A novel catalyst layer with carbon matrix for Pt nanowire growth in proton exchange membrane fuel cells (PEMFCs)

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Abstract

Novel catalyst layers for proton exchange membrane fuel cells (PEMFCs) were investigated by in-situ growing of Pt nanowires (Pt-NWs) on carbon matrix. The Pt-NWs grew on the matrix along the thickness direction with a length of 10–20 nm and a diameter of 4 nm. In-situ cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and polarization experiments were employed to characterize the electrochemical performance of the Pt-NWs electrodes. The results showed that the predominantly [111]-oriented facets and oxygen access of the Pt-NWs structure contribute to the higher performance in comparison with that of the conventional catalyst layers. This work is advantageous for fuel cell catalyst layer design by allowing the controlled modification of both Pt distribution and pore size.

Keywords:
Pt nanowires
Carbon matrix
In-situ growth
Catalyst layers
PEM fuel cells

1. Introduction

Despite significant advances on platinum-based and non-platinum catalyst, membrane electrode assemblies (MEAs) prepared by highly dispersed Pt nanoparticles (Pt-NPs) on carbon supports (Pt/C) are still being widely used in the state-of-the-art commercial PEMFCs. However, corrosion of the carbon support and Pt dissolution/aggregation/Oswald ripening can reduce the electrochemical surface area (ECSA) of Pt/C catalysts and then degrade fuel cell performance during operation [1].

Catalyst layers (CLs) in PEMFCs facilitate electrochemical reactions and therefore play a critical role in cell performance. In recent years, some techniques, such as Pt deposition [2,3], magnetron sputtering [4,5], electrodeposition [6] and piezoelectric printing technique [7] have been focused on the preparation of the CLs. Du [2] reported growing Pt nanowires (Pt-NWs) in-situ on GDLs at room temperature in aqueous
solution. Weissmann et al. [3] directly deposited platinum at different polymer electrolyte membranes by chemical reduction to increase the electrolyte/catalyst interface. But part of the deposited platinum, inside the membrane, was not accessible and non-electrocatalytically active. Chisaka et al. [4] controlled porosity of Pt catalyst layers by variable deposition angle in a magnetron sputtering process onto gas diffusion layer to achieve efficient reactant flow for high-current density operation. Lertviriyapaisan [6] prepared a substrate by applying a hydrophobic or a hydrophilic sublayer onto an uncatalyzed gas diffusion layer prior to the electrodeposition of the Pt catalyst. Saha et al. [7] developed an improved catalyst deposition methodology based on a piezoelectric printing technique and thus fabricated catalyst coated membranes (CCM) with thin catalyst layers (1.50 μm) and ultra-low Pt loadings (0.02–0.12 mgPt cm⁻²).

Many researchers [2,7–11] investigated 1D Pt nanostructures, such as nanowires and nanorods, by Pt growth methods. Compared to Pt nanoparticles, 1D Pt nanostructures have a better activity and durability for oxygen reduction due to their unique characters in morphologies. Sun et al. [8] showed the multiarmed starlike Pt-NWs on carbon as catalysts with good activity and durability. The growth density and length of Pt-NWs on carbon support could be adjusted by controlling the reduction condition [9]. Also the ordered CL structures improved cell performance due to oriented mass transport [4].

Here we describe a novel catalyst layer with in-situ grown Pt-NWs for PEMFCs, in particular in the cathodes. An ink of carbon powder + Nafion® resin was sprayed on the membranes as the matrix, then Pt-NWs were grown on this by chemical reduction of Pt precursor with formic acid. Compared with the conventional catalyst layers, in-situ grown Pt catalyst layers showed better performance.

2. Experimental

2.1. In-situ grown catalyst layer and MEA preparation

The in-situ grown Pt-NWs catalyst layers were used as the cathodes, and prepared as follows: Firstly, carbon powder (XC-72R, Cabot), Nafion® solution (DE1020, Ion Power) and iso-propanol (Sinopharm Chem. Reagent) (carbon:Nafion® resin = 4:1 wt.%) were well mixed to form ink, and the ink was sprayed onto one side of Nafion® membranes (NR212, DuPont) to form a carbon matrix with 0.20 mg cm⁻² carbon loading. Then the membrane with the painted surface up was immersed with the H₂PtCl₆ solution (Sinopharm Chem. Reagent) and HCOOH (Sinopharm Chem. Reagent). The reduction was left at room temperature for 72 h. Normally, 10.60 mg H₂PtCl₆·6H₂O deposited on this carbon matrix gave Pt loading of 0.40 mg cm⁻². The deposited membrane was rinsed with de-ionized water to remove any ions. After drying, Nafion® solution (dry basis loading of 0.025 mg cm⁻²) was painted onto the surface of Pt-NWs to enlarge the Triple Phase Boundary (TPB). For comparison purposes, a conventional catalyst layer in the cathode was made as described for the anode. The anode catalytic layers of all samples were prepared by the normal processes of spraying the ink of 50 wt.% Pt/C catalyst (9100 HiSPEC, Johnson & Matthey), Nafion® solution and iso-propanol (Pt/C:Nafion® resin = 4:1 wt.%) on Nafion® membranes. The Pt loading in the anode was 0.50 mg cm⁻². Ballard carbon papers (AvCarb GDS3250) were used as gas diffusion layers (GDLs). The catalyst-coated-membrane was “sandwiched” between two GDLs to obtain a MEA for a single cell test, hot pressed at 130 °C under 0.20 MPa for 2 min.

