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In-situ selective oxidation created Cr₂O₃ assisting CrMnFeCoNi for ultrahigh power density zinc-air batteries

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Abstract

Highly efficient and stable bifunctional catalysts toward sluggish oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are critical for practical applications of rechargeable zinc-air batteries (ZAB). Heterostructure engineering is effective in boosting catalytic performances of the bifunctional catalysts. Here, N-doped carbon supported quinary alloy-chromium oxide heterostructured catalysts, CrMnFeCoNi-(CrO_x)₁/NC, were created, through *in-situ* selective oxidation of Cr, to construct binder-free composite air electrodes for high-performance rechargeable ZABs. The CrMnFeCoNi-(CrO_x)₁/NC-based ZAB exhibited outstanding discharge-charge performances, delivering an ultrahigh discharge peak power density of 364 mW cm⁻² at 499 mA cm⁻², an ultra-narrow working voltage gaps of 0.78 V at 10 mA cm⁻² and 0.87 V at 50 mA cm⁻², and ultrastability of 765 h at 10 mA cm⁻² and 100 h at 50 mA cm⁻², which largely outperformed the (Pt/C+RuO₂)-based one. *In-situ* Raman and X-ray absorption spectroscopy studies revealed that Mn, Fe, and Co were the main active sites for ORR, whereas Mn, Co, and Ni played the key roles in catalysis of OER. The presence of Cr₂O₃ offers abundant oxygen vacancies, beneficial for enhanced oxygen adsorption to boost ORR. Further oxidation of the oxidation-prone Cr₂O₃ to CrO₃ during OER is advantageous for protection of OER-active intermediates from over-oxidation to enhance OER.

Keywords: Rechargeable zinc-air battery, binder-free composite air electrode, oxygen reduction reaction, oxygen evolution reaction, heterostructured catalyst



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INTRODUCTION

Rechargeable zinc-air batteries (ZABs) are considered a pivotal advancement in electrochemical energy storage technologies because of their high energy densities, environmental friendliness, and renewability. Nevertheless, the advancement of rechargeable ZABs is currently constrained by several technical challenges, with low catalytic activities and stability toward catalysis of sluggish oxygen reduction reaction (ORR) at discharging and oxygen evolution reaction (OER) at charging being the most critical. Although noble metal-based catalysts, for example, Pt/C for ORR and RuO₂ for OER, exhibit superior performances, their high cost, extremely limited availability, and mono-functionality toward catalysis of oxygen reactions, restrict their practical applications for rechargeable ZABs. Consequently, development of highly efficient, durable, and cost-effective bifunctional catalysts is essential for large scale applications of rechargeable ZABs.

Among the many previously explored electrocatalysts, transition metals, such as Mn, Fe, Co, and Ni, based materials are recognized for their low cost and abundant availability. When supported on N-doped carbons, these materials exhibited promising catalytic activities and stability toward both ORR and OER^[1,2]. N-doped carbons not only offer necessary electrical conductivities to facilitate relevant electrochemical processes, but also effectively tackle several detrimental issues, including catalyst corrosion, aggregation, and detachment under severe reaction conditions^[3-5].

For catalyst design, interface engineering is an effective strategy to enhance activities and stability of the catalysts. One common approach in interface engineering is the formation of heterostructures, where two or more different materials are combined to form interfaces of a microscopic scale^[6]. Charge transfer, occurring across the interface, helps regulate charge distribution near active sites and adsorption energies of reaction intermediates, thereby enhancing catalytic activities. Furthermore, formation of heterostructures can create a large number of defect sites, through lattice mismatch-induced local strains, on and around the interfaces, thus increasing the number of active sites on the catalyst surface^[7,8], beneficial for activity enhancement.

Metal-metal oxide heterostructures have been shown to modulate binding strength between intermediates and catalysts because of the strong electronic interactions occurring at the interface^[9]. Zhang *et al.*^[10] synthesized Co-CoO heterojunctions embedded in N-doped carbon nanospheres as the air electrode catalyst for rechargeable ZABs, achieving a potential gap (ΔE) of 0.83 V. Li *et al.*^[11] utilized a thermal decomposition method with dopamine precursors to prepare Co-MnO heterostructures for catalysis of ORR. It was found that MnO, upon forming a heterojunction with Co, exhibited a Mott-Schottky effect at the interface, modulating the charge distribution and thereby enhancing ORR activities. Luo *et al.*^[12] fabricated a multi-element heterostructure, FeNiCo-MnGaO_x, for applications in rechargeable ZABs. The heterostructured catalyst demonstrated excellent electrochemical performances with a half-wave potential ($E_{1/2}$) of 0.824 V and a remarkably low OER overpotential of 255 mV at 10 mA cm⁻², and the FeNiCo-MnGaO_x-based ZAB maintained stable operations for 158 h of discharge-charge cycling at 5 mA cm⁻². For heterostructured catalysts, there exist a huge number of design freedoms, particularly for multi-element-based ones. Developments of heterostructured catalysts for electrocatalytic processes are still in their early stage, and deserve extensive and intensive research efforts. Particularly, multi-element-based catalysts possess the unique advantages of atomic scale synergistic cocktail effects, to fine-tune the band structure of the catalyst for optimal adsorption/desorption of reaction intermediates and to team up constituent elements to undertake bond forming/breaking involved in multi-step reactions, potentially leading to further enhanced catalytic activities. The design of multi-element catalysts, in terms of the kinds and concentrations of the constituent elements, however, remains relatively unexplored.

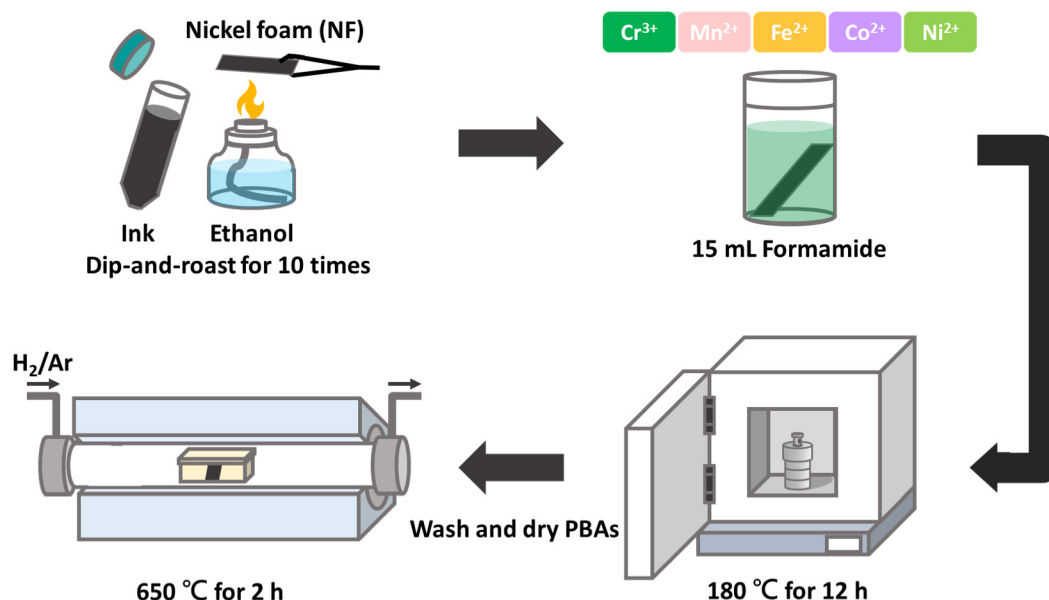
Here, a multi-element alloy-based alloy-oxide heterostructured catalyst, CrMnFeCoNi-CrO_x, was developed to serve as a highly active and stable bifunctional catalyst for the air electrode of a high-performance rechargeable ZAB. The multi-element material system of CrMnFeCoNi has been explored as bifunctional oxygen catalysts for ZABs^[13] and as electrocatalysts for OER^[14], exhibiting promising electrocatalytic performances. Introduction of heterostructure to the CrMnFeCoNi system is a rational extension to gain further improvements. The CrMnFeCoNi-CrO_x heterostructure was created through thermal reduction of a multi-element Prussian blue analogue [PBA, M_{1x}M_{2y}(CN)₆] precursor, CrMnFeCoNi PBA, in a reducing atmosphere, 5%H₂/95%Ar, in the presence of a dispersing support, carbon black (CB). CB, coated on skeleton surfaces of a conductive porous substrate, nickel foam (NF), was introduced to disperse the growth of the PBA and thus the final PBA-derived N-doped carbon supported multi-element alloy catalyst. The presence of CB also enabled *in-situ* selective oxidation during the subsequent thermal reduction treatment. Upon thermal treatment in a reducing atmosphere, metal ions and CN groups of the PBA were reduced to form N-doped carbon supported multi-element alloy nanoparticles dispersed on the CB layer. The oxygen-containing groups on the surface of CB, however, triggered partial oxidation of Cr, an oxidation-prone metal, to create the alloy-oxide heterostructure, CrMnFeCoNi-CrO_x. The chromium oxide, Cr₂O₃, thus formed, in an oxygen deficient environment, was with abundant oxygen vacancies, beneficial for oxygen adsorption in the ORR process. Furthermore, Cr₂O₃ is prone to further oxidation under anodic potentials to form CrO₃ of a high valence Cr(VI), thus protecting OER-active intermediates, such as NiOOH, from being overoxidized to form less OER-active species. The merits of the quinary alloy-metal oxide heterostructured catalyst, CrMnFeCoNi-CrO_x, were confirmed through comparison in electrochemical performances with the corresponding quaternary alloy catalyst, MnFeCoNi, and plain Cr₂O₃ catalyst. *In-situ* spectroscopic studies were conducted to gain insights on the catalytic mechanisms of the heterostructured catalyst toward ORR and OER.

RESULTS AND DISCUSSION

Materials characterizations

[Scheme 1](#) illustrates the fabrication of the N-doped carbon supported heterostructured catalyst, CrMnFeCoNi-(CrO_x)_n/NC. Detailed experimental procedures, including precursor formulas for syntheses of CrMnFeCoNi-(CrO_x)_n/NC [[Supplementary Table 1](#)] and mass loading of the sample catalysts [[Supplementary Table 2](#)], are offered in the [Supplementary Materials](#). Briefly, a CB loaded NF (CB@NF) was first prepared through a dip-and-roast procedure to serve as a substrate to accommodate the catalysts. A multi-element CrMnFeCoNi PBA was then grown on CB@NF with a solvothermal treatment, followed by calcination in a reducing atmosphere H₂/Ar to afford the heterostructured catalyst. [Supplementary Figure 1](#) shows the X-ray diffraction (XRD) pattern of the CrMnFeCoNi PBA, exhibiting a pronounced single phase pattern together with some peak overlapping for minor phase separation and thus confirming the successful formation of a multi-element PBA. Furthermore, three heterostructured catalysts of increasing Cr concentrations, termed CrMnFeCoNi-(CrO_x)_n/NC (n=0.5, 1, 3), were prepared to investigate the effect of Cr loading. And two control sample catalysts, MnFeCoNi/NC (without presence of Cr) and CrO_x/NC (Cr only sample), were also prepared for comparison purposes. Among the five catalysts, as shown later, CrMnFeCoNi-(CrO_x)₁/NC exhibited the best electrochemical performances and was thus treated as the main catalyst for detailed characterizations and discussion.

