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Construction of Molybdenum-Doped Cobalt-Sulfide as Environmentally Friendly Catalyst for Boosting Urea Oxidation in the Alkaline Seawater Electrolyte

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ABSTRACT: Electrocatalytic urea oxidation in alkaline seawater electrolytes presents a compelling, carbon-neutral strategy for grid-scale hydrogen generation. Yet, the broader deployment of this process is fundamentally hindered by the inherently sluggish kinetics of the urea oxidation reaction (UOR). In this work, we developed a robust and highly efficient Co-S-Mo electrocatalyst for UOR in 1 M KOH + 0.33 M urea seawater via a facile and binder-free electrodeposition strategy. The as-synthesized Co-S-Mo electrocatalyst requires only 1.384 V and 1.521 V (vs. RHE, reversible hydrogen electrode) to deliver 10 and 100 mA·cm⁻², respectively, with a low Tafel slope of 94.6 mV·dec⁻¹ and good stability in 1.0 M potassium hydroxide (KOH) + 0.33 M urea seawater. The introduction of molybdenum induces a synergistic Mo-Co-S interaction that reorganizes cobalt's electronic configuration, thereby simultaneously improving the electrical conductivity of the Co-S matrix, accelerating charge-transfer kinetics, and promoting the oxidation of Co²⁺ to active Co³⁺. In addition, the plentiful accessible active sites, together with the accelerated charge and mass transport enabled by the inter-element synergy, ensure outstanding electrocatalytic performance. This work establishes a cost-efficient and robust protocol for fabricating advanced anodes tailored for urea-assisted seawater splitting, offering pivotal insights for the scalable design of energy-saving hydrogen production technologies.

KEYWORDS: Molybdenum-doped cobalt-sulfide; seawater; urea oxidation reaction; electrodeposition; heteroatom doping

1 Introduction

Driven by surging population and accelerating industrialization, relentlessly rising energy consumption is rapidly exhausting finite reserves, rendering conventional carbon-based sources alone wholly insufficient to meet escalating global demand [1,2]. Hydrogen (H₂) is widely regarded as a key eco-friendly energy carrier because of its high energy density (~142 MJ·kg⁻¹), clean nature, and potential for large-scale renewable generation [3]. However, the vast majority of hydrogen is still obtained from fossil fuels through coal gasification and steam reforming, methods that release significant volumes of CO₂ [4]. These production pathways exacerbate environmental degradation and climate warming, thereby subverting the very purpose of adopting hydrogen as a clean energy vector. Hydrogen's advantages as a clean, adaptable, and high-efficiency energy medium can only be actualized when the gas is derived from renewable feedstocks. Electrolysis of water using intermittent renewable energy (wind, solar, or tidal) has emerged as a premier route for

generating high-purity green hydrogen, owing to its negligible pollutant release, zero CO₂ emissions, and overall environmental compatibility [5,6]. From the standpoints of resource availability and process economics, seawater is vastly more abundant than freshwater, and its direct use bypasses the costs and energy penalties of desalination. For these reasons, seawater electrolysis has recently gained prominence as a compelling industrial strategy for sustainable hydrogen production [7,8]. Nevertheless, two pivotal obstacles profoundly impede direct seawater electrolysis [9,10]: first, the intrinsically sluggish kinetics of the four-electron oxygen evolution reaction (OER, $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$, 1.23 V vs. RHE) imposes a substantial overpotential; second, at elevated current densities, the chlorine evolution reaction (CER, $\text{Cl}^- + 2\text{OH}^- \rightarrow \text{ClO}^- + 2\text{e}^-$, 1.72 V vs. RHE) competes with the OER, thereby diminishing electrolysis efficiency. To circumvent the limitations of conventional anodic processes, various alternative oxidation reactions, including the oxidation of hydrazine, alcohols, biomass-derived substrates, and sulfide ions, have been extensively explored, and among these, the urea oxidation reaction (UOR, $\text{CO}(\text{NH}_2)_2 + 6\text{OH}^- \rightarrow \text{N}_2 + 5\text{H}_2\text{O} + \text{CO}_2 + 6\text{e}^-$, 0.37 V vs. RHE) stands out. Thermodynamically, its theoretical potential (0.37 V vs. RHE) is substantially lower than that of the OER (1.23 V vs. RHE) and CER (1.72 V vs. RHE), which fundamentally reduces anodic overpotential, effectively suppresses chlorine generation, and yields stable, non-toxic products. Furthermore, unlike highly toxic alternatives such as hydrazine (N₂H₄) and sulfide (H₂S), urea is widely available in domestic and industrial wastewater, enabling the simultaneous production of hydrogen and the purification of urea-rich wastewater at lower costs. Beyond wastewater treatment, UOR also finds applications in direct urea fuel cells, thereby offering compelling energy and environmental benefits.

