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Bimetallic MnCo selenide yolk shell structures for efficient overall water splitting

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ABSTRACT

In this work, we systematically investigate and compare the activity of MnCo-based electrocatalysts (i.e. selenide, oxide, and hydroxide) for the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) in alkaline solutions. The result indicates that the selenides are oxidized upon OER and the surface generated oxides are the real OER active species. The MnCo selenides exhibit a significantly enhanced performance as compared to the oxide and hydroxide though the real active OER species of these three catalysts are essentially the same. The superior activity of MnCo selenides could be attributed to the high intrinsic conductivity and the high surface active area. Further, the synergy between Mn and Co lowers the energy barrier for catalysis and helps to stabilize the material. The bimetallic MnCo selenides with yolk shell structures possess the optimal electrochemical performance with a low cell voltage of 1.66 V at the current density of 50 mA cm^{-2}, outperforming most of the earth-abundant electrocatalysts. Our work provides a better understanding of the active species of metal selenides and the origin of the performance disparity between selenides (-derived oxides) and oxides electrocatalysts.

1. Introduction

Facing the challenges of energy crisis and the interrelated environmental issues, renewable and clean energy have attracted widespread attentions [1]. Hydrogen has been considered as a promising alternative to overcome our reliance on fossil fuels because of its cleanliness, high-energy density, and renewability [2]. Electrochemical water splitting ($2H_2O \rightarrow 2H_2 + O_2$) provides an effective way to convert electrical energy into chemical energy, which is an environmentally friendly method to meet the global energy demands [3–5]. Noble metal-based catalysts such as IrO_2 and RuO_2 for oxygen evolution reaction (OER) whereas Pt for hydrogen evolution reaction (HER) are currently state of the art but their large-scale adoption is seriously limited by their scarcity and high cost. Therefore, the development of robust and cost-efficient catalysts with high activity is crucial for the hydrogen economy yet remains a challenge. Over the past decades, numerous efforts have been devoted to designing and exploring highly active, stable, and low-cost alternatives based on earth-abundant materials.

To date, earth-abundant pyrite structured transition-metal dichalcogenides (TMDs) (MX_2: M = Fe, Co, or Ni and X = S or Se), which are found in sedimentary deposits or minerals within earth's crust, have been identified as efficient electrocatalysts for HER in acidic media [3,6–9]. Because of their intrinsic metallic properties, these coordinated surface cations (Fe^{2+}, Co^{2+}, and Ni^{2+}) as the active centers of pyrite electrocatalysts have been speculated to be the same as the active centers of hydrogenases with high catalytic activity towards the HER. Among the large family of TMDs, $CoSe_2$ exhibits the optimal activity and thus has attracted many research interests. For example, Kong et al. demonstrated that the $CoSe_2$ nanoparticles grown on carbon fiber paper can efficiently catalyze the HER with a low overpotential of 137 mV at 10 mA cm^{-2} in 0.5 M H_2SO_4 [10]. Recently, $CoSe_2$ has also been demonstrated to be a promising OER "precatalysts" [11,12] owing to its $t_{2g}^6 e_g^1$ electronic configuration that is close to an optimal e_g filling required for OER [13]. The real active OER species however, are the surface oxide layer that is *in situ* generated during OER under oxidative conditions [14]. Compared to the corresponding oxides or hydroxides, metal selenides generally possess enhanced electrocatalytic activity thanks to the intrinsic higher conductivity [15]. To further

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enhance the OER (might also apply for HER) activity of $CoSe_2$, many strategies have been proposed, such as improving the conductivity by heteroatom doping (e.g. Ag-$CoSe_2$) [16], increasing the surface active area by delicately nanostructuring (e.g. ultrathin nanoplates) [11], and creating electronic interactions by constructing hybrid structures (e.g. CeO_2-$CoSe_2$) [17]. We note that Mn containing Co-based catalysts, such as CoMn layered double hydroxides (LDHs) and CoMnP [18,19], exhibit significantly enhanced OER activity though Mn-based compounds (e.g. oxides) themselves are poor OER catalysts [20]. This probably is due to the fact that the presence of Mn could lower the energy barrier for catalysis on Co-based catalysts, whereas the presence of Co might also moderate the stability of Mn [19]. In view of these investigations, we expected that the bimetallic MnCo selenides should be a promising OER precatalyst but so far have not yet been explored. In addition, metal selenides generally show good HER performance in acidic solutions, their activity in alkaline media however, is much poorer because of the difficulty in water dissociation [4,21]. Hybridization of different selenides (e.g. $MnSe_2$ with $CoSe_2$) could presumably regulate the bond strength of the reaction intermediates (e.g. H_2O, OOH^-, OH^-) and therefore improve the catalytic activity [22]. Unfortunately, the use of metal selenide hybrids for HER in alkaline solution has considerably less been explored.

