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Synthesis of Platinum Particles from H_2PtCl_6 with Hydrazine as Reducing Agent

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ABSTRACT

Platinum nanoparticles were obtained by chemical reduction of hexachloroplatinic acid (H_2PtCl_6) with hydrazine at various temperature and pH values. Reducing agent was chosen depending on the oxidation reactions and potential values of chemical materials used in the experiment. The aim of this study was to investigate the effects of temperature and pH on the structure of platinum particles. The morphology of platinum nanoparticles was investigated by JEOL, JSM-5410LX scanning electron microscope (SEM). Malvern Zetasizer 3000 HSA was used to determine size and zeta potential of platinum nanoparticles. The parameters that correspond to the production of minimum size platinum particles were obtained in addition the corresponding distribution of particle size were determined. These parameters were assumed to be the optimum conditions to obtain platinum nanoparticles from H_2PtCl_6 using hydrazine as reducing agent.

Key Words: *Pt nanoparticle, H_2PtCl_6, Hydrazine, Chemical reduction.*

1. INTRODUCTION

Proton exchange membrane fuel cells (PEMFC) are a promising system for the conversion of chemical energy directly into electrical energy with high efficiency and low pollutant emissions at low temperature (80ºC) [1]. At the hearth of PEMFCs, in both the anode and cathode, noble metal electrocatalysts supported on carbon black are used [2]. Platinum nanoparticles and its alloys with less noble elements such as ruthenium, molybdenum, other transition metals and tin are the most common catalysts for PEMFCs [3, 4]. Platinum provides enough catalytic activity particularly in this type of cells where an oxygen reduction reaction takes place in the presence of an acid electrolyte at low temperature (80-100ºC) [2]. It is well known that catalytic activity of metals is strongly dependent on shape, size and size distribution of the metal particles [5]. Smaller particle sizes are more desirable for PEMFC electrodes because the smaller the particles, the greater the particle surface area to reduce hydrogen. The mechanism of hydrogen electrooxidation on Pt in acid electrolytes is thought to proceed by rate-determining dissociative electrosorption of molecular hydrogen (Reaction 1) followed by facile electron transfer (Reaction 2)[6]:

$$H_2 + 2Pt \longleftrightarrow 2Pt–H_{ads} \quad (1)$$

$$2Pt–H_{ads} \longleftrightarrow 2Pt + 2H^+ + 2e^- \quad (2)$$

Hexachloroplatinic acid (H_2PtCl_6) and tetraammineplatinum (II) chloride $[Pt(NH_3)_4]Cl_2$ have been traditionally used as platinum precursors, and supported on different carbonaceous materials using a range of different methods [2, 7, 8]. These compounds have decomposition temperatures of 350 and 375ºC, respectively, and are highly soluble in water [7, 8]. Platinum chlorides $PtCl_2$ and $PtCl_4$, which are sometimes used as Pt precursors, are not soluble in water at room temperature and have decomposition temperatures of 550 and 370ºC, respectively [8].

Hydrazine was chosen as reducing agent depending on the oxidation reactions and the potential values of chemical materials used in the experiment. Platinum nanoparticles were obtained by reduction of $(NH_4)_2PtCl_6$ [7,8] and (H_2PtCl_6) [9,10,11] using water-in-oil microemulsion [10] or sodium di-2-ethylhexylsulfosuccinate (AOT) [11].

