Copper Cobalt Selenide as a High-Efficiency Bifunctional Electrocatalyst for Overall Water Splitting: Combined Experimental and Theoretical Study

Xi Cao^a, Julia E. Medvedeva^{b*} and Manashi Nath^{a*}

^aDepartment of Chemistry, Missouri University of Science & Technology, Rolla, Missouri 65409, United States.

^bDepartment of Physics, Missouri University of Science and Technology, Rolla, Missouri 65409, United States.

*Email: nathm@mst.edu

Experimental Section

1. Electrodeposition of RuO₂ on Au coated glass:

In a previous reported procedure of electrodeposition of RuO_2 ,^{s1} $RuCl_3$ (0.452 g) and KCl (2.952 g) were mixed in 40 ml of 0.01M HCl, cyclic voltammetry from 0.015 to 0.915 V (vs Ag|AgCl) was applied for 100 cycles at a scan rate of 50 mV s⁻¹. Finally, the products were heated at 200 °C for 3 h under air.

2. Calculation of Tafel Slope. The Tafel slope is an important parameter to explain the kinetics of electrocatalytic performance of CuCo₂Se₄ and the equation is shown below.

$$\eta = a + \frac{2.3RT}{anF} \log(j)$$

Where η is the overpotential, α is transfer coefficient and the other symbols have their usual meaning. The Tafel slope is given by 2.3RT/anF.

3. Calculation of Turnover Frequency (TOF)

The turnover frequency (TOF) was calculated from the following equation:

$$TOF = \frac{I}{4 \times F \times m}$$

where I is the current in Amperes, F is the Faraday constant and m is the number of moles of the active catalyst.

4. Calculation of surface energy through DFT:

$$E_{Surface} = \frac{1}{2} \left(E_{Total \ surface} - E_{Bulk} \right)$$

5. Calculation of adsorption energy through DFT:

$$E_{Adsorption} = \left(E_{Surface with OH} - E_{Surface} - E_{OH} \right)$$



Figure S1. Cyclic voltammograms measured for CoSe (a), Cu_2Se (b) and $CuCo_2Se_4$ (c) in N₂-saturated 1.0 M KOH solution at different scan rates from 10 to 60 mV s⁻¹. The inset is a plot of both anodic and cathodic current measured at 0.01 V vs Ag|AgCl (KCl saturated) as a function of scan rate.

Table S1. Electrochemically active surface area (ECSA) and roughness factor (RF) of CoSe, Cu_2Se and $CuCo_2Se_4$.

| Catalysts | ECSA (cm ²) | RF |
|-----------------------------------|-------------------------|--------|
| Cu ₂ Se | 10.05 | 143.57 |
| CoSe | 8.875 | 126.79 |
| CuCo ₂ Se ₄ | 5.325 | 76.07 |



Figure S2. Zoom-in LSV curve of $CoCu_2Se_4@Au$ in N₂-saturated 1.0 M KOH at a scan rate of 10 mV s⁻¹ in order to obtain the onset potential.



Figure S3. Gravimetric current density for CuCo₂Se₄.



Figure S4. TOF of CuCo₂Se₄ and RuO₂.



Figure S5. LSV curves of $CoCu_2Se_4$ on Au and CFP in N₂-saturated 1.0 M KOH at a scan rate of 10 mV s^{-1} .



Figure S6. Comparison of OER LSVs of CoSe, Co_7Se_8 , Cu_3Se_2 , Cu_2Se and $CuCo_2Se_4$ measured in N₂-saturated 1.0 M KOH at a scan rate of 10 mV s⁻¹.



Figure S7. SEM images of as-synthesized CuCo₂Se₄ (a) and CuCo₂Se₄ after 8 h chronoamperometry in 1.0 M KOH.

