CoNi₂Se₄ as an Efficient Bifunctional Electrocatalyst for Overall Water Splitting

Bahareh Golrokh Amin^a, Abdurazag T. Swesi^a, Jahangir Masud^a, and Manashi Nath^{*,a}

Department of Chemistry, Missouri University of Science and Technology, Rolla, MO 65409.

*E-mail: nathm@mst.edu

Experimental & Methods

Materials were reagent grade and were used as received without further purification. Nickel acetate tetrahydrate [Ni (C₂H₄O₂)₂.4H₂O from J. T. Baker chemical company, USA and cobalt acetate tetrahydrate [Co (C₂H₄O₂)₂.4H₂O from Alfa Aesar, SeO₂ [Acros Chemicals] and lithium chloride (LiCl) [Aldrich] were used. Au-coated glass slide (purchased from Deposition Research Lab Incorporated (DRLI), Lebanon, Missouri) and Carbon fiber paper (CFP) and Carbon cloth (CC) (purchased from Fuel cells Etc company, college station, Texas) were used as substrates in electrodeposition.

Electrodeposition of CoNi₂Se₄

The electrolytes were prepared using analytical grade reagents and deionized (DI) water with a resistivity of 18 M Ω ·cm. Prior to electrodeposition, Au / glass substrates were cleaned by ultrasonic treatment in micro-90 detergent followed by rinse with isopropanol for three times and eventually rinsed with deionized water (15 min each step) to ensure clean surface. Au-coated glass was covered with a Teflon tape, leaving an exposed geometric area of 0.283 cm², and connected as the working electrode. An IviumStat potentiostat was used to control the electrodeposition process and to monitor the current and voltage profiles. NiCo₂Se₄ was electrodeposited on the substrate by a controlled-potential deposition at -0.8 V (vs Ag/AgCl) at room temperature from an aqueous solution containing 10 mM Ni (C₂H₄O₂)₂.4H₂O, 25 mM Co (C₂H₄O₂)₂.4H₂O and 40 mM SeO₂. The pH of the electrolytic bath was adjusted to ~ 2.5 with dilute HCl. After each electrodeposition, the electrodeposited films were washed with deionized water in order to remove impurities and adsorbents from the surface.

Electrochemical Measurements:

Oxygen and hydrogen (OER and HER) evolution reaction was performed in 1M KOH solution by using Iviumstat. Ag|AgCl|KCl (sat.) and Pt mesh were using as reference and counter electrode, respectively. The measured potential *vs*. the Ag/AgCl was converted to the reversible hydrogen electrode (RHE) *via* the Nernst equation (eq. 1):

 $E_{\rm RHE} = E_{\rm Ag|AgCl} + 0.059 \text{PH} + E^{\rm o}_{\rm Ag|AgCl} (1)$

Where E_{RHE} is the converted potential vs. RHE, $E_{\text{Ag}|\text{AgCl}}$ is the experimentally measured potential against Ag|AgCl reference electrode, and $E^{\circ}_{\text{Ag}|\text{AgCl}}$ is the standard potential of Ag|AgCl at 25 °C (0.199 V).

Surface Characterizations

SEM and EDS

A FEI Helios Nanolab 600 FIB/FESEM at an acceleration voltage of 10 kV and a working distance of 5.0 mm was employed to obtain SEM image of the modified electrode surfaces. Energy dispersive spectroscopy (EDS) accompanied by line scan analysis was also acquired from the SEM microscope.

XRD

The product was characterized through powder X-ray diffraction (pxrd) with Philips X-Pert utilizing CuK α (1.5418Å) radiation. Pxrd pattern was collected from the pristine product with no further treatments. Because the product formed a very thin layer on the substrate, the pxrd was collected at grazing angles in thin film geometry (GI mode with Göbel mirrors).

XPS

KRATOS AXIS 165 X-ray Photoelectron Spectrometer using monochromatic Al X-ray source was used for all XPS measurements of the catalyst.