Although noble-metal oxides (such as iridium dioxide and ruthenium dioxide) can serve as efficient catalysts for the UOR, their practical deployment is constrained by prohibitive cost and elemental scarcity [11]. More recently, transition metal compounds have exhibited remarkable stability and outstanding catalytic properties, confirming their potential as UOR catalysts, including oxides (and hydroxides) [12], sulfides [13], selenides [14], nitrides [15], and phosphides [16]. For example, cobalt chalcogenides have garnered extensive research focus, driven by their superior electronic conductivity, versatile valence states, diverse crystallographic phases, and complex redox behavior [17–19]. Moreover, the *in-situ* self-reconstruction that these materials undergo in alkaline electrolytes permits the *in-situ* electrochemical generation of highly active electrocatalysts. Wei et al. [20] reported a CoS₂ nanoneedle array grown on titanium mesh, prepared by a hydrothermal method followed by sulfidation under nitrogen. The as-prepared catalyst demonstrated excellent UOR activity, demanding only 1.4 V to drive 10 mA·cm⁻² in a 1 M KOH + 0.3 M urea electrolyte. Guided by the principle of orbital symmetry matching [21], Co centers that possess *e_g* orbitals are capable of engaging the lone electron pair situated in the sp³-hybridized orbital of –NH₂ groups, leading to the formation of sp³-dz² bonds and subsequent activation of the nitrogen atoms. For urea, the C=O moiety with its π electrons can coordinate to metal atoms that have available p orbitals through p-π bonding [22]. Consequently, engineering the electronic structure of CoS₂ by introducing heteroatoms to simultaneously activate the –NH₂ and C=O groups constitutes an effective strategy for boosting the UOR performance. For example, molybdenum (Mo) is strategically selected as the dopant to overcome the inherent limitations of Co-based sulfides in urea-assisted seawater oxidation. Incorporating high-valence Mo atoms significantly tunes the electronic properties via Mo 4d and Co 3d orbital coupling, which alters the local charge distribution near Co active sites and lowers the d-band center; such adjustments effectively reduce the overly strong binding of urea intermediates, thereby accelerating the otherwise slow C–N bond cleavage step required for the six-electron transfer pathway [23]. Concurrently, the formation of robust Mo-S co-ordinations stabilizes the catalyst architecture, where Mo species act as a redox buffer to mitigate the over-oxidation and leaching of Co sites. Furthermore, the involvement of Mo 4d orbitals enhances

electron delocalization and broadens the conductive band of the sulfide matrix, effectively lowering the charge transfer resistance and accelerating the overall reaction kinetics.

Herein, we report a straightforward strategy to directly grow a molybdenum-doped cobalt sulfide (Co-S-Mo) electrocatalyst on nickel foam (NF) via cyclic voltammetry (CV) electrodeposition method. Remarkably, the Co-S-Mo catalyst requires just 1.384 V and 1.521 V (vs. RHE) to drive 10 and 100 mA·cm⁻² for the UOR in 1.0 M KOH + 0.33 M urea seawater, while simultaneously delivering a favorable Tafel slope of 94.6 mV·dec⁻¹. This study presents a new and viable approach to substantially boost the intrinsic activity of cobalt sulfide catalysts, thus offering tremendous promise for large-scale hydrogen production from the vast, renewable resource of seawater.

2 Experimental Details

2.1 Reagents

Sodium molybdate dihydrate (Na₂MoO₄·2H₂O), ammonium chloride (NH₄Cl), cobalt chloride hexahydrate (CoCl₂·6H₂O), potassium hydroxide (KOH), sodium citrate (Na₃C₆H₅O₇·2H₂O), thiourea (CH₄N₂S), and saccharin (C₇H₅NO₃S) were obtained from Aladdin Industrial Co., Ltd. (Shanghai, China). The aforementioned reagents were used as obtained, with all being of analytical purity. Nickel foam (NF) was obtained from Changcheng Chemical Co., Ltd. All aqueous solutions were made using deionized water (resistivity ≥18 MΩ·cm) throughout. All seawater was obtained from the coastal waters off Qingdao in Shandong Province, China (Fig. S1), where the ambient pH was 7.9. Immediately before each experiment, the raw sample was filtered under reduced pressure over medium-speed filter paper, a step that removed suspended solids including phytoplankton and silt.

2.2 Synthesis of Co-S-Mo Electrocatalyst

Prior to the deposition process, NF (1 cm × 1 cm × 0.3 cm) was subjected to sequential ultrasonication in 10 wt% HCl, ethanol, and deionized water (20 min per step) to eliminate native oxide layers and physically adsorbed organic/inorganic contaminants. Subsequently, the washed NF substrates were placed in a vacuum oven and dehydrated at 60°C over a 12-h period.

Co-S-Mo electrocatalyst was electrodeposited at 40°C in a three-electrode cell run by a CHI660E workstation (Shanghai Chenhua Instrument Co., Ltd.). The pre-treated NF substrate functioned directly as the working electrode, whereas a graphite rod alongside a saturated calomel electrode (SCE) constituted the counter and reference electrodes, respectively. The electrodeposition electrolyte for Co-S-Mo electrocatalysts consists of 20 mM CoCl₂·6H₂O, 100 mM Na₂MoO₄·2H₂O, 2000 mM CH₄N₂S, 10 mM C₇H₅NO₃S, 500 mM NH₄Cl, and 600 mM Na₃C₆H₅O₇·2H₂O. The solution pH was tuned to 8.0, followed by nitrogen purging for 15 min before deposition to eliminate dissolved oxygen. Electrodeposition under CV mode was conducted in a potential range of -1.2 to 0.2 V (vs. SCE) at a 5 mV·s⁻¹ scan rate for 10 cycles. Following deposition, the working electrode was quickly washed with deionized water, blow-dried with nitrogen, and subsequently vacuum-dried at 60°C for 12 h. All tests were carried out at least three times to confirm good repeatability. The average catalyst loading on the NF was measured as 8.5 mg·cm⁻² by recording the weight difference of the substrate before and after the electrodeposition process. As a control, Co-S electrocatalyst was prepared similarly to Co-S-Mo electrocatalyst but without the addition of Na₂MoO₄·2H₂O.

