Electrochimica Acta 265 (2018) 10–18

Contents lists available at ScienceDirect

Electrochimica Acta

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

The role of Cr doping in Ni–Fe oxide/(oxy)hydroxide electrocatalysts for oxygen evolution

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ARTICLE INFO

Article history:
Received 27 October 2017
Received in revised form
28 December 2017
Accepted 23 January 2018

Keywords:
Oxygen evolution
Electrocatalysts
Nickel iron oxides
Chromium
Electrochemical impedance

ABSTRACT

Efficient and earth-abundant electrocatalysts for water oxidation are essential for renewable and sustainable energy conversion technologies. And Ni(Fe)O_xH_y especially attractive as a state-of-the-art best candidate catalyst for efficient electrochemical oxygen evolution reaction (OER). In previous research, Cr has been reported could benefit the Ni(Fe)O_xH_y catalysts with conflicting mechanism. Here, a series of ternary (Ni, Fe and Cr) amorphous metal oxide catalysts for OER are synthesized via a simple thermal decomposition method. We show that $Ni_{0.6}Fe_{0.3}Cr_{0.1}O_x$ has a turnover frequency of $0.046 \pm 0.004\ s^{-1}$ at 300 mV overpotential which is ~31% more active than an analogous $Ni_{0.6}Fe_{0.4}O_x$ film, $0.035 \pm 0.007\ s^{-1}$, in 0.1 M KOH media. Using electrochemical voltammetry and AC impedance analysis, we demonstrate that Cr increases the number of electrochemically available active sites, as a pore forming agent, but does not affect the intrinsic per metal atom activity. We find that the Cr begins to leach immediately upon electrochemical testing, and the Cr is almost completely depleted after a 24 h stability test. Importantly, along with the decreased content of Cr, the catalyst activity is further promoted. Although the Cr itself may not be responsible for the improvement, its dissolution results in an ideal type of pore and/or active sites. We further optimize the deposition of high-surface-area and high-mass-loading $Ni_{0.6}Fe_{0.3}Cr_{0.1}O_x$ on carbon-cloth electrodes and demonstrate an overpotential as low as 251 mV at 10 mA cm^{-2} in 1 M KOH.

1. Introduction

Hydrogen can be generated renewably with solar energy through photoelectrochemical water splitting or by water electrolysis. Water splitting reactions can be divided into two half-reactions: the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) [1]. The slow kinetics of the four-electron transfer process and the O═O double bond formation during the OER limits the overall performance of water splitting [2]. Multi-component metal oxides/(oxy)hydroxides containing Ni, Co, Fe, and Mn are the promising candidates for the high-efficiency and low-cost OER electrocatalysts [3–6]. Fundamentally understanding the function and effect of each element in these earth-abundant catalysts is essential for the development of electrocatalysts with improved activities.

Among earth-abundant OER catalysts studied, Ni–Fe oxides/(oxy)hydroxides are among the most active catalysts in basic electrolyte [3,6–9]. Historically, Ni oxide/(oxy)hydroxides have been considered very active catalyst materials [10,11]. However, Corrigan and Trotochaud et al. have demonstrated that Ni (oxy) hydroxides are actually poor catalysts and that co-deposition or

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https://doi.org/10.1016/j.electacta.2018.01.143
0013-4686/

unintentional contamination (high purity electrolyte, etc) of Fe increases the activity of Ni (oxy)hydroxides by three orders of magnitudes compared to the pure Ni (oxy)hydroxides in rigorously Fe-free conditions [9,12]. The role of Fe in these Ni(Fe) (oxy)hydroxides is still debated, however, Fe is clearly a critical component for high activity [9,13–15].

Previous research shows that the introduction of a third metal could further improve the OER activity in Ni–Fe oxides/(oxy)hydroxides. Smith et al. proposed a synergistic effect among ternary Ni, Co, and Fe (oxy)hydroxides through a photochemical route [16]. Zhang et al. found that the addition of Al into Ni–Fe could benefit the OER catalysts, and correlated the promoted activity to the high Lewis-acidity of Al^{3+} facilitating the concerted M-O bond formation and deprotonation [17]. It has been previously reported that incorporation of a certain amounts of Cr could promote the OER activity of Ni–Fe oxides/hydroxides [18–21]. Singh et al. synthesized a series of spinel-type $NiFe_{2-x}Cr_xO_4$ oxides by the precipitation method, and the best electrocatalytic activity of the oxide was achieved with $x = 0.8–1.0$ [18]. Diaz-Morales et al. demonstrated that NiCr LDH (with Fe impurities) had superior activity than Ni(Fe) hydroxides by a joint theoretical-experimental study, and doping with Cr could lower the overpotential through tuning adsorption energies of *O and *OH [21]. In a separate investigation, Lange and coworkers correlated OER activity of annealed $Ni_{1-y-z}Fe_yCr_zO_x$ with electronic/physical structure and suggested that the OER activity benefited from the addition of Cr due to an increased ratio of octahedral Fe^{III} to tetrahedral Fe^{III} [19]. Stahl and coworkers also observed that the NiFe oxide OER activity was enhanced with Cr-doping and they attributed the improved activity to the interactions between these redox-active ions and Lewis-acidity of the Cr cations [20]. In addition to the conflicting role of Cr, the stability of Cr in NiFeCr oxide/(oxy)hydroxide catalysts is unclear [18,19,21].

