

Integrated Co-Ni-Se network on Ni foam as an efficient electrocatalyst for Alkaline Hydrogen Evolution

Received Feb.15, 2019,
Accepted Mar.10, 2019,

DOI: 10.4208/jams.021519.031019a

<http://www.global-sci.org/jams/>

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Abstract. Hydrogen evolution reaction (HER) is long considered as a promising chemical reaction that can produce the clean fuel hydrogen to resolve the energy crisis and environmental pollution. Herein, we report the in situ growth of Co-Ni-Se network on a 3D porous Ni foam support (Co-Ni-Se/NF) as an efficient electrocatalyst for HER. The obtained Co-Ni-Se/NF electrode exhibits high HER activity that only needs a low overpotential of 106 mV at 10 mA cm⁻².

Keywords: Hydrogen evolution reaction; Ni foam; electrocatalyst.

1. Introduction

Facing the energy and environmental crisis, the grand challenge is to explore sustainable, carbon-neutral energy sources as a substitution for traditional fossil fuels [1]. The hydrogen evolution reaction (HER) is widely considered as a promising strategy to produce clean and renewable hydrogen energy [2]. The crucial conundrums are design and synthesis of catalysts with great efficiency and excellent stability. So far, most highly active catalysts are the noble metal-based materials, such as Pt for HER. But the high cost and poor stability seriously limit their large-scale commercial applications [3, 4]. Therefore, it is an emergency to develop highly active and inexpensive electrocatalysts for HER.

Over the past few years, a variety of non-noble based catalysts have been reported as electrocatalysts for HER, such as carbon materials [5], transition-metal hydroxides [6], sulfides [7], selenides [8], and so on. Among these materials, the 3D transition metal (3d-TM) selenides have exhibited the higher electrocatalytic activities and conductivities than their oxide or hydroxide counterparts [9]. Furthermore, compared with S²⁻, Se²⁻ has the larger size anions, which may endow suitable band gap thus enhance the electrochemical performance [10].

Herein, we synthesized Co-Ni-Se network on a nickel foam support (Co-Ni-Se/NF). The synergistic effect of cobalt and nickel atoms could effectively increases the electrocatalytic activity for HER. When the current density reach to 10 mA cm⁻², this material only needed the overpotential of 106 mV with superior stability.

2. Experimental section

The overall synthesis of Co-Ni-Se/NF was synthesized by two step hydrothermal method. Primarily, Co precursor/NF was synthesized by Co(CH₃COO)₂·4H₂O, NH₄F, and urea at 120°C for

6 h with the presence of the Ni foam. Secondly, Co-based/NF precursor reacted with NaHSe at 160 °C or 10 h and converted into Co-Ni-Se/NF.

3. Results and discussion

The chemical composition of the product was carried out by X-ray powder diffraction (XRD). As shown in **Figure 1a**, the three marked peaks from left to right matches to the (111), (200), and (220) planes of metallic nickel (JCPDS: 070-0989), which are attributed to the Ni foam substrate. Moreover, the diffraction patterns are very consistent with those of CoNiSe₂ (JCPDS: 65-7038). Remarkably, except for three strong peaks stemming from the Ni substrate, the (101) diffraction peak displays the highest intensity, indicating the preferential growth of (101) planes. The morphological and structural evolution of the electrode was investigated by scanning electron microscopy (SEM). **Figure 1b** reveals that the nano-architecture uniformly distributes on the NF surface. Noticeably, those nanorods interconnecting with each other are beneficial for electron transfer, which lays the foundation for high electrocatalytic activity. Furthermore, the inset of **Figure 1b** is the high-resolution transmission electron microscopy (HRTEM) of the Co-Ni-Se/NF, the lattice fringe of 0.27 nm is readily indexed to the (101) planes of CoNiSe₂, completely coinciding with the result of XRD.

XPS was employed to further refine the composition and

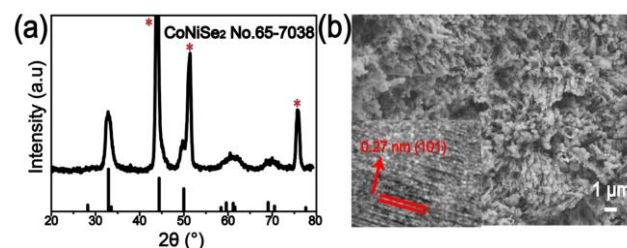


Figure 1 (a) XRD pattern of Co-Ni-Se/NF (b) the SEM images of the Co-Ni-Se/NF nano-architecture directly grown on the nickel foam, the inset in (b) shows the HRTEM of the Co-Ni-Se/NF.

