Preparation of the vulcan XC-72R-supported Pt nanoparticles for the hydrogen evolution reaction in PEM water electrolysers

Huy Du Nguyen¹, T Thuy Luyen Nguyen¹, Khac Manh Nguyen¹, Thuc Huy Ha¹ and Quoc Hien Nguyen²

¹ University of Science, Vietnam National University in Ho Chi Minh City, 227 Nguyen Van Cu Street, Ho Chi Minh City, Vietnam
² Research and Development Center for Radiation Technology, Vietnam Atomic Energy Commission, 202A, Street 11, Linh Xuan Ward, Thu Duc District, Ho Chi Minh City, Vietnam

E-mail: hien7240238@yahoo.com

Received 14 January 2015
Accepted for publication 26 January 2015
Published 20 February 2015

Abstract
Pt nanoparticles on vulcan XC-72R support (Pt/vulcan XC-72R) were prepared by the impregnation–reduction method. The Pt content, the morphological properties and the electrochemical catalysis of the Pt/vulcan XC 72R materials have been investigated by ICP-OES analysis, FESEM, TEM, and cyclic voltammetry. These materials were then used as catalyst for hydrogen evolution reaction at the cathode of proton exchange membrane (PEM) water electrolysers. The best catalyst was Pt/vulcan XC-72R prepared by the impregnation–reduction method which is conducted in two reducing steps with the reductants of sodium borohydride and ethylene glycol, respectively. The current density of PEM water electrolysers reached 1.0 A cm⁻² when applying a voltage of 2.0 V at 25 °C.

Keywords: proton-exchange membrane, platinum nanoparticles, carbon support, impregnation-reduction method

Classification numbers: 4.02, 6.00

1. Introduction
Proton-exchange membrane (PEM) water electrolysis can contribute to the development of a hydrogen infrastructure network [1–3]. Hydrogen can be produced efficiently using electricity from renewable energy sources such as solar and wind [1, 2, 4]. In conventional PEM water electrolysers, precious metals have been used as electrocatalysts such as platinum or palladium at the cathode for the hydrogen evolution reaction (HER) and iridium (or its oxides) at the anode for the oxygen evolution reaction (OER) [1, 2, 5]. One of the main challenges in PEM technology is minimizing of noble metal loading in PEM cell without decreasing its efficiency and lifetime. This can be achieved by using the electrocatalysts consisting of the nanoparticles of the noble metals on the low-cost electronic carriers with large surface area [1, 2]. The platinum and palladium nanoparticles supported by vulcan-XC 72 [1] or graphitic nanofibers [2] have been successfully used as electrocatalysts at the cathode for HER. However, it is not easy to fabricate the noble metal nanoparticles spreading on the whole surface of the carbon carriers because the surface area of the carbon carriers is very large, e.g. 170 m² g⁻¹ and 250 m² g⁻¹ for graphitic nano-fibers and vulcan XC-72R, respectively. To date, the impregnation–reduction method has been considered as the best method to prepare the noble metal nanoparticles on carbon carriers. There are some impregnation–reduction methods using different reductants such as formaldehyde (FD) [1, 2], ethylene glycol (EG) [6], and sodium borohydride (SB) [7]. Therefore, the aim of this study is screening and improving the impregnation–reduction method to prepare the platinum nanoparticles on vulcan XC-72R carrier which is
2.2.1. Ethylene glycol reductant. Platinum nanoparticles were dispersed on Vulcan XC-72R carbon powder (98%), nitric acid (65%), hydrochloric acid (37%), hydrogen peroxide (30%), potassium hydroxide, sodium hydroxide, sodium borohydride, chloroplatinic acid hexahydrate (H₂PtCl₆ · 6H₂O), iridium(III) chloride hydrate (IrCl₃ · xH₂O), ethylene glycol, ethanol, acetone, nafion 117 solution (5 wt. %) and nafion 117 membrane were purchased from Sigma-Aldrich Corporation (USA). De-ionized water (millipore) with 18 MΩ cm⁻¹ resistivity was used throughout all the experiments.

Iridium oxide was prepared from IrCl₃ · xH₂O by thermal decomposition method [5, 8]. Then, iridium black catalyst was prepared by reducing the colloid of iridium oxide (diameter about 200 nm, figure 1) in water with the excess of sodium borohydride. The reduction was carried out overnight under continuous stirring. The stirring was switched off and the precipitate of iridium black is obtained by centrifuging.

