Pt/C electrocatalyst synthesis from recycling of the spent PEMFC membrane electrode assembly – a closed loop circular economy

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Abstract

Large-scale commercialization and sustainable growth of proton exchange membrane fuel cells (PEMFCs) technology depends largely on availability of the raw materials. Here, technical details of a closed loop recycling of spent electrocatalyst from a PEMFC electrode is demonstrated. The process includes electrochemical dissolution of the Pt nanoparticles in dilute acidic bath, precipitation of the dissolved Pt in form of a Pt-salt and synthesis of carbon supported Pt (Pt/C) electrocatalyst through reduction of the Pt-salt. Spent electrocatalysts from PEMFC electrodes, owing to their high activity, were subjected to dissolution through potentiodynamic treatment in dilute (0.1 M or 1 M) HCl bath to attain a Pt concentration of ~0.7 mg/mL. Pt was recovered from the electrolyte by precipitation in form of ammonium hexachloroplatinate, which was converted to Pt/C electrocatalyst (20 wt. % Pt) through reduction by refluxing in an ethylene glycol/water (1:1 v/v) mixture. Electrochemical surface area measurement and accelerated stress test of the synthesized Pt/C exhibit performances similar to or better than that of commercial Pt/C (20 wt.% Pt). With a demonstrated recovery efficiency >90%, the process may be utilized for large-scale recycling of the spent electrocatalysts, especially suitable for PEMFC electrodes.
1. Introduction

Owing to its scarcity and high cost, recovery of Pt /Pt group metals from the industrial wastes such as the spent catalysts from automobiles, chemical plants, fast growing renewable industries etc. is essential for a sustainable society.\textsuperscript{1-4} However, the well-established pyrometallurgical and/or hydrometallurgical routes,\textsuperscript{3, 4} owing to their high power consumption, high initial investment, toxic emissions, etc., may not be optimal for the recovery of Pt from such spent catalysts. For example, nanoparticulate Pt supported on high surface area supports (e.g. carbon) is the common electrocatalyst used in polymer electrolyte membrane fuel cells (PEMFCs) and electrolyzers\textsuperscript{5}, which represents key players for hydrogen economy. During operation, the electrocatalyst nanoparticles lose their catalytic activity due to degradation of the catalyst layer through various mechanisms.\textsuperscript{6-9} Particularly, the active surface area of the electrocatalysts degrades due to the growth of particle size, the altered size distribution and the loss of electronic or protonic contact in the electrode through mechanisms including Ostwald ripening, migration, coalescence and agglomeration, etc.\textsuperscript{10, 11}, though the overall catalyst mass loss is less than 1%. Pt nanoparticles of such a spent catalyst, still having an average particle size of 5 to 10 nm,\textsuperscript{12} have sufficient activity enabling their recovery under less hazardous conditions compared to those employed for the metal extraction from ore or secondary resource of low surface area. Hence, high activity of the nanoparticles (due to high surface/volume ratio) may be utilized for their environmentally friendly recovery from the industrial waste.\textsuperscript{13}

Dedicated research efforts towards environmentally friendly recovery of Pt form the PEMFC electrodes have been made recently.\textsuperscript{14-23} Approaches such as the use of the ionic liquids\textsuperscript{24} or the ion exchange resins\textsuperscript{25} have been applied respectively to improve the leaching efficiency or the recovery of the leached Pt from the solution. However, synthesis of Pt/C electrocatalyst based on precursor recycled from spent PEMFC Pt/C electrocatalysts is not well reported. Such a closed loop circular
economy is of significant interest owing to various practical issues such as concentration of platinum content, presence of impurities affecting the dissolution and/or recovery of the Pt nanoparticles, etc.

Here, we demonstrate a process to recover and recycle the spent Pt/C electrocatalyst from a PEMFC electrode. Since recycling of the Pt/C electrocatalyst for reuse in similar applications has to be performed in a way to restore their activity, i.e., reconstructing the Pt/C electrocatalysts to attain a particle size distribution and Pt loading suitable for PEMFCs. In the 3-step process (Fig. 1), spent Pt/C electrocatalysts from a PEMFC electrode are dissolved by potentiodynamic treatment under mild conditions to form a Pt-complex in weak acidic aqueous bath. Further, Pt was recovered from the bath by precipitation in form of a non-hygroscopic Pt-salt and finally, the Pt/C electrocatalysts having particle size distribution and Pt-loading suitable for PEMFC electrodes are synthesized by using the Pt-salt as the precursor in a polyol synthesis route. The process shows high overall recovery efficiency of > 90%, suitable for industrial upscaling, at least for the studied class of MEAs.
2. Materials and Methods