2.3 Characterization

Surface morphology and microstructure were observed via a Zeiss EVO18 scanning electron microscope (SEM). Surface composition and elemental distribution were mapped using an Oxford XmaxN energy-

dispersive X-ray spectrometer (EDS). Powder X-ray diffraction (XRD) data were collected using a Bruker D8 Venture device with Cu K α radiation ($\lambda = 0.15406$ nm) at a $4^\circ \cdot \text{min}^{-1}$ scan speed. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific EscaLab 250Xi spectrometer equipped with monochromatic Al K α X-rays ($h\nu = 1486.6$ eV). Calibration of binding energies was performed by setting the adventitious carbon C 1 s peak at 284.87 eV as an internal standard. Data deconvolution and peak fitting were executed using XPSPEAK software.

2.4 Electrochemical Measurements

Electrochemical characterizations were conducted with a CHI660F potentiostat (Shanghai Chenhua Instrument Co., Ltd., China) in a standard three-electrode setup. The working electrode was the as-prepared electrocatalysts, while a graphite rod and a SCE served as the counter and reference electrodes, respectively. All measured potentials in this study were referenced to the RHE scale via the equation below [24]:

$$E_{\text{RHE}} = E_{\text{SCE}} + 0.244 + 0.059 \times \text{pH}.$$

UOR tests were performed in a seawater medium containing 0.33 M urea and 1.0 M KOH. Catalytic activity was measured using linear sweep voltammetry (LSV) at a sweep rate of $2 \text{ mV} \cdot \text{s}^{-1}$, where the potentiostat applied 85% iRs compensation automatically. For electrochemical impedance spectroscopy (EIS), data were gathered between 0.01 Hz and 1 MHz with a 5 mV AC perturbation. Catalyst stability was checked via continuous CV sweeps at $100 \text{ mV} \cdot \text{s}^{-1}$.

3 Results and Discussion

Fig. 1 depicts the preparation procedure for the Co-S-Mo electrocatalyst. In conventional configurations, powdered catalysts must be deposited onto the electrode by drop-casting and require polymeric binders to ensure adhesion; this introduces substantial interfacial resistance between the catalyst and the support, ultimately impairing catalytic activity. To overcome this drawback, we employed porous nickel foam as a scaffold and directly grew the catalyst on its surface through an *in-situ* approach. This strategy simultaneously boosted the material loading and facilitated faster electron transport.

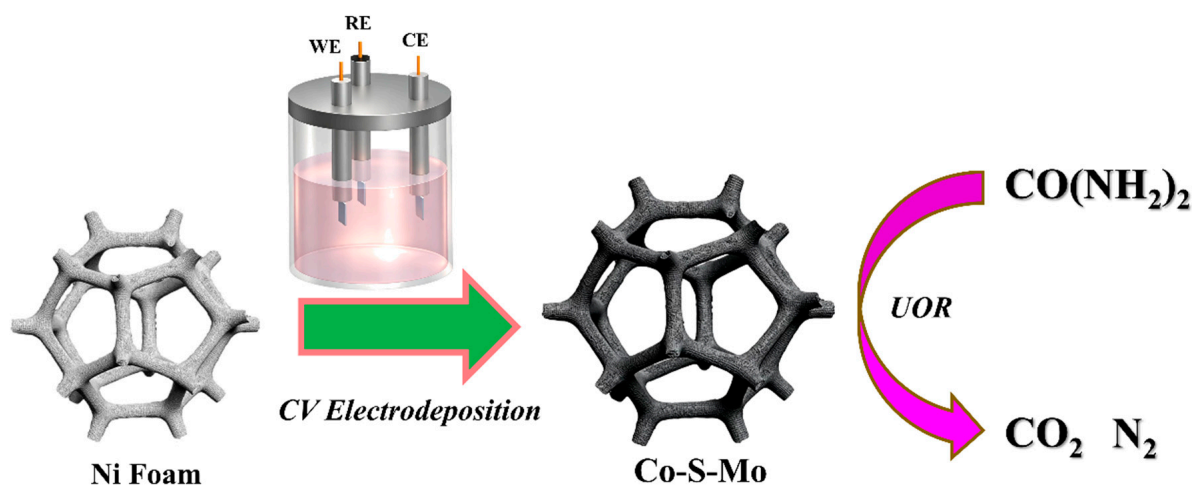


Figure 1: Synthesis scheme of Co-S-Mo electrocatalyst. (NF: nickel foam; CV: cyclic voltammetry; WE: working electrode; RE: reference electrode; CE: counter electrode).

The morphology of the Co-S-Mo electrocatalyst was investigated by SEM. As shown in Fig. 2a,b, the Co-S electrocatalyst exhibits a flat, dense substrate with scattered white particles. In contrast, after Mo incorporation (Fig. 2c,d), the surface becomes extensively cracked. Cracking of the deposited layer likely arises from residual stress caused by electrodeposition, which itself may be due to lattice substitution of smaller atoms by larger ones, generating internal stress. Alternatively, the crack initiation could stem from compressive stresses induced by gas bubbles entrapped during the electrochemical reduction process [25]. Furthermore, EDS mappings (Fig. 2e–g) validate the homogeneous surface dispersion of Co, S, and Mo across the catalyst, while the corresponding quantitative spectrum (Fig. S2) determines their exact atomic proportions to be 88.57, 7.31, and 4.12 at%, respectively.

