Journal of Power Sources 399 (2018) 337–342

Contents lists available at ScienceDirect

Journal of Power Sources

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

Short communication

In situ prepared amorphous FeCoO-Polyaniline/multiwalled carbon nanotube nanohybrids as efficient oxygen evolution catalysts for rechargeable Zn-air batteries

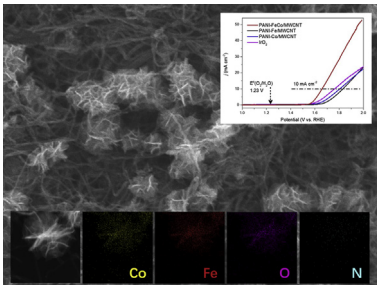
Chenchen Zhao[a,*], Yuhong Jin[a], Xian Du[b], Wenbo Du[b,**]

[a] Beijing Guyue New Materials Research Institute, Beijing University of Technology, Beijing, 100124, PR China
[b] College of Materials Science and Engineering, Beijing University of Technology, Beijing, 100124, PR China

HIGHLIGHTS

- Novel polyaniline-amorphous FeCo oxide-MWCNT nanohybrids are designed for OER.
- The hybrid materials are synthesized via a facile *in situ* procedure.
- The optimal hybrid material exhibits beneficial OER activities.
- The material shows remarkable efficiency and cycle stability for Zn-air battery.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Amorphous iron cobalt oxide
Polyaniline
Carbon nanotube
Oxygen evolution reaction
Zn-air battery
Air electrode

ABSTRACT

Efficient catalyst with low overpotential and small Tafel slope for oxygen evolution reaction is the key factor to improve overall efficiency of Zn-air battery. In the present study, a novel hybrid catalyst with polyaniline and amorphous iron-cobalt-binary oxide supporting on multiwalled carbon nanotubes is prepared via a simple *in situ* method by mixing Fe^{3+}, Co^{2+}, aniline and multiwalled carbon nanotubes together followed by subsequent borohydride reduction with citrate as protective stabilizer. The optimal sample exhibits remarkable activity for oxygen evolution reaction in 0.1 M KOH solution, accompanied by a low overpotential of 440 mV at a current density of 10 mA cm^{-2}, and a small Tafel slope of 55 mV dec^{-1}. Such catalyst can endow rechargeable Zn-air battery with a high peak power density of 287.4 mW cm^{-2} and long-term cycling performance over 100 h with high efficiency and stability, demonstrating its promising feasibility as highly active electrocatalyst for rechargeable metal-air batteries.

1. Introduction

Increasing demand for reliable devices for electrochemical energy storage and conversion has emerged with the development of low-carbon economy [1]. Zn-air battery (ZAB), as one of the most promising candidates for continuous utilization of electricity, has attracted much attention due to its prominent advantages like high energy density, environmental compatibility and low cost [2,3], whereas the scalable application of ZAB has been greatly hindered by its low overall efficiency which mainly because of the sluggish kinetics of oxygen evolution reaction (OER) at the electrode [4]. The OER process involves 4-electron oxidation to form a dioxygen molecule, which is often

* Corresponding author.
** Corresponding author.
E-mail addresses: zhaochenchen@bjut.edu.cn (C. Zhao), duwb@bjut.edu.cn (W. Du).

https://doi.org/10.1016/j.jpowsour.2018.07.111
Received 30 April 2018; Received in revised form 23 July 2018; Accepted 29 July 2018
0378-7753/

accompanied by a large reaction energy barrier [5]. Thus, an efficient OER catalyst with low overpotential and small Tafel slope is the key factor to improve overall efficiency of ZAB. Ir and Ru-based materials are known to be the most efficient catalysts for OER, but the scarcity and high cost of the precious metals prohibit their wide commercialized application [6].

Transition metal-based nano-materials have been widely investigated as alternatives to precious Ir or Ru catalysts for OER, especially mixed transition metal oxides (TMOs) [7–9]. Among them, iron-cobalt binary oxides are shown to have high catalytic efficiency, especially spinel and perovskite structured catalysts [9]. However, amorphous metal oxide materials are reported to exhibit better electrocatalytic performance than their crystalline counterparts [10], but research on amorphous iron-cobalt-oxide as active OER catalyst for ZAB is lacking.

On the other hand, a further improvement of electrochemical activity of TMOs for OER has been hampered by the poor intrinsic electrical conductivity which greatly impedes the electron and/or proton transport as well as decreases the amount of available catalytic active sites [11]. An effective way to overcome this shortcoming is to combine catalytic oxides with conductive supports to create hybrid composites. Multiwalled carbon nanotubes (MWCNTs) have attracted tremendous research interest as catalyst substrate materials due to their large surface area, prominent electronic conductivity and high chemical stability [12]. Decorating carbon nanotube (CNT) with conducting polymer, such as polyaniline (PANI), will not only further promote the electron transfer but also improve the stability, while the original properties of MWCNTs are kept [13]. Nevertheless, in most of the reported literature the TMOs-PANI-MWCNTs composite materials are synthesized via at least two steps: the first is wrapping CNTs with PANI and the second step is to load TMOs onto the surface of PANI-wrapped CNTs [13]. Guo and co-workers have developed a rapid and efficient procedure to prepare nano-composite structures of metal nanoparticles embedded in porous PANI matrix at ambient temperature by spontaneous molecular self-assembly [14]. In our previous research we have successfully synthesized a nanostructured PANI-Pd nanoparticles-CNT nanohybrid material via a similar facile *in situ* procedure by reducing Pd^{2+} in a mixture of CNTs and aniline with the sodium citrate as protective stabilization [15].