**Materials:** Hydrochloric acid (1 M HCl; Reagent Ph. Eur.; BDH chemicals®), sulfuric acid (H₂SO₄; EMSURE® grade, assay > 95 – 97%, Merck, Germany), ethylene glycol (HOCH₂CH₂OH; EMSURE® grade, assay > 99.5%, Merck, Germany), were used as-received, while Milli-Q water (resistivity ≥ 18.2 MΩ·cm at 25 °C) was used to prepare different electrolytes/solutions. The spent PEMFC MEAs were extracted from a 120 cell stack that had been running for several thousand hours in a Serenergy 5kW H3-5000 module, which had been operating normally and the MEAs had shown ordinary degradation behaviour. The MEAs consisted of the carbon cloth (CC)-based gas diffusion layers (GDLs), the catalyst layers (CLs) made of a carbon-supported Pt (60 wt.% Pt on C) catalyst and Nafion® ionomer ink having a catalyst/ionomer weight ratio of ~7:3 and the proton conductive membrane (Nafion®) as the electrolyte. The 20% Pt supported on Vulcan XC-72 carbon procured from BASF Chemicals (hereafter 20% Pt/C-(BASF)) was used for comparison of electrochemical performance of the recycled Pt/C catalyst from MEA (hereafter Pt/C-MEA-CC).

**Delamination of MEAs:** Unless otherwise stated, the delamination of MEAs was performed by subjecting the samples (10 mm diameter or larger) to number of wetting cycles (~15 min in water or 0.1 M HNO₃) followed by drying at 80 °C in air. The numbers of wetting cycles for complete delamination were 3 and 5 for the 10 mm diameter and the 5 × 5 cm² MEA samples, respectively.

**Electrochemical dissolution studies:** A three-electrode setup consisting of a working electrode (WE), a counter electrode (CE; Graphitic carbon rod; ~5 mm diameter) and a reference electrode (RE; Hg/Hg₂SO₄; REF 601 Radiometer®) was used for the electrochemical dissolution of spent Pt catalyst and the electrochemical characterizations of the Pt/C catalyst synthesized from the recovered
Pt. For electrochemical dissolution of the spent catalyst, 10 mm diameter circular discs (unless otherwise stated) from the electrode (CL coated on GDL; obtained by delaminating the MEAs) were used as the WE (hereafter MEA-CC). The potentials were measured w.r.t. the Hg/Hg₂SO₄ RE and reported w.r.t. the reversible hydrogen electrode (RHE). Potentiodynamic dissolution of Pt was performed through potential cycling of the MEA-CC WE between 0.4 - 1.6 V (starting and end potential values: 1.2 V) at a scan rate of 100 mV/s in different electrolytes using a Zahner® IM6e electrochemical workstation. Further, UV-vis spectroscopy (Perkin Elmer; Lambda 900 UV/VIS/NIR spectrometer) was employed to determine the oxidation state of the Pt complexes formed through the electrochemical dissolution process.

**Dissolution quantification:** The Pt-loading on the MEA-CC electrodes was measured using an X-ray fluorescence spectrometer (XRF; Thermo Scientific Niton XL3t GOLDD+ XRF analyzer) calibrated for the same. The amounts of dissolved Pt were also estimated through Pt concentration measurements of the post-dissolution electrolytes by atomic absorption spectroscopy (AAS; Graphite Furnace Agilent 200 Series AA analyzer).

The %dissolution of Pt from an electrode subjected to an electrochemical treatment was calculated by using the relation-

\[
\%dissolution = \frac{W_0 - W_f}{W_0} \times 100 \tag{1}
\]

where, \(W_0\) and \(W_f\) are the Pt-loadings on the electrode before and after the electrochemical treatment, respectively.

**Structural characterizations:** Evolution of average particle size and morphology of the Pt-nanoparticles from MEA-CCs during electrochemical dissolution was studied through transmission electron microscope (TEM) imaging using a JEOL JEM-2010F TEM, while TEM imaging of the Pt/C-MEA-CC electrocatalysts was performed using a FEI/Tecnai T20 TEM with a LaB6 emitter.
(200kV). X-ray diffraction (XRD) patterns of the MEA-CCs and the Pt/C-MEA-CC catalysts were collected using a Rigaku Miniflex 600 X-ray diffractometer (Cu Kα (λ = 1.5418 Å) radiation).