In recent works, Thompson et al. [12, 13] obtained platinum particles by impregnation and electrodeposition methods. They used $[Pt(NH_3)_4]Cl_2$ and $H_3[Pt(SO_3)_2OH]$ solution as Pt precursor. Kim et al.[14] obtained about 1,6-3,4 nm sized platinum particles using H_2PtCl_6 as Pt precursor. Verde et al. [8] obtained platinum particles smaller than 5 nm using $(NH_4)_2PtCl_6$ as Pt precursor. Wang et al. [15] prepared platinum nanoparticles on carbon nanotubes by hydrothermal method. There are almost no Pt

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aggregations. The shape of Pt grain is round. The size of the Pt nanoparticles is uniform, only 1-3 nm. Zhao et al.[16] obtained platinum nanoparticles sized between 6.89-9.5 nm by H_2PtCl_6 as Pt precursor. Wang et al. [5] synthesized Pt nanoparticles supported on carbon nanotubes by using ^{60}Co gamma irradiation in the presence of surfactants and a scavenger. The diameter of the Pt nanoparticles is about 2.5-4 nm. Ismagilov et al. [17] developed active catalysts for low Pt loading cathodes of PEMFC by surface tailoring of nanocarbon materials. Pt particles with size in the range of 3.2-5 nm are obtained by using H_2PtCl_6 as Pt precursor. Tan et al. [18] prepared platinum colloids through the reduction of H_2PtCl_6 by potassium bitartrate in the presence or absence of protective agents. Their investigations reveal that the sizes of platinum nanoparticles are sensitive to not only the concentration but also the type of the protective agents (stabilizers). The observed sizes of the nanoparticles decrease when the ratio of the concentration of the metal to the stabilizer is decreased. The extremely small Pt nanoclusters with a mean diameter of <1.5 nm are obtained when the concentration ratios of protective agents to metal ions are higher at a fixed concentration of metal ions.

Platinized titanium dioxide electrodes and particles are of particular importance due to their photocatalytic behavior in redox reactions such as photodecomposition of water and photocatalytic oxidation employed for biotechnological resource regeneration. Previously, it was shown that photocatalytic properties of metalized semiconductors are enhanced when pattern dimensions are reduced to micrometer size. To understand the photocatalytic behavior of micro-electrodes, one should consider charge transfer on the nm-scale at the TiO_2/Pt/electrolyte interface. Fabrication of nanometer scale Pt patterns is inevitable for such tasks [19]. Juodkazis et al. [19] reported enhancement in the spatial resolution of TiO_2 surface patterning by Pt up to sub-micrometer dimensions. Single particles of Pt as small as 100 nm could be grown. They showed the possibility of fabricating well-defined Pt patterns and free-standing single particles of sub-micrometer dimensions by photocatalytic reduction of $PtCl_4^{2-}$.

The occurrence of superconductivity in compacted platinum powders is an interesting phenomenon since bulk platinum, in contrast, has not been found to superconduct even at the lowest accessible temperatures of solid matter ($T \approx 1.5 \mu K$). The superconducting transition temperature and critical magnetic field observed in compacted Pt powder samples with sub-micrometer grain size are as high as 20 mK and 18 mT and thus more than one order of magnitude larger than for those with larger (micrometer) grain size. Superconductivity of compacted platinum powders was previously reported for two different commercially available high purity platinum powders with average grain sizes in the micrometer range. The sub-micrometer samples exhibit strong lattice strain and significantly smaller Debye temperatures compared to bulk platinum [20]. Schindler et al. [20] extended their studies to platinum powders with average grain sizes in the sub-micrometer range ($300 \geq d \geq 100$ nm) [20].

In this paper, the synthesis of platinum nanoparticles by chemical reduction of H_2PtCl_6 with hydrazine is reported. Due to their widespread application as catalysts, metals precipitated from aqueous solutions continue to be a thoroughly investigated subject. The precipitation of metals from aqueous or non-aqueous solutions typically requires the chemical reduction of a metal cation [21]. H_2PtCl_6 was chosen as Pt precursor due to the ease of its synthesis, high water solubility and relatively low decomposition temperature [8]. The aim of this study was to investigate effects of temperature and pH on the structure of platinum by using hydrazine as the reducing agent. In all experiments, deionized water was used as solvent and any other surfactant was not included to the solution. The morphology of platinum nanoparticles was investigated by JEOL, JSM-5410LX scanning electron microscope (SEM). Malvern Zetasizer 3000 HSA was also used to determine the size and the zeta potential of platinum nanoparticles.