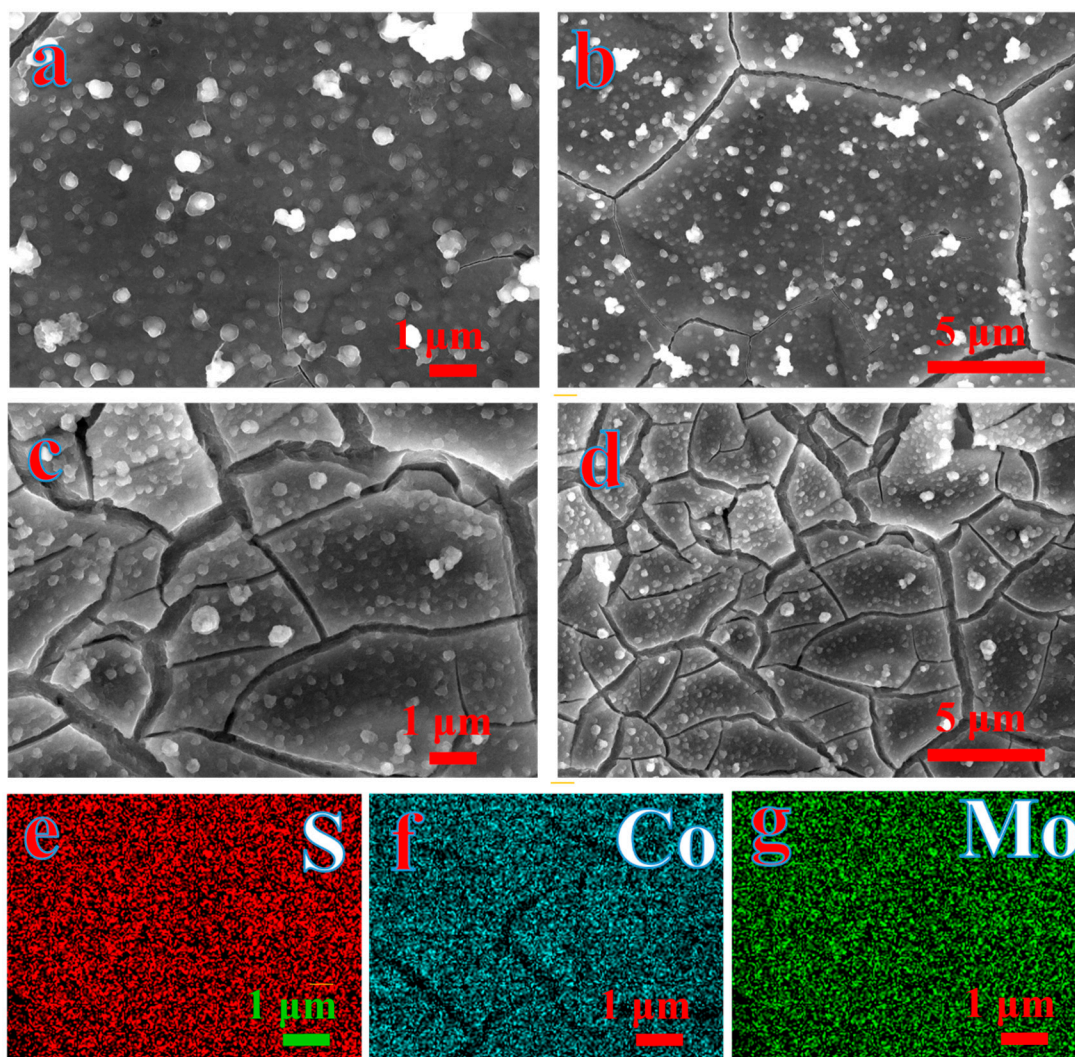


Figure 2: SEM images of (a,b) Co-S, (c,d) Co-S-Mo electrocatalysts. (e–g) elemental mapping images of S, Co, and Mo elements for Co-S-Mo electrocatalyst.

XRD was used to examine the crystal structures of the as-prepared catalysts. As displayed in Fig. 3a, the Co-S and Co-S-Mo electrocatalysts exhibit only three discernible reflections, located at 44.5° , 52.0° , and 76.7° . These signals are indexed to the (111), (200), and (220) facets, respectively, and originate from the underlying nickel foam substrate (PDF #04-0850). Additionally, a weak diffraction peak at 30.5° in the Co-S electrocatalyst

is assigned to (100) for Co_4S_3 (PDF#02-1458). The Co-S-Mo sample shows no observable Co_4S_3 reflections, probably because Mo doping introduces substantial lattice distortion and strain owing to the size mismatch between Mo and Co cations. The severe lattice distortion disrupts the cubic symmetry and long-range ordering of Co_4S_3 , indicating a structural reconstruction into Co-S-Mo solid solution. This amorphization can be rationalized by non-equilibrium deposition kinetics: the pronounced cathodic overpotential (-1.2 V vs. SCE) and citrate complexation favor instantaneous nucleation while restricting adatom diffusion. Consequently, the rapid deposition flux is proposed to kinetically trap atoms within a metastable, short-range-ordered state, thereby bypassing the crystallization of the thermodynamically preferred Co_4S_3 .

Additionally, X-ray photoelectron spectroscopy (XPS) was employed to probe the elemental chemical states of the as-synthesized catalyst. The corresponding fitting results are summarized in Tables S1 and S2. As depicted in Fig. 3b, the high-resolution Co 2p spectrum features characteristic spin-orbit split doublets. Peak deconvolution unambiguously validates the coexistence of Co^{3+} (780.12 eV for $2p_{3/2}$ and 795.26 eV for $2p_{1/2}$) and Co^{2+} (781.35 eV for $2p_{3/2}$ and 796.54 eV for $2p_{1/2}$) within the Co-S-Mo electrocatalyst. The satellite features centered at 784.85 and 803.51 eV serve as signatures of Co^{2+} and Co^{3+} , respectively [26,27]. The S 2p spectrum (Fig. 3c) displays a prominent feature at 163.03 eV, a binding energy typical of metal-sulfur bonds, verifying that the as-prepared material consists primarily of sulfide phases [28]. An additional contribution located at 168.54 eV indicates a small fraction of oxidized sulfur species, likely surface-bound sulfates (SO_x), which could affect the electrode's long-term stability in chloride-containing seawater electrolytes [29]. The Mo 3d XPS profile shown in Fig. 3d exhibits characteristic peaks. The peaks at 231.73 eV and 234.90 eV are assigned to Mo^{4+} $3d_{5/2}$ and its $3d_{3/2}$ spin-orbit partner, respectively [30]. The specific binding energies confirm the presence of Mo-O-S species in the Co-S-Mo electrocatalyst. Mo incorporation into Co-S induces a positive shift (≈ 0.1 – 0.2 eV) in Co 2p binding energies, indicating electron-depleted Co sites and improved charge transfer. The relative sulfate-to-sulfide ratio decreases from ca. 6.36 to 2.65 upon Mo incorporation, indicating suppressed sulfur over-oxidation, although oxidized sulfur species remain non-negligible. This suggests that while surface oxidation occurs during catalyst preparation, the Mo atoms effectively stabilize the active sulfide phase, which is beneficial for the HER process.

