



# RuCo alloy nanoparticles supported on mesoporous hollow carbon as a catalyst for the chlorine evolution reaction

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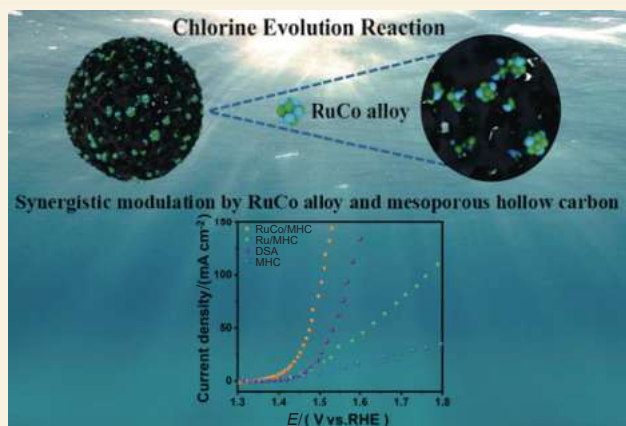
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**Abstract:** The chlorine evolution reaction (CER) is the primary anodic process in chlor-alkali electrolysis for industrial chlorine production. Developing electrocatalysts that produce a high current density at a low overpotential remains a significant challenge. We report a RuCo alloy supported on mesoporous hollow carbon (RuCo/MHC) as an efficient CER electrocatalyst. The mesoporous carbon framework provides abundant defect sites and promotes a uniform dispersion of RuCo alloy nanoparticles. Electronic interactions between the RuCo alloy and the carbon matrix produce an interfacial charge redistribution, which changes the electronic structure of unsaturated oxygen species and optimizes Cl<sup>-</sup> adsorption, thereby accelerating CER kinetics. The material requires an overpotential of only 59 mV to produce a current density of 10 mA cm<sup>-2</sup> and gives better kinetics and a stable electrochemical performance. This work indicates a practical way to design durable, low-noble-metal CER anodes through combining alloy engineering and porous carbon supports.

**Key words:** Chlorine evolution reaction; RuCo alloy; Mesoporous hollow carbon; Interfacial charge redistribution; Electrocatalysis



## 1 Introduction

Chlorine is an essential bulk chemical for the chemical, pharmaceutical, disinfection and organic-synthesis industries<sup>[1–3]</sup>. Industrially, chlorine is produced primarily by electrolysis, in which the chlorine evolution reaction (CER) is the dominant anodic process<sup>[4]</sup>. The most widely used anodes are dimensionally stable anodes (DSAs), which typically comprise mixed metal oxides containing ruthenium and iridium<sup>[5–6]</sup>. However, noble metals can form thermodynamically stable soluble species (e.g., soluble RuO<sub>x</sub> or IrO<sub>x</sub>) under harsh anodic conditions, leading to

catalyst degradation<sup>[7–8]</sup>. Therefore, developing anodic catalysts that combine high activity, high selectivity and long-term stability remains a central objective in electrochemical chlorine production.

In recent years, carbon-based materials have attracted broad interest in electrocatalysis owing to their high electrical conductivity, large specific surface area

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and structural tunability<sup>[9–11]</sup>. Mesoporous hollow carbon (MHC), which combines a nanometer-scale framework with a hollow mesoporous morphology, provides abundant sites for dispersing metal nanoparticles with effectively suppressed particle aggregation<sup>[12–13]</sup>. Its open pore network also facilitates reactant transport and rapid removal of gaseous products, enabling stable performance under high current-density operation<sup>[14–15]</sup>. Moreover, MHC can modulate electronic interactions at the metal-carbon interface by tuning pore architecture, specific surface area and surface chemistry, thereby affecting the adsorption behavior of reaction intermediates and improving overall catalytic efficiency<sup>[13]</sup>. Therefore, MHC provides an attractive platform for CER catalysis, offering opportunities to simultaneously optimize mass transport, active-site dispersion, and interfacial electronic structure.

In addition to optimizing the support architecture, alloying to tune the electronic structure of active sites also represents an effective strategy to enhance electrocatalytic performance<sup>[16–17]</sup>. Ruthenium exhibits excellent activity for a range of anodic reactions. However, its high cost and limited abundance hinder large-scale application. Alloying Ru with transition metals can reduce noble-metal loading. Through inter-metallic electronic interactions, alloy surface electronic states can be modified to optimize intermediate binding and reaction kinetics. Su et al. encapsulated RuCo nanoalloys within nitrogen-doped graphene layers, where the graphene shell suppresses nanoparticle aggregation and dissolution while preserving efficient charge transfer at the metal-carbon interface<sup>[18]</sup>. Cai et al. prepared ultrathin RuCo alloy nanosheets with interfacial charge redistribution between Ru and Co<sup>[19]</sup>. Tang et al. synthesized Ru-Co solid-solution nanoparticles in which strong metal-metal electronic coupling facilitates electron transfer to surface oxygen species and helps stabilize the catalytic surface under oxidative conditions<sup>[20]</sup>. Nevertheless, alloy nanoparticles remain susceptible to sintering and leaching at high anodic potentials. Therefore, immobilizing them on appropriate supports is essential to achieve both high activity and long-term durability for CER.

Herein, we report RuCo alloy nanoparticles supported on MHC (RuCo/MHC) as a high-performance electrocatalyst for CER. The RuCo nanoparticles are uniformly dispersed within the mesoporous shell framework with a narrow size distribution. Meanwhile, the porous, highly conductive carbon scaffold effectively anchors the alloy nanoparticles, preventing their aggregation and suppressing their detachment owing to the confinement of the nano carbon framework, while also facilitating charge transport to enhance catalytic performance. Ru-Co alloying induces interfacial charge redistribution, which modulates the electronic structure of unsaturated oxygen species ( $O^{2-}/O^-$ ) at the catalyst surface, thereby optimizing Cl adsorption/desorption and enhancing CER kinetics. As a result, the RuCo/MHC electrode requires an overpotential of only 59 mV to reach  $10 \text{ mA cm}^{-2}$  and exhibits a relatively low Tafel slope of  $73.36 \text{ mV} \cdot \text{dec}^{-1}$ . This work demonstrates that combining alloy engineering with mesoporous hollow carbon supports offers a viable route to load low-noble-metal to attain high-activity and durable CER anodes.

## 2 Experiment

### 2.1 Chemicals and materials

Ammonium hydroxide solution ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ ), tetrapropyl orthosilicate (TPOS,  $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Si}$ ), ruthenium(III) chloride trihydrate ( $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ ), Cobalt(II) nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), sodium chloride (NaCl) and resorcinol ( $\text{C}_6\text{H}_6\text{O}_2$ ) were purchased from Shanghai Aladdin Biological Technology Co., Ltd. Formaldehyde solution ( $\text{CH}_2\text{O}$ ) and Nafion 117 were purchased from Macklin Biochemical Technology Co., Ltd. Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), lithium fluoride (LiF) and hydrochloric acid (HCl) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents were directly used without further purification. The water used for all experiments was prepared by a Merck Millipore Milli-Q system (resistivity  $18.2 \text{ M } \Omega \text{ cm}$ ).