[Figure 1A](#) and [Supplementary Figure 2](#) show the XRD patterns of the three heterostructured catalysts, CrMnFeCoNi-(CrO_x)_n/NC (n=0.5, 1, 3), and the two control sample catalysts, MnFeCoNi/NC and CrO_x/NC. Evidently, CrMnFeCoNi-(CrO_x)_n/NC and MnFeCoNi/NC exhibit prominent diffraction peaks at 2θ of 44.4, 51.7, and 76.1°, corresponding to crystalline planes of (111), (200), and (220) of face-centered cubic (FCC) metals, without peak splitting or impurity peaks observed, indicating single phase multi-element alloys. As to the XRD pattern of CrO_x/NC, characteristic diffraction peaks located at 2θ of



Scheme 1. Schematic illustration of fabrication of CrMnFeCoNi-(CrO_x)_n/NC. PBA: Prussian blue analogue.

33.8°, 36.4°, 41.6°, and 54.9°, corresponding to crystalline planes of (104), (110), (113), and (116) of Cr₂O₃ (JCPDS #038-1479), are identified. The metallic compositions of CrMnFeCoNi-(CrO_x)_n/NC and MnFeCoNi/NC were also determined with inductively coupled plasma optical emission spectrometry (ICP-OES) and summarized in [Supplementary Table 3](#) for comparison. Evidently, the multi-element alloys are CoNi-based, with Cr, Mn, and Fe included as minor components. Note that, the presence of Cr₂O₃ in the heterostructured samples however is not revealed with the XRD characterization, simply because of its low concentrations and possibly poor crystallinity. Further investigation on the presence of Cr₂O₃ with advanced characterization techniques, such as transmission electron microscopy (TEM) and X-ray absorption spectroscopy (XAS), is presented in a later section.

The morphologies of these sample catalysts were next investigated with scanning electron microscope (SEM) imaging. [Figure 1B](#) and [C](#) shows the SEM images of the main catalyst, CrMnFeCoNi-(CrO_x)₁/NC, loaded on the substrate CB@NF, at increasing magnifications. At a low magnification [[Figure 1B](#)], a segment of the skeleton of the NF is observed, which is uniformly coated with a CB layer, and on top of the CB layer numerous nanoparticles reside, appearing as tiny white dots in [Figure 1B](#). When zoomed in to a high magnification [[Figure 1C](#)], these nanoparticles, with an average size of 530±130 nm, appear to be decorated with even smaller-sized nanoparticles (6.0±2.2 nm), designated by yellow arrows. There are also some sheet structures observed around these nanoparticles. These sheet structures are later identified as N-doped carbon sheets, derived from carbonization of the CN group of the PBA. SEM images of other samples were also collected for comparison as shown in [Supplementary Figure 3](#). The morphologies of CrMnFeCoNi-(CrO_x)_{0.5}/NC and CrMnFeCoNi-(CrO_x)₃/NC resemble that of CrMnFeCoNi-(CrO_x)₁/NC, whereas MnFeCoNi/NC and CrO_x/NC show distinct morphological features as compared to those of CrMnFeCoNi-(CrO_x)_n/NC. For MnFeCoNi/NC, nanoparticles populate uniformly over the CB layer, without decoration of smaller-size nanoparticles. On the contrary, CrO_x/NC appears as sparsely and uniformly distributed smaller-size nanoparticles decorated on the CB nanoparticles. These SEM images suggest that introduction of the Cr precursor leads to formation of smaller-size nanoparticles, presumably the Cr₂O₃ nanoparticles as inferred from the XRD characterization of CrO_x/NC [[Supplementary Figure 2](#)].

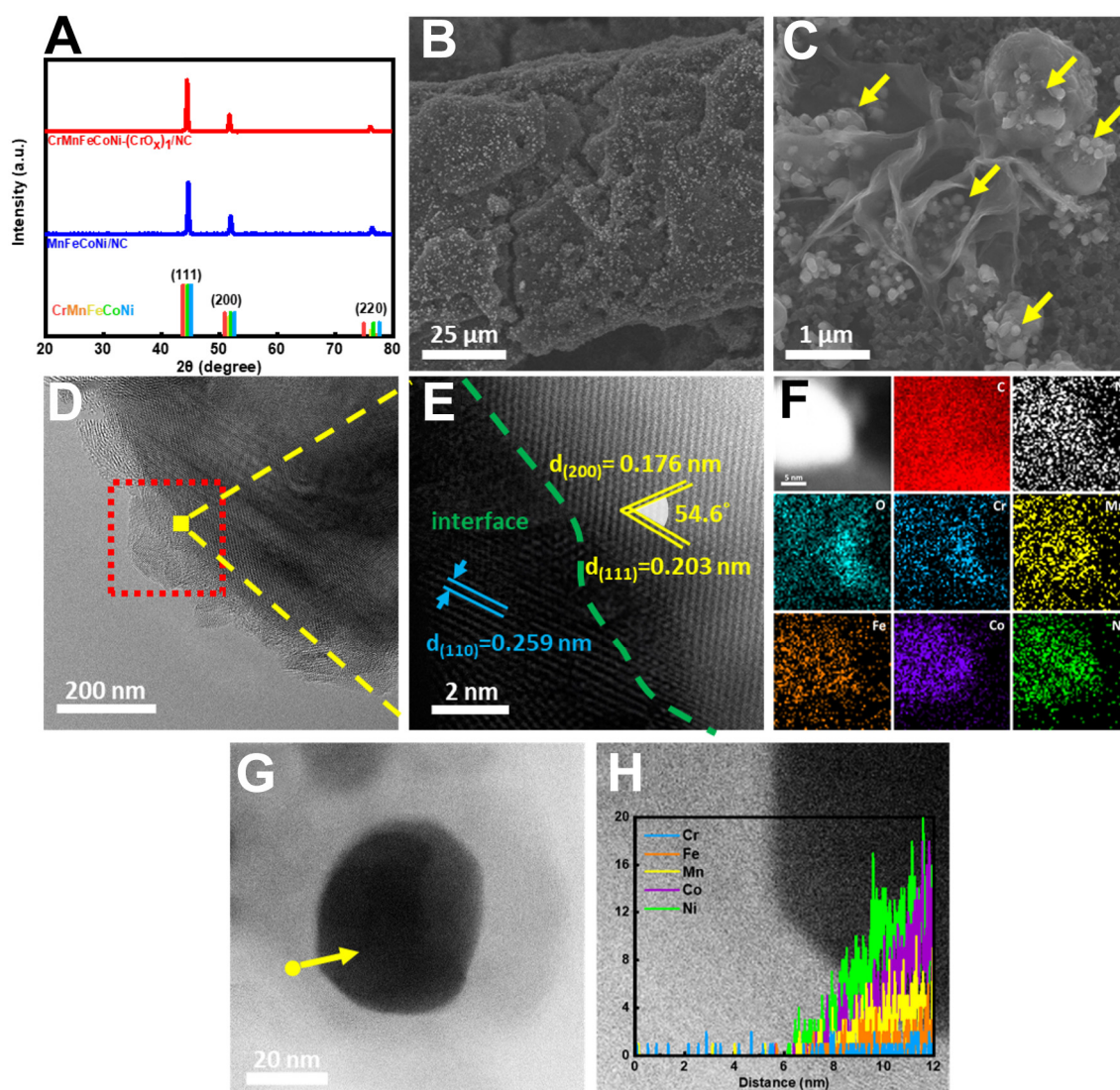


Figure 1. (A) XRD patterns of MnFeCoNi/NC and CrMnFeCoNi-(CrO_x)₁/NC; (B and C) SEM images of CrMnFeCoNi-(CrO_x)₁/NC on CB@NF; (D) HR-TEM image and (E) HAADF-STEM image of CrMnFeCoNi-(CrO_x)₁/NC nanoparticle; (F) TEM-EDS elemental mapping of CrMnFeCoNi-(CrO_x)₁/NC nanoparticle; (G and H) TEM elemental line scan of CrMnFeCoNi-(CrO_x)₁/NC nanoparticle. XRD: X-ray diffraction; HR-TEM: high-resolution-transmission electron microscopy; HAADF-STEM: high-angle annular dark-field scanning transmission electron microscopy; TEM-EDS: transmission electron microscopy-energy dispersive X-ray spectroscopy; SEM: scanning electron microscope.

TEM imaging analyses were conducted on CrMnFeCoNi-(CrO_x)₁/NC [Figure 1D and E, Supplementary Figure 4A and B] and CrO_x/NC [Supplementary Figure 4C] nanoparticles to examine their detailed compositions. Figure 1D and E shows high-resolution (HR)-TEM and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of a CrMnFeCoNi-(CrO_x)₁/NC composite nanoparticle, revealing attachment of a smaller-size nanoparticle, highlighted with a red dashed square, to the surface of a larger nanoparticle [Figure 1D] and the existence of an interface between the two nanoparticles [Figure 1E], respectively. Distinct lattice fringes were observed on the two sides of the interface. An interlayer distance of 0.259 nm, in good agreement with the d-spacing of the (110) planes of Cr₂O₃, was determined for the attachment domain, indicating the attached smaller-size nanoparticle to be a Cr₂O₃ nanoparticle. In addition, interlayer distances of 0.176 nm and 0.203 nm, in good agreement with the

d-spacing of the (200) and (111) planes of an FCC phase, respectively, were determined for the larger size nanoparticle domain. The two crystalline planes have a dihedral angle of 54.6° , closely matching the theoretical value of 54.7° for the dihedral angle between the (200) and (111) planes of an FCC phase, further confirming the nanoparticle to be a single FCC phase multi-element alloy nanoparticle. In addition to Cr_2O_3 decoration, the CrMnFeCoNi alloy nanoparticle is also coated with a thin layer of poorly crystallized N-doped carbons as shown in [Supplementary Figure 4A](#) and [B](#). An average interlayer distance of 0.342 nm is determined, in good agreement with the d-spacing of the (002) planes of N-doped carbons. As for sample CrO_x/NC , [Supplementary Figure 4C](#) shows an HR-TEM image of a nanoparticle, highlighted in a red dashed square, in sample CrO_x/NC , revealing lattice fringes with an interlayer distance of 0.253 nm, in good agreement with the d-spacing of the (110) planes of Cr_2O_3 . This further confirms the composition of Cr_2O_3 for sample CrO_x/NC . Furthermore, the elemental distributions of CrMnFeCoNi- $(\text{CrO}_x)_1/\text{NC}$ and CrO_x/NC were characterized by transmission electron microscopy-energy dispersive X-ray spectroscopy (TEM-EDS) elemental mapping, as shown in [Figure 1F](#) and [Supplementary Figure 4D](#). If examined closely, Cr and O exhibit similar spatial distributions in both CrMnFeCoNi- $(\text{CrO}_x)_1/\text{NC}$ and CrO_x/NC , consistent with the existence of Cr_2O_3 in both samples. By the same token, Mn, Fe, Co, and Ni show similar distributions in CrMnFeCoNi- $(\text{CrO}_x)_1/\text{NC}$. In addition, the presence of the N-doped carbon sheet support, formed from thermal reduction of the CN groups of the PBA, in both CrMnFeCoNi- $(\text{CrO}_x)_1/\text{NC}$ and CrO_x/NC is confirmed with the uniform distributions of C and N over the entire sample domain, not just over the particle domain. The detailed elemental distribution for a single CrMnFeCoNi- $(\text{CrO}_x)_1$ nanoparticle was further examined with TEM elemental line scan [[Figure 1G](#) and [H](#)]. Evidently, the exterior of the CrMnFeCoNi- $(\text{CrO}_x)_1$ nanoparticle is primarily composed of Cr, with a small amount of Mn present within the Cr layer. This outcome is consistent with the Cr_2O_3 decoration on the surface of the CrMnFeCoNi alloy nanoparticles, and implies possible presence of a minor amount of manganese oxides in the decoration layer. As to the interior of the nanoparticle, Ni and Co dominate, consistent with the ICP-OES measurements, with Cr, Mn, and Fe existing as minor components. This outcome shows that Cr exists not only in the Cr_2O_3 decoration layer but also in the multi-element CrMnFeCoNi alloy nanoparticles. In conclusion, CrMnFeCoNi- $(\text{CrO}_x)_1/\text{NC}$ features a heterostructure of Cr_2O_3 decorated multi-element CrMnFeCoNi alloy nanoparticles supported on N-doped carbons.

