



Trimetallic Prussian blue analog/sulfonated carbon cloth electrodes for enhanced and selective Pb^{2+} capture from solution via capacitive deionization

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ARTICLE INFO

Editor Name: Choe Earn Choong

Keywords:

Electrochemical desalination
Structural tailoring
Nanoframe architecture
Heavy metal
Selectivity

ABSTRACT

Severe lead ion (Pb^{2+}) pollution necessitates efficient electrochemical remediation technologies, yet conventional capacitive deionization (CDI) is often hindered by inadequate electrode capacity and selectivity. Herein, we rationally design two sets of Cu-based Prussian blue analogs (PBAs) with cubic, nanobox, and nanoframe structures (CuMnHCF and $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF}$) integrated with sulfonated carbon cloth (sCC) for selective Pb^{2+} extraction via a rocking-chair CDI (RCDI) platform. Through structural tailoring, the nanoframe (NF) architecture provides shortened ion diffusion pathways and mitigates structural strain, while the sCC substrate contributes high conductivity and abundant ion-exchange sites. Electrochemical evaluations reveal that the nanoframe-structured electrodes exhibit optimal ion transport, improved specific capacitance, and robust stability. Notably, the CuMnHCF-NF/sCC electrode achieves an exceptional Pb^{2+} capture capacity of 354.5 mg g^{-1} at 1.2 V in 500 mg L^{-1} of Pb^{2+} solution. Furthermore, both nanoframe electrodes demonstrate durable performance, retaining 77.7% (CuMnHCF-NF) and 75.9% ($\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF}$) of their capacity over 40 consecutive intercalation/deintercalation cycles. Importantly, the $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF/sCC}$ electrode exhibits outstanding Pb^{2+} selectivity over competing ions, achieving separation factors of 2.5 for Pb^{2+} over Na^+ , 10.9 over Ca^{2+} , and 8.53 over Mg^{2+} in equivalent systems. This selectivity is fundamentally attributed to the lower hydration energy and higher polarizability of Pb^{2+} , coupled with the synergistic Faradaic lattice intercalation of the tailored PBA framework and non-Faradaic electrosorption of sCC. This work demonstrates that structurally tailored trimetallic PBA/sCC composites overcome traditional CDI trade-offs, offering a promising material platform for targeted heavy metal remediation.

1. Introduction

The pervasive contamination of global water systems by heavy metals represents one of the most severe environmental and public health challenges of the modern era [1]. Of these pollutants, lead (Pb^{2+}) is particularly notorious for its acute toxicity, chronic bioaccumulative nature, and environmental persistence [2]. To mitigate Pb^{2+} pollution, conventional water treatment technologies such as chemical precipitation, adsorption, membrane filtration, and ion exchange have been widely deployed [3]. However, these traditional methods suffer from

critical limitations: chemical precipitation generates substantial secondary sludge requiring further disposal; adsorption processes often exhibit sluggish kinetics and poor regenerability; membrane filtration demands high transmembrane pressures leading to exorbitant energy costs; and ion exchange resins are highly susceptible to fouling and exhibit diminished efficiency at trace concentrations [3,4]. These inherent limitations underscore the urgent need for advanced, energy-efficient, and highly selective alternative technologies capable of effectively remediating Pb^{2+} -contaminated water matrices.

Capacitive deionization (CDI) has arisen as a highly promising and

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<https://doi.org/10.1016/j.seppur.2026.140341>

Received 26 July 2026; Received in revised form 8 September 2026; Accepted 25 September 2026

Available online 26 September 2026

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energy-efficient technology for desalination and water treatment, offering a viable alternative to address the limitations of conventional methods [5–8]. Generally, CDI operates by removing charged ions from water through their electrosorption into the electrical double layers (EDLs) of porous electrodes under an applied electric field, a process that is inherently low-energy, reagent-free, and reversible [9]. The efficacy of CDI hinges critically on the development of high-performance electrode materials, with carbonaceous materials like activated carbon and carbon nanotubes being the most extensively studied due to their high surface areas and good electrical conductivity [10–12]. However, for the specific challenge of heavy metal removal, carbon-based electrodes exhibit substantial drawbacks, including poor selectivity and limited adsorption capacity for divalent ions such as Pb^{2+} , as well as degradation of performance in the presence of competing cations often found in real water matrices [7,13]. To address these limitations, for instance, surface modification of carbonaceous electrodes with specific functional groups is a primary strategy for enhancing Pb^{2+} capture [13–18]. Besides, integration of two-dimensional (2D) graphene, reduced graphene oxide (rGO), or 1D carbon nanotubes (CNTs) into electrode architectures was found to significantly improve affinity for Pb^{2+} and thus the adsorption capacity [19–22]. Apart from carbon-based and bio-derived materials, faradaic or intercalation-type electrode materials (e.g., metal oxides/sulfides, MXene) that utilize redox reactions and intercalation have gained considerable attention in boosting the adsorption capacity for Pb^{2+} from solutions [23–29]. Prussian blue analogs (PBAs), with their open 3D framework and general formula $\text{A}_x\text{M}_1[\text{M}_2(\text{CN})_6]_y \cdot n\text{H}_2\text{O}$ (A = alkali or alkaline-earth metals, M_1 and M_2 are transition metals, $0 \leq x \leq 2$, $y < 1$), are a leading example, enabling efficient and selective ion storage via reversible intercalation/deintercalation [30–32]. Despite this promise, binary metal PBAs, such as copper hexacyanoferrate (CuHCF) and nickel hexacyanoferrate (NiHCF), have demonstrated practical limitations for Pb^{2+} capture [33,34]. Their performance is often constrained by insufficient capacity, structural instability during repeated electrochemical cycling, and, critically, a lack of preferential selectivity for Pb^{2+} over other common cations like Ca^{2+} , Mg^{2+} , and Na^+ [34,35].

