

Preparation of highly active and stable polyaniline-cobalt-carbon nanotube electrocatalyst for oxygen reduction reaction in polymer electrolyte membrane fuel cell



Zhong-shu Yin^a, Tian-hang Hu^a, Jian-long Wang^a, Cheng Wang^a,
Zhi-xiang Liu^b, Jian-wei Guo^{a,*}

^a Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, PR China

^b School of Electrical Engineering, Southwest Jiaotong University, Chengdu 610031, PR China

ARTICLE INFO

Article history:

Received 6 September 2013

Received in revised form

13 December 2013

Accepted 13 December 2013

Available online 27 December 2013

Keywords:

Oxygen reduction reaction

Non-noble-metal electrocatalyst

Carbon nanotube

Citrate acid

In-situ synthesis

ABSTRACT

This paper established an *in-situ* synthesis strategy that the mixing solution of aniline, CNTs and CoCl_2 was directly reduced to prepare polyaniline-cobalt-carbon nanotube (PANI-Co-CNT) electrocatalyst. Furthermore, this strategy was effectively modified by pretreating CoCl_2 precursor with citric acid (CA), forming 2–4 nm cobalt nanoparticles uniformly distributed on PANI-CNT support with porous structure. The control experiments revealed various PANI states in the growth stage, further proposing the self-assembly mechanisms in these two routes with and without CA pretreatment. These two PANI-Co-CNT electrocatalysts were also checked by oxygen reduction reaction (ORR) in acid environment, to corroborate their basically 4-electron processes. Inspiringly, the large activity and stability for the pretreated route could be comparable with those of the advanced electrocatalysts. All these progresses lay a bottom-up approach for future electrocatalysts.

Crown Copyright © 2013 Published by Elsevier Ltd. All rights reserved.

1. Introduction

The polymer electrolyte membrane fuel cells (PEMFCs) are highly regarded as energy converting systems for power fields in stationary and mobile devices [1–3], but their low kinetics in oxygen reduction reaction (ORR) is a major limiting factor especially in acid media [4]. Up to now, platinum (Pt)-based catalysts show remarkable improvements in activity and stability [5–9] though these progresses cannot yet meet future targets. Moreover, Pt is scarce in reserve and its cost is too expensive to meet large applications, so it is still urgent to prepare non-noble-metal electrocatalysts with high activity and stability towards ORR.

As a promising candidate, cobalt has long been focused on its macrocycles, oxides, chalcogenides and carbon-based structures [10–14], whose activity and stability cannot be achieved simultaneously. It is expected these drawbacks can be improved by loading these structures on supports, which is a general strategy for most electrocatalysts. As an ideal support, carbon nanotube (CNT) is notable for its excellent properties [15,16] in high

conductivity, large surface area and high stability [17]. If CNTs are wrapped with conducting polymers such as polyaniline (PANI), the composite support of PANI-CNT not only keeps most properties of CNTs, but also composes of the basis for metal-nitrogen-carbon (M-N-C) electrocatalyst [10]. The electrocatalysis activities are usually restricted by many structural factors. Generally, the miniaturization of nanoparticles is beneficial to enhance activity due to large surface areas and quantum effects. For example, the activity of platinum nanoparticles is effective when their size lies in the range of 2–5 nm [18], and it will be enhanced significantly when their size is less than 1 nm [19,20]. However, to obtain small nanoparticles should deliberately control their nucleation-growth paths in most aqueous synthesis. Additionally, the stable core-shell structure has been designed to improve the electrocatalysis activity. For example, Wei *et al.* found that the activity and durability of PANI-Pt-C electrocatalyst with core-shell structure are sensitive to the thickness of the PANI shell [6]. Thus, to pursue PANI-Co-CNT electrocatalysts is deduced to decrease nanosizes and stable composite structure, which are expected to enhance electrocatalysis remarkably.

