



Short Communication

A Facile Route for Polymer Electrolyte Membrane Fuel Cell Electrodes with in situ Grown Pt Nanowires

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ABSTRACT

Novel Gas Diffusion Electrodes (GDEs) for Polymer Electrolyte Membrane Fuel Cells (PEMFCs) were prepared by in situ growing Pt nanowires on carbon paper using a facile deposition method at room temperature. Pt nanowires, with a length 100–150 nm, were uniformly coated on the carbon fiber surfaces in carbon paper. This route was much simpler than the traditional method for preparing GDEs because there were no processes needed to make the ink or print the catalysis layer. Membrane Electrode Assemblies (MEAs) were made with the as-prepared GDEs and tested in a 25 cm² PEMFC fed by hydrogen/air. The impedance spectroscopy and polarization curve measurement showed that the as-prepared GDE possessed a lower charge transfer resistance and a higher power density than did the conventional one with ELAT® GDE LT120EW. The excellent performance obtained and the simple steps made the process a promising technique for preparing GDEs in PEMFCs for commercial applications.

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1. Introduction

As a clean power generator at low temperature, the polymer electrolyte membrane fuel cell (PEMFC) is very attractive. However, PEMFCs still cannot compete commercially in many applications owing to the high cost, the poor durability and reliability [1].

As the key component in PEMFC, the electrocatalyst layer is the place where the electrochemical reactions take place and the electrical energy is produced, exhibiting a great influence on the total performance and durability [2]. Moreover, this catalyst layer is also the most expensive component in the system, including the material cost and the spending on the preparation [3]. The current method for manufacturing the electrocatalyst layer is to make the catalyst ink from the synthesized catalysts supported on the different carbon materials, and then paint it onto the gas diffusion layer (GDL) [4]; or spray it onto a PTFE blank sheet, and then transfer the dried catalyst layer onto the electrolyte membrane [5]. Both methods are complex and the processes need careful controls, which thereby increase the cost and detract from performance and durability [6].

Nanostructured materials are becoming increasingly important in recent years due to their excellent catalytic performances [7,8]. To lower the cost of Pt catalysts, great effort has focused on the devel-

opment of novel nanostructures of Pt catalysts with an enhanced surface area to achieve a high catalytic performance and utilization efficiency [9–11]. Xia and co-workers have directly grown Pt nanowires on Pt or W gauze by a polyol process in the presence of Fe²⁺ or Fe³⁺ and poly(vinyl pyrrolidone) (PVP). The products indicated a higher tolerance to CO-like intermediates and showed a great activity toward methanol oxidation. However, this method needed a high temperature of 110 °C, with surfactant and polyol as solvent [12]. Recently, Sun and co-workers developed a facile wet-chemical method to grow single-crystalline Pt nanowires on the nanospheres of a carbon black via a simple chemical reduction of hexachloroplatinic acid (H₂PtCl₆) with formic acid (HCOOH) at room temperature in aqueous solution. Such Pt nanowire/C nanocomposites showed an enhanced catalytic activity for the oxygen reduction reaction (ORR) compared with a state-of-the-art Pt/C catalyst made of Pt nanoparticles [13]. The method has also been used to synthesize 3D flower-like platinum nanostructures on carbon paper [14], or to prepare urchinlike Pt nanoelectrocatalysts at 30 °C in the presence of PVP [15].

By a small modification of this facile formic acid method, here we demonstrate a very simple and effective wet-chemical route to prepare GDEs for PEMFCs, by growing Pt nanowires in situ on GDLs, which were carried out by simply immersing carbon paper in a mixed solution of hexachloroplatinic acid, formic acid and PVP at room temperature in aqueous solution. The as-prepared GDEs were used as cathodes and tested in 25 cm² PEMFCs fed by hydrogen/air.

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2. Experimental

2.1. Materials

All chemicals were used as accepted without further purification. H_2SO_4 , H_2O_2 , poly(vinyl pyrrolidone) (PVP, M.W. = 55,000), 2-propanol, Ethanol, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (99.95%) and HCOOH (98%) were used as received from Sigma–Aldrich. Nafion® solution DE 1021 10 wt%, E-TEK ELAT® GDE LT120EW (Pt loading 0.5 mg cm^{-2}) and Nafion NRE212 membrane were bought from Fuel Cell Store. Freudenberg GDL H2315 I6 was obtained from Freudenberg FCCT KG. All aqueous solutions were prepared with ultrapure water from an Aquatron D40 Nanopure water system.

