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Iron and nickel doped CoSe₂ as efficient non precious metal catalysts for oxygen reduction

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ABSTRACT

Iron and nickel doped CoSe₂ were prepared by solvothermal method, and they were proved to be ternary chalcogenides by series of physical characterization. The effects of the iron and nickel contents on the oxygen reduction reaction were investigated by electrochemical measurements, and the highest activities were obtained on Co_{0.7}Fe_{0.3}Se₂ and Co_{0.7}Ni_{0.3}Se₂, respectively. Both Co_{0.7}Fe_{0.3}Se₂ and Co_{0.7}Ni_{0.3}Se₂ presented four-electron pathway. Furthermore, Co_{0.7}Fe_{0.3}Se₂ exhibited more positive cathodic peak potential (0.564 V) and onset potential (0.759 V) than these of Co_{0.7}Ni_{0.3}Se₂ (0.558 V and 0.741 V). And Co_{0.7}Fe_{0.3}Se₂ displayed even superior stability and better tolerance to methanol, ethanol and ethylene glycol crossover effects than the commercial Pt/C (20 wt% Pt).

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Introduction

Nowadays, non-precious metal-based electrocatalysts have exhibited promising activities towards oxygen reduction reaction (ORR) [1–4]. Among them, cobalt based selenides (CoSe_x) are attracting enormous interest as new ORR electrocatalysts. For example, CoSe₂/C obtained by Feng et al. [5,6] showed superior electrocatalytic activity towards ORR with an open circuit potential of 0.81 V in 0.5 M H₂SO₄, and higher methanol tolerance than that of Pt/C. Susac et al. [7] exhibited that cobalt–selenium (Co–Se) with varying content of Se obtained by magnetron sputtering and chemical methods

indicated a electrocatalytic activity towards ORR in an acidic electrolyte.

However, the ORR activities of these materials are still far from proton exchange membrane fuel cells' practical applications [8–11]. To further improve electrocatalytic activity, doping of transition metal is crucial to the Co-based chalcogenides. Zhao et al. [12] exhibited the tungsten doped Co–Se electrocatalysts synthesized by decarbonylation of carbonyl compounds in 1,6-hexanediol solvent, and indicated high ORR electrocatalytic activity in 0.5 M H₂SO₄. Nanosized particles of Ru_xFe_ySe_z were prepared by Solorza-Feria [13] showed higher electrocatalytic activity towards ORR than that of the Ru_xSe_y.

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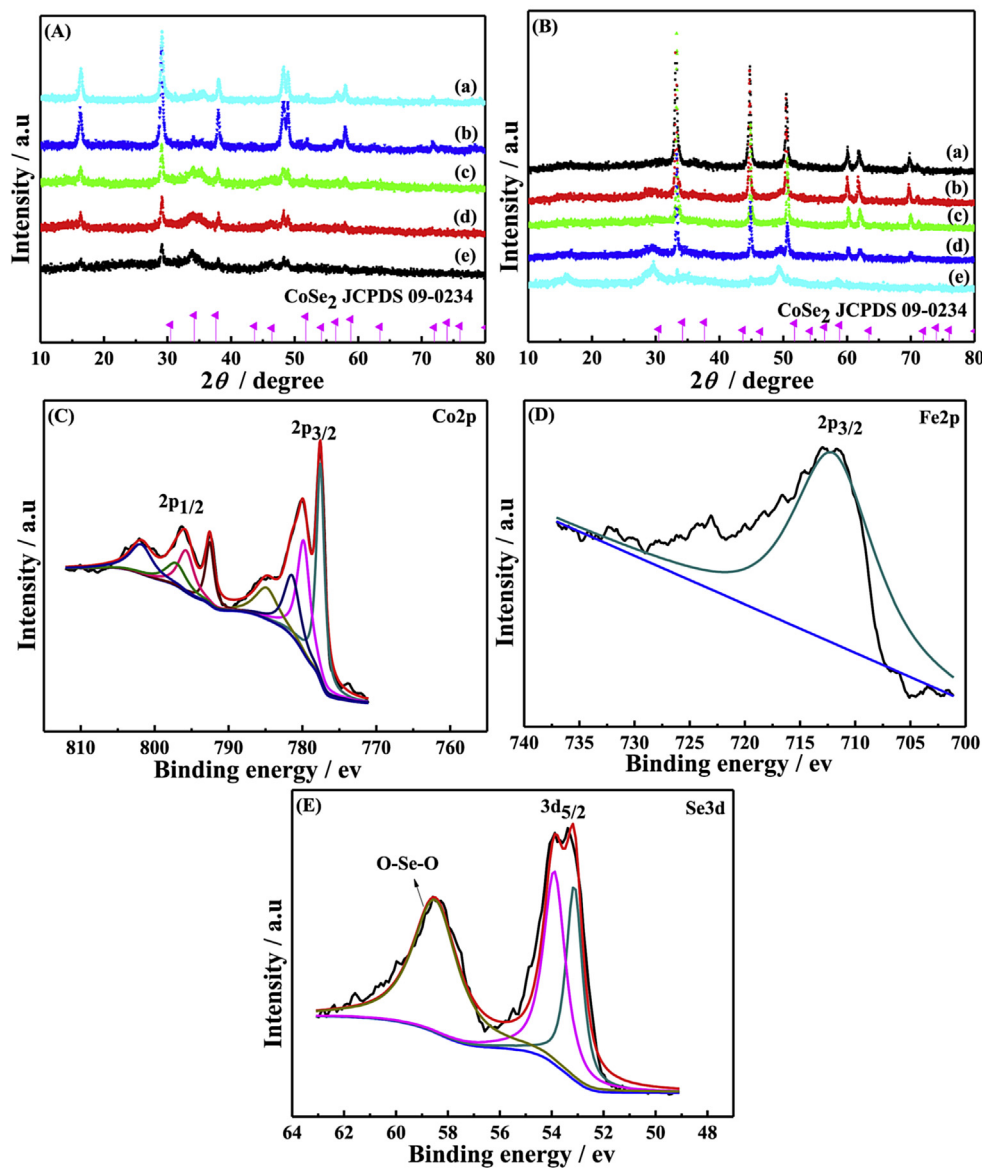