### 2.2 Preparation of MHC

First, 65 mL of ethanol, 15 mL of deionized (DI) water, and 3.0 mL of ammonium hydroxide were mixed under ambient conditions. Then, 3.45 mL of

tetrapropyl orthosilicate (TPOS) was introduced into the mixture. After stirring for 15 min, 0.4 g of resorcinol and 0.56 mL of formaldehyde solution (37%) were added to the solution. After continuous agitation for 24 h, silica@resorcinol-formaldehyde ( $\text{SiO}_2\text{@RF}$ ) nanospheres were collected by centrifugation, thoroughly washed sequentially with DI water and ethanol, and finally dried overnight at 60 °C. Next,  $\text{SiO}_2\text{@RF}$  powder was annealed at 700 °C for 5 h with a heating rate of 5 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere. A 500 mg portion of the  $\text{SiO}_2\text{@C}$  composite was treated with an in situ-generated HF solution (prepared from 0.8 g LiF and 10 mL of 9 mol L<sup>-1</sup> HCl) at 35 °C for 24 h to remove silica, obtaining MHC after centrifugation, washed with DI water and then dried at 60 °C in vacuum overnight.

### 2.3 Preparation of RuCo/MHC

First, 20 mg of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 5 mg of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  were added to 5 mL of deionized water and sonicated until completely dissolved. Subsequently, 50 mg of MHC was introduced into the above solution and stirred for 2 h. The resulting precursor was washed three times alternately with ethanol and deionized water, collected by centrifugation at 10 000 r min<sup>-1</sup>, and dried in a vacuum oven at 60 °C. Finally, the dried RuCo oxide/MHC was placed in the center of a tubular furnace and reduced/calcined under a H<sub>2</sub>/Ar mixed gas atmosphere at 700 °C for 2 h to obtain RuCo/loaded mesoporous hollow carbon nanospheres (RuCo/MHC). The Ru/MHC was prepared following the process similar to that of RuCo/MHC except the absence of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .

### 2.4 Characterization

Field-emission scanning electron microscopy (FESEM, JEOL JSM-7800F) and transmission electron microscopy (TEM, JEOL JEM-F200) were utilized to evaluate the morphology of the prepared samples. The crystal structures were characterized by X-ray diffraction (XRD, Rigaku, D-MAX 2500/PC) using a high-intensity Cu K $\alpha$  radiation source ( $\lambda = 1.54 \text{ \AA}$ ) and operating at a voltage of 40 kV and a current of 30 mA. Specific surface areas and pore size distributions were obtained from nitrogen sorption

isotherms at 77 K (Micromeritics ASAP2460, USA). The actual Ru and Co contents were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). XPS data were collected on a Kratos Axis ULTRA X-ray photoelectron spectrometer, and the binding energy of the C 1s peak at 284.6 eV was used as an internal reference. Raman spectra were recorded using a Horiba LabRAM HR Evolution with a 532 nm Ar laser. Electron paramagnetic resonance (EPR) spectra were recorded using a Bruker EMXplus spectrometer.

### 2.5 Electrochemical measurements

Electrochemical measurements were performed in a standard three-electrode configuration on a Gamry electrochemical workstation. The working electrode was carbon paper (1 cm × 1 cm) loaded with 1.5 mg of catalyst. A saturated Ag/AgCl electrode was served as the reference and a carbon rod was used as the counter electrode. Experiments were carried out in an H-type electrolyzer containing freshly prepared 5 mol L<sup>-1</sup> NaCl electrolyte adjusted to pH=2 with hydrochloric acid. The iR compensation was performed at 95% using the solution resistance determined by the workstation before each measurement. The catalyst ink was prepared by dispersing 5 mg of catalyst in 1.0 mL of anhydrous ethanol containing 50  $\mu\text{L}$  of 5% Nafion, followed by ultrasonication for 30 min to obtain a homogeneous suspension. Subsequently, 300  $\mu\text{L}$  of the catalyst ink was drop-cast onto carbon paper with a geometric area of 1 cm × 1 cm to achieve a catalyst loading of 1.5 mg cm<sup>-2</sup>. The electrode was dried under ambient conditions before electrochemical measurements. Both the synthesized catalysts and DSA were tested under identical conditions to ensure comparability. The saturated Ag/AgCl reference electrode was calibrated prior to electrochemical measurements, and all potentials were converted to the reversible hydrogen electrode (RHE) scale according to:

$$E_{\text{RHE}} = E_{(\text{Ag}/\text{AgCl})} + 0.197 \text{ V} + 0.0592 \times \text{pH}$$

The linear sweep voltammetry (LSV) was recorded at a scan rate of 5 mV·s<sup>-1</sup>. Electrochemical impedance spectrum (EIS) was measured over the frequency range from 1 mHz to 100 kHz. Cyclic voltam-

mograms (CVs) were collected at scan rates of 20, 40, 60, 80, 100 and 120 mV·s<sup>-1</sup>.

The electrochemical double-layer capacitance ( $C_{dl}$ ) was determined from CV curves collected in a non-Faradaic potential window of 0.5–0.6 V at scan rates of 20–120 mV s<sup>-1</sup>. The capacitive current density, defined as ( $\Delta j/2$ ), was extracted at a fixed potential and plotted against the scan rate. The slope of the linear fit was taken as the  $C_{dl}$  value. The ECSA was estimated according to

$$ECSA = \frac{C_{dl} \times S}{C_s}$$

where  $C_s$  is assumed to be 0.02 mF cm<sup>-2</sup>.