It is worthy mentioned that the modification of CNT usually depends on covalent methods whose chemical treatments inevitably destroy the CNT surface. As a non-covalent method, π - π stacking based on two aromatic molecules interaction provides non-destructive route for aniline adsorption on CNT surface

* Corresponding author. Institute of Nuclear and New Energy Technology, Beijing 100084, PR China. Tel.: +86 1080194009; fax: +86 1080194009.

E-mail address: jwguo@mail.tsinghua.edu.cn (J.-w. Guo).

[21–23]. This route also helps PANI wrap CNT surfaces completely under the condition of aniline polymerization. Moreover, the functional group of NH_2 in aniline can be coordinated with cobalt precursor and play capping role for cobalt nanoparticles [24], thus controlling cobalt nanosize effectively. As a bridge between CNT and cobalt precursor, the aniline is deduced to open an *in-situ* route for composite PANI-Co-CNT structure. We also noticed there are many capping agents such as citric acid (CA) [25–28], whose extension for *in-situ* route is expected.

Herein, we disclosed that the mixing solution of aniline, CNTs and cobalt chloride (CoCl_2) precursor can be *in-situ* reduced to prepare polyaniline-cobalt-carbon nanotube (PANI-Co-CNT) electrocatalyst. We found 2–4 nm cobalt nanoparticles could be mounted in the porous PANI-CNT structure, but the CoCl_2 precursor pretreated by CA improves nanoparticles distribution significantly. Our control experiments revealed the differences for CoCl_2 precursor with and without pretreatment, thus proposing their preparation mechanisms as the self-assembly manner. We also related the basically 4-electron processes in ORR behaviors to their porous structures, determining the large activity and stability for pretreated PANI-Co-CNT sample. All these progresses help to make a complete breakthrough for future electrocatalysts.

2. Experiment

2.1. Materials and sample synthesis

Multiwall carbon nanotubes (MWCNTs) without any surface groups were purchased from Sciencetech Corporation. Aniline, cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), sodium citrate tribasic dehydrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$), ethanol, sodium borohydride (NaBH_4) were all bought from Sigma-Aldrich and 5 wt% Nafion were procured from DuPont. All chemicals were analytical grade reagents and used as received.

Synthesis of PANI-Co-CNT: First, 0.05 g of CNTs and 0.03 g aniline were mixed in 12.5 ml ethanol and 12.5 ml DI water, dispersed via ultrasonication for 3 hours. The amount of aniline was excess for complete PANI coverage on CNT surface. Then, 5 ml CoCl_2 (0.1 mol L^{-1}) was added into the above solution and further ultrasonicated for 2 hours. Next, 1.5 g NaBH_4 reducer was poured into the mixture solution and allow the reaction to last for at least 2 hours until no bubbles appeared. Finally, the solution was filtered to obtain suspended solids, which was dried at 60°C to achieve prepared samples. To extend synthesis, the above procedures were same except that CoCl_2 precursor was pretreated by CA, which was carried out to mix 5 ml CoCl_2 (0.1 mol L^{-1}) and $0.15 \text{ g C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ into 25 ml water and ultrasonicated for at least 5 hours. Thus we obtained two PANI-Co-CNT samples, namely Co+CA and Co-CA, corresponding to the pretreated and non-pretreated with CA species.

To probe the growth manners, we made control experiments whose procedures were the same as the above synthesis except that no CNTs were added, so we acquired another two samples, named as PANI-Co (+CA) and PANI-Co (-CA) respectively.

