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Short Communication

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.

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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

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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 electro-deposition 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 H_2PtCl_6 solution (Sinopharm Chem. Reagent) and HCOOH (Sinopharm Chem. Reagent). The reduction was left at room temperature for 72 h. Normally, 10.60 $\text{mg H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ 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

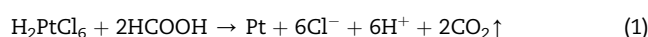
Scanning electron microscopy (SEM) observations were performed with a Hitachi S-4800 microscope, operating at 15 kV. Pt line scanning over the thickness region of the catalyst layers was determined by energy-dispersive X-ray spectroscopy (EDS). High-Resolution Transmission Electron Microscopy (HRTEM) 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 cm^2 . Cell activation, polarization curve and electrochemical impedance spectroscopy (EIS) measurements were carried out at 70 °C and atmosphere pressure, with pure H_2 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 N_2 and H_2 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:



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.

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