2. MATERIALS AND METHODS

2.1. Synthesis of Platinum Particles

Platinum nanoparticles were obtained by chemical reduction of H_2PtCl_6 (Sigma-Aldrich, ~%38Pt) with hydrazine (Sigma-Aldrich, 35 wt. % in H_2O). The temperature was controlled using a water bath (Julabo, Ultratemp FP35-HC). 250 mg H_2PtCl_6 was dissolved in deionized water. The solution was stirred by magnetic stirrer (IKA® RH-KT/C) during the experiment. The reduction of the metal ions was accomplished by adding hydrazine solution as reducing agent. Platinum precipitate was separated by centrifuge (Nüve®, NF 615) at 3000 rpm for 5 minutes. The precipitate formed by the metallic nanoparticles was washed several times [22] with deionized water and acetone, then put in acetone as a suspension. Then, the acetone and water in liquid phase was vaporized in an oven at 110 ºC. Experiments were repeated at various temperatures and pH values. The parameters that correspond to the production of minimum size platinum particles were obtained in addition the corresponding distribution of particle size were determined. These parameters were assumed to be the optimum conditions to obtain platinum nanoparticles from H_2PtCl_6 using hydrazine as reducing agent.

2.2. Zeta Potential Measurement and Particle Size Analysis

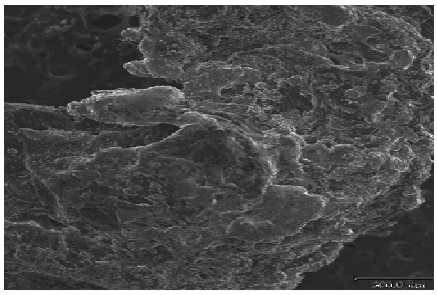
Malvern Zetasizer 3000 HSA was also used to determine size and zeta potential of platinum nanoparticles. This instrument allows the measurement of particle size distributions in the range 2 nm to 3 μm and can also be used to measure the distribution of zeta potentials for dispersed

particles in a similar size range. The zeta potential is determined by measuring the electrophoretic particle velocity in an electrical field. During the particle movement the diffuse layer is shorn off, hence the particle obtains a charge due to the loss of the counter ions in the diffuse layer. This potential at the plane of shear is called the zeta potential. As this electric potential approaches zero, particles tend to aggregate.

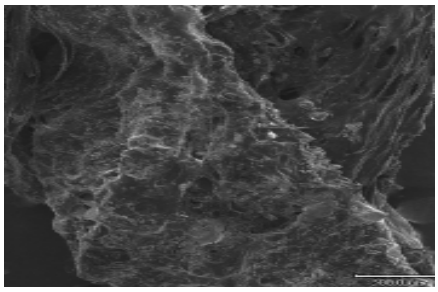
3. RESULTS AND DISCUSSION

3.1. Morphology

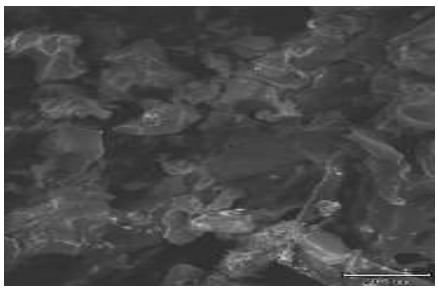
SEM micrographs of the platinum particles obtained from 25ºC, 40ºC and 50ºC temperatures were shown in Figure 1-3, respectively. As can be seen from Figure1, no characteristic platinum structure was observed until pH=10. Increasing the temperature and pH values has affected the structure, size and uniform distribution of platinum particles. It was observed that the morphological distribution changes remarkably for particles obtained at high temperature and high pH values compared to particles obtained at lower temperature and lower pH values. Cubic crystal structure of platinum particles can be seen from Figure 2-3.