2.2. GDE preparation

Freudenberg GDL H2315 I6 carbon paper was used as gas diffusion layer (GDL) and support for growing Pt nanowires. To grow Pt nanowires on the carbon fiber surface, a piece of carbon paper of $5 \text{ cm} \times 5 \text{ cm}$ was used each time. The wet carbon paper was immersed with the aqueous solution of H_2PtCl_6 , HCOOH and PVP in a 10 cm glass Petri dish at room temperature. Typically, for the growth of 0.4 mg cm^{-2} Pt on the carbon paper, $26.6 \text{ mg H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (10 mg Pt, 0.4 mg cm^{-2} on GDL), 1 mL HCOOH and 4 mg PVP were added to 20 mL of water. The solution was added into the glass Petri dish with the carbon paper and stored at room temperature for 72 h. After completion of the Pt reduction reaction and the growth of nanowires onto the substrate, the product was rinsed with D.I. water 3 times and ethanol 2 times, followed by drying at 65°C for 24 h. The loading of Pt on the carbon paper was controlled by monitoring the weight of the Pt precursor versus the support area.

The as-prepared GDE nanostructures were characterized by field emission scanning electron microscope (FESEM, JEOL 7000F, operating at 20 kV). X-ray Diffraction (XRD) pattern were recorded on Bruker D8 ADVANCE diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) at 40 kV and 40 mA.

2.3. MEA assembling

The Nafion NRE-212 membrane was pretreated by boiling in 3% H_2O_2 , D.I. Water, 1 M H_2SO_4 and D.I. Water, respectively, and each for 1 h. One of the as-prepared GDEs was sonicated in water–ethanol (1:1, volume ratio) mixed solution for 2 h ((Langford Sonomatic 375H, 40 kHz)) before the membrane electrodes assembly (MEA) mounting to investigate the catalyst durability. Then the as-prepared GDE was assembled as the cathode with Nafion NRE-212 membrane in a MEA, while the anode was an E-TEK ELAT® GDE LT120EW with the catalyst loading of 0.5 mg cm^{-2} Pt onto which a thin Nafion layer of 0.6 mg cm^{-2} was painted followed by drying at 90°C for 1 h. The electrodes were then hot-pressed against the Nafion membrane at 140°C (1 min without pressure, 50 s under the pressure of 17 MPa). A comparing MEA with the Nafion NRE-212 membrane, and the E-TEK ELAT® GDE LT120EW (Pt loading 0.5 mg cm^{-2}) as both electrodes, was made simultaneously. The hard Teflon gasketing with a thickness of $254 \mu\text{m}$ was used for sealing the fuel cells.

2.4. Fuel cell measurement

The MEAs with the as-prepared and commercial GDEs as the cathodes were tested in a 25 cm^2 PEM fuel cell at a temperature of 65°C , with pure H_2 and air gases humidified at 75°C before entering the cell and gas flows larger than 120 mL min^{-1} and 300 mL min^{-1} and the stoichiometry of 1.5/2.0, respectively. The gas pressure of the water-saturated H_2 or air (identical at anode and cathode) was

2.5 bars absolute (1.5 bar backpressure). Measurements were controlled and recorded with a PaxiTech and Bio-logic FCT-50S test station. The MEA was activated by a break-in at 0.6 V for 6 h. Then the polarization curve was recorded with a sweep rate of 2 mV s^{-1} . The impedance spectroscopy measurement was performed in the frequency range from 10 kHz to 0.1 Hz with an amplitude of 100 mV.