## 2.6 Chlorine evolution reaction selective test method

Chlorine selectivity was quantified by iodometric titration and expressed as:

$$S_{Cl_2}(\%) = \frac{Y_{\text{experimental}}}{Y_{\text{theoretical}}} \times 100\% \quad (1)$$

45 mL of electrolyte is added to the electrolysis cell and purged with argon for 15 min. Chronoamperometry (CA) was then performed at an applied potential corresponding to a current density above 10 mA·cm<sup>-2</sup> for 120 s. The theoretical amount of Cl<sub>2</sub> produced was calculated from the CA current by:

$$Y_{\text{theoretical}}(\text{mol}) = \int \frac{id}{2F} \times dt \quad (2)$$

Where  $i$  is current,  $t$  is time (s),  $F$  is the Faraday constant, and the factor 1/2 accounts for the 2 electrons transferred per Cl<sub>2</sub> molecule. Immediately after CA, a 10 mL aliquot of the electrolyte was transferred to a glass bottle and excess NaI was added. The solution turned yellow-brown due to I<sub>2</sub> formation via:



The liberated I<sub>2</sub> was titrated with standardized 0.01 mol L<sup>-1</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. When the yellow solution became colorless, a few drops of 1% (w/v) starch indicator were added (the solution turns blue), and titration was continued with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> until the blue color disappeared. The experimental Cl<sub>2</sub> yield (mol) was calculated from the volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> consumed:

$$Y_{\text{experimental}}(\text{mol}) = 0.01 \times V_{Na_2S_2O_3}(L)/2 \quad (4)$$

## 3 Results and discussion

### 3.1 Structural and phase compositions of RuCo/MHC, Ru/MHC and MHC

Fig. 1a shows the synthesis procedure of samples. First, silica@resorcinol-formaldehyde (SiO<sub>2</sub>@RF) nanospheres were prepared via a modified Stöber method (Fig. S1)<sup>[21]</sup>. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images show that the as-prepared SiO<sub>2</sub>@RF nanospheres are highly uniform with an average diameter of approximately 300 nm (Fig. S2). After carbonization and selective etching (Fig. S3), mesoporous hollow carbon (MHC) spheres were obtained. SEM and TEM images further confirm that the MHC possesses open surface channels and a well-defined hollow morphology (Fig. 1b). The as-synthesized MHC was dispersed in deionized water by ultrasonication to form a homogeneous suspension. Ruthenium and cobalt salt precursors were then added in a defined ratio, allowing the metal ions to adsorb within the mesoporous network of the MHC. Owing to its high specific surface area and abundant pore architecture, the MHC provides ample adsorption sites for uniform metal loading<sup>[22]</sup>. The resulting material was dried and subjected to high-temperature reduction under a H<sub>2</sub>/Ar atmosphere. During this treatment, the metal ions were reduced to the metallic state and underwent in-situ alloying, yielding stably anchored RuCo alloy nanoparticles on the carbon support and producing the RuCo/MHC composite.

SEM image (Fig. 1c) shows that RuCo/MHC retains an intact hollow-spherical morphology. TEM image further reveals that the nanoparticles exhibit an average size of ~ 10 nm. Most particles are uniformly dispersed across the sample, suggesting that the hollow mesoporous architecture exerts a confinement effect that helps suppress excessive particle agglomeration (Fig. 1d). High-resolution TEM (HRTEM) image clearly reveals well-defined lattice fringes (Fig. 1e). The enlarged HRTEM image in Fig. 1f shows a lattice spacing of 0.211 nm, corresponding to the (111) plane of alloy RuCo<sup>[23]</sup>. The corresponding Fourier transform image is shown in

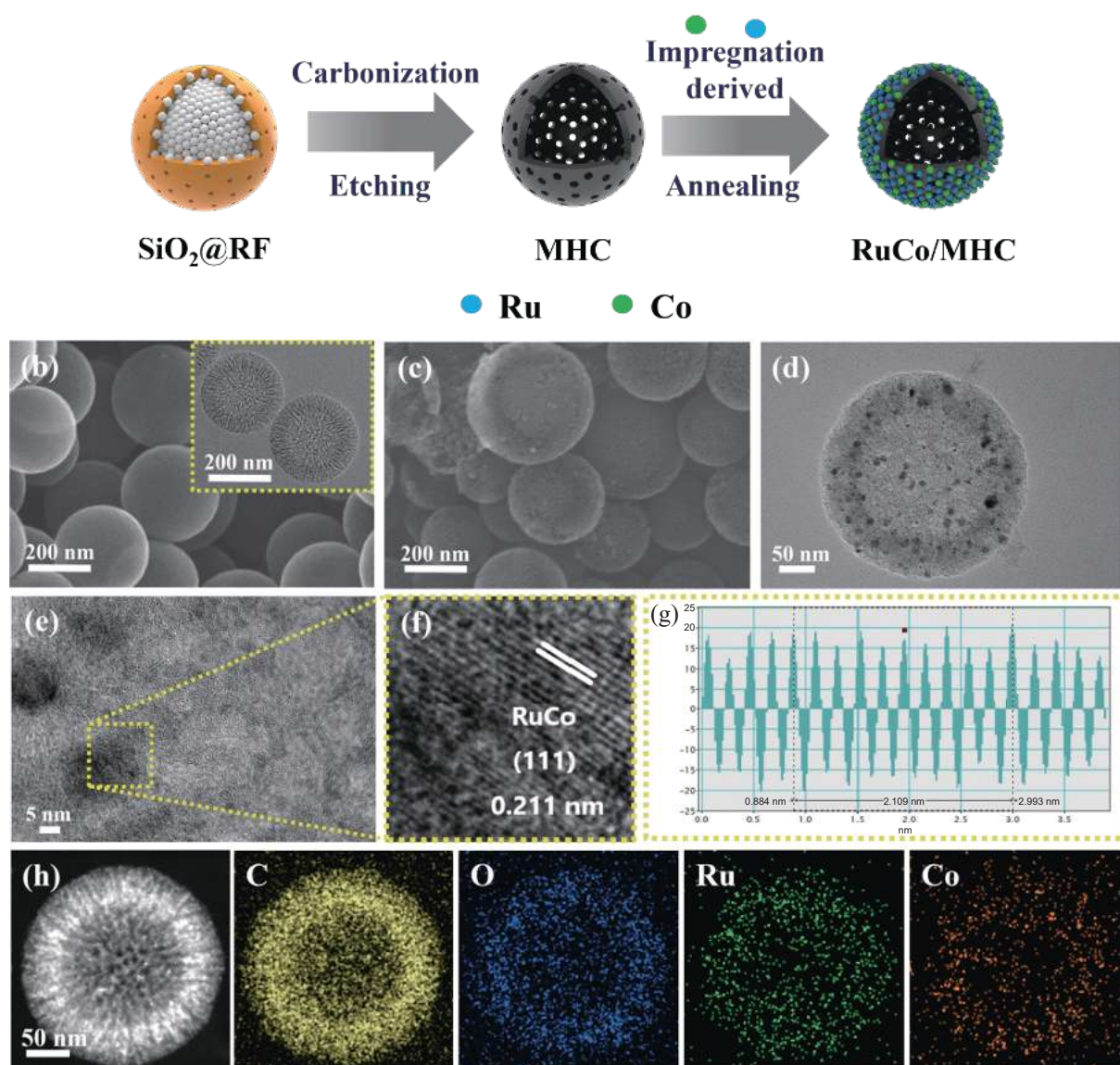


Fig. 1 (a) Schematic diagram of synthesis of RuCo/MHC. (b) SEM image of MHC, TEM image of MHC (inset of Fig. 1b). (c) SEM image of RuCo/MHC. (d) TEM image of RuCo/MHC. (e, f) HRTEM image and (g) corresponding Fourier transform image of RuCo/MHC. (h) EDS elemental mapping of RuCo/MHC

