Iron-cobalt bimetallic selenide as effective and durable catalyst for HER and OER

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Abstract. As a way of energy conversion with zero carbon emission, water splitting plays a crucial role in the green and efficient energy utilization. Reasonable design of suitable catalysts for hydrogen evolution reaction and oxygen evolution reaction is conducive to the wide-ranging application of water splitting. Double metallic composite is superior to single-metal and non-metal materials due to the unique electronic configuration. In this work, we synthesized a Fe-Co-Se catalyst on carbon cloth (Fe-Co-Se/CC) for HER and OER. Fe-Co-Se/CC shows an overpotential of 131 mV@10 mA cm$^{-2}$, 177 mV@100 mA cm$^{-2}$ and 215 mV@500 mA cm$^{-2}$ in 1.0 M HClO$_4$ for HER and 300 mV@100 mA cm$^{-2}$, 365 mV@500 mA cm$^{-2}$ and 416 mV@1000 mA cm$^{-2}$ in 1.0 M KOH for OER. Fe-Co-Se/CC also exhibits excellent stability in HER and OER measurements. This work demonstrates that Fe-Co-Se/CC is a promising candidate catalyst for water splitting.

1. Introduction

Nowadays, the energy demand grows swiftly, but the reserves of fossil fuel are limited and environmental pollution becomes more serious. Building a global-scale environment-friendly sustainable energy system has become the most modern and urgent scientific challenge [1]. In 1874, Jules Verne claimed that "water will be the coal of the future"[2]. Water splitting as a green and sustainable energy conversation approach, converting the electricity which is produced by other renewable resources (like solar energy, wind energy, tidal energy) into chemical energy for storage, avoiding the inconvenience caused by the discontinuity of renewable energy itself. It will play a critical role in the development of a sustainable energy system. Overall water splitting (OWS) can be divided into two reactions, one is hydrogen evolution reaction (HER) occurs at the cathode, another is oxygen evolution reaction (OER) occurs at the anode.

Transition metal (TM) is widely concerned due to its advantages of low price, high reserves, rich and adjustable 3D orbital electrons. Fe, Ni, Co, Mo, and their alloys, sulfides, phosphates, carbides, nitrides, and oxides are the most widely studied electrolytic water catalysts[3-5]. Analogy with sulfides, the 3D orbit of selenium in metal selenides may be involved in the bonding with metal atoms. This electronic structure makes the transition metal selenides favorable for electron transfer and reaction. Ni et al.[6] prepared NiSe$_2$, NiSe, and Ni$_3$Se$_2$ on Ni foam by using the electrodeposition method. NiSe$_2$ showed the best HER and OER performances among these catalysts, and the good electrocatalytic activity is phase-dependent. Yin et al.[7] obtained 1T-MoSe$_2$ of disordered structure with plenty of unsaturated defects by adding excessive reductant NaBH$_4$ in the solvothermal method under lower reaction temperature. 1T-MoSe$_2$ achieved a current density of 10 mA cm$^{-2}$ at 152 mV for HER. Zhao et al.[8] controlled the mass ratio of Co and Se to tune the Co charge state. And they found
a low Co charge state is positive for HER, while a high Co charge state is beneficial for OER. The bifunctional electrocatalyst exhibits 10.3 mA cm$^{-2}$ at 1.8 V vs. RHE, 7.4 mA cm$^{-2}$ higher than commercial Ir–C and Pt–C electrodes at 1.8 V. However, the exposure of the active sites number of the pure monometallic selenides is insufficient and leads to the low catalytic activity.

Electronic configuration controlling can improve the activity of electrocatalyst. It is a common strategy to regulate the electronic configuration of the catalyst by doping or introducing defects, to reduce the reaction energy barrier and enhance the catalytic activity[9-12]. Transition metal elements such as Co, Ni, Fe, Mo, Zn, and non-metal elements such as S, O, P, Se often as dopants. Premnath et al.[13] synthesized a series of coral-like Ni$_{1-x}$Mo$_x$Se. The Ni$_{0.5}$Mo$_{0.5}$Se performed electrochemical activity of 197 mV at 10 mA cm$^{-2}$ towards HER and 340 mV@10 mA cm$^{-2}$ for OER. Gao et al.[14] incorporated Fe into NiSe nanorod/nanosheet hierarchical array on Ni foam, the introduction of Fe$^{3+}$ could realize the dual adjustment of electronic structure and morphology at the same time. The optimal Fe$_{7.4\%}$Ni$_{92.6\%}$Se presents the low overpotential of 163 mV@10 mA cm$^{-2}$, 296 mV@500 mA cm$^{-2}$ for HER, 231 mV@50 mA cm$^{-2}$, 269 mV@500 mA cm$^{-2}$, 291 mV@1000 mA cm$^{-2}$ toward OER. Li et al.[15] prepared hollow Mn$_{0.1}$Co$_{0.9}$Se$_{2}$ polyhedrons by Co-based bimetallic organic frameworks (BM-ZIFs), the introduction of a transition metal element enhances the electrocatalytic ability via the Jahn–Teller effect. The Zn$_{0.1}$Co$_{0.9}$Se$_{2}$ showed small overpotentials of 140 mV@10 mA cm$^{-2}$ and 340 mV@10 mA cm$^{-2}$ with excellent catalytic stability towards HER in acidic and OER in alkaline.

In this work, we synthesized a catalyst of iron-cobalt-selenium on carbon cloth (Fe-Co-Se/CC) by hydrothermal method followed with a high-temperature selenylation approach. The Fe-Co-Se/CC catalyst exhibits the excellent HER and OER activity and durable stability.

