Sulfide doped cobalt oxide nanosphere as a highly efficient electrocatalyst for oxygen evolution reaction

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Abstract. Electrochemical water splitting has been known as a promising and environmental approach to produce hydrogen by avoiding relying on fossil fuels. Unfortunately, the efficient and large-scale \( \text{H}_2 \) production is still hindered by the sluggish kinetics of the oxygen evolution reaction (OER) at the anode side of a water electrolyzer. Herein, we report a novel amorphous sulfide doped cobalt oxide (amorphous Co-S-O) nanosphere as an efficient electrocatalyst for OER. The Co-S-O electrode exhibits high HER activity and good stability.

Keywords: OER; Electrocatalyst; Sulfide Cobalt; Nanosphere;

1. Introduction

Electrochemical splitting of water provides an attractive way to produce hydrogen fuel.\textsuperscript{[1-4]} The efficiency of this hydrogen generation depends enormously on the anodic oxygen evolution reaction (OER).\textsuperscript{[5]} However, by the reason of multistep reaction involving four e\textsuperscript{-} transfers, OER has high kinetic barrier, large overpotential and low efficiency.\textsuperscript{[6]} As is known to all, Pt- and Ru-based materials are the benchmark catalysts for OER, but the resource scarcity, high cost and poor stability of Pt- and Ru-based catalysts hinder their large scale application.\textsuperscript{[7-9]} To meet these challenges, great effort has been given to reduce the overpotentials of OER kinetics, using cheaper earth abundant materials.\textsuperscript{[10]}

Catalytic activity is of great important indicator in evaluation the efficacy of electrocatalysts. Activities are controlled by two factors: the number of active sites and more efficient mass transportation.\textsuperscript{[11]} With this in mind, it is very necessary to logically design and prepare hollow structure catalysts, which maximize the specific surface area and provide abundant active sites for OER.

Herein, we synthesized novel amorphous sulfide doped cobalt oxide (amorphous Co-S-O) nanosphere. The Co-S-O shows more remarkable OER activity than pure Co\textsubscript{3}O\textsubscript{4} in 1.0 M KOH. The Co-S-O with a low overpotential of 285 mV at the current density of 10 mA cm\textsuperscript{-2} and satisfied durability.

2. Experimental section

Firstly, \( \text{Co(CH}_3\text{COO)}_2\cdot4\text{H}_2\text{O, NaHCO}_3 \) and polyvinylpyrrolidone were dissolved into ethylene glycol under stirring to form a clear solution, Then the solution was transferred into a Tefion-lined stainless autoclave (50 mL). Then the autoclave was sealed and placed in an oven at 200 °C for 20 h. Then, The Co\textsubscript{3}O\textsubscript{4} was synthesized by calcined the pink precipitate at 300 °C for 2 h Finally, above resultant Co\textsubscript{3}O\textsubscript{4} with thioacetamide was dispersed in deionized water at 160 °C for 3 h.

3. Results and discussion

Figure 1. (a) XRD patterns of amorphous Co-S-O, and Co\textsubscript{3}O\textsubscript{4} precursor; (b) The SEM images of the Co\textsubscript{3}O\textsubscript{4}, precursor; (c) The SEM images of the amorphous Co-S-O.

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product. Figure 1b shows that the precursor is a burr sphere. Figure 1c shows that amorphous Co-S-O is a hollow sphere.

As we all know, X-ray photoelectron spectroscopy (XPS) analysis can detect the surface composition and chemical states. The XPS analyses reveal that Co-S-O include Co, S, and O elements without other impurities (Figure 2a). The Co 2p XPS spectrum of Co-S-O is displayed in Figure 2b. The Co 2p spectra peaks at 778.4 eV and 793.5 eV correspond to spin-orbit splitting values of Co 2p3/2. The Co 2p spectra peaks at 781.4 eV and 797.5 eV correspond to spin-orbit splitting values of Co 2p1/2. In Figure 2c, the two peaks at 161.5 and 162.2eV are attributed to the S 2p3/2 and S 2p1/2 of Co-S, respectively. The peaks at 168.5 and 169.1eV correspond to S-O bond.

The OER catalytic activity of amorphous Co-S-O and Co3O4 were investigated in 1 M KOH with the three electrode system. The linear sweep voltammograms (LSV) of Co-S-O exhibits the highest electrocatalytic activity with the lowest overpotential of 285 mV to reach 10 mA cm−2, smaller than that of Co3O4 (320mV) (Figure 3a). The Tafel slope of the Co-S-O are only about 49.67 mV dec−1 (Figure 3b), which is much lower than that of the Co3O4 (72.63 mV dec−1) and RuO2 (61.05 mV dec−1). Amorphous Co-S-O has a low Tafel slope, which indicates that it has great reaction kinetics in the OER.

To assess the OER reaction kinetics, the electrochemical impedance spectroscopy (EIS) tests were conducted (Figure 4a). The Nyquist plots suggest that Co-S-O possess the smaller interfacial charge transfer resistance and faster electron transfer process than Co3O4. The stability of Co-S-O electrode was studied using chronogrammetry. The tested result (Figure 4d) at 1.52 V vs RHE suggests that the electrocatalytic activity of Co-S-O electrode can be maintained for a long time without obvious change. The above results confirm that Co-S-O is a stable and highly active electrocatalyst for OER.

4. Conclusion

In summary, amorphous Co-S-O is demonstrated excellent electrocatalytic performance and catalytic stability for OER in alkaline medium. To approach a current density of 10 mA cm−2, amorphous Co-S-O only needs the overpotential of 285 mV. This work breaks a new path for the single metal sulfides and opens up an avenue in designing other advanced electrocatalysts.

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**Figure 2.** (a) XPS survey spectrum for amorphous Co-S-O and (b) Co 2p, (c) S 2p.

**Figure 3.** (a) polarization curves for OER at a scan rate of 10 mV s−1 in 1.0 M KOH and (b) corresponding Tafel plots.

**Figure 4.** (a) Nyquist plots of different electrodes at an overpotential of 300 mV for HER; (b) Chronoamperometric response of amorphous Co-S-O in 1 M KOH solution at the applied potential of 1.52 V versus RHE.