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Aligned polyaniline nanorods in situ grown on gas diffusion layer and their application in polymer electrolyte membrane fuel cells

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ABSTRACT

Catalyst layers (CLs) with spatially ordered structure can improve mass transport of reactants/products, which is essential for the high performance of polymer electrolyte membrane fuel cells (PEMFCs). In this study, aligned polyaniline (PANI) nanorods grown on gas diffusion layers by in situ polymerization are used as supports for platinum to fabricate ordered CLs. The length and diameter of the PANI nanorods can be controlled by optimizing the reaction temperatures or the aniline concentrations during the in situ polymerization process. With the optimized aligned PANI nanorods as supports of cathode, the mass specific power density of the PEMFC reaches 2.5 kW g_{Pt}^{-1}, which is 21% higher than that of the conventional PEMFC without PANI. This improvement can be attributed to the reduced oxygen transport resistance revealed by oxygen gain and electrochemical impedance spectroscopy.

Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have gained numerous attentions because of their high energy density, low temperature operation and environmental benefits [1–4]. However, the large amount of Pt used for catalyzing the oxygen reduction reaction at the cathode has hampered the widespread application of PEMFCs. The reduction of the Pt usage is considered to be a critical challenge for widely commercialization of PEMFCs. Unfortunately, reducing Pt loading generally could induce the cell performance loss, partially due to the increased oxygen transport resistance [5]. Minimizing the oxygen transport resistance in the cathode is one of the effective solutions to enhance the cell performance for low Pt loading membrane electrode assembly (MEA). It is generally accepted that the oxygen transport from the flow field to the catalyst layer (CL) in the cathode of a PEMFC follows two diffusion processes: molecular diffusion dominates in the carbon paper and Knudsen diffusion dominates in the microporous layer (MPL) and the CL. The effective diffusion coefficient of molecular diffusion is three orders of magnitude

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higher than that of Knudsen diffusion. Hence, the oxygen transport resistance of the cathode is mainly resulted from the diffusion of oxygen across the MPL and CL. Many efforts have been carried out to improve the oxygen transport in cathodes of PEMFCs. Yang and Middelman found that oxygen mass transport could be improved with networked MPL [6,7] and ordered CL [8], respectively. Inspired by the research work related to ordered CL of Middelman, diverse types of spatially ordered CLs were fabricated, which were based on nanostructured thin films [9], columnar carbon layer [10], vertically aligned carbon nanotubes or nanofibers (VACNT/VACNF) arrays [11,12] and vertically aligned metal oxides [13] et al., yet these ordered CLs commonly needed complex preparation process such as plasma sputter deposition [9,10], chemical vapor deposition [11,12] and glancing angle deposition [13].

The low cost of polyaniline (PANI), combined with its high conductivity in partially oxidized state [14], high chemical stability in acid medium [15], good thermal conductivity [16,17], as well as its facile to be constructed in ordered nanostructure, e.g. nanorod array, nanotube array etc, make it an appealing electrocatalyst support in PEMFCs. It is reported that aligned PANI nanorods can be assembled by electrochemical method [18] and dilute polymerization method [19]. The electrochemical method is limited to a small scale, because the current distribution may be uneven in different positions of the substrate, leading to an undesired structure of the PANI nanorods. Compared with electrochemical method, dilute polymerization method is much more facile for the synthesis of large area aligned PANI nanorods. But the method is limited to flat substrates, such as polytetrafluoroethylene (PTFE), polystyrene (PS) and glass, and there are few reports about the aligned PANI nanorods obtained on porous substrates up to now. In this article, for the first time, we report that aligned PANI nanorods are grown on porous gas diffusion layer (GDL) by in situ polymerization. The length and diameter of the PANI nanorods can be controlled by tuning the reaction temperatures or the aniline concentrations during the polymerization. With the optimized aligned PANI nanorods as supports of cathode, performance of the PEMFC single cell is improved, and the mechanism for performance improvement is investigated by oxygen gain and electrochemical impedance spectroscopy (EIS).