**Recovery of dissolved Pt:** Pt dissolved from MEA-CC in the acidic electrolyte through the electrochemical treatment was further recovered in form of ammonium hexachloroplatinate by addition of ammonium chloride in the electrolyte to a concentration of 1 M. The bright yellow precipitate was separated by centrifuging and washing with ethanol several times to remove the ammonium chloride impurity. Finally, the precipitate was dried at 80 °C for ~1h. Pt recovery efficiency was estimated by measuring the Pt concentration in the extract through AAS.

**Pt/C-MEA-CC synthesis:** Pt/C electrocatalyst was synthesized through a modified polyol synthesis. In a typical synthesis, 25 mg of the (NH₄)₂PtCl₆ obtained through MEA-CC recycling was added to 5.6 ml of ethylene glycol in a 100 ml flask to obtain a Pt concentration of ~10 mM (solution A). 44 mg of Vulcan XC 72 carbon dispersed in 5.6 mL of milli-Q water (solution B) through ultrasonication using a Hielscher UP200St ultrasonic homogenizer for 60 s was mixed to solution A at room temperature to obtain a Pt concentration of ~5mM and a Pt/C ratio of 1/4 (w/w). The mixture was then refluxed for 3 h under constant magnetic stirring and cooled to room temperature before centrifugal separation of the Pt/C electrocatalyst. The sample was washed with milli-Q water (three times) and dried at 80 °C in air for 2 h.

**Electrochemical characterizations of Pt/C-MEA-CC:** Comprehensive characterization of the synthesized Pt/C was carried out and compared with the commercial equivalent catalyst i.e. 20% Pt/C (BASF). Catalyst inks of the Pt/C-MEA-CC and the 20% Pt/C (BASF) were prepared using the standard procedure described elsewhere. In brief, a stock solution of isopropanol, 5 wt. % Nafion solution (Ion Power, Dupont D521) and Milli-Q water in their respective volumetric proportion of 20, 0.4 and 79.6 was used as the solvent. Catalyst ink was prepared by mixing 10 mg of the Pt/C catalyst with 5 mL of the stock solution through ultrasonic agitation for 60 s.
For electrochemical characterizations, the catalyst inks (10 µl) were drop-casted on a polished (0.5 µm alumina) glassy carbon (GC) rotating disc electrode (RDE; 5 mm diameter; Pine instruments) and dried in air at by rotating the RDE at 700 rpm for 30 min. The catalyst loadings on GC electrode (pre-AST and post-AST) were estimated by using a Thermo Scientific Niton XL3t GOLDD+ X-ray fluorescence analyzer calibrated for the same.

Electrochemical surface area (ECSA) and durability assessments of the modified GC RDE were performed through cyclic voltammetry in N₂ saturated 1 M H₂SO₄ electrolyte using a three-electrode setup (similar to that used for dissolution of Pt from MEA-CC) attached to the Zahner® IM6e electrochemical workstation. The GC WE was subjected to an accelerated stress test (AST). During AST, linear sweep potential cycling, consisting of stress cycles (between 0.4 and 1.6 V at a scan rate of 1 V/s with start and end potentials being 1.2 V for a total of 1600 stress cycles) and intermediate observational cycles (2 cycles between 1.2 and 0.02 V at a scan rate of 10 mv/s with start and end potentials being 1.2 V) at every 0, 20, 100, 200, 300, 400, 500, 600, 800, 1000, 1200, 1400 and 1600 number of stress cycles, was applied on the modified GC. The area under H adsorption peak during cathodic scan was used for the ECSA estimation (surface charge density for H adsorption on polycrystalline Pt: 210 µC/cm²). The durability of the catalyst was accessed through % loss of ECSA with the number of stress cycles.