**Fig. 1g.** For comparison, the lattice spacing of Ru (002) in standard metallic Ru is approximately 0.214 nm (PDF #06-0663), while typical Co-related lattice spacing is around 0.201 nm. The observed intermediate spacing of 0.211 nm suggests lattice contraction caused by the incorporation of smaller Co atoms into the Ru lattice, which is consistent with the formation of RuCo alloy nanoparticles rather than separated Ru and Co phases. EDS elemental mapping indicates a high degree of spatial overlap between Ru and Co across the entire particle, with no obvious phase separation, further supporting the uniform an-

choring of the RuCo alloy on the MHC (Fig. 1h). Collectively, the morphological and structural characterization confirms that the impregnation-high-temperature reduction strategy achieves controlled loading of RuCo alloy nanoparticles on the hollow mesoporous carbon support. The hollow and mesoporous architecture of the MHC not only provides abundant exposed interfaces but also confines and stabilizes the metal particles, offering a solid structural foundation and interfacial advantages for subsequent electrocatalytic reactions<sup>[24]</sup>.

XRD patterns (Fig. 2a) of RuCo/MHC, Ru/MHC

and MHC show a diffraction peak at  $2\theta \approx 22.5^\circ$ , which corresponds to the graphitic (002) plane. Compared with Ru/MHC (PDF #06-0663), the corresponding peak for RuCo is slightly shifted to higher angles (Fig. 2b), suggesting that Co atoms enter the Ru lattice and induce lattice contraction<sup>[25]</sup>. According to Bragg's law, the shift toward higher  $2\theta$  values corresponds to a reduced lattice spacing, further supporting the lattice contraction inferred from the HRTEM analysis. In addition, no distinct diffraction peaks corresponding to metallic Co or cobalt oxides are observed, suggesting the absence of obvious phase segregation. Together with the homogeneous Ru and Co distributions revealed by EDS mapping, these results further support the successful formation of RuCo alloy nanoparticles on the MHC support. Raman spectra (Fig. 2c) show characteristic *D* and *G* bands at  $\sim 1350\text{ cm}^{-1}$  and  $1580\text{ cm}^{-1}$ , respectively, reflecting structural disorder and the  $\text{sp}^2$  graphitic framework<sup>[26]</sup>. The  $I_D/I_G$  ratios for RuCo/MHC, Ru/MHC and MHC are 1.11, 1.08 and 0.92, respectively, indicating a higher defect density in RuCo/MHC<sup>[27]</sup>. EPR spectra (Fig. 2d) display a pronounced signal at  $g = 2.003$  for all samples. The sample RuCo/MHC shows the strongest intensity, which is consistent with the Ra-

man results and indicates more unpaired electrons associated with defects<sup>[28]</sup>.

$\text{N}_2$  adsorption-desorption isotherms of RuCo/MHC (Fig. 2e) exhibit a typical type-IV isotherm with a hysteresis loop in the medium-high relative pressure region ( $p/p_0 \approx 0.5\text{--}0.9$ ), indicating abundant mesoporosity<sup>[29]</sup>. The adsorbed volume increases markedly with increasing relative pressure, reflecting a large pore volume and high specific surface area. The pore size distribution calculated using the nonlocal density functional theory model (Fig. 2f) reveals a hierarchical pore structure, with micropores centered at  $\sim 1.3\text{ nm}$  and mesopores centered at  $\sim 7.6$  and  $8.8\text{ nm}$ . Such a hierarchical micro/mesoporous architecture is favorable for exposing accessible active sites and facilitating electrolyte penetration and mass transport during CER<sup>[30]</sup>. The sample has a specific surface area of  $895.4\text{ m}^2\text{ g}^{-1}$  (Table S2). Such a large surface area combined with the hierarchical mesoporosity facilitates electrolyte penetration and promotes transport of reactants and products, thereby improving the accessibility of catalytically relevant interfacial sites<sup>[31]</sup>. To further clarify the role of the hollow porous structure,  $\text{N}_2$  adsorption-desorption isotherms and pore-size distribution curves of the control

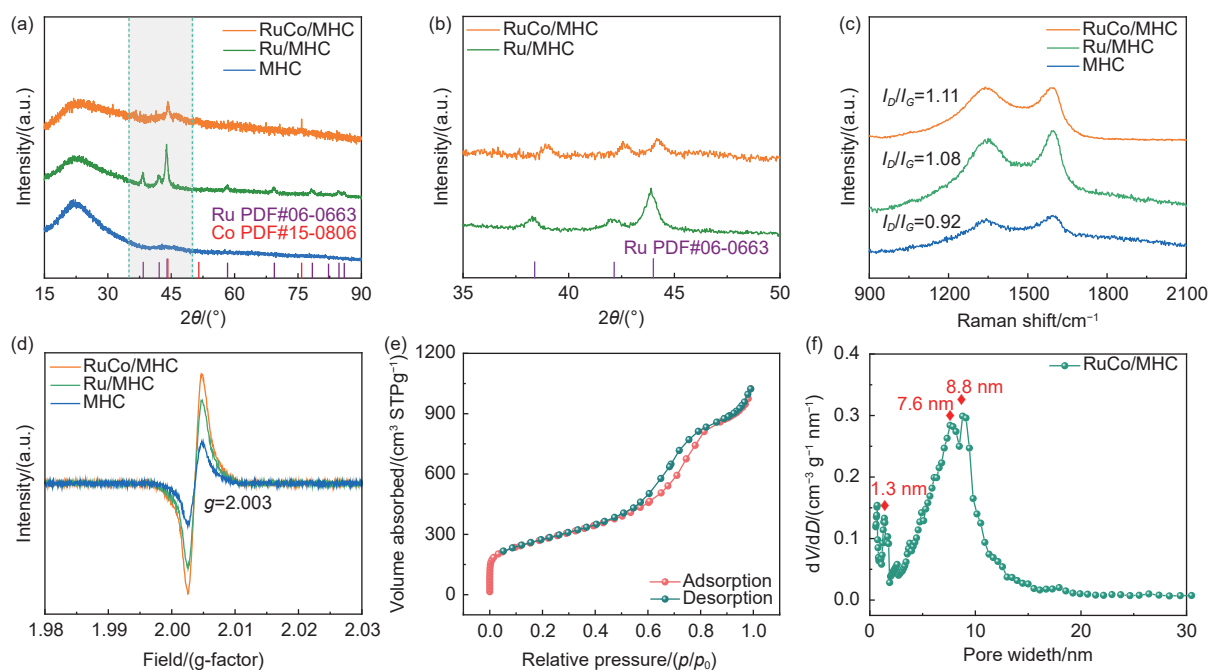


Fig. 2 (a,b) XRD patterns. (c) Raman spectra. (d) EPR spectra of RuCo/MHC, Ru/MHC and MHC. (e)  $\text{N}_2$  adsorption-desorption isotherms of RuCo/MHC. (f) Pore-size distribution of RuCo/MHC