2.2. Physical characterization

Scanning electron microscopy (SEM) observations were performed with a Hitachi S-4800 microscope, operating at 15 kV. Pt line scanning over the thickness region of the catalyst layers was determined by energy-dispersive X-ray spectroscopy (EDS). High-Resolution Transmission Electron Microscopy (HRTEM) images were taken to examine the in-situ grown Pt-NWs on a JEOL 2100F microscope at an accelerating voltage of 200 kV. Inductively Coupled Plasma Mass Spectrometer (ICP-OES) (7500a, Agilent) was used to determine Pt loading of the samples.

2.3. Single cell measurement

A two-serpentine graphite flow field plate was used with an active area of 10 cm². Cell activation, polarization curve and electrochemical impedance spectroscopy (EIS) measurements were carried out at 70 °C and atmosphere pressure, with pure H₂ and air gases fully humidified at 65 °C and flow rates of 150 mL min⁻¹ and 300 mL min⁻¹ (1.5/2.0 stoics), respectively. Before all the tests, freshly assembled cells were activated by repeating two times and eight times of the following cycles, respectively: 0.60 V, 20 min/0.70 V, 20 min/0.80 V, 20 min/0.85 V, 20 min/0.90 V, 20 min/OCV, 20 min, and 0.20 V, 10 min/OCV, 30 s. The polarization curves were conducted with a sweep rate of 20 mV s⁻¹ from OCV to 0.30 V. The EIS measurements were performed at 0.80 V, 0.60 V and 0.40 V in the frequency range from 10 kHz to 0.1 Hz with an AC amplitude of 10% of DC current. In-situ CV experiments were conducted at 35 °C by simultaneously flushing the fuel cell cathode and anode with N₂ and H₂ with fixed flow 75 mL min⁻¹ and 300 mL min⁻¹, respectively. The CV curves for the cathode were recorded by applying the potential range of 0.05 and 1.00 V vs. RHE at a sweep rate of 25 mV s⁻¹. Above measurements were controlled and recorded with an 850e Multi-Range Fuel Cell Test System (Scribner Associates).

3. Results and discussion

Pt was deposited and grown via the chemical reduction of hexachloroplatinic acid with formic acid on the carbon matrix at room temperature. Pt nanonuclei were reduced by the following chemical reaction:

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

The Pt nanonuclei moved into, deposited and grew on the carbon matrix. Pt precursor concentration, reduction time and temperature could affect the length and growth density of the Pt-NWs.
HR-TEM image and Fast Fourier transform (FFT) were used to investigate the morphology and crystallinity of the in-situ grown Pt-NWs. Fig. 1 shows that the Pt-NWs synthesized have a length of 10–20 nm and a diameter of 4 nm. The FFT image of the atomic lattice, in the inset to Fig. 1, further demonstrates the crystallinity of the nanowires grown along the [111] facets, which is in agreement with the results reported by Sun et al. [9].

Compared to the middle and bottom side, the freshly formed nanonuclei would preferentially deposit and grow on the upper side of the catalyst layers. A downward gradient Pt profile in Fig. 2a along the depth towards the membrane is found in the novel in-situ Pt growth catalyst layer by Pt line scanning, as compared with constant Pt contents in Fig. 2b in the conventional catalyst layer. Fig. 3 shows SEM images of novel in-situ grown Pt catalyst layer at the upper side and middle region of the catalyst layers. It can be seen that at the upper side area (Fig. 3a), Pt-NWs coated on the carbon blacks densely, and with the increase of depth only partially covered (Fig. 3b). As the Nafion® content in the catalyst layers will influence their microstructure, the Pt profile can be controlled by adjusting the carbon matrix to get the desired CL structure.

We benchmarked the electrochemical properties of the MEAs with Pt-NWs catalyst layers (Pt loading 0.20 mg cm$^{-2}$ and 0.40 mg cm$^{-2}$) against that with the conventional Pt/C catalyst layer (Pt loading 0.50 mg cm$^{-2}$).