The composition of CrMnFeCoNi- $(\text{CrO}_x)_1$ was further examined with XAS, which offers information on coordination environments of atoms to reveal constituent components of the material. For comparison purposes, XAS spectra of MnFeCoNi/NC were also collected. [Figure 2A-E](#) shows the K-edge extended X-ray absorption fine structure (EXAFS) spectra of each constituent element for MnFeCoNi and CrMnFeCoNi- $(\text{CrO}_x)_1$. For Cr in CrMnFeCoNi- $(\text{CrO}_x)_1$, two coordination shells are identified, with the first one located at the coordination distance of 1.5 Å, contributed by the Cr-O coordination, and the second one located at 2.4 Å, slightly longer than 2.2 Å of the typical Cr-Cr coordination distance in an FCC structure. This discrepancy in the coordination distance of the second shell of Cr is to be further discussed. For Mn, Fe, Co, and Ni, they appear in both MnFeCoNi and CrMnFeCoNi- $(\text{CrO}_x)_1$, and thus comparison on the corresponding EXAFS spectra can be made to gain information on the compositional difference between the two samples. For Mn in MnFeCoNi, only one coordination shell located at 2.2 Å, contributed by the Mn-metal coordination, is observed, indicating that Mn exists predominately in its metallic form in MnFeCoNi. On the contrary, in CrMnFeCoNi- $(\text{CrO}_x)_1$, in addition to the major coordination shell at 2.2 Å, contributed by the Mn-metal coordination, a minor coordination shell at 1.5 Å, contributed by the Mn-O coordination, appears, suggesting existence of a minor amount of oxidized Mn in the sample. This observation is consistent with the TEM elemental line scan results, which reveal existence of a minor amount of Mn in the exterior of the CrMnFeCoNi- $(\text{CrO}_x)_1/\text{NC}$ nanoparticle, presumably oxide decoration on the CrMnFeCoNi nanoparticle surface. As for Fe, Co, and Ni in both MnFeCoNi and CrMnFeCoNi- $(\text{CrO}_x)_1$, only coordination shells at 2.2 Å, contributed by the metal-metal coordination, are

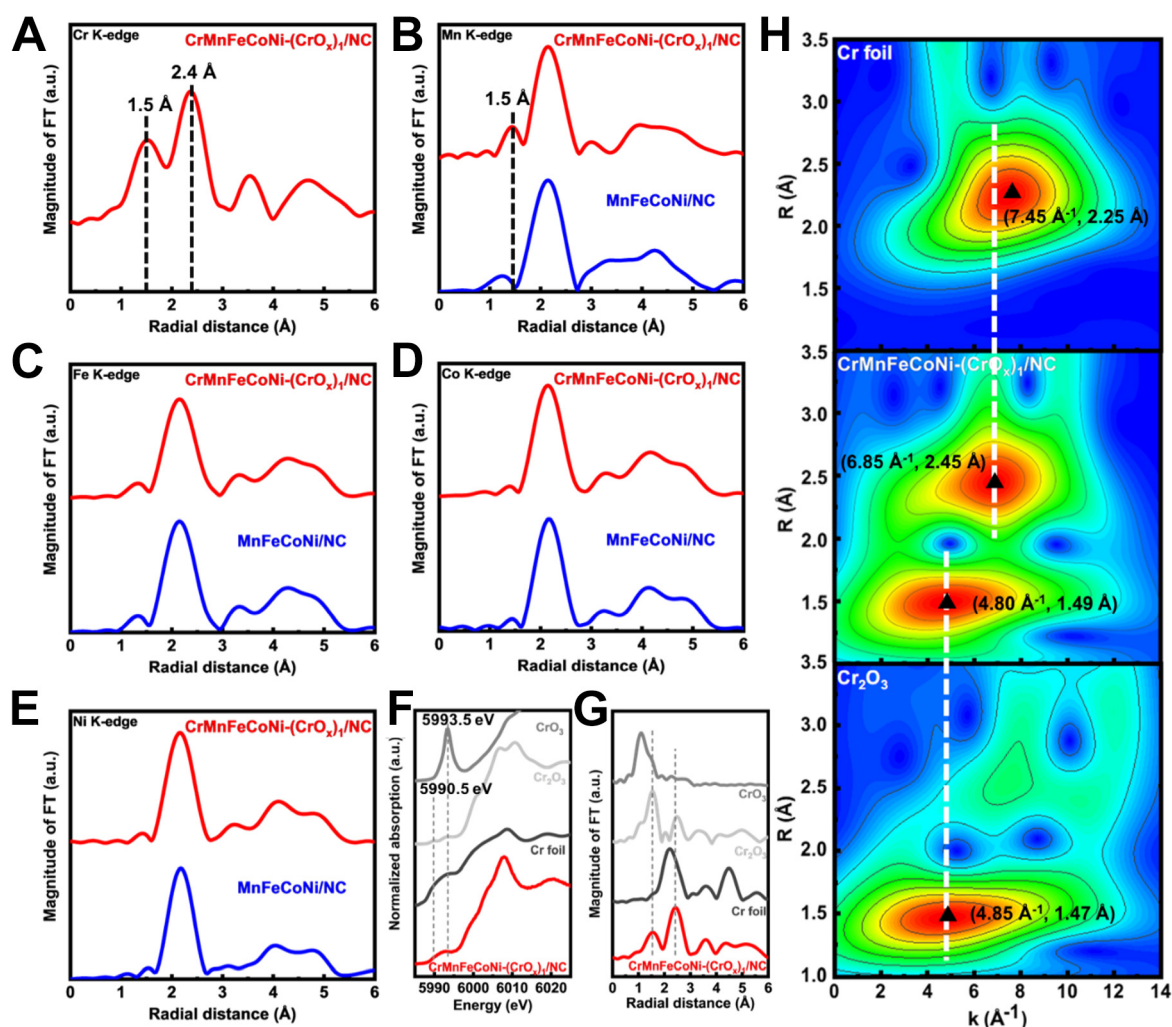


Figure 2. K-edge EXAFS spectra of MnFeCoNi/NC and CrMnFeCoNi-(CrO_x)₁/NC in R space: (A) Cr, (B) Mn, (C) Fe, (D) Co, and (E) Ni; (F) Cr pre-edge and (G) EXAFS spectra of CrMnFeCoNi-(CrO_x)₁/NC, Cr foil, and Cr₂O₃ in R space; (H) WT-EXAFS k-R contour plots of CrMnFeCoNi-(CrO_x)₁/NC, Cr foil, and Cr₂O₃. EXAFS: Extended X-ray absorption fine structure; WT-EXAFS: wavelet transform-EXAFS.

observed, affirming that these elements exist in their metallic states in the two samples.

The distinct coordination environment of Cr in CrMnFeCoNi-(CrO_x)₁ is further discussed with a more detailed analysis of the XAS spectra. [Supplementary Figure 5](#) shows the K-edge X-ray absorption near edge structure (XANES) spectrum of Cr in CrMnFeCoNi-(CrO_x)₁/NC, along with those of Cr metal foil and Cr₂O₃ standard for comparison. The absorption edge of CrMnFeCoNi-(CrO_x)₁/NC is close, but with a slight left shift, to that of the Cr₂O₃ standard, indicating that the oxidation state of Cr in the sample is slightly less than 3+ of Cr in Cr₂O₃. This slight left shift in absorption energies is to be further discussed. The shape and intensity of the pre-edge features provide insights into the geometry and symmetry of the local structure of the sample. The pre-edge features are compared across CrMnFeCoNi-(CrO_x)₁/NC, Cr foil, Cr₂O₃ standard, and CrO₃ standard as shown in [Figure 2F](#). For CrO₃, a prominent feature peak is observed at 5,993.5 eV. This peak is contributed by the allowed 1s to 3d transition of the tetrahedral Cr (VI), which does not possess a center of symmetry. The empty d-orbitals of Cr (VI) greatly increase the transition probability. On the contrary, Cr₂O₃ has Cr (III) in a centrosymmetric octahedral structure, forbidding the 1s to t_{2g} and 1s

to e_g transitions, respectively. These weak features are caused by vibronic coupling, which increases the transition probability even though the transition is typically forbidden. Nevertheless, the transition probability remains low because of the half-filled t_{2g} orbitals of Cr (III), resulting in relatively weak peak intensity^[15,16]. The pre-edge of the Cr K-edge XANES spectrum of CrMnFeCoNi-(CrO_x)₁/NC shows a single broad characteristic peak at 5,992.9 eV, falling in between 5,990.5 and 5,993.5 eV. This suggests the presence of a small amount of Cr in the form of CrO₃ in CrMnFeCoNi-(CrO_x)₁/NC, contributing to the observed peak at 5,992.9 eV.

To further elucidate the coordination state of Cr in CrMnFeCoNi-(CrO_x)₁/NC, Cr K-edge EXAFS spectra of CrMnFeCoNi-(CrO_x)₁/NC, Cr foil, Cr₂O₃ standard, and CrO₃ standard were compared as shown in Figure 2G. CrMnFeCoNi-(CrO_x)₁/NC shows two major coordination shells. The first coordination shell is located at 1.5 Å, contributed by the Cr-O coordination, same as the first coordination shell of Cr₂O₃. The second coordination shell is located at 2.4 Å, falling in-between the Cr-Cr coordination shell of Cr foil and the Cr-O-Cr coordination shell of Cr₂O₃, implying that Cr of CrMnFeCoNi-(CrO_x)₁/NC exists in both metallic and oxidized states. This also explains the slight left shift in absorption energies, experienced by Cr of CrMnFeCoNi-(CrO_x)₁/NC, from those of Cr₂O₃ [Supplementary Figure 5]. Furthermore, comparison on wavelet transform-EXAFS (WT-EXAFS) k-R contours of CrMnFeCoNi-(CrO_x)₁/NC, Cr foil, and Cr₂O₃ [Figure 2H] gives further evidences on the simultaneous presence of Cr and Cr₂O₃ in CrMnFeCoNi-(CrO_x)₁/NC. High k-number oscillations identify metal-metal coordination and coordination between heavy elements, whereas low k-number oscillations elucidate metal-oxygen coordination and coordination of metal with light elements. CrMnFeCoNi-(CrO_x)₁/NC exhibits two prominent contour peaks, one at a low k-value (4.8 Å⁻¹, 1.49 Å) and the second one at a high k-value (6.85 Å⁻¹, 2.45 Å), indicating mixed Cr species in the sample. The low k-value contour peak aligns closely with the contour peak of Cr₂O₃ (4.85 Å⁻¹, 1.47 Å), showing the presence of Cr₂O₃ in the sample. As for the high k-value contour peak, it is located at a k-value slightly lower than that of the Cr foil (7.45 Å⁻¹, 2.25 Å). This down-shift in k-values suggests interference, caused by the Cr-O-Cr coordination of Cr₂O₃, to the Cr-metal coordination of the sample, shifting the contour peak to a slightly lower k-value location. These observations further confirm that Cr of CrMnFeCoNi-(CrO_x)₁/NC exists in both metallic and oxidized states.

