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Highly active platinum electrocatalyst towards oxygen reduction reaction in renewable energy generations of proton exchange membrane fuel cells

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HIGHLIGHTS

- Porous carbon nanofibers (PCNFs) with multiform mesoporous structure could be superior to carbon black as the support to grow platinum.
- PCNF may construct reasonable catalyst layer (CL) which benefit for mass transfer and water management.
- The combination of excellent support and special morphological fabrication of platinum guarantee the high activity and durability of platinum catalyst.
- PCNF or Pt nanowires could be as a reliable replacement to conventional support or Pt nanoparticles.

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ABSTRACT

Reducing platinum usage and increasing its electrocatalytic durability are the key issues for the successful application of PEMFC. Fabricating platinum into specific morphologic structure and combining with the superior support is one of effective resolutions. In this paper, porous carbon nanofibers supported platinum nanowires (PtNW/PCNF) were synthesized via a simple and inexpensive template-free methodology and used oxygen reduction reaction (ORR) electrocatalyst. As a comparison, Pt nanowires supported on commercial carbon black (PtNW/Vulcan) was also prepared in the same condition. High-resolution transmission electron microscopy (TEM) shows that the single-crystal Pt nanowires were successfully grown on the support. The electrocatalytic activity and stability of the resultant catalysts along with the commercial one (JM20) were investigated by using cyclic voltammetry (CV) and liner sweep voltammetry (LSV) with a rotating disk electrode (RDE). As a result, the PtNW/PCNF exhibited much enhanced electrocatalytic activity and stability compared with the PtNW/Vulcan and JM20. The mass activity (at 0.80 V vs. RHE) of the PtNW/PCNF is about 1.7 and 2.3 times higher than that of PtNW/Vulcan and JM20, respectively. The remnant ECSA of the PtNW/PCNF after 1000 cycles was about 32% compared with the initial one whereas JM20 and PtNW/Vulcan retained only 10% and 23%. Furthermore, after ADT test for the three electrocatalysts, PtNW/PCNF lost 51 mV in half-wave potential, significantly better than the 150 mV half-wave potential loss for PtNW/Vulcan and almost complete loss of performance for commercial JM20. These results indicate controlled growth of Pt nanowires as a potential choice for conventional Pt nanoparticles and PCNFs a promising candidate as catalyst supports for the enhancement of PEMFC performance.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are considered as promising sustainable energy conversion technologies because of their outstanding advantages including high energy conversion efficiencies, quick start-up times and zero by-product emissions when they are operating [1]. In order to commercialize this technology widely, some challenges such as water managing [2–5], insufficient oxygen reduction reaction (ORR) [6,7], and short lifecycle [8] must be overcomed. Therefore, reasonable catalyst layers (CLs) and high performance ORR electrocatalysts designing are quite significant for promoting the wide applications of PEMFCs [9].

At the current state of the technology, precious metal catalysts typically platinum-based catalysts have been recognized as the

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efficient catalysts [10,11]. As of now, state-of-the-art catalysts consisting of platinum nanoparticles supported on carbon blacks (Pt/C) were used widely. However, some fatal problems still need to be addressed [12,13]. Pt nanoparticles are susceptible to agglomeration or dissolution because of their high surface energies during the operation of PEMFC, along with the inevitable corrosion of carbon support [1,14]. Therefore, their catalytic performance including ORR activity and stability are still needed to be further improved [15]. Various methods have been developed to improve the electrocatalytic activity and durability of the Pt-based electrocatalysts, including the fabrication of new catalyst supports [15,16] and the design of precious metal structures [13].

In general, the materials used as catalyst supports should own some characters including large surface area, high electronic conductivity and excellent electrochemical stability as well as reasonable pore structures [16]. Although CBs are the most popularly used as the catalysts supports, they are still not sufficient to resist carbon corrosion during long time operation, which may lead to the aggregation or elapsing of Pt nanoparticles, in turn to decrease the activity and durability of the electrocatalyst [17]. In the last decade, a large number of new carbonaceous materials such as carbon nanotubes (CNTs) [18–21], carbon nanofibers (CNFs) [22–24], carbon aerogels (CAs) [25] and graphene [26–28] have been exploited into catalyst design. Even some researches indicate that supports with reasonable structure can not only benefit for depositing mental nanoparticles but also can construct new CLs, among them porous carbon nanofibers (PCNF) act as a promising one [29,30]. Song et al. [29] used PCNFs as the assistant support to re-disperse commercial electrocatalyst (JM40). When fabricating MEA, they found that with the addition of PCNFs, the catalyst layer was quite different from traditional JM20 as the catalyst layer. The catalyst layer with PCNFs displayed a loose 3-D structure which could reduce mass transfer resistance and act as microporous layer (MPL) so that facilitating water drainage to prevent the cathode from flooding. The same results were also obtained when PCNFs were used as support to prepare Pt nanoparticles catalysts [30].

