Particle Size-Controlled Growth of Carbon-Supported Platinum Nanoparticles (Pt/C) through Water-Assisted Polyol Synthesis

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ABSTRACT: A water-assisted control of Pt nanoparticle size during a surfactant-free, microwave-assisted polyol synthesis of the carbon-supported platinum nanoparticles (Pt/C) in a mixture of ethylene glycol and water using (NH₄)₂PtCl₆ as the Pt precursor is demonstrated. The particle size was tuned between ∼2 and ∼6 nm by varying either the H₂O volume percent or the Pt precursor concentration during synthesis. The electrochemical surface area (ECSA) and the oxygen-reduction reaction activity obtained for the Pt/C electrocatalyst show a catalytic performance competitive to that of the state-of-the-art commercial Pt/C electrocatalysts used for polymer electrolyte membrane fuel cell electrodes (ECSA: ∼70 m²/g; half-wave potential for oxygen reduction reaction: 0.83 V vs reversible hydrogen electrode). The synthesized Pt/C electrocatalysts show durability equivalent to or better than that of the commercial Pt/C. The durability was found to improve with increasing particle size, with the ECSA loss values being ∼70 and ∼55% for the particle sizes of 2.1 and 4.3 nm, respectively. The study may be used as a route to synthesize Pt/C electrocatalysts from a convenient and economic Pt precursor (NH₄)₂PtCl₆ and avoiding the use of alkaline media.

1. INTRODUCTION

Nanoparticulate platinum supported on carbon (Pt/C) is a key catalyst for numerous state-of-the-art renewable energy technologies such as the polymer electrolyte membrane (PEM) fuel cells (PEMFCs) and the PEM electrolyzers.¹⁻⁵ The synthesis of Pt/C catalysts is generally achieved through various physical, chemical, or physicochemical routes using Pt precursors such as [PtCl₆]²⁻.²⁻⁶⁻¹⁰ The metal precursor and the synthesis routes are important from both the processing and the catalyst performance points of view. A Pt/C synthesis route that is less costly and involves environmentally friendly processing is preferred for the commercial production of the catalysts. For example, use of (NH₄)₂PtCl₆, an intermediate product of the Pt extraction/refining process, as the Pt precursor to synthesize Pt/C electrocatalysts may be considered a more convenient, cost-effective, and greener approach. Similarly, as parameters such as the loading size, surface morphology, and state of distribution of the Pt nanoparticles affect the catalytic performance of the Pt/C catalysts significantly,¹¹⁻¹₃ their synthesis with desired structural parameters has remained a topic of significant interest.¹⁴⁻²⁰

The size and their agglomeration state of the Pt nanoparticles may be controlled essentially by varying the synthesis parameters. For example, variations of either of the parameters such as the strength and concentration of reducing agent, the Pt precursor concentration, presence of surfactants, etc. may be used to control the particle size and agglomeration state of the Pt nanoparticles during their synthesis through a chemical route.²¹⁻²³ Use of surfactants such as poly(vinylpyrrolidone) (PVP) during chemical synthesis has been shown to control the particle size and prevent agglomeration successfully.²⁰,²⁴⁻²⁶

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Table 1. Summary of the Experimental Parameters For Various Pt/C Samples Synthesized (Reaction Temperature: 140 °C; Reaction Time: 150 s, max. MW Power: 200 W)