3. Results and discussion

At room temperature, H_2PtCl_6 reduction occurred very slowly in the presence of a weak reducing agent, formic acid, which favored the growth of {1 1 1} plane, and led to the formation of 1D nanowires [16]. Surfactant PVP was present as a capping agent to prevent the particle aggregation [15]. In reaction, the color of the solution changed from yellow to colorless very slowly, indicating the slow reduction of Pt(IV) to Pt(0) species. Reduction took place according to the following reaction:

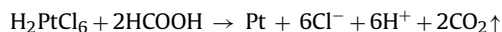


Fig. 1 shows the SEM images of the surface morphology of the Pt/carbon paper integrated GDE. It can be observed that the packed nanowire arrays were densely grown on the fiber surface, with a length of 100–150 nm and a diameter of a couple of nanometers, possessing a very similar morphology to the Pt nanowires grown on the carbon black surfaces [13]. XRD pattern of the as-prepared GDE is shown in Fig. 2, revealing that the Pt nanowires grown on the carbon substrate were crystallized in a face-centered-cubic (fcc) structure similar to bulk Pt. From the analysis results of Sun and his co-workers, the entire nanowire prepared by this method is a single Pt crystal and grows along (1 1 1) direction, possessing an enlarged electrochemical surface area and higher performance for Oxygen Reduction Reactivity (ORR) [13].

To check the ORR performance, the as-prepared GDE with dense Pt nanowires coated carbon paper (Pt loading 0.4 mg cm^{-2}) was tested as compared to the commercial E-TEK ELAT® GDE LT120EW (Pt loading 0.5 mg cm^{-2}) in MEAs in 25 cm^2 PEMFCs fed by hydrogen/air. The electrochemical impedance spectroscopy measurement was performed in the PEMFC test station, and the spectrum for each MEA was recorded at four potentials of 0.41 V, 0.55 V, 0.68 V and 0.80 V. The spectra were shown in Fig. 3. It can be observed that the diameter of the first impedance semicircle of the MEA with the as-prepared GDE is significantly smaller than that with the commercial GDE, indicating a substantially lower charge transfer resistance; that is, the catalytic activity of the Pt nanowires is much higher, as was also conformed by the cathode polarization measurement shown in Fig. 4. At 1.0 A cm^{-2} , in the same operating conditions, the MEA with the as-prepared GDE exhibits a better performance than that with the commercial GDE, about 240 mV higher even with a lower catalyst Pt loading. The maximum power density of the MEA with the as-prepared GDE (Pt loading 0.4 mg cm^{-2}) was about 25% higher compared to that with the commercial one (Pt loading 0.5 mg cm^{-2}). This pronounced difference can be explained by several possible mechanisms, for example the good contact between the catalyst and substrate, and the large ratio of length to diameter of the Pt nanowires giving higher catalytic performance through improved diffusion of air to the catalyst surface [13].

To investigate the durability of the as-prepared GDE, one of the samples was treated with sonication for 2 h in water–ethanol (volume ratio, 1:1) mixed solution. According to literature [12], if the adhesion of the nanowires to the substrate was weak, they would be easily released by a sonication treatment; Moreover, if the Pt nanowires were not stable enough themselves, they would suffer from a crystallinity destruction process when being treated with sonication in the aqueous and alcoholic solution [17], of which both would result in a lower catalytic performance. The cathode

