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Facile synthesis of Co-based selenides for oxygen reduction reaction in acidic medium

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ABSTRACT

Co-based selenides with different selenium contents were successfully synthesized by a one-pot solvothermal method. The physical properties of the prepared catalysts were characterized by X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy and thermogravimetric analysis. While their electrocatalytic performances were evaluated by cyclic voltammetry, linear sweep voltammetry, electrochemical impedance spectroscopy and chronoamperometry. The results showed that the Co-Se-75 displayed better electrocatalytic activity towards the oxygen reduction reaction with higher onset potential (0.708 V vs. RHE), reduction current (2.81 mA cm^{-2}) and a four-electron oxygen reduction process. Furthermore, the catalyst exhibited better stability, stronger resistance to methanol, ethanol and ethlene glycol than that of the Pt/C (20 wt% Pt) catalyst.

Introduction

Proton exchange membrane fuel cells (PEMFCs) are an electrochemical device that converts the chemical energy of a fuel directly into electrical energy [1]. They are regarded as one of the most promising power sources for transportation, generation of power, and portable electronic devices, etc., due to their high energy-conversion efficiency, low temperature of operation, and zero or low emission [2–6]. Among various PEMFCs, direct methanol fuel cells (DMFCs) have received the most extensive attention and efforts [7–10]. Compared with the oxidation reaction of fuels at the anode, developing effective catalysts for oxygen reduction reaction (ORR) at the cathode of DMFCs is a severe technological bottleneck [11]. Although platinum (Pt) and its alloys have been recognized as the most active catalysts for ORR, the prohibitive cost, scarcity, weak durability, deactivation by CO poisoning and fuel crossover effect hindered the large-scale application of DMFCs [12–16].

In recent year, the global research efforts were directed toward the search for broad-range alternative catalysts based on non-precious metal (NPM) [17–37], especially in developing cheap transition metal oxides [25–30], nitrogen-coordinated metal [31,32] and metal-free carbon-based nanostructures [33–37]. It is well-known, developing NPM electrocatalysts for ORR in acidic medium is of practical significance and highly desired. Transition metal chalcogenides

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such as Co_9S_8 [38], Co_3S_4 [39], $Co_{1-x}Se$ [40], FeS_2 [41], (Co, Fe) S_2 [42], and $CoSe_2$ [43,44] show high ORR acitivities and stabilities. In addition, the transition metal chalcogenides are insensitive to methanol [45], halide ions [46], ethanol and ethylene glycol [47].

In this work, the Co-based selenides were synthesized by a one-pot solvothermal strategy. Furthermore, the prepared Co-based selenides exhibited good electrocatalytic activity towards ORR.

Materials and methods

Chemical and reagents

Cobalt nitride hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), hydrazine hydrate ($N_2H_4 \cdot H_2O$), sulfuric acid (H_2SO_4), methanol (CH_3OH), ethanol (C_2H_5OH) and ethylene glycol ($(CH_2OH)_2$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium selenite (Na_2SeO_3) was purchased from Xiya Reagent Research Center. Diethylenetriamine (DETA) was purchased from Aladdin. All aqueous solutions were prepared with analytical grade chemicals and deionized water (DIW).

Catalysts preparation

The catalysts were synthesized by a solvothermal method similar to previous reports [48], Briefly, appropriate $Co(NO_3)_2 \cdot 6H_2O$ and Na_2SeO_3 were added into a 30 mL mixed solution of DETA and DIW ($V_{DETA}/V_{DIW} = 2:1$), Se molar ratio in the catalysts was chosen at 66.7 mol%, 71.4 mol%, 75 mol%, 77.8 mol% and 80 mol% according to the reference [49]. After half an hour, 8.5 mL 50% $N_2H_4 \cdot H_2O$ was added in the above solution, then transferred into a Teflon-lined autoclave and maintained at 140 °C for 24 h. Finally, the prepared materials were washed with ethanol and distilled water, then dried at 60 °C under vacuum overnight. The resulting samples were denoted as Co-Se-66.7, Co-Se-71.4, Co-Se-75, Co-Se-77.8, and Co-Se-80, respectively. As a comparison, the electrochemical performance of the commercial Pt/C catalyst BASF (20% Pt supported on Vulcan XC-72 carbon, BASF Chemical) was also examined.