| variable                  | sample code | H2O volume percent | H2O/EG (mol/mol) | H2O/Pt (mol/mol) | EG/Pt (mol/mol) | Pt conc. (mM) | developed pressure (bar) | reaction completion (%) |
|---------------------------|-------------|--------------------|------------------|------------------|-----------------|---------------|--------------------------|------------------------|
| H2O volume percent        | 95          | 95                 | 59.03            | 10.297           | 174             | 5             | 2.5                      | 100.0                  |
| 90                        | 90          | 27.96              | 9755             | 349              | 5               | 2.5           | 99.99                    |
| 80                        | 80          | 12.43              | 8671             | 698              | 5               | 2.2           | 99.99                    |
| 70                        | 70          | 7.25               | 7588             | 1047             | 5               | 1.9           | 99.95                    |
| 60                        | 60          | 6.66               | 6504             | 1306             | 5               | 1.7           | 99.97                    |
| 50                        | 50          | 3.11               | 5556             | 1788             | 5               | 1.2           | 99.92                    |
| 40                        | 40          | 2.07               | 4336             | 2093             | 5               | 0.8           | 99.99                    |
| 30                        | 30          | 1.33               | 3252             | 2442             | 5               | 0.7           | 99.98                    |
| 20                        | 20          | 0.78               | 2168             | 2791             | 5               | 0.0           | 99.97                    |
| 10                        | 10          | 0.35               | 1084             | 3140             | 5               | 0.0           | 99.19                    |
| 05                        | 05          | 0.16               | 542              | 3315             | 5               | 0.0           | 96.27                    |
| 00                        | 00          | 0.00               | 0                | 3489             | 5               | 0.0           | 84.67                    |
| Pt conc. (mM)             |             |                    |                  |                  |                 |               |                          |                         |
| 05 mM                     | 70          | 7.25               | 7588             | 1047             | 5               | 1.9           | 99.91                    |
| 10 mM                     | 70          | 7.25               | 3794             | 523              | 10              | 1.9           | 99.96                    |
| 15 mM                     | 70          | 7.25               | 2529             | 349              | 15              | 1.9           | 99.98                    |
| 20 mM                     | 70          | 7.25               | 1897             | 262              | 20              | 1.9           | 99.99                    |
| 25 mM                     | 70          | 7.25               | 1518             | 209              | 25              | 1.9           | 99.98                    |
| 30 mM                     | 70          | 7.25               | 1265             | 174              | 30              | 1.9           | 99.98                    |

However, the requirement to remove the surfactant from the synthesized Pt/C adds extra processing steps. Hence, other parameters such as pH of the synthesis bath, presence of water, Pt concentration, etc. may be used to control the Pt particle size. Li et al. have demonstrated significant effects of the pH of the solution on carbon nanotube-supported Pt nanoparticles.16 Similarly, Schrader et al. have reported the effect of OH− concentration of the particle size of colloidal Pt nanoparticles synthesized through a surfactant-free polyol route in alkaline solutions of ethylene glycol (EG).17 The particle size was found to decrease with increasing NaOH concentration. Quinson et al. have recently shown that with a variation in the NaOH/Pt molar ratio from 2.5 to 3 during a surfactant-free synthesis in alkaline solutions of EG, the Pt nanoparticle size can be varied from 1 to 5 nm.18 Apart from alkaline solutions, particle size-controlled growth of Pt nanoparticles through varying the H2O/methanol ratio during their synthesis in aqueous solutions of methanol has also been reported.15,21,29,30 Teranishi et al. have demonstrated the synthesis of monodispersed Pt nanoparticles of controlled size by changing the alcohol/water and PVP/Pt ratio during alcohol reduction of H2 PtCl6.21 The Pt particle size was found to decrease with increasing alcohol or PVP concentration. Similarly, Quinson et al. have shown the effect of the methanol/water ratio on the Pt particle size to be dependent on the Pt concentrations of the synthesis bath.15 At a lower Pt concentration of 0.5 mM, the particle size remained unaffected by the methanol/water ratio, while smaller particles were obtained for a higher methanol content at the Pt concentration of 2.5 mM. The effect of the presence of water on the particle size may be likely due to different reaction pathways as demonstrated by Chen et al. that the presence of water changes the [PtCl6]2− reduction pathway and accelerates the reduction reaction during the synthesis of Pt nanoparticles in a methanol/water mixture.22 Such a water-assisted control of Pt nanoparticles may be of significant industrial importance over the use of alkaline solutions. Owing to their industrial importance, such a simple size-controlled synthesis of supported Pt (especially Pt/C) nanoparticles (2−5 nm) is of interest, though optimizations at low Pt concentrations (<5 mM) may be of little significance for large-scale synthesis.

