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Synthesis of Pt/C Electrocatalyst from a User-Friendly Pt Precursor -
Ammonium Hexachloroplatinate through Microwave-Assisted Polyol
Synthesis

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Abstract

Ammonium hexachloroplatinate (NH$_4$)$_2$PtCl$_6$, owing to its low solubility in NH$_4$Cl containing aqueous solutions, is an intermediate compound during the hydrometallurgical extraction of platinum. As a rare example of a water soluble and air stable platinum(IV) salt that is not hygroscopic, (NH$_4$)$_2$PtCl$_6$, may be a convenient and economic platinum precursor for large-scale catalyst production. This report investigates the feasibility of (NH$_4$)$_2$PtCl$_6$ as Pt precursor for synthesis of the electrocatalysts for polymer electrolyte membrane fuel cells (PEMFCs), i.e., the Pt supported on high surface area carbon (Pt/C). The Pt/C electrocatalysts with \textasciitilde 20 wt.\% Pt loading are synthesized through a microwave assisted polyol synthesis approach. The reaction parameters, namely the reaction time and the reaction temperature are optimized. In terms of the electrochemical surface area, Pt/C electrocatalyst synthesized at a reaction temperature of 140 °C and a reaction time of 150 s using a Pt concentration of 5 mM exhibited the optimal performance. The process may be used to synthesize Pt/C electrocatalysts having electrochemical performance equivalent to the Pt/C catalyst available commercially or that synthesized using the common precursors such as H$_2$PtCl$_6$. 

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Key words: ammonium hexachloroplatinate, Pt precursor, Pt catalyst, polyol synthesis, microwave synthesis, PEMFC

Highlights:

- Convenient & economic Pt precursor (NH₄)₂PtCl₆ was used for electrocatalyst synthesis
- Parameters for microwave assisted polyol synthesis are optimized
- The synthesized electrocatalyst has shown competitive performance to other equivalents

1. Introduction

Supported nanoparticulate platinum is of great technological interest for applications including automobile emission control, hydrogenation reaction and the electrocatalysts for polymer electrolyte membrane (PEM) fuel cells (PEMFCs) and electrolyzers, etc.¹⁻⁶ With increasing environmental concerns, clean power technologies, especially the PEMFCs and PEM electrolyzers are becoming more relevant with a significant market share in near future.⁷ However, their projected large-scale applications are throttled by the high cost and scarcity of Pt and hence, sustainable primary production and strategic recycling of the Pt containing products, especially Pt/C based electrodes are inevitable for advancement of the industries relying on it.⁸⁻¹⁰ Moreover, engineering and capacity for large-scale production are decisive factors, which contribute significantly to the overall cost of the catalysts.¹¹

Synthesis of the Pt and other platinum group metal (PGM) nanoparticles of desired physical characteristics has been already achieved with a great control over various parameters such as particle size, shape,¹² porosity,¹³⁻¹⁵ crystallinity, etc., with hollow and core-shell structures as further advancements.¹⁵⁻¹⁶ Commonly, the Pt/C electrocatalysts can be synthesized through various physical (e.g. sonication, microwave irritation), chemical (e.g. polyol, impregnation, electrochemical) or physicochemical routes¹⁷⁻¹⁸ by reduction of appropriate metal precursor such as H₂PtCl₆¹⁻², ⁴, ¹⁹⁻²²
K₂PtCl₆, Na₂PtCl₆ and Pt(acac)₂. Ammonium hexachloroplatinate ((NH₄)₂PtCl₆), owing to its low thermal decomposition point, non-hygroscopic nature and low solubility in aqueous solutions of NH₄Cl, is an important intermediate compound in various platinum extraction/recycling processes. In view of this, synthesis of Pt/C from the intermediate compound (NH₄)₂PtCl₆ instead of the conventionally used Pt precursors is of significant technical importance. Verde et al. have shown the synthesis of Pt/C electrocatalysts by impregnation of high surface area carbon with aqueous solution of (NH₄)₂PtCl₆, followed by thermal decomposition to obtain Pt/C with Pt loadings of ≤4 wt.%. However, as a Pt loading ≤20 wt.% Pt and uncontrolled Pt nanoparticle surface properties are not suitable for typical PEMFC and electrolyzer electrocatalysts. Alternative routes to synthesize the Pt/C of higher Pt loading and well dispersed Pt nanoparticles by using the (NH₄)₂PtCl₆ precursor may be explored.