Recall that, in the TEM elemental line scan, a small amount of Mn was detected in the CrO_x layer of CrMnFeCoNi-(CrO_x)₁/NC. The situation was further examined with XAS studies on CrMnFeCoNi-(CrO_x)₁/NC and MnFeCoNi/NC, along with those on Mn foil and MnO₂. It is evident from the Mn K-edge XANES spectra of the four samples [Supplementary Figure 6A] that Mn of CrMnFeCoNi-(CrO_x)₁/NC and MnFeCoNi/NC has a valence state close to that of Mn foil. Nevertheless, the absorption edge energy of Mn in CrMnFeCoNi-(CrO_x)₁/NC is slightly higher than that in MnFeCoNi/NC, indicating a slightly higher valence state of Mn in CrMnFeCoNi-(CrO_x)₁/NC. Furthermore, from the EXAFS spectra in R-space [Supplementary Figure 6B], it is evident that CrMnFeCoNi-(CrO_x)₁/NC, in addition to the pronounced Mn-metal coordination shell at 2.2 Å, exhibits a minor Mn-O coordination shell at 1.5 Å, which is absent from that of MnFeCoNi/NC, suggesting that a minor amount of Mn in CrMnFeCoNi-(CrO_x)₁/NC exists in oxidized states. Supplementary Figure 6C shows the EXAFS spectra in k-space for Mn, Fe, Co, and Ni of CrMnFeCoNi-(CrO_x)₁/NC. All four elements show similar oscillation profiles at high k-values, indicating comparable coordination environments for the four elements in CrMnFeCoNi-(CrO_x)₁/NC. At lower k-values, the oscillation profile of Mn differs slightly from those of Fe, Co, and Ni, caused by the minor extent of Mn-O coordination. The above observations confirm that Mn of CrMnFeCoNi-(CrO_x)₁/NC exists predominately in its metallic state, with a small amount of Mn oxidized.

Surface chemical states of CrMnFeCoNi-(CrO_x)₁/NC and MnFeCoNi/NC were also examined with high-resolution X-ray photoelectron spectroscopy (HR-XPS). **Figure 3A** shows the HR-XPS spectra of N 1s, which are deconvoluted to reveal five distinct N states, including pyridinic N, pyrrolic N, graphitic N, metal-N_x, and oxidized N. Among these states, pyridinic N has been shown to contribute to superior ORR activities and stability^[3-5]. Interestingly, CrMnFeCoNi-(CrO_x)₁/NC has a high pyridinic N content of 39.5%, 4.3% higher than that of MnFeCoNi/NC, indicating a more favorable nitrogen environment for catalysis of ORR [**Supplementary Table 4**]. The presence of N species also further confirms the N-doping of the carbon support. **Figure 3B** shows the O 1s spectra, which are deconvoluted to identify four O species, including lattice O, O vacancy, hydroxyl O, and carbonyl O^[17]. It is to be noted that metallic samples are inevitably surface oxidized when exposed to ambient atmosphere before X-ray photoelectron spectroscopy (XPS) measurements, resulting in showing of lattice O and O vacancies. As for the hydroxyl O and carbonyl O, they come from surface adsorption of oxygen-containing species. As expected, CrMnFeCoNi-(CrO_x)₁/NC, containing a minor amount of Cr₂O₃, shows a higher lattice O concentration of 8.2%, 1.4% higher than that of MnFeCoNi/NC [**Supplementary Table 5**]. Additionally, CrMnFeCoNi-(CrO_x)₁/NC possesses a high O vacancy concentration of 30.8%, 6.9% higher than that of MnFeCoNi/NC [**Supplementary Table 5**], attributable to formation of Cr₂O₃ in an oxygen-deficient environment. These O vacancies help alleviate the interfacial strain caused by lattice mismatch between CrMnFeCoNi and Cr₂O₃ to stabilize the heterostructure and also enhance oxygen adsorption to boost ORR activities^[11]. **Figure 3C** shows the Cr 2p spectra for CrMnFeCoNi-(CrO_x)₁/NC, revealing binding energy peaks at 575.0 and 584.4 eV for metallic Cr, at 576.6 and 585.9 eV for Cr(III), and at 579.1 and 588.2 eV for Cr(VI)^[18,19]. The result is consistent with the finding that Cr of CrMnFeCoNi-(CrO_x)₁/NC exists in both metallic and oxidized states. **Figure 3D** shows the Mn 2p spectra, which are identified binding energy peaks at 638.9 and 639.2 eV for metallic Mn, at 640.8 and 641.1 eV for Mn(II), and at 642.7 and 642.8 eV for Mn(III), along with satellite peaks at 645.5 eV^[20-22]. Interestingly, the proportion of metallic Mn in CrMnFeCoNi-(CrO_x)₁/NC is significantly lower than that in MnFeCoNi/NC, indicating higher Mn oxidation extent in CrMnFeCoNi-(CrO_x)₁/NC. This observation is consistent with the findings drawn from the XAS and TEM elemental line scan analyses that a minor amount of Mn is oxidized and present in the Cr₂O₃ layer. **Figure 3E** shows the Co 2p spectra, which are deconvoluted to reveal peaks at 778.3 and 793.5 eV for metallic Co, at 779.3 and 794.9 eV for Co(III), at 781.4 and 797.4 eV for Co(II), and satellite peaks of Co(II) at 784.8 and 802.7 eV^[22,23]. Note that Co(II) possesses higher binding energies than Co(III), attributable to the unique electronic configuration, nuclear charges, and shielding effect^[24]. **Figure 3F** shows the Ni 2p spectra, which are deconvoluted to exhibit peaks at 853.2 and 870.3 eV for metallic Ni, at 855.1 and 872.6 eV for Ni(II), and satellite peaks at 860.5 and 877.0 eV^[22,23]. Interestingly, the proportion of metallic Ni in CrMnFeCoNi-(CrO_x)₁/NC is significantly higher than that in MnFeCoNi/NC. This may be attributed to the protection effect of Cr oxidation on Ni from being oxidized.

Electrochemical characterizations

Electrochemical properties of the five sample catalysts, two control samples, and three heterostructured samples, along with the benchmark catalysts, Pt/C for ORR and RuO₂ for OER, toward ORR and OER were characterized in 0.1 M KOH. **Supplementary Figure 7** shows the cyclic voltammetry (CV) curves recorded for the five sample catalysts under the conditions of both O₂ and N₂ saturation to examine their capabilities toward catalysis of ORR. Evidently, reduction peaks appear only in O₂-saturated electrolytes, implying occurrence of ORR and confirming ORR-activeness of these catalysts. Among all characterized samples, CrMnFeCoNi-(CrO_x)₁/NC shows the highest oxygen reduction peak potential of 0.816 V, thus the lowest ORR overpotential, indicating its superior efficiency in reducing oxygen.

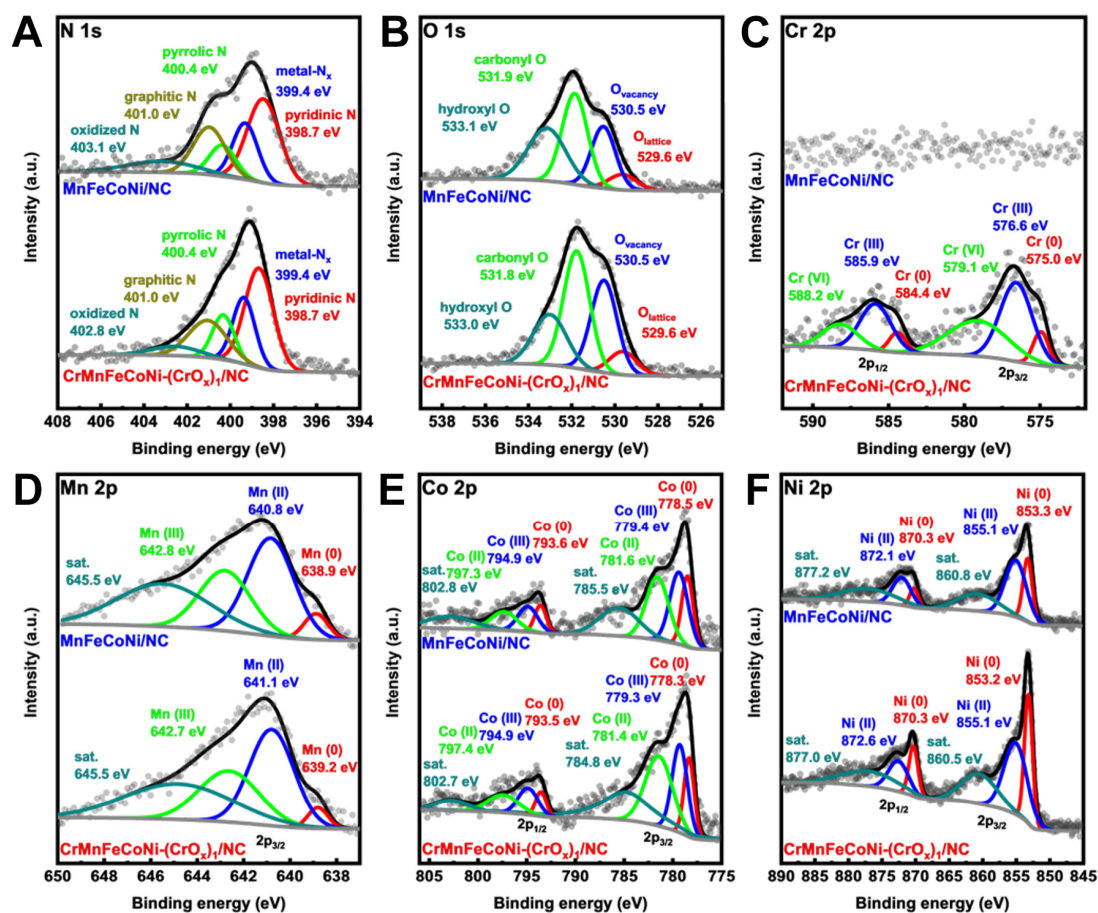


Figure 3. HR-XPS spectra of MnFeCoNi/NC and CrMnFeCoNi-(CrO_x)₁/NC: (A) N 1s, (B) O 1s, (C) Cr 2p, (D) Mn 2p, (E) Co 2p, and (F) Ni 2p. HR-XPS: High-resolution X-ray photoelectron spectroscopy.

