 mg of carbon in 0.3 ml of hydrogen peroxide and allowed to dry. Later 1 ml of the colloidal dispersion prepared with 2.61 m mol of $PtCl_4$ was added to this while continuing the drying process. The resulting powder was annealed for 20 minutes at 330 °C in N_2 atmosphere. Finally the baked powder was pulverized and

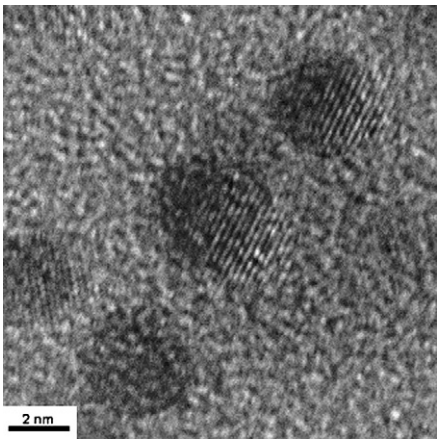

Fig. 3 – Typical high resolution TEM images of the Pt nanoparticles synthesized by wet chemical method. Crystallinity of the nanoparticles is clear from the well ordered lattice planes.

mixed with isopropanol and Nafion solution in an ultrasonic agitator. Five micro liter of the above ink was deposited onto the rotating disk electrode. Different electrodes were prepared with three sets of nanoparticles dispersions prepared with 2.61, 1.3 and 0.71 m mol $PtCl_4$.

4.2. *Cyclic voltamperometry*

Cyclic voltammetry measurements were carried out at a sweeping speed of 30 mVs^{-1} in inert atmosphere of nitrogen. The electrolyte in all cases was 0.5 M H_2SO_4, and prior to the voltammetry measurements, the electrolyte was de-oxygenated by bubbling N_2 for 30 minutes. The cyclic voltammogram of the three electrodes are shown in Fig. 4. The peaks corresponding to the adsorption and desorption of hydrogen atoms as well as the region where monolayers of oxides are formed can be seen in Fig. 4. It was possible to observe the reversible hydrogen electrode performance associated to a metallic oxide, the H-adatoms adsorption and desorption are not observed symmetrically in the cyclic voltammetry for the Pt based catalysts supported on carbon, it was not proper to calculate specific areas from that mechanism and it is possible to assume that the process could be controlled by diffusion desorption processes in order to maintain similar charge capacity as function of cyclic scans. For simplicity, the specific surface areas were calculated from cathodic reactions.

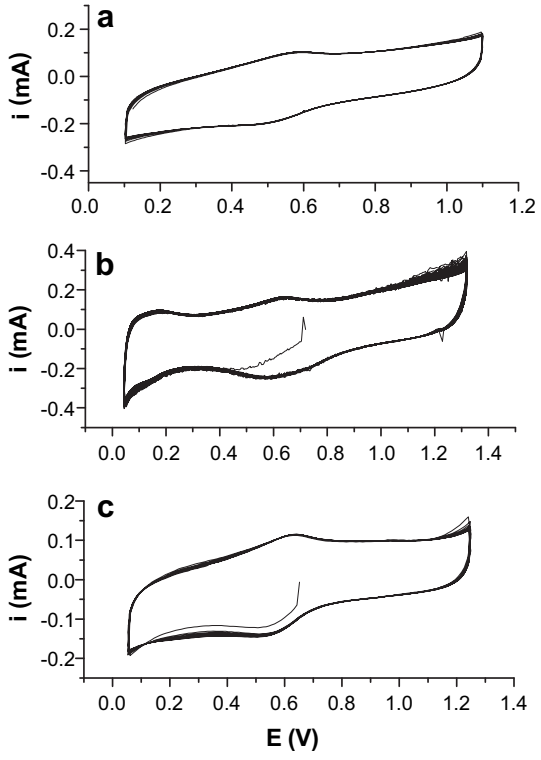

Fig. 4 – Cyclic voltammograms for the carbon supported platinum catalyst prepared with different amounts of $PtCl_4$: a) 0.71 m mol, b) 1.3 m mol and c) 2.61 m mol.