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chemical state of the Co-Ni-Se/NF, as shown in **Figure 2a**, the XPS survey spectrum shows the Co, Ni, and Se signals in addition to those from oxides and adventitious C species. The Co 2p spectra peaks at 781.2 and 796.8 eV (**Figure 2b**) correspond to spin-orbit splitting values of Co 2p_{3/2} and Co 2p_{1/2}, which are associated with Co²⁺ [11]. The Ni 2p region (**Figure 2c**) exhibits two peaks at 855.5 and 873.3 eV are assigned to the Ni 2p_{3/2} and Ni 2p_{1/2}, confirming the signal of Ni²⁺ at the surface [12]. The Se 3d XPS spectrum in **Figure 2d** shows the peak for Se 3d at 54.4 eV (Se 3d_{5/2}) is originated

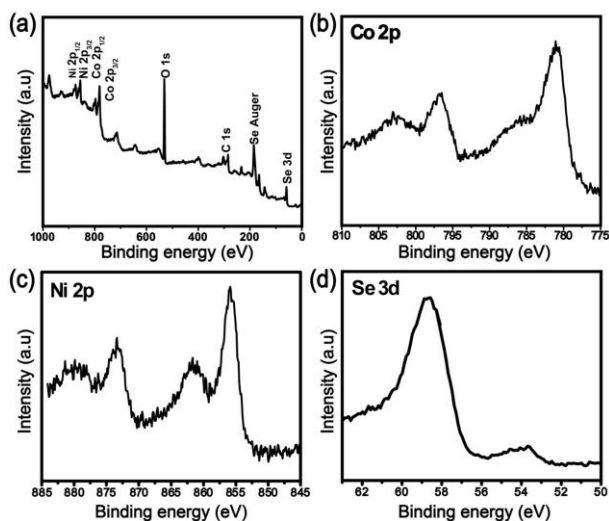


Figure 2 (a) The full scan XPS survey spectrum for Co-Ni-Se/NF and the high resolution (b) Co 2p, (c) Ni 2p and (d) Se 3d XPS survey spectrum for Co-Ni-Se/NF.

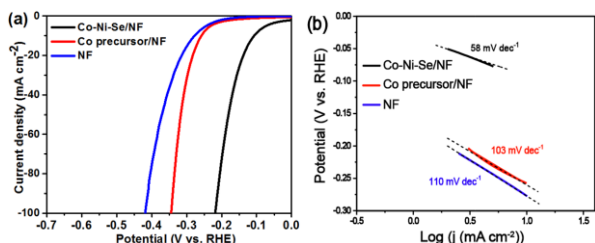


Figure 3 (a) Polarization curves for HER at a scan rate of 5 mV s⁻¹ in 1.0 M KOH and (b) corresponding Tafel plots.

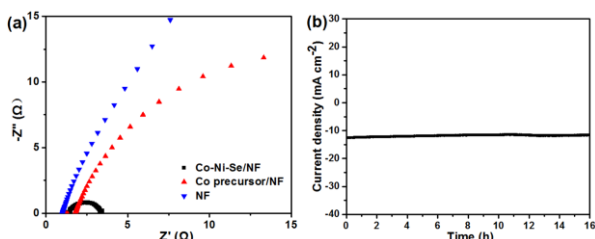


Figure 4 (a) Nyquist plots of different electrodes at an overpotential of 200 mV for HER; (b) time dependent-current density of Co-Ni-Se/NF for HER at an overpotential of 120 mV.

from the state of Se²⁻ and the peak at 58.8 eV is attributed to oxidation of surface Se species (SeO_x). Based on XPS data, this sample has a composition of Co²⁺, Ni²⁺ and Se²⁻ cation, which is consistent with the XRD result.

The HER performance of all samples was evaluated in 1M KOH solution with a three-electrode system. As shown in **Figure 3a**, the LSV curves of Co-Ni-Se/NF displayed a low overpotential of 106 mV at a current density of 10 mA cm⁻². It is obviously smaller than Co precursor/NF (256 mV) and bare NF (278 mV), indicating the highly efficient catalytic activity of Co-Ni-Se/NF. The corresponding Tafel plots are displayed in **Figure 3b**, the Co-Ni-Se/NF shows the smallest Tafel slope among the other samples, verifying that the Co-Ni-Se/NF catalyst follows a faster HER kinetics with efficient HER catalytic properties.

Meanwhile, the electrochemical impedance spectroscopy (EIS) was shown in **Figure 4a**, the observed Rct value of Co-Ni-Se/NF (2.05Ω) was visibly smaller than Co precursor/NF (28.38Ω) and NF (77.15Ω), indicating that the Co-Ni-Se/NF catalyst possess a much faster electron transfer thus resulting in a better HER catalytic activity. In addition, the stability of electrocatalyst as shown in **Figure 4b**, the Co-Ni-Se/NF electrode displays insignificant degradation of current density after a long period, demonstrating the superior stability of Co-Ni-Se/NF for HER.

4. Conclusion

In conclusion, in situ growth of Co-Ni-Se on a 3D porous conductive Ni foam support (Co-Ni-Se/NF) exhibits efficient electrocatalytic performance and catalytic stability for HER in strongly alkaline solutions. Bimetallic synergy is conducive to increase active site concentration, making the binder-free Co-Ni-Se electrode only a low overpotential of 106 mV to reach a current density of 10 mA cm⁻² for HER. Our work offers one of a new insight to design non-noble bimetal electrocatalyst with highly activity for HER.

Acknowledgements

This work was supported by Chongqing Municipal Natural Science Foundation (cstc2018jcyjAX0625).

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