Electrochimica Acta 178 (2015) 767–777

Contents lists available at ScienceDirect

Electrochimica Acta

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

Characterization of local electrocatalytical activity of nanosheet-structured $ZnCo_2O_4$/carbon nanotubes composite for oxygen reduction reaction with scanning electrochemical microscopy

Li Ma[a,1], Han Zhou[a,1], Shuli Xin[a], Chunhui Xiao[a,b], Fei Li[a,b,*], Shujiang Ding[a,b,*]

[a] Department of Chemistry, School of Science, State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China
[b] Institute of Chemistry for New Energy Materials, Xi'an Jiaotong University, Xi'an 710049, China

ARTICLE INFO

Article history:
Received 10 July 2015
Received in revised form 7 August 2015
Accepted 12 August 2015
Available online 17 August 2015

Keywords:
Oxygen reduction reaction
Electrocatalysts
$ZnCo_2O_4$ nanosheets/carbon nanotubes
Scanning electrochemical microscopy

ABSTRACT

A novel nanosheet-structured $ZnCo_2O_4$/carbon nanotubes (*i.e.*, $ZnCo_2O_4$ nanosheets/carbon nanotubes ($ZnCo_2O_4$ NSs/CNTs)) composite is successfully synthesized. Its catalytic activity towards oxygen reduction reaction (ORR) in alkaline electrolyte is evaluated by both cyclic voltammetry (CV) and scanning electrochemical microscopy (SECM). The CV results demonstrate that the $ZnCo_2O_4$ NSs/CNTs composite has good ORR catalytic activity, which is better than those of $ZnCo_2O_4$, CNTs, physically mixed $ZnCo_2O_4$ and CNTs, and Co_3O_4 NSs/CNTs. It could attribute to the unique ultrathin nanosheet structure and the synergetic effects of $ZnCo_2O_4$ and CNTs. Through recording the ORR currents using a microelectrode above the catalyst sample surfaces with applying different sample potentials, the differences in the local catalytic activities of these catalysts are simultaneously investigated and visualized by SECM. The obtained SECM results agree well with the CV results and also as important complements to the CV measurements. Our work proves the good ORR catalytic performance of the nanosheet-structured $ZnCo_2O_4$ /CNTs composite and introduces the SECM technique as a rapid screening method for predicting the ORR catalytic performances of the mixed transition metal oxides hybrids with providing both qualitative and quantitative local catalytic activity information.

1. Introduction

Oxygen reduction reaction (ORR), as one of the most extensively studied electrochemical reactions in electrochemical energy conversion devices (*e.g.*, metal-air batteries, fuel cells) as well as electrochemical oxygen sensors, has drawn much attention in both fundamentals and applications in the past several decades [1–6]. But its sluggish kinetics and the high cost, scarcity and low durability of traditional platinum catalyst as the two major barriers limit its research development. Tremendous efforts have been made on developing low-cost non-precious metal catalysts with high ORR catalytic performance [7–14], among which transition metals oxides (TMOs) with spinel structure and considerable advantages of low cost, environmental friendliness, prominent stability have long been proved to be electrocatalytically active for ORR from both the experimental and theoretical studies [11–14]. Cobalt-based oxides, such as Co_3O_4, as the most extensively investigated TMOs, has been studied as a highly efficient and stable ORR catalyst in alkaline electrolyte for several years [12–14]. More recently, incorporations of cheaper and eco-friendly element atoms, such as Fe, Ni, Mn and Zn, into Co_3O_4 were performed to form the mixed transition metal oxides (MTMOs) with spinel-like structures, such as $CoFe_2O_4$ [15], $NiCo_2O_4$ [16], $MnCo_2O_4$ [17] and $ZnCo_2O_4$ [18]. And through further growing MTMOs on highly conductive carbon nanomaterials, such as carbon nanotubes (CNTs), graphene and reduced graphene oxide (rGO), the obtained MTMOs/CNTs (or graphene, rGO) hybrids show higher ORR catalytic activities than TMOs [16–22]. Therefore, synthesis of Co-based MTMOs hybrids with various compositions and structures and discover their ORR catalytic activities and potential applications have become a recent research interest for developing novel non-precious metal ORR catalysts [15–22].