The ORR activities of these sample catalysts, along with the benchmark ORR catalyst, Pt/C, were characterized by half-wave potentials ($E_{1/2}$) derived from the polarization curves recorded in 0.1 M KOH [Figure 4A and Supplementary Figure 8A]. The main catalyst, CrMnFeCoNi-(CrO_x)₁/NC, not only achieves a limiting current density comparable to that of Pt/C, but also acquires the highest $E_{1/2}$ of 0.834 V, outperforming all catalysts tested, including Pt/C (0.820 V). Notably, the two control sample catalysts, MnFeCoNi/NC and CrO_x/NC, have the lowest $E_{1/2}$ of 0.780 and 0.720 V, respectively, whereas the three heterostructured catalysts consistently show improved $E_{1/2}$ values, highlighting the effectiveness of the alloy-oxide heterostructure in enhancing ORR activities. Furthermore, as shown in Figure 4B and Supplementary Figure 8B, CrMnFeCoNi-(CrO_x)₁/NC achieves a Tafel slope of 47.7 mV dec⁻¹, significantly lower than that of Pt/C (79.9 mV dec⁻¹), suggesting its enhanced ORR kinetics. Figure 4C and Supplementary Figure 8C present the electron transfer numbers (n) and hydrogen peroxide yields (H₂O₂%) for the sample catalysts within the potential window of 0.2 V to 0.8 V [vs. reversible hydrogen electrode (RHE)]. Pt/C, as expected, exhibits an average electron transfer number of 3.96, close to 4, and an ultralow hydrogen peroxide yield of 1.82%, closely aligning with the theoretical limiting values (4 for n and 0 for H₂O₂%) of a pure four-electron transfer ORR route. For CrMnFeCoNi-(CrO_x)₁/NC, the average electron transfer number and hydrogen peroxide yield are 3.92% and 4.28%, respectively, comparable to those achieved by Pt/C, indicating a predominately four-electron transfer ORR mechanism. The average electron transfer number can also be estimated from Koutecky-Levich (K-L) analyses. Supplementary Figure 9A-D shows the linear sweep voltammetry (LSV) curves recorded for the sample catalysts at increasing rotating speeds from 400 to

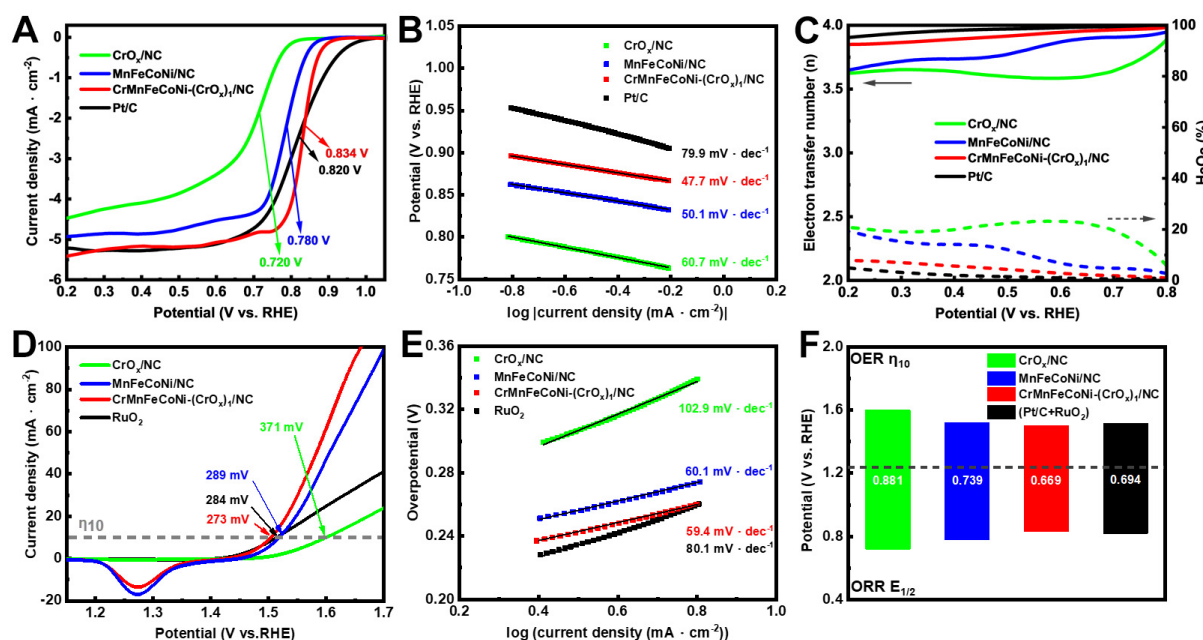


Figure 4. Electrochemical performances of CrO_x/NC , $\text{MnFeCoNi}/\text{NC}$, $\text{CrMnFeCoNi}-(\text{CrO}_x)_1/\text{NC}$, and benchmark catalysts in 0.1 M KOH: (A) ORR LSV curves recorded at 1600 rpm with scan rate of 5 mV s^{-1} ; (B) ORR Tafel slopes; (C) ORR electron transfer numbers (n) and hydrogen peroxide yields ($\text{H}_2\text{O}_2\%$); (D) OER LSV curves at scan rate of 1 mV s^{-1} ; (E) OER Tafel slopes; (F) potential gap (ΔE) between η_{10} of OER and $E_{1/2}$ of ORR. ORR: Oxygen reduction reaction; LSV: linear sweep voltammetry; OER: oxygen evolution reaction.

2400 rpm, from which the K-L plots [Supplementary Figure 9E] can be constructed to estimate the average electron transfer numbers. $\text{CrMnFeCoNi}-(\text{CrO}_x)_1/\text{NC}$ again achieves an average electron transfer number of 3.98, almost 4, the same as that acquired by Pt/C, confirming again the four-electron transfer mechanism driven by $\text{CrMnFeCoNi}-(\text{CrO}_x)_1/\text{NC}$. Notably, the two control sample catalysts show significantly lower average electron transfer numbers (less than 3), indicating poor selectivity toward the preferred four-electron transfer reaction route. This outcome shows that formation of the $\text{CrMnFeCoNi}-\text{CrO}_x$ heterostructure enhances not only the activity and reaction kinetics, but also selectivity toward catalysis of ORR. Furthermore, electrochemical impedance spectroscopy (EIS) was conducted to investigate charge transfer resistances (R_{ct}) involved in ORR catalyzed by the product catalysts. The Nyquist plots recorded are fitted with an equivalent circuit model (inset of Supplementary Figure 10A) to extract the values of R_{ct} . As a result, $\text{CrMnFeCoNi}-\text{CrO}_x/\text{NC}$ exhibits a significantly lower R_{ct} of 132Ω than that of $\text{MnFeCoNi}/\text{NC}$ (158Ω), confirming the merit of the alloy-oxide heterostructure in accelerating the ORR kinetics.

Figure 4D and E, Supplementary Figure 11 display the OER polarization curves and corresponding Tafel slopes. It is to be noted that the LSV for OER [Figure 4D] was conducted in a negative scan mode to avoid possible interference from pre-OER oxidation toward determination of overpotentials at 10 mA cm^{-2} (η_{10}). For metallic alloy samples, the surface oxide layer of high-valence metals formed at high applied potentials is reduced to oxides of low-valence metals at low applied potentials, leading to the showing of the reduction peak observed. Among the tested catalysts, CrO_x/NC shows the poorest performance. The formation of the $\text{CrMnFeCoNi}-\text{CrO}_x$ heterostructure significantly reduces the OER overpotential, with $\text{CrMnFeCoNi}-(\text{CrO}_x)_1/\text{NC}$ performing the best, achieving the lowest overpotential (273 mV) at 10 mA cm^{-2} (η_{10}) and Tafel slope (59.4 mV dec^{-1}), even lower than those of the benchmark catalyst, RuO_2 (284 mV and 80.1 mV dec^{-1}). The superiority of the heterostructured catalyst becomes more pronounced with increasing applied potentials [Figure 4D], beneficial for practical operations at high current densities.

Electric double layer capacitances (C_{dl} 's), a direct measure of electrochemical surface areas (ECSAs), were also determined to normalize the LSV curves for examination of the intrinsic activities of the catalysts. To determine C_{dl} , CV curves [Supplementary Figure 12] recorded within a non-Faradaic potential window at increasing scan rates were collected, from which C_{dl} 's were calculated as halves of the slopes of the current density difference versus scan rate plots, obtained through linear regression. Interestingly, all multi-element alloy-containing samples exhibit much higher C_{dl} 's ($> 12 \text{ mF cm}^{-2}$) than CrO_x/NC (6.2 mF cm^{-2}), correlating well with their morphological characteristics. Recall that CrO_x/NC has a morphology of sparsely distributed small-size nanoparticles decorated on CB nanoparticles, whereas the multi-element alloy-containing samples have a morphology of densely populated nanoparticles, with/without decoration of small-size nanoparticles, uniformly distributed on top of the CB layer, giving higher amounts of exposed surface areas of the catalysts. These C_{dl} 's were used to normalize the OER LSV curves [Supplementary Figure 13] to exclude the effect of electrochemical surface areas, thus quantity of active sites, from the LSV curves to reveal the intrinsic activities of the catalysts. Evidently, the main catalyst, $\text{CrMnFeCoNi}-(\text{CrO}_x)_1/\text{NC}$, exhibits the lowest overpotentials, indicating its highest intrinsic activities. Furthermore, the charge transfer resistances involved in OER catalyzed by the product catalysts were examined with EIS [Supplementary Figure 10B]. As evident from Supplementary Figure 10B, $\text{CrMnFeCoNi}-\text{CrO}_x/\text{NC}$ exhibits a significantly lower R_{ct} of 8.0Ω than that of $\text{MnFeCoNi}/\text{NC}$ (12.2Ω), confirming the merit of the alloy-oxide heterostructure in accelerating the OER kinetics.

Efficiency of the bifunctionality of the sample catalysts toward catalysis of ORR and OER was characterized by the potential gap between η_{10} values of OER and $E_{1/2}$ values of ORR as shown in Figure 4F. $\text{CrMnFeCoNi}-(\text{CrO}_x)_1/\text{NC}$ exhibits an exceptionally low potential gap of 0.669 V , even lower than 0.694 V achieved by the noble metal-based benchmark composite catalyst ($\text{Pt}/\text{C}+\text{RuO}_2$). $\text{MnFeCoNi}/\text{NC}$ and CrO_x/NC , without the presence of the alloy-oxide heterostructure, exhibit much larger potential gaps of 0.739 and 0.881 V , respectively. This further confirms that presence of the alloy-oxide heterostructure effectively boosts the catalytic performance toward both OER and ORR.

Catalyst robustness, critical to practical applications of ZABs, was also characterized by a 20 h chronoamperometric test as shown in Supplementary Figure 14. For both ORR and OER, $\text{CrMnFeCoNi}-(\text{CrO}_x)_1/\text{NC}$ exhibits only 4.3 and 5.0% decay, respectively. As for the two benchmark catalysts, Pt/C and RuO_2 experience severer decay of 7.3% for ORR and 17.1% for OER, respectively. This indicates that $\text{CrMnFeCoNi}-(\text{CrO}_x)_1/\text{NC}$ possesses not only superior bifunctional catalytic activities, but also superior operational stability.

Zinc-air battery characterizations

Electrochemical characterizations on ZABs, constructed by using the present developed catalysts as the catalysts for the air electrode, were conducted to further show the merits of the alloy-oxide heterostructured catalysts on ZABs. Figure 5A and B, Supplementary Figure 15A and B show the discharge-charge curves and corresponding power density curves of the two control and the three heterostructured sample catalysts-based ZABs, along with the benchmark composite catalyst ($\text{Pt}/\text{C}+\text{RuO}_2$)-based one, in a two-electrode full-cell setting. For charging, at a charging cutoff voltage of 2.4 V , the $\text{CrMnFeCoNi}-(\text{CrO}_x)_1/\text{NC}$ -based ZAB achieves the highest charging current density of 399.1 mA cm^{-2} , outperforming all other characterized ZABs, 258.3 , 211.1 , 163.2 , 326.1 , and 198.1 mA cm^{-2} for the $\text{MnFeCoNi}/\text{NC}$, ($\text{Pt}/\text{C}+\text{RuO}_2$), CrO_x/NC , $\text{CrMnFeCoNi}-(\text{CrO}_x)_{0.5}/\text{NC}$, and $\text{CrMnFeCoNi}-(\text{CrO}_x)_3/\text{NC}$ -based ones, respectively. For discharging, the $\text{CrMnFeCoNi}-(\text{CrO}_x)_1/\text{NC}$ -based ZAB achieves an exceptionally high peak power density of 364.2 mW cm^{-2} at 499.1 mA cm^{-2} , significantly outperforming the $\text{MnFeCoNi}/\text{NC}$ (302.6 mW cm^{-2} at 420.0 mA cm^{-2}), CrO_x/NC (214.0 mW cm^{-2} at 302.1 mA cm^{-2}), $\text{CrMnFeCoNi}-(\text{CrO}_x)_{0.5}/\text{NC}$ (344.6 mW cm^{-2} at 485.4 mA cm^{-2}), $\text{CrMnFeCoNi}-(\text{CrO}_x)_3/\text{NC}$ (315.7 mW cm^{-2} at 448.0 mA cm^{-2}), and ($\text{Pt}/\text{C}+\text{RuO}_2$).

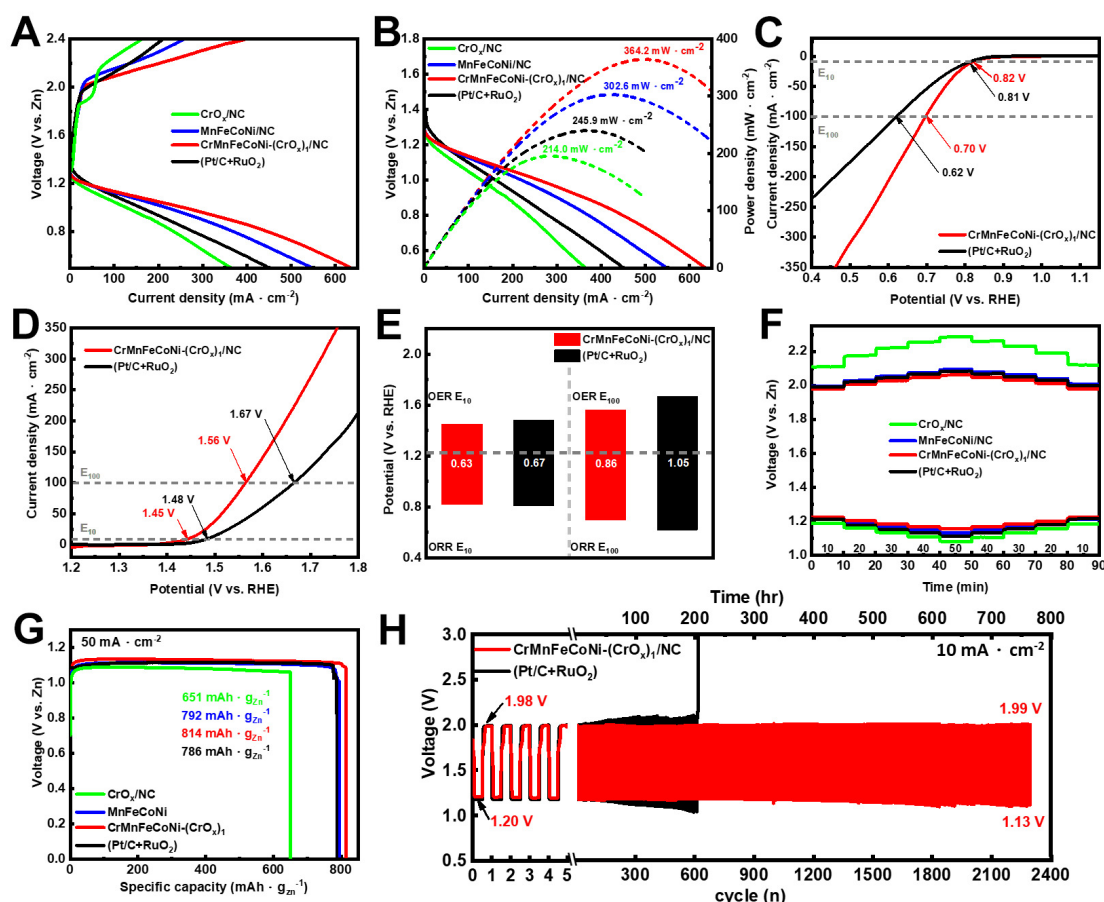


Figure 5. Electrochemical characterizations of CrO_x/NC , $\text{MnFeCoNi}/\text{NC}$, $\text{CrMnFeCoNi}-(\text{CrO}_x)_1/\text{NC}$, and $(\text{Pt}/\text{C}+\text{RuO}_2)$ -based ZABs: (A) discharge-charge polarization curves and (B) corresponding power density curves at current ramping rate of 1 mA s^{-1} ; (C) ORR LSV curves, (D) OER LSV curves, and (E) potential gaps (ΔE_{10} and ΔE_{100}) of $\text{CrMnFeCoNi}-(\text{CrO}_x)_1/\text{NC}$ and $(\text{Pt}/\text{C}+\text{RuO}_2)$ -based air electrodes in 6.0 M KOH at scan rate of 1 mV s^{-1} ; (F) Step voltage diagrams of CrO_x/NC , $\text{MnFeCoNi}/\text{NC}$, $\text{CrMnFeCoNi}-(\text{CrO}_x)_1/\text{NC}$, and $(\text{Pt}/\text{C}+\text{RuO}_2)$ -based ZABs working at varying charge/discharge current densities from 10 to 50 and then back to 10 mA cm^{-2} ; (G) Specific capacities achieved by CrO_x/NC , $\text{MnFeCoNi}/\text{NC}$, $\text{CrMnFeCoNi}-(\text{CrO}_x)_1/\text{NC}$, and $(\text{Pt}/\text{C}+\text{RuO}_2)$ -based ZABs at 50 mA cm^{-2} ; (H) Galvanostatic cycling discharge-charge stability tests of $\text{CrMnFeCoNi}-(\text{CrO}_x)_1/\text{NC}$ and $(\text{Pt}/\text{C}+\text{RuO}_2)$ -based ZABs at 10 mA cm^{-2} with duration of 20 min per cycle (10 min discharge + 10 min charge). ORR: Oxygen reduction reaction; LSV: linear sweep voltammetry; OER: oxygen evolution reaction; ZABs: zinc-air batteries.

($245.9 \text{ mW} \cdot \text{cm}^{-2}$ at $359.8 \text{ mA} \cdot \text{cm}^{-2}$)-based ones. Furthermore, as evident from Figure 5A, the $\text{CrMnFeCoNi}-(\text{CrO}_x)_1/\text{NC}$ -based ZAB functions with the narrowest charge-discharge voltage gaps, largely outperforming all other characterized ZABs, and its superiority turns more pronounced with increasing working current densities. These results indicate outstanding discharge-charge performances of the $\text{CrMnFeCoNi}-(\text{CrO}_x)_1/\text{NC}$ -based ZAB.

In this study, the air electrode was fabricated by pressing firmly a gas diffusion carbon paper layer with a porous catalyst-loaded NF layer to form a composite binder-free air electrode. Unlike the traditional binder assisted catalyst ink drop-casting process, the catalyst in this work was grown *in-situ* on the skeleton surface of NF, thus being binder-free. To examine the merit of the binder-free approach in loading catalysts, the discharge-charge polarization curve and the corresponding discharge power density curve of the drop-cast $\text{CrMnFeCoNi}-(\text{CrO}_x)_1/\text{NC}$ -based ZAB were collected for comparison with those achieved by the $\text{CrMnFeCoNi}-(\text{CrO}_x)_1/\text{NC}$ and $(\text{Pt}/\text{C}+\text{RuO}_2)$ -based ZABs [Supplementary Figure 15C and D]. For the

drop-cast CrMnFeCoNi-(CrO_x)₁/NC-based ZAB, a current density of 263.7 mA cm⁻² at a charging potential of 2.4 V and a discharge peak power density of 299.1 mW cm⁻² at 451.1 mA cm⁻² are obtained, significantly inferior to those of the CrMnFeCoNi-(CrO_x)₁/NC-based ZAB. These results indicate that catalyst-loading through drop-casting catalyst inks, that contain generally non-conductive polymer binders, leads to reduced catalytic efficiency toward ORR and OER, attributable to the reduced exposure of the catalyst and electrical conductivity of the air electrode. Furthermore, non-uniform loading and aggregation of the catalyst worsen the situation. [Supplementary Figure 16](#) shows the SEM images of the drop-cast CrMnFeCoNi-(CrO_x)₁/NC particles on skeleton surfaces of the NF substrate. Evidently, the catalyst coverage is not uniform, with some part of the skeleton surface uncovered with catalysts, and aggregation of the catalyst particles occurs, reducing the exposed catalyst surface, both detrimental to the catalytic efficiency of the catalyst.

Electrochemical performances of the sample catalysts toward ORR and OER were further characterized in a half-cell setting, in which the catalyst loaded air electrode served as the working electrode and 6 M KOH served as the electrolyte, to more accurately assess the catalytic efficiency of the sample air electrode catalysts in an air electrode setting. [Figure 5C](#) and [D](#) shows the LSV curves recorded for the sample air electrode catalysts toward ORR and OER, respectively. Evidently, the CrMnFeCoNi-(CrO_x)₁/NC-based air electrode outperforms the (Pt/C+RuO₂)-based one, with the superiority of the CrMnFeCoNi-(CrO_x)₁/NC-based air electrode turns more pronounced at increasing applied potentials/current densities. The superiority of the CrMnFeCoNi-(CrO_x)₁/NC-based air electrode over the (Pt/C+RuO₂)-based one, can be more clearly comprehended in terms of applied potentials needed to achieve specific current densities, such as E₁₀ for 10 mA cm⁻² and E₁₀₀ for 100 mA cm⁻². For the CrMnFeCoNi-(CrO_x)₁/NC-based air electrode, E₁₀ and E₁₀₀ are 0.82/1.45 V and 0.70/1.56 V for ORR/OER, respectively, significantly higher/lower than 0.81/1.48 V and 0.62/1.67 V achieved by the (Pt/C+RuO₂)-based air electrode. The charge-discharge potential gaps at 10 and 100 mA cm⁻², ΔE₁₀ and ΔE₁₀₀, respectively, achieved by the CrMnFeCoNi-(CrO_x)₁/NC-based air electrode (0.63 and 0.86 V) thus are significantly narrower than those obtained by the (Pt/C+RuO₂)-based one (0.67 and 1.05 V) [[Figure 5E](#)]. The above results are the main reasons to explain why the CrMnFeCoNi-(CrO_x)₁/NC-based ZAB performs much better than the (Pt/C+RuO₂)-based one, with much narrower charge-discharge voltage gaps and a much higher discharge peak power density. And the superiority of the CrMnFeCoNi-(CrO_x)₁/NC-based ZAB turns more pronounced with increasing working current densities.

[Figure 5F](#) and [Supplementary Figure 17A](#) present the step voltage diagrams for each sample ZAB working at varying charge/discharge current densities from 10 to 50 and then back to 10 mA cm⁻². The CrMnFeCoNi-(CrO_x)₁/NC-based ZAB consistently exhibits superior charge/discharge platforms and narrower voltage gaps, as compared to those of the MnFeCoNi/NC, CrO_x/NC, and even (Pt/C+RuO₂)-based ones, with the superiority turning more pronounced at increasing working current densities. The voltage recovery rates of the tested ZABs at the end of the tests are summarized in [Supplementary Table 6](#) for comparison. The CrMnFeCoNi-(CrO_x)₁/NC-based ZAB exhibits the highest voltage recovery rates, 99.99% for the discharging and 99.95% for the charging. The above results indicate that the CrMnFeCoNi-(CrO_x)₁/NC-based ZAB achieved not only outstanding charge/discharge efficiency but also outstanding voltage recovery characteristics, relevant to enhanced stability, high reversibility, and sustained catalytic performances. Furthermore, at a working current density of 50 mA cm⁻², the CrMnFeCoNi-(CrO_x)₁/NC-based ZAB achieves a specific capacity of 814 mAh g_{Zn}⁻¹ and an energy density of 918 Wh kg_{Zn}⁻¹, surpassing 786 mAh g_{Zn}⁻¹ and 874 Wh kg_{Zn}⁻¹, respectively achieved by the (Pt/C+RuO₂)-based one, and approaching the theoretical limits of 820 mAh g_{Zn}⁻¹ and 1312 Wh kg_{Zn}⁻¹, respectively [[Figure 5G](#) and [Supplementary Figure 17B](#)]. In comparison, ZABs constructed based on catalysts without the heterostructure, MnFeCoNi/NC and CrO_x/NC, show lower specific capacities of 792 and 651 mAh g_{Zn}⁻¹, respectively, with corresponding lower

energy densities of 878 and 702 Wh kg_{Zn}⁻¹, respectively, than those acquired by the three heterostructured catalyst-based ZABs [Supplementary Figure 17C and D].

Finally, the durability of the ZABs was assessed with long-term cycling operations. Figure 5H shows the cycling discharge-charge profiles of the CrMnFeCoNi-(CrO_x)₁/NC and (Pt/C+RuO₂)-based ZABs at a current density of 10 mA cm⁻² with a duration of 20 min per cycle. Initially, the CrMnFeCoNi-(CrO_x)₁/NC-based ZAB exhibits charging and discharging plateaus of 1.98 and 1.20 V, respectively, giving a voltage gap of 0.78 V. In comparison, the (Pt/C+RuO₂)-based ZAB shows slightly inferior initial charging and discharging plateaus of 2.00 and 1.18 V, respectively with a voltage gap of 0.82 V. After approximately 600 cycles, the (Pt/C+RuO₂)-based ZAB experiences a noticeable operation failure, whereas the CrMnFeCoNi-(CrO_x)₁/NC-based one continues to operate stably. Even after approximately 2,300 cycles, the discharging plateau of the CrMnFeCoNi-(CrO_x)₁/NC-based ZAB shows only a slight decrease to 1.13 V, whereas the charging plateau increases only marginally to 1.99 V, leading to an overall voltage gap decay of only 10.2%. Given the outstanding cycling discharge-charge stability of the CrMnFeCoNi-(CrO_x)₁/NC-based ZAB at 10 mA cm⁻², an additional cycling test was conducted at a high current density of 50 mA cm⁻² [Supplementary Figure 18]. The CrMnFeCoNi-(CrO_x)₁/NC-based ZAB exhibits far superior discharge-charge efficiency to the (Pt/C+RuO₂)-based one right from the beginning, with initial charging and discharging plateaus of 2.00 and 1.13 V, respectively, and a narrow voltage gap of 0.87 V, significantly better than the initial charging and discharging plateaus of 2.10 and 1.13 V, respectively and the initial voltage gap of 0.97 V achieved by the (Pt/C+RuO₂)-based ZAB. After 120 cycles, the (Pt/C+RuO₂)-based ZAB fails, whereas the CrMnFeCoNi-(CrO_x)₁/NC-based one maintains stable operations even after 300 cycles, highlighting its superior durability even at high current densities.

In-situ spectroscopic analyses

In-situ Raman spectroscopy and *in-situ* XAS were conducted to gain insights on the mechanisms of ORR and OER catalyzed by CrMnFeCoNi-(CrO_x)₁/NC. Figure 6 shows the *in-situ* XANES and EXAFS spectra and *in-situ* Raman spectra collected for CrMnFeCoNi-(CrO_x)₁/NC toward catalysis of ORR. Figure 6A-E presents the *in-situ* XANES spectra of constituent metal elements of CrMnFeCoNi-(CrO_x)₁/NC at open-circuit potential (OCP) and 0.6 V (*vs.* RHE), with the XANES spectra of corresponding metallic foils and metal oxide standards included for comparison. Note that some colored curves are not observed because of close curve overlapping. When the electrode is immersed in the electrolyte without applications of biases (*i.e.*, at OCP), the valence state of Cr is close to that of Cr₂O₃, whereas the absorption edges of Mn, Fe, Co, and Ni align well with those of the corresponding metal foils, indicating that the valence states of these elements do not change upon contact with the electrolyte. Upon elevating the applied potential to 0.6 V (*vs.* RHE), no significant shifts in the absorption edges are observed for any of the elements, suggesting that Cr oxide remains unreduced under the ORR conditions and that Mn, Fe, Co, and Ni retain their metallic states. Figure 6F-J displays the corresponding EXAFS spectra in R-space. At 0.6 V (*vs.* RHE), reductions in intensity of the metal-metal coordination peak located at around 2.2 Å are observed for Mn, Fe, and Co. This phenomenon may be attributed to adsorption of oxygen-containing intermediates of weaker backscattering abilities, leading to reductions in metal-metal coordination strength. This observation suggests that Mn, Fe, and Co serve as active catalytic sites during the ORR.

Figure 6K presents *in-situ* Raman spectra of CrMnFeCoNi-(CrO_x)₁/NC under varying applied potentials. Initially, no signals other than the D and G bands of the N-doped carbon supports are observed for the dry samples. Upon contact with the electrolyte, the spectra remain unchanged at OCP and the applied potential of 0.9 V (*vs.* RHE). Further lowering the applied potential to 0.8 V, corresponding to an increase in reducing powers, a pronounced peak appears at 1,056 cm⁻¹, attributable to vibrations of superoxo (O₂⁻) intermediates^[25,26], indicating proceeding of the ORR. The intensity of this characteristic peak increases with

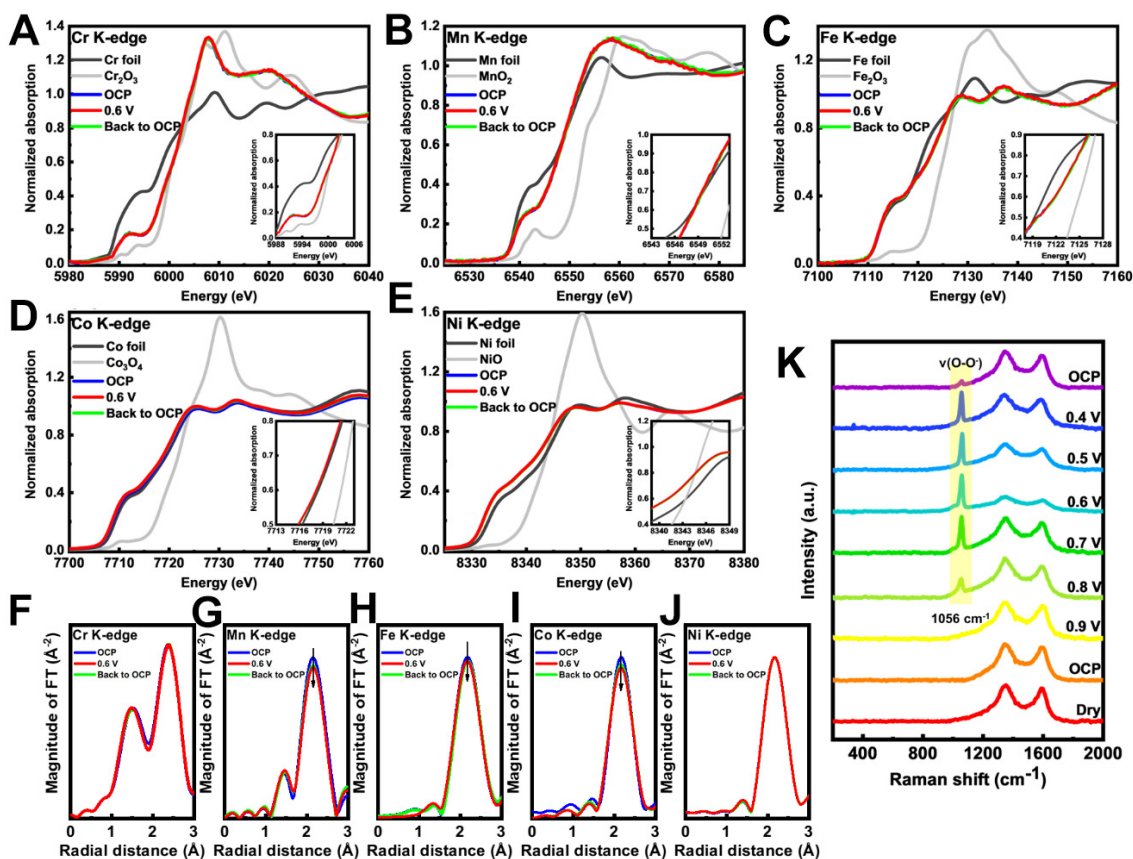


Figure 6. *In-situ* XANES spectra for ORR catalyzed by CrMnFeCoNi-(CrO_x)₁/NC at (A) Cr K-edge, (B) Mn K-edge, (C) Fe K-edge, (D) Co K-edge, and (E) Ni K-edge; Corresponding EXAFS spectra in R space ($k=2$) for (F) Cr K-edge, (G) Mn K-edge, (H) Fe K-edge, (I) Co K-edge, and (J) Ni K-edge; (K) *In-situ* Raman spectra of ORR catalyzed by CrMnFeCoNi-(CrO_x)₁/NC. XANES: X-ray absorption near edge structure; ORR: oxygen reduction reaction; EXAFS: extended X-ray absorption fine structure.

further decreasing applied potentials (i.e., increasing reducing powers), reaching its maximum at 0.6 V, indicating increasing extent of ORR. The intensity of this characteristic peak slightly decreases with further decreasing applied potentials from 0.6 V to 0.4 V and drops significantly upon returning to the OCP. The observed variations in peak intensity can be correlated to the coverage of the superoxo intermediate on the catalyst surface. At high applied potentials (i.e., low reducing powers), the catalyst surface is only partially covered by the superoxo intermediate. As the applied potential decreases (i.e., increasing reducing powers), more superoxo intermediates adsorb onto the catalyst surface, resulting in an increase in peak intensity. Subsequently, at even lower applied potentials (i.e., even higher reducing powers), part of the superoxo intermediates are successfully reduced to hydroxide ions, leading to a slight decrease in peak intensity. Upon ceasing application of the potential, the superoxo intermediates largely desorb from the catalyst surface, resulting in a sharp drop in intensity of the characteristic peak.

Figure 7 presents the *in-situ* XANES and EXAFS spectra and *in-situ* Raman spectra collected for CrMnFeCoNi-(CrO_x)₁/NC toward catalysis of OER. Figure 7A shows the Cr K-edge XANES spectra, which reveal a significant increase in intensity of the pre-edge absorption peak, accompanied by a 0.4 eV upshift in peak positions from 5,992.9 eV to 5,993.3 eV, upon application of a 1.6 V (vs. RHE) potential. This phenomenon suggests a structural transformation wherein part of the octahedral Cr₂O₃ of CrMnFeCoNi-(CrO_x)₁/NC is converted to tetrahedral CrO₃ of a higher-valence Cr. This transformation

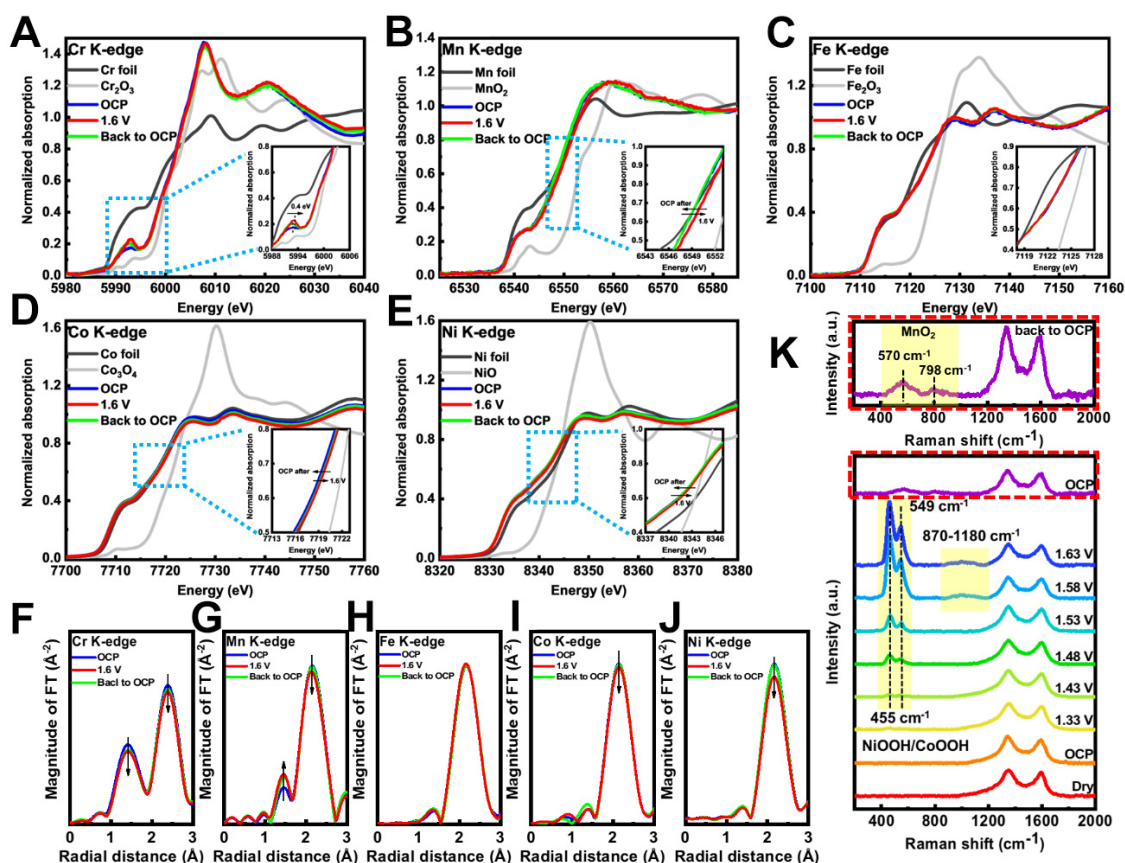


Figure 7. In-situ XANES spectra for OER catalyzed by CrMnFeCoNi-(CrO_x)₁/NC at (A) Cr K-edge, (B) Mn K-edge, (C) Fe K-edge, (D) Co K-edge, and (E) Ni K-edge. Corresponding EXAFS spectra in R space ($k=2$): (F) Cr K-edge, (G) Mn K-edge, (H) Fe K-edge, (I) Co K-edge, and (J) Ni K-edge; (K) In-situ Raman spectra of OER catalyzed by CrMnFeCoNi-(CrO_x)₁/NC. XANES: X-ray absorption near edge structure; OER: oxygen evolution reaction; EXAFS: extended X-ray absorption fine structure.

allows part of the forbidden 1s to 3d transition in the octahedral Cr₂O₃ structure to become permitted in the tetrahedral CrO₃ structure, resulting in a pronounced increase in intensity of the pre-edge peak under the applied anodic bias. Upon removal of the anodic bias, the driving force for this structural transformation is lost, and the tetrahedral CrO₃ reverts to the octahedral Cr₂O₃.

Furthermore, the K-edge XANES spectra of Mn, Co, and Ni (Figure 7B, D and E, respectively) show significant shifts in absorption edge positions to higher energies under anodic conditions, indicating slight oxidation of Mn, Co, and Ni of CrMnFeCoNi-(CrO_x)₁/NC during OER. Figure 7F-J depicts the K-edge EXAFS spectra in R-space for constituent metal elements of CrMnFeCoNi-(CrO_x)₁/NC under anodic conditions. Under the applied anodic bias, both the first and second coordination shells of Cr exhibit a decrease in peak intensity. The intensity reduction of the first shell located at 1.5 Å is attributed to the transformation of part of the octahedral Cr₂O₃ to tetrahedral CrO₃ during OER. For CrO₃, the number of oxygen atoms coordinating with Cr (4 Cr-O) is less than that in Cr₂O₃ (6 Cr-O), thereby reducing the intensity of the first coordination shell. Furthermore, in the tetrahedral crystalline structure (CrO₃), Cr and O are more loosely packed than in the octahedral crystalline structure (Cr₂O₃), and thus partial conversion of Cr₂O₃ to CrO₃ results in a decrease in intensity of the second coordination shell (Cr-O-Cr). The above observations conclude that partial conversion of Cr₂O₃ to CrO₃ occurs during OER^[27]. In addition, it has been proposed that oxidation of Cr₂O₃ protects β-NiOOH, a highly OER-active intermediate, from being

overoxidized into γ -NiOOH, a less OER-active species, during the OER process^[28,29]. For Mn, Co, and Ni, their K-edge EXAFS spectra in R-space exhibit intensity reductions for the metal-metal coordination shell located at 2.2 Å upon application of the anodic potential. For Mn, its Mn-O coordination shell located at 1.4 Å receives a boost in intensity. These phenomena may be attributed to adsorption of oxygen-containing species of weaker backscattering abilities, leading to reductions in metal-metal coordination strength and boost in metal-O coordination strength. This observation suggests that Mn, Co, and Ni serve as active catalytic sites during the OER process.

In-situ Raman spectra recorded for CrMnFeCoNi-(CrO_x)₁/NC at varying applied anodic potentials were used to investigate potential intermediates involved in the OER process [Figure 7K]. In the dry state and at low anodic potentials, no characteristic peaks other than the D and G bands of the N-doped carbon support are observed. Upon elevating the anodic potential to 1.43 V (vs. RHE), weak characteristic peaks emerge at 455 and 549 cm⁻¹, which turn more pronounced with increasing anodic potentials. These peaks are attributed to Ni/Co oxyhydroxides (NiOOH and CoOOH), which are well-recognized as favorable intermediates for OER^[30-32]. As the anodic potential increases to 1.58 V, an additional broad weak peak appears in the range of 870-1,180 cm⁻¹, attributable to the vibration of superoxide intermediates (M-O₂) interacting laterally with metal sites. These superoxide intermediates, formed from oxyhydroxides, can only be observed at high enough anodic potentials^[30,33]. Upon ceasing application of the anodic potential, characteristic peaks for Ni/CoOOH and corresponding superoxides almost disappear, whereas peaks at around 570 and 798 cm⁻¹, attributable to MnO₂^[30,34], emerge. The driving force for formation of Ni/CoOOH and corresponding superoxides disappears upon returning the bias to the OCP, leading to desorption of oxygen-containing species from the catalyst surface and thus disappearance of the associated peaks. As to the emergence of characteristic peaks associated with MnO₂, it can be explained as follows. The concentration of Mn in CrMnFeCoNi-(CrO_x)₁/NC is quite low, and thus the concentration of MnO₂ derived from Mn is even lower. Consequently, the peaks associated with MnO₂ cannot be observed under the relatively strong showing of the peaks associated with Ni/CoOOH. These peaks however become pronounced upon disappearance of the Ni/CoOOH peaks. The findings concluded from the *in-situ* Raman study align well with those from the *in-situ* XAS investigation, revealing that Mn, Co, and Ni serve as the primary active sites for OER.

CONCLUSION

A non-precious quinary alloy-metal oxide heterostructured catalyst, CrMnFeCoNi-(CrO_x)₁/NC, was developed as an outstanding bifunctional catalyst for a binder-free composite air electrode, based on which a high-performance ZAB was fabricated. The heterostructured catalyst showed outstanding catalytic efficiency toward catalysis of ORR and OER, achieving a high $E_{1/2}$ of 0.834 V for ORR and a low η_{10} of 273 mV for OER in 0.1 M KOH, outperforming the noble metal-based benchmark catalysts, Pt/C for ORR (0.820 V) and RuO₂ (284 mV) for OER. The CrMnFeCoNi-(CrO_x)₁/NC-based ZAB exhibited an ultrahigh discharge peak power density of 364 mW cm⁻², an ultra-narrow working voltage gap of 0.78 V at 10 mA cm⁻², and ultra-stability of 765 h at 10 mA cm⁻², largely outperforming the (Pt/C+RuO₂)-based one (246 mW cm⁻², 0.82 V, 200 h). [Supplementary Table 7](#) summarizes electrochemical performances of state-of-the-art non-precious heterostructure-based catalysts and ZABs reported in recent years. Evidently, the CrMnFeCoNi-(CrO_x)₁/NC heterostructured catalyst-based ZAB stands out with the narrowest charge-discharge voltage gap, highest discharge peak power density, and longest stability.

In-situ Raman and XAS spectroscopy studies revealed that Mn, Fe, and Co served as the primary ORR active sites, and Mn, Co, and Ni worked as the main active sites for catalysis of OER. The presence of Cr₂O₃ helped boost the ORR and OER performances by offering abundant oxygen vacancies to enhance oxygen

adsorption for ORR and by protecting OER-active intermediates from over-oxidation through its oxidation-prone characteristics. Heterostructure engineering proves to be an effective approach to boost activities and stability of bifunctional catalysts to elevate discharge-charge performances of ZABs. Multi-element-based alloy-metal oxide heterostructured catalysts are particularly promising because of the unique atomic scale synergies between constituent elements to further enhance the electrocatalytic performances of the bifunctional catalysts.

DECLARATIONS

Authors' contributions

Data curation, formal analysis, investigation, methodology, software, validation, writing - original draft: Yen, F. Y.

Data curation, formal analysis, investigation: Chang, S. I.; Ting, Y. C.; Chang, C. W.; Lee, K. A.

Conceptualization, funding acquisition, project administration, supervision, validation, visualization, writing - review and editing: Lu, S. Y.

Availability of data and materials

The detailed materials and methods in the experiment are available within the [Supplementary Materials](#). Further data are available from the corresponding author upon reasonable request.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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