3. Results and discussion

3.1 Delamination of MEA-CC

Recycling of the spent electrocatalysts through electrochemical route essentially requires them to be accessible both electronically and chemically (electrolyte accessibility). The as-received MEAs (Fig. 2a) consist of the PEM sandwiched between two electrodes, each containing a catalyst layer (CL) and a hydrophobic carbon cloth (CC)-based GDL (CC1/CC2), with the CL facing the PEM, as shown in schematic of Fig. 2b. Hence, being obscured by the CC-based GDL, the catalyst layer of the as-
received MEA remains inaccessible to the aqueous electrolyte to be used for electrochemical recycling of the catalyst nanoparticles. In order to perform electrochemical recycling of the electrocatalyst, delamination of the electrodes from the PEM needs to be performed. However, a mechanical delamination of dry or wet MEA leads to a random attachment of the catalyst layer to the CC-based GDL or to the PEM, with a third possibility of the catalyst layer being separated from both of the PEM and the GDL in form of powder. As shown in Fig. 2c, mechanical separation of the MEA wetted by immersing in Milli-Q water for ~15 min by pulling the two layers apart manually distributes the catalyst layer on the PEM and on the GDL randomly (black color of PEM is due to presence of the CL patches on both sides). Such a delamination is not suitable for electrochemical recovery as it becomes difficult to provide electronic connectivity to the nanoparticles on the PEM.

In another approach, a preferential delamination with the catalyst layer being attached preferentially to the CC-based GDL, has been attained by subjecting the MEA with wetting/drying cycles, as described in the Materials and Methods section. In the cyclic wetting process, delamination takes place with preferential attachment of the CLs to their respective CC-based GDLs, as confirmed through the optical photographs of Fig. 2d and the XRF measurements of the Pt loading values for the three components (Table 1). Here the values in table do not add exactly to a constant Pt loading because the Pt loading of the as-received MEAs shows small variations possibly due to initially inhomogeneous Pt loading at different parts of the MEA.

Table 1: Pt loading values of the three components of the CC-based MEA delaminated through single or cyclic wetting

<table>
<thead>
<tr>
<th>Delamination type</th>
<th>Pt loading (mg/cm²)</th>
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<tr>
<td></td>
<td>CC1</td>
</tr>
<tr>
<td>Single wetting</td>
<td>0.98</td>
</tr>
<tr>
<td>Cyclic wetting</td>
<td>1.07</td>
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Fig. 2: (a) Optical photograph of as-received MEA. (b) Schematic of the cross-sectional view of (a) showing the components CC1, CC2, PEM and the catalyst layers (CL). Optical photographs of the components CC1, CC2 and PEM after delamination through (c) single and (d) cyclic wetting routes. PEM of (c) contains patches of the CLs on both sides while that of (d) has no attached patches.
3.2 Pt dissolution

Electrochemical dissolution of end-of-life PEMFC electrode containing platinum catalyst is carried out according to the procedure described in our earlier work. In brief, MEA-CC electrodes have been stressed under potential cycling between 0.4 and 1.6 V at a scan rate of 100 mV/s in 1 M HCl. Fig. 3a shows a typical cyclic voltammogram of the MEA-CC electrode in 1 M HCl electrolyte for 50 cycles between 0.4 and 1.6 V. Fig. 3b shows a typical UV-Vis spectrum of the electrolyte after potentiodynamic dissolution of Pt from CC-MEA in 1 M HCl. UV-visible spectra of the post-dissolution electrolyte (1 M HCl). UV-vis spectra of commercial Pt precursors H₂PtCl₆ and K₂PtCl₄ have also been shown w.r.t. identical background. For the MEA-CC electrolyte, presence of the absorption peak at 265 nm, identical to that for [PtCl₆]²⁻, suggest the dissolved Pt species to be in form of [PtCl₆]²⁻.

![Cyclic voltammogram and UV-Vis spectra](image)

