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N-doped porous carbon derived from biomass as an advanced electrocatalyst for aqueous aluminium/air battery

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ARTICLE INFO

Article history:

Received 11 August 2015

Received in revised form

13 September 2015

Accepted 19 September 2015

Available online xxx

Keywords:

N-doped porous carbon

Aluminium/air battery

Electrocatalyst

ABSTRACT

A metal-free N-doped porous carbon (N-PC) derived from tapioca was fabricated and used as an enhanced electrocatalyst for aqueous metal/air battery. The electrochemical performance of N-doped porous carbon material as well as undoped porous carbon (PC) was studied by galvanostatic discharge measurements and steady-state linear polarization. Because of the existence of doping N atom, the N-PC exhibits a nice electrocatalytic activity in alkaline solutions. In addition, the N-PC loaded air electrode performs a high discharge voltage of 1.36 V at a current density of 50 mA cm⁻² in aluminium/air battery, which should be attributed to highly efficient, new and active sites created by N doping. N-PC could be used as an advanced electrocatalyst for high power aluminium/air battery.

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Introduction

Growing energy demands have aroused extensive research on high-efficiency, low-cost and environmental-friendliness energy storage system [1–3]. Aqueous metal/air batteries, especially aluminium/air batteries, have been identified as the next generation energy storage devices for their high energy density, low cost and low environmental contamination [4–6]. The theoretical energy density of aluminium/air battery is 8135 Wh kg⁻¹, and the actual energy density can reach up to 600–800 Wh kg⁻¹, which is extremely high compared with the lithium ion battery [6]. What interests us most is that it is a kind of flexible device by changing the structure and materials

[7]. Beyond that, aluminium is cheaper than lithium because of its abundance in earth crust. Therefore, aqueous metal/air battery comes to be one of the most fascinating device for the power of electric vehicle.

The air electrode is of great significance in aqueous metal/air battery. One of the present bottleneck of the metal-air battery lies in the sluggish kinetics of oxygen reduction reactions [8,9]. Although the Pt-based catalysts have superb ORR activity, they are restricted by their high price. The alternative catalysts based on non-precious metal oxides [10–12] and metal-free materials [13–16] have become the preferred choice. Therefore, catalysts which perform as the heart role of the air electrode are facing great challenges that it needs to improve ORR activity and reduce cost at the same time.

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<http://dx.doi.org/10.1016/j.ijhydene.2015.09.054>

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N-doped porous carbon based catalysts have been sustaining studied as a result of their admirable ORR electrochemical properties, relatively low cost, excellent stabilization as well as CO and methanol tolerance [17–20]. According to the literature and the experimental experience, a proper porous structure with high surface area and many catalytic sites often enhances the ORR activity of N-doped carbon material [21,22]. There exist many strategies to improve the surface area of various carbon materials, such as the use of various high surface area carbon materials (e.g., mesoporous carbon [23], carbon fiber [24], graphene [25]) and the addition of template in the process of carbon material preparation [26]. On the basis of the literature, a porous structure often refers to a higher surface area and more catalytic sites, then an improved ORR catalytic efficiency is obtained [27]. And the N-doped carbon materials are attracted because of their admirable electrochemical properties [28].

Moreover, the N-doped carbon materials have made sense in enhancing the performance of aqueous zinc/air batteries [27]. However, the catalysts in aluminium/air batteries mainly remain to be the metal oxide and their carbon hybrid [29], such as MnO_2 [30], NiCo_2O_4 /carbon nanotubes hybrid [31] and LiMn_2O_4 /N-rGO Nano hybrid [32] etc. The simplex doped porous carbon material has never been applied in aluminium/air batteries. Porous carbon materials based on biomass have been arousing considerable interests since biomass is widely accessible, reused and recyclable, furthermore, it is suitable for preparation in a large scale. The carbonization of biomass is pivotal as the inner structures and morphology of carbon is of great importance for its application [33,34]. Tapioca, commonly known as cassava starch, it can be found all over the world, and it has been able to gather abundant organotrophy from earth and air without any extra cost [35]. As a result, the tapioca can offer a good basis for the inexpensive growing trend of metal-free electrocatalysts for aluminium/air batteries.