The present work aims to investigate the suitability of (NH₄)₂PtCl₆ as the precursor for synthesis of the Pt/C electrocatalysts with 20 wt.% Pt loading. A microwave assisted polyol process, owing to its short processing times is adopted for the synthesis of Pt/C from (NH₄)₂PtCl₆ precursor. Impact of the process parameters, namely reaction time, and reaction temperature on the electrocatalytic activity of the Pt/C electrocatalysts has been studied to obtain the optimal Pt/C electrocatalyst accompanied with comprehensive physiochemical and electrochemical characterizations.

2. Materials and methods

Materials: Vulcan XC 72 carbon, ethylene glycol (HOCH₂CH₂OH; EMSURE® grade, assay > 99.5%, Merck, Germany), ammonium hexachloroplatinate ((NH₄)₂PtCl₆, Alfa Aesar, Pt: 43.4 wt.%) Sulfuric acid (H₂SO₄; EMSURE® grade, assay > 95 – 97%, Merck, Germany) and potassium
hydroxide (KOH, Sinopharm A.R. China) were used as-received, while different electrolytes/solutions were prepared using Milli-Q water (resistivity $\geq 18.2$ M$\Omega$·cm at 25 °C).

**Pt/C synthesis:** Pt/C electrocatalyst was synthesized through a microwave (MW) assisted modified polyol synthesis,$^{28-30}$ using a CEM Discovery SP® microwave synthesizer. The instrument was operated in dynamic mode with maximum MW power being 200 W with a temperature control. Table 1 shows a summary of the reaction parameters for various Pt/C samples synthesized in the present study. In a typical synthesis, 25 mg of the (NH$_4$)$_2$PtCl$_6$ and 44 mg of Vulcan XC 72 carbon were added to 11.2 mL of ethylene glycol: milli-Q water 1:1 (v/v) mixture in a 35 ml glass reaction vessel. The mixture was ultrasonicated using a Hielscher UP200St ultrasonic homogenizer for 60 s at room temperature to obtain a Pt concentration of 5 mM and a Pt/C ratio of 1:4 (w/w). The mixture was then transferred to the microwave synthesizer and subjected to a MW treatment under closed conditions for varying the reaction temperatures and the dwell times under constant magnetic stirring. For comparison, a Pt/C electrocatalyst using the common Pt precursor H$_2$PtCl$_6$ was also synthesized. The vessel was air cooled to room temperature and the Pt/C electrocatalyst was separated from the dispersion by centrifuging and repeated (3 ×) washing with milli-Q water before dried at 80 °C in air for ~2 h. The degree of completion of the [PtCl$_6$]$^{2-}$ complex reduction to the Pt$^0$ in form of Pt nanoparticles deposited on the support carbon is determined through measuring the Pt concentration of the extract solvent through atomic absorption spectroscopy (AAS) using a Graphite Furnace Agilent 200 Series AA analyzer.

Table 1: Summary of the experimental parameters for various Pt/C samples synthesized through MW –assisted polyol route (H$_2$O/EG volume ratio: 1/1; max. MW power: 200 W)

