Full paper

Ultrahigh electrocatalytic oxygen evolution by iron-nickel sulfide nanosheets/reduced graphene oxide nanohybrids with an optimized autoxidation process

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ABSTRACT

Iron-nickel-based electrocatalysts are a group of noble-metal-free and high-performance candidate for oxygen evolution reaction (OER), and autoxidation always occurs in their OER process. Autoxidation is a double-edged sword: it could in-situ generate high-catalytic activity sites to accelerate OER, but it also results in the attenuation of conductivity and the dissolution of active components. In this work, we propose a new strategy to relieve the negative impacts of autoxidation on OER through designing three-dimensional (3D) iron-nickel sulfide nanosheets/reduced graphene oxide (FeNiS$_2$ NS/rGO) nanohybrids via a one-pot colloidal method, which enabled the well dispersion and strong coupling of FeNiS$_2$ NS on the rGO. Such an interconnected 3D architecture could facilitate excellent electron transport, provide large amounts of active sites and prevent the dissolution of active components. The FeNiS$_2$ NS/rGO delivered extremely low overpotentials of 270 mV and 200 mV to reach a current density of 10 mA cm^{-2}, and rapid kinetics with Tafe slope of 38 mV dec^{-1} and 40 mV dec^{-1} for OER in 0.1 and 1.0 M KOH, respectively. Moreover, they could retain a great stability without activity loss over long-term continuous electrolysis and long-ageing time under air conditions. This work provides an efficient approach to resolve the autoxidation problem of FeNiS$_2$ NS in the OER process and develops a promising earth-abundant OER electrocatalyst towards practical applications.

1. Introduction

Up to date, tremendous efforts have been made to develop earth-abundant and high-powered catalysts for oxygen evolution reaction (OER), which is an important half-cell reaction for many energy conversion technologies, including solar water-splitting devices, water electrolyzers, and metal-air batteries [1–4]. The difficulty in non-noble-metal catalysts design originates from the sluggish kinetics of the 4-electron and proton transfers in the OER process to form an oxygen-oxygen bond. Early studies demonstrated that Fe impurities in the nickel hydroxide electrodes could cause detrimental effects on the Ni-based alkaline batteries by greatly lowering their OER overpotential [5,6]. Such a discovery has inspired many researches to explore the mechanism, optimize the Fe content and synthesize various FeNi mixed compounds in order to obtain better OER electrocatalysts. Especially, FeNi-based oxides and hydroxides [7–13] with distinct chemical structures and physical morphologies have been extensively studied as

potential catalysts alternatives because of their attractive OER activity. However, low electrical conductivity is the major drawback of these electrocatalysts. In order to solve this problem, great efforts have been devoted to pursue FeNi oxides and hydroxides electrocatalysts with improved conductivity, such as dimension adjustment [14], surface atom incorporation [15], and hybridization with conductive matrixes [16]. Our recent work showed that ternary iron-nickel sulfide nanosheet (FeNiS$_2$ NS) catalysts, with the assistance of sulfur atom and unique two-dimensional structure to enhance the conductivity, offered a promising alternative to OER catalysts with excellent performance [17]. In fact, it is notable that the FeNiS$_2$ NS catalysts are much more active for OER than that of either binary Ni$_9$S$_8$ or FeS alone, and even is comparable to that of commercial RuO$_2$ because of the synergistic effect of Fe/Ni and good transport properties.

