In situ grown nanoscale platinum on carbon powder as catalyst layer in proton exchange membrane fuel cells (PEMFCs)

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Abstract
An extensive study has been conducted on the proton exchange membrane fuel cells (PEMFCs) with reducing Pt loading. This is commonly achieved by developing methods to increase the utilization of the platinum in the catalyst layer of the electrodes. In this paper, a novel process of the catalyst layers was introduced and investigated. A mixture of carbon powder and Nafion solution was sprayed on the glassy carbon electrode (GCE) to form a thin carbon layer. Then Pt particles were deposited on the surface by reducing hexachloroplatinic (IV) acid hexahydrate with methanoic acid. SEM images showed a continuous Pt gradient profile among the thickness direction of the catalytic layer by the novel method. The Pt nanowires grown are in the size of 3 nm (diameter) × 10 nm (length) by high solution TEM image. The novel catalyst layer was characterized by cyclic voltammetry (CV) and scanning electron microscope (SEM) as compared with commercial Pt/C black and Pt catalyst layer obtained from sputtering. The results showed that the platinum nanoparticles deposited on the carbon powder were highly utilized as they directly faced the gas diffusion layer and offered easy access to reactants (oxygen or hydrogen).

Key words
platinum; catalyst layer; carbon powder layer; proton exchange membrane fuel cells

1. Introduction
Polymer electrolyte membrane fuel cells (PEMFCs) are being considered for wide commercial and military applications, such as portable electronic devices, automobiles, backup power sources and residential power systems, due to their high energy density, reliability and zero emission. Their commercialisation steps largely rely on the cost of electrolyte membrane and platinum (Pt) catalyst. Two ways to lower the catalyst cost are to reduce the loading amount of Pt or replace it with non-noble metals [1−8] while keeping their performance. Recently, efforts directed at improving the utilization efficiency of Pt catalyst have been focused on finding the optimal material configuration subjected to the requirement of the minimum Pt loading while satisfying the conditions of proton access, gas access, and electronic continuity.

The common method to fabricate the catalyst layer is to mix Pt/C catalyst with a solubilized polymer electrolyte, e.g. Nafion ionomer, and then apply the ink on a diffusion layer or a piece of electrolyte membrane by blade, decal or spray method. In this case, inactive catalyst sites are always present in catalyst layers, especially the part far from diffusion layers (i.e., near the membrane), causing reactant transport resistance. These inactive sites are not available for fuel cell reaction because they are not at the interface between polymer electrolyte (e.g., Nafion) and Pt catalyst which is exposed to reactant. Therefore, thickness of the catalyst layer is reduced by adopting Pt/C catalyst with high Pt content, for example with 50%−70% Pt, compared with 10%−30% previously.

Recently, in situ growth or deposition of Pt, including reducing impregnation, spraying, electrodeposition, and sputter deposition, directly on the membrane or the diffusion layer has been suggested by a number of workers [9−20]. Lee et al. [11] prepared low Pt loading electrodes by galvanostatic pulse electrodeposition on a Nafion-bonded carbon layer. Since the electrodeposition of Pt in aqueous solution occurred only on the carbon surface with some ion conductivity (Nafion-Na+), it was possible to significantly reduce the thickness of the catalyst layer as well as the amount of Pt loading. Thus, it provided enhanced utilization efficiency of catalyst. Saha et al. [12] developed an improved catalyst deposition methodology.
based on a piezo-electric printing technique and thus fabricated catalyst coated membranes (CCM) with thin catalyst layers (1.5 μm) and ultra-low Pt loadings (0.02–0.12 mg Pt/cm²). Yoo et al. [13] used a RF magnetron sputter technique at high pressure to deposit Pt nanocatalyst on gas diffusion layer for high utilization of Pt. Kreidler et al. [14] reported a fabrication method in which Pt and Pt alloy thin films were sputter-deposited onto carbon/Nafion decals. The results showed that improved mass performance and catalyst utilization were observed with Pt thin films and that increased mass activities were achieved with PtCo (76 : 24) and PtCr (80 : 20) alloys compared with pure Pt. Choe et al. [21] introduced a procedure to locate the Pt nanostructure inside the hydrophilic channel of Nafion membrane in order to enhance Pt utilization in PEMFCs.