Experimental

Materials

All chemicals were used as received without further purification. Aniline and $(NH_4)_2S_2O_4$ (APS) were purchased from Tianjin Damao Reagent. $HClO_4$ was purchased from Tianjin Zhengcheng Reagent. Pt black and 60 wt.% Pt/C were purchased from Johnson Matthey Co., Ltd. Nafion® solution (5 wt.%) and Nafion® 212 membrane were purchased from DuPont Corporation. Carbon paper (TGP-H-060) with a porosity of 78% was purchased from Toray, Japan [17]. All aqueous solutions were prepared with ultrapure water from a Unique-R20 water system.

Preparation of aligned PANI nanorods on GDLs

The GDL was made up of hydrophobic carbon paper and MPL. The hydrophobic carbon paper was prepared by spraying the 1 wt.% PTFE solution onto the carbon paper, dried in air, and sintered at 340 °C. The amount of PTFE in hydrophobic carbon paper was approximately 10 wt.%. Then, the carbon powder (Vulcan XC-72, Cabot Corp.), 60 wt.% PTFE, and ethanol were ultrasonically mixed with a weight ratio 3:2 of carbon to solid PTFE content. The viscous mixture was coated onto hydrophobic carbon paper and then heated at 340 °C for 1 h. The carbon powder of MPL was controlled at 0.5 mg cm^{-2}.

Aligned PANI nanorods were synthesized by a modified dilute polymerization method as previously reported [19]. In a typical procedure, aniline monomer or oxidant (APS) was added into 100 ml $HClO_4$ solution (aqueous, 1 mol L^{-1}) and stirred for 5 min to form a uniform solution, respectively, where the molar ratio of aniline to APS was 1.5. The two solutions were kept in a certain temperature. The polymerization was performed by rapidly adding the oxidant solution to the aniline solution and a piece of GDL (4×4 cm^2) was immersed into the mixed solution, where the MPL of the GDL faced to the solution while the other side was sealed. Then, the mixture remained still for 24 h. Finally, the GDL was taken out and washed with ultrapure water. The samples polymerized at −5 °C, 0 °C, 10 °C or 25 °C with an aniline concentration of 10 mmol L^{-1} were denoted as PANI-T-5, PANI-T0, PANI-T10 or PANI-T25, respectively. To investigate the effect of aniline monomer concentration on the morphology of PANI, the concentrations of aniline monomer were kept at 5 mmol L^{-1}, 8 mmol L^{-1}, 10 mmol L^{-1}, 12 mmol L^{-1}, 15 mmol L^{-1} and 20 mmol L^{-1} while the temperature was kept at 0 °C. The PANI in the solution was filtrated and washed several times with ultrapure water, and finally dried at 60 °C to obtain green powder. The corresponding samples were denoted as PANI-C5, PANI-C8, PANI-C10, PANI-C12, PANI-C15 or PANI-C20, respectively.

Characterizations of the aligned PANI nanorods

Characterizations of the aligned PANI nanorods on GDLs were investigated by Scanning Electron Microscope (SEM, JSM-7800F, JEOL), Attenuation Total Reflection Fourier Transformed Infrared Spectroscopy (ATR-FTIR, Nicolet 6700, Thermo Fisher). The in-plane conductivity of the PANI was characterized by four point probe method (SZ-82, Suzhou Telecommunication). Considering the conductivity of the PANI nanorods on the GDLs was the same as PANI powder obtained from the solution. The detailed measure process was as follows: First, the PANI powder was pressed to a disk. Then three different points of every disk were tested and the mean value was taken.

Fabrication of MEA

The GDLs with aligned PANI nanorods were cut into 2×2 cm^2. The cathodes were obtained by spraying catalyst ink composed of commercial Pt black and Nafion® ionomer onto the GDLs with PANI nanorods. For comparison, the GDL without PANI was used to prepare cathode following the