The oxide formation occurs between 0.4 and 1.2 V while the reduction starts approximately at 1.0 V. Takasu et al. found that the position of hydrogen adsorption/disorption peak and the oxygen reduction peak changes with the average size of the particles [26–32]. It should be noticed that the increase in size of the Pt particle is proportional to the molarity of the colloidal dispersion, and as the particle size increases, the oxygen reduction peak becomes well defined indicating that a change happens with the size of the particles in the electrode. This effect is more pronounced in Fig. 4b and c. There are different observations reported in literature in this respect; some reports say that the specific activity decreased and the slope of Tafel plot increased with the decrease in particle size [26–30], but some reports show different results [31,32]. Watanabe et al. discussed that the effect of the particle size is not truly dependant on the dimensions of the Pt crystallites but it is dependant on the inter-crystalline distance [32]. According to this hypothesis, the specific activity was also increased with the decrease in the size of the platinum particle when the separation of the crystals is less than 18 nm. On the other hand, Kinoshita et al. have observed that the specific activity diminishes steeply with the decrease in the size of the particles [27–30].

4.3. *Oxygen reduction reaction*

Fig. 5 shows hydrodynamic voltammograms for the ORR at the platinum working electrode in O_2 saturated 0.5 M H_2SO_4, at a sweeping rate of 5 mVs^{-1} and with rotation speed in the range of 100 rpm to 1800 rpm at of 25 °C. Fig. 5a and b shows the polarization curves obtained for the ORR for different catalyst concentrations, 0.71 m mol and 1.3 m mol $PtCl_4$ in the precursor solution respectively. An increase in current is observed as the rotation speed increases, until about 600 rpm, for higher rotation speeds the increase in current is not very significant. This type of behavior, where the current increases significantly until arriving to a certain rotational speed is attributed to processes of mixed control, is to say, convection and diffusion process, while the graphs for which the current is independent of the speed of rotation is attributed to the processes of activation [26]. The polarization curves obtained for the catalyst samples prepared with of 2.61 m mol $PtCl_4$ is shown in Fig. 5c. It can be observed

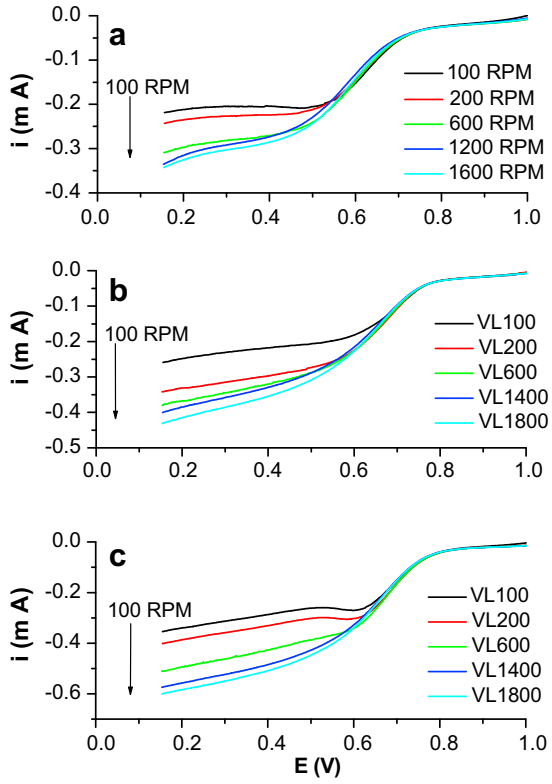

Fig. 5 – Polarization curve of oxygen reduction on the rotating disk electrode prepared with a) 0.71 m mol, b) 1.3 m mol, and c) 2.61 m mol of $PtCl_4$.

that the ORR potential shows a cathodic displacement and an increase in current. It can be noted that at high rotation speeds the polarization curves of oxygen reduction curves appear inclined, this phenomenon is associated with an irreversible process happened at the electrode when the catalyst is impregnated on the electrode [33]. The results of the calculations of the different electrochemical parameters of the Pt catalyst prepared with different molar concentrations of $PtCl_4$ in the precursor solution are shown in Tables 1–3.