2.2.3. Sodium borohydride reductant. With sodium borohydride (SB) reductant, the synthesis method was done as described by Sung et al [7]. Briefly, 255 mg of carbon was dispersed in 200 mL water by stirring and sonicating. Then 8.7 mL of 0.1 M H₂PtCl₆ aqueous solution was added drop wise into the dispersion under continuous stirring. The pH of the mixture was adjusted to about 9 by 1 M KOH solution and stirred overnight under atmosphere of nitrogen. The resultant Pt40/C (E) catalyst (where 40 denotes the content (wt.%) of platinum, C denotes the vulcan XC72R carbon carrier and E denotes EG reductant) was washed several times by water and acetone and dried at 80 °C in an oven.

2.2.2. Formaldehyde reductant. With formaldehyde (FD) reductant, the impregnation–reduction method was carried out as described by Grigoriev et al [1, 2]. In brief, 255 mg of carbon was dispersed in 30 mL of EG by sonicating. Then 8.7 mL of 0.1 M H₂PtCl₆ aqueous solution was added drop wise into the dispersion under continuous stirring. The pH of the mixture was adjusted to about 9 by 1 M KOH solution and then 110 mL of EG was added to the mixture. The reduction was initiated by stirring and pre-heating the dispersion to 75 °C. After adding 87 mL of a FD solution (37%) drop wise into the dispersion, the temperature of the mixture was kept at 95 °C for 3 h. Then the heating was switched off and the dispersion was cooled down to ambient temperature for 2 h under continuous stirring. The remaining deposit was washed with water (7 to 8 times) by centrifuging. Then, it was dried at 70 °C. As a result, Pt40/C (F) catalyst (F denotes FD reductant) was obtained.

2.2.4. Step-by-step sodium borohydride and ethylene glycol reductants. Step 1: The Pt25/C material (where 25 denotes the content (wt.%) of platinum) was synthesized by the impregnation–reduction method with SB reductant, as described by Sung et al [7].

Step 2: Platinum nanoparticles were adhered further to the Pt25/C material by the impregnation–reduction method with EG reductant, as described by Kumar et al [6].

The resultant Pt40/C (B–E) catalyst (where 40 denotes the content (wt.%) of platinum and B–E denotes the synthesis method using two reducing steps with SB and EG reductants) was washed several times with water and acetone and then dried at 80 °C in an oven.

2.2.1. Ethylene glycol reductant. Platinum nanoparticles deposited onto vulcan XC-72R carbon were synthesized by the impregnation–reduction method with ethylene glycol (EG) reductant, described by Kumar et al [6]. Briefly, the vulcan XC-72R carbon powder (255 mg) was dispersed with 70 mL of EG in a three-neck flask by a magnetic stirring bar. Then 35 mL of 0.025 M H₂PtCl₆ solution in water was added drop wise into the dispersion under continuous stirring. The pH of this mixture was adjusted to about 9 by 1 M KOH solution. After that, the mixture was refluxed at 110 °C for 3 h and stirred overnight under atmosphere of nitrogen. The resultant Pt40/C (E) catalyst (where 40 denotes the content (wt.%) of platinum, C denotes the vulcan XC72R carbon carrier and E denotes EG reductant) was washed several times by water and acetone and dried at 80 °C in an oven.

2.2.2. Formaldehyde reductant. With formaldehyde (FD) reductant, the impregnation–reduction method was carried out as described by Grigoriev et al [1, 2]. In brief, 255 mg of carbon was dispersed in 30 mL of EG by sonicating. Then 8.7 mL of 0.1 M H₂PtCl₆ aqueous solution was added drop wise into the dispersion under continuous stirring. The pH of the mixture was adjusted to about 9 by 1 M KOH solution and then 110 mL of EG was added to the mixture. The reduction was initiated by stirring and pre-heating the dispersion to 75 °C. After adding 87 mL of a FD solution (37%) drop wise into the dispersion, the temperature of the mixture was kept at 95 °C for 3 h. Then the heating was switched off and the dispersion was cooled down to ambient temperature for 2 h under continuous stirring. The remaining deposit was washed with water (7 to 8 times) by centrifuging. Then, it was dried at 70 °C. As a result, Pt40/C (F) catalyst (F denotes FD reductant) was obtained.