The composition and construction of the MTMOs hybrids in the local area, such as the microstructures (*e.g.*, defect), micro-compositions (*e.g.*, non-uniform local composition), and the homogeneity degree between MTMOs and support (*e.g.*, CNTs, graphene) have significant effects on their ORR catalytic performance. The classical electrochemical techniques for evaluating ORR catalyst activities, such as cyclic voltammetry (CV) and

---

* Corresponding authors.

E-mail addresses: feili@mail.xjtu.edu.cn (F. Li), dingsj@mail.xjtu.edu.cn (S.J. Ding).

[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.electacta.2015.08.060
0013-4686/© 2015 Elsevier Ltd. All rights reserved.

rotating disk electrode (RDE) techniques, mainly provide average information of ORR catalytic performance of samples [23–27]. And the CV and RDE methods can only evaluate one sample in one experiment, which can't meet the need of rapidly screening large amount of catalysts [23–27]. The increasing interest on developing novel MTMOs hybrids as ORR catalyst candidates thus raises a new request on high throughput electrochemical screening methods with high spatial resolution and also providing local electrocatalytic activity information of the MTMOs catalysts. Scanning electrochemical microscopy (SECM), as a kind of scanning probe microscope with using a microelectrode as probe, can provide the local reactivity of sample with high spatial and temporal resolutions based on the recorded probe currents [28–34]. And since only small amount of sample needed in SECM experiment and its rapid experimental process, SECM has the capability of quickly and simultaneously evaluating reactivities of different catalysts within one single experiment. In recent years, based on the advantages in rapid screening and providing local catalytic activities of samples, SECM has been applied to screen catalytic performances of several ORR catalyst arrays containing different catalysts and investigate their local catalytic activities [35–47].

In this work, we firstly synthesized $ZnCo_2O_4$ nanosheets (NSs) on CNTs to form a novel nanosheet-structured $ZnCo_2O_4$/CNTs composite (*i.e.*, $ZnCo_2O_4$ nanosheets/carbon nanotubes ($ZnCo_2O_4$ NSs/CNTs)). The composition of the synthesized $ZnCo_2O_4$ NSs/CNTs was well defined by X-ray diffraction (XRD) and thermogravimetric analysis (TGA), and its hierarchical and sheet-like structure was proven by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) characterizations. From the cyclic voltammograms recorded in 0.1 M KOH solution, the $ZnCo_2O_4$ NSs/CNTs composite was found to exhibit high ORR catalytic activity, better than the catalytic performances of $ZnCo_2O_4$, CNTs, physically mixed $ZnCo_2O_4$ and CNTs, and Co_3O_4 NSs/CNTs. The SECM technique was further applied to simultaneously investigate and visualize the local catalytic activities of the catalyst arrays with applying different sample potentials. The SECM results agree well with the CV results and additionally provide the differences in the local catalytic activities of these catalysts. Our work proposes the hierarchical and sheet-like structured $ZnCo_2O_4$ NSs/CNTs composite as a novel MTMO hybrid ORR catalyst and the feasibility of SECM technique as a rapid screening method of predicting the ORR catalytic performances of novel MTMO hybrids with providing local catalytic activity information.

2. Experimental

2.1. Chemicals

All chemicals were used as received. CNT-OH was purchased from Chengdu Organic Chemicals Co. Ltd. (China). Maleic anhydride, toluene, azobisisobutyronitrile (AIBN), acetone, styrene, ethanol, H_2SO_4, $Zn(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, hexamethylenetetramine, citric acid trisodium salt dehydrate, KOH were all obtained by Aladdin Ltd. (China). Nafion (5 wt%) and Pt/C (20 wt%) were purchased from Alfa-Aesar and E-TEK, respectively. Ferrocenemethanol (FcMeOH, 97%) and KCl ($\geq$99.5%) were obtained from Sigma-Aldrich. Glass carbon electrode (GCE), Ag/AgCl reference and Pt wire counter electrodes were obtained from Xianren Co. Ltd. (China). All aqueous solutions used for electrochemical experiments were prepared from Milli-Q reagent water (Millipore Corp., resistivity > 18.2 MΩ cm).