The gradient distribution of Pt, electrolyte and porosity along the thickness in the catalyst layers effectively depressed the transport resistance of proton and gas. Zhu et al. [22] demonstrated a functionally graded catalyst layer based on a double-layered carbon nanotube/nanofiber film-(bucky paper) supported Pt composite catalyst to approach an idealized microstructure. They used a pulse electrodeposition technique to deposit Pt nanoparticles onto the bucky paper. To decrease the conflict between improving mass transfer and maintaining good Pt utilization, Su et al. [23] suggested a novel DCL cathode structure which was prepared using catalysts with two different amounts of Pt; the catalyst with higher Pt content was used in the inner layer to concentrate the Pt, and the catalyst containing less Pt was used in the outer layer to maintain a suitable layer thickness.

Some authors considered coating the Pt catalyst on the membrane. Li et al. [24] presented a method that combined coating Pt seeds on the C-Nafion substrate and introducing polyethylene glycol (PEG) into the deposition solution. The result showed that Pt seeds and PEG play an important role in the morphology of the Pt deposit and the active surface area and electrocatalytic activity of the Pt catalyst prepared towards oxygen reduction reaction (ORR) were improved remarkably. Haug et al. [17] showed that sputter-depositing a single layer of Pt on the gas diffusion layer provided better performance with ~0.28 A/cm² at 0.6 V than that of sputtering the Pt directly onto a Nafion membrane with ~0.065 A/cm² at 0.6 V and the two methods equaled the performance of the baseline for an equivalent Pt loading.

Du et al. [9,10] introduced an in situ grown Pt on gas diffusion layer (GDL) by chemical reduction. But the condensed layer of deposited Pt near the GDLs could lead to high resistance for reactant diffusion, which might produce insufficient oxygen feeding at high current densities. To make reactant access to Pt surface easier, in this work, a novel in situ Pt growth method was introduced for catalyst layer preparation. In detail, a catalyst layer with in situ grown nanoscale platinum particles on carbon powder coated on the membrane surface was prepared. This method was compared with conventional methods of Pt/C catalyst and sputtering Pt by SEM, TEM, XRD and CV characterization.

2. Experimental

2.1. Preparation of catalyst layer on glassy carbon electrodes (GCEs)

A mixture of carbon powder (XC-72R, Cabot) and Nafion (DuPont) in isopropanol solution was sprayed on GCEs (CH Instruments, Inc.) to form a thin layer of carbon powder. Then a catalyst layer was coated on the above layer by three methods as following: (a) Pt particles were reduced by methanoic acid (Sinopharm Chemical Reagent Co., Ltd) from hexachloroplatinic (IV) acid hexahydrate (Shanghai Chemical Reagent Research Institute) and deposited on the carbon layer surface at room temperature for 24 h; (b) the mixture of 50 wt% Pt/C catalyst (9100 HispecTM, Johnson-Matthey) and Nafion in isopropanol solution was directly dropped on the carbon layer of GCEs; (c) the platinum was loaded on conductive adhesive by JS-1600 sputtering device (Beijing HTCY Technology Co.).

2.2. Fabrication of membrane electrode assembly (MEA)

50% Nanoscale Pt/C catalyst (Johnson Matthey, Hispec 8000 catalyst) was chosen as anode catalyst. On the other side, reduced Pt deposited on carbon powder was as cathode catalyst.