Physical characterizations

X-ray diffraction (XRD) patterns were obtained with a GBC MMA X-ray diffractometer with Cu Kα radiation. The

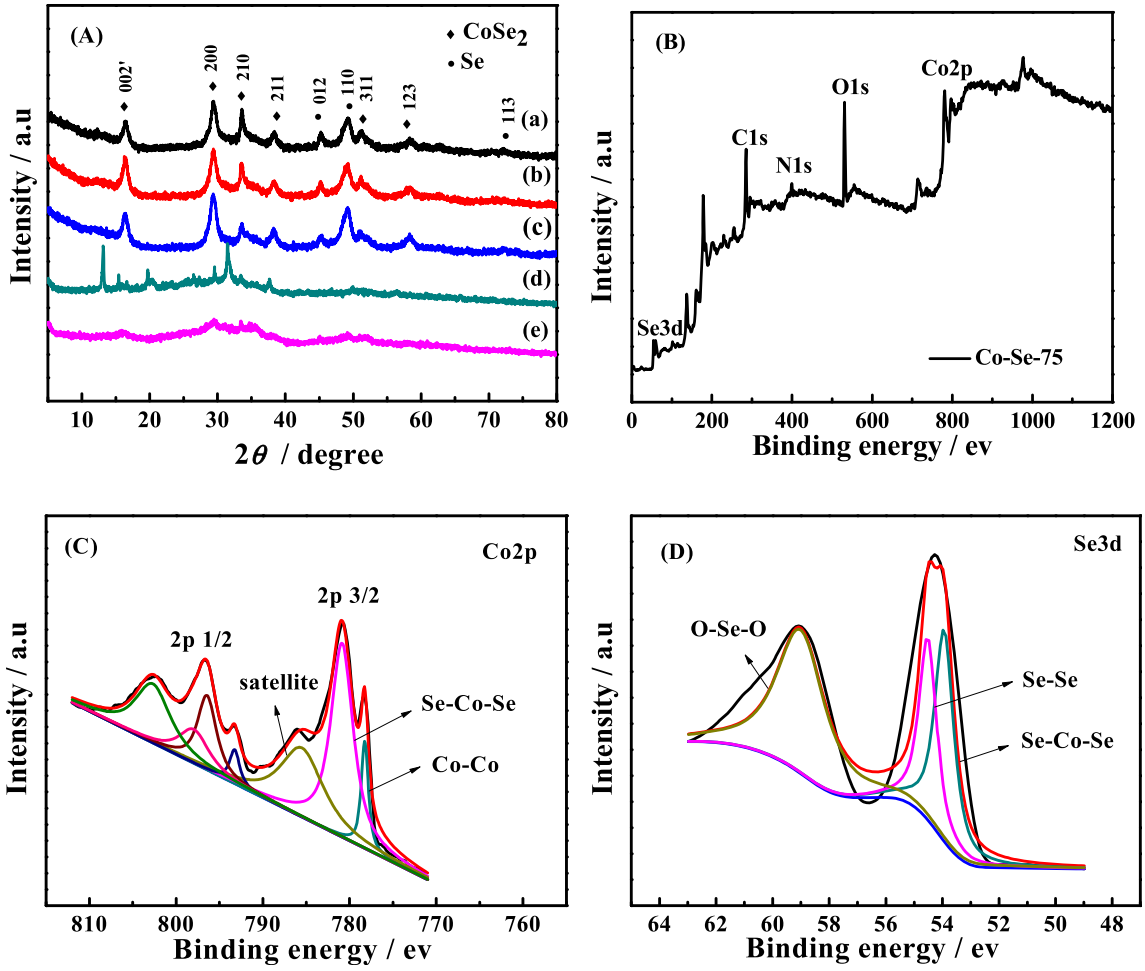

Fig. 1 – (A) X-ray diffraction patterns of Co-based selenides (a) Co-Se-66.7, (b) Co-Se-71.4, (c) Co-Se-75, (d) Co-Se-77.8 and (e) Co-Se-80. (B) XPS spectra of Co-Se-75, and the corresponding high resolution XPS spectra of (C) Co2p and (D) Se3d.