2.2. Synthesis of CNT-SPS (CNT with sulfonated polystyrene layer)

The synthesis procedure of CNT-SPS is described as follows. 0.4 g CNT-OH was dispersed in 60 mL acetone by sonication, then 8.25 mg maleic anhydride was added. The reaction mixture was stirred for 12 h at 25 °C. The black production was obtained and collected by centrifugation, completely washed with dry acetone for several times, and dried at 60 °C overnight. 0.127 g as-prepared black production was dispersed in 30 mL anhydrous toluene by sonication and transferred into a three-necked round-bottom flask. 0.8 g AIBN, followed by 4.2 mL styrene, was slowly added into the above suspension and then stirred for 3 h at 70 °C under a nitrogen flow to ensure complete reaction. The black powder (named as CNT-PS) was obtained by centrifugation and washed fully with deionized water and ethanol for three times, then dried at 60 °C overnight. Then 3 g of the obtained CNT-PS was well dispersed in 90 g concentrated sulfuric acid by sonication for 10 min. After being stirred at 40 °C for 10 min, the obtained CNT-SPS was filtered off and washed with deionized water and ethanol until the production was neutral.

2.3. Synthesis of catalyst samples

The $ZnCo_2O_4$ NSs/CNTs composite was synthesized by the following procedure. 15 mg CNT-SPS was well dispersed in 40 mL deionized water by sonication treatment. 0.25 mM $Zn(NO_3)_2{\cdot}6H_2O$, 0.5 mM $Co(NO_3)_2{\cdot}6H_2O$, 0.25 mM hexamethylenetetramine and 0.025 mM citric acid trisodium salt dehydrate were dissolved into the above dispersion to form a light green solution. The resulting solution was transferred into a 100 mL round bottom flask. After slowly stirring at 90 °C for 6 h, the flask was cooled down to room temperature naturally. The product was collected by centrifugation and washed with deionized water and ethanol for several times then dried at 60 °C for 12 h under vacuum. Finally, the powder was heated to a temperature of 400 °C with a heating ramp of 1 °C min^{-1} for 2 h under nitrogen atmosphere. The synthesis methods of Co_3O_4 NSs/CNTs and $ZnCo_2O_4$ are similar to the synthesis procedure of $ZnCo_2O_4$ NSs/CNTs, only without adding $Zn(NO_3)_2{\cdot}6H_2O$ to the reaction solution for the Co_3O_4 NSs/CNTs synthesis, or without adding CNTs to the reaction solution for the $ZnCo_2O_4$ synthesis.

2.4. Morphology and composition characterizations

The morphology of the prepared samples was characterized by field-emission scanning electron microscopy (FESEM; HITACHI, SU-8010) and TEM (JEOL, JEM-2100). Crystallographic information of the samples was examined using powder XRD (SHIMADZU, Lab X XRD-6000). The SPS layer on CNT surface was characterized by fourier transform infrared spectroscopy (FTIR, BRUKER, TENSOR 27). TGA was conducted with a Perkin-Elmer TGA7 thermogravimetric analyzer in temperature range from room temperature to 800 °C with a heating rate of 10 °C min^{-1} under air flow.

2.5. Cyclic voltammetric measurements

Cyclic voltammetric measurements were performed on a CHI760D electrochemical workstation (Chenhua Co. Ltd., China) with a three-electrode cell. A GCE (Ø 3 mm) modified with 3 μL of 4 mg mL^{-1} catalyst suspension and a Pt wire were served as the working electrode (WE) and the counter electrode (CE), respectively. A Ag/AgCl (KCl, saturated) electrode was used as the reference electrode, and the potential values reported were all adjusted to the reversible hydrogen electrode (RHE). The catalyst suspensions were prepared by dispersing 4 mg of different samples in 1 mL mixture solvent of ethanol and deionized water (V:V = 1:4), then added with 20 μL Nafion solution and sonicated for 10 min to form a homogeneous suspension. A commercial Pt/C catalyst suspension for comparison was prepared with the same quantity and method as described above. All the CV measurements were