With respect to the design of the precious metal structure, Pt-based nanoarrays [31], nanowire networks [32,33], nanoflowers [34,35], and single crystal nanowires [36] have recently been proved capable of markedly improving the ORR activity and/or durability compared with commercial Pt/C catalyst. Liang et al. [32] successfully fabricated free-standing Pt nanowire membranes via a multistep templating process and they exhibited high durability and activity than commercial supported or unsupported catalysts. Meng et al. [37] used the carbon powders as the support to grow the Pt nanowires on them via a template-free method and control the Pt growth by adjusting the pH values. The novel catalysts showed better activity and durability in catalyzing methanol oxidation. Recently, Shuhui et al. reported Pt-based nanowires by substituting carbon nanospheres with new carbonaceous support such as carbon nanotubes (CNTs) [38] and carbon papers [36], and these catalysts can provide significantly improved specific and mass activities, coupled with durability in comparison to commercial Pt/C. Hoque et al. [39] even exploited the sulfur-doped graphene (SG) as the support to anchor the multigrain platinum nanowires on and used as the ORR catalyst. Their research found that the PtNW/SG catalysts are comprised of numerous single crystalline nanoparticles oriented along the <111> direction, and provide much increased Pt-mass-based ORR activity and durability in comparison to commercial Pt/C and PtNW/G.

Inspired by the above, the electrocatalytic performance can be further enhanced by combining better Pt nanostructure with rational support. Furthermore, when the catalysts were fabricated into the MEA they can construct better CLs which can benefit for the water management. Herein, PCNFs were employed as the support to grow Pt nanowires via a simple and inexpensive template-free method. The synthesized PtNW/PCNF used as the ORR electrocatalyst was studied, along with the electrocatalytic activity and durability in comparison to PtNW/Vulcan and commercial Pt/C (JM20).

2. Experimental

2.1. Materials

Methanol, formic acid, and hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) in analytical purity. Commercial Pt/C electrocatalyst (JM20) was purchased from Johnson Matthey Corp. Commercial carbon support Vulcan XC-72 can be achieved from Cabot Corp. and 5% Nafion® solution were purchased from Dupont. All the chemicals were used in the experiments directly without any further purification.

2.2. Preparation of the electrocatalysts

The carbon support, PCNFs, were prepared in the lab via electrospinning method followed by pre-oxidation and carbonization as we have reported previously [40]. The Pt nanowires supported on carbon support were prepared via a simple and inexpensive template-free method as reported elsewhere [41,42]. Typically, 255 μl of $H_2PtCl_6 \cdot 6H_2O$ aqueous solution (7.53 mg ml^{-1} of Pt) and 1.5 ml HCOOH were added into 20 ml water. 7.5 mg carbon support was then dispersed in the above solution by mild ultrasonication for about 1 h. After that, the suspension was displaced at room temperature for at least three days in order to ensure the completely reduction reaction and the growth of Pt nanowires onto the carbon support. The slurry was separated from the solution and

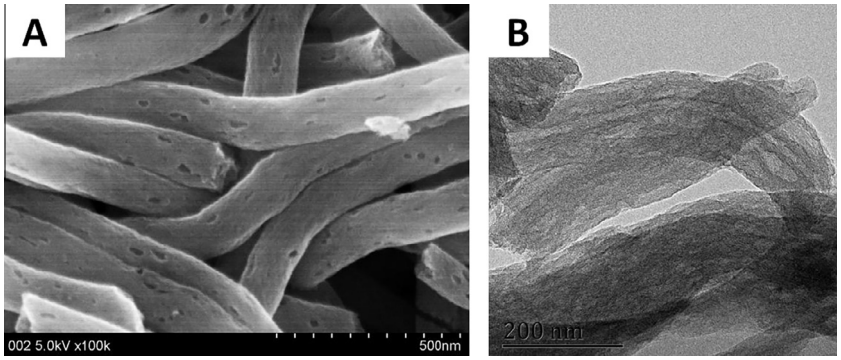

Fig. 1. FESEM (A) and TEM (B) image of PCNFs.