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Article

Chemistry

Metal-free porous nitrogen-doped carbon nanotubes for enhanced oxygen reduction and evolution reactions

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Abstract Developing efficient metal-free bi-functional electrocatalysts is required to reduce costs and improve the slow oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) kinetics in electrochemical systems. Porous N-doped carbon nanotubes (NCNTs) were fabricated by KOH activation and pyrolysis of polypyrrole nanotubes. The NCNTs possessed a large surface area of more than 1,000 $m^2\ g^{-1}$. NCNT electrocatalysts, particularly those annealed at 900 °C, exhibited excellent ORR electrocatalytic performance. Specifically, they yielded a more positive onset potential, higher current density, and long-term operation stability in alkaline media, when compared with a commercially available 20 wt% Pt/C catalyst. This resulted from the synergetic effect between the dominant pyridinic/graphitic-N species and the porous tube structures. The NCNT electrocatalyst also exhibited good performance for the OER. The metal-free porous nitrogen-doped carbon nanomaterials were prepared from low cost and environmentally friendly precursors. They are potential alternatives to Pt/C catalysts, for electrochemical energy conversion and storage.

Keywords N-doped porous carbon · Polypyrrole · Electrocatalyst · Oxygen reduction reaction · Oxygen evolution reaction

1 Introduction

Increasing energy demands are promoting the development of clean energy conversion technologies such as fuel cells and metal-air batteries, because of their high efficiency and low environmental impact. The essential component of these electrochemical energy conversion technologies is highly active and durable bi-functional electrocatalysts, for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) [1]. However, the ORR and OER typically have very high overpotentials, with sluggish reactions dynamics. Thus, they require a large amount of precious metal electrocatalyst to achieve satisfactory activity and durability [2, 3]. Platinum-based catalysts [4–9] including facet-controlled Pt catalysts, Pt alloys, and core-shell Pt-based nanoparticles are currently considered to be the most active ORR catalysts. However, these catalysts suffer from high cost and scarce precursors, methanol crossover/CO poisoning, and poor OER performance [10]. Various non-noble metal or metal-free materials have recently been reported as ORR catalysts [11–14]. They exhibit excellent activity, but their OER performance still requires further study. Iridium and ruthenium-based nanostructures are highly efficient OER catalysts, but are less effective for the

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reverse ORR. A bi-functional electrocatalyst for both ORR and OER typically requires low overpotentials and high activities for both the ORR and OER. Developing stable and highly active bi-functional electrocatalysts for the ORR and OER remains a significant challenge.

Nanostructured transition metals have received much attention as electrocatalysts for ORR and OER, because of their relatively low-cost and good electrocatalytic activity. These include Fe, Ni and Co and their oxides [15–18]. Wu and co-workers [19] reported that CoO–NiO–NiCo bi-functional nanocomposites supported by carbon nanotubes exhibited excellent activity and stability towards the ORR and OER in alkaline media. Wei and co-workers [20] prepared cobalt carbonate hydroxide supported on carbon black (CCH/C) via a hydrothermal method. CCH/C exhibited excellent ORR catalytic activity compared with a commercial Pt/C catalyst, and also showed a small overpotential of 0.509 V at a current density of 10 mA cm^{-2} in the OER, which were attributed to the stable one-dimensional nanostructure of CCH. Yang and co-workers [21] reported that co-embedded nitrogen-doped carbon nanotubes exhibited a surprisingly high OER activity, that outperformed that of IrO_2. The nanotubes exhibited a comparable ORR catalytic activity to that of a commercial Pt/C catalyst, in alkaline and neutral media. Various metal-free carbon materials reportedly function as bi-functional electrocatalysts. These have attracted much attention, because of their low cost, long durability, high abundance, and favorable catalytic activity. Yuan et al. [22] prepared a N-doped carbon sheet from chitin, as an efficient non-metal electrocatalyst. It exhibited excellent ORR catalytic activity, comparable to that of a commercial Pt/C catalyst. It also exhibited high catalytic activity towards the OER, with a small onset potential of (1.64 ± 0.02) V versus RHE. Lin et al. [23] prepared N-doped graphene by the pyrolysis of GO and polypyrrole (PPy), which exhibited excellent catalytic activities for the ORR and OER. These studies demonstrated that N doping of carbon nanomaterials enhanced the electron conductivity and surface hydrophilicity. This facilitated charge–transfer and electrolyte–electrode interactions, making these materials potential bi-functional catalysts for the ORR and OER.

N-doped carbon nanomaterials are typically prepared by the direct carbonization of N-containing precursors, or post treatment methods including thermal treatment in NH_3 atmosphere [24], nitrogen plasma treatment [25], and hydrazine hydrate treatment [26]. The N-containing precursor method can achieve the in-situ homogeneous incorporation of N into carbonaceous materials, without pre- or post-processing. PPy is a conjugated heterocyclic conducting polymer. It is an effective precursor for N-doped carbon nanomaterials which exhibit effective catalytic activity towards the ORR [27, 28], but less than that of commercial Pt/C. There are few reports of N-doped carbon nanomaterials derived from PPy as a bi-functional electrocatalysts towards the ORR and OER.

Herein, we report N-doped porous carbon nanotubes (NCNTs) with large surface areas. The NCNTs were fabricated using PPy nanotubes as a carbon precursor, by chemical activation with KOH and subsequent carbonization under a nitrogen atmosphere. The activation and pyrolysis formed hierarchical porous structures with in-situ N doping. The porous structure could facilitate the transport of gas molecules, and N-doping could provide abundant active sites for enhancing catalytic activity. The catalyst annealed at 900 °C (NCNT-900) exhibited a high ORR activity, with positive onset and reduction potentials at −0.012 and −0.136 V (vs. SCE), respectively. NCNT-900 also exhibited a high catalytic current density compared to commercial 20 wt% Pt/C, in alkaline conditions. For OER activity, the NCNT-900 catalyst exhibited a lower overpotential at the current density of 10 mA cm^{-2}, than that of commercial Pt/C. The NCNT-900 catalyst exhibited superior tolerance to methanol, and durability under alkaline conditions, than the commercial 20 wt% Pt/C catalyst. The excellent ORR and OER performances were attributed to synergistic effect of N doping and the porous tube structure. The method is simple yet effective for preparing N-doped electrochemical catalysts for the ORR and OER. It has potential in electrochemical energy conversion applications such as fuel cells, metal-air batteries, and water splitting.

2 Experimental

2.1 Synthesis of PPy nanotubes

PPy nanotubes were synthesized by the chemical oxidative polymerization of pyrrole, in the presence of $FeCl_3$ as an oxidant, and p-toluene sulfonic acid (TsOH) as a dopant. In a typical synthesis, pyrrole (0.14 mol) and TsOH (0.2 mol) were dissolved in 150 mL of deionized water by vigorous magnetic stirring for 15 min, to form a uniform emulsion. 50 mL of $FeCl_3$ (0.2 mol) aqueous solution was added dropwise over 24 h, under stirring at room temperature. After polymerization, the mixture was collected by filtration, and thoroughly washed with deionized water and ethanol until the filtrate was colorless. The as-produced powder was dried at 70 °C for 12 h.

The PPy powder was chemically activated by KOH aqueous solution (5 mol L^{-1}), in a 50 °C water bath for 3.5 h. After cooling to ambient conditions, the suspension was filtered and the solid material was washed with 50 mL of ethanol several times, before being dried at 70 °C for 12 h. The as-activated PPy powder was then annealed