Journal of Power Sources 288 (2015) 128–135

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Template-free synthesis of hierarchical yolk-shell Co and N codoped porous carbon microspheres with enhanced performance for oxygen reduction reaction

Shujun Chao [a, b, 1], Qian Cui [a, 1], Kui Wang [a], Zhengyu Bai [a], Lin Yang [a, *], Jinli Qiao [a, c, *]

[a] School of Chemistry and Chemical Engineering, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Collaborative Innovation Center of Henan Province for Fine Chemicals Green Manufacturing, Henan Normal University, Xinxiang 453007, PR China
[b] Department of Chemistry, Xinxiang Medical University, Xinxiang 453007, PR China
[c] College of Environmental Science and Engineering, Donghua University, 2999 Ren'min North Road, Shanghai 201620, PR China

HIGHLIGHTS

- The yolk-shell Co and N codoped porous carbon microspheres have been synthesized.
- The formation process of the yolk-shell precursor is discussed in-depth.
- YS-Co/N-PCMs display high ORR and OER performance in alkaline medium.
- The integrated yolk-shell and porous structure ensures superior ORR performance.
- The YS-Co/N-PCMs outperform Pt/C in methanol resistance ability and stability.

ARTICLE INFO

Article history:
Received 29 January 2015
Received in revised form
22 March 2015
Accepted 9 April 2015
Available online

Keywords:
Template-free synthesis
Yolk-shell
Porous structure
Transition metal and N codoped carbon materials
Oxygen reduction reaction
Oxygen evolution reaction

ABSTRACT

The structures and compositions of materials have important influences on their performance. Herein, hierarchically structured yolk-shell Co and N codoped porous carbon microspheres (YS-Co/N-PCMs) have been successfully synthesized by using low-cost melamine, formaldehyde and cobalt acetate as raw materials *via* a facile template-free hydrothermal method and a subsequent pyrolysis. The formation process of the yolk-shell precursor is systematically investigated, involving a morphological evolution process from solid microspheres, ultrathin and wrinkled shells wrap, to yolk-shell structure formation. More importantly, the unique structure combines the favorable features towards oxygen reduction reaction (ORR), such as high surface area, sufficient Co-Nx and graphitic N active sites and suitable pore structures. As a result, the YS-Co/N-PCMs catalyst shows high catalytic activity for ORR in alkaline media for fuel cells, which not only outperforms commercial Pt-based catalysts in terms of resistance to methanol crossover and long-time stability, but is also better than many non-precious metal doped carbon-based catalysts reported previously. In addition, the YS-Co/N-PCMs catalyst also has high catalytic activity toward oxygen evolution reaction (OER). Therefore, the YS-Co/N-PCMs catalyst may serve as a promising alternative to Pt/C catalyst for ORR and OER in alkaline media.

1. Introduction

Yolk-shell structure is a special class of core–shell structure with a distinctive core@void@shell configuration. Owing to the intriguing properties of movable cores, interstitial hollow spaces and diverse functionalities of shells, yolk-shell micro/nanomaterials have shown great application potentials in various electrochemical systems. For example, they can be used as electrocatalysts for oxygen reduction reaction (ORR) in fuel cells [1–3] and electrode materials of lithium ion batteries and supercapacitors [4–6]. Specially, with regard to yolk-shell micro/nanostructured ORR catalysts [1–3], the functionalized movable cores are able to meet different needs; the shells allow transport of reactants and reaction products and the hollow space between core and shell may provide a relatively homogeneous

---

[*] Corresponding authors. School of Chemistry and Chemical Engineering, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Collaborative Innovation Center of Henan Province for Fine Chemicals Green Manufacturing, Henan Normal University, Xinxiang 453007, PR China.
E-mail addresses: yanglin1819@163.com (L. Yang), qiaojl@dhu.edu.cn (J. Qiao).
[1] Shujun Chao and Qian Cui contributed equally to this work.

http://dx.doi.org/10.1016/j.jpowsour.2015.04.049
0378-7753/

reaction environment. However, the yolk-shell structure exhibits limited external accessible surface area and a small amount of micropores and mesopores. On the other aspect, the porous structure can afford high surface area for a large number of accessible active sites and abundant pores for facilitated mass transfer and electron transfer [7,8]. Therefore, a rational combination of the yolk-shell structure and porous structure is highly desired to form hierarchical nanoarchitectures with the inherited advantages of the component structures or even with unexpected properties. For this reason, we attempt to synthesize the highly efficient ORR catalysts with integrated yolk-shell and porous structure.

In recent years, various kinds of non-precious metal ORR catalysts, such as transition metal (Fe or Co) and N codoped carbon (M/N—C) materials [9–13], transition metal chalcogenides [14], metal oxides/carbides/nitrides/oxynitrides/carbonitrides [15–19], conductive polymer-based catalysts [20] and metal-free catalysts [21–23], have been developed. Among them, M/N—C materials [9–13] with relatively high ORR catalytic activities, long-time stabilities and low costs have been considered as the most promising cathode candidates for fuel cells. Studies have shown that the following two requirements are essential for achieving high performance of M/N—C materials: (i) the materials should possess abundant micro/mesopores and micrometer-sized macropores to ensure high surface area and fast transport of mass and charge; (ii) there should be sufficiently available active sites to facilitate their redox-reaction with the ions from the electrolyte.