The home-made MEAs were prepared as follows: (a) A mixture of 5 wt% Nafion solution, Pt/C catalyst and isopropanol (Nafion: Pt/C = 1 : 5) was dispersed to form a slurry in ultrasound agitator for 10 min and then the slurry was sprayed over a Nafion membrane (NR212, Dupont) at temperature range from 35 °C to 40 °C under infrared lamp to form the anode; (b) A mixture of carbon powder and Nafion solution was sprayed on the cathode side of the membrane. After drying for 30 min, the membrane was moved to a hexachloroplatinic (IV) acid hexahydrate solution with the cathode side on the top. Methanoic acid was added to the solution. Then the solution was stored at room temperature for 24 h; (c) Two pieces of carbon paper (TGP-H-060, Toray) were treated with 10%–20% PTFE solution (TF-5203Z, 3M) and then baked out in an oven at 380 °C for 2 h; (d) After drying, the Nafion membrane with one catalyst layer on each side was hot-pressed together with the above two pieces of carbon-coated carbon paper.

2.3. Physical characterization

An X-ray diffractometer from Rigaku Corporation D/max-2200/PC was used to measure the X-ray diffraction (XRD) patterns of the catalyst sample. Scans were acquired with a rate of 0.1 °/s over 2θ range of 20°–90° with Cu-Kα radiation (λ = 1.54056 Å).

A specimen for electron microscopy was prepared by ultrasonic dispersion in ethanol, taking a droplet of electrocatalyst suspension in ethanol on a 3mm-size copper grid, and dry-
ing under an infrared lamp for 5 min at 40 °C. For high resolution electron microscopy, a JEM-2010 transmission electron microscope was used.

The surface image of the catalyst layer with deposited platinum was characterized by SEM (SP2600, Hitachi), compared with commercial Pt/C and sputtering platinum samples, and Pt profile at different positions of a in situ grown catalyst layer was characterized by SEM (S-4800, Hitachi). And the elementary analysis of the regions on the surface of catalyst layers was determined by energy-dispersive X-ray spectroscopy (EDS). A 7500a Inductively Coupled Plasma Mass Spectrometer (Agilent) was used to determine the catalyst loading on different samples.

2.4. Cyclic voltammetry (CV) tests

The GCEs were tested in a three-electrode cell by a Potentiostat/Galvanostat (Model 1287A, Solartron) in 0.5 M H2SO4 (GR, Sinopharm Chemical Reagent Co., Ltd). Cyclic voltammograms were obtained at a potential sweep rate of 50 mV s−1 vs saturated calomel electrode (SCE). All the samples were scanned for 30 sweep circles before the steady-state curves were recorded.

2.5. Performance evaluation of the fuel cell

Performance evaluation was carried out in a single cell with an active area of 33×33 mm². The cell was operated at 60 °C at atmospheric pressure. And the reactant feeds were kept at constant rates of 300/600 mL/min (H2/O2), respectively. The humidification temperatures of H2 and O2 were 60 °C, the same as that of the cell. Minitest 3000 fuel cell test system (TOYO Co.) was used. The fuel cell set consists of an MEA, two graphite plates with serpentine flow-channels (1 mm in width and 1 mm in depth), two gold-plated copper plates and two titanium end plates.

3. Results and discussion

3.1. Three catalyst layer structures

Figure 1 demonstrates three different catalyst layer structures. In conventional structure (model a), the catalyst ink is sprayed onto the membrane or carbon paper and then hot-pressed together with the other, shown in Figure 1(a). Recently, some researchers developed sputtering or deposition method (model b) to achieve high utilization of platinum, shown in Figure 1(b) [9,14,15]. Compared with conventional catalyst coating method, model b is simpler as no catalyst spraying process is needed. Its catalysts are directly loaded on gas diffusion layer. But in hot-pressing procedure, part of the platinum surface exposed could be covered by the membrane. Moreover, it could produce large diffusion resistance to prevent the reactant going through the carbon powders. This will result in insufficient fuel or oxygen feed to the three phase boundaries, i.e. lack of catalyst exposure to gases.