The present work aims to use the existing knowledge of water-assisted synthesis of colloidal Pt nanoparticles of the desired size for the large-scale synthesis of well-dispersed and size-controlled Pt/C electrocatalysts. Here, a modified polyol route to synthesize Pt/C electrocatalysts of the desired size has been proposed. Unlike the conventional route, where the desired particle size and uniform distribution of Pt nanoparticles are achieved through, for example, use of surfactants or alkaline media (concentration up to 5 M), etc. during the synthesis of Pt/C by reducing a Pt precursor under optimal conditions, the present study uses water-assisted control over the particle size and particle distribution on the carbon support. The average size of the Pt nanoparticles is tuned by varying either of the synthesis parameters, namely, the H2O volume percent and the Pt precursor concentration, essentially varying both the H2O/Pt and the EG/Pt molar ratios. Moreover, the catalyst was achieved using (NH4)2PtCl6 as a precursor. Comprehensive structural and electrochemical characterizations of the synthesized samples confirm their catalytic performance competitive to the state-of-the-art commercial Pt/C electrocatalysts used for PEMFC electrodes.

2. RESULTS AND DISCUSSION

2.1. Propagation of the Pt/C Synthesis Reaction. Synthesis of various Pt/C samples through the microwave (MW)-assisted polyol route was performed in a closed vessel capable of sustaining a pressure of up to 10 bar. As the final temperature (140 °C) and the holding time (150 s) were maintained constant for all of the samples, some of the samples were synthesized under supercritical conditions with a pressure (Δp) developed in the vessel. On changing the H2O volume fraction between 0.95 and 0.20, Δp showed a corresponding variation between 2.5 and 0.0 bar, as shown in Table 1. The percent conversion of the [PtCl6]2− → Pt6 reduction reaction was determined by atomic absorption spectroscopy (AAS) of the residual Pt concentration in the reaction bath after centrifuging the Pt/C catalyst (Table 1). The presence of
H₂O clearly affected the reduction reaction significantly, leading to lower percent conversion for samples containing H₂O volume fractions below 0.10. No effect of increased Pt concentration was observed on the percent conversion.

2.2. Structural Characterizations of Pt/C Electrocatalysts. Microscopic analysis of selected Pt/C catalysts through transmission electron microscopy (TEM) reveals a uniform distribution of the Pt nanoparticles supported on carbon. A comparison of the typical TEM images of Pt/C catalysts synthesized with varying H₂O/EG ratios is shown in Figure 1. It suggests larger particle sizes for 95 and 00% samples (sample code: Table 1) as compared to those for the 70 and 50% Pt/C catalysts. With a smaller particle size (~2 nm) and uniform distribution of the Pt nanoparticles, the 70 and 50% Pt/C catalysts exhibit a comparable microstructure. Moreover, the 95 and 00% samples exhibit a relatively uneven distribution with a significant agglomeration of the Pt nanoparticles on carbon. This particle size variation is in contrast to that observed for the alcohol-water system, where a consistent decrease in the particle size with increasing alcohol content during synthesis has been reported.11 Similarly, typical TEM images of the Pt/C catalysts synthesized by varying the Pt concentration during synthesis shown in Figure 2 reveal significant variations in the size and agglomeration state of the Pt nanoparticles. With increasing Pt concentration, both the particle size and the degree of agglomeration increase significantly.

Further, X-ray diffraction (XRD) patterns of the Pt/C catalysts synthesized by varying the H₂O volume percent and the Pt concentration are shown in Figure 3a,c, respectively. The broad peak centered at 2θ ~ 26° is attributed to the carbon support, while the relatively intense peaks at 2θ values of 39.8, 46.1, and 67.9° correspond to diffraction from the Pt(111), Pt(200), and Pt(220) planes, respectively. The XRD data were analyzed further to estimate the average crystallite size of the Pt nanoparticles. Variations of the crystallite sizes of Pt nanoparticles for the Pt/C catalysts synthesized by varying the H₂O volume percent and the Pt concentration are shown in Figure 3b,d, respectively. It is clear that both the H₂O volume percent as well as the Pt concentration show significant effects on the Pt crystallite size. Variation of the crystallite size with H₂O volume percent (Figure 3b) suggests larger crystallite size values for the H₂O volume fractions <0.4 and >0.8 as compared to those for the H₂O volume fractions between 0.4 and 0.8. This is unlike that in alkaline electrolytes, where increasing the OH⁻ concentration leads to a consistent decrease in the Pt nanoparticle size.16 Further, the crystallite size variation with the Pt concentration shown in Figure 3d suggests increasing Pt particle/agglomerate size with increasing Pt concentration during synthesis. Combining the XRD and TEM results, it is clear that for the 50 or 70% Pt/C catalyst, the crystallite size matches well with the corresponding particle size. This suggests the Pt nanoparticles to be single crystalline with a low degree of agglomeration.