**Fig. 3:** (a) Cyclic voltammogram of MEA-CC electrode in 1 M HCl at a scan rate of 100 mV/s. (b) shows UV-Vis spectra of the electrolyte after potentiodynamic dissolution of Pt from CC-MEA in 1 M HCl and the commercial Pt precursors H₂PtCl₆ [PtCl₆]²⁻ and K₂PtCl₄. Absorption peaks at 265 nm and 225 nm correspond respectively to [PtCl₆]²⁻ and [PtCl₄]²⁻ complexes.
Comparison of the Pt dissolution rates in three different electrolytes has been demonstrated in Fig. 4a. Irrespective of the electrolyte used, %dissolution as high as 98% could be achieved. Since for the application of the potentiodynamic treatment, a Pt nanoparticle must have electronic connectivity to the external circuit, their high %dissolution confirms high electronic connectivity of the Pt nanoparticles from MEA-CC samples. Further, since achieving a fast rate of dissolution by increasing the HCl concentration may not be a preferable route, comparable dissolution rates can be achieved in presence of low concentrations (0.01 – 0.1 M or less) of Cu^{2+} in the electrolyte through inhibition of the redeposition of the dissolved Pt species on the source Pt nanoparticles. Further, XRD patterns of as-received and post-dissolution MEA-CC electrodes (with 80% and 95% dissolution) have been shown in Fig. 4. As compared to that for the as-received sample, the intensities of the diffraction peaks corresponding to Pt decrease significantly for the sample with 80% dissolution, while the peaks disappear for that with 95% dissolution. The average crystallite size (L) of the Pt nanoparticles estimated by using Scherrer formula \( L = \frac{0.9 \lambda}{\beta \cos \theta} \) with \( \lambda \), \( \theta \) and \( \beta \) being the X-ray wavelength, the Bragg’s diffraction angle and peak width (2\( \Delta \theta \)) of Pt (111) diffraction peak, respectively is 2.9 and 2.6 nm for the as-received and the 80% dissolution electrodes, respectively. Here, the integral width (FWHM\( \times \pi/2 \)) of the Lorentzian fit to the XRD data has been taken as \( \beta \), without corrections for the instrument broadening etc.
Fig. 4: (a) Variations of %dissolution of Pt with number of potential cycles in three different electrolytes (electrode> 10 mm diameter MEA-CC with total Pt loading ~1 mg; electrolyte volume: 12 mL). (b) XRD patterns of as-received and post-dissolution MEA-CC electrodes. The later were treated electrochemically treated by potential cycling between 0.4 and 1.6 V at a scan rate of 100 mV/s in 0.1 M HCl+0.1 M CuCl₂ electrolyte for 50 (80% dissolution) and 100 cycles (95% dissolution).

Evolutions of the Pt nanoparticle density and the particle size during the fuel cell operation have been revealed through TEM images of Fig. 5a-5b. TEM images of the pristine Pt/C electrocatalyst (60 wt.% Pt on C) and of the as-received MEA-CC samples are shown respectively in Fig. 5a and 5b. During fuel cell operation the average size of the Pt nanoparticles exhibits significant growth from 2.6 nm for pristine electrocatalyst to 7.3 nm for the as-received MEA-CC electrocatalyst. Moreover, the larger particle size of the as-received MEA-CC as compared to the XRD crystallite size (2.9 nm) may be attributed to the polycrystalline nature of the Pt nanoparticles. Further, similar to that revealed by XRD studies, the average particle size decreases with Pt dissolution (Fig. 5c-5d), indicating negligible Ostwald ripening through redeposition of Pt during the dissolution process. Further, the
total number of Pt nanoparticles decreases with increasing %dissolution, as expected. Moreover, the
catalyst support, carbon spheres appear intact after the dissolution process.

Fig. 5: (a) TEM images of (a) the pristine Pt/C catalyst (60 wt.% Pt on C) used to fabricate the MEA-
CC electrodes and (b) the as-received MEA-CC electrodes (used in fuel cell). The size distribution
histogram of the Pt nanoparticles of (a) and (b) are shown as inset graphs. (c) and (d) show the TEM
images of the MEA-CC electrodes electrochemically treated by potential cycling between 0.4 and 1.6
V at a scan rate of 100 mV/s in 0.1 M HCl+0.1 M CuCl₂ electrolyte for 50 and 100 cycles,
respectively.
To study the recovery of Pt from MEA-CC, electrochemical dissolution of Pt from a MEA-CC electrode (9.5 × 7.5 cm²) with average Pt loading of 1.19 mg/cm² is performed by potential cycling for 500 cycles between 0.4 and 1.6 V in 70 mL of 1 M HCl, dissolving ~50 mg of Pt (~60% dissolution), to obtain a Pt concentration of ~0.71 mg/mL. The Pt is recovered from the electrolyte in form of (NH₄)₂PtCl₆ by precipitation through addition of ammonium chloride to a concentration of 1 M, as the amount of (NH₄)₂PtCl₆ precipitation is found to saturate for the ammonium chloride concentrations > 0.5 M. Fig. 6 shows the XRD diffraction patterns of the recovered (NH₄)₂PtCl₆ and a high purity (>99.5%) commercial (NH₄)₂PtCl₆ sample. The precursor solution for the recovered (NH₄)₂PtCl₆ was prepared by electrochemical treatment of the MEA-CC electrode by potential cycling between 0.4 and 1.6 V at a scan rate of 100 mV/s in 1 M HCl for 1000 cycles. Diffraction peaks at identical positions in the two diffraction patterns confirms the recovered product to be (NH₄)₂PtCl₆. The peak intensity differences between the two compounds might be due to different processing parameters leading to different texture.³¹ Also, absence of ‘extra’ peaks in the recovered (NH₄)₂PtCl₆ indicate absence of any crystalline impurities. Purity of the recovered (NH₄)₂PtCl₆ is determined by dissolving a known amount of the salt in 0.1 M HCl and measuring the Pt concentration through AAS, showing a purity of ~100 % (Details: supplementary information: S2).
**Fig. 6:** XRD patterns of (NH₄)₂PtCl₆ samples, with (NH₄)₂PtCl₆ –C and (NH₄)₂PtCl₆ –MEA-CC corresponding respectively to the commercial and the synthesized samples.