2.4. Cyclic voltammetry (CV) tests

Through modification of model b, model c is introduced in this work. In this method, Pt is reduced and grown on a thin carbon layer which is coated on the membrane. Pt surface faced carbon paper and the gases access it in the shortest route. High platinum utilization can be expected. As the thin catalyst layer close to the membrane, resistance in proton transfer is less than conventional ways like in model a. Moreover, this method is much simpler than the conventional CCM method because there was no process needed to make the ink or print the catalyst layers.

The reduction in model c takes place according to the following reaction [9]:

\[
\text{H}_2\text{PtCl}_6 + 2\text{HCOOH} \rightarrow \text{Pt} + 6\text{Cl}^- + 6\text{H}^+ + 2\text{CO}_2
\]

In this reaction, the color of the solution slowly changed from yellow to colorless. At room temperature, H2PtCl6 can slowly be reduced by a weak reducing agent such as methanoic acid and platinum favored the growth of specific crystal faces [9,10]. Pt particle size and morphology can be controlled by adjusting the reaction condition, such as the temperature, reactant concentration and reductive agent.

3.2. SEM, TEM and XRD characterization

The surface morphology of three catalyst layers was shown by SEM images (Figure 2). It can be seen that for the in situ Pt growth sample in (c), the Pt particles reduced (light spots) from hexachloroplatinic (IV) acid were well distributed onto carbon particles. Compared to commercial Pt/C catalyst and sputtered platinum, the surface of carbon particles where Pt grows is much coarse, meaning that fine platinum particles were obtained. Regional EDS results showed that there were more Pt particles loaded on the carbon powder layer in in situ grown sample (67.06% Pt) than in the commercial 50% Pt/C sample (52.49% Pt) and the sputtering sample (26.23% Pt). The Pt contents from EDS to some extent demonstrated a similar Pt dispersion between the commercial 50% Pt/C and the in situ grown Pt sample.

Figure 3 showed SEM images of different regions of the catalyst layer with present method among thickness direction, which faced to the diffusion layer (a) was with a dense Pt
nano-wire distribution, and that near the membrane (c) was with a sparse particles distribution. Therefore, a Pt catalyst gradient for the active layer with Pt loading 0.4 mg/cm$^2$ from high to low concentration was as the order: (a) outer (near diffusion layer)→(b) middle→(c) inner (near membrane). This gradient structure is with a continuous Pt profile and can be easily adjusted by the carbon matrix and deposition condition, different from multilayer structure with a non-continuous Pt profile [22,23].

Figure 2. SEM images of surface morphology of three different catalyst layers: (a) commercial Pt/C, (b) sputtering Pt, (c) in situ grown Pt

As shown in Figure 4, the in situ grown Pt is nanowire with size of 3 nm (diameter)×10 nm (length) by high solution TEM image. Sun S et al. [25] proved those Pt nanowires are with both better catalytic activity and durability than those of commercial Pt/C catalysts. In Figure 5, the XRD patterns indicated that the in situ grown Pt had narrower peaks than that of commercial Pt/C catalyst (Johnson Matthey, HiSPEC 8000 catalyst). This confirmed that the in situ grown Pt nanowires are with crystal structure and more stable than amorphous Pt/C.

Figure 3. Pt profile of a catalyst layer with Pt loading of 0.4 mg/cm$^2$ by SEM images: (a) outer (near diffusion layer), (b) middle, (c) inner (near membrane)

Pt wires shown in Figure 4 were shorter than that reported in reference [9], where their nanowires can be as long
as 100−150 nm [9,10]. As described in reference [20], on-membrane deposition was different with on-GDL deposition by electrospray for the preparation of catalyst layers. The catalyst layer deposited on membrane is globular morphology as compared with the dendritic morphology on GDL. As reported in reference [24], through adjusting the reaction condition, e.g. the temperature, reagent concentration or adding active agents, larger surface area and the coarseness of catalyst surface could be expected. For example the result in reference [24] showed that Pt seeds and PEG play an important role in the morphology of Pt deposit and the active surface area.