2.3. Electrochemical Performance of Pt/C Electrocatalysts of Varying Particle Sizes. Estimating the electrochemical surface area (ECSA) of the Pt nanoparticles (area/g of Pt; m²/gPt) through measurement of the charge associated with certain redox peaks such as the H, CO, or Cu adsorption/
stripping is a quick and convenient route to determine their actual potential activity.\textsuperscript{31,32} Provided the electrode structure and the crystallinity of the Pt nanoparticles are comparable, the method may be used to estimate the relative variation of the particle/agglomerate size of different Pt/C samples. Figure 4 summarizes the ECSA measurement results for the Pt/C catalysts synthesized by varying the H\textsubscript{2}O volume percent and the Pt concentration during the MW synthesis. The current values have been normalized to the Pt loading on the electrode measured through X-ray fluorescence (XRF).\textsuperscript{33} The variation among the double layer capacitance (DLC) values, i.e., the absolute difference between cathodic and anodic currents in the double-layer regime (\textasciitilde0.5 V) for various Pt samples (Figure 4a,c), may be attributed to factors such as small variations in the Pt/C weight ratios, changes in DLC due to the MW-induced surface modification of the support carbon, etc. The estimation of ECSA is made through measurement of the area under the H adsorption peak between the double-layer region and the onset of hydrogen evolution during a cathodic scan (shown as the gray shaded area in the inset of Figure 4b) and using eq 1, with the specific charge for H adsorption on polycrystalline Pt being 210 \( \mu \)C/cm\(^2\).\textsuperscript{34}

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ECSA = \frac{\text{H adsorption peak area (VC/s)}}{\text{scan rate (V/s) \times Pt loading (g}_Pt\text{) \times specific charge (C/m}^2\})}
\]

Variation of the ECSA with H\textsubscript{2}O volume percent (Figure 4b) suggests low ECSA for both the low and the high fractions of

\textbf{Figure 2.} TEM images of the Pt/C catalysts (a, b) 05 mM, (c, d) 20 mM, and (e, f) 30 mM, showing the effect of the Pt concentration during syntheses on the catalyst morphology.
H₂O, with high ECSA for the H₂O volume fractions between 0.4 and 0.8. Further, cyclic voltammograms of the Pt/C samples synthesized through MW treatment (time: 150 s; temp.: 140 °C; H₂O volume percent: 7/3 (v/v); Pt/C weight ratio: 1/4) by varying the Pt concentration between 05 and 30 mM are shown in Figure 4c. The corresponding variation of the ECSA with the Pt concentration shown in Figure 4d exhibits decreasing ECSA values with increasing Pt concentration, with a sharp decrease in ECSA for the Pt concentration >25 mM. The variations of the ECSA with both the synthesis parameters show a trend in line with the crystallite sizes determined using XRD. Hence, the ECSA variation may be attributed to the variation of the particle size and hence the physical surface area, with no significant contributions from factors such as electronic connectivity of the Pt nanoparticles, surface crystallite orientation, etc.

Stability of the Pt/C catalysts under working conditions is affected significantly by the Pt particle size. Electrodes consisting of larger catalyst particles show higher durability as compared to that for the smaller particles. Durability assessment of the selected Pt/C catalysts was performed by subjecting the electrodes with an accelerated stress test (AST) consisting of a potential cycling treatment (0.4−1.6 V; 1 V/s) in 1 M H₂SO₄ along with intermediate measurements of the ECSA through observational cycles (0.02−1.2 V; 100 mV/s). As shown in Figure 5, Pt/C catalysts with lower ECSA (95 and 00% Pt/C catalysts) have higher durability (retention of ECSA after AST) as compared to that for the 70% Pt/C catalyst with lower ECSA, which are more prone to growth through dissolution/redeposition (Ostwald ripening) under electrochemical potential cycling.35−37

Electrochemical performance evaluation of the Pt/C catalysts was further supplemented by the measurement of their oxygen reduction reaction (ORR) activity in both acidic and basic media. Linear sweep voltammetry (LSV) plots (normalized with Pt loading on glassy carbon rotating disc electrode (GC RDE)) of the 95, 70, and 00% Pt/C catalysts recorded at a scan rate of

Figure 3. XRD patterns of the Pt/C catalysts synthesized with (a) the H₂O/EG and the (b) Pt concentration variations. Crystallite size variations of the Pt/C catalysts obtained from the XRD patterns of (a) and (c) are shown in (b) and (d), respectively.

Figure 4. Cyclic voltammograms of the Pt/C catalysts recorded in 1 M H₂SO₄ (N₂ saturated) at a scan rate of 10 mV/s with variation of (a) the H₂O volume percent and (c) the Pt concentration during the MW-assisted synthesis. Corresponding variations of the ECSA with the H₂O volume percent and the Pt concentration during the MW-assisted synthesis are shown in (b) and (d), respectively.
10 mV/s at a rotation speed of 1600 rpm in 0.5 M H₂SO₄ and 0.1 M KOH are shown in Figure 6a,b, respectively. In both the acidic and the basic media, the 00% Pt/C catalyst shows the lowest half-wave potential and mass activity values, with the specific activity being the highest (Table 2). Furthermore, despite their comparable ECSA values, the 00% Pt/C catalyst exhibits ORR performance significantly lower than that of the 95% Pt/C catalyst. Moreover, ORR performance of the latter is comparable to those of the 50 and 70% Pt/C catalysts. The different ORR performances of the 95 and the 00% Pt/C catalysts in terms of the half-wave potentials may be due to different Pt(111), Pt(100), and Pt(220) textures as the ORR activity is known to vary as Pt(110) > Pt(100) > Pt(111) in H₂SO₄ and as Pt(110) > Pt(111) > Pt(100) in HClO₄. The
Pt(111)/Pt(200) XRD peak intensity ratios for the 00 and the 95% Pt/C catalysts are 2.14 and 2.41, respectively. The lower ORR activity of the 00% Pt/C catalyst as compared to that for the 95% Pt/C catalyst suggests a lower fractional contribution of the (111) facets for the former. Further, the variation in the diffusion-limiting current around 0.4 V shows that it is related to how species travel to or leave a catalytic surface and may be attributed to the different agglomeration states and distributions of the Pt nanoparticles on the support carbon. For example, relatively lower values of the diffusion-limiting current for the 95 and 30 mM Pt/C samples may be due to large agglomerates of the Pt nanoparticles (revealed by the respective TEM images), hindering their accessibility to the reaction species.

Further, the effect of the Pt concentration on the ORR performance is demonstrated by studying the ORR performances of the 05 mM, 20 mM, and 30 mM Pt/C samples. LSV curves corresponding to these Pt/C catalysts in 0.5 M H$_2$SO$_4$ and 0.1 M KOH are shown, respectively, in Figure 6c,d, while the corresponding ORR performance data have been provided in Table 2. A decreasing ORR performance trend with increasing Pt concentration is observed in both acidic and basic media, which could be attributed to the increasing particle size and/or agglomeration, as suggested by the ECSA values.

### 2.4. Synthesis Parameter/Material Property Correlation

Figure 7 demonstrates the correlations between the synthesis parameters, namely the H$_2$O/EG ratio (D1; in red) and the Pt concentration (D2; in black), and the material properties, namely the ECSA and the Pt crystallite size. Since the H$_2$O/Pt and the EG/Pt molar ratios are varied either (D1) by using different reaction bath compositions (H$_2$O/EG ratios) with fixed Pt concentrations or (D2) by using different Pt concentrations in reaction baths of a fixed H$_2$O/EG ratio, the data of material properties from these two datasets are termed D1 and D2, respectively.

As shown in Figure 7, the datasets D1 and D2 follow relatively different trends w.r.t. the H$_2$O/Pt molar ratio, while similar trends of D1 and D2 are observed w.r.t. the EG/Pt ratio. Also, with identical EG/Pt ratios (<1000), a decrease in particle size is