Fig. 1 – (A) XRD patterns of (a) $\text{Co}_{0.9}\text{Fe}_{0.1}\text{Se}_2$, (b) $\text{Co}_{0.8}\text{Fe}_{0.2}\text{Se}_2$, (c) $\text{Co}_{0.7}\text{Fe}_{0.3}\text{Se}_2$, (d) $\text{Co}_{0.6}\text{Fe}_{0.4}\text{Se}_2$ and (e) $\text{Co}_{0.5}\text{Fe}_{0.5}\text{Se}_2$, (B) XRD patterns of (a) $\text{Co}_{0.9}\text{Ni}_{0.1}\text{Se}_2$, (b) $\text{Co}_{0.8}\text{Ni}_{0.2}\text{Se}_2$, (c) $\text{Co}_{0.7}\text{Ni}_{0.3}\text{Se}_2$, (d) $\text{Co}_{0.6}\text{Ni}_{0.4}\text{Se}_2$ and (e) $\text{Co}_{0.5}\text{Ni}_{0.5}\text{Se}_2$. XPS spectra of $\text{Co}_{0.7}\text{Fe}_{0.3}\text{Se}_2$ in the (C) Co 2p, (D) Fe 2p, and (E) Se 3d regions.

In order to enhance ORR electrocatalytic activity, two series of ternary non-noble metal chalcogenides were synthesized in this work. The electrocatalytic activity towards ORR and stability of the chalcogenides were investigated in 0.5 M H_2SO_4 . Furthermore, the relationships between the content of doping transition metals and electrocatalytic activity were investigated.

Experimental

Electrocatalyst synthesis

All chemicals were purchased from Sigma–Aldrich.

$\text{Co}_x\text{Fe}_{1-x}\text{Se}_2$ ($x = 0.9, 0.8, 0.7, 0.6, 0.5$) were obtained via a solvothermal method. Briefly, 0.291 g cobalt nitride

hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and different iron (II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) (Table S1) were dissolved in 30 mL diethylenetriamine (DETA) and deionized water (DIW) ($V_{\text{DETA}}/V_{\text{DIW}} = 2:1$). Then, 0.591 g sodium selenite (Na_2SeO_3) and 8.5 mL hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) were added into the solution, and stirred for 30 min. Finally, the mixture was transferred into an autoclave and treated at 140 °C for 24 h.

$\text{Co}_x\text{Ni}_{1-x}\text{Se}_2$ ($x = 0.9, 0.8, 0.7, 0.6, 0.5$) were prepared by the similar method, only using nickel nitride hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (Table S2) instead of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. CoSe_2 was prepared with no addition of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ [14].

Characterization

X-ray diffraction (XRD) experiments were carried out on a GBC MMA X-ray diffractometer with Cu $K\alpha$ radiation. X-ray

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