2.2.3. Sodium borohydride reductant. With sodium borohydride (SB) reductant, the synthesis method was done as described by Sung et al [7]. Briefly, 255 mg of carbon was dispersed in 200 mL water by stirring and sonicating. Then 8.7 mL of 0.1 M H₂PtCl₆ aqueous solution was added drop wise into the dispersion under continuous stirring. Then, metal precursors were reduced by the excess of SB, which was added drop wise into the dispersion (5 times larger than the stoichiometric amount of metal precursors). The obtained Pt40/C (B) catalyst (B denotes SB reductant) was washed by water several times and dried by freeze-drying without any heat treatment.

2.2.4. Step-by-step sodium borohydride and ethylene glycol reductants. Step 1: The Pt25/C material (where 25 denotes the content (wt.%) of platinum) was synthesized by the impregnation–reduction method with SB reductant, as described by Sung et al [7].

Step 2: Platinum nanoparticles were adhered further to the Pt25/C material by the impregnation–reduction method with EG reductant, as described by Kumar et al [6].

The resultant Pt40/C (B–E) catalyst (where 40 denotes the content (wt.%) of platinum and B–E denotes the synthesis method using two reducing steps with SB and EG reductants) was washed several times with water and acetone and then dried at 80 °C in an oven.
The two platinized titanium micro grids (1 mm in thickness and 1.2 × 1.2 cm²) were placed as current distributor on both sides of the membranes supported electrocatalysts and two titanium sheets (1 mm in thickness and 1.2 × 4 cm²) were used as end plates. The above items were clamped together with two polystyrene end plates (1 cm in thickness and 4 × 4 cm²). The 1.0 cm² single electrolysis cells were immersed in water sink. The current–voltage curves were recorded at 25 °C.

3. Results and discussion

3.1. The Pt content

The Pt content of the obtained Pt40/C catalyst is able to significantly affect its electrocatalyst [9]. In the impregnation–reduction, the formation of the Pt nanoparticles in the bulk solution makes the Pt content in the catalysts lower. The experiment result (table 1) shows that the Pt content in the obtained Pt40/C catalysts efficiency of the deposition Pt on Vulcan XC-72R increases with the strength of the reductant (EG < FD < SB) and the surface tension of the solvent (EG < EG/H2O < H2O).

In addition, the Pt content of the Pt40/C (B–E) catalyst is highest (table 1) and reaches 97.75% of the Pt content calculated following the total amount of the loading Pt (IV) salt. Therefore, the impregnation–reduction method will get the higher efficiency of the deposition Pt on Vulcan XC-72R when the loading Pt (IV) salt is decreased. However, with the lower loading of Pt (IV) salt, the impregnation–reduction method has to be carried out several times to reach the Pt content desired.

3.2. Morphological characterization

In aiming to fabricate the Pt/C catalysts compared to the Pt black catalyst powder, the Pt nanoparticles should be distributed over the entire surface of the carbon carrier in tiny and homogeneous size. Experimentally, platinum can be distributed over the entire surface of the carbon carrier when the concentration of chloroplatinic acid has to be high enough during the impregnation step, which in turn yields the Pt nanoparticles of large size. The Pt nanoparticles of large size were observed by FESEM images (figure 2), while the distribution of the Pt nanoparticles of small size on the surface of the carbon carrier were illustrated by TEM images (figure 3). FESEM and TEM images show that the Pt40/C (E) and Pt40/C (B) catalysts consist of many Pt nanoparticles in large numbers.
Figure 2. FESEM image of catalyst: (a) Pt40/C (E); (b) Pt40/C (F); (c) Pt40/C (B) and (d) Pt40/C (2S).

Figure 3. TEM images of catalysts: (a) Pt40/C (E); (b) Pt40/C (F); (c) Pt40/C (B) and (d) Pt40/C (B–E).
size (figures 2(a) and (c)); the diameter of the Pt nanoparticles of small size is above 5 nm and the coverage ratios of Pt nanoparticles is not high (figures 3(a) and (c)).

Although the Pt nanoparticles of large size exist little in the Pt40/C (B-E) catalyst (figure 2(d)), the diameter of the Pt nanoparticles of small size is below 3 nm and the coverage ratios of Pt nanoparticles are quite high (figure 3(d)). Therefore, the decreasing of the loading of Pt (IV) salt also helps to lessen the diameter of the Pt nanoparticles on vulcan XC-72R.