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Table 2. Summary of Oxygen Reduction Reaction (ORR) Activity Parameters of the Electrocatalysts Synthesized by Varying the H$_2$O Volume Percent or the Pt Concentration

| samples | Pt loading (μg) on GC | specific activity (mA/cm$^2$) | mass activity (mA/mg) | half-wave potential (V) |
|---------|-----------------------|-------------------------------|-----------------------|------------------------|
|         |                       | acidic | basic | acidic | basic | acidic | basic |
| 95%     | 6.04                  | 0.79   | 1.26  | 171    | 174   | 0.82   | 0.8    |
| 70%     | 6.12                  | 0.39   | 0.62  | 162    | 179   | 0.81   | 0.83   |
| 50%     | 6.08                  | 0.31   | 0.79  | 170    | 183   | 0.82   | 0.83   |
| 0%      | 6.02                  | 1.49   | 1.61  | 160    | 166   | 0.74   | 0.78   |
| 05 mM   | 6.12                  | 0.36   | 0.63  | 166    | 180   | 0.81   | 0.83   |
| 20 mM   | 6.20                  | 0.54   | 0.99  | 161    | 172   | 0.8    | 0.82   |
| 30 mM   | 6.14                  | 1.14   | 1.55  | 155    | 172   | 0.76   | 0.8    |
| BASF    | 6.12                  | 0.41   | 0.91  | 166    | 176   | 0.82   | 0.83   |
observed with increasing H₂O/Pt ratio. In contrast, with identical H₂O/Pt ratios (∼8000), an increase in particle size is observed with increasing EG/Pt ratio. Hence, both the H₂O/Pt and the EG/Pt ratios are important to determine the Pt nanoparticle size.

As a note on the underlying mechanisms leading to the observed particle size variation with the H₂O/EG ratio, it has been reported that in the presence of the support carbon, nanoparticles are formed through heterogeneous nucleation on active sites of support, while in the absence of support (colloidal synthesis), the particles are formed through homogeneous nucleation in the reaction bath. Here, assuming the formation of Pt nanoparticles through a heterogeneous nucleation route and no significant change in the chemical route due to the fact that all of the samples (except the 00%) have been synthesized in an H₂O/EG mixture with both H₂O/Pt and EG/Pt molar ratios >150, there could be several physical parameters controlling the Pt nanoparticle size. As the particle size depends on the number of stable nuclei formed during synthesis, availability of the active sites and the reagents are of significant importance. Hence, the particle size variation may be explained by considering the interplay among the parameters such as the EG/Pt ratio, the diffusivity of the [PtCl₆]²⁻ complex, and the wettability and strength of EG adsorption on the support, with the former and the latter parameters being associated with the availabilities of the reagents and the active sites, respectively. A schematic illustration of the interplay of various parameters and the Pt nanoparticle size is shown in Figure 8.

![Image](image_url)

Figure 8. Schematic showing the proposed underlying mechanisms leading to the observed particle size variation with the H₂O/EG ratio.

There are three possible scenarios:

- **On the other hand, for high water content**, a small amount of larger particles are formed due to the relatively lower number of accessible active sites (low wettability) in contact with the reaction mixture, leading to fewer heterogeneous nuclei, and the lower concentration of the reducing agent, i.e., EG, leading to a decreased rate of nucleation.

- **Finally, for the intermediate H₂O/EG contents**, relatively moderate values of wettability, viscosity, and EG adsorption strength, along with sufficient reducing agent concentration, lead to deposition of the smaller Pt nanoparticles by the formation and growth of a large number of stable nuclei.

3. CONCLUSIONS

In conclusion, a water-assisted synthesis of size-controlled Pt nanoparticles supported on carbon (Pt/C) electrocatalysts was demonstrated. Pt/C catalysts with 20 wt % Pt loading and a uniform distribution of Pt nanoparticles (∼2 nm) were synthesized in the surfactant-free aqueous solutions of ethylene glycol without additional modification of pH. A variation in the Pt nanoparticle size from ∼2 to ∼5 nm is achieved by varying either the H₂O volume percent of the synthesis bath between 95 and 0% or the Pt concentration in the synthesis bath between 5 and 30 mM. With a Pt nanoparticle size of ∼2 nm, an ECSA value of ∼70 m²/g, and a half-wave potential of 0.83 V, the electrocatalyst prepared with an optimal H₂O volume percent of 70% shows an electrocatalytic performance comparable to that of its commercial equivalent.