To evaluate the advantage of Co-S-Mo for UOR, the electrocatalytic activity was tested by LSV in a standard three-electrode configuration. Fig. 4a compares the UOR polarization curve of the Co-S-Mo electrocatalyst with its OER activity. The OER requires 1.566 V (vs. RHE) to deliver $10 \text{ mA}\cdot\text{cm}^{-2}$, whereas UOR achieves this current density at only 1.384 V, confirming a reduced kinetic barrier and a clear preference for UOR. Moreover, the onset potential for urea oxidation is synchronized with the formation of CoOOH , providing mechanistic evidence that the electrochemically generated high-valence Co^{3+} species serve as the catalytically active centers for the UOR process [31]. The mechanistic pathways underlying UOR diverge from those of OER, which involves continuous electrochemical oxidation. UOR proceeds via a dual-step process: an initial electrochemical oxidation ($\text{M}^{2+}(\text{OH})_2 + \text{OH}^- \rightarrow \text{M}^{3+}\text{OOH} + \text{H}_2\text{O} + \text{e}^-$) followed by a chemical oxidation step ($6\text{M}^{3+}\text{OOH} + \text{CO}(\text{NH}_2)_2 + \text{H}_2\text{O} \rightarrow 6\text{M}^{2+}\text{OH} + \text{N}_2 + \text{CO}_2$). In the Co-S-Mo electrocatalyst, the intrinsic Co^{3+} sites, modulated by electron-withdrawing effects, preferentially trigger UOR at reduced potentials. Here, the low-valence cobalt species are readily oxidized to higher oxidation states, facilitating the reaction. This electronic tuning, imparted by Mo doping, synergistically optimizes the catalyst's electroactive landscape for efficient urea electro-oxidation.

To benchmark the UOR performance, the activity of Co-S and Co-S-Mo electrocatalysts was also examined. Bare NF exhibits poor UOR performance in 1.0 M KOH + 0.33 M urea seawater (Fig. S3). As revealed in Fig. 4b, the Co-S-Mo catalyst needs only 1.384 V (vs. RHE) to deliver $10 \text{ mA}\cdot\text{cm}^{-2}$, whereas Co-S requires 1.408 V; at $100 \text{ mA}\cdot\text{cm}^{-2}$, the respective potentials are 1.521 and 1.640 V. Additionally, comparative evaluation

against recent reports (Table S3) validates the exceptional UOR performance of Co-S-Mo electrocatalyst, establishing a new benchmark for catalyst efficiency in alkaline seawater electrolysis.