<table>
<thead>
<tr>
<th>Variable</th>
<th>Dwell time (s)</th>
<th>Reaction temperature (°C)</th>
<th>Pressure developed (bar)</th>
<th>Pt precursor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dwell time</td>
<td>150</td>
<td>180</td>
<td>~7.9</td>
<td></td>
</tr>
</tbody>
</table>
Electrochemical characterizations of Pt/C: Electrochemical characterizations of the synthesized Pt/C samples were performed, and the performance was compared with that of the commercial 20% Pt/C (BASF) equivalent catalyst. Catalyst inks of the synthesized and the 20% Pt/C (BASF) catalysts were prepared using the recipe described elsewhere.\textsuperscript{31} In brief, a stock solution was prepared by mixing isopropanol, 5 wt. % Nafion solution (Ion Power, Dupont D521) and Milli-Q water in volumetric ratios of 20, 0.4 and 79.6, respectively. Typical catalyst ink was prepared by ultrasonic dispersion (Hielscher UP200St ultrasonic homogenizer; 60 s) of Pt/C catalyst (10 mg) in the stock solution (5 mL). Electrodes were prepared by spin coating (rpm: 700, time: 30 min) the catalyst inks (10 µl on a polished (0.5 µm alumina) glassy carbon (GC) rotating disc electrode (RDE; 5 mm diameter; Pine instruments). The Pt loadings on the GC electrode were estimated by using a calibrated X-ray fluorescence (XRF) analyzer (Thermo Scientific Niton XL3t GOLDD+), as described in our previous study.\textsuperscript{32}

Electrochemical surface area (ECSA) and durability of the Pt/C catalysts were accessed through cyclic voltammetry in N\textsubscript{2} saturated 1 M H\textsubscript{2}SO\textsubscript{4} electrolyte using a three-electrode setup, comprising of the modified GC RDE as working electrode (WE), a counter electrode (CE; Graphitic carbon rod; ~5 mm diameter) and a reference electrode (RE; Hg/Hg\textsubscript{2}SO\textsubscript{4}; REF 601 Radiometer®). The measurements were performed using a Zahner® IM6e electrochemical workstation. Prior to the electrochemical measurements, the catalyst coated GC RDE electrode was activated by potential cycling for 20 cycles between 0.02 and 1.2 V at a scan rate of 100 mV/s in the same electrolyte. For
the durability assessment, the GC WE was subjected to an accelerated stress test (AST) through linear sweep potential cycling, using a protocol described in our earlier work. In brief, the AST consisted of 1600 stress cycles between 0.4 and 1.6 V at a scan rate of 1 V/s along with intermediate observational cycles between 1.2 and 0.02 V at a scan rate of 10 mV/s (2 cycles per observation). The ECSA was estimated from the area under H\(^+\) adsorption peak during cathodic scan, while the variation of ECSA with the number of stress cycles (N) was used as a measure of durability.

Further, oxygen reduction reaction (ORR) measurements of the Pt/C catalysts were performed using linear sweep voltammetry (LSV) with a multichannel potentiostate (Biologic VMP3 France), for the accuracy of ORR measurements, all the tests were performed on the same channel. The scan rate was set in 10mV/s. The RDE system was carried out with PINE, the rotation speed was set at 1600 rpm. A catalyst coated glassy carbon (GC) electrode (\(\Phi=5\)mm) was used as working electrode (WE); a carbon rod was used as counter electrode (CE); a saturated calomel electrode (SCE) was used as reference electrode (RE) in 0.5M H\(_2\)SO\(_4\) electrolyte; and a Hg/HgO electrode was used as RE in 0.1M KOH electrolyte. For easy comparison, all the values of potential were converted to vs. reversible hydrogen electrode (RHE). Before the ORR measurements, the electrolyte was O\(_2\) purged for 15 min every time. The background currents were measured by recording the LSV plots for the electrodes in argon-saturated electrolytes and the ORR data were corrected by subtracting the corresponding background data.

**Structural characterizations:**

Thermogravimetric analysis (TGA) of typical Pt/C samples was performed using a NETZSCH STA449 F3 thermal analyzer (between 50 to 1000 °C at a temperature scan rate: 10 °C/min) in an O\(_2\) atmosphere with O\(_2\) and N\(_2\) flow rates of 4 and 16 mL/min, respectively. Transmission electron microscope (TEM) imaging using a JEOL JEM-2010F TEM was employed to study the average particle size and morphology of the Pt-nanoparticles of the as-synthesized Pt/C samples.
software was employed for the Pt nanoparticle size distribution analysis by setting an appropriate
threshold to define the particles and by selecting the area having the most obvious distribution of
individual particles. At least 150 nanoparticles were measured to determine the size distribution. X-
ray diffraction (XRD) patterns of the as-synthesized Pt/C catalysts were collected using a Rigaku
Miniflex 600 X-ray diffractometer (Cu Kα (λ = 1.5418 Å) radiation). The average crystalline size (L)
was calculated using Scherrer formula (L = 0.9λ/βCosθ; with λ, θ and β being the X-ray
wavelength, the diffraction angle and the FWHM (2Δθ), respectively) for Pt (111) peak. Atomic
absorption spectroscopy (AAS; Graphite Furnace Agilent 200 Series AA analyzer) was employed to
determine the Pt concentration in the extract solution to determine the degree of completion of the
Pt/C synthesis reaction during MW treatment.