In this respect, we presented the N-doped porous carbon which used silica as template and the tapioca as carbon precursor. The N element comes from NH_3 in the post heat treatment process. After the high temperature carbonization under the NH_3 atmosphere, then the silica template was removed by hydrogen fluoride acid. Since then, the porous N-doped porous carbon was obtained. The results of electrochemical measurement indicated that N source doping can sharply improve the ORR properties. And it was easy to find that the catalyst performed a quite high ORR activity in alkaline media and nice discharge characteristics. Moreover, the metal-free N-PC derived from tapioca, a kind of biomass, is cheap and easy to obtain.

Experimental

Synthesis of N-PC catalyst

All reagents were of analytical grade and used without further purification. All stock solutions were freshly obtained with the solvent of deionized water. In a typical experiment, 15 g of starch was completely dissolved in 50 mL deionized water under stirring, and followed by the addition of 20 g silica

template (20 nm). The reaction was conducted for 40 min under stirring at 90 °C in a water bath. The transparent mixture then was poured into culture dish, then dried at 50 °C for 2 h. The light yellow gel solid would be gotten after 100 °C desiccation. In the following processes, the gel solid was pre-carbonized in an argon flow at 400 °C for 60 min with a heating rate of 5 °C min^{-1} to form a pre-carbonized starch with silica (named PS@SiO_2). The PS@SiO_2 was dispersed by ball milling for 3 h. To obtain the product pre-carbonized porous carbon (PPC), dilute hydrofluoric acid (30 wt %) was used to remove SiO_2 in PS@SiO_2 . The preparation of PS@SiO_2 materials with different structures was conducted with the same process by only changing the dosage of silica template.

The final product N-doped PPC was carbonized under NH_3 atmosphere at 700 °C for 60 min with a heating rate of 5 °C min^{-1} . The final product was labeled as N-PC catalyst. For comparison, another sample without N doped was prepared and labeled as PC.

Physicochemical characterization

The morphology analysis was conducted with a field emission scanning electron microscopy (FESEM, FEI Quanta-200) and a scanning transmission electron microscopy (STEM, Tecnai G2 F20 S-TWIX). The surface morphology of the as-prepared porous N-PC was analyzed with scanning electron microscopy (SEM, JSM-6360LV). N_2 adsorption/desorption measurements were employed by using a Quantachrome instrument (Quabrasorb SI-3MP) at 77 K. The surface area was evaluated by the Brunauer–Emmett–Teller (BET) method and the pore size distribution was obtained by the desorption branch using the Barrett–Joyner–Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS, ESCA LAB 250Xi) was used to characterize the chemical state of the nitrogen in the material. Raman spectrum data were recorded from Labram-HR 800 in the wavenumber range of 1000–2000 cm^{-1} .

Electrochemical characterization

The ORR activity of the catalysts was measured on an electrochemical workstation (Solartron 1470E) at room temperature, using a five electrolysis pool. A spiral platinum wire and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. All the electrochemical properties of the catalysts were measured in O_2 -saturated aqueous solution (0.1 M KOH). All catalyst electrodes were prepared as the method reported in literature [36,37]. The working electrode was prepared by loading catalyst of 80 mg cm^{-2} . The ORR activity was performed using rotating disk electrode (RDE) technique on a pine modulated speed rotator (PINE AFMSRCE 3406) by linear sweep voltammetry (LSV) in the potential range of 0.1–1.0 V with a scan rate of 5 mV s^{-1} .

To better characterize the electrochemical properties of the sample, catalysts were loaded onto air electrodes. The as-prepared air cathode is composed of a gas diffusion layer, current collector, and a catalytic layer. The catalytic layer was assembled as here under mentioned: catalysts and acetylene black, as conductive additive, polytetrafluoroethylene emulsion (PTFE, 60 wt %), as binder, were mixed uniformly in a weight ratio of 6:1:3.

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