(a)

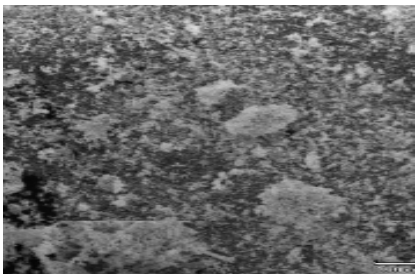


(b)

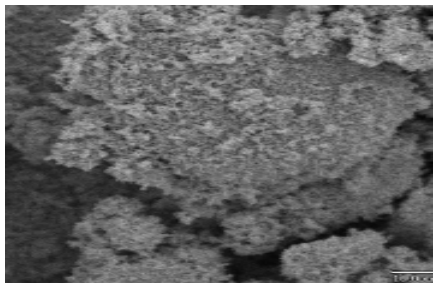


(c)

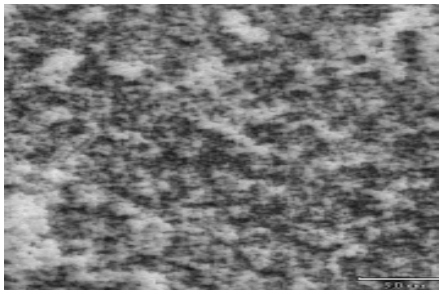
Figure 1. SEM micrographs at 25ºC: (a) pH=4, (b) pH=7, (c) pH=10.



(a)

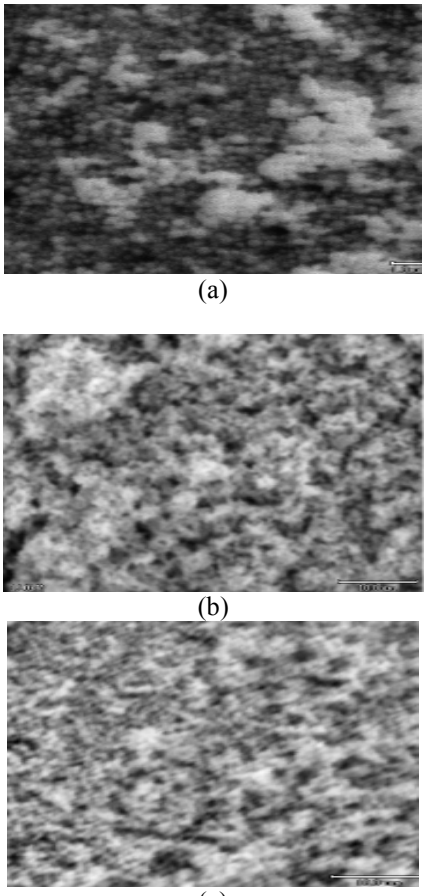


(b)



(c)

Figure 2. SEM micrographs at 40ºC: (a) pH=4, (b) pH=7, (c) pH=10.



(a) (b) (c)

Figure 3. SEM micrographs at 50ºC: (a) pH=4, (b) pH=7, (c) pH=10.

3.2. Particle Size and Zeta Potential

The particle size and zeta potential distributions obtained by random counting from the Malvern Zetasizer 3000 HAVE are presented in Table 1, 2, respectively. The minimum particle size (293 nm) was obtained at 40˚C temperature and pH=7. Similar size particles were obtained at various pH values at constant temperature of 40˚C; and also similar size particles were obtained at various temperatures at constant pH value of pH=10. It was observed that particle size was stable at 40˚C for changing pH values and also stable at pH=10 during changing temperature.

Table 1. The average particle size of platinum obtained at various temperature and pH values.

Particle Size (nm)		**T=25˚C**	**T=40˚C**	**T=50˚C**
pH=4	**Pt+Water**	1174	318	1235
pH=7	**Pt+Water**	2778	293	361
pH=10	**Pt+Water**	557	302	639

Table 2. The average zeta potential of platinum particles obtained at various temperature and pH values.