From the CV test shown in Fig. 4, the peak charge densities of the novel cells are obviously smaller than that of the conventional cell with commercial Pt/C catalyst. The hydrogen
desorption peaks were used to calculate the electrochemical specific area (ECSA) and the results are listed in Table 1. ECSAs of 35.42 m² g⁻¹ (0.20 mg cm⁻²) and 35.33 m² g⁻¹ (0.40 mg cm⁻²) are got for the Pt-NWs catalyst layers respectively, smaller than that 47.00 m² g⁻¹ for the Pt/C catalyst layer (0.50 mg cm⁻²). It is as expected due to the smaller Pt particle size (2–5 nm) of Pt/C than that of the Pt-NWs.

Fig. 5 shows the EIS measured at three different potentials. At a high potential of 0.80 V in Fig. 5a, the Nyquist plots of the three cells with the Pt-NWs catalyst or Pt/C catalyst present almost perfect semicircles, which are attributed to the kinetic impedance. Because of its low catalyst loading in the cathode, the cell with 0.20 mg cm⁻² Pt-NWs has the larger charge transfer resistance than the other cells with 0.50 mg cm⁻² Pt/C and 0.40 mg cm⁻² Pt-NWs. The cell with 0.40 mg cm⁻² Pt-NWs has a smaller arc diameter than that of 0.50 mg cm⁻² Pt/C, indicating the higher catalytic activity of the in-situ grown Pt than that of the Pt-NPs of Pt/C catalyst. With the potential decreasing, the kinetic impedances decrease while the diffusion impedances increase, as shown in Fig. 5b and c. Progressively the cell with 0.20 mg cm⁻² Pt-NWs had the least arc diameter (kinetic impedances + diffusion impedances) compared to the others. This may be due to the fact that Pt-NWs are stretching out from the surface of the carbon nanospheres, oxygen diffusion toward the Pt surface is improved. In addition, excess Pt loading in the carbon matrix may block pores and hinder oxygen access.

The polarization curves of the three cells with different cathodes were investigated and the results are shown in Fig. 6. Compared with the conventional cell of 0.50 mg cm⁻², the novel cell of 0.40 mg cm⁻² has a significant improvement in the performance when the current density is more than 0.40 A cm⁻², and the maximum power density is 15% increased (0.39 W cm⁻²–0.34 W cm⁻²). Even for the cell with 0.20 mg cm⁻², its current density is higher than that of the conventional one when the cell voltage is less than 0.40 V. The

<table>
<thead>
<tr>
<th>Cathode (Pt loading) [m/mg Pt cm⁻²]</th>
<th>Current density at 0.90 V [j] [mA cm⁻²]</th>
<th>ORR activity at 0.90 V per Pt mass [j_m]/A g⁻¹ Pt</th>
<th>Pt ECSA [**] [s/m² g⁻¹ Pt]</th>
<th>ORR activity at 0.90 V per Pt area [j_s]/µA cm⁻² Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-NWs (0.20)</td>
<td>8.87</td>
<td>44.35</td>
<td>35.42</td>
<td>125.21</td>
</tr>
<tr>
<td>Pt-NWs (0.40)</td>
<td>17.52</td>
<td>43.80</td>
<td>35.33</td>
<td>123.97</td>
</tr>
<tr>
<td>Pt/C (0.50)</td>
<td>11.68</td>
<td>23.36</td>
<td>47.00</td>
<td>49.70</td>
</tr>
</tbody>
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** As measured in Fig. 5; [***] as measured in Fig. 3. Here j_m = j/m and j_s = 100 * j_m/s.
specific activities of both cathodes for oxygen reduction reaction (ORR) are summarized in Table 1. From a practical viewpoint, the mass activity expressed in A per gram of Pt, at a given voltage (third column in Table 1) is the figure-of-merit of a Pt catalyst. This figure is the result of the electrochemically active Pt surface area (fourth column, Pt area per mass Pt) times the specific activity of Pt (fifth column, ORR current per Pt area at given potential). Although a 34% lower ECSA, the Pt-NWs catalysts show higher specific activities, 1.5-fold mass or 1-fold area of specific ORR activity better than the conventional cathode. The high specific activity of the Pt-NWs was explained by the preferential exposure of certain crystal facets of the former and/or less surface defects bearing [12,13].

4. Conclusions

In this work, we presented a novel catalyst layer structure with carbon matrix for in-situ grown Pt NWs. Pt-NWs grow in the pores along the thickness direction with a length of 10–20 nm and a diameter of 4 nm. The predominantly [111]-oriented facets and oxygen access contribute to the higher performance than that of the conventional CLs. This work thus opens up a new direction for fuel cell catalyst layer design by allowing the controlled modification of both Pt distribution and pore size (diameter and length).

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