samples Ru/MHC and MHC are shown in Fig. S5a, c. All samples exhibit typical type-IV isotherms with distinct hysteresis loops, confirming the presence of mesoporous structures. The corresponding pore size distributions reveal hierarchical micro/mesoporous structures, with micropores centered at approximately 1.3 nm and mesopores mainly centered at approximately 7.3–7.6 and 8.8 nm (Fig. S5b, d). These results indicate that the hollow porous architecture is well preserved after metal incorporation. Such accessible hierarchical pores facilitate electrolyte infiltration,  $\text{Cl}^-$  diffusion, and  $\text{Cl}_2$  release during CER, thereby contributing to the improved CER performance.

The XPS survey spectra of RuCo/MHC and Ru-MHC (Fig. S6, S7) confirm their expected elemental compositions. RuCo/MHC contains C, O, Ru and Co, whereas Ru/MHC contains C, O and Ru. These results are consistent with the EDS analysis. High-resolution C 1s fitting (Fig. 3a) exhibits peaks at 284.7, 286.6 and 288.8 eV, attributable to C–C, C–O and

O–C=O, respectively<sup>[32]</sup>. Additional features at  $\sim 280.6$  and  $281.3$  eV in this region are ascribed to overlap with Ru 3d signals. The O 1s high-resolution spectrum can be deconvoluted into three components, O1 (530.3–530.6 eV) associated with oxygen species related to C–O/C=O functional groups, O2 ( $\sim 531.9$  eV) assignable to low-coordination or unsaturated oxygen species ( $\text{O}^{2-}/\text{O}^-$ ), and O3 (532.3–533.2 eV) related to hydroxyl groups or adsorbed surface water (Fig. 3b and S8b)<sup>[33]</sup>. To avoid ambiguity from C 1s / Ru 3d overlap, the Ru 3p region is further examined (Fig. 3c). The high-resolution Ru 3p spectrum displays Ru  $3p_{3/2}$  and Ru  $3p_{1/2}$  peaks at approximately 462.8 and 484.8 eV, respectively. Deconvolution reveals that the peaks at 462.8 and 484.8 eV correspond to metallic Ru(0), while those at 464.5 and 486.8 eV are assigned to Ru (IV)<sup>[34]</sup>.

Compared with the reference Ru/MHC (Ru  $3p_{3/2} \sim 462.5$  eV, Ru  $3p_{1/2} \sim 484.5$  eV), the Ru 3p peaks in RuCo/MHC are shifted to higher binding energies, in-

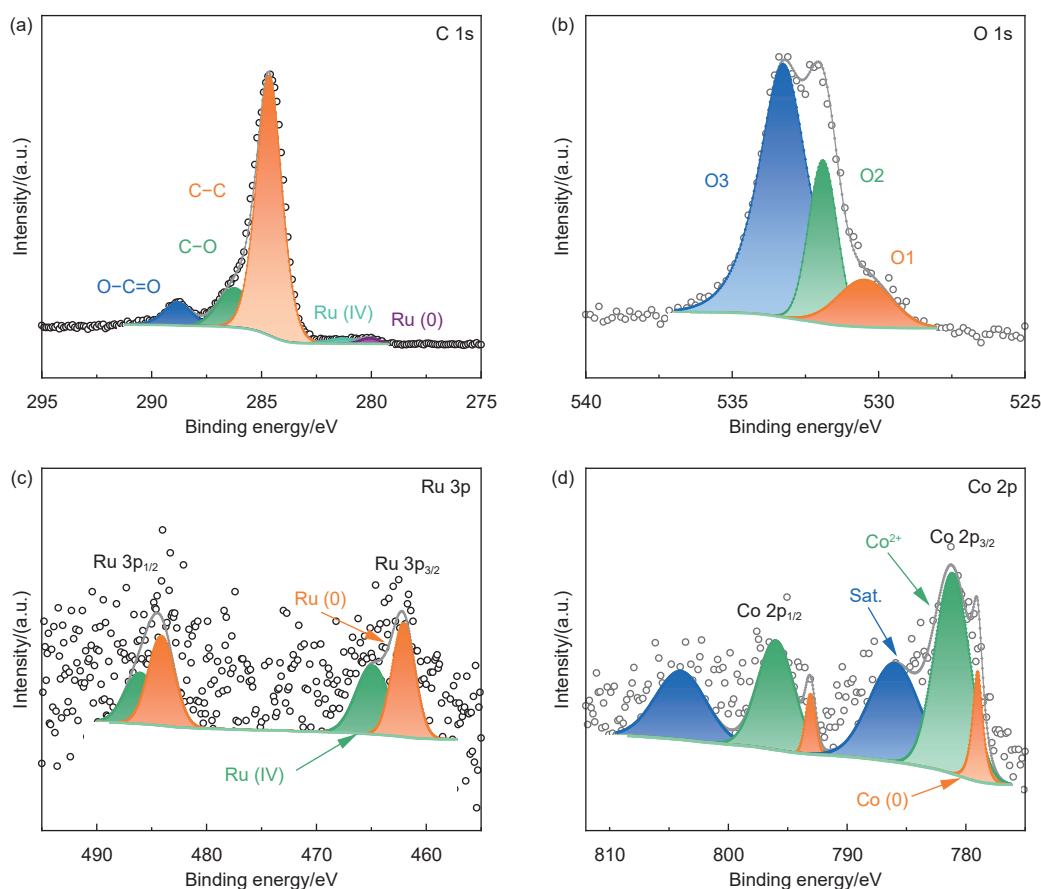


Fig. 3 High-resolution XPS spectra of (a) C 1s, (b) O 1s, (c) Ru 3p and (d) Co 2p for RuCo/MHC

dicating reduced electron density at Ru sites and electronic redistribution at the Ru-Co interface (Fig. S8c). The observed Ru (IV) component is likely attributable to partial surface oxidation of Ru upon air exposure. In the Co 2p region (Fig. 3d), peaks at 778.5 and 793.4 eV are assigned to metallic Co (0) Co 2p<sub>3/2</sub> and Co 2p<sub>1/2</sub>, respectively<sup>[35]</sup>. The peaks at 782.5 and 797.7 eV are assigned to Co(II) 2p<sub>3/2</sub> and Co(II) 2p<sub>1/2</sub>, respectively<sup>[36]</sup>. The presence of Co (II) is likely due to partial surface oxidation of Co (0) in air. Notably, the O2 component in the O 1s spectrum of RuCo/MHC (~ 531.7 eV) shifts to lower binding energy relative to that of Ru/MHC (~ 532.0 eV). The XPS data demonstrate electronic interactions and interfacial charge modulation among Ru, Co and O in RuCo/MHC<sup>[37–38]</sup>. ICP-OES analysis further shows that the Ru and Co contents in RuCo/MHC are 7.72% and 2.62%, respectively, while the Ru content in Ru/MHC is 7.61% (Table S1). The comparable Ru loading between RuCo/MHC and Ru/MHC suggests that the enhanced CER performance of RuCo/MHC mainly originates from Ru-Co alloying-induced electronic modulation rather than increased Ru content.