In this study we design and fabricate a novel hybrid catalyst with polyaniline and amorphous iron-cobalt-binary oxide supporting on multiwalled carbon nanotube (denoted as PANI-FeCo/MWCNT) via a simple *in situ* method. Due to the multisynergistic effects of the heterostructure containing different electrocatalytically active sites, the optimal sample exhibits remarkable OER activity and stability in alkaline KOH solution. Moreover, the ZAB fabricated with this hybrid catalyst demonstrates high performance and cycling durability.

2. Experimental section

2.1. Preparation of catalysts

The MWCNTs were purchased from Kumho Petrochemical Co., Ltd. The aniline, $CoCl_2{\cdot}6H_2O$, $FeCl_3{\cdot}6H_2O$, sodium citrate tribasic dehydrate and KBH_4 were supplied from Sinopharm Chemical Reagent Co. Ltd and used as received. All solutions were prepared with deionized water (18.2 MΩ cm). Commercial IrO_2 (Alfa Aesar) were used as benchmark catalysts.

The amorphous PANI-FeCo/MWCNT nanohybrids were prepared via a simple *in situ* method [15]. Briefly, 75 mg MWCNTs and 100 mg aniline were mixed in 25 mL water/ethanol (volume ratio:1/1) solution and ultrasonicated for 3 h to achieve the MWCNT suspension. 0.01 mol $FeCl_3$ was dissolved in 100 mL deionized water containing 3 g sodium citrate and ultrasonicated for at least 1 h to form a clean $FeCl_3$ solution. $CoCl_2$ solution was prepared in the same way. The two solutions were mixed together at different volume ratio under continuous magnetic stirring, and then 10 mL of the mixed $FeCl_3/CoCl_2$ solution was poured into the MWCNT suspension and ultrasonicated for 1.5 h. 2 g KBH_4 powder was added slowly and under ultrasonication the reduction process lasted at least 1.5 h. Finally, the product was filtered, washed and dried in a 50 °C oven. According to different molar ratios of Fe:Co (1:0, 3:1, 1:1, 1:3, and 0:1), the synthesized samples were denoted as PANI-Fe/MWCNT, PANI-3FeCo/MWCNT, PANI-FeCo/MWCNT, PANI-Fe3Co/MWCNT, and PANI-Co/MWCNT, respectively. In addition, the PANI-FeCo/MWCNT was heat-treated under Ar atmosphere at 750 °C for 4 h to obtain a high-crystalline sample, labeled as PANI-FeCo/MWCNT(750). A counterpart without addition of aniline was also prepared, labeled as FeCo/MWCNT.

2.2. Physicochemical analysis

The synthesized materials were physicochemically characterized by powder X-ray diffraction using Kα radiation (XRD, Bruker D8 Advance), X-ray photoelectron spectroscopy with Al-Kα source (XPS, ESCALAB 250Xi), scanning and transmission electron microscopy (SEM and TEM, Hitachi SU-9000) and high-resolution transmission electron microscopy equipped with energy dispersive X-ray spectroscopy (HRTEM and EDX, JEOL JEM 2100), respectively.

2.3. Electrochemistry and Zn-air battery performance

The electrochemical performance of catalysts was evaluated in a 3-electrode system with a rotating disk electrode (RDE, PINE Instrument Co.) under the control of a CHI 660 E electrochemical workstation (Chenhua Instruments Co.), having KCl saturated Ag/AgCl as reference electrode, Pt plate (4 cm^2) as counter electrode and 0.1 M or 1 M KOH as electrolyte [13]. To prepare the working electrode, 5 mg of catalyst powder, 1.9 mL of ethanol and 0.1 mL of Nafion solution (5 wt%, Dupont) were ultrasonicated to form a homogenous ink. Then 10 μL of as-prepared ink was pipetted onto the surface of the polished glassy carbon RDE (5 mm in diameter) and dried to form a thin catalytic layer.

ZAB evaluation was done with a multichannel LAND CT2001A testing system (Wuhan Land Electronic Co.), using pure Zn plate as the anode and 6 M KOH solution as the electrolyte. 0.2 M $Zn(CH_3COO)_2$ was added in electrolyte to facilitate the reversible electrochemical reactions of zinc. To fabricate the air electrode, 10 mg of catalyst was dispersed in 1 mL of deionized water, 0.6 mL of ethanol and 0.4 mL of Nafion by grinding to form a uniform ink. The ink was then sprayed onto the surface of carbon paper (Toray™) at a loading of 5 mg cm^{-2}. Porous nickel foam was used as the current collector. Wet-proofing gas diffusion layer was made by mixing acetylene black and 10 wt% PTFE (Dupont) into a sticky mixture and rolling into thin slices with a roller mixer machine. For comparison, a conventional Pt/C (20 wt%, HISPEC 3000, Johnson Matthey) and IrO_2 mixture catalyst was also tested under the same conditions.

3. Results and discussions

The fabrication process of catalyst is depicted in Fig. 1. Firstly, the aniline monomer was evenly absorbed on the MWCNT by π-π stacking effect under ultrasonication [14–16]. Subsequently, with the pretreatment of sodium citrate as protective stabilizer, the Fe or Co atoms were attacked by citrate, resulting in the formation of Fe (or Co)-citrate complex structures. When mixing the MWCNTs suspension and Fe/Co solution together, strong COO^--NH_2 bonds originated from the COO^- from citrate and NH^- from aniline were established [16]. During the whole fabrication process, the aniline polymer units were first oxidized by Fe^{3+} and Co^{2+}, leading to the formation of fully oxidized pernigraniline oligomer and radical cation segments [14–16]. Then excess KBH_4 powder as reducer was slowly added to obtain the final hybrids. The leucoemeraldine state of PANI was attained during this borohydride reduction [15].