While the ultrathin two-dimensional sulfides have been designed with enhanced conductivity, it is particularly important to note that an autoxidation of the FeNiS$_2$ NS catalysts prior to the OER catalysis exists

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in the OER process, which is commonly observed for Ni-based catalysts [18,19]. So far, the structural or chemical characteristics of FeNi oxides and hydroxides catalysts, particularly in OER process, which is related to the real active sites and mechanistic studies for OER catalysis have been explored [6,8,20–22]. For example, NiOOH was found to be present in films containing up to ~50% Fe, and in situ Raman spectroscopic characterization of the electro chemically grown Ni-Fe films showed an increasing mixture of FeOOH and Fe_2O_3 at higher Fe contents [20,22]. Furthermore, operando X-ray absorption spectroscopy (XAS) analysis using high energy resolution fluorescence detection revealed that Fe^{3+} in $Ni_{1-x}Fe_xOOH$ occupied octahedral sites with unusually short Fe-O bond distances, which was induced by edge-sharing with surrounding $[NiO_6]$ octahedra. Besides, XAS was used to evaluate the oxidation states and local atomic structure motifs of the Ni and Fe K-edges of the electrocatalysts under OER conditions [21]. The XAS data indicated that up to 75% of the Ni centers increased their oxidation state from +2 to +3, while up to 25% reached the +4 state for the NiOOH catalyst and the high valence state Ni would be consumed under OER catalysis. While the Fe centers consistently remain in the +3 state, regardless of potential and composition.

These results indicate that the autoxidation of the FeNi-based catalysts inevitably occurs. Such an autoxidation process causes the change of structure, valence and composition during the OER process, resulting in the transformation of the real active sites and the acceleration of the OER performances. However, these changes simultaneously have some negative consequences, e.g., poor conductivity derived from the in-situ generated actives sites [21]. Therefore, evaluation of the effects of these changes on the OER performance of $FeNiS_2$ NS and efficient strategies to take the advantage of autoxidation while avoid its negative effects are greatly desired.

With the above considerations, in this work we initially investigated the $FeNiS_2$ NS-catalyzed OER process in alkaline electrolyte via characterizing the structure and composition changes of the $FeNiS_2$ NS catalysts by using ex-situ HRTEM and EDX. With the identification of the problems caused by the autoxidation in OER process, e.g., amorphization of structures, formation of oxides and dissolution of active components, a new OER electrocatalyst, $FeNiS_2$ NS in-situ hybridization with reduced graphene oxide (rGO) (denoted as $FeNiS_2$ NS/rGO), was designed and synthesized. Then, the phase, composition and structure of the prepared $FeNiS_2$ NS/rGO were characterized. Furthermore, the OER activity and stability of the $FeNiS_2$ NS/rGO were evaluated using a suite of electrochemical measurements, and the mechanisms for its ultrahigh activity and excellent stability were elucidated. In this way, a novel electrocatalyst $FeNiS_2$ NS/rGO with ultrahigh-performance for OER was prepared and one efficient strategy to address the autoxidation issue and optimize the OER performance was also developed.

2. Experimental section

2.1. Preparation of GO

Nickel (II) acetylacetonate [$Ni(acac)_2$, 98%], Iron(III) 2,4-pentanedionate [$Fe(acac)_3$, 98%], oleylamine [OAM, 70%] and 1-octanethiol [OTT, 98%] were purchased from Aladdin Co., USA. All reagents were used as received without any purification.

GO was prepared using a modified Hummers method [23,24]. Briefly, 0.5 g of graphite powders (< 30 μm) and 0.5 g of $NaNO_3$ were stirred with concentrated H_2SO_4 (23 mL) in an ice bath. Then, 3 g of $KMnO_4$ was added slowly within 10 min. In the subsequent 1 h, the mixture was maintained in 35 °C with vigorous stirring. After that, 40 mL of deionized water was dosed into the reaction mixture and further heated to 90 °C for 30 min. Thereafter, the mixture was removed from the water bath, and 100 mL of water was added. The unreacted $KMnO_4$ and residual manganese species were removed by the addition of 3% H_2O_2. The suspension was stirred at room temperature for 4 h and purified by repeated centrifugation until a negative reaction

on the sulfate ion [with $Ba(NO_3)_2$] was achieved. The final precipitate was dispersed in 50-mL water and ultrasonicated for 10 min. The insoluble solids were crushed by centrifugation, and a brown homogeneous supernatant was collected (the GO solution was 4.65 mg mL^{-1}) and freeze-dried to obtain the GO powder.