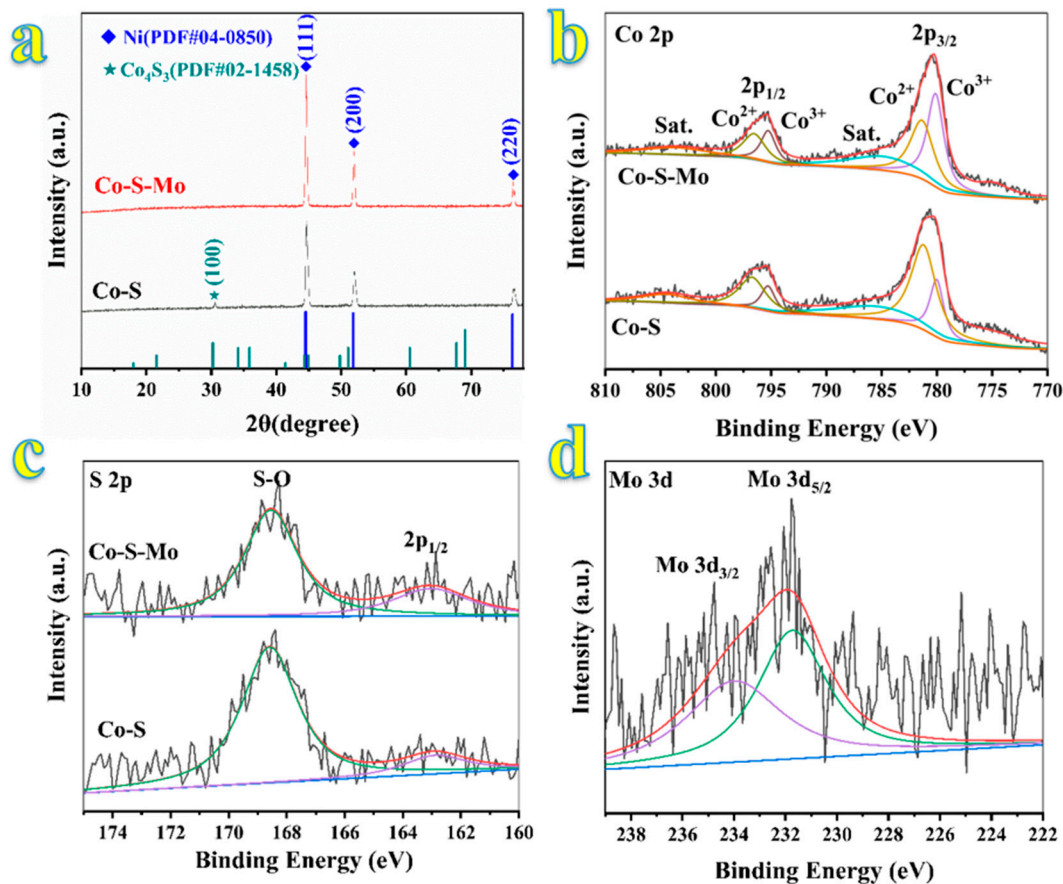


Figure 3: (a) XRD patterns, (b) Co 2p XPS spectra, (c) S 2p XPS spectra of Co-S and Co-S-Mo electrocatalysts. (d) Mo 3d XPS spectra of Co-S-Mo electrocatalyst.

The UOR kinetics were assessed by Tafel analysis based on the corresponding polarization curves. A lower Tafel slope signifies a faster UOR rate as the applied potential increases, indicating reduced electrode resistance during polarization [32]. As can be seen from Fig. 4c, the Tafel slopes for Co-S and Co-S-Mo electrocatalysts were 180.8 and 94.6 mV·dec⁻¹, respectively. The reduced Tafel slope observed for Co-S-Mo implies enhanced reaction kinetics, meaning the current density climbs much faster as the potential increases.

The charge transfer coefficient α , which serves as an intrinsic measure of how efficiently activation energy is utilized in the electrode reaction, was obtained from the following equation [33]:

$$\alpha = \frac{2.3RT}{bF} \quad (1)$$

here, F , R , and T denote the Faraday constant, universal gas constant, and experimental temperature, respectively. An α close to 0.5 denotes an ideal symmetric energy barrier; thus, the value of 0.63 for Co-S-Mo reflects a relatively symmetric barrier that promotes UOR, whereas the much lower α of 0.33 for Co-S reveals a highly asymmetric barrier accompanied by slow charge transfer. This highlights the markedly better kinetic compatibility of Co-S-Mo electrocatalysts for UOR.

An expanded electrochemically active surface area (ECSA) generally reflects a higher density of active sites at the boundary between the electrode and electrolyte. To estimate this parameter for a given catalyst, the double-layer capacitance (C_{dl}) is normally measured via CV method [34]. These CV measurements were carried out in a non-Faradaic region at scan rates ranging from 10 to 100 $\text{mV}\cdot\text{s}^{-1}$ (Fig. S4). As shown in Fig. 4d, the Co-S-Mo electrocatalyst shows a C_{dl} of $10.2 \text{ mF}\cdot\text{cm}^{-2}$, which is much higher than the $1.6 \text{ mF}\cdot\text{cm}^{-2}$ recorded for Co-S. This notably higher capacitance suggests a considerably enlarged ECSA and, therefore, a greater number of exposed active sites that enhance UOR activity.