In this work, we report the synthesis of MnCo bimetallic selenides for both the OER and HER and further the full water splitting electrocatalysis in 1 M KOH. The MnCo selenides can efficiently catalyze HER/OER and full water splitting at low overpotentials and the performance achieved herein is comparable to those obtained on noble metal-based catalysts and superior to most of the earth-abundant catalysts. Specifically, the MnCo selenides-based two-electrode alkaline water-splitting system achieves 50 mA cm^{-2} at a cell voltage of 1.66 V, outperforming the Pt/C||RuO_2 couple. More importantly, we have systematically investigated the electrochemical performance of MnCo selenides and carefully discussed the possible reasons for the superior performance in comparison to MnCo oxides/hydroxides (noting that the real OER active species for selenides are the surface oxides). This work not only presents a highly efficient water splitting electrocatalyst but also provides an effective strategy for enhancing the performance of monometallic selenide (or chalcogenides in general) electrocatalysts.

2. Experimental

2.1. Materials synthesis

2.1.1. Preparation of MnCo glycolate

0.25 mmol $Mn(CH_3COO)_2 \cdot 4H_2O$, 0.5 mmol $Co(NO_3)_2 \cdot 6H_2O$, and 8 mmol urea were dissolved in 15 mL ethylene glycol under continuous stirring to form a homogeneous solution. After that, the mixed solution was transferred into a 30 mL Teflon-lined autoclave, which was then sealed and maintained at 180 °C for 6 h. After reaction, the product was collected and cleaned using ethanol and deionized water for several times, and then dried at 60 °C overnight under vacuum to get the MnCo glycolate powder.

2.1.2. Preparation of MnCo selenide

The as-synthesized MnCo glycolate was thermally converted to MnCo selenide. Typically, 30 mg MnCo glycolate powder and 300 mg Se powder were placed at the downstream and upstream sides of a tube furnace, respectively. The furnace was heated at 450 °C for 2 h with a heating ramp of 5 °C min^{-1} in Ar atmosphere.

2.1.3. Preparation of MnCo hydroxide

50 mg of MnCo glycolate was dissolved in 20 mL of 2 M NaOH aqueous solution, which was then mixed with 30 mL ethanol under magnetic stirring for several minutes. Finally, the precipitate was obtained by washing with deionized water and ethanol several times, and dried at 60 °C for 12 h.

2.1.4. Preparation of MnCo oxide

The as-prepared MnCo glycolate was thermally annealed in Ar flow at 450 °C for 2 h to give the MnCo oxide.

2.2. Fabrication of electrodes

The electrodes were prepared by ultrasonically mixing 3 mg of the catalyst powder with the mixture of 1 mL ethanol and Nafion (0.5 wt.%, 30 μL) for 30 min to form a homogeneous ink, which was then drop-casted onto a pre-cleaned Ni foam. The typical catalyst loading was about 0.9 mg cm^{-2}.

2.3. Characterizations

The materials were characterized using X-ray diffraction (XRD, Rigaku) with Cu K_α radiation ($\lambda = 1.54056$ Å), scanning electron microscopy (SEM, ZEISS Sigma), and transmission electron microscopy (TEM). X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI Quantum-2000 XPS (US). The composition of the catalyst was determined by inductively couple plasma mass spectrometry (ICP-MS, Thermo Fisher).

2.4. Electrochemical measurements

All electrochemical measurements were performed on a CHI 660E electrochemical workstation at room temperature in 1 M KOH (pH = 13.6) using a standard three-electrode configuration, where MnCo-based catalysts, a Pt plate (for OER) or a graphite rod (for HER), and a saturated calomel electrode (SCE) were used as the working electrode, counter electrode, and reference electrode, respectively. Before the linear sweep voltammogram (LSV) tests, the working electrodes were activated by using cyclic voltammetry (CV) test at a scan rate of 100 mV s^{-1} for 200 cycles. After that, LSVs were recorded at a scan rate of 3 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) measurements were performed at open-circuit voltage from 100 KHz to 0.1 Hz with an AC amplitude. For the estimation of the double-layer capacitance, CV curves at various scan rates (20, 40, 60, 80, 100 and 120 mV s^{-1}) were recorded. All potentials were measured against the SCE electrode and converted to the reversible hydrogen electrode (RHE) using $E_{RHE} = E_{SCE} + 0.241 + 0.059 \times pH$. All polarization curves were *IR*-corrected using $E_{corr} = E_{mea} - IR_s$, where E_{corr} is *IR*-corrected potential, E_{mea} is experimentally measured potential, and R_s is the equivalent series resistance extracted from the electrochemical impedance spectroscopy measurements.

The faradaic efficiency of catalysts describes the transfer efficiency of charge (electron) in HER and OER by calculating the ratio of theoretical value and measured value. The water splitting electrocatalysis was conducted using an H-type cell, where two working electrodes were put in different chambers. The H_2 and O_2 gases generated at 50 mA cm^{-2} were first quantitatively collected by water drainage method. Assuming that the HER and OER were the only process that took place on the working electrode, the corresponding theoretical value was calculated by faraday law, which claims that 1 equivalent reaction occurs, accompanied by the passage of 96485.309 C charge. The theoretical value of H_2 and O_2 were calculated as follows: