

Localized Ru-induced interfacial electronic reconstruction enables highly reversible Li-CO₂ batteries

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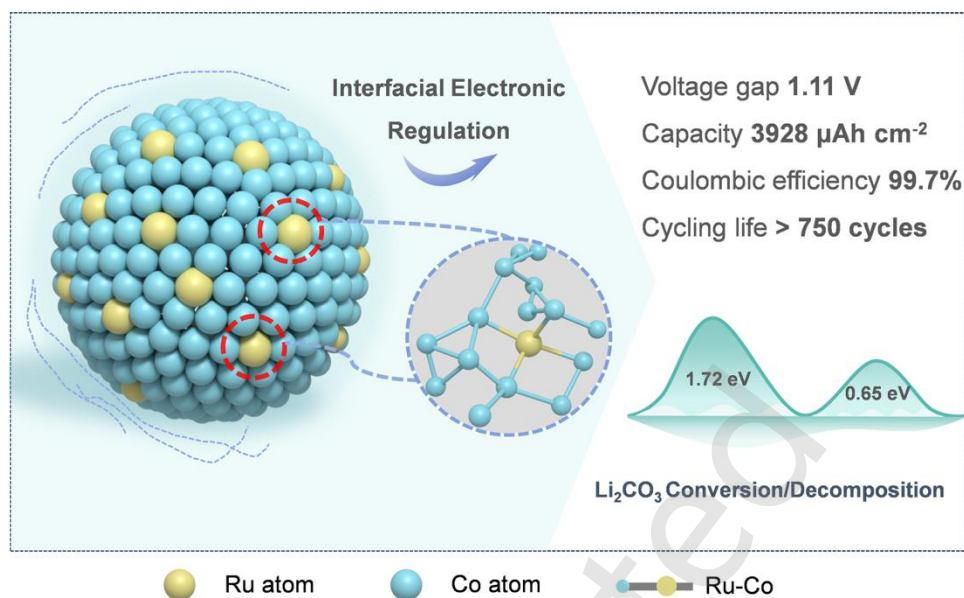
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Moderate localized Ru incorporation regulates the interfacial electronic environment of Co sites to facilitate reversible Li_2CO_3 conversion/decomposition, enabling Li- CO_2 batteries with low voltage gap (1.11 V), high coulombic efficiency (99.7%), and long-term cycling stability (3100 h, > 750 cycles).

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ABSTRACT: Li-CO₂ batteries are promising for integrating energy storage with CO₂ utilization, yet their practical application is limited by poor reversibility of discharge products formation/decomposition. Rational regulation of interfacial electronic environments is therefore crucial for improving reaction reversibility and enhancing electrochemical performance. Herein, a Co-based catalyst with localized Ru incorporation was constructed through a ZIF-67-derived structural confinement strategy. Localized Ru incorporation effectively reconstructs the local electronic environment of neighboring Co sites and induces interfacial electronic modulation. The Li-CO₂ battery with the Ru₁₅Co₈₅ nanoparticles (Ru₁₅Co₈₅-NPs) cathode delivers a low voltage gap of 1.11 V, a high coulombic efficiency of 99.7%, and stable cycling over 750 cycles (3100 h), significantly superior to those with Co-NPs and Ru₅₀Co₅₀-NPs counterparts. The optimized Ru₁₅Co₈₅ catalyst exhibits regulated interfacial reaction, enabling more efficient Li₂CO₃-related conversion and decomposition processes. Density functional theory calculations further reveal that moderate Ru incorporation lowers the free-energy barrier of the rate-determining Li₂CO₃ formation step and reduces the Li₂CO₃ dissociation barrier to 0.65 eV. This work provides an effective strategy for regulating interfacial electronic environments through moderate Ru incorporation and offers new insights into the design of highly reversible Li-CO₂ battery catalysts.

KEYWORDS: Li-CO₂ batteries, reversibility, long cycle, localized Ru, interfacial electronics

1 Introduction

Carbon dioxide, as a typical greenhouse gas, its massive emissions impose long-term pressure on energy structures and ecological environments. In this context, achieving efficient conversion and resource utilization of CO₂ has emerged as an urgent scientific and technological demand. Electrochemical conversion is regarded as one of the most promising pathways owing to its compatibility with renewable energy sources, mild operating conditions, and controllable efficiency [1–3]. Among various systems, the lithium-carbon dioxide (Li-CO₂) battery stands out as a representative technology. The reaction follows the chemical equation $4\text{Li}^+ + 3\text{CO}_2 + 4\text{e}^- \leftrightarrow 2\text{Li}_2\text{CO}_3 + \text{C}$, which not only exhibits a high theoretical energy density of up to 1876 Wh kg⁻¹ but also enables efficient CO₂ conversion, thereby offering the unique advantage of integrating energy storage with carbon capture [4–7]. However, the performance enhancement of Li-CO₂ batteries remains constrained by the slow kinetics of the cathode reaction, particularly the difficult reversible decomposition of the discharge product Li₂CO₃ during the charging process [8–11]. This issue primarily stems from the high thermodynamic stability and electronic insulating properties of Li₂CO₃, leading to significant charge-discharge potential differences, low energy efficiency, and limited cycle life [12–16].

In recent years, extensive efforts have been devoted to

developing efficient catalysts to improve the sluggish cathode reaction kinetics and reversibility of Li-CO₂ batteries [17–18]. Among them, Ru-based catalysts have attracted considerable attention owing to their remarkable capability for promoting Li₂CO₃ decomposition and suppressing charge polarization during cycling [19–22]. However, most reported Ru-based systems still rely on high Ru loadings to compensate for insufficient intrinsic activity or limited active-site utilization, resulting in high cost and low atomic efficiency [23,24]. Rational regulation of localized interfacial electronic environments has recently emerged as an important strategy for promoting reversible discharge-product conversion chemistry in metal-CO₂ battery systems. For example, Deng and co-workers demonstrated that interfacial sulphilic enrichment can effectively regulate the interfacial Li₂CO₃ conversion behavior by enriching sulfur-affinitive reaction environments, thereby facilitating reversible discharge-product evolution and improving the cycling reversibility of Li-CO₂ batteries [25]. Meanwhile, Guo, et al. reported that electronically localized RuNi nanosheet assemblies can optimize local electronic structures and regulate interfacial CO₂ conversion chemistry in Mg-CO₂ batteries, resulting in significantly reduced overpotential and enhanced electrochemical reversibility [26]. These recent advances

highlight the critical role of localized interfacial electronic regulation in governing reversible discharge-product conversion chemistry in metal- CO_2 battery systems. Nevertheless, precise modulation of localized interfacial electronic environments toward highly reversible Li_2CO_3 conversion/decomposition processes in Li- CO_2 batteries remains highly challenging.

Herein, a Co-based catalyst with localized Ru incorporation was constructed through a ZIF-67-derived structural confinement strategy. Structural characterizations including X-ray absorption spectroscopy (XAS) analyses reveal evident electronic interaction between localized Ru species and neighboring Co sites, indicating effective modulation of the local electronic environment after Ru incorporation. The Li- CO_2 battery with the $\text{Ru}_{15}\text{Co}_{85}$ nanoparticles ($\text{Ru}_{15}\text{Co}_{85}$ -NPs) cathode delivers a low voltage gap of 1.11 V, substantially lower than those of Co-NPs (1.72 V) and $\text{Ru}_{50}\text{Co}_{50}$ -NPs (1.59 V). Moderate Ru incorporation in $\text{Ru}_{15}\text{Co}_{85}$ effectively regulates the Co-derived electronic states and reconstructs the local interfacial electronic environment, thereby enabling more favorable Li_2CO_3 -related conversion and decomposition processes. Density functional theory calculations further reveal that $\text{Ru}_{15}\text{Co}_{85}$ surface exhibits the lowest thermodynamic barrier (1.72 eV) along the favorable Li_2CO_3 formation pathway, together with a reduced Li_2CO_3 dissociation barrier of 0.65 eV, both more favorable than those of Co and $\text{Ru}_{50}\text{Co}_{50}$ surfaces. As a consequence, the Li- CO_2 battery with $\text{Ru}_{15}\text{Co}_{85}$ -NPs shows stable operation over 750 cycles with a voltage gap of only 1.41 V, whereas Co-NPs and $\text{Ru}_{50}\text{Co}_{50}$ -NPs fail after 122 and 74 cycles, respectively, accompanied by severe polarization increase. These results collectively establish a direct correlation between localized Ru-induced interfacial electronic regulation and the reversible conversion/decomposition of Li_2CO_3 , providing mechanistic insight into the design of highly reversible Li- CO_2 battery catalysts.

2 Results and discussion

Following the synthesis route illustrated in **Fig. S1**, Ru_xCo_y nanoparticles (Ru_xCo_y -NPs) synthesized through a ZIF-67-derived structural confinement strategy involving solvent-phase ion exchange and subsequent hydrogen reduction. Pristine ZIF-67 exhibited a well-defined dodecahedral morphology with high crystallinity (**Figs. S2 and S3**). After Ru/Co ion exchange, the resulting $\text{Ru}_x\text{Co}_y\text{O}_z$ precursors largely retained the polyhedral framework, while their structural integrity showed a strong dependence on the Ru incorporation level. Specifically, the $\text{Co}_{100}\text{O}_z$ preserved the intact dodecahedral structure, while $\text{Ru}_{15}\text{Co}_{85}\text{O}_z$ retained the polyhedral framework with only slight distortion. In contrast, excessive Ru incorporation ($\text{Ru}_{50}\text{Co}_{50}\text{O}_z$) led to pronounced polyhedral collapse and edge blunting (**Fig. S4**), indicating that excessive Ru disrupts the structural stability of the ZIF-derived framework during precursor evolution. These observations suggest that moderate Ru incorporation is beneficial for preserving structural confinement during precursor transformation. Furthermore, Energy-dispersive spectroscopy (EDS) analysis of $\text{Ru}_{15}\text{Co}_{85}\text{O}_z$ revealed the homogeneous spatial distribution of Ru, Co, and O throughout the polyhedral framework (**Fig. S5**). The

homogeneous elemental distribution suggests effective incorporation of Ru species within the Co-based precursor, which is likely facilitated by the porous confinement environment of ZIF-67 that promotes uniform distribution of Ru^{3+} and Co^{2+} species [27]. Subsequent hydrogen reduction induced significant contraction of the dodecahedral framework and morphological reconstruction, leading to the formation of Ru_xCo_y -NPs (**Figs. S6 and 1(a)**). This transformation can be primarily attributed to framework decomposition and the migration/rearrangement of metal species at elevated temperatures. EDS mapping after thermal reduction revealed that both Ru and Co species remained uniformly distributed without obvious elemental segregation, suggesting negligible metal loss during the reduction process (**Figs. S7-S9**). Taking $\text{Ru}_{15}\text{Co}_{85}$ -NPs as an example, transmission electron microscopy (TEM) images revealed a typical nanoparticle structure with distribution and well-defined interfaces. Corresponding EDS mapping confirmed intimate spatial coupling between Ru and Co species without observable macroscopic phase separation (**Fig. 1(b)**). Similarly, for undoped Co-NPs and high-Ru-content $\text{Ru}_{50}\text{Co}_{50}$ -NPs, Ru and Co maintained good homogeneity (**Figs. S10 and S11**). High-resolution TEM (HRTEM) of $\text{Ru}_{15}\text{Co}_{85}$ -NPs displayed clear lattice fringes with an interplanar spacing of approximately 0.20 nm, which can be assigned to the Co (002)-related metallic lattice plane (**Fig. 1(c)**). Combined with the homogeneous Ru/Co distribution revealed by EDS mapping, these results suggest the formation of a RuCo-based metallic framework with intimate local interfacial coupling. N_2 adsorption-desorption measurements were further conducted to determine the specific surface areas of the catalysts. As shown in **Fig. S12**, all three samples exhibit similar N_2 adsorption-desorption isotherms, with BET specific surface areas of 21.56, 10.05, and 17.35 $\text{m}^2 \text{g}^{-1}$ for Co-NPs, $\text{Ru}_{15}\text{Co}_{85}$ -NPs, and $\text{Ru}_{50}\text{Co}_{50}$ -NPs, respectively. As shown in X-ray diffraction (XRD) patterns (**Fig. 1(d)**), there are three diffraction peaks appeared at $2\theta = 41.68^\circ$, 44.76° , and 47.56° in the undoped Co-NPs, consistent with the diffraction pattern of hexagonal close-packed (hcp) cobalt (PDF#05-0727). A weak diffraction peak near 51.5° can also be indexed to the (200) plane of face-centered cubic (fcc) Co (PDF#15-0806), suggesting a minor contribution from the fcc Co phase. Accordingly, the diffraction feature around 44° is likely associated with overlapping contributions from hcp Co(002) and fcc Co(111). Upon Ru incorporation, the major characteristic diffraction peaks gradually shift toward lower diffraction angles. This progressive shift is attributed to lattice expansion and local structural distortion associated with Ru incorporation, which increase the average interplanar spacing of the neighboring Co lattice [28-30]. To quantify the actual Ru/Co composition, the reduced samples were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES). The results showed that the actual molar ratio of Ru to Co in $\text{Ru}_{15}\text{Co}_{85}$ -NPs was approximately 14:86, while that in $\text{Ru}_{50}\text{Co}_{50}$ -NPs it was about 53:47 (**Table S1**). These values closely matched the initial feeding proportions, demonstrating that this synthesis strategy enables effective control over the bimetallic composition.

To elucidate the electronic structure and coordination

environment of the metal sites, further characterization was performed on the three aforementioned materials. As shown in the Fourier-transform infrared (FTIR) spectra (**Fig. S13**), the three samples exhibited highly similar absorption peaks across the entire wavenumber range, indicating that Ru incorporation neither introduces new functional groups nor disrupts the overall chemical structure of the Co-based material. X-ray photoelectron spectroscopy (XPS) results further verified the coexistence of Ru and Co species in the obtained nanoparticles, consistent with the EDS and ICP-OES analyses (**Figs. S14** and **S15**). Furthermore, the C 1s spectra of all samples exhibited consistent carbon support structures without surface organic contamination (**Fig. S16**). The high-resolution Ru 3p and Co 2p XPS spectra indicate that both Ru and Co predominantly exist in metallic states within the $\text{Ru}_x\text{Co}_y\text{-NPs}$ [31,32]. In the Co 2p spectrum (**Fig. 1(e)**), the peak located at 778.8 eV is assigned to metallic Co^0 , while the peak at 781.9 eV corresponds to oxidized Co species. The oxidized Co species are likely associated with residual Co-N/O coordination environments or surface oxidation upon air exposure. Correspondingly, Raman spectra (**Fig. S17**) exhibited several characteristic bands located at approximately 472, 516, and 678 cm^{-1} , which are associated with surface metal-oxygen vibrational modes in the Co-based framework [28]. After Ru incorporation, characteristic Ru metallic-state signals appeared at 461.83 and 484.01 eV in the Ru 3p spectra (**Figs. S15** and **1(f)**). Notably,

progressive Ru incorporation induced an evident shift of the Co-related peaks toward lower binding energies, accompanied by an opposite shift of the Ru-related peaks toward higher binding energies [33,34]. Compared with Co-NPs, the Co^0 peak in $\text{Ru}_{15}\text{Co}_{85}\text{-NPs}$ shifted negatively by 0.13 eV. With further Ru incorporation, the Co^0 peak in $\text{Ru}_{50}\text{Co}_{50}\text{-NPs}$ exhibited an additional negative shift of 0.15 eV, while the Ru^0 peak shifted positively by 0.12 eV. These opposite binding-energy shifts suggest pronounced interfacial charge redistribution between Ru and Co species, with electron transfer from localized Ru sites to neighboring Co sites. Such electronic redistribution reflects localized interfacial coupling induced by Ru incorporation rather than significant changes in the dominant metallic states of Ru and Co [35-37]. X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses were further employed to probe the local electronic configuration and coordination environment of Co sites in Co-NPs and $\text{Ru}_{15}\text{Co}_{85}\text{-NPs}$. Metallic Co foil and CoO were used as reference samples for Co valence-state and coordination-environment analysis.

As shown in **Fig. 1(g)**, the absorption edge of Co-NPs is close to that of Co foil, indicating that Co predominantly retains a metallic character. In contrast, $\text{Ru}_{15}\text{Co}_{85}\text{-NPs}$ show a slight positive shift of the Co K-edge together with an enhanced white-line intensity, suggesting a reduced average

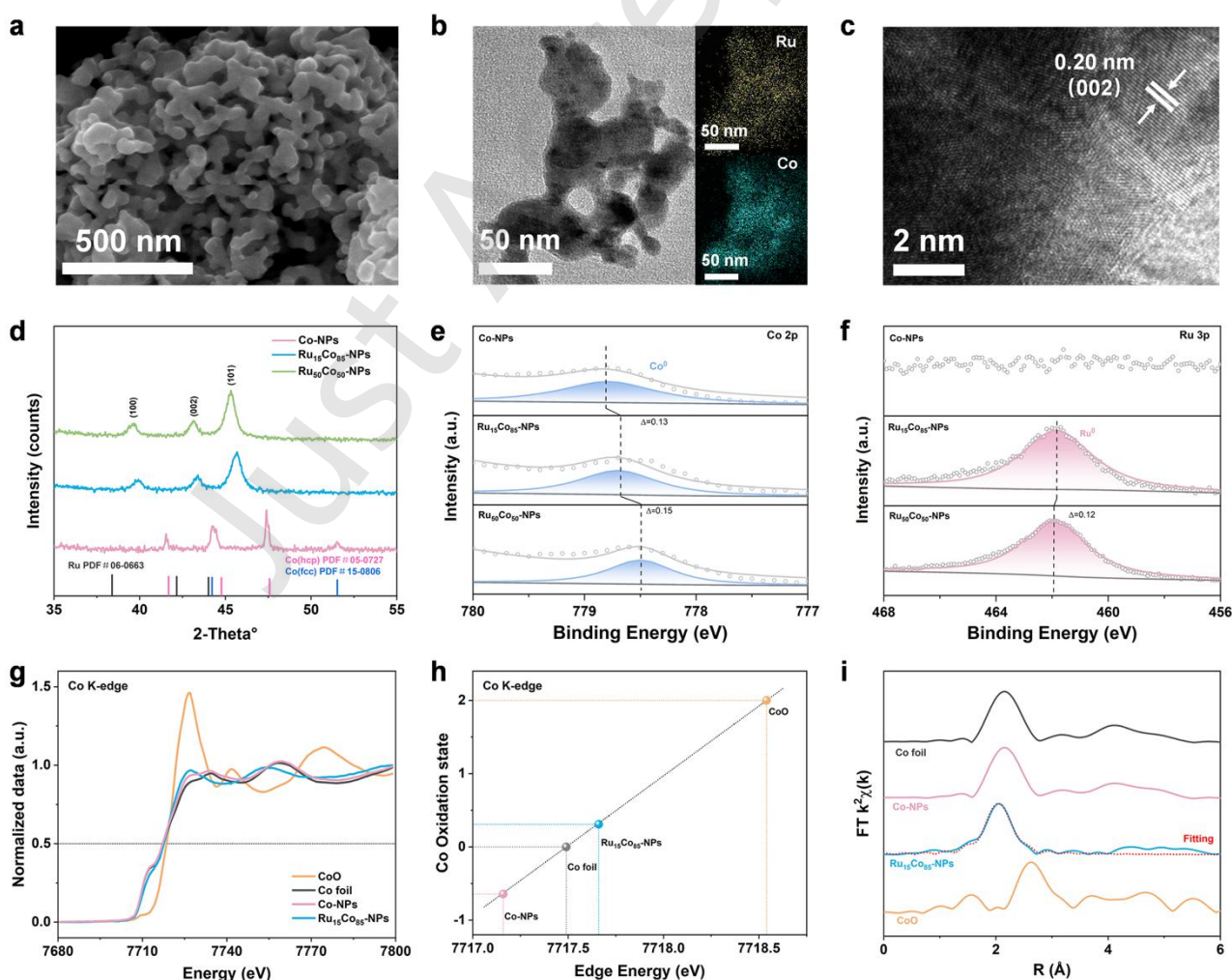


Fig 1. Microstructure and electronic structure characterization of the $\text{Ru}_{15}\text{Co}_{85}$ -NPs catalyst. (a) SEM image, (b) TEM image and EDS mappings of Ru and Co elements, (c) HRTEM image of $\text{Ru}_{15}\text{Co}_{85}$ -NPs. (d) XRD patterns, (e) Locally enlarged Co 2p and (f) Ru 3p XPS curves of three NPs samples. (g) Co K-edge XANES results for Co-NPs, $\text{Ru}_{15}\text{Co}_{85}$ -NPs, and reference samples (Co foil and CoO). (h) Relation between the Co K-edge absorption energy and valence states. (i) The FT-EXAFS spectra and the fitting results of $\text{Ru}_{15}\text{Co}_{85}$ -NPs.

electron density around Co sites relative to Co-NPs. This spectral evolution reflects Ru-induced reconstruction of the local electronic environment around Co sites while preserving the predominantly metallic coordination feature. As shown in **Fig. 1(h)**, the average Co valence state was further estimated from the absorption-edge energy at 0.5 normalized intensity using Co foil (Co^0) and CoO (Co^{2+}) as references. The estimated Co valence state of $\text{Ru}_{15}\text{Co}_{85}$ -NPs is slightly higher than that of Co-NPs but remains close to the metallic state. The apparently negative valence value estimated for Co-NPs should be ascribed to nanoscale electronic effects and edge-position calibration uncertainty, rather than the formation of true negatively charged Co species. The Fourier-transform EXAFS (FT-EXAFS) spectra further reveal the local coordination environment of Co sites (**Fig. 1(i)**). The dominant Co-Co scattering peaks observed for both Co-NPs and $\text{Ru}_{15}\text{Co}_{85}$ -NPs indicate that Co predominantly exists in a metallic coordination environment. EXAFS fitting was further performed to evaluate the influence of Ru incorporation on the local bond distances and coordination numbers around Co sites (**Table S2**). The fitted Co-Co distance in $\text{Ru}_{15}\text{Co}_{85}$ -NPs remains comparable to

that of Co foil, indicating that the metallic Co framework is largely preserved after Ru incorporation. The coordination numbers (CN) for Co-Co and Ru-Co paths in $\text{Ru}_{15}\text{Co}_{85}$ -NPs are 4.1 and 0.35, respectively. Notably, the relatively low Ru-Co coordination number suggests that Ru species are present in localized interfacial environments rather than forming a fully homogeneous Ru-Co alloy structure. Meanwhile, the reduced coordination number around Co relative to the Co foil reference suggests a locally unsaturated coordination environment in $\text{Ru}_{15}\text{Co}_{85}$ -NPs. These partially undercoordinated Co sites, together with localized Ru-Co interfacial coupling, are expected to provide a favorable local electronic environment for interfacial CO_2 reduction/evolution reactions ($\text{CO}_2\text{RR}/\text{CO}_2\text{ER}$) structures. Finally, the fitted curves for the Co edge in k-space showed good agreement with the experimental data (**Fig. S18**), which validates the reliability of the fitting model.

The electrochemical performance of Li- CO_2 batteries with different catalysts as cathodes was systematically evaluated toward interfacial $\text{CO}_2\text{RR}/\text{CO}_2\text{ER}$. As shown in the cyclic voltammetry (CV) curves (**Fig. 2(a)**), the $\text{Ru}_{15}\text{Co}_{85}$ -NPs cathode exhibited the most pronounced electrochemical

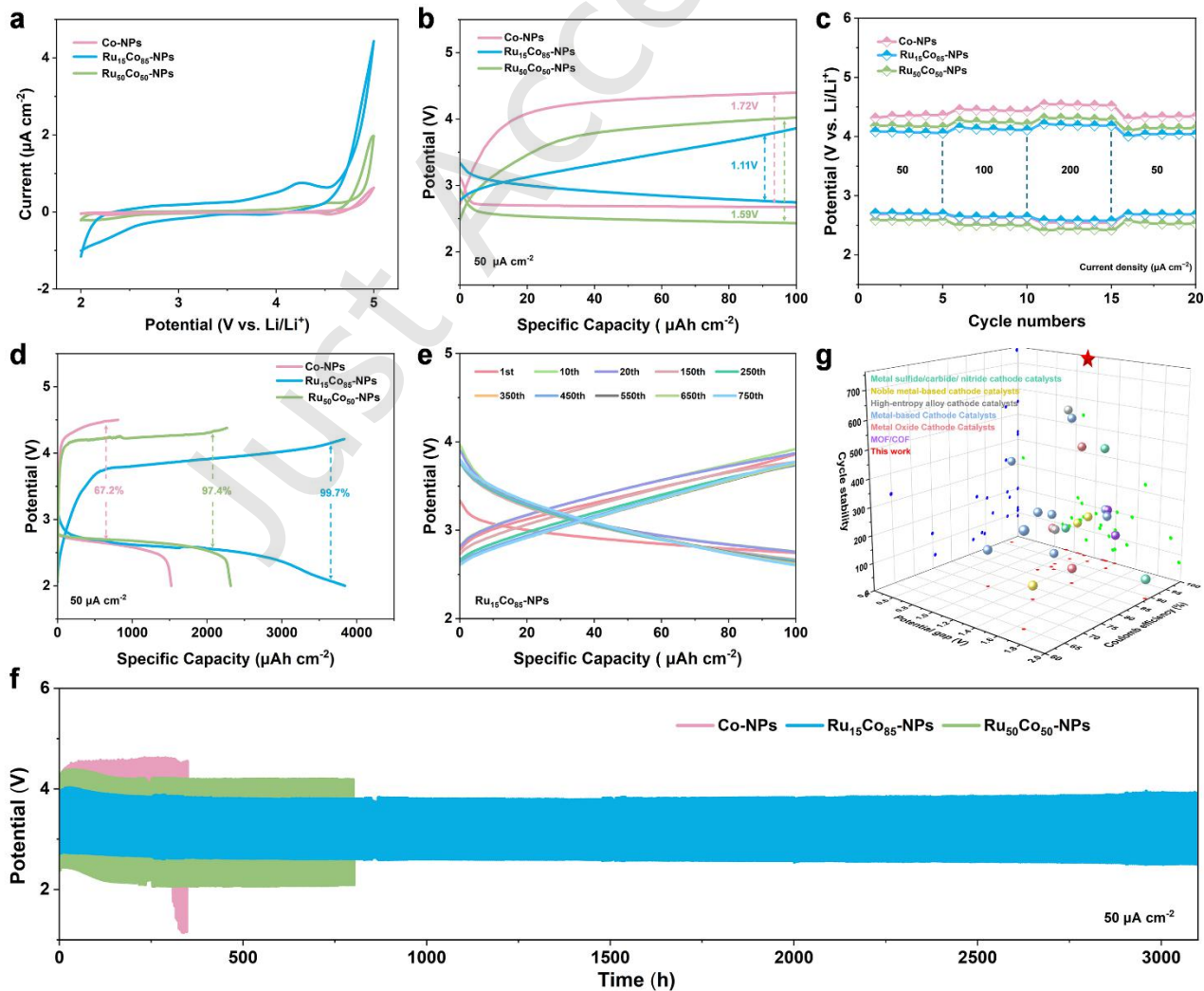


Fig 2. Electrochemical performance characterization of Li-CO₂ batteries with different cathodes. (a) The CV curves of Co-NPs, Ru₁₅Co₈₅-NPs, and Ru₅₀Co₅₀-NPs cathodes upon operation at a scan rate of 0.2 mV s⁻¹ with a potential voltage of 2.0 ~ 5.0 V. (b) GDC curves of three cathodes with a limited capacity of 100 μAh cm⁻² at a current density of 50 μA cm⁻². (c) The rate performance comparison at various current densities for three cathodes. (d) The full discharge and charge capacities of three cathodes at 50 μA cm⁻². (e) Recyclability of Li-CO₂ battery with Ru₁₅Co₈₅-NPs at 50 μA cm⁻². (f) Cycling performance of three cathodes at 50 μA cm⁻². (g) Performance comparison toward terminal voltage gaps, cycle stability and energy efficiency between Li-CO₂ batteries with Ru₁₅Co₈₅-NPs cathode and other reported catalysts.

response among the three samples. Both the oxidation and reduction peak currents were significantly higher than those of Co-NPs and Ru₅₀Co₅₀-NPs, indicating the superior capability of Ru₁₅Co₈₅-NPs in facilitating cathode reaction kinetics. Notably, an additional oxidation feature centered at approximately 4.3 V was observed for Ru₁₅Co₈₅-NPs, which is tentatively attributed to the initial decomposition of Li₂CO₃ during charging. Furthermore, Ru₁₅Co₈₅-NPs exhibited the smallest redox peak separation, indicating reduced polarization and enhanced electrochemical reversibility. The initial galvanostatic discharge-charge (GDC) profiles of batteries with different catalysts were compared at a current density of 50 μA cm⁻² with a limited capacity of 100 μAh cm⁻² (**Fig. 2(b)**). The results showed that the battery based on the Ru₁₅Co₈₅-NPs cathode exhibited the smallest discharge/charge voltage gap of 1.11 V, significantly lower than those of the Co-NPs-based (1.72 V) and Ru₅₀Co₅₀-NPs-based (1.59 V) batteries. This reduced polarization suggests that moderate Ru incorporation effectively optimizes the local interfacial electronic environment, thereby promoting reversible CO₂RR/CO₂ER kinetics. In contrast, excessive Ru incorporation in Ru₅₀Co₅₀-NPs may disrupt the optimized local electronic environment and interfacial reaction balance, leading to inferior electrochemical reversibility. Within the current density range of 50 to 200 μA cm⁻², the Ru₁₅Co₈₅-NPs cathode maintained a low voltage gap, demonstrating favorable rate performance (**Fig. 2(c)**). It is noteworthy that when the current density is restored to 50 μA cm⁻², the voltage gap does not increase but instead slightly decreases, suggesting gradual activation of the interfacial reaction process during cycling. Furthermore, as illustrated in the deep charge-discharge profile presented in **Fig. 2(d)**, the Ru₁₅Co₈₅-NPs cathode exhibited the highest discharge capacity (3928 μAh cm⁻²/11097 mAh g⁻¹), while maintaining a coulombic

efficiency as high as 99.7%. In comparison, the Co-NPs and Ru₅₀Co₅₀-NPs cathodes delivered significantly lower discharge capacities of only 1739 and 2556 μAh cm⁻² (4913 and 7721 mAh g⁻¹), respectively, accompanied by notably larger voltage gaps and lower coulombic efficiencies. Interestingly, despite its lower discharge capacity and larger voltage gap, the Ru₅₀Co₅₀-NPs cathode still exhibited a relatively high coulombic efficiency, suggesting partially reversible formation and decomposition behavior of discharge products. However, the interfacial reaction process in Ru₅₀Co₅₀-NPs remains less optimized than that in Ru₁₅Co₈₅-NPs, resulting in increased polarization and limited discharge capacity.

The electrochemical stability and reversibility of the aforementioned three catalysts were further evaluated through long-term cycling tests. As shown in **Fig. 2(e)** and **2(f)**, the Li-CO₂ battery based on Ru₁₅Co₈₅-NPs exhibited stable performance over 750 cycles (3100 h) at a current density of 50 μA cm⁻², with a voltage gap as low as 1.41 V. In contrast, the Ru₅₀Co₅₀-NPs and Co-NPs cathodes achieved only 74 and 122 cycles, respectively, accompanied by significantly enlarged voltage gaps of 2.76 V and 2.35 V (**Figs. S19 and S20**). As illustrated in **Figs. S21 and S22**, the energy efficiency of the battery with the Ru₁₅Co₈₅-NPs cathode reached as high as 88.7%, markedly surpassing those of the Co-NPs (56.9%) and Ru₅₀Co₅₀-NPs (60.5%) cathodes. Even at an elevated current density of 100 μA cm⁻², the Ru₁₅Co₈₅-NPs cathode maintained a stable voltage gap of approximately 1.70 V for over 650 hours (**Fig. S23**), further highlighting its stable interfacial reaction kinetics under demanding operating conditions. The low voltage gap and high discharge capacity further demonstrate the distinct advantage of Ru₁₅Co₈₅-NPs in improving the energy-utilization efficiency of

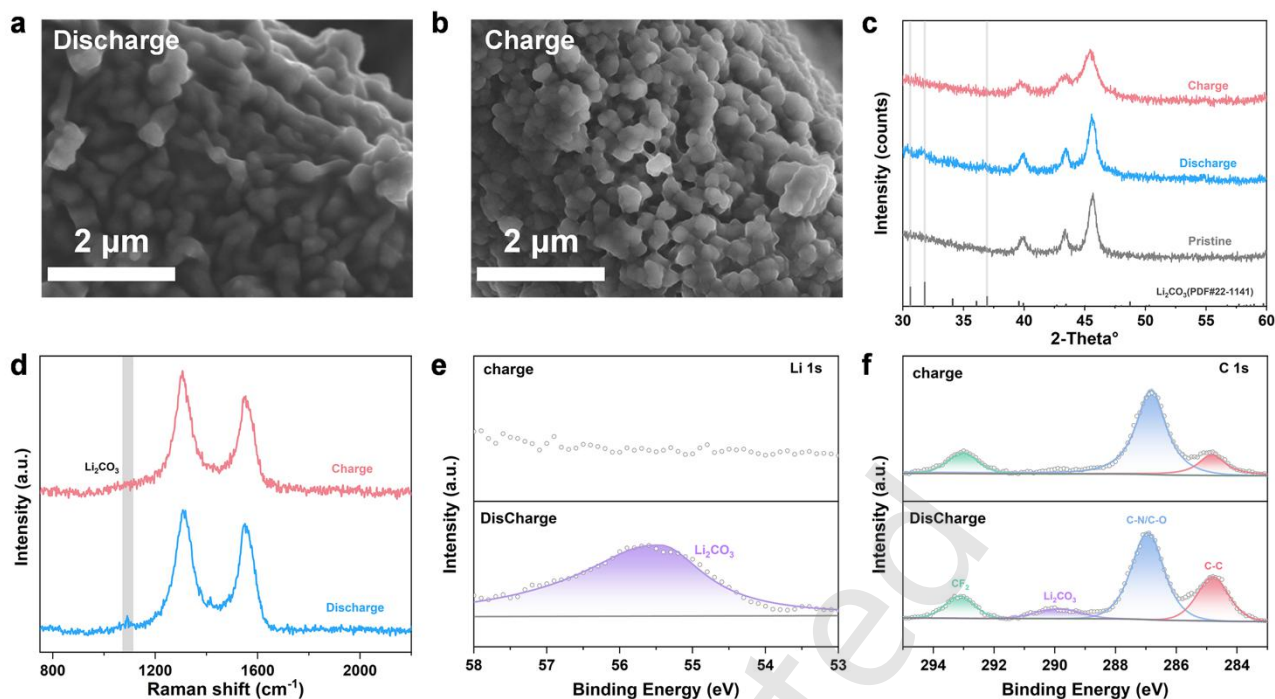


Fig 3. Ex situ characterization of the Ru₁₅Co₈₅-NPs cathode after discharge and charge. (a-b) SEM images of the morphological changes for the Ru₁₅Co₈₅-NPs cathode at a discharged and charged state of 1 mAh. (c) XRD patterns, (d) Raman spectra, (e) Li 1s and (f) C 1s XPS spectra of discharged/charged Ru₁₅Co₈₅-NP.

Li-CO₂ batteries. Compared with previously reported Li-CO₂ battery systems, the present system demonstrates competitive performance in key metrics including voltage gap, coulombic efficiency, and cycle life (**Fig. 2(g)** and **Table S3**). Collectively, these electrochemical results demonstrate that moderate Ru incorporation effectively reconstructs the local interfacial electronic environment, thereby facilitating reversible CO₂RR/CO₂ER kinetics and suppressing interfacial polarization during cycling. As a result, Ru₁₅Co₈₅-NPs achieve an optimized balance between reaction kinetics and electrochemical reversibility, leading to superior electro-performance.

To further elucidate the evolution of discharge products and the reversibility of the reactions, a series of characterizations were performed on cathodes at different discharge/charge states. After discharging to 1 mAh at a current density of 50 $\mu\text{A cm}^{-2}$, distinct differences in the morphology and distribution of discharge products were observed on different cathodes. After discharge, the Ru₁₅Co₈₅-NPs cathode was uniformly covered by finely distributed discharge products. These particles exhibited relatively uniform sizes and a dense yet non-blocking distribution (**Fig. 3(a)**), indicating the formation of highly dispersed Li₂CO₃. Such a morphology is favorable for maintaining accessible interfacial reaction pathways during cycling. In contrast, the discharge products formed on Ru₅₀Co₅₀-NPs and Co-NPs exhibited obvious agglomeration. The discharge products were larger, unevenly distributed, and partially accumulated into dense aggregates that locally blocked the active surface (**Figs. S24** and **S25**). During the subsequent charging process, the discharge products on Ru₁₅Co₈₅-NPs were almost completely removed, and the electrode morphology was largely restored to its initial state (**Figs. S26** and **3(b)**). In contrast, residual undecomposed products remained on Ru₅₀Co₅₀-NPs and Co-NPs after charging, leading to rougher and more heterogeneous surface morphologies. XRD measurements were further performed to identify the solid discharge products formed during cycling. The XRD patterns (**Fig. 3(c)**) revealed characteristic diffraction peaks assignable to Li₂CO₃ (PDF#22-1141) after discharging to 1 mAh [38]. These peaks disappeared during charging, confirming the reversible formation and decomposition of Li₂CO₃ during the discharge-charge process. Additionally, a characteristic Raman band at 1090 cm^{-1} , corresponding to the C–O stretching vibration of Li₂CO₃, appeared after discharge and disappeared after subsequent charging on the Ru₁₅Co₈₅-NPs cathode (**Fig. 3(d)**), confirming the reversible formation and decomposition of Li₂CO₃ [39]. Electrochemical impedance spectroscopy (EIS) was further employed to probe the interfacial kinetics associated with the formation and decomposition of discharge products. As shown in **Fig. S27**, the battery impedance exhibited an increase-decrease evolution during the discharge-charge process. This trend is attributed to the progressive formation of discharge products during discharge and its decomposition during charge. Notably, the Ru₁₅Co₈₅-NPs cathode showed only a limited increase in charge transfer resistance after discharge, which rapidly recovered to a level close to its initial state upon charging. In contrast, the Co-NPs and Ru₅₀Co₅₀-NPs cathodes maintained a higher charge transfer resistance

even after charging. These results indicate that Ru₁₅Co₈₅-NPs promote the uniform deposition and effective removal of discharge products, thereby maintaining favorable interfacial reaction kinetics during cycling.

Building upon this foundation, XPS analyses were further performed to investigate the composition and evolution of discharge products at different electrochemical states. As shown in **Figs. 3(e)** and **3(f)**, a characteristic peak at 290.0 eV, attributable to the CO₃²⁻ species in Li₂CO₃, emerged in the C 1s spectrum of the Ru₁₅Co₈₅-NPs cathode after discharge. Simultaneously, a characteristic peak at 55.6 eV was observed in the Li 1s spectrum, further confirming the formation of Li₂CO₃ as the discharge product [40,41]. During the subsequent charging process, these characteristic peaks in both the C 1s and Li 1s spectra nearly vanished completely, indicating efficient decomposition of Li₂CO₃ on Ru₁₅Co₈₅-NPs during charging. In contrast, the Co-NPs (**Fig. S28**) and Ru₅₀Co₅₀-NPs (**Fig. S29**) cathodes retained clear C 1s (290.0 eV) and Li 1s (55.6 eV) signals even after charging. These results collectively demonstrate the efficient formation and decomposition of Li₂CO₃ on Ru₁₅Co₈₅-NPs, which correlates well with its low voltage gap and excellent cycling stability. The Co 2p and Ru 3p XPS spectra collected at different electrochemical states (**Figs. S30-S32**) showed highly similar peak positions and spectral profiles, suggesting that the chemical states of Ru and Co remain largely stable during cycling. These results further suggest that localized Ru incorporation effectively regulates the interfacial formation/decomposition behavior of Li₂CO₃ during cycling.

Density functional theory (DFT) calculations were further performed based on representative Co (002), Ru₁₅Co₈₅ (002), and Ru₅₀Co₅₀ (002) surface models (**Fig. S33**). The pristine Co model was constructed from the hcp Co crystal, using a four-layer 5 × 5 Co (002) slab. Ru incorporation was introduced by substituting surface Co atoms with Ru atoms to generate Ru₁₅Co₈₅ (002) and Ru₅₀Co₅₀ (002) models, corresponding to Ru contents of approximately 15 at.% and 50 at.%, respectively. These models were constructed according to the experimentally observed metallic Co framework and corresponding Ru incorporation environments revealed by XRD, XPS, and XAS analyses. After structural relaxation, all slabs reached stable surface configurations, providing reasonable models for subsequent electronic-structure and reaction-pathway analyses. Spin-polarized projected density of states (PDOS) calculations were subsequently performed to investigate the electronic-state evolution induced by Ru incorporation (**Fig. 4(a)**). Compared with pristine Co (002), Ru incorporation induces evident redistribution of Co-derived electronic states near the Fermi level, indicating substantial modulation of the local electronic environment around Co sites. In particular, Ru₁₅Co₈₅ (002) preserves the dominant Co-derived electronic features, whereas Ru₅₀Co₅₀ (002) exhibits stronger perturbation of the Co electronic states. Correspondingly, the Co d-band center shifts from -1.24 eV for pristine Co (002) to -1.16 eV for Ru₁₅Co₈₅ (002), while it shifts downward to -1.47 eV in Ru₅₀Co₅₀ (002). To further elucidate the electronic redistribution induced by Ru incorporation, charge density difference and Bader charge analyses were performed (**Fig. S34**). The charge density difference maps reveal evident electron redistribution

around the Ru–Co interface, while the corresponding Bader analysis quantitatively confirms the evolution of the local electronic environment. Specifically, the representative Co site in the Ru₅₀Co₅₀ (002) model exhibits a higher Bader electron population (3.73 e[−]) than that in the Ru₁₅Co₈₅ (002) model (3.12 e[−]), indicating a higher local electron density around the Co site. This trend is consistent with the progressively larger negative shift of the Co 2p binding energy observed in the XPS spectra. These results suggest that moderate localized Ru incorporation effectively regulates the electronic environment of Co sites, which may favor balanced interactions with the intermediates.

Favorable adsorption configurations of key intermediates involved in the two possible reaction pathways were first optimized on Co (002), Ru₁₅Co₈₅ (002), and Ru₅₀Co₅₀ (002) surfaces (**Fig. 4(b)** and **Figs. S35–S39**) [18,42,43]. The optimized structures indicate that all key intermediates can be stably accommodated on the three catalyst surfaces, whereas their adsorption configurations and interfacial interaction distances vary with the Ru incorporation level, suggesting distinct surface reaction energetics. Considering that the lithiation and CO₂ conversion process may proceed through different elementary reaction process sequences, two possible reaction pathways (Path 1 and Path 2) were systematically evaluated (**Figs. 4(c)** and **S40**). Comparison of the Gibbs free-energy profiles reveals that Path 2 exhibits consistently lower reaction barriers than Path 1 on all three catalyst surfaces, indicating that Path 2 is thermodynamically more favorable and therefore selected as the representative reaction pathway for subsequent discussion. The Gibbs free-energy changes (ΔG) along the energetically preferred Path 2 are shown in **Fig. 4(c)**. In this pathway, CO₂ is initially activated through coupling and successive lithiation to generate the Li₂C₂O₄ intermediate,

which is subsequently converted into Li₂CO₃ through Li₂CO₃-related surface intermediates accompanied by the formation of surface carbon species. Overall, the initial CO₂ activation and lithiation processes are thermodynamically favorable on all three catalyst surfaces, whereas the subsequent conversion of the Li₂C₂O₄-containing intermediate exhibits the largest uphill free-energy change, identifying it as the thermodynamically most demanding step. Among the three catalysts, Ru₁₅Co₈₅ (002) exhibits the lowest reaction barrier (1.72 eV), which is lower than those of Co (002) (1.98 eV) and Ru₅₀Co₅₀ (002) (1.82 eV). These results indicate that moderate Ru incorporation effectively lowers the energy barrier of the key Li₂CO₃ formation step. Although Ru₅₀Co₅₀ (002) also reduces the reaction barrier compared with pristine Co, its activity remains inferior to that of Ru₁₅Co₈₅ (002), consistent with the PDOS and Bader analyses showing that excessive Ru incorporation induces over-perturbation of the Co electronic structure. To further evaluate the Li₂CO₃ decomposition behavior, the dissociation pathway and corresponding energy barriers were analyzed (**Fig. S35** and **Fig. 4(d)**). The calculated Li₂CO₃ dissociation energy barriers on Co (002), Ru₁₅Co₈₅ (002), and Ru₅₀Co₅₀ (002) are 0.89, 0.65, and 0.79 eV, respectively. The reduced dissociation barrier on Ru₁₅Co₈₅ suggests facilitated Li₂CO₃ decomposition during charging, which is beneficial for lowering charge polarization and improving electrochemical reversibility in Li–CO₂ batteries. Overall, these theoretical results suggest that moderate Ru incorporation effectively regulates the interfacial electronic environment of Co sites, thereby lowering the energy barrier of Li₂CO₃-related conversion processes and facilitating Li₂CO₃ decomposition. This interfacial electronic regulation provides

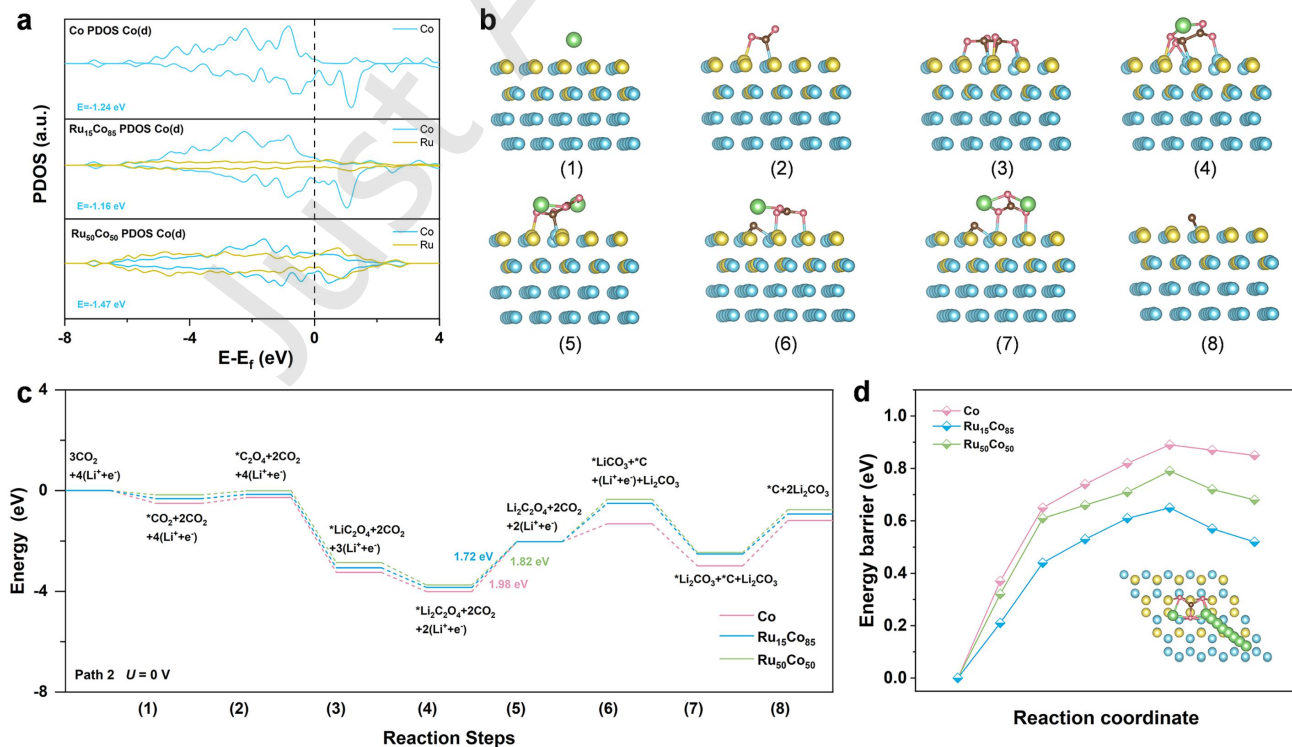


Fig. 4. Theoretical calculations of reaction pathways and diffusion behaviors on different cathodes. (a) The d-orbital PDOS for Co and Ru atoms of Co (002), Ru₁₅Co₈₅ (002) and Ru₅₀Co₅₀ (002). (b) The side views of adsorption systems on the Ru₁₅Co₈₅ (002) according to the most possible reaction

pathway. (c) Gibbs free energy changes of the most favorable reaction pathways in Li-CO₂ batteries with three cathodes. (d) Diffusion energy barriers of Li₂CO₃ on Co (002), Ru₁₅Co₈₅ (002) and Ru₅₀Co₅₀ (002).

a mechanistic basis for the reduced polarization and enhanced electrochemical reversibility experimentally observed for Ru₁₅Co₈₅-NPs.

3 Conclusion

In summary, a Co-based catalyst with localized Ru incorporation was successfully developed through a ZIF-67-derived structural confinement strategy. Structural characterizations reveal preserved morphology together with localized Ru-induced modulation of the local coordination and electronic environment. The absorption-edge shift in the XANES spectra together with the Ru-Co scattering path identified from EXAFS fitting provide direct evidence for localized electronic interaction between Ru and neighboring Co sites. Electrochemical evaluations demonstrate that moderate Ru incorporation is critical for achieving optimized Li-CO₂ battery performance. The optimized Ru₁₅Co₈₅-NPs cathode delivers a low voltage gap of 1.11 V, a high coulombic efficiency of 99.7%, and stable cycling over 750 cycles (3100 h). In addition, it achieves a high discharge capacity of 3928 $\mu\text{Ah cm}^{-2}$ with a coulombic efficiency of 99.7%, and maintains stable operation for over 650 h at 100 $\mu\text{A cm}^{-2}$, outperforming both Co-NPs and Ru₅₀Co₅₀-NPs counterparts. DFT calculations further reveal that moderate Ru incorporation effectively regulates the Co-derived electronic states and reconstructs the local electronic environment of Co sites. Moreover, mechanistic investigations demonstrate that moderate Ru incorporation lowers the highest uphill free-energy change along the favorable Li₂CO₃ formation pathway and reduces the Li₂CO₃ dissociation barrier to 0.65 eV, thereby facilitating formation and decomposition Li₂CO₃ and improving electrochemical reversibility. This work provides an effective strategy for regulating interfacial electronic environments through moderate noble-metal incorporation and offers new insights into the design of highly reversible Li-CO₂ battery catalysts.

Electronic Supplementary Material: Supplementary material (synthesis procedures, other characterization data (SEM, TEM images, FT-IR spectra, etc.), electrochemical performance, and theoretical calculation details) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909068>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing author(s) report(s) no conflict of interests in this work.

Author contribution statement

X. Z.: Conceptualization, investigation, experimental design, visualization, writing-original draft. X. Z.: Investigation, data curation, validation, writing-review & editing. J. Z.: Investigation, formal analysis. J. L.: Supervision, formal analysis. A. Y.: Resources, funding acquisition, project administration, supervision, writing-review & editing. All authors approved the final version of the manuscript.

Use of AI statement

None.

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Electronic Supplementary Material

Localized Ru-induced interfacial electronic reconstruction enables highly reversible Li-CO₂ batteries

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Experimental section Informed consent

1. Chemicals

Cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AR), 2-methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$, AR), cobalt(II) chloride (CoCl_2 , AR), ruthenium(III) chloride trihydrate ($\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, AR), N-methyl-2-pyrrolidone ($\text{C}_5\text{H}_9\text{NO}$, AR), polyvinylidene fluoride ($[(\text{CH}_2\text{CF}_2)]_n$, AR), methanol (CH_3OH , AR), ethanol ($\text{C}_2\text{H}_5\text{OH}$, AR).

2. Methods

2.1 Synthesis of ZIF-67: Under continuous stirring, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (300 mg) was dissolved in a mixed solvent of 50 mL H_2O and 50 mL methanol (solution A), and 2-methylimidazole (5 g) was dissolved in another 50 mL H_2O and 50 mL methanol mixture (solution B). After stirring both solutions at room temperature for 30 minutes, Solution A was rapidly added to solution B, followed by an additional 30 minutes of stirring. The resulting dodecahedral ZIF-67 crystals were collected by centrifugation and washed three times with water and methanol. Finally, the ZIF-67 powder was dispersed in 30 mL of methanol to form a ZIF-67 suspension.

2.2 Synthesis of $\text{Ru}_x\text{Co}_y\text{O}_z$: A total of 720 μmol of RuCl_3 and CoCl_2 (with varying molar ratios) was dissolved in a mixed solvent of 30 mL H_2O and 30 mL methanol. Under continuous stirring, 8 mL of the as-prepared ZIF-67 suspension was added to this solution. After stirring at 60°C for 2 hours, the resulting $\text{Ru}_x\text{Co}_y\text{O}_z$ were collected by centrifugation and washed three times with water and methanol. Note: they are named based on the molar ratio of raw materials. The 'x' is the theoretical percentage of Ru, and the 'y' is the theoretical percentage of Co. ($x=0$ and $y=100$, it corresponds to $\text{Co}_{100}\text{O}_z$, i.e., CoO_z .)

2.3 Synthesis of Ru_xCo_y NPs: Following overnight drying, the powder ($\text{Ru}_x\text{Co}_y\text{O}_z$) was annealed at 360°C for 2 hours under a 5% H_2/Ar atmosphere (5 vol% H_2) to yield Ru_xCo_y nanoparticle (NPs).

3. Materials characterizations

X-ray diffraction (XRD, Rigaku Corporation) was used to determine the crystal structure. X-ray photoelectron spectroscopy (XPS, Thermo Scientific Nexsa) was employed to measure the chemical state spectra, with binding energies calibrated against the C 1s peak at 284.8 eV. The morphology of the samples was characterized by scanning electron microscopy (SEM, HITACHI HT-7800) and transmission electron microscopy (TEM, Thermo Fisher Scientific Talos F200X G2). Fourier-transform infrared spectroscopy (FTIR, Thermo Fisher Scientific) was used to examine the molecular structure. Raman microscopy (Bruker Corporation) with a laser excitation wavelength of 532 nm was utilized to characterize the products on the electrode. The actual molar ratio of Ru to Co elements in the samples was quantified using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Thermo Fisher Scientific ICAP7400). Nitrogen adsorption-desorption measurements were performed using a Quantachrome Autosorb-iQ2-XR analyzer. Prior to analysis, the samples were degassed under vacuum at 200°C for 8 h. The specific surface areas were determined according to the Brunauer-Emmett-Teller (BET) method. Co K-edge (7709 eV) X-ray absorption spectroscopy (XAS) were measured at Rapid XAFS 2M (Anhui Absorption Spectroscopy Analysis Instrument Co., Ltd.) by transmission mode at 20 kV and 40 mA, and the Si (533) spherically bent crystal analyzer with a radius of curvature of 500 mm was used for Co. Co foil served as reference samples. The obtained XAFS data was processed in Athena (version 0.9.26) for background, pre-edge line and post-edge line calibrations. Then Fourier transformed fitting was carried out in Artemis (version 0.9.26). The k^2 weighting, k-range of $3 \sim 11 \text{ \AA}^{-1}$ and R range of $1 \sim 2.4 \text{ \AA}$ were used for the fitting. The four parameters, coordination number, bond length, Debye-Waller factor and E_0 shift (CN, R, σ^2 , ΔE_0) were fitted without anyone was fixed, constrained, or correlated.

4. Electrochemical measurements

The obtained Ru_xCo_y and Co NPs material was homogeneously mixed and ground with the binder polyvinylidene fluoride (PVDF) at a mass ratio of 9:1 in an agate mortar. An appropriate amount of N-methyl-2-pyrrolidone (NMP) was added, and grinding was continued to form a uniform slurry. This slurry was then evenly coated onto punched carbon paper (diameter: 12 mm). The coated electrode was dried in a vacuum oven at 80°C for 12 hours to completely remove the solvent. The final catalyst loading on each cathode was approximately 0.4 mg (equivalent to $\sim 0.3 \text{ mg cm}^{-2}$).

Li-CO₂ batteries were assembled into CR2032-type coin cells, where the cathode housing featured uniformly distributed micro-holes to facilitate gas diffusion. Each cell consisted of a lithium metal anode ($\Phi 15.8 \times 0.50$ mm), a glass fiber separator (GF) soaked with 80 μ L of electrolyte (1M LiTFSI in TETRAGLYME=100 Vol%), and the porous cathode. All assembly steps were carried out in an argon-filled glovebox with H₂O and O₂ concentrations below 0.1 ppm, and the cells were sealed under a pressure of 10–15 MPa. After sealing, the cells were transferred inside the glovebox into a sealed testing chamber, which was then purged and filled with pure CO₂ gas and allowed to equilibrate. Electrochemical performance tests were conducted using a LAND CT2001A battery testing system and a CHI760E electrochemical workstation (Chenhua Instruments).

5. Computational details

Spin-polarized electronic structure calculations were performed using the plane-wave basis set approach as implemented in the Vienna ab initio simulation package (VASP)[1]. The projector augmented wave (PAW) method was used to represent the ion–core electron interactions[2]. The valence electrons were represented with a plane wave basis set with an energy cutoff of 450 eV. Electronic exchange and correlation were described with the Perdew-Burke-Ernzerhof (PBE) functional[3]. DFT-D3 method was used to treat the van der Waals interaction[4]. 15 Å vacuum space was included to avoid interactions between surface slabs. A 3×3×1 Monkhorst-Pack scheme was used to generate the k-point grid for the modeled surfaces[5]. Zero-point vibrational energy (ZPVE) corrections are calculated by assuming a quantum harmonic oscillator possessing the calculated vibrational frequency. The convergence criteria for the self-consistent electronic structure and geometry were set to 10⁻⁵ eV and 0.05 eV/Å, respectively. Transition state calculations were performed using the climbing image nudged elastic band (CI-NEB) method with the transition state identified to have an absolute tangent force below 0.05 eV/Å[6].

Supplementary Figures

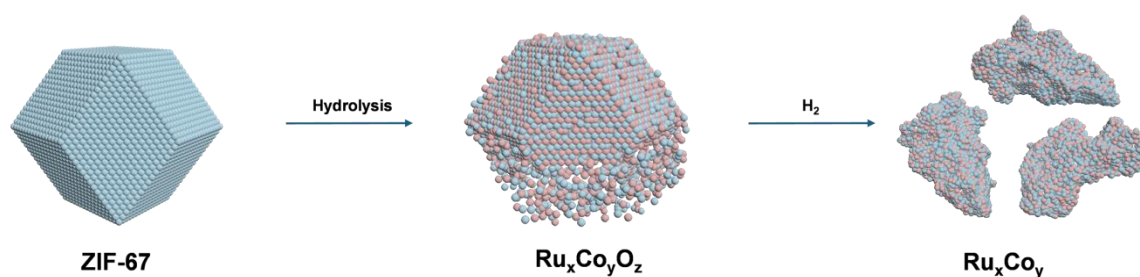


Figure S1. Schematic of Ru_xCo_y -NPs synthesis.

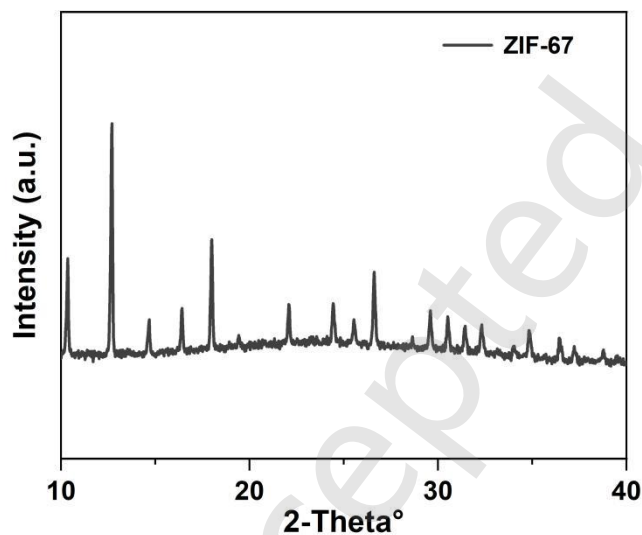


Figure S2. XRD pattern of ZIF-67.

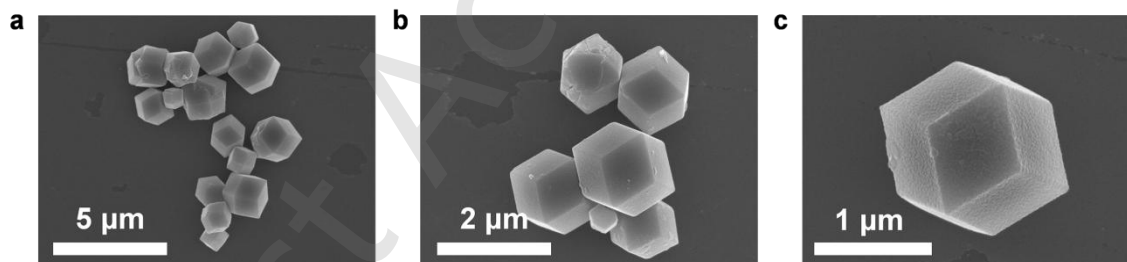


Figure S3. SEM images of ZIF-67.

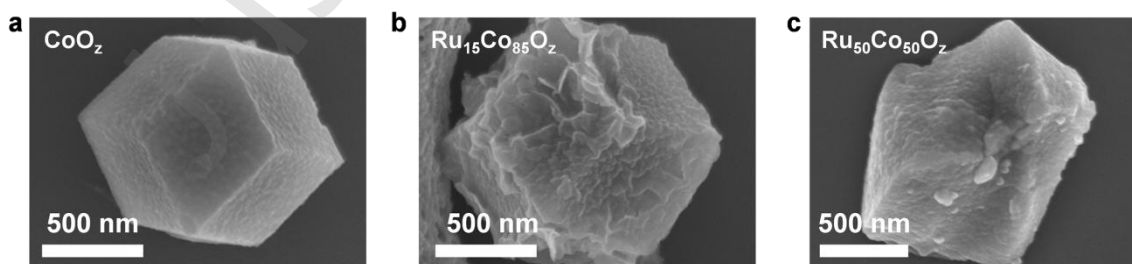


Figure S4. SEM images of CoO_z (a), $\text{Ru}_{15}\text{Co}_{85}\text{O}_z$ (b), and $\text{Ru}_{50}\text{Co}_{50}\text{O}_z$ (c).

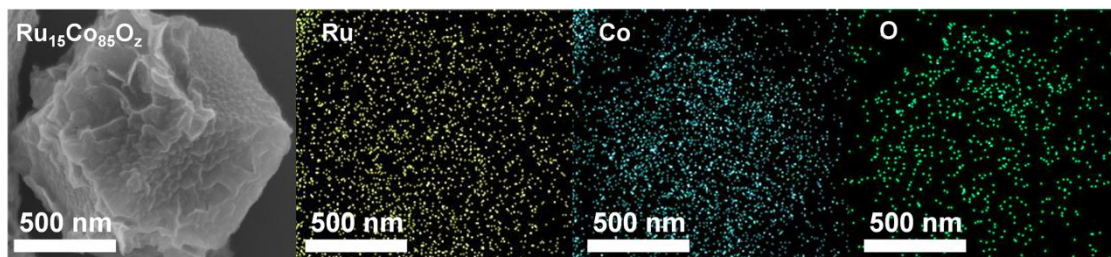


Figure S5. EDS mappings of $\text{Ru}_{15}\text{Co}_{85}\text{O}_z$ for Ru, Co, and O elements.

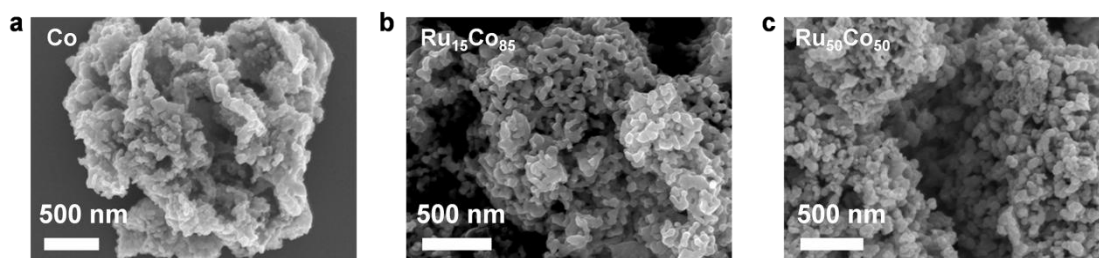


Figure S6. SEM images of Co-NPs (a), Ru₁₅Co₈₅-NPs (b), Ru₅₀Co₅₀-NPs (c).

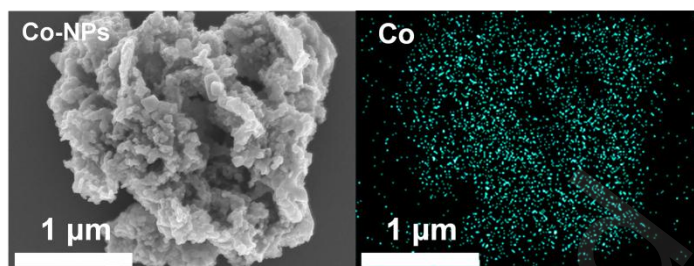


Figure S7. SEM image and EDS mappings of Co-NPs.

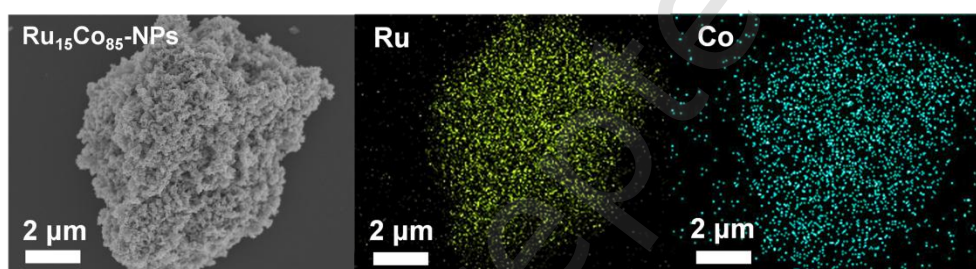


Figure S8. SEM image and EDS mappings of Ru₁₅Co₈₅-NPs.

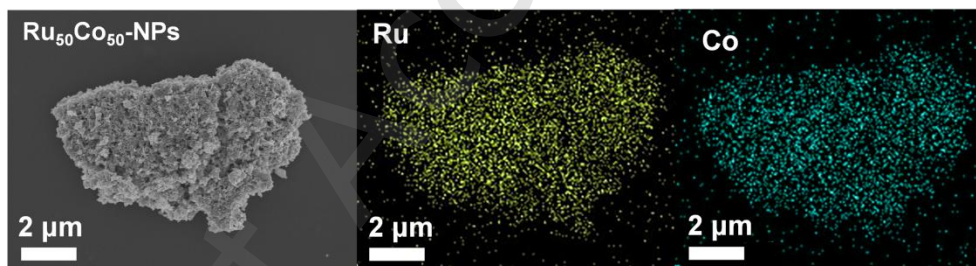


Figure S9. SEM image and EDS mappings of Ru₅₀Co₅₀-NPs.

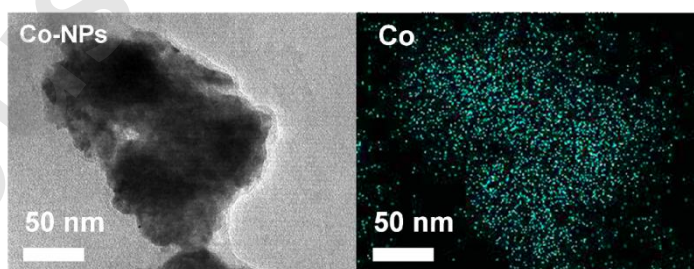


Figure S10. TEM image and EDS mappings of Co-NPs.

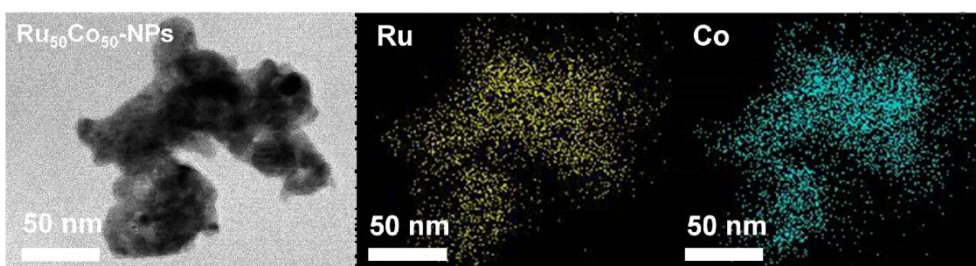


Figure S11. TEM image and EDS mappings of Ru₅₀Co₅₀-NPs.

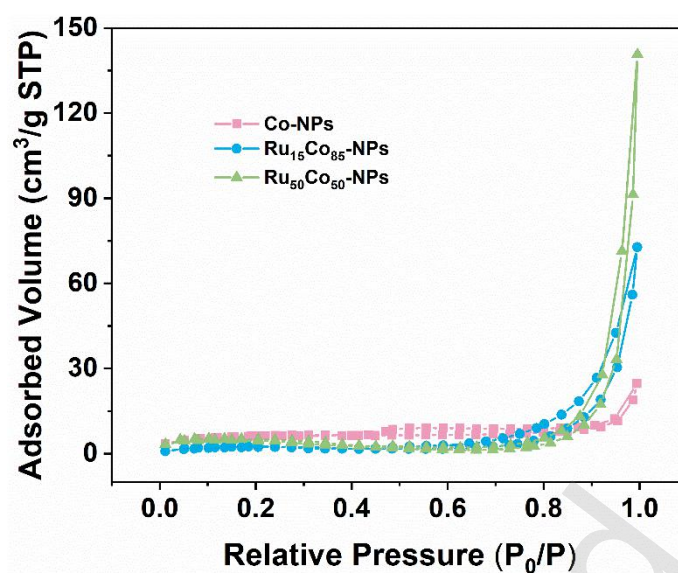


Figure S12. Nitrogen adsorption-desorption isotherm curves of three $\text{Ru}_x\text{Co}_y\text{-NPs}$.

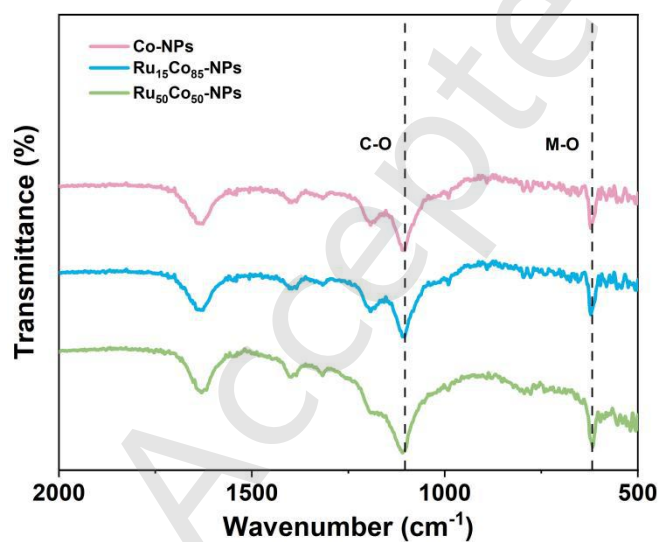


Figure S13. FTIR spectra of $\text{Ru}_x\text{Co}_y\text{-NPs}$.

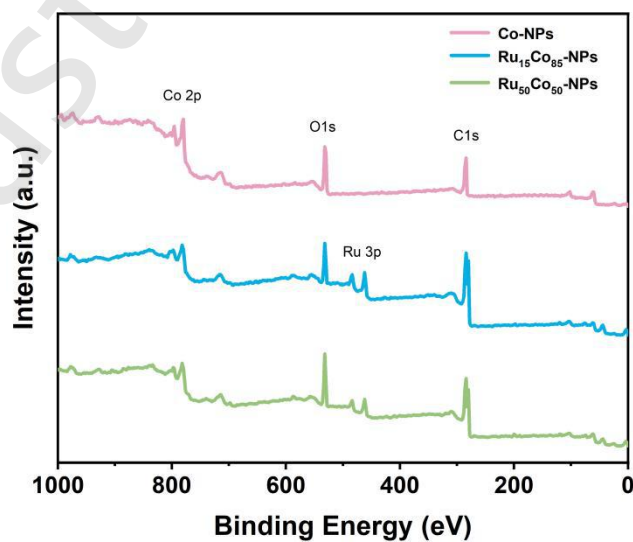


Figure S14. The full XPS curves of three $\text{Ru}_x\text{Co}_y\text{-NPs}$.

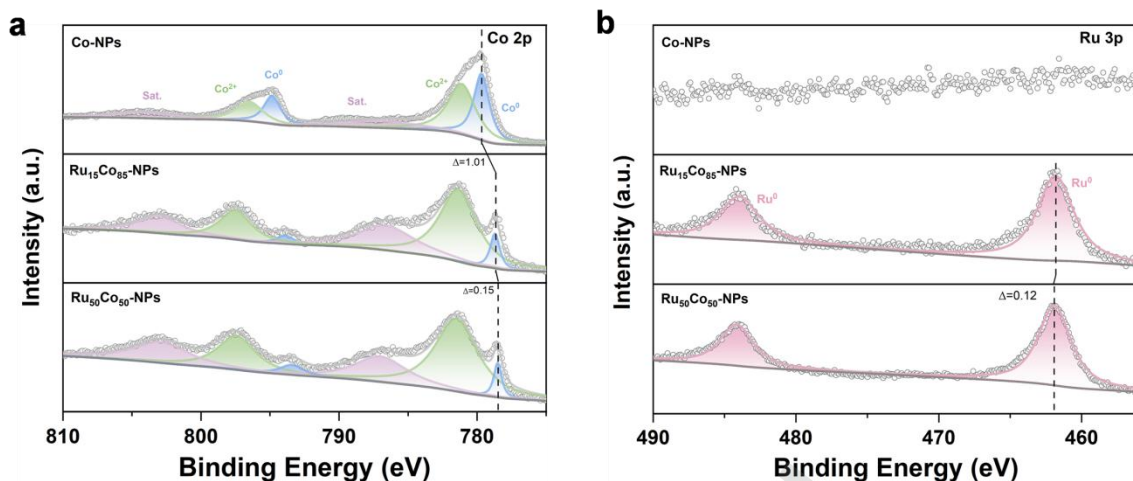


Figure S15. Co 2p (a) and Ru 3p (b) XPS spectra of $\text{Ru}_x\text{Co}_y\text{-NPs}$.