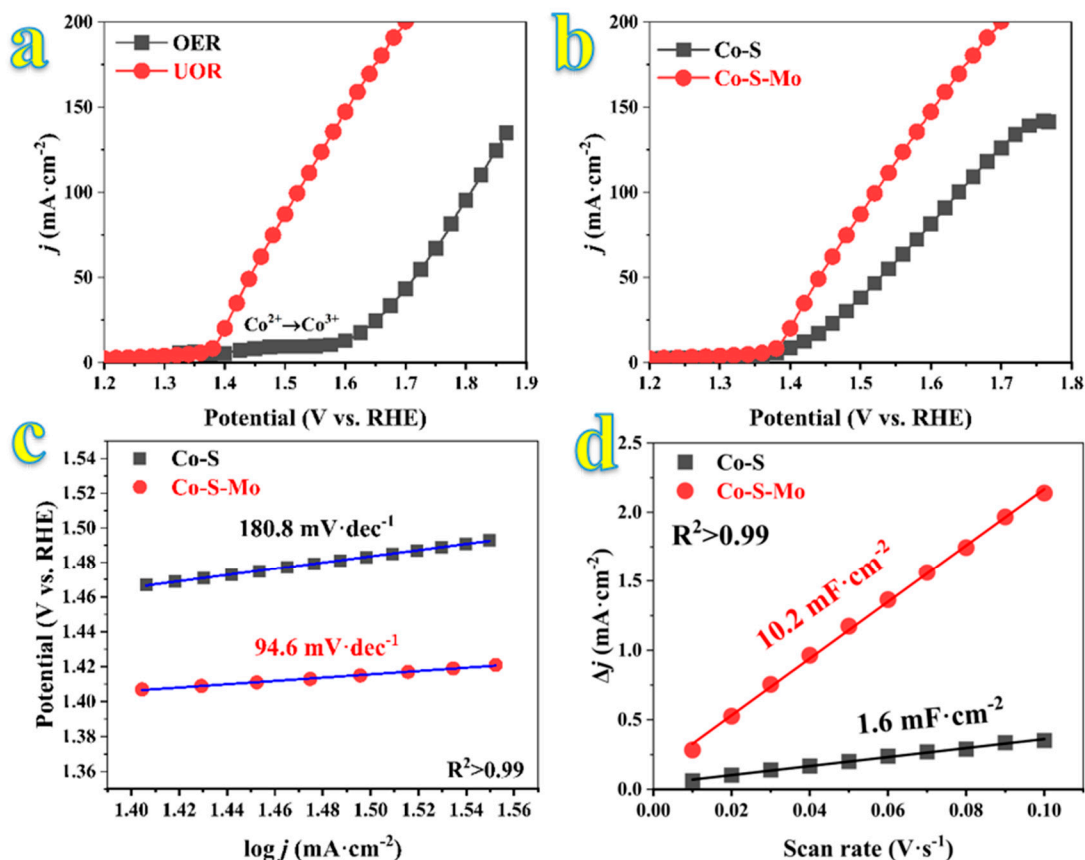


Figure 4: (a) OER and UOR polarization curves of Co-S and Co-S-Mo measured in seawater containing 1 M KOH, with or without 0.33 M urea. (b) LSV responses of Co-S and Co-S-Mo in seawater containing 1 M KOH and 0.33 M urea. (c) Tafel plots derived from the LSV data in (b). (d) Calculated C_{dl} based on the slope of current density against scan rate. (UOR: urea oxidation reaction; OER: oxygen evolution reaction).

To gain insight into interfacial charge-transfer behavior during urea oxidation, EIS measurements were also performed. The impedance spectra of both catalysts, acquired in 1.0 M KOH seawater with 0.33 M urea (Fig. 5a,b), were interpreted using the equivalent circuit shown in Fig. S5, which consisted of R_s (solution resistance), R_f (film resistance), R_{ct} (charge-transfer resistance), and a CPE (constant-phase element). As observed, R_{ct} value of Co-S and Co-S-Mo electrocatalysts is 1.14Ω and 0.39Ω , respectively. The smaller R_{ct} value of Co-S-Mo electrocatalyst corresponds to a faster reaction rate [35,36]. The results agreed well with the observation of smaller Tafel slope and superior UOR kinetics of Co-S-Mo electrocatalyst. The Bode phase plots of Co-S and Co-S-Mo electrocatalysts (Fig. 5c) reveal distinct electrochemical kinetics. Both spectra exhibit two well-defined relaxation peaks, indicating the presence of two time constants associated with charge transfer and ion diffusion processes, respectively. Notably, the Co-S-Mo electrocatalyst exhibits

an increased phase angle magnitude at low frequencies ($\sim 38^\circ$) compared to pristine Co-S ($\sim 36^\circ$). This increase can be attributed to the substantially larger ECSA of Co-S-Mo, which introduces a stronger capacitive response. Despite this capacitive enhancement, the fitted Rct value confirms that Co-S-Mo possesses a much smaller charge-transfer resistance (0.39Ω vs. 1.14Ω), directly demonstrating that Mo doping effectively optimizes the electronic structure and accelerates the interfacial charge transfer kinetics. Furthermore, the high-frequency relaxation peak of Co-S-Mo shifts toward higher frequencies with a diminished magnitude, suggesting that the incorporation of Mo alters the ion diffusion pathways within the electrode matrix, thereby facilitating more efficient mass transport. Moreover, the Rct/ECSA ratio (Fig. 5d) of Co-S-Mo electrocatalyst is lower than that of Co-S electrocatalyst, which further implies that the Co-S-Mo electrocatalyst has higher intrinsic catalytic activity.

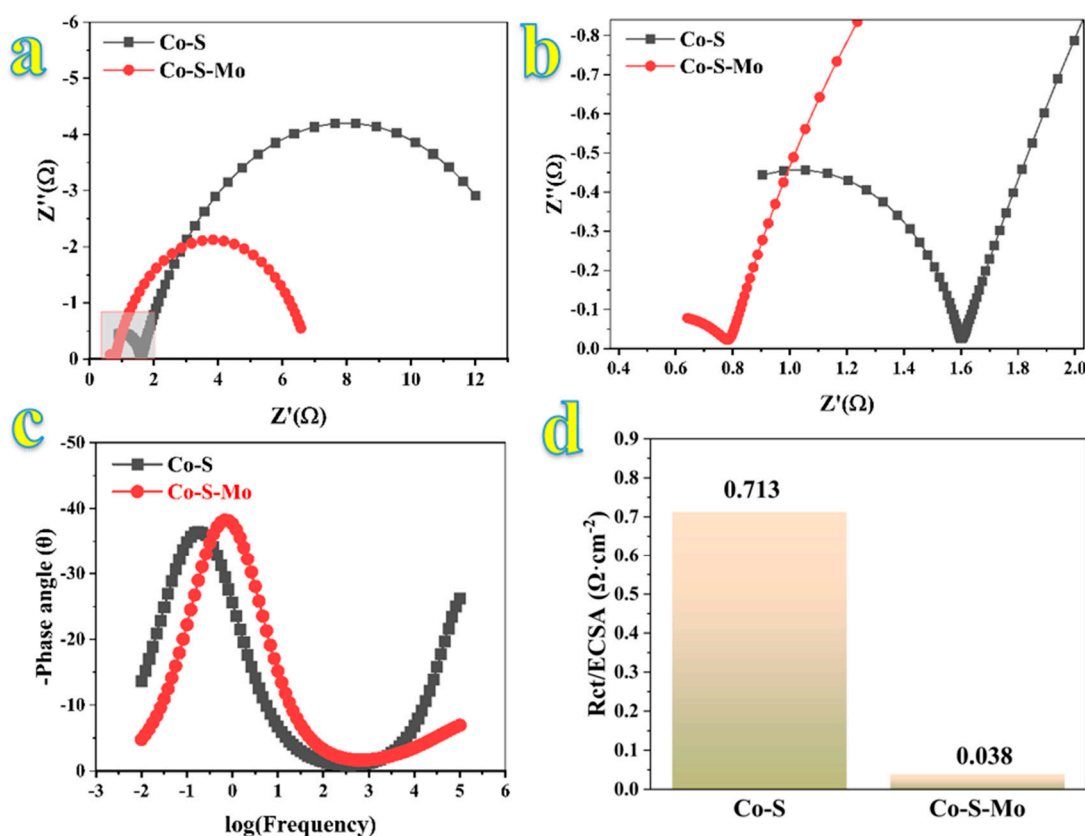


Figure 5: (a) Nyquist plots of Co-S and Co-S-Mo electrocatalysts at 1.35 V vs. RHE for UOR. (b) An enlarged view of the high-frequency area. (c) Bode phase plots of Co-S and Co-S-Mo electrocatalysts. (d) Rct/ECSA.