Zeta Potential Analysis (mV)		**T=25˚C**	**T=40˚C**	**T=50˚C**
pH=4	**Pt +Water**	-14.5	-43.8	-29.4
pH=7	**Pt +Water**	-20.7	-50.8	-55.7
pH=10	**Pt +Water**	-78.1	-45.4	-52.4

Zeta potential measurement gives an idea of the surface charge associated with the particles. The particle charge is one of the factors determining the physical stability of emulsions and suspensions. If all the particles in suspension have a large negative or positive zeta potential then they will tend to repel each other and there is no tendency to flocculate. However, if the particles have low zeta potential values then there is no force to prevent the particles from coming together and flocculating. The general dividing line between stable and unstable suspensions is generally taken at either +30mV or -30mV. Particles with zeta potentials more positive than +30mV or more negative than -30mV are normally considered stable. As can be seen from SEM micrographs and zeta potentials, there is no stability on platinum particles obtained at 25ºC temperature until pH = 10. For decreasing of particle size, the absolute value of zeta potential increases.

Figure 4. showed that particle size was stable and very similar to each other for all pH values at 40ºC temperature. At 40ºC temperature, particle size was apparently not influenced by changing pH. Figure 5. showed that particle size decreased by increasing temperature until 40ºC temperature, after this value, particle size increased. All experiments were performed open to atmosphere and hydrazine is a very volatile solution. Due to decreasing of hydrazine concentration by volatilizing, particle size increased by increasing temperature after 40ºC temperature. Because of these reasons, experiments were not performed at higher temperatures.

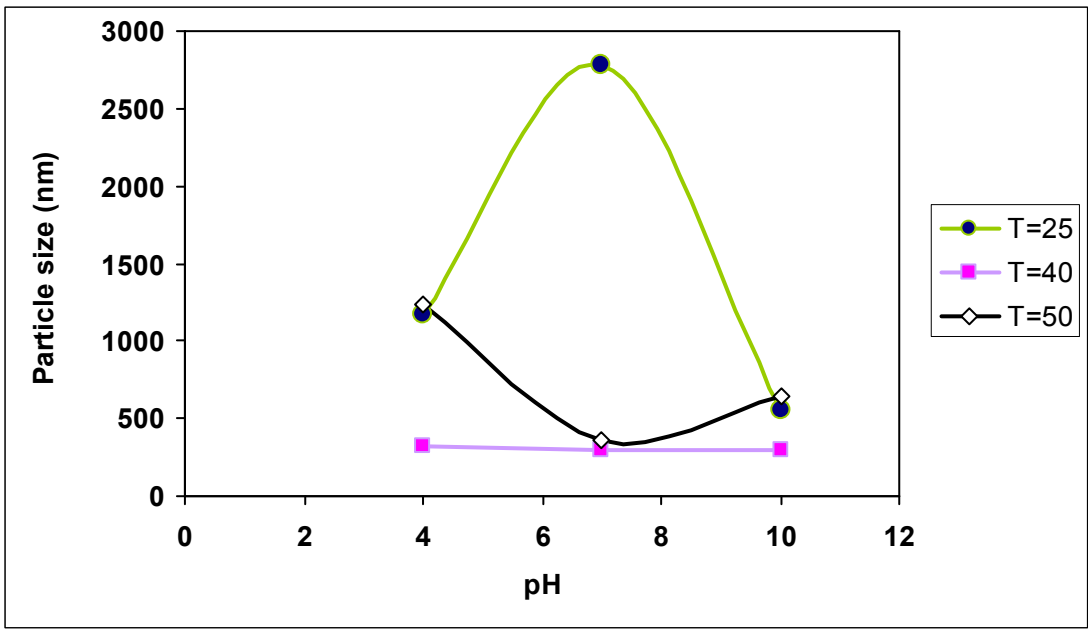


Figure 4. Particle size-pH curves.