Table S2. Comparison of EDS atomic ratio of the catalyst before and after 8 h chronoamperometry.

| | EDS (Atomic %) | | |
|----------------------------|------------------|------|------|
| | Со | Cu | Se |
| As-deposited | 30.9 | 17.0 | 52.1 |
| After 8h chronoamperometry | 30.9 | 17.5 | 51.6 |



Figure S8. Comparison of XPS of CuCo₂Se₄ before and after stability (a) Co 2p, (b) Cu 2p, (c) Se 3d and (d) O 1s.



Figure S9. Zoom-in Figure of HER plots in order to measure the HER onset potential.



Figure S10. TOF of CuCo₂Se₄ for HER process.



Figure S11. Overall water splitting of CuCo₂Se₄@Au in N₂-saturated 1.0 M KOH solution.



Figure S12. LSV curves of water electrolysis at a scan rate of 10 mV s⁻¹ in N₂-saturated 1.0 M KOH solution. Black curve shows $CuCo_2Se_4$ catalyst as both anode and cathode, red one represents $CuCo_2Se_4$ catalyst as anode while Pt as cathode, and blue curve shows RuO_2 as anode while Pt as cathode.

Energy Efficiency for overall water splitting

| Catalyst | OER, V ^a | HER, V ^a | E_{cell} / V | Energy efficiency ^b / % |
|-----------------------------------|---------------------------|---------------------------|---------------------------|------------------------------------|
| | at 50 mA cm ⁻² |
| CuCo ₂ Se ₄ | 1.55 | 0.232 | 1.782 | 83.05 |
| Pt | | 0.08 | 1.74 | 95.06 |
| RuO ₂ | 1.66 | | 1./4 | 83.00 |

 Table S3. Calculation of energy efficiency of water electrolyzer (%)

^aAll voltages are vs RHE. ^bEnergy efficiency of water electrolysis \cong (1.48 *V*/*Ecell*) ×100.



Figure S13. (a) The total density of states (DOS) of bulk $CuCo_2Se_4$ and (b-d) partial density of states (PDOS) of Cu 3d, Co 3d and Se 4p calculated using GGA (dashed line) and GGA+U with U = 6 eV for Co d-states and U = 4 eV for Cu d-states (solid line).

Table S4. Comparison of total energy, magnetic moment, distance of Co-Se and bond length distortion at different layers among bulk CoCu₂Se₄, (100) surface and (111) with Co/Cu and Co termination as calculated from GGA+U.

| | $E_{surface} / eV$ | Magnetic Moment/ μ_B | | Distance (Co-Se) / Å | Distortion (bond length) |
|--------------|--------------------|--------------------------|---------|----------------------|--------------------------|
| Bulk | | 0.79 | | 2.4 | 0 |
| | | 2.1 | Layer 0 | 2.26 | 0.018 |
| | | | | 2.35 (2×) | |
| | | | | 2.3 | |
| | | | | 2.4 | |
| | | 0.9 | Layer 1 | 2.35 (2×) | 0.0099 |
| | | | | 2.40 (2×) | |
| | | | | 2.39 | |
| 100 | 136 | | | 2.42 | |
| | | 0.86 | Layer 2 | 2.4 | 0.0044 |
| | | | | 2.41 | |
| | | | | 2.38 (4×) | |
| | | 0.78 | Layer 3 | 2.37 (2×) | 0.0029 |
| | | | | 2.39 (4×) | |
| | | 2.29 | Layer 0 | 2.23 (3×) | 0.0002 |
| | | 1.47 | Layer 1 | 2.36 (3×) | 0.0087 |
| | | | | 2.41 | |
| | | | | 2.40 (2×) | |
| 111 Co/Cu | 280 | 2.07 | Layer 2 | 2.39 (4×) | 0.0018 |
| | | | | 2.38 (2×) | |
| | | 2.13 | Layer 3 | 2.38 (2×) | 0.0009 |
| | | | | 2.39 (4×) | |
| | | 2.23 | Layer 0 | 2.22 | 0.0175 |