Individual and overall efficiency of Pt recovery from the spent fuel cell electrode is summarized in the table 2. The efficiency losses are assigned to various process steps, namely (1) delamination of MEA, (2) dissolution of Pt from CC-MEA, (3) precipitation of dissolved Pt and (4) reduction of the precipitated Pt-salt.

<table>
<thead>
<tr>
<th>Step</th>
<th>Efficiency</th>
<th>Comment on efficiency loss</th>
</tr>
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<tbody>
<tr>
<td>(1) Delamination of MEA</td>
<td>0.96</td>
<td>Imperfect separation of CL from PEM and/or Pt nanoparticles being entrapped inside the PEM</td>
</tr>
<tr>
<td>(2) Dissolution of Pt</td>
<td>0.98</td>
<td>Imperfect dissolution possibly due to presence of inaccessible Pt nanoparticles or unoptimized experiment conditions</td>
</tr>
<tr>
<td>(3) Precipitation of dissolved Pt</td>
<td>0.96</td>
<td>Imperfect precipitation due to solubility of (NH₄)₂PtCl₆</td>
</tr>
<tr>
<td>(4) Reduction of (NH₄)₂PtCl₆</td>
<td>1.00</td>
<td>Complete reduction is achieved (reflux time: 2h)</td>
</tr>
<tr>
<td>Overall</td>
<td>0.90</td>
<td>Higher efficiency may be achieved by improving delamination/precipitation steps.</td>
</tr>
</tbody>
</table>
Here, firstly, the delamination loss is the fractional Pt loading on the delaminated PEM, may be subdivided to (i) the loss due to imperfect separation of CL from PEM, leading to fraction of the CL being attached to the PEM and (ii) the loss due to Pt nanoparticles inside the PEM, grown by reduction of mobile Pt-ions inside the PEM during the PEMFC operation. While the former may be minimized by optimizing the delamination process, a separate recovery of Pt from the PEM could be applied to minimize the latter contribution. Secondly, the loss due to imperfect dissolution may be minimized by optimizing the electrochemical treatment (cycle number, potential range, potential form, current distribution, electrolyte, etc.). Thirdly, recovery of the dissolved Pt through precipitation in form of (NH₄)₂PtCl₆ leads a loss of 4%. However, this could either be minimized by increasing the Pt concentration in the electrolyte and/or decreasing the (NH₄)₂PtCl₆ solubility (e.g. by lowering the bath temperature) or be averted by using alternative Pt/C synthesis route avoiding the precipitation step. One such alternative approach to synthesize Pt/C through ethanol reduction (Pt precursor/ethanol ratio: 1/1 v/v) of the dissolved Pt on Vulcan XC 72 carbon by refluxing (2h) in a basic bath (pH adjustment through NaOH) has been studied here (Details: supplementary information: S1). However, the Pt/C synthesized through direct reduction show a relatively poor electrochemical performance due to larger particle size. Last, reduction of the (NH₄)₂PtCl₆ salt gives 100% efficiency. This non hydroscopic salt turned out to be an excellent Pt precursor for catalyst synthesis, which is further optimized and discussed in detail in a separate work.