The electrochemically active surface area was calculated in the kinetic region for the oxygen reduction reaction using the experimental Koutecky–Levich slope. The equation used for this calculation is:

$$A_{EA} = \frac{1}{0.2nFB_{K-L}\upsilon^{-1/6}C_{O_2}D_{O_2}^{2/3}} \quad (1)$$

where n is the number of electrons transferred ($n = 4$), F is Faraday constant ($F = 96485$ C/mol), B_{K-L} is the experimental Koutecky–Levich slope, υ is the kinematic viscosity ($\upsilon = 0.01$ cm^2/s), C_{O2} is the Oxygen concentration close to the electrode surface ($C_{02} = 1.1 \times 10^{-6}$ mol/cm^3), and D_{O2} is the oxygen diffusion coefficient ($D_{O2} = 1.4 \times 10^{-5}$ cm^2/s). The specific surface area for the three Pt based catalysts ((a) 2.61 m mol of $PtCl_4$, (b) 1.3 m mol of $PtCl_4$, (c) 0.71 m mol of $PtCl_4$) was estimated at 0.042, 0.066 and 0.0071 cm^2, respectively. The active surface area can also be determined from the UPD H-adatoms desorption peaks provided the particle size is below 2 nm [34]. However, in the present case the particle size is larger than 2 nm and hence we didn't adopt this method.

We have intended to associate the size of the platinum particles in the electrode with respect to the change in their electrochemical properties. From the tables it is possible to observe that the Tafel slope (b) is increased with the decrease in the size of the particle, similar observation was reported by Takasu and collaborators [26]. In the present case, the samples show an increase in the slope of Tafel and in the exchange current density as the speed of rotation of the EDR increases, while the coefficient of mass transfer shows a decrease in its value conforms to the increase in the number of revolutions per minute.

Table 1 – Electrochemical parameters of the sample prepared with 0.71 m mol of $PtCl_4$.

RPM	Tafel slope	i_o	n_α
100	0.207	0.000160	0.284
200	0.215	0.000192	0.274
400	0.216	0.000199	0.273
600	0.219	0.000215	0.269
800	0.226	0.000252	0.260
1000	0.228	0.000256	0.258
1200	0.243	0.000342	0.242
1400	0.244	0.000354	0.242
1600	0.244	0.000369	0.242
Average	0.226	0.000259	0.260

Table 2 – Electrochemical parameters of the sample prepared with 1.3 m mol of $PtCl_4$.

RPM	Tafel slope	i_o	n_α
100	0.178	0.000108	0.331
200	0.179	0.000114	0.328
400	0.183	0.000134	0.322
600	0.188	0.000148	0.314
800	0.188	0.000151	0.314
1000	0.193	0.000173	0.305
1200	0.197	0.000192	0.299
1400	0.198	0.000196	0.298
1800	0.198	0.000197	0.298
Average	0.189	0.000157	0.312

Table 3 – Electrochemical parameters of the sample prepared with 2.61 m mol of $PtCl_4$.

RPM	Tafel slope	i_o	n_α
100	0.166	0.000105	0.353
200	0.167	0.000116	0.352
400	0.168	0.000117	0.350
600	0.169	0.000122	0.349
800	0.169	0.000121	0.348
1000	0.172	0.000131	0.343
1200	0.173	0.000131	0.340
1400	0.173	0.000134	0.340
1600	0.174	0.000134	0.339
1800	0.174	0.000140	0.338
Average	0.170	0.000125	0.345

5. Conclusions

We have synthesized Pt nanoparticles with size in the range 2.5 to 8.5 nm. The electrochemical characteristics of the prepared Pt nanoparticles were investigated by analyzing the response of the nanostructured catalyst to the oxygen reduction reaction. The reactivity of our carbon supported catalyst was comparable to that of the commercially available carbon supported Pt for the oxygen reduction reaction. Catalytic parameters like charge transfer coefficient, Tafel constants and exchange current density were calculated for the prepared catalyst.

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