3. Results and discussion

3.1 Effect of reaction time and temperature

Figures 1a-1c show the cyclic voltammograms of the Pt/C samples synthesized with variation of
different parameters during MW synthesis. The cyclic voltammograms of the Pt/C coated GC RDEs,
recorded in 1 M H₂SO₄ at a scan rate of 10 mV/s, show the characteristic redox peaks for the Pt/C
electrocatalysts. The cathodic peak centered at a potential ~0.7 V correspond to Pt-Oxide reduction,
while the peaks for potentials between ~0.4 and ~0.05 V are related to H⁺ adsorption on various
crystallographic faces of Pt. Similarly, anodic peaks correspond to the H⁺ desorption for potentials
between ~0.05 and ~0.4 V, and to the Pt/oxide formation for potentials ≥1.0 V.

No significant difference among the shapes of the voltammograms is observed for the Pt/C
synthesized by variation of dwell time between 150 and 600 s. This suggests relatively comparable
Pt loadings (Pt wt.%) of the samples. This is also confirmed by the measurement of Pt concentration
in the extract solution, which suggests conversion of ~99.9% of the Pt⁴⁺ from the batch to Pt⁰.
(supporting information S1), with negligible difference of the %removal for different dwell times. Hence, the reduction reaction completes within the initial 150 s. Further, fig. 1b suggests decreasing ECSA values with increasing dwell time. This may be due to increase of the average size of the Pt nanoparticles due to Ostwald ripening during prolonged MW treatment. In a separate study, MW treatment of the 20 wt.% Pt/C (BASF) has suggested significant growth of Pt nanoparticles with MW irradiation. Hence, a dwell time of 150 s was used to synthesize the Pt/C samples for the optimization of other parameters.

Fig. 1: Cyclic voltammograms of the Pt/C catalysts recorded in nitrogen-saturated 1 M H₂SO₄ at a scan rate of 10 mV/s with variation of (a) the dwell time and (c) the temperature during the MW
assisted synthesis. Corresponding variations of the ECSA of Pt/C with the dwell time and the temperature during the MW assisted synthesis are shown in (b) and (d), respectively.

Voltammograms of Fig. 1c show the effect of reaction temperature on the electrochemistry of the synthesized Pt/C samples. The voltammograms show similar characteristics except for the synthesis temperature of 100 °C, where no peaks characteristic to Pt are observed due to the incomplete (~3%) reduction of Pt^4 to Pt^0, in contrast to the high conversion rates (~99.9%) for temperatures ≥120 °C (supporting information S2). The ECSA vs. temperature plot shown in Fig. 1d reveals the optimal temperature to be 140 °C having a marginally higher ECSA. Here, the decreasing ECSA for temperatures > 140 °C may be assigned to the larger size of the Pt nanoparticles, possibly due to Ostwald ripening during the MW treatment.

Combining all observations, the optimized condition for the microwave assisted polyol synthesis using (NH₄)₂PtCl₆ as Pt precursor (5 mM) is MW time: 150 s and temperature: 140 °C and referring to Pt/C -(NH₄)₂PtCl₆ for the rest. The catalyst is produced in a closed glass vessel with a developed pressure of <1.5 bar at 140 °C. The production can be further up-scaled using solvothermal/supercritical flow synthesis.³¹,³⁵