3.3. CV measurements

In this section, three different kinds of catalyst layers were compared by electrochemical cyclic voltammetry (CV) measurement. Figure 6 and Figure 7 show the voltammograms of platinum electrode prepared with commercial Pt/C catalyst, in situ grown Pt and sputtering Pt in nitrogen and oxygen atmosphere respectively. The current peaks of the hydrogen region and the formation-reduction of oxidized platinum slowly increased after several scans. Steady-state curves were obtained after 30 potential sweeps. The Pt loadings of the samples were obtained from ICP tests.

In Figure 6(a), the area of hydrogen absorption-desorption peak increased with the Pt loading (0.26, 0.52, and 0.77 mg/cm²) of the in situ deposition samples. The maximum geometric area was obtained at a loading of 0.77 mg/cm², slightly larger than that of commercial Pt/C (0.29 mgPt/cm²). Considering the loading, the electrochemical activity surface area (ECSA) of the in situ grown Pt was smaller than that of the Pt/C.

In Figure 6(b), the initial potential of oxygen reduction peak for in situ grown sample was the same as that for the commercial sample, and the peak intensity for 0.77 mg/cm² loading sample was slightly larger, indicating the former catalyst was more active than the latter. It is noticed that the in situ grown samples have narrower oxygen reduction peaks compared with Pt/C catalyst.

In Figure 7, the sputtering sample showed a much lower current response in both nitrogen and oxygen atmospheres. And as the platinum was sputtered onto a piece of conductive adhesive tape, a blank CV measurement was taken for comparison with the sputtering sample. The results showed hydrogen adsorption-desorption peak was obviously wider than that of the blank, and the oxygen peak of the former was accompanied with some side reactions. This was due to the low loading (0.07 mg/cm²) and the smaller surface area of sputtered platinum, and small amount Pt was active for the organic compounds in the conductive adhesive tape.
By comparing CV results, the areas of hydrogen absorption-desorption peak of the four samples are in the order: commercial Pt/C (0.29 mg Pt/cm²) > the in situ deposition sample (0.26 mg Pt/cm²) > the sputtering sample (0.07 mg Pt/cm²) > the conductive adhesive tape (blank test). This is consistent with that smaller Pt particle size, the larger surface area in the condition of the same loading.

3.4. Performance test with the novel cathode

Figure 8 is a polarization curve of the fuel cell with the novel cathode catalyst layer with in situ grown nanoscale Pt. It could be seen that the open circuit voltage was 0.995 V. The current density reached 1.3 A/cm² at the voltage of 0.5 V in hydrogen/oxygen feeds. The max power density was 0.64 W/cm². Through optimizing Pt growth and MEA structure, better performance could be expected.

4. Conclusions

A novel method of in situ Pt growth was introduced in this paper. Pt was reduced and deposited on a thin carbon layer coated on the polymer electrolyte membrane. SEM showed the platinum nanoparticles grew uniformly on carbon surface in dendritic morphology and were a continuous Pt gradient profile among the thickness direction of the reaction layer. The Pt nanowires are in the size of 3 nm (diameter) × 10 nm (length) by high solution TEM images. Similar roughness was observed for in situ grown Pt and commercial Pt/C, while the sputtering sample showed a smoother surface. CV tests demonstrated the electrochemical surface area (ECSA) of the samples in the order of Pt/C > in situ grown Pt > sputtering Pt. Considering easier oxygen access to the in situ grown Pt, this method offered a route for making high performance PEM-FCs. Further works are suggested on optimizing Pt growth and MEA structure to achieve an ultra-low Pt loading.

Acknowledgements

This work was financially supported by award from the Royal Academy of Engineering, UK. ICP characterization was completed at the Instrumental Analysis Center of Shanghai Jiao Tong University (IAC-SJTU).

References