On the other hand, the Pt40/C (F) catalyst only consists of a few Pt nanoparticles in large size (figure 2(b)), the diameter of the Pt nanoparticles of small size is about 3 nm and the coverage ratios of Pt nanoparticles are quite high (figure 3(b)). Following image analysis, the Pt40/C (F) catalyst can be the best of the obtained catalysts. This obtained result is similar to the result reported by Grigoriev et al [1]. The preeminence of FD reductant may be due to the absorption of FD on the Pt cluster [10] forming in the impregnation–reduction process. This absorption may prevent the Pt cluster from the size increasing.

3.3. Electrochemical characterization

Cyclic voltammograms recorded on the working electrode, which is the glassy carbon electrode, are modified by the thin film of the Pt40/C catalysts and nafion binder. These cyclic voltammograms are shown in figure 4. The cyclic voltammetry curves of the Pt40/C catalysts are similar to that of Pt black powder catalyst (figure 4). Therefore, the Pt40/C catalysts are expected to behave as Pt black powder catalyst for the HER.

Electrochemically active surface areas (EAS) of Pt40/C catalysts were estimated from the cyclic voltammetry curves in figure 4. The EAS of Pt40/C (F) catalysts is the same as that of the Pt40/C (B–E) catalyst and higher than those of the Pt40/C (E), Pt40/C (B) or Pt black catalysts (table 2). Therefore, to enhance the EAS of the catalysts, the impregnation–reduction method is necessary to use FD reductant or decrease the loading of Pt (IV) salt in each impregnation–reduction step.

3.4. Water electrolysis

During PEM water electrolysis, the typical current–voltage curves are recorded at 25 °C and plotted in figure 5. All our PEM water electrolyzers illustrated the current density of 1.0 A cm\(^{-2}\) when the applied voltages were about 2.0 V. So our PEM water electrolyzers operate similarly to those designed by Grigoriev et al [11]. Their conversion efficiency reaches about 75% at 1.0 A cm\(^{-2}\) and 25 °C. Therefore, their conversion efficiency can show the cathodic catalysis of the synthesized Pt40/C catalyst.

The PEM electrolyser with the Pt40/C (B-E) catalyst at cathode offers the best efficiency (figure 5) in comparison with those with the other Pt40/C or Pt black catalyst at cathodic cathode. Cathodic catalysis of the Pt40/C (F) catalyst was a little lower than the Pt40/C (B–E) catalyst, although the Pt40/C (F) and Pt40/C (B–E) catalyst possess the same EAS. This unexpected behavior could result from the absorption of
FD on the Pt nanoparticles of Pt40/C (F) catalyst [10]. Further study should be carried out to clarify this phenomenon.

4. Conclusions

The results show that Pt40/C (F) has the highest coverage ratio and the Pt nanoparticles are almost those of homogeneous size while the Pt40/C (B-E) catalyst has the highest cathode catalysis. These results lead to the conclusion that the impregnation–reduction method consisting of two steps with the Pt loading about 20% of carbon weight per step is a promising approach for the preparation of the cathodic catalysts which possess Pt nanoparticles on vulcan XC-72R carrier.

Acknowledgments

This work is financially supported in part by the Department of Science and Technology of Ho Chi Minh City, Vietnam.

References

[1] Grigoriev S A et al 2011 Int. J. Hydrogen Energy 36 4143
[2] Grigoriev S A et al 2008 J. Power Sources 177 281
[3] Jang I Y et al 2008 J. Membr. Sci. 322 154
[4] Millet P et al 2011 Int. J. Hydrogen Energy 36 4134
[5] Balaji R et al 2011 Int. J. Hydrogen Energy 36 1399
[6] Kumar S M S et al 2011 Int. J. Hydrogen Energy 36 5453
[7] Choi B et al 2007 Carbon 45 2496
[8] Trasatti S 1991 Electrochim. Acta 36 225
[9] Marshall A T et al 2007 Int. J. Hydrogen Energy 32 2320
[10] Gomes J R B and Gomes J A N F 2000 J. Electroanal. Chem. 483 180
[11] Grigoriev S A et al 2006 Int. J. Hydrogen Energy 31 171