### 3.2 Catalytic CER performance

In a standard three-electrode configuration with

5 mol L<sup>-1</sup> NaCl (pH=2) as the electrolyte, the electrocatalytic performance of the catalysts for CER was systematically evaluated. LSV curves (Fig. 4a) and overpotential bar charts (Fig. 4b) indicate distinct activities under identical testing conditions. Specifically, RuCo/MHC requires overpotentials of 59 and 148 mV to reach 10 and 100 mA cm<sup>-2</sup>, respectively, which are substantially lower than those of Ru/MHC (119 and 261 mV). Moreover, at these current densities RuCo/MHC also outperforms the commercial DSA (110 and 226 mV). The lower overpotentials demonstrate that RuCo/MHC requires less energy to drive CER, reflecting superior electrocatalytic activity<sup>[39]</sup>. Notably, comparison with recent reports (Fig. S9 and Table S3) further highlights the competitive CER performance of RuCo/MHC. The actual Ru and Co contents of RuCo/MHC were determined by ICP-OES to be 7.72% and 2.62%, respectively, corresponding to a Ru loading of 0.116 mg cm<sup>-2</sup> at a catalyst loading of 1.5 mg cm<sup>-2</sup>. At 1.42 V vs RHE, RuCo/MHC delivers a mass activity of 0.086 A mg<sup>-1</sup> Ru, while the apparent turnover frequency TOF is estimated to be 0.045 s<sup>-1</sup> based on the total Ru content, suggesting efficient noble-metal utilization and improved cost-effectiveness enabled by Co alloying.

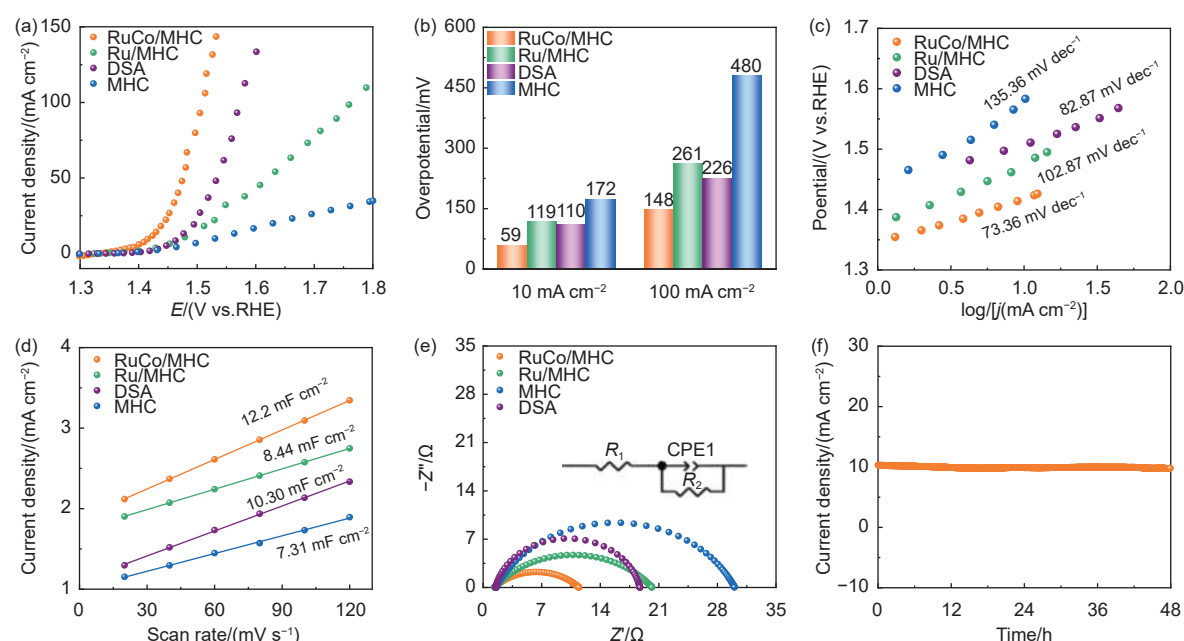


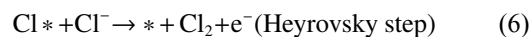
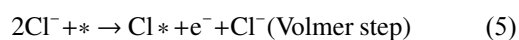
Fig. 4 (a) LSV curves of RuCo/MHC, Ru/MHC, DSA and MHC at 5 mol L<sup>-1</sup> NaCl (pH=2). (b) Comparison of overpotential of catalysts at 10 and 100 mA cm<sup>-2</sup>. (c) Tafel slopes of different catalysts. (d) C<sub>dl</sub> of different catalysts. (e) EIS Nyquist diagram for different catalysts. (f) Chronoamperometric stability test of RuCo/MHC at 10 mA cm<sup>-2</sup> for 48 h

Overall, RuCo/MHC delivers high current densities at relatively low overpotentials, demonstrating excellent catalytic performance and practical potential.

