NAFION-STABILIZED PT NANOPARTICLES AND THE EFFECT OF PT DISTRIBUTION ON THE ELECTROCHEMICAL REDUCTION OF OXYGEN

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ABSTRACT

Nafion stabilized Pt sols was prepared by using methanol to reduce the precursor H2PtCl6. No other ingredient was used in the preparation and Pt nanoparticles of 2 -3 nm size were obtained. Platinum nanoparticles were found to form aggregates. The aggregate size and the stability of Pt sols could be changed by solvent treatment. This suggests that SO3$^-$ *functional groups of Nafion stabilized Pt nanoparticles and that the aggregates formed due to the formation of ionic clusters of Nafion. The electrochemical reduction of oxygen was examined with carbon supported Nafion-Pt catalysts of different aggregate size. At low overpotential, the kinetic rate was not changed by the aggregate size. At high overpotential region where mass-transfer limitation phenomenon was observed, the reaction rate increased with decreasing aggregate size. It indicates that smaller aggregates, i.e., the more even Pt distribution, are less subjected to mass-transfer limitation and could consequently provide better electrode performance.*

KEYWORDS*: Pt nanoparticles, Nafion, Solvent, Aggregate, Oxygen reduction.*

1.0 INTRODUCTION

Platinum nanoparticles are of interest for applications such as electrocatalysts (B.C. Sih *et. al.*, 2005; L. Niu *et. al.*, 2003;M.R. Khan *et. al.*, 2006), chemical sensors (E. Bakker *et. al.*, 2006; S. Hrapovic *et. al.*, 2004), electrochemical capacitors (C.-C. Hu *et. al.*, 2002) and protective coatings against corrosion (M.A. Malik *et. al.*, 1999). Both dry and wet processes have been utilized in preparing Pt nanoparticles. Among them, the sol-gel method is popular because through it, the size, shape, and dispersion of nanoparticles can be easily controlled. One important ingredient in sol-gel preparation is the stabilizing agent, which prevents nanoparticles from coalescing. The most used stabilizing agents are polymers with functional groups (T. Teranishi *et. al.*, 2000; CW Chen *et. al.*., 2000; P.J. Kulesza *et. al.*, 2004; K.V. Sarathy *et. al.*, 1997) which can provide both electrostatic stabilization and steric stabilization. However, removal of polymer stabilizers, usually by severe conditions such as high temperatures, is needed for applications in which polymers become detrimental. Consequently, the polymer stabilizing agent has to either be easily removable or result in no detrimental consequence.

Nafion® is the most popular perfluoroionomers used as polymer electrolytes for fuel cells (T. Herricks *et. al.*, 2004), electrolysis (P. Costamagna *et. al.*, 2001; Y.L. Chen *et. al.*, 1994), and catalysis (V.R. Sarsani *et. al.*, 2005). Nafion in solution form is used to prepare catalyst ink for preparing the membrane-electrode assembly (MEA) of fuel cells. The chemical structure of Nafion consists of polytetrafluoroethylene backbone and ether side chains with sulfonate groups at the ends. It can be used as a stabilizer for preparing nanoparticles and there will be no need to remove Nafion because its ion conductivity can be useful for fuel cell applications. Nafion-stabilized Pt sols for fuel cell applications may provide an improved ion-transfer interface and consequently better performance.

A few studies have reported the use of Nafion in solution as a stabilizer for preparing Pt nanoparticles (Z.Q. Tian *et. al.*, 2007; Z. Liu *et. al.*,2006; P-C. Lee *et. al.*, 2009). They all prepared nanoparticles at a pH of 8.5 or higher.Sarma *et. al.* reported Pt-Ru/C preparation using Nafion and methanol with metal precursors and carbon black at a pH of 11. None has described in details how Nafion or pH influenced the prepared Pt nanoparticles. In this study, we report the preparation of Pt nanoparticles using Nafion as the stabilizer without pH adjustment. Our results show that Pt particles of 2-5 nm were formed and the Pt particles formed aggregates. Furthermore, the aggregate size could be changed by treatment with selected solvent. This provides an opportunity to test how the Pt distribution may affect the electrochemical reactivity while the Pt particle size is not changed. The results of this study indicate that mass transfer limitation is more severe when the aggregate size becomes larger.