The role of crystallinity has also been thoroughly studied and highly crystalline and rigid electrocatalysts generally underperform more-disordered so-called “amorphous” catalyst films [16,22]. This is likely because the active phases in many cases are (oxy)hydroxides under OER conditions regardless of the initial as-synthesized structure [3]. Amorphous oxides appear easier to convert to active (oxy)hydroxides phases than highly crystalline oxide catalysts [3,23–26]. Here we investigate a series of amorphous ternary metal oxides containing well-defined compositions (Ni, Fe, and Cr) prepared by a thermal decomposition method. The overpotentials of the ternary metal catalysts for water oxidation are mapped as a function of composition. The role of Cr in activity and long-term stability was tested via cyclic voltammetry and polarization. X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma optical emission spectrometry (ICP-OES) were used to monitor the surface and bulk compositions. We find that Cr leaches from the catalyst system during the course of the water oxidation process, which increases the performance of the Ni–Fe oxides/(oxy)hydroxides electrocatalyst by increasing the number of electrochemically available active sites. This indicates that Cr itself is unrelated with the high performance OER catalysts outside of its role as a pore-forming agent. The elucidation of the working mechanism of Cr content provides insight that will enable understanding the function of other thermodynamically unstable elements in multicomponent catalysts and designing effective porous/disordered electrocatalysts for water oxidation.

2. Experimental

2.1. Synthesis of amorphous films on planar substrates

Precursor solutions were prepared from nickel (II) 2-ethylhexanoate (78% w/w in 2-ethylhexanoic acid, Strem Chemicals), iron (III) 2-ethylhexanoate (50% w/w in mineral spirits, Strem Chemicals) and chromium (III) 2-ethylhexanoate (50% w/w in 2-ethylhexanoic acid, Alfa Aesar). Amorphous metal oxide films were prepared on fluorine-doped tin oxide (FTO) coated glass substrates (TEC-15, Pilkington) or Au/Ti through a modified near-infrared-driven (NIR) decomposition of metal-complex method (Scheme 1a) [27]. First, the solutions were prepared by dissolving the precursors in hexane to produce the total metal-complex concentration of 15 wt%. The mixed precursors were sonicated for 10 min to achieve homogeneous mixing. Then the solutions were spin-coated on FTO at 3000 rpm for 45 s. Second, the films were placed under a near-infrared lamp (Philips BR125 IR 150 W) with different irradiation time, where the bottom of the lamp was positioned 2 cm above the substrate that was set on an Al_2O_3 ceramic wafer to dissipate the heat. The temperature of substrate is about 220 °C, determined by a thermocouple.

2.2. Construction of catalysts/carbon cloth electrode

The electrocatalyst was loaded on carbon cloth (CC) by an impregnation method (Scheme 1b). The CC was dipped in the precursor solution for 5 s. Then the sample was treated with the NIR lamp irradiation (by the above-mentioned preparation method).

2.3. Electrochemical characterization

As-prepared electrodes were masked with a 60 μm Surlyn film (Solaronix) with a 0.25 cm^2 square hole to explore the active areas. Surlyn films were adhered to the electrodes after heating to 115 °C. The electrochemical measurements were performed using Zennium workstation (Zarhner, Inc.) or BioLogic SP200/SP300 in a home-built three-electrode electrochemical system in 0.1 M KOH electrolyte (Semiconductor grade, Sigma-Aldrich, without further purification). High-purity oxygen was bubbled through the electrolyte 20 min before and during the electrochemical test. A platinum wire and standard Hg/HgO were employed as a counter electrode (CE) and reference electrode (RE), respectively. The potential of the Hg/HgO reference electrode (*vs.* RHE) was calibrated against a reversible hydrogen electrode.

All potentials reported here were normalized to the overpotential (according to Equation (1)). The cyclic voltammetry for the integration of the Ni redox wave was performed with a scan rate of 10 mV s^{-1}. The onset-potential ($J = 0.1$ mA cm^{-2}), stable catalytic potential ($J = 1$ mA cm^{-2}) and Tafel slopes were measured by the galvanostatic method. Electrochemical impedance spectroscopy (EIS) was measured in the 0.1 M KOH solution with an amplitude of 5 mV and frequencies between 0.1 Hz and 1 MHz at a potential of 0.6 V *vs* Hg/HgO. The electrochemical measurements were corrected for R_u, the uncompensated series resistance. R_u was determined by equating R_u to the minimum impedance between 1 kHz and 1 MHz, where the phase angle was closest to zero. Typically, for the catalyst on FTO electrodes in 0.1 M KOH, R_u was ~30–50 Ω.

$$\eta = \boldsymbol{E}_{\text{measured}} - \boldsymbol{E}_{\text{rev}} - \boldsymbol{i}\boldsymbol{R}_u \text{ with } \boldsymbol{E}_{\text{rev}} = 0.30\text{ V at }25\,^{\circ}\text{C} \quad (1)$$

The average total turnover frequency (TOF), i.e. the number of O_2 formed per s per metal ion, is calculated based on the number total metal atoms (including Ni, Fe and Cr) and the steady-state current at 300 mV iR-compensated overpotential according Equation (2). The number of total metal is measured by ICP-OES from the dissolved sample following electrochemical analysis.