2.2. Preparation of $FeNiS_2$ NS and $FeNiS_2$ NS/rGO

$FeNiS_2$ NSs were prepared following a method reported previously [17]. In brief, $Fe(acac)_3$ (0.10 mmol, 0.0375 g), $Ni(acac)_2$ (0.10 mmol, 0.0258 g) and OTT (0.2 mL) were mixed into a solution of OAM (1.0 mL) and ODE (5.0 mL) in a 100 mL three-neck flask. Under a N_2 flow, the mixture was initially heated to 120 °C, kept at this temperature for 30 min, and subsequently the mixture was raised to 220 °C at a ramping rate of 10 °C min^{-1} and maintained for 60 min. Finally, the products were allowed to cool down to room temperature naturally, precipitated by adding 10 mL of ethanol and centrifuged at 8000 rpm for 5 min, washed several times with absolute ethanol and hexane (v/v = 4:1), and then dried at 60 °C under vacuum for further characterization. The synthesis route to $FeNiS_2$ NS/rGO was similar to the above method except that additional GO (5 mg) was dosed and the solvent was changed to OAM (6.0 mL). After drying under vacuum, the products were heated to 400 °C in a NH_3/Ar (v/v = 1:9) atmosphere for 2 h to reduce the GO in the compositions.

2.3. Characterization of the catalysts

The purity and phases of the products were identified by X-ray diffraction (XRD) patterns on a Philips X'Pert Pro Super diffractometer with graphite-monochromatized Cu-Ka radiation (λ = 1.541874 Å) (Rigaku TTR-III, PHLIPS Co., the Netherlands). The morphologies of the products were examined by field emission scanning electron microscopy (SEM) (Supra 40, Zeiss Co., Germany). Raman spectra were excited by radiation of 514.5 nm from a confocal laser micro-Raman spectrometer (LABRAM-HR, Jobin-Yvon Co., France). The transmission electron microscopy (TEM) images of the samples were recorded on a TEM (H-7650, Hitachi Co., Japan), using an electron kinetic energy of 100 kV. The chemical compositions and the valence states of constituent elements were analyzed by X-ray photoelectron spectroscopy (XPS) (ESCALAB250, Thermo Fisher Inc., USA). The high resolution transmission electron microscopy (HRTEM), high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images and corresponding energy dispersive spectroscopic (EDS) mapping analyses were performed on a JEOL JEM0ARF200F TEM/STEM with a spherical aberration corrector (Talos F200X, FEI Co., USA). The surface areas of the samples were measured by the Brunauer-Emmett-Teller (BET) method with a Builder 4200 instrument (Tristar II 3020 M, Micromeritics Co., USA). TGA measurements are tested in an air environment from room temperature to 800 °C at a heating rate of 10 °C min^{-1} (SDT Q600, TA Inc., USA).

2.4. Electrochemical tests of the catalysts

All electrochemical tests were conducted with a rotating disk electrode (RDE) (Pine Research Instrumentation Inc., USA) connected to a CHI 760E potentiostat (Chenhua Instrument Co., China). The diameter of RDE was 5.0 mm and the disk geometric area was 0.196 cm^2. Ag/AgCl (3.0 M KCl) electrode and platinum wire were used as the reference electrode and counter electrode, respectively. To prepare the working electrode, 4.0 mg as-prepared pure $FeNiS_2$ NSs, the mixture of $FeNiS_2$ NS with rGO (denoted as $FeNiS_2$ NSs+rGO) and $FeNiS_2$ NSs/rGO and 10 μl Nafion solution (Sigma Aldrich Co., USA, 5 wt%) were dispersed in 1.0-mL water-ethanol solution with a volume ratio of 3:1 by sonicating for 1 h to form a homogeneous ink. Then, 10 μl of the catalyst ink containing 20 μg of catalyst was loaded onto a RDE with a loading of ~0.10 mg cm^{-2}. For comparison, 4.0 mg RuO_2 (Sigma