As shown in Fig. 4c, RuCo/MHC exhibits a Tafel slope of  $73.36 \text{ mV dec}^{-1}$ , which is significantly lower than those of Ru/MHC ( $102.87 \text{ mV dec}^{-1}$ ), commercial DSA ( $82.87 \text{ mV dec}^{-1}$ ) and MHC ( $135.36 \text{ mV dec}^{-1}$ ), indicating faster reaction kinetics<sup>[40]</sup>.  $C_{dl}$  values are obtained from non-Faradaic CVs at different scan rates (Fig. 4d). RuCo/MHC shows a  $C_{dl}$  of  $12.2 \text{ mF cm}^{-2}$ , which is higher than Ru/MHC ( $8.44 \text{ mF cm}^{-2}$ ), DSA ( $10.30 \text{ mF cm}^{-2}$ ) and MHC ( $7.31 \text{ mF cm}^{-2}$ ). This result implies a larger electrochemically active surface area and improved accessibility of catalytically relevant interfacial sites (Fig. S11)<sup>[41]</sup>. Furthermore, EIS Nyquist plots and equivalent-circuit fitting (Fig. 4e) indicate an interfacial charge-transfer resistance of  $11.6 \Omega$  for RuCo/MHC, consistent with the lower charge-transfer impedance and faster interfacial electron transport<sup>[42]</sup>. Collectively, RuCo/MHC displays advantages in kinetics, electrochemical active area and charge transport, which together promote its excellent CER performance<sup>[43]</sup>. Chronoamperometry (Fig. 4f) shows that RuCo/MHC maintains stable electrochemical behavior during continuous operation at  $10 \text{ mA cm}^{-2}$  for 48 h, indicating good operational stability and durability. After the 48 h stability test at  $10 \text{ mA cm}^{-2}$ , post-reaction SEM and TEM images show that the spherical morphology and hollow mesoporous structure of RuCo/MHC are largely preserved, without obvious structural collapse or noticeable nanoparticle aggregation (Fig. S12a, b). XPS analysis of the used catalyst further reveals that the characteristic chemical states of Ru and Co are largely retained. The O 1s spectra confirm the preserved oxygen-associated surface species after the reaction (Fig. S13b). The Ru 3p spectra show the coexistence of metallic Ru and oxidized Ru species, indicating surface oxidation under anodic conditions (Fig. S13c), while the Co 2p spectra retain the characteristic Co species (Fig. S13d). To further evaluate the durability under high current-density conditions, an additional chronoamperometric test was performed at  $100 \text{ mA cm}^{-2}$

(Fig. S14). RuCo/MHC maintains a relatively stable potential during continuous operation, indicating stable electrochemical performance at the elevated current density. In addition, SEM and TEM images collected after the  $100 \text{ mA cm}^{-2}$  stability test show that the hollow spherical morphology and dispersed nanoparticle structure are still maintained (Fig. S15). These results suggest that the RuCo alloy structure and interfacial chemical environment remain relatively stable during the CER process, without obvious phase segregation or significant surface loss of Ru/Co.

The oxygen evolution reaction (OER) activity of RuCo/MHC is assessed using the LSV method in  $1.0 \times 10^{-2} \text{ mol L}^{-1}$  HCl (pH=2) (Fig. 5a). The OER overpotential at  $10 \text{ mA cm}^{-2}$  is 348 mV, revealing a considerable potential difference as compared with that of CER (59 mV). The CER Faradaic efficiency is measured by constant-current electrolysis followed by standard iodometric titration, with each measurement independently repeated three times<sup>[44]</sup>. At  $10 \text{ mA cm}^{-2}$ , RuCo/MHC exhibits an average  $F_E$  of 97.2%, higher than Ru/MHC (94.2%), MHC (91.3%) and the commercial DSA (96.0%) (Fig. 5b). These results indicate that RuCo/MHC effectively suppresses competing side reactions and achieves high selectivity for chlorine evolution. The CER is generally considered to proceed via a Volmer-Heyrovský pathway<sup>[45]</sup>. In the Volmer step, chloride ions undergo electrochemical adsorption on the catalytic active site, generating the surface intermediate  $\text{Cl}^*$ . Subsequently,  $\text{Cl}_2$  is produced through the Heyrovský step, in which the adsorbed  $\text{Cl}^*$  species reacts with  $\text{Cl}^-$  from the electrolyte accompanied by electron transfer<sup>[46]</sup>:



The variation of the rate-determining step (RDS) during CER can be evaluated by analyzing the surface coverage of  $\text{Cl}^*$  ( $\theta_{\text{Cl}}$ ), which correlates with both the Tafel slope and the reaction order according to the following relations<sup>[39, 47]</sup>:

$$b = \frac{RT}{F} \left[ \frac{1}{\beta + 1 - \theta_{\text{Cl}}} \right] \quad (7)$$

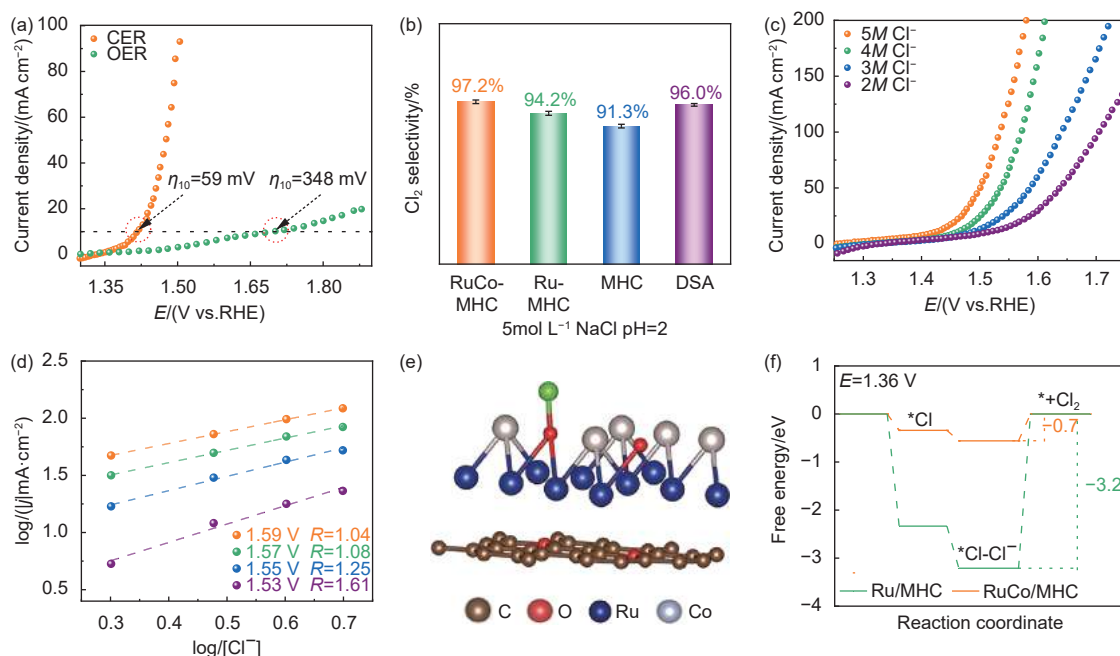


Fig. 5 (a) LSV curves for CER and OER of RuCo/MHC. (b) The CER selectivity of RuCo/MHC, Ru/MHC, MHC and DSA catalysts in 5 mol L<sup>-1</sup> NaCl (pH = 2) electrolyte is determined by iodometric titration. (c) LSV curves of RuCo/MHC at different  $[\text{Cl}^-]$ . (d)  $\log j$  vs.  $\log [\text{Cl}^-]$  plots of RuCo/MHC. (e) Structural model of chlorine intermediates adsorbed on RuCo/MHC. (f) Gibbs free energy of CER process

$$\mathfrak{R} = \left( \frac{\partial \log j}{\partial \log [\text{Cl}^-]} \right)_{E,T} = 2 - \theta_{\text{Cl}} \quad (8)$$

Here,  $\mathfrak{R}$  represents the reaction order,  $b$  is the Tafel slope,  $T$  is the temperature (K),  $R$  is the gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>),  $F$  is the Faraday constant,  $\beta$  is the symmetry factor of charge transfer in the RDS (typically 0.5), and  $[\text{Cl}^-]$  denotes the chloride concentration in the electrolyte. A reaction order approaching 2 indicates a low  $\text{Cl}^*$  surface coverage, suggesting that the Volmer step dominates the reaction kinetics.