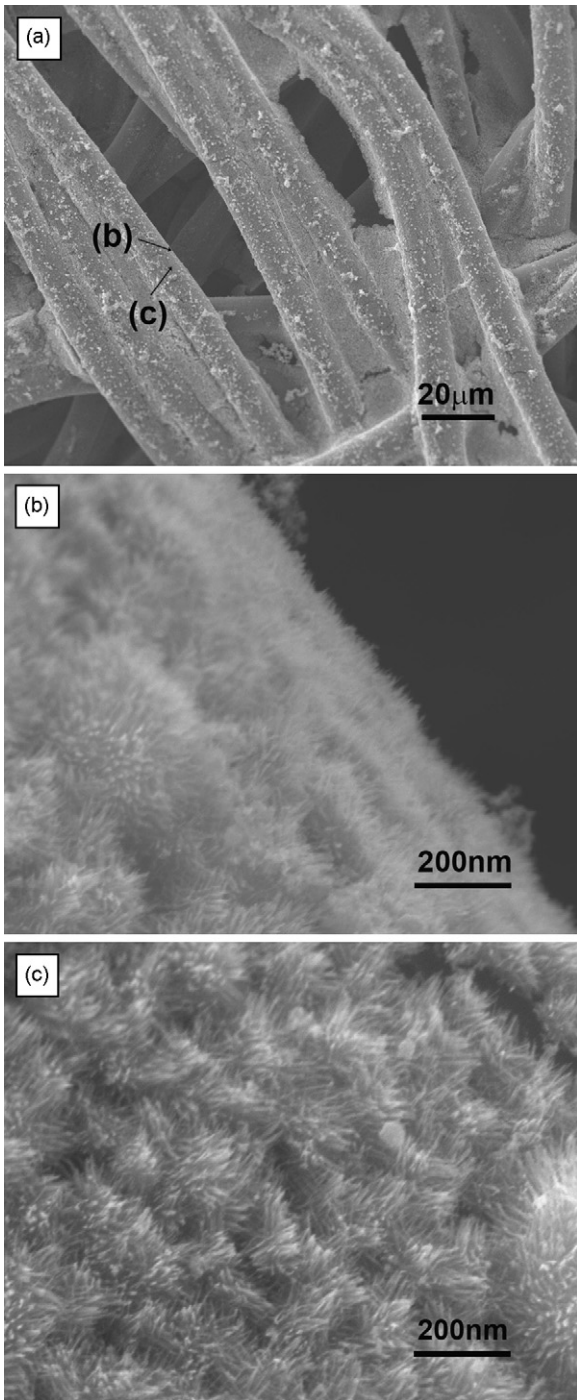


Fig. 1. SEM images of carbon fibres in the carbon paper in situ coated with Pt nanowires.

polarization plot of the MEA with the as-prepared GDE after the sonication treatment (Fig. 4) showed the performance did drop a little, about 10% on the maximum power density, while the SEM images (not shown here) exhibited a very similar morphology to the sample without the sonication treatment (Fig. 1). So, this drop in power density came from the release of some Pt nanowires with a relative poor adhesion to the carbon substrate. But, this drop in the power density is so small after such a long-time sonication, revealing the very good contact of the Pt nanowires with the carbon support and the high stability of the catalyst nanowires, meeting the demands of the electrocatalysts in PEMFCs for commercial applications.

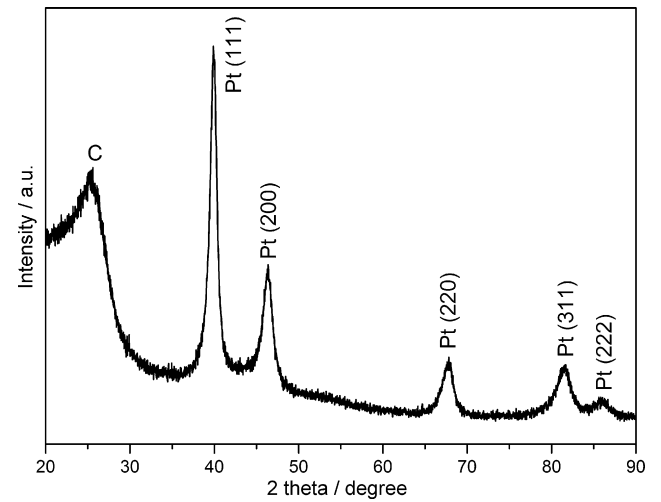


Fig. 2. XRD pattern of the carbon paper with in situ grown Pt nanowires.