4. MATERIALS AND METHODS

4.1. Materials. For the Pt/C catalyst synthesis, Vulcan XC 72 carbon, ethylene glycol (HOCH₂CH₂OH; EMSURE grade, assay >99.5%, Merck, Germany), and ammonium hexachloroplatinate ((NH₄)₂PtCl₆, Alfa Aesar, Pt: 43.4 wt %) were used as-received. For electrochemical characterization, electrolytes were prepared by diluting sulfuric acid (H₂SO₄; EMSURE grade, assay >95–97%, Merck, Germany) or potassium hydroxide (KOH, Sinopharm A.R. China) with ultrapure water (Milli-Q; resistivity ≥18.2 MΩ-cm at 25 °C).

4.2. Pt/C Synthesis. A microwave (MW)-assisted modified polyol synthesis approach was adopted to prepare the Pt/C electrocatalysts. The CEM Discovery SP microwave synthesizer was operated in the dynamic mode (maximum MW power: 200 W) using a closed vessel (35 mL). In a typical Pt/C synthesis, appropriate amounts of the (NH₄)₂PtCl₆ and Vulcan XC 72 carbon were added to 10 mL of an ethylene glycol/milli-Q water 1:1 (v/v) mixture to obtain a Pt/C weight ratio of 1/4. A uniform dispersion of the reactants was performed through ultrasonication using a Hielscher UP200St ultrasonic homogenizer for 60 s at room temperature. As shown in Table 1, Pt/C catalysts were synthesized by varying two of the reaction parameters, namely the H₂O volume percent and the Pt concentration, systematically, while maintaining the reaction time (150 s) and the reaction temperature (150 °C) constant. Optimizations on the reaction time and the reaction temperature for the Pt/C synthesis from (NH₄)₂PtCl₆ can be found in our previous publication. Constant magnetic stirring was used during the MW treatment, while the vessel was cooled to 50 °C using compressed air jet before opening. For the Pt concentration study, the amounts of (NH₄)₂PtCl₆ and Vulcan XC 72 carbon were varied appropriately while maintaining the
ethylene glycol/mill-Q water volume ratio constant at 3/7. The synthesized Pt/C catalyst was separated from the dispersion by centrifuging and repeated (3×) washing with mill-Q water and dried completely at 80 °C in air.

4.3. Characterization of Pt/C. Atomic absorption spectroscopy (AAS; Graphite Furnace Agilent 200 Series AA analyzer) was employed to estimate the Pt concentration of the extract solution and hence the degree of completion of the [PtCl₆]²⁻ → Pt⁰ reduction reaction. Morphology of the synthesized Pt/C catalysts was unveiled through transmission electron microscope (TEM) imaging using an FEI/Techni T20 TEM with an LaB₆ emitter (200 kV), while their X-ray diffraction (XRD) patterns were collected using a Rigaku Miniflex 600 X-ray diffractometer (Cu Ka λ (λ = 1.5418 Å) radiation). Crystallite size (L) values of the Pt nanoparticles were calculated using Scherer’s formula ([L = 0.9λ/β cos θ], with λ, θ, and β being the X-ray wavelength, the diffraction angle, and the full width at half maximum (FWHM) (2Δθ), respectively) by using the most intense Pt (111) diffraction peak at 2θ = 39.9°. For determination of the FWHM, the XRD data for 2θ values between 35 and 45° were fitted with Gaussian distributions for 2 peaks at 2θ ~ 39.8 and ~46.1°, corresponding, respectively, to the Pt (111) and Pt (200) planes.

Electrochemical characterizations of the Pt/C samples were performed for assessment of the electrochemical surface area (ECSA), durability, and oxygen-reduction reaction (ORR) activity parameters. For catalyst ink preparation, the Pt/C catalyst (10 mg) was dispersed ultrasonically (Hielscher UP200St ultrasonic homogenizer; 60 s) in a stock solution (5 mL) consisting of isopropanol (20 vol %), 5 wt % Na₂CO₃ (Thermo Scientific), and 5 wt % H₂O (79.6 vol %). The typical working electrode (WE) was synthesized Pt/C catalyst was separated from the dispersion by centrifuging and repeated (3×) washing with mill-Q water (79.6 vol %). The typical working electrode (WE) was centrifuged and repeated (3×) washing with mill-Q water (79.6 vol %). The typical working electrode (WE) was synthesized using magnetron sputtering for application in PEM electrochemical systems. *Int. J. Hydrogen Energy* 2013, 38, 426—430.

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