2.0 EXPERIMENTAL

2.1 Pt Sols Preparation

The preparation was performed using methanol as the reducing agent and Nafion as the stabilizing agent following a protocol reported earlier (C.-S. Lin *et. al.*, 2006). The temperature was controlled using a water bath. The required amount of Nafion (DuPont, 5 wt% solution) and H_2PtCl_6 (Alfa Aesar, 99.95% metals basis) aqueous solution were added to methanol (90 vol% in final solution) at 85 °C under reflux and constant stirring. The reaction was stopped by immersing the flask in an ice-water bath immediately after the solution turned black. Several solvents, namely, methanol, ethanol, *n*-propanol, and DMAc (dimethyl acetamide) were used to examine the solvent effect. To prepare the Nafion-Pt/C catalyst, the required amount of carbon black powder (Cabot, XC72) was added to Nafion-Pt sols, ultrasonicated for 30 min and then freeze-dried.

2.2 Pt Sols Characterization

UV–visible spectroscopy measurements were performed from 200 to 600 nm using a commercial spectrophotometer (Shimadzu UV-2550) at room temperature with a 1-cm optical length cuvette. Pt sols prepared as mentioned above were diluted by water to 0.1 mMPt before measurement. The absorbance intensity at 261 nm was used to gauge the persistence of $PtCl_6^{2-}$, while the Pt particle absorbance was monitored at 450 nm. The $PtCl_4^{2-}$ intermediate shows negligible absorption at 261 nm (A.J. McCaffery *et. al.*, 1968). Transmission electron microscopy (TEM) was performed using JEOL JEM-2000EXII operated at 100 kV. Specimens were prepared by dipping the 300-mesh carbon-coated copper grid into the sols twice, followed by drying at room temperature. Electrochemical reduction of oxygen was examined by using a rotating-disc electrode (RDE, Pine Instrument) and a potentiostat (CHI, 627). A one-compartment glass cell was used at room temperature for the electrochemical tests with 1 M H_2SO_4 as the electrolyte, Pt wire as the counter electrode and a reversible hydrogen reference electrode. The Nafion-Pt/C catalyst was loaded with 6 μg Pt onto a clean glassy carbon (GC, 5 mm diameter) electrode, then covered by 10μl of 0.05 wt % Nafion solution (diluted from 5 wt % DuPont solution). After N_2 (Sanfu, 99.995%) purge and cycling between 0.05 and 1.2 V until steady-state voltammetry was reached, O_2 (Sanfu, 99.98%) was introduced and the reduction current was recorded at different rotating speeds. All voltammetry was collected at a scan rate of 10 mV/s. The reported ORR currents were corrected by subtracting the background currents measured under N_2 at identical potential scan settings.

3.0 RESULTS AND DISCUSSION

All previous studies (Z.Q. Tian *et. al.*, 2007; Z. Liu *et. al.*, 2006; P-C. Lee *et. al.*, 2009) of Nafion-stabilized Pt sols preparation applied pH adjustment to 8.5 or higher. Our preparation used no pH adjustment and Nafion, methanol, Pt precursor, and water (as the solvent) were the only ingredients used. Figure 1(a) shows the UV-visible spectra during the preparation at a Pt/Nafion ratio of 1/0.11 (wt) and 85 °C. The characteristic peak of $PtCl_6^{2-}$ at 261 nm started decaying as the reaction proceeded.

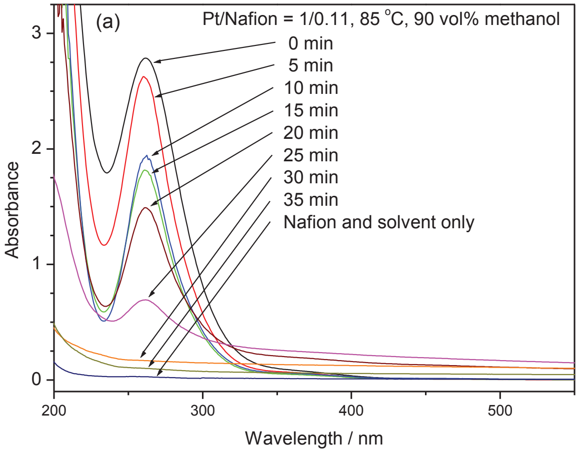

Figure 1 (a) UV-visible spectra during the preparation of Nafion-stabilized Pt sols

The solution changed in color from pale yellow to brown after an induction period of 15–17 min; thereafter, the change was rapid and resulted in a black-brown sol after 25 min of reflux time. The relative concentrations of $PtCl_6^{2-}$ and Pt sols were plotted against the reaction time, as shown in Figure 1(b), and a sharp rise inPt particle formation at 20–25 min was clearly observed. The absorbance of $PtCl_6^{2-}$ completely diminished after 30 min but the relative nanoparticle concentration decreased after 25 min when phase separation was observed.

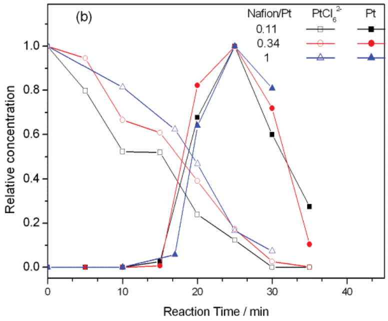

Figure 1 (b) The evolution of the normalized concentration of $PtCl_6^{2-}$ and Pt nanoparticles based on the maximum absorbance at 261 and 450 nm, respectively, during preparation at 85 °C.

Preparations with different Pt/Nafion ratios were examined, and the results are included in Figure 1(b). Increasing Nafion content resulted in a decreased rate in the reduction of Pt precursor; the maximum Pt particle concentration was observed at 25 min for all tests at 85 °C. When the reaction was carried out at 75 °C with a Pt/Nafion ratio of 1/0.11 (not shown), the maximum nanoparticle formation was observed at 40 min. The 40-min sol obtained at 75 °C was similar to the 25-minsol prepared at 85°C with the same Pt/Nafion ratio.

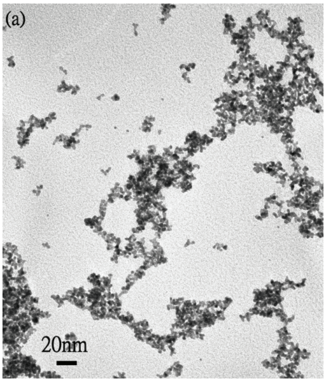

Figure 2 (a) TEM images of Pt sols prepared with Nafion stabilizer. The Pt sols preparation conditions: Pt/Nafion = 1/0.34; 90 vol% methanol; T = 85 °C.

The black solutions obtained by quenching at the maximum nanoparticles formation showed similar stability regardless of the Pt/Nafion ratio or the preparation temperature. They maintained the same status for hours at room temperature and signs of phase separation began after 8 h.

Figure 2(a) presents the TEM image of Pt nanoparticles prepared by this method. Without Nafion, methanol-reduced Pt nanoparticles gradually coated the surface of the flask during preparation. Nafion clearly acts as the stabilizer with its SO_3^- functional groups stabilizing Pt nanoparticles.

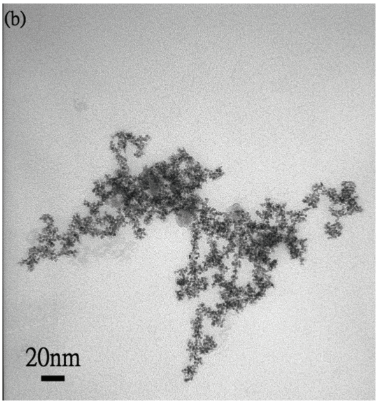

Figure 2 (b) TEM images of Pt sols diluted by DMAc solvent at a 1:1 (vol) ratio, The Pt sols preparation conditions: Pt/Nafion = 1/0.34; 90 vol% methanol; T = 85 °C.

Figure 2 shows that Pt particles with an average size of 2–3 nm formed aggregates. The average Pt particle size was consistent with a Pt-Pt coordination number of 7.2 analyzed from the sols at 25 min using EXAFS (extended X-ray absorption fine structure). The formation of aggregates can be expected as a consequence of SO_3^--stabilized Pt nanoparticles, because ionic clusters are known to form in Nafion solutions (H. Li, S. Schlick, 1995; S.-J. Lee *et. al.*, 2004; C.-H.Ma *et. al.*, 2009). Han *et. al.* 2006., reported the formation of Au nanoparticles in ionic clusters of Nafion and the particles showed similar aggregates. Nafion-stabilized Pt sols prepared at pH 8.5 or higher showed similar aggregate morphology (Z.Q. Tian *et. al.*, 2007; Z. Liu *et. al.*,2006; P-C. Lee *et. al.*, 2009).

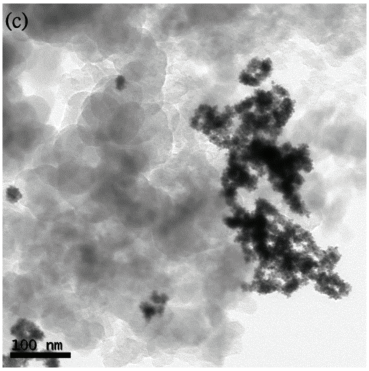

Figure 2 (c) TEM images of Pt sols mixing with carbon black to make 5% Pt/C, and (d) Pt/C after re-dispersing (c) in DMAc and then being freeze-dried. The Pt sols preparation conditions: Pt/Nafion = 1/0.34; 90 vol% methanol; T = 85 °C.

If Pt aggregates are formed via a mechanism similar to the ionic clusters formation in Nafion solution, the aggregate size can be changed by the solvent according to the studies of Nafion solution (S.-J. Lee *et. al.*, 2004; C.-H. Ma *et. al.*, 2009).

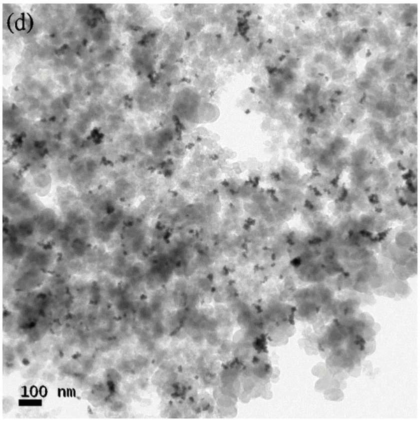

Figure 2 (d) TEM images of Pt/C after re-dispersing (c) in DMAc and then being freeze-dried. The Pt sols preparation conditions: Pt/Nafion = 1/0.34; 90 vol% methanol; T = 85 °C.

Therefore, the Nafion-Pt sols prepared in this study were diluted at 1:1 volume ratio with methanol, ethanol, propanol or DMAc.

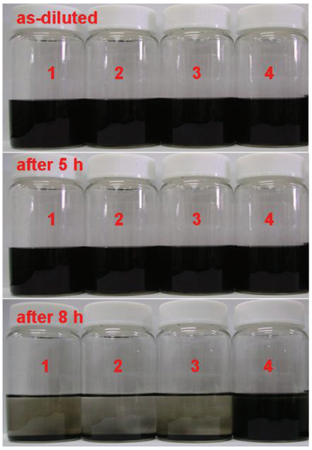

Figure 3 Effect of diluent solvents on the stability of Pt sol at a 1:1 (vol) ratio at room temperature; 1: methanol; 2: ethanol; 3 n-praopanol; 4: DMAc.

Figure 3 shows that the stability of the diluted sols was affected by the diluent solvent. All diluted sols maintained a homogeneous appearance for several hours at room temperature. After 8 h, all sols showed precipitation except for the one diluted with DMAc, which showed signs of precipitation after 40 h. The solubility parameter of DMAc is the closest to that of the backbone of Nafion, which consequently caused Nafion to be well dispersed in the solution (C.-H. Ma *et. al.*, 2009). The TEM image of Pt sols after dilution with DMAc is shown in Figure 2(b). The size of the Pt particles remained the same but the size of aggregates seemed smaller than that of the non-diluted sols, which may consequently improve the stability as the test results shown in Figure 3.

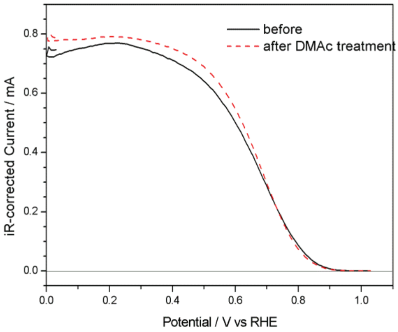

Figure 4 Effect of DMAc-treatment on the electrochemical reduction of oxygen over Nafion-Pt/C catalysts. The ORR currents were recorded under O_2 at 25 ^{o}C, 1600 rpm, and 10 mV s^{-1}.