To address these issues, special attention has been paid to the fabrication of porous M/N—C catalysts [9–13,24,25]. In many reported porous M/N—C catalysts, the porous carbon materials, such as porous Ketjenblack EC-300J, porous Vulcan XC-72R, ordered mesoporous carbon, hierarchically porous carbon, carbon nanofibers and Black Pearls 2000, mostly play a role of the support or a platform for creating the catalytically active sites [9–12,24,25]. Only a few of M/N—C materials possess the porosity in themselves for the direct use as the ORR catalysts [13,26]. What's more, the porous M/N—C catalysts are commonly prepared by the template-assisted synthesis route [12,26,27]. The complexity of synthesis seriously hinders the large-scale commercialization of these catalysts.

Based on these considerations, here we develop a template-free and scalable route to synthesize hierarchical yolk-shell Co and N codoped porous carbon microspheres (YS-Co/N-PCMs). The resulting YS-Co/N-PCMs exhibit high ORR activity in alkaline media better than many non-precious metal doped carbon-based catalysts reported previously (Table S1). Besides, the YS-Co/N-PCMs outperform commercial Pt/C catalyst in methanol tolerance ability and long-time stability. The high surface area, abundant Co-Nx and graphitic N active sites and suitable pore structures caused by the yolk-shell and porous structure make a synergetic contribution to the high ORR performance of the YS-Co/N-PCMs. In addition to ORR, we also examine the electrocatalytic activity of YS-Co/N-PCMs for oxygen evolution reaction (OER), an important reaction for many energy storage and conversion processes in regenerative fuel cells and rechargeable metal—air batteries, etc. [28,29]. The results indicate that the YS-Co/N-PCMs catalyst can also effectively catalyze the oxygen evolution reaction (OER) in alkaline medium. Moreover, this work provides a new path for preparation of yolk-shell transition metal and N codoped carbon micro/nanomaterials.

2. Experimental

2.1. Synthesis of YS-Co/N-PCMs

1.2 g melamine (99.5%), 9.4 g formaldehyde solution (37%) and 1.246 g $Co(CH_3COO)_2\cdot 4H_2O$ were added into 60 mL double distilled water (DD water) and ultrasonicated for 5 min to form a homogeneous suspension. Subsequently, the suspension was stirred at 60 °C for 10 min and then the clear pink solution was formed. After heating to 90 °C and maintaining at this temperature for 10 min, the solution was transferred into a 100 mL Teflon-lined autoclave, which was treated at 180 °C for 6 h. Finally, the product was collected by filtration, washed several times with DD water and ethanol, respectively, and dried at 40 °C overnight. The dried product was pyrolyzed at 800 °C for 2 h under N_2 atmosphere with a ramp rate of 3 °C min^{-1}. After that, YS-Co/N-PCMs were obtained. For comparison, Co-free sample (N-doped carbon (N—C)) was also prepared under the same conditions, apart from $Co(CH_3COO)_2\cdot 4H_2O$ as the metal precursor.

2.2. Characterization

The morphologies of the samples were determined by scanning electron microscopy (SEM, JEOL JSM-6390LV), field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6701F) and transmission electron microscopy (TEM, Hitachi JEM-2100). The elemental mappings were obtained from a scanning transmission electron microscope (STEM) unit with a high-angle annular dark-field (HAADF) detector (HITACHI S-5500) operating at 30 kV. The phases and crystallinities of YS-Co/N-PCMs and N—C were investigated by a Bruker D8 ADVANCE X-ray diffractometer (XRD) with a CuKα radiation source (λ = 0.15406 nm). Raman spectra were recorded using a RM2000 Microscopic Confocal Raman Spectrometer (Renishaw PLC, England) with an Ar laser at a wavelength of 514.5 nm. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG Scientific ESCALab220i-XL electron spectrometer using 300 W AlKα radiation as the photosource. The surface areas and pore size distributions of YS-Co/N-PCMs and N—C were determined from the results of N_2 adsorption/desorption measurements at 77 K (model: Micromeritics ASAP 2020) using the BET (Brunauer—Emmet—Teller) and BJH (Barrett—Joyner—Halenda) models, respectively.

2.3. Electrochemical measurements

Cyclic voltammetry (CV) and steady-state polarization measurements were performed by using a CHI660D potentiostat equipped with a model 616 electrode rotator (Princeton Applied Research) with a conventional three-electrode cell. The reference and counter electrodes were a saturated calomel electrode (SCE) and a platinum foil (1 cm^2), respectively. The working electrode was fabricated as follows: 2 mg as-prepared catalyst or commercial 20 wt% Pt/C catalyst was ultrasonically dispersed in a mixed solvent of 1 mL N,N-dimethylformamide and 40 μL 5 wt% nafion. Next, 18 or 12 μL of the ink suspension was deposited on a pre-cleaned rotating disk electrode (RDE, 4 mm in diameter) made of glass carbon and allowed to dry under an infrared lamp. The loadings of the catalysts were 272.4 or 181.6 μg cm^{-2}.

The electrolyte was 0.1 M KOH solution. Cyclic voltammograms (CVs) were recorded in the potential range of −1.0–0.2 V at a scan rate of 50 mV s^{-1} after purging the electrolyte with O_2 for 30 min. ORR steady-state polarization curves were obtained by scanning the potential from 0.2 to −1.0 V in O_2-saturated 0.1 M KOH solution with a scan rate of 10 mV s^{-1} at different rotating speeds from 400 rpm to 2500 rpm.

The stabilities of the YS-Co/N-PCMs and commercial Pt/C catalysts were investigated by cycling the two catalysts in O_2-saturated 0.1 M KOH solution between −1.0 and 0.2 V at 200 mV s^{-1}. After 8000 cycles, ORR steady-state polarization measurements were carried out at 10 mV s^{-1} at 1600 rpm.