| | | | | 2.25 | |
|--------|-----|------|---------|-----------|---------|
| | | | | 2.27 | |
| | | | | 2.35 | |
| | | 2.16 | Layer 1 | 2.36 | 0.00381 |
| | 242 | | | 2.37 (2×) | |
| | | | | 2.39 | |
| 111 Co | | 0.91 | Layer 2 | 2.37 (2×) | 0.00307 |
| | | | | 2.38 (2×) | |
| | | | | 2.39 | |
| | | 0.84 | Layer 3 | 3.38 (2×) | 0.00193 |
| | | | | 2.39 (4×) | |



Figure S14. Comparison of partial electronic density of states (PDOS) of Co atoms in the surface top layer with the one in the center layer in the (100) slab (a) and (111) slab with Co/Cu termination (b).



Figure S15. Partial density of states (PDOS) of Cu atom in (100) surface before OH⁻ attachment (a), Cu atom after OH⁻ attachment (b), OH⁻ after attached on Cu atom (c). PDOS of Cu atom in (111) surface before OH⁻ attachment (d), Cu atom after OH⁻ attachment (e), OH⁻ after attached on Cu atom (f).

| Surface | Atom attached with OH ⁻ | Adsorption Energy / eV |
|---------|------------------------------------|------------------------|
| (100) | Со | -2.96 |
| | Cu | -2.43 |
| (111) | Со | -10.02 |
| Co/Cu | Cu | -7.99 |

Table S5. OH⁻ adsorption Energy on Co and Cu atoms in (100) and (111) Co/Cu surfaces.

| | | OFP | | T | | |
|---|------------------------------|----------------------------------|--|----------------------------------|--|-----------|
| | | (| JEK | Г | 1EK | |
| Electrocatalyst | Electrolyte | Onset potential (V vs RHE) | Overpotential (mV vs RHE) @ 10 mA·cm ⁻² | Onset potential (V vs RHE) | Overpotential (mV vs RHE) @ 10 mA·cm ⁻² | Reference |
| CuCo ₂ Se ₄ | 1 M KOH | 1.43 | 320ª | 0.07 | 120 | This work |
| Co ₇ Se ₈ | 1 M KOH | 1.45 | 290 | 0.317 | 472 | S2 |
| Cu ₂ Se | 1 M KOH | 1.50 | 320 | _d | - | S3 |
| CuCo ₂ O ₄ /NrG O | 1 M KOH | 1.52 | 360 | - | - | S4 |
| CuCo ₂ S ₄ | 1 M KOH | 1.43 | 310 | - | - | S5 |
| (Ni, Co) _{0.85} Se | 1 M KOH | 1.47 | 255 | - | - | S6 |
| CoSe ₂ | 1 M KOH | 1.55 | 430 | 0.1 ^b | 160 | S7 |
| CuO | 1 M KOH | 1.59 | 470 | - | - | S8 |
| CuO | 1 M KOH | 1.57 | 420 | | | S9 |
| CuCo ₂ S ₄ /CF | 1 M KOH | 1.43 | 295° | - | - | S10 |
| Cu ₃ P/NF | 1 M KOH | 1.49 | 320 | 0.12 | 150 | S11 |
| CuO– TCNQ/CF | 1 M KOH | 1.55 | 355 ^a | - | - | S12 |
| Co ₃ O ₄ /NiCo ₂ O ₄ | 1 M KOH | 1.53 | 340 | - | - | S13 |
| Cu ₂ MoS ₄ | 0.1 M phosphate buffer | - | - | 0.55 | 750 | S14 |

 Table S6. Comparison of catalytic activity for different Co and/or Cu based OER / HER
 electrocatalysts in alkaline medium.

^a Overpotential at 50 mA cm⁻². ^b HER was studied in 0.5 M H₂SO₄. ^c Overpotential at 100 mA cm⁻². ^d – indicates no relevant values reported in the corresponding literature.

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