3.4 Characterizations on Pt/C based on the recycled precursor

XRD pattern of the Pt/C synthesized through polyol route from the recovered (NH₄)₂PtCl₆ exhibits diffraction peaks corresponding to the support carbon and to the polycrystalline Pt similar to that of 20% Pt/C (BASF), as shown in Fig. 7a and 7b. The crystalline sizes of the Pt nanoparticles calculated
using Scherrer formula for Pt (111) peaks are 2.3 and 2.1 nm, for the Pt/C-MEA-CC and the 20% Pt/C (BASF) samples, respectively. These may be compared with the particle size values obtained from microscopic analysis of the samples. TEM images and corresponding particle size histograms (Inset) of the pristine Pt/C-MEA-CC and 20% Pt/C (BASF) samples are shown in Fig. 7c and Fig. 7d, respectively, with their respective average particle sizes of 2.6 and 3.0 nm. In general, the larger particle size (TEM determination) as compared to the corresponding crystallite size values (XRD determination) of the two samples may be attributed to the agglomeration of single crystalline Pt nanoparticles and/or the presence of polycrystalline particles with multiple crystallites. Comparatively larger difference between the crystallite and the particle sizes for the 20% Pt/C (BASF) sample suggests a higher degree of agglomeration, which is evident in the TEM image as well (Fig. 7d). No significant agglomeration of the Pt nanoparticles is observed for the Pt/C-MEA-CC sample, as reflected through the corresponding TEM image showing a uniform distribution of the Pt nanoparticles without agglomeration.
Fig. 7: XRD patterns of (a) the Pt/C-MEA-CC and (b) the 20% Pt/C (BASF) samples. TEM images of (c) the Pt/C-MEA-CC and (d) the 20% Pt/C (BASF) samples along with corresponding particle size distribution histograms (Inset).

Fig. 8 (a) shows the cyclic voltammograms corresponding to Pt/C-MEA-CC and 20% Pt/C (BASF) electrocatalysts collected in N₂ saturated 1 M H₂SO₄ at a scan rate of 10 mV/s before AST. The current values have been normalized to the Pt loadings on the electrode. The voltammograms exhibit cathodic peaks corresponding to Pt/oxide reduction (∼0.7 V) and H⁺ adsorption (between ∼0.4 and ∼0.05 V) and anodic peaks corresponding to the H⁺ desorption (between ∼0.05 and ∼0.4 V) and Pt/oxide formation (≥1.0 V). The initial ECSA values for Pt/C-MEA-CC and 20% Pt/C (BASF)
samples are observed to be 80.6 and 58.8 m²/g, respectively. This may be attributed to the smaller average Pt nanoparticle size for the Pt/C-MEA-CC sample (2.6 nm) as compared to that for the 20% Pt/C (BASF) sample (3.0 nm), as revealed by the TEM imaging. Fig. 8b shows the observational cyclic voltammograms of the GC modified with the Pt/C-MEA-CC electrocatalyst synthesized from the recycled (NH₄)₂PtCl₆ collected at different number of stress cycles during AST in N₂ saturated 1 M H₂SO₄. With stress cycling, the peak intensities vary due to change in ECSA of the Pt electrocatalyst.

Variations of the %ECSA with number of stress cycles during AST of the Pt/C-MEA-CC and 20% Pt/C (BASF) electrocatalysts have been shown in Fig. 8c. The Pt/C-MEA-CC electrocatalyst appears less durable as compared to 20% Pt/C (BASF). Further, the lower durability (Higher loss of %ECSA during AST) of the Pt/C-MEA-CC may also be attributed to its smaller initial particle size as compared to that of the Pt/C 20% (BASF). TEM image of the post-AST Pt/C-MEA-CC sample has been shown in Fig. 8d, along with the corresponding particle size histogram (Inset). The Pt nanoparticles grow significantly during AST to an average particle of 5.5 nm as compared to that of 2.6 nm for the pristine Pt/C-MEA-CC sample. Similar growth of Pt nanoparticles has been observed previously for the commercial Pt/C electrocatalysts as well. However, we would like to point out that such particle growth phenomenon is a dominant and artificially amplified degradation mechanism for catalyst AST evaluation in aqueous electrolyte, which is significantly reduced in solid electrolyte environment.
Fig. 8: (a) cyclic voltammograms corresponding to Pt/C-MEA-CC and 20% Pt/C (BASF) electrocatalysts (current normalized to Pt loading on electrode) collected in N2 saturated 1 M H2SO4 at a scan rate of 10 mV/s (without stress cycling). (b) Cyclic voltammograms recorded at a scan rate of 10 mV/s in nitrogen-saturated 1 M H2SO4 during AST (0.4–1.6 V; scan rate: 1 V/s) of a Pt/C-MEA-CC electrocatalyst modified GC. Legends show the number of stress cycles applied before the CV recording. (c) Variations of %ECSA values with number of stress cycles during AST of the GC electrodes modified with (i) Pt/C-MEA-CC and (ii) 20% Pt/C-BASF electrocatalysts (1600 cycles between 0.4–1.6 V at a scan rate of
1 V/s in N\textsubscript{2}-saturated 1 M H\textsubscript{2}SO\textsubscript{4}). (d) TEM image and corresponding particle size distribution histogram (Inset) of the Pt nanoparticles from the post/AST Pt/C-MEA-CC sample.