Electrochemically active surface area (ECSA)

The ECSA of the NiCo₂Se₄ can be determine by measuring the double layer charging current at different scan rates following here:

$$ECSA = C_{DL}/Cs$$
 (2)

Where C_s is the specific capacitance (0.040 mF cm⁻²) in N₂ saturated 1 M KOH solution. C_s is the specific capacitance which is reported in a range between 0.022 to 0.130 mF cm⁻² in alkaline solutions.^[S1] Here, the value of 0.040 mF cm⁻² was used based on previously reported Ni-based OER catalysts.^[S1]

 C_{DL} was calculated as a slop of the plot of capacitive current (i_{DL}) from a non-faradaic double-layer region against scan rate v (V s⁻¹). The ECSA was measured to be 10.8 cm² on CFP.



Fig. S1 Elemental analysis of as prepared $CoNi_2Se_4$ by using EDS



Fig. S2 TEM image (a) and SAED pattern (b) of $CoNi_2Se_4$ catalyst.



Fig. S3 Comparison of OER catalytic activity of $CoNi_2Se_4$ grown on different substrates. All measurements were done in 1M KOH solution.



Fig. S4 Comparison of pxrd before and after chronoamperometry.



Fig. S5 EDS analysis after 10h of chronoamperometry



Fig. S6 Comparison of XPS (Ni 2p, Co 2p and Se 3d) before and after Chronoamperometry for 10h.

Electrocatalyst	Catalyst Loading	Electrolyte	Overpotential (mV vs. RHE) @ 10 ^a , 20 ^b or 50 ^c mA cm-2	Reference
NiCo ₂ Se ₄ @CFP	4.7 mg cm ⁻²	1 M KOH	160ª, 210 ^c	This work
NiCo ₂ S ₄ @graphene	-	0.1 M KOH	470 ^a	S2
NiCo ₂ S ₄ NA/CC	4.0 mg cm ⁻²	1 M KOH	340 mV (100 mA	S 3
			cm ⁻²)	
NiCo ₂ S ₄ NW/NF	-	1 M KOH	260ª	S4
NiCo ₂ O ₄ hollow	$\sim 1 \text{ mg cm}^{-2}$	1 M NaOH	290ª	S5
microcuboids				
Ni-Co-O@Ni-Co-S	-	1 M KOH	300 ^b	S 6
NA				
NiCo ₂ O ₄	-	1 M KOH	391 ^b	S7
(a-CoSe/Ti)	3.8 mg cm ⁻²	1 M KOH	292ª	S 8
Co _{0.85} Se	-	1 M KOH	324 ^a	S9
(Ni,CO) _{0.85} Se	-	1 M KOH	255ª	S9
Co _{0.13} Ni _{0.87} Se ₂ /Ti	1.67 mg cm ⁻²	1 M KOH	320 mV (100 mA	S10
			cm ⁻²)	
NiSe ₂ /Ti	-	1 M KOH	350 mV (100 mA	S10
			cm ⁻²)	
NiSe ₂	1 mg cm^{-2}	1 M KOH	250ª	S11
$CoSe_2$	1 mg cm^{-2}	1 M KOH	430 ^a	S11
NiS/ Ni foam	-	1 M KOH	335°	S12
Ni ₃ Se ₂ /Cu foam	-	1 M KOH	343°	S13
CoSe/Ti mesh	3.8 mg cm ⁻²	1 M KOH	341°	S14
Fe-doped NiSe	4.8 mg cm^{-2}	1 M KOH	264 mV (100 mA	S15
			cm ⁻²)	
Ni(OH) ₂	142 µg cm ⁻²	1 M KOH	313 ^b	S16
NiO nanoparticles	-	1 M KOH	347 ^b	S16
Amorphous NiO	0.1 mg cm ⁻²	1 M KOH	>470 ^b	S17
NiO _x /C	-	1 M KOH	335 ^a	S18
$(Ni_{0.69}Fe_{0.31}O_x/C)$	-	1 M KOH	280ª	S18
NiOOH	-	1 M KOH	525 ^a	S19
NiCo LDH	$\sim 0.17 \text{ mg cm}^{-2}$	1 M KOH	393 ^b	S20

ST1: Comparison of OER activity of the NiCo₂Se₄@ C.P. with recently reported catalysts

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