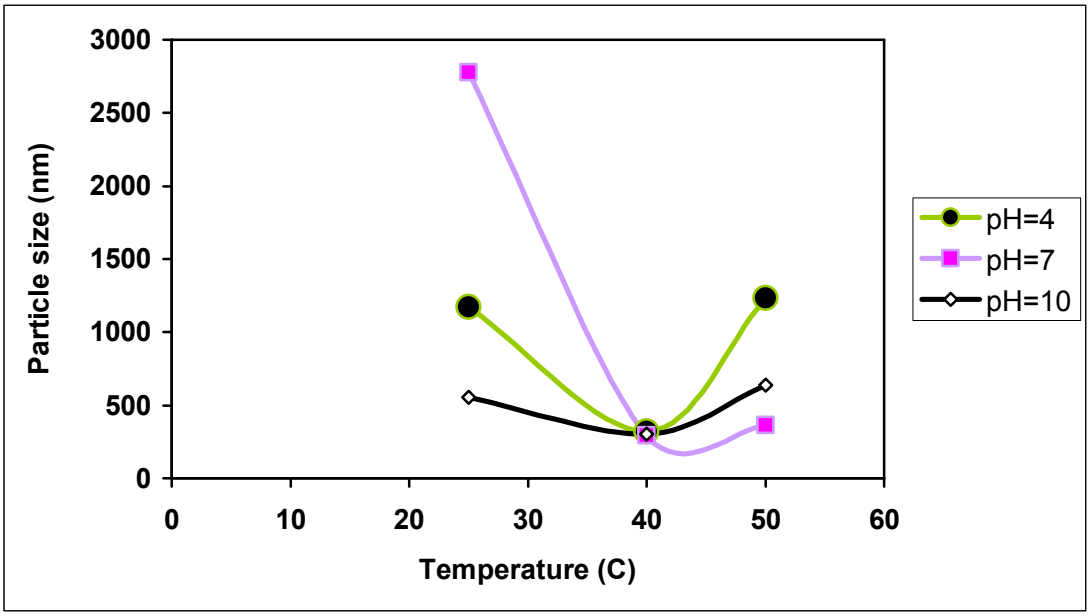


Figure 5. Particle size-temperature curves.

As can be seen from Figure 5, particle size visibly decreased by increasing pH value. During reduction reaction of hydrazine, concentration of H^+ ions increased. At higher pH values, concentration of OH^- ions increased. Due to reacting H^+ ions with OH^- ions, forward rate of reaction increased and the equilibrium shifted to the right.

$$H_2PtCl_6.6H_2O + N_2H_5OH \rightarrow Pt + N_2 + 7H_2O + 6HCl \quad (3)$$

Acceleration of reaction interrupts particle growth rates and smaller platinum particles are obtained at higher pH values.

4. CONCLUSION

The effects of reducing agents, pH, temperature and concentration on particle size of platinum were investigated. It was shown that 302 nm particle size and relatively homogenous size distribution could be obtained from experiment performed at 40ºC temperature and pH=10 value. The relative optimum conditions were obtained at 40ºC temperature and pH=10 for platinum particles formation from H_2PtCl_6 by using hydrazine as reducing agent. The average platinum particle size decreased with increasing temperature and increasing pH values. The reaction rate was accelerated by increasing temperature and pH value. It is conjectured that the acceleration of reaction interrupts particle growing and smaller platinum particles are obtained at higher temperature and pH values. All experiments were performed open to atmosphere. At temperatures higher than 40ºC, particle size began to increase possibly due to volatilizing of hydrazine. Because of decreasing of hydrazine concentration by volatilizing, experiments were not performed at temperatures higher than 50ºC. Hydrazine concentration was calculated analytically from the measurement of the hexachloroplatinic acid concentration. Hydrazine was used as the reducing agent as the N_2 gas, formed during hydrazine's reduction reaction, is an inert gas which does not interact with platinum particles.

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