2.2. Physical characterizations

The UV-vis spectroscopies were made on a UV-2101 (Shimadzu) to evaluate solution properties in control experiments. Some techniques were used to realize the prepared PANI-Co-CNT samples: (1) Both Thermogravimetric analysis (TGA) on STA 490 PC (Netzsch) and ICP-OES measurements on IRIS Intrepid II XSP (ThermoFisher) were coordinately conducted to determine cobalt amount. TGA was carried out at 5°C min^{-1} in air from room temperature to 1000°C , then the residues were dissolved in hydrochloric acid whose cobalt

ion contents were detected by ICP-OES. (2) The morphologies were observed by transmission electron microscope (TEM) and scanning transmission electron microscope (STEM) on Tecnai G2 Transmission Electron Microscope (FEI). (3) The X-ray diffraction (XRD) patterns were acquired on a Bruker D8-advance X-ray diffractometer. (4) X-ray photoelectron spectroscopy (XPS) equipped with PHI Quantera Scanning X-ray Microprobe (ULVAC-PHI, Inc) was used to determine element content and the valence state of cobalt species. (5) Surface areas and pore size distributions were measured by nitrogen adsorption at 77 K on a NOVA 3200e Analyzer (Quantachrome).

2.3. Electrochemical characterizations

A three-electrode system was composed of glassy carbon electrode (GCE) with an area of 0.1256 cm^2 as the working electrode, Pt wire as the counter electrode and saturate calomel electrode (SCE) as the reference electrode. The catalyst ink was composed of 5 mg prepared sample and $950 \mu\text{L}$ ethanol containing $50 \mu\text{L}$ of 5 wt% Nafion, and ultrasonicated for at least an hour. The GCE surface was initially polished with alumina suspension, then pipetted with $20 \mu\text{L}$ catalyst ink and finally covered with a drop of 0.1 wt% Nafion, with the catalyst loading at $0.8 \text{ mg}_{\text{catalyst}} \text{ cm}^{-2}$.

Cyclic voltammetry (CV) and rotating disk electrode (RDE) measurements were carried out on potentiostat (EG&G Princeton, Model 263). CV experiments were conducted at room temperature in $0.5 \text{ M H}_2\text{SO}_4$ solution saturated with nitrogen or oxygen. Before each experiment, the working electrode was cycled at least 10 times with 50 mV s^{-1} from 1.19 V to 0 V vs. RHE until data stabilization. Then the ORR was made at a scan rate of 5 mV s^{-1} , from 1.19 V to 0 V vs. RHE, accompanied with RDE at the rotating speed from 400–3600 rpm controlled by Pine instrument. Normalized currents were labeled as (mA cm^{-2}) in this paper.

To evaluate durability, we made some accelerated degeneration tests which were carried out by CV in the range of 1.19 V–0 V vs. RHE at scan rate of 150 mV s^{-1} in the O_2 saturated $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution at 0 rpm. After every 90 cycles, the ORR was made at the scan rate of 5 mV s^{-1} and the rotation speed at 1600 rpm. The final retention ratio for current was defined as the ratio of the last current to the initial current under various potentials.

3. Results and discussion

3.1. Physicochemical characterizations

Fig. 1 displays the TGA curves in the air for both Co-CA and Co+CA samples. A typical three-step loss for PANI has been

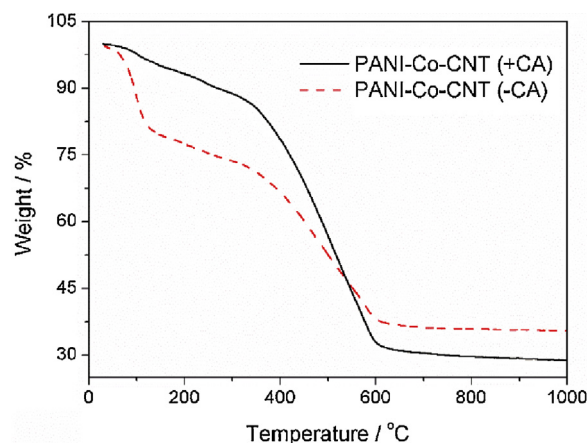


Fig. 1. TGA curves for PANI-Co-CNT (+CA, -CA) samples in the air from 25°C to 1000°C .

Download English Version:

<https://daneshyari.com/en/article/186409>

Download Persian Version:

<https://daneshyari.com/article/186409>

[Daneshyari.com](https://daneshyari.com)