4. Conclusions

In conclusion, recycling of carbon supported Pt (Pt/C) electrocatalysts from a spent PEMFC electrode through recovery of the spent Pt by electrochemical dissolution in dilute acidic bath, precipitation of the dissolved Pt in form of (NH\textsubscript{4})\textsubscript{2}PtCl\textsubscript{6}, a non-hygrosopic Pt-salt, and synthesis of Pt/C electrocatalyst from the precipitated Pt-salt by polyol route has been demonstrated. The carbon cloth-based GDLs of the high-temperature PEMFC can be delaminated by cycling wetting to get the catalyst-layer being preferentially attached to the GDL (efficiency: 96%). Pt nanoparticles from the catalyst layer, owing to their (i) high surface/volume ratio leading to high activity and (ii) electronic connectivity to the GDL, are dissolved (efficiency: 98%) electrochemically in dilute acidic (HCl) bath to achieve a Pt concentration of \(\sim0.7\ mg/mL\). Recovery of Pt from such dilute baths is achieved in form of (NH\textsubscript{4})\textsubscript{2}PtCl\textsubscript{6} (efficiency: 96%), which is finally used to form Pt/C electrocatalyst by reduction through ethylene glycol (efficiency: 100%). Overall, the electrochemical performance of the Pt/C-MEA-CC electrocatalysts is comparable to that of the commercial Pt/C electrocatalysts. The scalable process, with an overall efficiency \(>90\%\), may be used for large-scale industrial recycling of the spent Pt-based catalysts, especially from the PEMFCs.

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References


Supplementary information on

Pt/C electrocatalyst synthesis from recycling of the spent PEMFC membrane electrode assembly – a closed loop circular economy

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S1: Synthesis of Pt/C from dissolved Pt precursor (Alternative approach)

Pt/C was synthesized by reduction of the Pt precursor obtained by dissolving Pt from CC-MEA electrochemically (500 cycles between 0.4 and 1.6 V; scan rate: 100 mV/s) in 1 M HCl. Firstly, pH of the precursor was adjusted to 12 by adding NaOH pallets. A purification step (centrifuging at 500 RPM for 20 min) was applied to remove any precipitate from the bath. Further, Vulcan XC 72 carbon dispersed ultrasonically in equal volume of ethanol was mixed with the pH adjusted Pt precursor bath. The Pt to C weight ratio was set to be ¼ to obtain a 20 wt.% Pt/C catalyst. The mixture was refluxed for 2h and cooled overnight before centrifugal separation of the Pt/C. Catalyst ink preparation and electrochemical measurements were performed according to the procedures described in the main text of the manuscript.

Figures S1 and S2 respectively show the cyclic voltammogram and XRD pattern of the Pt/C synthesized through ethanol reduction (Pt/C-CC-MEA (Ethanol)). The electrochemical surface area (ECSA) of the Pt/C-CC-MEA (Ethanol) is observed to be 27 m²/g, significantly lower than that of
the Pt/C-CC-MEA (synthesized by precipitation of ($\text{NH}_4$)$_2\text{PtCl}_6$ and ethylene glycol reduction), owing to its larger Pt nanoparticle size (5.1 nm).

Fig. S1: Cyclic voltammogram of Pt/C-CC-MEA (Ethanol)
**S2: Determination of (NH₄)₂PtCl₆ purity**

The (NH₄)₂PtCl₆ purity was determined by dissolving a known amount of the salt in 0.1 M HCl and measuring the Pt concentration through AAS. Table S1 shows the details of the purity measurement.

Table S1: Purity determination of synthesized (NH₄)₂PtCl₆

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount of (NH₄)₂PtCl₆</th>
<th>Pt weight</th>
<th>Solution vol.</th>
<th>Dilution factor</th>
<th>AAS reading</th>
<th>Pt concentration (mg/mL)</th>
<th>Total Pt (mg)</th>
<th>Pt purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH₄)₂PtCl₆</td>
<td>7.12</td>
<td>3.13</td>
<td>5.0</td>
<td>2000</td>
<td>315.5</td>
<td>0.63</td>
<td>3.16</td>
<td>100.8</td>
</tr>
</tbody>
</table>

Fig. S2: XRD pattern of Pt/C-CC-MEA (Ethanol)