2. Experiment section

2.1. Material synthesis

Synthesis of Fe-Co-Se/CC: In a typical synthesis, 4.5 mmol FeCl$_3$ꞏ6H$_2$O and CoCl$_2$ꞏ6H$_2$O, 16 mmol NH$_4$F, and 30 mmol urea were dissolved in deionized water via sonicating 15 minutes. Before transferring the transparent solution into a 100 mL Teflon-lined autoclave, putting a piece of 6 cm$^2$ carbon cloth inside. Then, keeping the reaction oven at 120°C for 6 h. After the autoclave was cooled naturally, the carbon cloth was taken out carefully and washed with deionized water and ethanol alternately, then dried in a vacuum oven at 60°C for 6 h. The product is marked as Fe-Co-pr/CC. After selenylation the Fe-Co-pr/CC at 450°C for 2 h with a ramp of 2°C min$^{-1}$, Fe-Co-Se/CC was obtained. Synthesis of Fe-Se/CC: All the steps are the same to Fe-Co-Se/CC, in the absence of cobalt precursor.

2.2. Electrochemical measurements

Electrochemical measurements were conducted in a single cell by using a three-electrode system with CHI660E electrochemical station. The linear sweep voltammetry (LSV) measurements were performed at a scan rate of 20 mV s$^{-1}$. The as-prepared catalysts were cut into 0.5 × 0.5 cm$^2$ as the working electrode. A piece of graphite rod was used as the counter electrode, the Ag/AgCl was used as a reference electrode in 1.0 M HClO$_4$, and Hg/HgO was used as a reference electrode in 1.0 M KOH, respectively. Before the test, the electrolyte should be bubbled with Ar gas for more than 30 minutes to purge oxygen and calibrated to vs. reversible hydrogen electrode (RHE). The HER performance measurements were carried out in an Ar-saturated 1.0 M HClO$_4$ solution, and the OER measurements were carried out in the O$_2$-saturated 1.0 M KOH solution.

3. Result and discussion

The morphology of the sample was characterized by scanning electron microscope (SEM). Figure 1a-b show that bare carbon cloth is composed of smooth carbon fiber. Fe-Co-pr is the particle with irregular morphology and uniformly attached to carbon cloth, is shown in Figure 1c-d. After selenylation, compare to Fe-Co-pr, the morphology of Fe-Co-Se almost unchanged.
HER measurements were performed in 1.0 M HClO₄ electrolyte. As shown in Figure 2a, the catalytic current density of bare CC is extremely small, indicating that the substrate has no effect on performance evaluation. The Fe-Co-Se/CC achieves a current density of 10 mA cm⁻², 100 mA cm⁻² and 500 mA cm⁻² at 131 mV, 177 mV and 215 mV, which is superior to Fe-Se/CC of 207 mV, 298 mV and 359 mV at corresponding current density (with 90% iR correction). The results demonstrated that the addition of Co is a positive effect on HER.

Stability is a major parameter for performance evaluation. After the accelerated degradation test (ADT) was conducted between -0.2 and 0.3 V by taking continuous cyclic voltammetry (CV) with a sweep rate of 100 mV s⁻¹, the LSV curves also can overlay well (Figure 3b), manifesting the excellent stability. The SEM images of Fe-Co-Se/CC are presented in Figure 3c-d.
Fe-Co-Se/CC also reveals good OER performance. In 1.0 M KOH, the overpotential of Fe-Co-Se/CC is 300 mV@100 mA cm\(^{-2}\) (with 90\% iR correction), 30 mV and 164 mV less than Fe-Co-pr/CC and Fe-Co-Se/CC. As well as the performance of Fe-Co-Se/CC at high potential is excellent, it can achieve 500 mA cm\(^{-2}\) and 1000 mA cm\(^{-2}\) at an overpotential of 365 mV and 416 mV.

Figure 3. Electrochemical performance of Fe-Co-Se/CC in O\(_2\)-saturated 1.0 M KOH.

The durability of Fe-Co-Se/CC is extremely good. After 10h i-t test at 1.634 V, the current retention is ~95.6\%, and the LSV curves before and after i-t test show no difference. The SEM images exhibited the morphology of Fe-Co-Se/CC little changed.

![Figure 3](image1)

Figure 4. (a) i-t curves of Fe-Co-Se/CC; (b) LSV curves of Fe-Co-Se/CC before and after i-t test in 1.0 M KOH; (c-d) SEM images of Fe-Co-Se/CC after i-t test.

4. Conclusion
In conclusion, we used a hydrothermal followed high-temperature selenylation method to obtain Fe-Co-Se/CC catalyst. It exhibited a good HER performance in acid system and OER performance in an
alkaline solution. The overpotential of Fe-Co-Se/CC is 131 mV@10 mA cm\(^{-2}\), 177 mV@100 mA cm\(^{-2}\) and 215 mV@500 mA cm\(^{-2}\) in 1.0 M HClO\(_4\) for HER and 300 mV@100 mA cm\(^{-2}\), 365 mV@500 mA cm\(^{-2}\) and 416 mV@1000 mA cm\(^{-2}\) in 1.0 M KOH for OER. Fe-Co-Se/CC also shows excellent stability both in HER and OER measurements. This work demonstrates that cobalt addition is beneficial for electrocatalytic enhancement. The bimetallic selcnides are promising candidates as electro-catalytic overall water splitting materials and offer a new way to rationally design effective catalysts.

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