The clustering of Pt nanoparticles through Nafion ionic clusters was further demonstrated by its mixing with carbon black powders. After mixing with carbon, sonification and freeze-drying, the obtained Nafion-Pt/C powders (at 5 wt% Pt loading) were examined by TEM as shown in Figure 2(c). The aggregate morphology of Nafion-stabilized Pt sols appeared in the vicinity or attached to the carbon surface. This indicates that the Pt aggregates was not changed by the presence of carbon black powders. Again, the aggregate size can be reduced by solvent treatment. The Nafion-Pt/C powders were dispersed in DMAc, sonificated and freeze-dry and the TEM image is shown in Figure 2(d). Not only the aggregate size decreased but also the Pt distribution became more even.

The electrochemical reduction of oxygen over the Nafion-Pt/C before and after DMAc treatment was tested using RDE (rotating disk electrode). The specific electrochemical surface area was not affected by the different aggregate size. The ORR currents at 1600 rpm are compared in Figure 4. At low overpotential, no significant difference was observed and it indicates that both catalysts had the same kinetic performance. At high overpotential where mass-transfer-limited reaction phenomenon was observed, the DMAc-treated Nafion-Pt/C catalyst had higher reaction rates than that without DMAc treatment. It indicates that smaller aggregates, i.e., more even Pt distribution, resulted in higher ORR current in the mass-transfer-limited regime. This can be explained based on the territory model proposed previously by Watanabe *et. al.* 1989. Smaller Pt aggregates can have a larger "territory" for receiving reactants for electrochemical reaction. Consequently, better electrode performance can be expected over electrodes of more uniform Pt distribution.

The results of this study indicate that Pt nanoparticles stabilized by Nafion form aggregates due to the ionic cluster formation of Nafion molecules. This phenomenon is found in solutions of Nafion or other polyelectrolytes (S-J. Lee *et. al.*, 2004, C.-H. Ma *et. al.*, 2009, P.A. Cirkel et.al, 1999, S. Jiang *et.al.*, 2001). Studies on the ionic clusters in Nafion and similar polyelectrolytes indicate that both the solubility parameter and ionic strength (dielectric property) of solvents can affect the distribution of polyelectrolyte molecules. For example, Lee *et. al.*, 2004, reported that the primary particle size of Nafion in methanol-water mixed solvent was around 2000 nm which was attributed to aggregation of through solvophobicperfluoro backbones. This size could be reduced to ~100 nm in the presence of NaCl. Heat-treatment temperature was noted to change the aggregate size of Nafion solution (Y. Kang *et. al.*, 2010). The aggregation of Nafion included catalyst inks affected the Pt distribution in the prepared electrodes of polymer electrolyte fuel cells and the aggregate size (in tens of μm range) could be reduced by the addition of NaOH. In this context, the distribution of Pt nanoparticles when prepared using polyelectrolyte stabilizers can be tuned by carefully adjusting the solvent environment. This may provide a method to control pattern formation from nanoparticles.

4.0 CONCLUSIONS

Platinum nanoparticles of 2–3 nm size could be prepared without pH adjustment by methanol reduction of hexachloroplatinic acid in the presence of Nafion. The rate of precursor reduction decreased with increasing Nafion/Pt ratio and with decreasing reaction temperature. Aggregates of Pt particles were found in the Nafion-Pt sols because of the stabilization by SO_3^- functional groups and the formation of SO_3^- ionic clusters. The aggregate size and the stability of Nafion-stabilized Pt sols can be changed by solvent treatment, which could change the size of ionic clusters. Smaller aggregates were found when the Nafion-stabilized Pt nanoparticles were diluted by DMAc than that diluted by methanol or ethanol. The Nafion-Pt/C catalyst obtained from mixing Pt sols with carbon powders showed similar aggregate morphology and the aggregate size can be reduced by a following treatment with DMAc. The solvent-induced reduction of aggregate size can be attributed to an improved solubility of the Nafion fluorocarbon backbone. The aggregate size of Nafion-Pt/C did not influence the electrochemical reduction rate of oxygen at low overpotential. The reaction rate at high overpotential region was found to increase with decreasing aggregate size. It indicates that electrodes with more even Pt distribution could experience less mass-transfer limitation.

5.0 ACKNOWLEDGEMENT

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