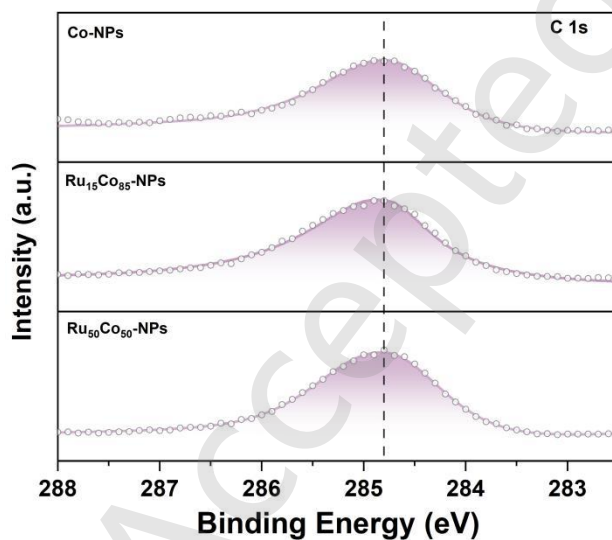


Figure S16. C 1s XPS spectra of $\text{Ru}_x\text{Co}_y\text{-NPs}$.

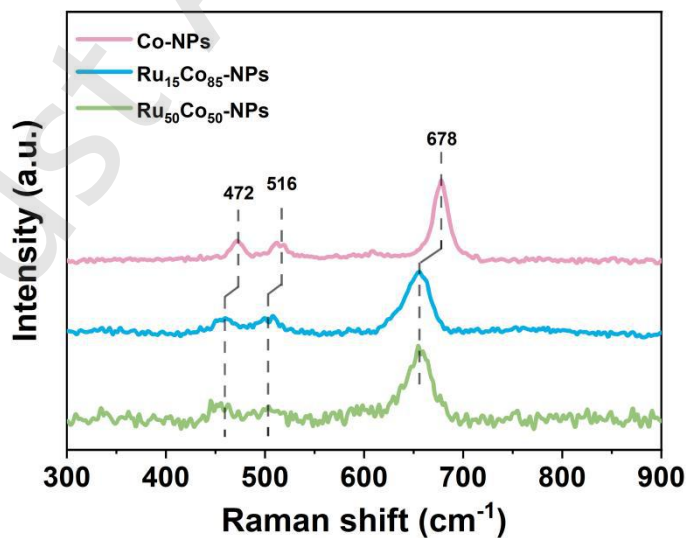


Figure S17. Raman spectra of $\text{Ru}_x\text{Co}_y\text{-NPs}$.

The Raman spectra show several characteristic bands located at approximately 472, 516, and 678 cm^{-1} , which are associated with surface metal–oxygen vibrational modes in the Co-based framework. Compared with Co-NPs, the Raman bands of $\text{Ru}_{15}\text{Co}_{85}\text{-NPs}$ and $\text{Ru}_{50}\text{Co}_{50}\text{-NPs}$ exhibit noticeable peak shifts and broadening after Ru incorporation. In particular, the broad band centered around 678 cm^{-1} becomes slightly broadened and shifted toward lower wavenumbers, while the shoulder

feature in the 520 – 560 cm^{-1} region becomes more pronounced. These spectral changes suggest that Ru incorporation modifies the local coordination environment and oxygen-related bonding characteristics in the Co-based framework.

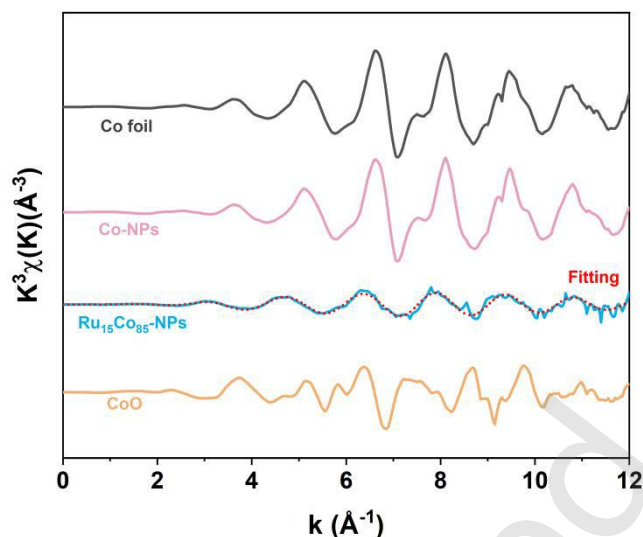


Figure S18. K space experimental of the EXAFS for Co-NPs, $\text{Ru}_{15}\text{Co}_{85}$ -NPs, CoO and Co foil.

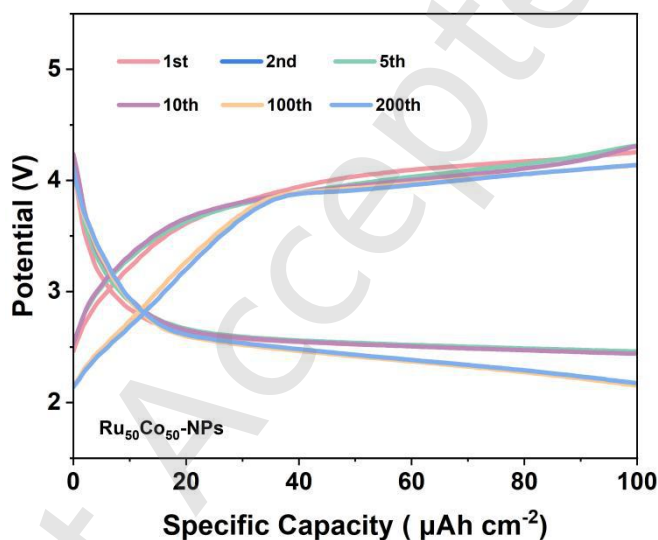


Figure S19. Cycling performance of the battery with a $\text{Ru}_{50}\text{Co}_{50}$ -NPs cathode with selected typical discharge and charge profiles.

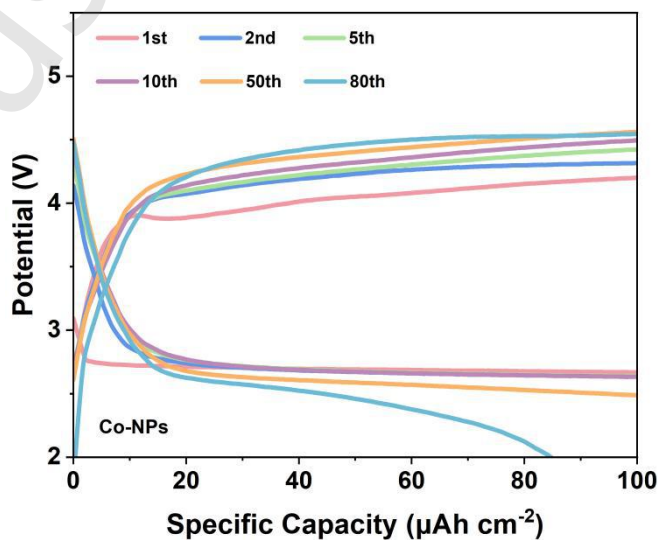


Figure S20. Cycling performance of the battery with a Co-NPs cathode with selected typical discharge and charge profiles.

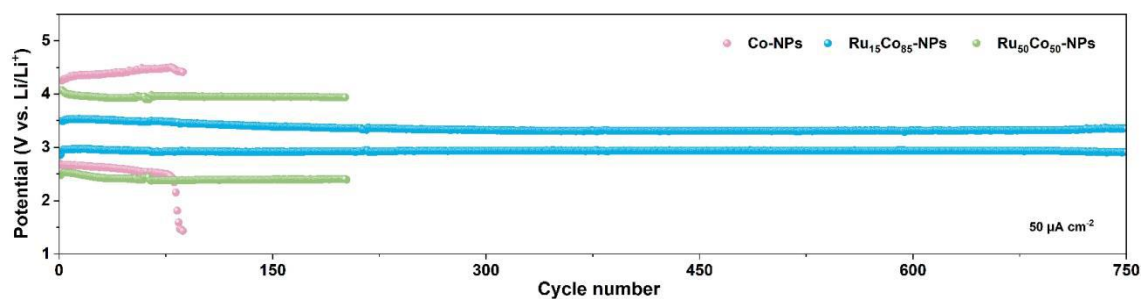


Figure S21. Discharge and charge middle voltage of three cathodes at the current densities of $50 \mu\text{A cm}^{-2}$.

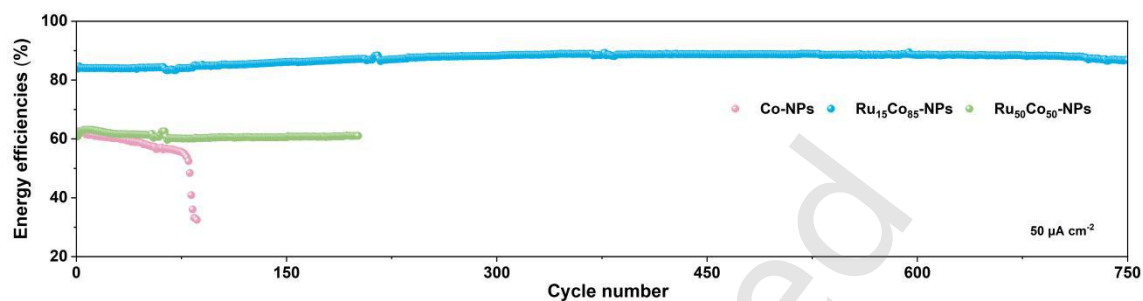


Figure S22. Energy efficiency of three cathodes at the current densities of $50 \mu\text{A cm}^{-2}$.

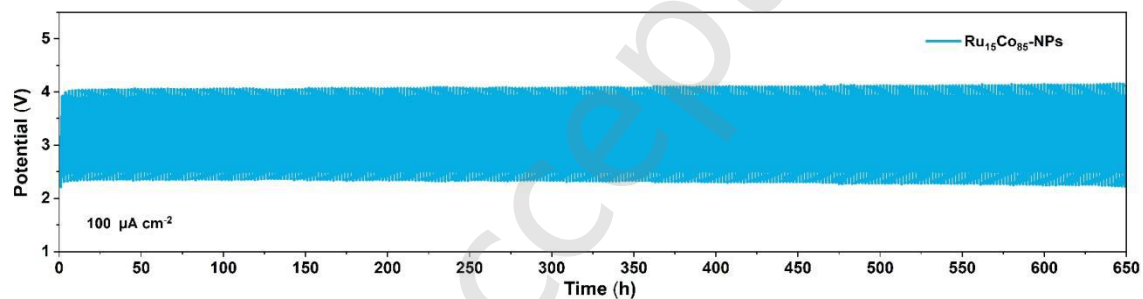


Figure S23. Cycling performance of $\text{Ru}_{15}\text{Co}_{85}\text{-NPs}$ at $100 \mu\text{A cm}^{-2}$ with a capacity limit of $100 \mu\text{Ah cm}^{-2}$.

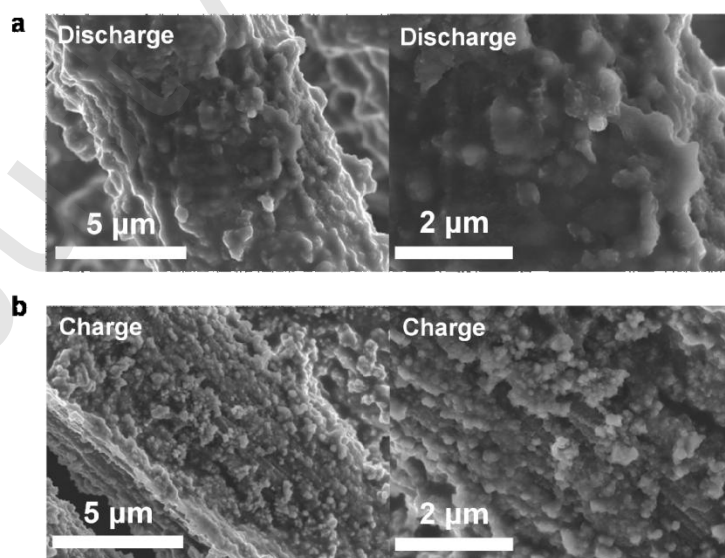


Figure S24. SEM images of $\text{Ru}_{50}\text{Co}_{50}\text{-NPs}$ in discharge and charge.

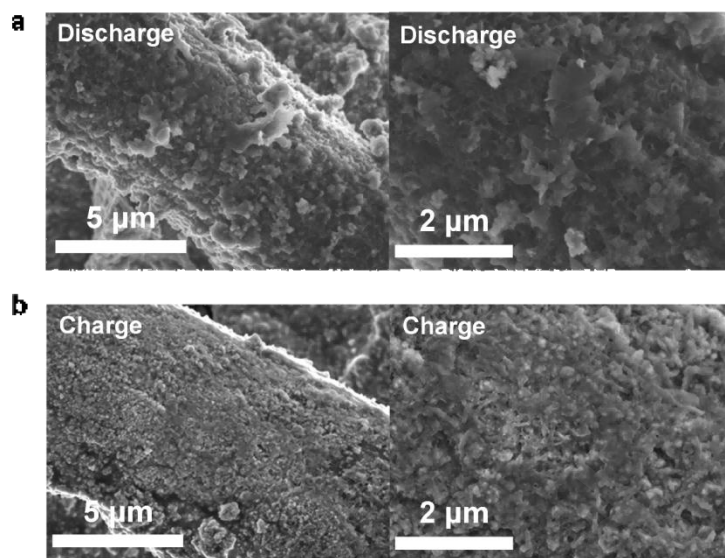


Figure S25. SEM images of Co-NPs in discharge and charge.

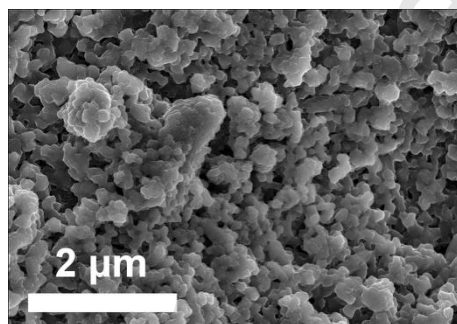


Figure S26. SEM image of the pristine $\text{Ru}_{15}\text{Co}_{85}$ -NPs cathode.

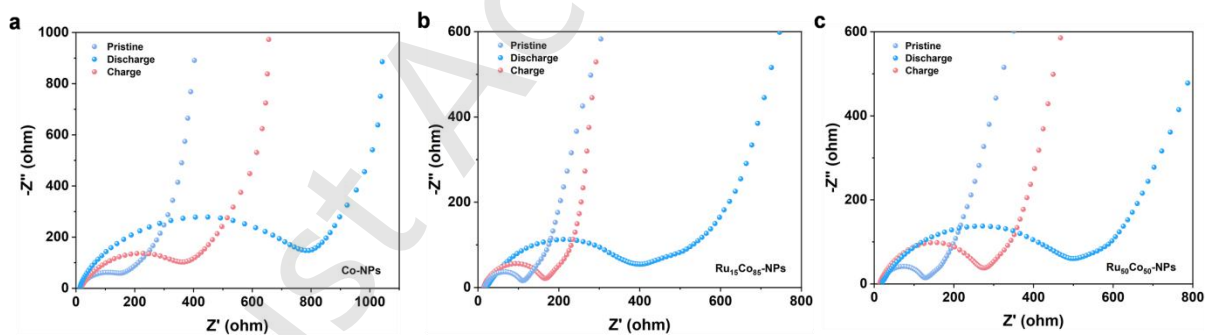


Figure S27. Nyquist plots of the Ru_xCo_y -NPs cathodes after discharge and charge.