To examine the stability of Co-S-Mo electrocatalyst toward the UOR, the accelerated degradation test (ADT) is performed in 1.0 M KOH + 0.33 M urea seawater at room temperature at $100 \text{ mV} \cdot \text{s}^{-1}$. As can be seen from Fig. 6, the UOR polarization curve of the Co-S-Mo electrocatalyst after 3000 CV cycles coincides well with the initial curve, indicating favorable structural stability under this cycling condition. After 4000 cycles, we conducted a quantitative analysis of the current densities at various potentials. The results reveal that: (1) At the low potential of 1.30 V, the current density increases from 1.828 to $3.807 \text{ mA} \cdot \text{cm}^{-2}$, representing a retention of 208%, indicating significant electrochemical activation of the catalyst. This is mainly attributed to the continuous *in-situ* transformation of Co^{2+} to active Co^{3+} species during prolonged cycling, along with further optimization of the Mo-doping-induced electronic structure; (2) Within the intermediate potential

window of 1.35 to 1.45 V, the current retention ranges from 70% to 87%. Remarkably, at a practically relevant current density of approximately $10 \text{ mA}\cdot\text{cm}^{-2}$, the retention ratio remains as high as 86.7%; (3) At higher potentials ($>1.50 \text{ V}$), more pronounced attenuation is observed (retention of approximately 60%–75%), which may be associated with slight surface structural reconstruction or mass loss under prolonged potential-cycling conditions. This characteristic of “activation at low potentials and attenuation at high potentials” precisely reflects the complex dynamic evolution of the catalyst during long-term service. Overall, within the operational potential window of 1.35–1.45 V, the Co-S-Mo catalyst maintains good catalytic activity after 4000 cycles, demonstrating acceptable durability under the potential range relevant to practical UOR applications. However, it should be explicitly noted that qualitative and quantitative analyses of potential byproducts and the exact Faradaic efficiency were not conducted in this study, which requires further in-depth investigation.

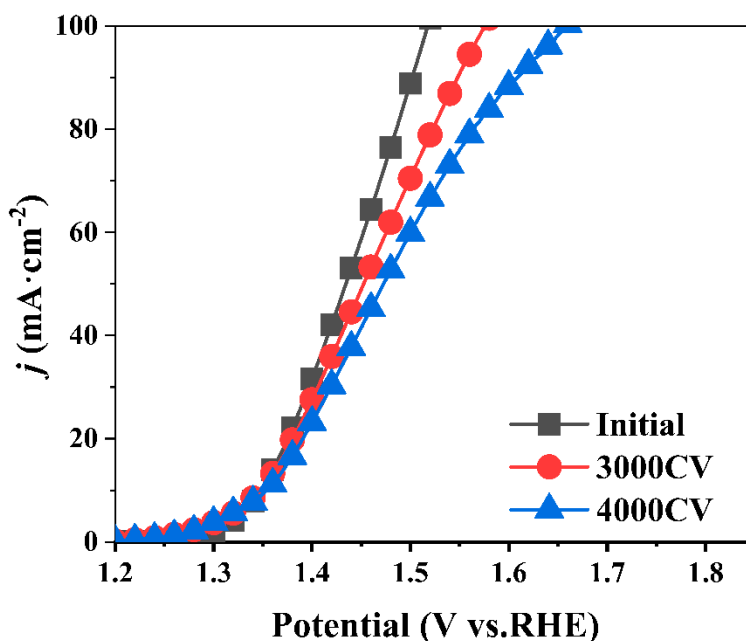


Figure 6: LSV curves of Co-S-Mo electrocatalyst before and after 3000 or 4000 CV cycles.

4 Conclusion

In summary, binder-free Co-S-Mo electrocatalyst on nickel foam has been synthesized via electrodeposition. The electrocatalyst exhibits outstanding UOR activity in seawater-based electrolyte containing 1.0 M KOH and 0.33 M urea, requiring only 1.384 and 1.521 V (vs. RHE) to deliver current densities of 10 and $100 \text{ mA}\cdot\text{cm}^{-2}$, respectively. It also features a low Tafel slope of $94.6 \text{ mV}\cdot\text{dec}^{-1}$ along with good durability, outperforming most UOR catalysts reported to date. Such outstanding UOR capabilities originate from the synergistic coupling of enhanced intrinsic conductivity, accelerated charge transfer kinetics, and abundant exposed active sites. This study not only delivers an economical electrocatalyst for urea oxidation in alkaline seater but also establishes practical guidelines for the targeted engineering of transition-metal-sulfide catalysts toward energy-efficient hydrogen production.

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Availability of Data and Materials: The data supporting the findings of this study are available from the corresponding author upon reasonable request.

Ethics Approval: Not applicable.

Conflicts of Interest: The authors declare no conflicts of interest.

Supplementary Materials: The supplementary material is available online at <https://www.techscience.com/doi/10.32604/cl.2026.089661/s1>. Refs. [37–42] are cited in the Supplementary Materials.

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