3.2 Comprehensive characterizations on the electrocatalysts

3.2.1 Electrochemical performance

Cyclic voltammograms of the commercial Pt/C catalyst (20 wt.% Pt) and the Pt/C catalysts synthesized from H₂PtCl₆ and (NH₄)₂PtCl₆ precursors through MW route (Pt conc.: 5 mM; MW time: 150 s, temperature: 140 °C) have been shown in Fig. 2a. The identical voltammogram characteristics and the relatively similar ECSA values of the H₂PtCl₆ and (NH₄)₂PtCl₆-sourced Pt/C catalysts suggest
the suitability of the later for the large-scale synthesis of Pt/C. The ECSA values of the Pt/C catalysts may be further enhanced by applying previously reported strategies. For example, ECSA values as high as 140-150 m²/g have been reported by Alekseenko et al (2017; 2018) by using CO as the growth inhibitor during synthesis of Pt/C from H₂PtCl₆ precursor through wet-chemical route. However, no such attempt has been made in the present study due to the fact that such high ECSA Pt/C might not be suitable for real-life PEMFC electrodes due to their lower stability.

Fig. 2: (a) Cyclic voltammograms and (b) ECSA values of the commercial Pt/C catalyst (20 wt.% Pt) and the Pt/C catalysts synthesized from H₂PtCl₆ and (NH₄)₂PtCl₆ precursors through MW route (Pt conc.: 5 mM; MW time: 150 s, temperature: 140 °C).

Durability studies of the Pt/C catalysts synthesized from H₂PtCl₆ and (NH₄)₂PtCl₆ precursors through MW route (Pt conc.: 5 mM; MW time: 150 s, temperature: 140 °C) and the commercial Pt/C (20 wt.% Pt) catalyst have been performed through AST by potential cycling (0.4-1.6 V; 1 V/s) in 1 M H₂SO₄. Figures 3a-3c show the evolution of cyclic voltammograms of the Pt/C catalysts during the AST. Variations of the %ECSA values with N (Fig. 3d) suggest both the H₂PtCl₆ and the (NH₄)₂PtCl₆-sourced Pt/C catalysts to be equally durable. The commercial Pt/C (20 wt.% Pt) catalyst, owing to its
initially low ECSA and hence larger particle size, shows higher stability as compared to that of the MW synthesized catalysts.

Fig. 3: (a-c) Evolution of the observational cyclic voltammograms of the GC RDE modified with (a) the H$_2$PtCl$_6$-sourced, (b) the (NH$_4$)$_2$PtCl$_6$-sourced and (c) the commercial Pt/C-BASF catalysts during AST in 1 M H$_2$SO$_4$ for 1600 cycles. The observational voltammograms are recorded at a scan rate of 10 mV/s. (d) Corresponding % ECSA loss with increasing number of stress cycles.
Oxygen reduction reaction (ORR) activities of the H₂PtCl₆ and (NH₄)₂PtCl₆-sourced and the commercial Pt/C (20 wt.% Pt) catalysts in the acidic (0.5M H₂SO₄) and basic (0.1M KOH) media have been studied through LSV in oxygen saturated electrolytes. Background current subtracted LSV plots of the samples in acidic and basic media are shown in Fig. 4a and Fig. 4b, respectively, while the corresponding ORR performance parameters are summarized in Table 2. Here, the (NH₄)₂PtCl₆-sourced catalyst shows an ORR performance comparable to that of the commercial and the H₂PtCl₆-sourced Pt/C electrocatalysts. The variations of the limiting current (Iₗ) values, i.e. in acidic media, the lower Iₗ values for the H₂PtCl₆-sourced and the commercial Pt/C catalysts as compared to that for the (NH₄)₂PtCl₆-sourced Pt/C catalyst, may be originated to different mass transport limitations at the ionomer/catalyst interfaces having different characteristics due to factors such as the distribution of Pt nanoparticles on the support. Furthermore, the H₂PtCl₆-sourced Pt/C has a comparatively lower Pt wt.% on C (TGA), which could explain its poor ORR performance.

Fig. 4: Linear sweep voltammograms of the GC RDE modified with either of the (NH₄)₂PtCl₆-sourced, the H₂PtCl₆-sourced or the commercial Pt/C (Pt/C-BASF) catalysts, recorded at a scan rate of 10 mV/s in oxygen saturated (a) acidic (0.5 M H₂SO₄) and (b) basic (0.1 M KOH) electrolytes and corrected for the background current in absence of oxygen.
Table 2: summary of oxygen reduction reaction activities of the electrocatalysts

<table>
<thead>
<tr>
<th>Samples</th>
<th>Specific activity in acidic mA/cm²</th>
<th>Specific activity in basic mA/cm²</th>
<th>Mass activity in acidic mA/mg</th>
<th>Mass activity in basic mA/mg</th>
<th>Half wave potential acidic V/ vs.RHE</th>
<th>Half wave potential basic V/ vs.RHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>BASF</td>
<td>0.33±0.002</td>
<td>0.75±0.012</td>
<td>134±1.0</td>
<td>146±2.5</td>
<td>0.82</td>
<td>0.87</td>
</tr>
<tr>
<td>(NH₄)₂PtCl₆-sourced</td>
<td>0.30±0.002</td>
<td>0.80±0.008</td>
<td>166±1.3</td>
<td>186±1.9</td>
<td>0.82</td>
<td>0.86</td>
</tr>
<tr>
<td>H₂PtCl₆-sourced</td>
<td>0.53±0.014</td>
<td>1.03±0.014</td>
<td>147±3.8</td>
<td>176±2.4</td>
<td>0.78</td>
<td>0.84</td>
</tr>
</tbody>
</table>

3.2.2 Structural analysis

TGA plots of the Pt/C-BASF (20 wt.% Pt) and the Pt/C catalysts synthesized from H₂PtCl₆ and (NH₄)₂PtCl₆ precursors through MW route (Pt conc.: 5 mM; MW time: 150 s, temperature: 140 °C) have been shown in Fig. S1 (supporting information S3). Assuming the residual mass corresponding to pure Pt (after thermal oxidation of the support carbon), the Pt wt. % values of the (NH₄)₂PtCl₆ – sourced, the H₂PtCl₆-sourced, and the commercial Pt/C samples are estimated to be ~23.7, ~19.5 and ~18.8 wt.%, respectively. The obtained Pt wt.% values of the H₂PtCl₆-sourced and the (NH₄)₂PtCl₆-sourced Pt/C samples suggest nearly complete attachment of the Pt nanoparticles formed during synthesis to the carbon support. A relatively lower Pt wt.% for the H₂PtCl₆-sourced Pt/C may be due to the highly hygroscopic nature of the Pt precursor leading to inaccurate measurement of the precursor amount during synthesis. Nevertheless, as XRF analysis is used for the Pt loading determination on the GC electrodes, the determined electrochemical performance parameters remain valid despite the variation of Pt wt.% from TGA.

Figures 5a-5c show the TEM images of the H₂PtCl₆ and (NH₄)₂PtCl₆-sourced and the commercial Pt/C (20 wt.% Pt) catalysts, exhibiting a comparatively uniform distribution of the synthesized Pt
nanoparticles without agglomeration. Particle size distribution histograms obtained by using the
*Analyze Particle* tool in ImageJ software after setting an appropriate threshold are shown as insets of
the corresponding TEM images. The average particle sizes of the Pt nanoparticles for the
(NH$_4$)$_2$PtCl$_6$-sourced, the H$_2$PtCl$_6$-sourced and the commercial Pt/C (20 wt.% Pt) catalysts are
observed to be 2.1, 2.0 and 2.3 nm, respectively. The larger particle size of the commercial Pt/C is
also reflected in the ECSA measurements as well. Further, the XRD patterns of the (NH$_4$)$_2$PtCl$_6$-
sourced and the commercial Pt/C (20 wt.% Pt) catalysts shown in Fig. 5d show the diffraction peaks
at $2\theta = 39.8^o$ and Pt 46.1$^o$, corresponding respectively to the Pt (111) and Pt (200) planes, while the
broad peak centered at $2\theta \sim 26^o$ corresponds to the support carbon. The XRD data for $2\theta$ values
between 35$^o$ and 45$^o$ have been fitted for 2 peaks (Lorentz distribution) corresponding to the Pt (111)
and Pt (200) planes. The average crystalline sizes ($L$) calculated from XRD patterns using *Scherrer*
formula for Pt (111) peak are ca. 1.9, 2.0 and 1.7 nm for the (NH$_4$)$_2$PtCl$_6$-sourced, the H$_2$PtCl$_6$-sourced
and the commercial Pt/C (20 wt.% Pt) catalysts, respectively. Here, the lower values of the $L$ as
compared to the corresponding average particle size values of the Pt/C catalysts may be attributed to
the presence of agglomerated individual single crystalline particles, suggesting higher agglomeration
for the 20% Pt/C (BASF) catalyst. Furthermore, there may be an underestimation of the $L$ value due
to the fact that the FWHM of Pt (111) peak is assigned to the crystalline size broadening and no
corrections for factors such as instrumental broadening have been applied.
Fig. 5: (a-c) TEM images of the (a) (NH$_4$)$_2$PtCl$_6$-sourced, (b) H$_2$PtCl$_6$-sourced and (c) the commercial Pt/C (20 wt.% Pt) catalysts. (d) XRD patterns of the (NH$_4$)$_2$PtCl$_6$-sourced and the commercial Pt/C catalysts.

4. Commercial/large-scale feasibility

Large-scale production of Pt/C from the (NH$_4$)$_2$PtCl$_6$ precursor should be possible through various state-of-the-art routes for Pt/C synthesis. As synthesis of other Pt precursors such as H$_2$PtCl$_6$ requires
additional processing steps such as thermal decomposition of (NH₄)₂PtCl₆, the intermediate product, followed by dissolution of the Pt-sponge in concentrated acidic media (e.g. aqua regia) and removal of excess electrolytes to obtain solid H₂PtCl₆, etc., use of (NH₄)₂PtCl₆ as Pt precursor is quite interesting. One of the possible drawbacks of using (NH₄)₂PtCl₆ as Pt precursor might be its low solubility as compared to that of H₂PtCl₆. However, typical synthesis routes report a Pt concentration ranging between 0.5-50 mM, preferentially ~10 mM, which can be achieved by using the (NH₄)₂PtCl₆ Pt precursor. Here, it is noteworthy that the low solubility of (NH₄)₂PtCl₆ at room temperature may not be necessarily hinder its application as Pt precursor at the synthesis conditions involving higher temperatures. Moreover, the (NH₄)₂PtCl₆ solubility may be enhanced by an order of 2 or more in alkaline solutions (e.g. in presence of NaOH).

3 Conclusions

In conclusion, microwave assisted polyol synthesis of the Pt/C electrocatalysts using ammonium hexachloroplatinate (NH₄)₂PtCl₆ as a convenient and economic Pt precursor is investigated. The process may be used to synthesize Pt/C electrocatalysts with 20 wt.% or higher loadings of Pt on C, having electrochemical performance and durability equivalent to the Pt/C catalyst available commercially or that synthesized using the common precursors such as H₂PtCl₆. Lower reaction temperatures (T < 120 °C) are found inadequate for the activation of the reduction of Pt precursor, while those higher than 160 °C lead to larger particle size of Pt and hence lower electrochemically active surface area. Similarly, a reaction time of 150 s was found adequate for completion of the reaction. Microwave exposure for prolonged times leads to increased particle size. The presented process to synthesize Pt/C is of significant interest for PEMFC electrocatalyst production, owing to the (NH₄)₂PtCl₆ precursor being an intermediate of various Pt extraction/recycling processes.
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Associated content

Supporting Information Available: S1: Pt/C synthesis parameters – dwell time; S2: Pt/C synthesis parameters – temperature; S3: Thermogravimetric analysis of Pt/C

References


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Conventional Precursor

Pt source \rightarrow Pt extraction • (NH₄)₂PtCl₆ \rightarrow Calcination • Pt sponge

Pt/C \rightarrow Concentrate • H₂PtCl₆ \rightarrow Dissolve in aqua-regia

This study

Pt source \rightarrow Pt extraction • (NH₄)₂PtCl₆ \rightarrow Pt/C