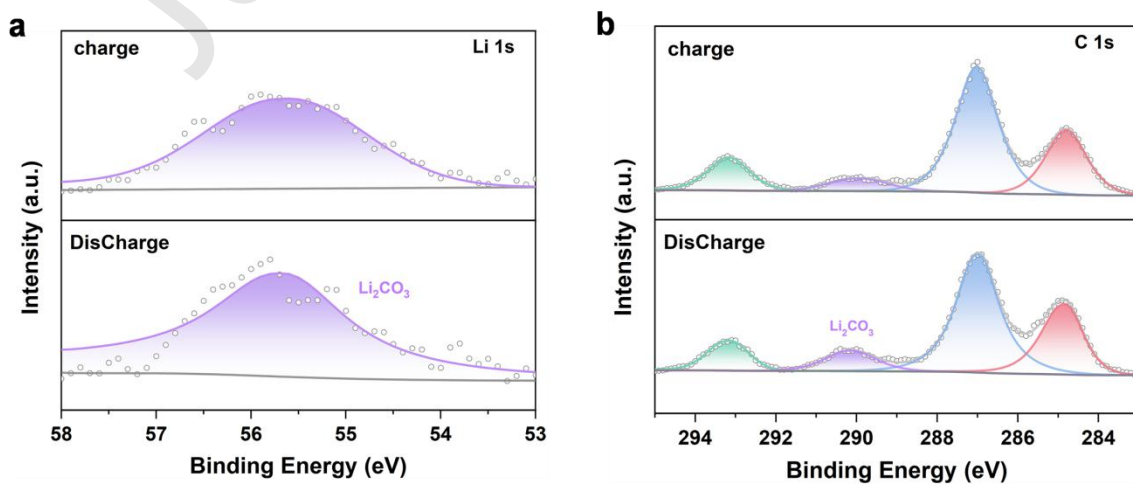


Figure S28. Li 1s (a) and C 1s (b) XPS spectra of the discharged and charged Co-NPs cathode.

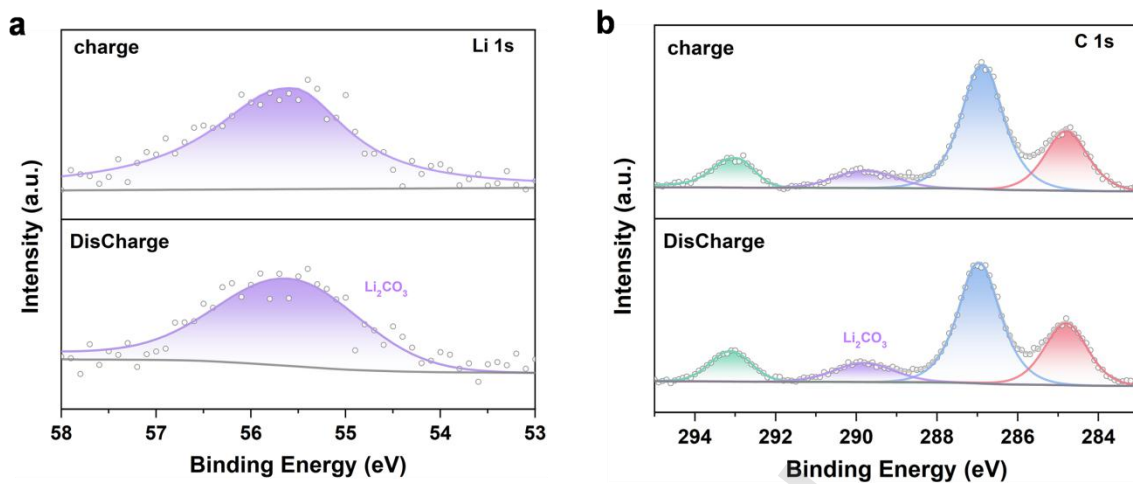


Figure S29. Li 1s (a) and C 1s (b) XPS spectra of the discharged and charged Ru₅₀Co₅₀-NPs cathode.

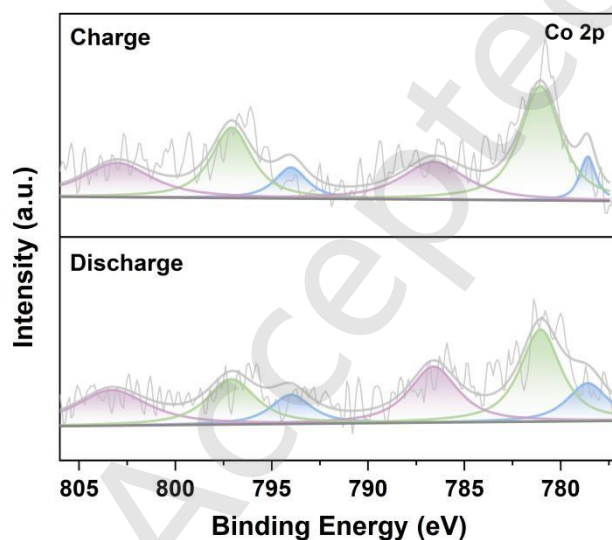


Figure S30. Co 2p XPS spectra of the discharged and charged Co-NPs cathode.

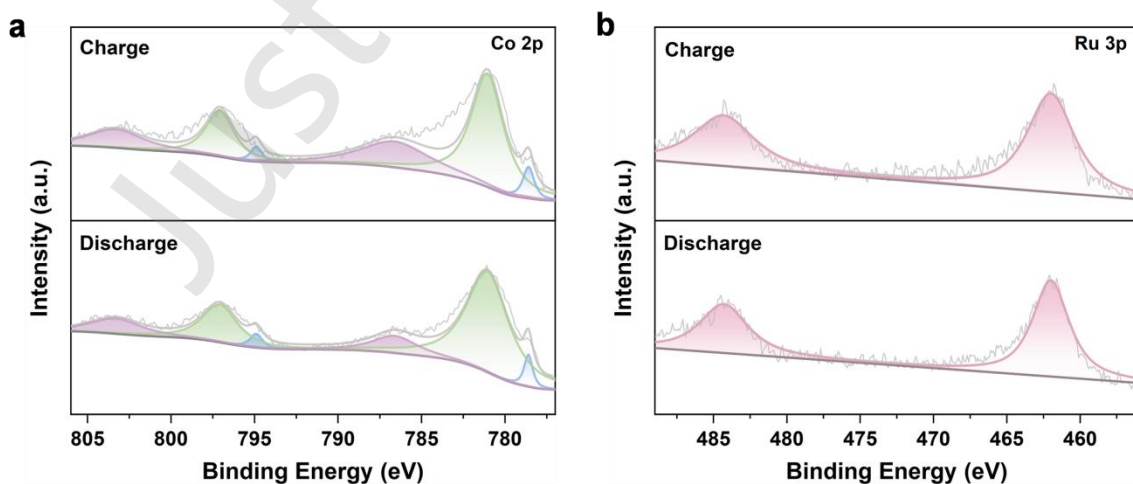


Figure S31. Co 2p (a) and Ru 3p (b) XPS spectra of the discharged and charged Ru₁₅Co₈₅-NPs cathodes

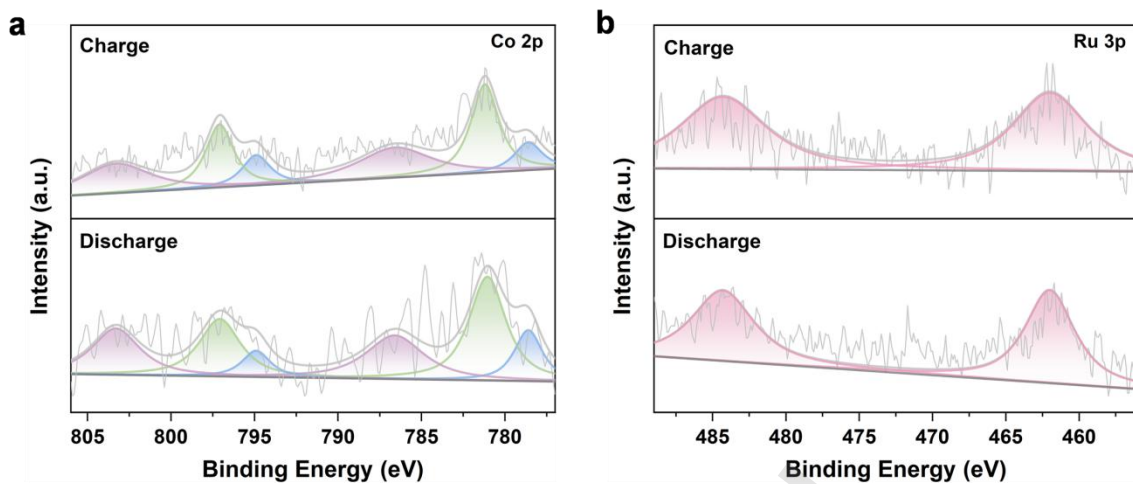


Figure S32. Co 2p (a) and Ru 3p (b) XPS spectra of the discharged and charged $\text{Ru}_{50}\text{Co}_{50}$ -NPs cathode.

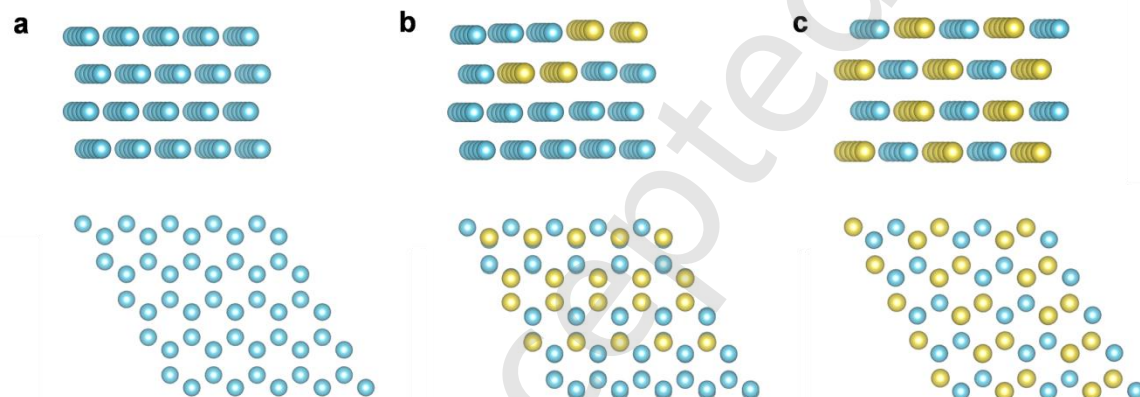


Figure S33. The top and side views of the optimized material structure (Co (002) (a), $\text{Ru}_{15}\text{Co}_{85}$ (002) (b) and $\text{Ru}_{50}\text{Co}_{50}$ (002) (c)).

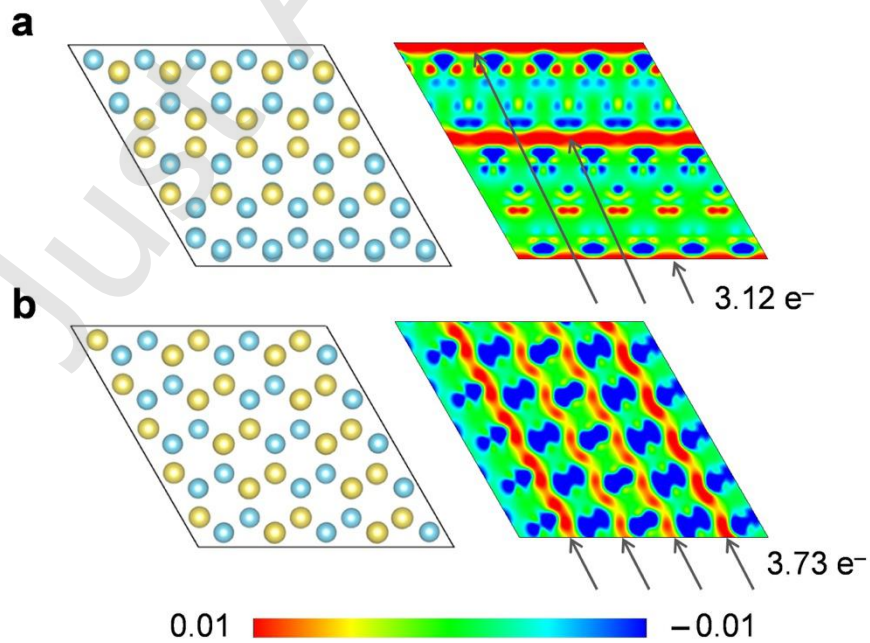


Figure S34. Differential density of charge and Bader charge of $\text{Ru}_{15}\text{Co}_{85}$ (002) (a) and $\text{Ru}_{50}\text{Co}_{50}$ (002) (b).

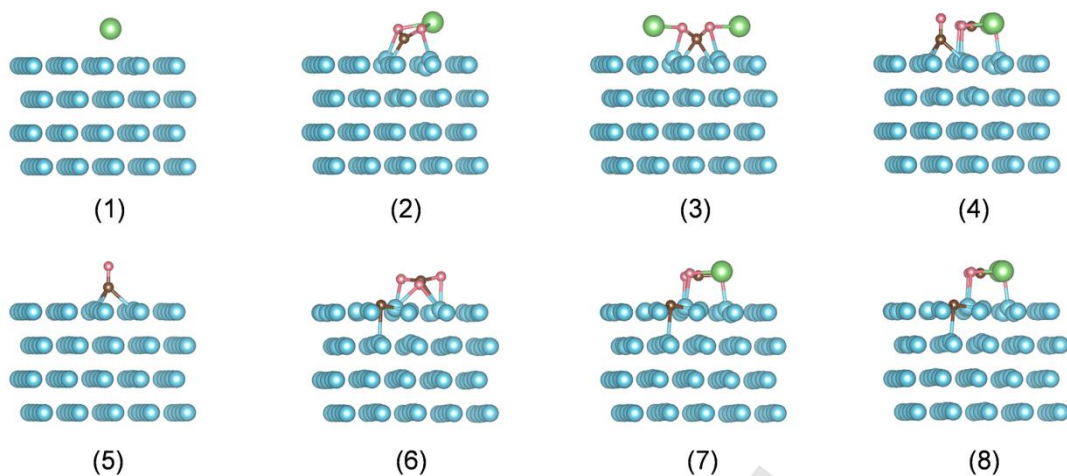


Figure S35. The side views of adsorption systems on the Co (002) according to the possible reaction path 1.