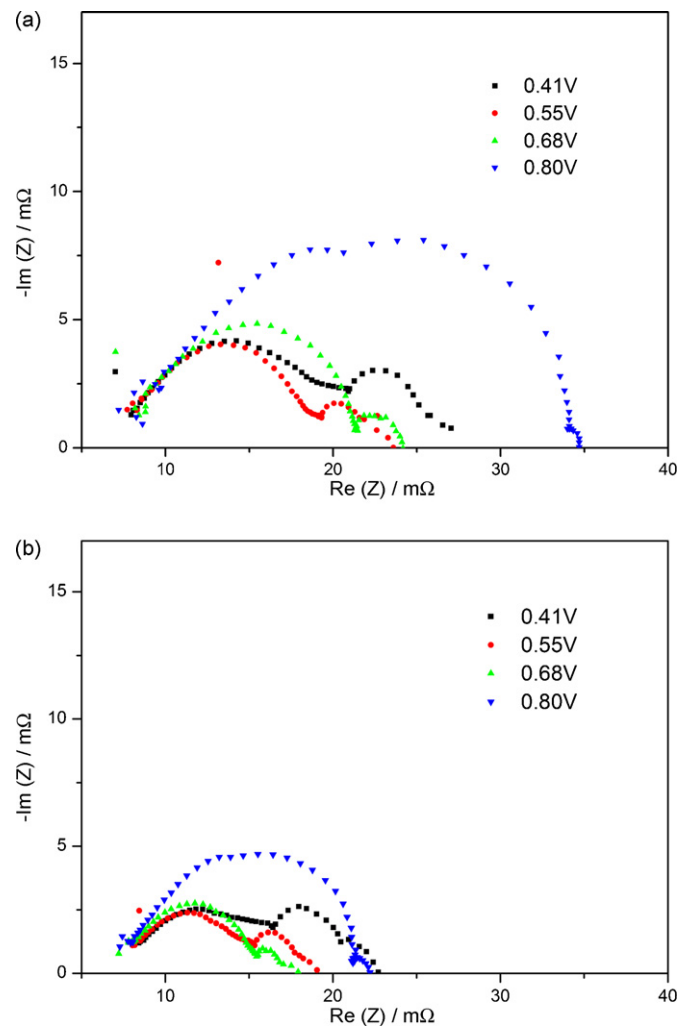


Fig. 3. Electrochemical impedance spectra of two MEAs with the cathodes of (a) E-TEK ELAT® GDE LT120EW (Pt loading 0.5 mg cm^{-2}) and (b) the as-prepared GDE with Pt nanowires on Freudenberg H2315 I6 GDL carbon paper (Pt loading 0.4 mg cm^{-2}), respectively, in the presence of NRE 212 membrane.

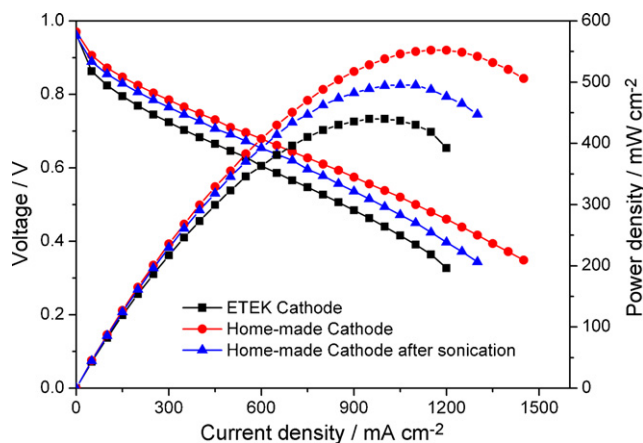


Fig. 4. Comparison of the cathode polarization curves of three MEAs with the cathodes of E-TEK ELAT[®] GDE LT120EW (Pt loading 0.5 mg cm^{-2}) and the as-prepared GDEs with Pt nanowires on Freudenberg H2315 I6 GDL carbon paper (Pt loading 0.4 mg cm^{-2}) before and after a 2 h sonication in water–ethanol mixed solution, respectively.

4. Conclusions

A very simple and effective process for preparing GDEs in PEMFCs has been demonstrated in this paper, where dense Pt nanowires were grown on the carbon fibers in the carbon paper by reducing chloroplatinic acid with formic acid in the presence of PVP at room temperature, without using any template or catalyst. The Pt nanowires were uniformly distributed on the support surface, with a length of 100–150 nm. The PEMFC with the cathode of the as-prepared GDE (Pt loading 0.4 mg cm^{-2}) showed a smaller charge transfer resistance and expressed about 25% higher maximum power density than that with the conventional E-TEK ELAT[®] GDE LT120EW (Pt loading 0.5 mg cm^{-2}), and the as-prepared GDE showed a very good durability in the long-time sonication treatment in water–ethanol mixed solution. The simple manufacturing process and high performance make the method a promising method for MEA preparation in PEMFCs for commercial applications.

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