To further elucidate this behavior, LSV measurements were carried out for RuCo/MHC at different chloride concentrations. As shown in Fig. 5c, the CER polarization curves shift progressively with increasing  $\text{Cl}^-$  concentration, accompanied by an increase in the catalytic current density. It indicates that the catalytic activity depends on chloride concentration. This trend can be explained by the Nernst relationship of CER, where the equilibrium potential ( $E_{\text{CER}}$ ) varies with  $\text{Cl}^-$  concentration. As illustrated in Fig. 5d, the reaction order  $\mathfrak{R}$  decreases gradually with increasing applied potential, implying a continuous increase in  $\text{Cl}^*$  surface coverage. Consequently, the RDS shifts from the Volmer step at lower potentials to the Heyrovský step at higher potentials, indicating a dy-

namic transition in the kinetic control of the RuCo/MHC system during CER.

The above results demonstrate that the superior CER performance of RuCo/MHC arises from the synergistic interplay between its optimized electronic structure and unique architecture. Previous studies have demonstrated that CER on Ru-based catalysts generally involves the adsorption and transformation of chlorine-containing intermediates, such as  $\text{Cl}^*$  and  $^*\text{OCl}$ , and that the binding strength of these intermediates plays a key role in determining catalytic kinetics and selectivity<sup>[50–53]</sup>. In addition, heteroatom or multimetal modulation of Ru-based catalysts has been reported to redistribute the electronic structure of Ru sites and optimize the adsorption behavior of chlorine-related intermediates<sup>[54–56]</sup>. For example, Eu-doped  $\text{RuO}_2$  enhances CER performance through charge redistribution and optimized  $^*\text{OCl}$  adsorption, while Ru-Sn-Ti electrodes strengthen the Ru-Cl interaction by modulating the Ru  $d$ -band center<sup>[54–56]</sup>. Consistent with these reports, the Ru-Co electronic interaction in RuCo/MHC may induce interfacial charge redistribution and modulate the electronic environment of oxygen-associated interfacial sites, thereby optimizing the

adsorption/desorption behavior of Cl-containing intermediates and facilitating  $\text{Cl}_2$  evolution. Meanwhile, the oxygen-associated surface species identified by XPS may participate in the adsorption of reaction intermediates or Ru-O-Cl-related interfacial evolution during CER. Similar oxygen-related active-site effects have also been reported in CER catalysts, including carbon-based systems<sup>[57–59]</sup>. The surface oxygen species in RuCo/MHC are mainly derived from residual oxygen-containing functional groups in the carbon matrix and partial surface oxidation. The relative content of unsaturated oxygen species is further estimated from the area ratio of the O2 component in the O 1s spectra. RuCo/MHC shows a higher O2 proportion than Ru-MHC and MHC, indicating that Ru-Co alloying promotes the formation or stabilization of low-coordination oxygen species (Table S4). Among these oxygen species, the unsaturated oxygen species are considered catalytically relevant, and Ru-Co alloying increases their electron density, thereby modulating the local electronic structure and interfacial polarization of the catalyst surface<sup>[47]</sup>. Such electronic redistribution may optimize the adsorption/desorption behavior of reaction intermediates, thus promoting CER activity.

To further understand the role of Ru-Co electronic interaction in modulating CER intermediates, adsorption models of Cl-related intermediates on RuCo-MHC and Ru/MHC are constructed, as shown in Fig. 5e and Fig. S16, and the corresponding Gibbs free-energy profiles for the CER pathway are calculated at an applied potential of 1.36 V. As shown in Fig. 5f, Ru/MHC exhibits more negative free-energy levels for the adsorbed chlorine intermediates, especially the  $\ast\text{Cl}-\text{Cl}$  state, indicating excessively strong stabilization of chlorine-containing species. Such strong adsorption may hinder the subsequent  $\text{Cl}_2$  release process. In contrast, RuCo/MHC shows a moderated free-energy profile with more balanced stabilization of  $\ast\text{Cl}$  and  $\ast\text{Cl}-\text{Cl}$  intermediates. This optimized adsorption strength is more favorable for the adsorption-desorption balance required by the Volmer-Heyrovsky pathway, thereby facilitating  $\text{Cl}_2$  evolution.

These results suggest that Co alloying effectively modulates the electronic structure of oxygen-associated interfacial sites and alleviates excessively strong binding of chlorine intermediates. This is consistent with the improved CER kinetics of RuCo/MHC. In addition to the electronic modulation induced by Ru-Co alloying, the hollow mesoporous carbon framework plays a pivotal role in enhancing catalytic efficiency<sup>[48]</sup>. Specifically, its high specific surface area and abundant porous structure improve the accessibility of catalytically relevant interfacial sites, while the interconnected mesoporous channels facilitate efficient electrolyte penetration and  $\text{Cl}^-$  transport. Meanwhile, the hollow architecture promotes the rapid detachment of generated  $\text{Cl}_2$  bubbles, effectively mitigating bubble accumulation and reducing mass-transfer resistance under high current densities<sup>[49]</sup>. Furthermore, the confinement effect of the porous carbon matrix helps suppress nanoparticle aggregation, thereby maintaining structural integrity and catalytic stability during long-term operation. Collectively, these structural advantages endow RuCo/MHC with enhanced activity, improved mass-transport kinetics, and robust durability, making it a highly promising catalyst for CER.

## 4 Conclusion

A Ru-Co alloy supported on MHC was successfully constructed as an efficient electrocatalyst for CER. Benefiting from the porous hollow carbon framework, RuCo nanoparticles are uniformly dispersed and stabilized, improving the accessibility of catalytically relevant interfacial sites and facilitating mass transport during the reaction. Alloy formation induces interfacial electronic redistribution, optimizing intermediate binding and accelerating CER kinetics. As a result, RuCo/MHC exhibits excellent catalytic performance in acidic NaCl electrolyte, requiring only about 59 mV overpotential to achieve a current density of  $10 \text{ mA cm}^{-2}$ , together with favorable kinetics and good operational stability. This work demonstrates that integrating alloy engineering with porous carbon supports provides an effective strategy for de-

veloping low-noble-metal, high-performance CER electrocatalysts.

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