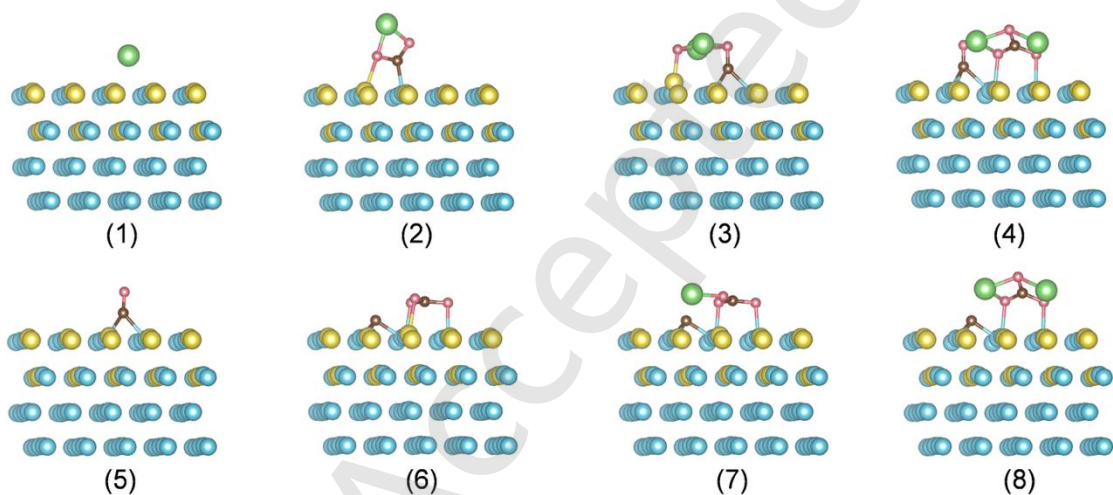


Figure S36. The side views of adsorption systems on the $\text{Ru}_{15}\text{Co}_{85}$ (002) according to the possible reaction path 1.

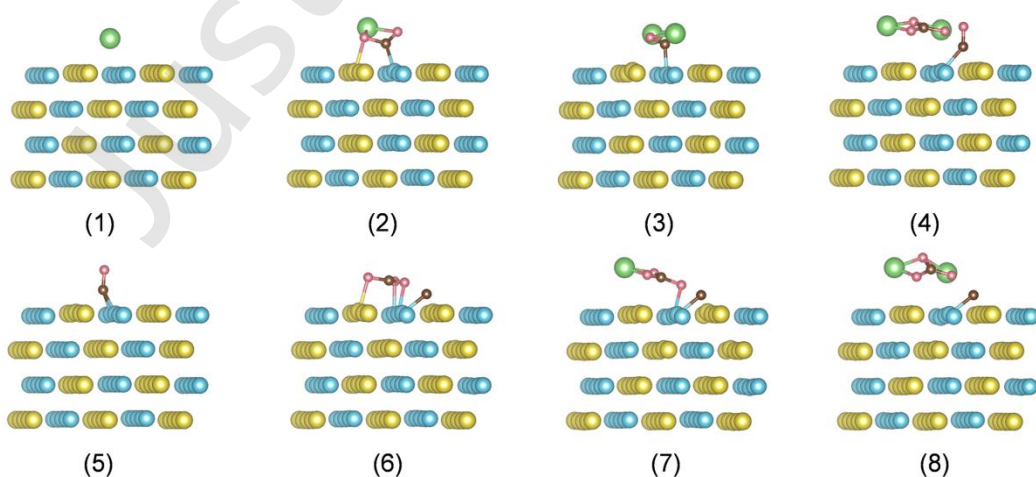


Figure S37. The side views of adsorption systems on the $\text{Ru}_{50}\text{Co}_{50}$ (002) according to the possible reaction path 1.

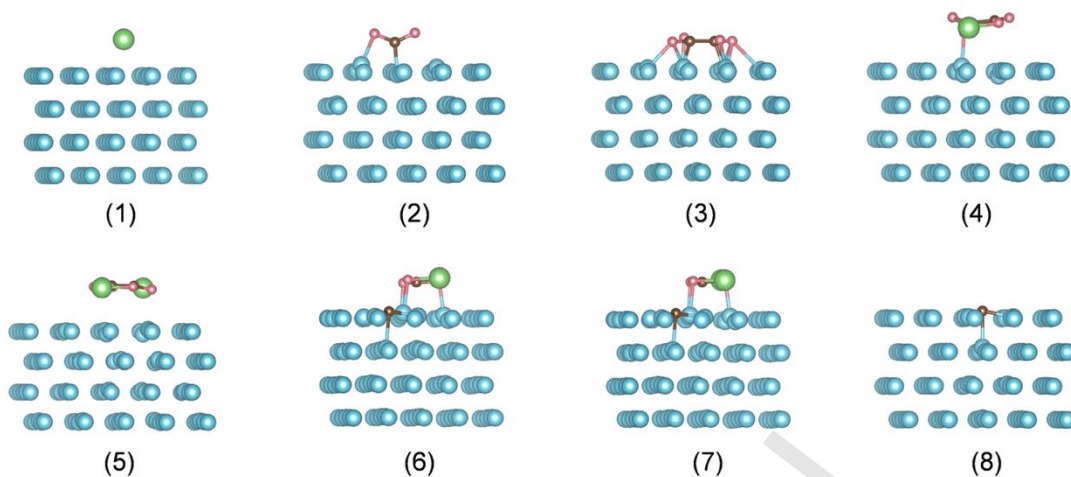


Figure S38. The side views of adsorption systems on the Co (002) according to the possible reaction path 2.

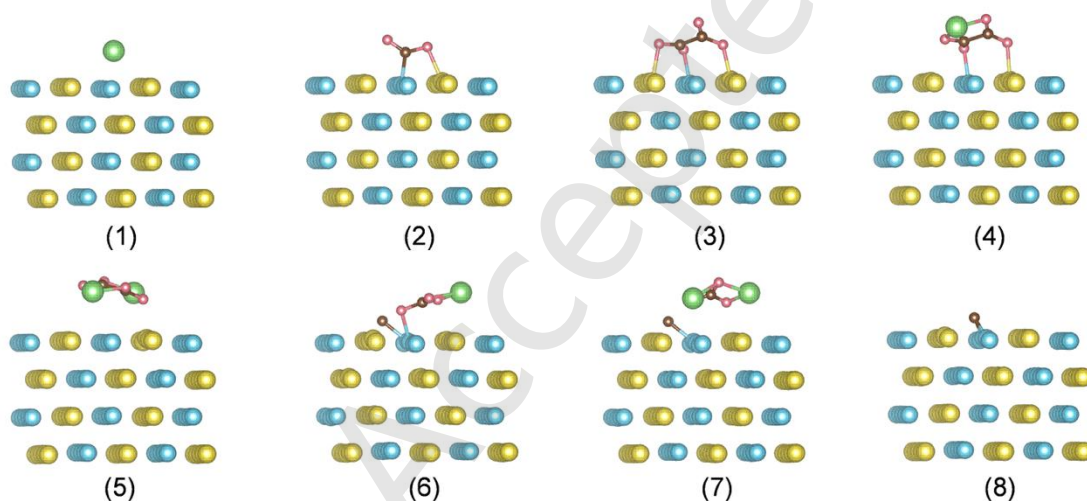


Figure S39. The side views of adsorption systems on the $\text{Ru}_{50}\text{Co}_{50}$ (002) according to the possible reaction path 2.

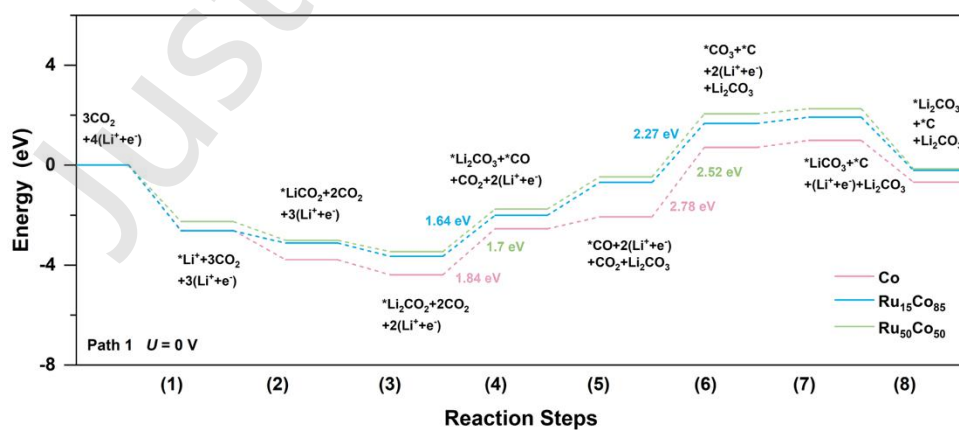


Figure S40. Gibbs free energy changes of the possible reaction path 1 in Li- CO_2 batteries with three cathodes.

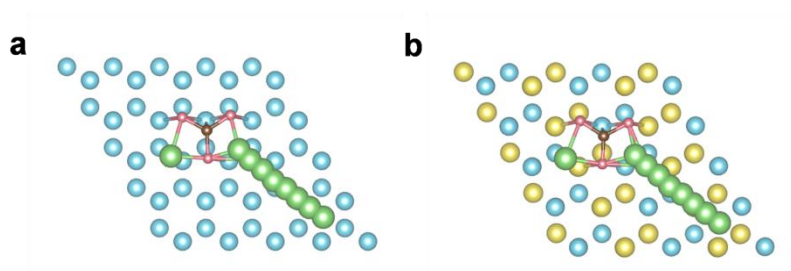


Figure S41. Detailed decomposition paths of Li_2CO_3 on Co (002) (a) and $\text{Ru}_{50}\text{Co}_{50}$ (002) (b).

Supplementary Tables

Table S1. ICP-OES analysis of Ru₁₅Co₈₅-NPs and Ru₅₀Co₅₀-NPs

Sample	Average Ru concentration (mg L ⁻¹)	Average Co concentration (mg L ⁻¹)	Calculated Ru:Co molar ratio
Ru ₁₅ Co ₈₅ -NPs	0.471	1.663	14:86
Ru ₅₀ Co ₅₀ -NPs	1.857	0.976	53:47

Table S2. EXAFS fitting parameters at the Co K-edge various samples ($S_0^2 = 1.0$)

Sample	Path	C.N. ^a	R (Å) ^b	$\sigma^2 \times 10^3$ (Å ²) ^c	ΔE (eV) ^d	R factor ^e
Co foil	Co-Co	9.3 ± 0.6	2.49±0.01	6.9±0.6	8.17±0.6	0.005
Ru ₁₅ Co ₈₅ -NPs	Co-Co	4.1 ± 2.3	2.48±0.01	9.3±6.9	-11.70±2.20	0.018
	Ru-Co	0.35± 0.3	2.68±0.01	9.9±1.1	-6.70±2.44	0.018

^aC.N.: coordination numbers; ^bR: bond distance; ^c σ^2 : Debye-Waller factors; ^d ΔE : the inner potential correction. ^eR factor: goodness of fit. * the experimental EXAFS fit of metal foil by fixing CN as the known crystallographic value.

Table S3. Comparison of the discharge/charge voltage gap and cycle number in Li-CO₂ batteries.

Cathodes	Current density	voltage gap	Cycle stability	Energy efficiency	Coulomb efficiency	Reference
Metal-based Cathode Catalysts						
FeMn ₂ O ₄ -rGO	100mA g ⁻¹	1.07 V	202 cycles	68.0%	90.5%	[7]
Pd ₅ Cu ₃	100 mA g ⁻¹	1.07V	540 cycles	73.1%	96.3%	[8]
CoPt@NCNF	100 μ A cm ⁻²	0.97 V	135 cycles	74.6%	75.0%	[9]
N-C/Fe ₃ C/Fe	300 mA g ⁻¹	1.41 V	200 cycles	65.4%	96.7%	[10]
Co@N-hCNT	500 mA g ⁻¹	1.03 V	220 cycles	65.8%	87.5%	[11]
NMO@CC	100 mA g ⁻¹	1.30 V	200 cycles	61.5%	100%	[12]
Mo _{1.33} C@rGO (MGA)	20 μ A cm ⁻²	0.46 V	330 cycles	78.3%	96.3%	[13]
Ni-Fe- δ -MnO ₂	100 mA g ⁻¹	1.34 V	100 cycles	68.7%	—	[14]
MOC@NMCNF	50 μ A cm ⁻²	1.66 V	327 cycles	63.4%	64.9%	[15]
Fe-CoP@N-CC	200 mA g ⁻¹	1.12 V	62 cycles	74.3%	89.7%	[16]
KB/HP-NiMnAl alloy/MnAlLDH	200mA g ⁻¹	1.26 V	135 cycles	97.2%	—	[17]
Metal Oxide Cathode Catalysts						
Cu-Co ₃ O ₄	50 μ A cm ⁻²	0.88 V	100 cycles	78.3%	96.7%	[18]
Mg _{0.34} @CuO	200 mA g ⁻¹	1.90 V	153 cycles	65.0%	—	[19]
V-ACO/CC	50 μ A cm ⁻²	1.06 V	420 cycles	73.3%	100%	[20]
NiFe ₂ O ₄ /MoS ₂ /MWCNTs	500 mA g ⁻¹	1.55 V	195 cycles	64.0%	—	[21]
Co ₃ O ₄	50 μ A cm ⁻²	1.40 V	55 cycles	—	86.3%	[22]
Metal sulfide/carbide/ nitride cathode catalysts						
MnS	100 mA g ⁻¹	1.28 V	430 cycles	74.7%	100%	[23]
tp-NiS	20 μ A·cm ⁻²	1.09 V	150 cycles	92.0%	—	[24]
TC500	200 mA g ⁻¹	1.98 V	70 cycles	54.5%	88.9%	[25]
Co _{0.1} Mo _{0.9} N	500 mA g ⁻¹	1.06 V	135 cycles	74.0%	—	[26]
N-MoSe ₂ /C	100 mA g ⁻¹	0.91 v	87 cycles	75.7%	100%	[27]

CoMoN/C@PPy	100 mA g ⁻¹	1.51 V	85 cycles	68.7%	—	[28]
ANCS	200 mA g ⁻¹	1.40 V	130 cycles	66.3%	—	[29]
Noble metal-based cathode catalysts						
MWCNT/nf-NRO ₅₅	100 mA g ⁻¹	1.25 V	122 cycles	67.5%	—	[30]
CBRu	20 μ A cm ⁻²	1.03 V	120 cycles	76.0%	100%	[31]
CoRu-CeO ₂	100 mA g ⁻¹	1.21 V	175 cycles	71.8%	97.4%	[32]
Ru-AHCNs	100 mA g ⁻¹	1.38 V	50 cycles	76.3%	75.6%	[33]
High-entropy alloy cathode catalysts						
PBA-FeMnNiCoCu	50 mA g ⁻¹	0.95 V	100 cycles	74.9%	—	[34]
FeCoNiCuRu HEA/CNFs	100 mA g ⁻¹	0.92 V	550 cycles	74.8%	100%	[35]
FeCoNiMnCuAl@C-600	100 mA g ⁻¹	1.05 V	134 cycles	84.5%	92.2%	[36]
Metal-Organic Framework/Covalent Organic Framework						
Cu-TDCOF	200 mA g ⁻¹	1.40 V	110 cycles	70.7%	100%	[37]
Ni-Fc	200 mA g ⁻¹	1.32 V	200 cycles	66.6%	100%	[38]
c-p-MOF-5	1000 mA g ⁻¹	1.70 V	250 cycles	65.4%	—	[39]
Ru ₁₅ Co ₈₅ -NPs	50 μ A cm ⁻² ~ 141 mA g ⁻¹	1.11 V	750 cycles	88.7%	99.7%	This work

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