These shortcomings of binary PBA materials suggest that a more sophisticated materials design strategy is needed to holistically enhance the adsorption capacity, structural stability, and selectivity of PBA electrodes toward Pb^{2+} ions. Recent materials science has highlighted that ternary metal doping can be a powerful tool to modulate and optimize the properties of PBA frameworks [35]. Introducing a third transition metal into the binary PBA structure offers a multifaceted strategy for performance enhancement [36,37]. Despite this scientific promise, the application of ternary metal PBA materials as CDI electrodes for targeted Pb^{2+} capture remains largely unexplored. There is a clear deficiency in the fundamental understanding of how the composition and microstructure of a ternary metal PBA influence its Pb^{2+} capture performance, and what the dominant mechanism for Pb^{2+} selectivity is in such a system. This missing knowledge is the central impediment to the rational design of ingenious PBA-based electrodes for this application. This knowledge gap is particularly important because the performance of PBA-based electrodes depends not only on their open-framework chemistry but also on the coupled effects of metal composition and hierarchical architecture [38]. Thus, a systematic comparison of trimetallic composition and morphology is needed to determine how these parameters regulate Pb^{2+} transport, capture, selectivity, and cycling behavior.

This study aims to bridge this knowledge gap by designing and preparing two sets of Cu-based trimetallic PBAs (i.e., CuMnHCF and CuNiHCF) with diverse shapes—cubic, nanobox, and nanoframe—and systematically evaluating the CDI performance of PBA-integrated sulfonated carbon cloth (PBA/sCC) electrodes for Pb^{2+} capture. The choice of a Cu-based PBA is strategically motivated by its excellent structural integrity and favorable electrochemical kinetics, which serve as an ideal platform for tertiary metal integration. The research encompasses three

integrated phases: first, the controlled synthesis and physicochemical characterization of the trimetallic Cu-based PBA properties; second, the evaluation of electrochemical properties; and third, comprehensive CDI deionization experiments, including kinetic analysis, capacity determination, selectivity tests, and cycling stability assessments. Mn and Ni were introduced as two representative dopants to probe composition-dependent electrochemical Pb^{2+} capture behavior based on previously established recipes or ratios [39,40], probably due to their electronic and lattice-regulating abilities [38,41]. By integrating experimental validation with mechanistic analysis, this work establishes a novel electrode design strategy for efficient and selective heavy metal capture. More broadly, it offers essential theoretical and experimental support for the practical application of PBA-based CDI systems, advancing the frontier of lead-contaminated water remediation.

2. Experimental section

All chemicals are of at least reagent purity and were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) unless otherwise specified. All solutions were prepared using ultrapure deionized water ($\text{DI H}_2\text{O}$) with resistivity $\geq 18 \text{ M}\Omega\cdot\text{cm}$ at 25°C .

2.1. Preparation and characterization of the trimetallic Cu-based PBAs

Two groups of trimetallic Cu-based PBAs, i.e., CuMnHCF and $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF}$, with microstructures of cubic (C), nanobox (NB), and nanoframe (NF) were prepared using chelator-assisted co-precipitation coupled with acid etching and cation exchange approach [40] (Fig. 1a), and evaluated as electrodes for enhanced and selective Pb^{2+} capture from solution on a rocking-chair capacitive deionization (RCDI) platform in the present work. The preparatory procedures of the PBAs and sCC are detailed in Supplementary Text S1 (Supplementary data). The crystallography, surface composition, surface functional groups, and morphological properties of the as-prepared PBAs were characterized comprehensively. Specifically, X-ray diffraction (XRD) analysis was performed on an XRD-6100 diffractometer (Shimadzu, Japan) at a tube voltage of 40 kV and a tube current of 30 mA with Cu-K α radiation. X-ray fluorescence spectroscopy (XRF) analysis was conducted on a portable DELTA DC-4000 analyzer (Olympus, USA) in soil mode. Fourier transform infrared (FTIR) spectroscopic measurement was carried out following the KBr method on an infrared spectrometer (Nicolet iS5, Thermo Fisher, USA). Thermogravimetric analysis (TGA) was conducted using a LABSYS EVO thermal analyzer (Setaram, France) under a nitrogen atmosphere from room temperature to 700°C at a heating rate of $10^\circ\text{C min}^{-1}$. The morphology of all trimetallic PBA samples was examined on a ZEISS Gemini 300 field emission scanning electron microscope (SEM, ZEISS, Germany).

2.2. Electrochemical measurements

Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) tests were performed in a 0.5 mM PbCl_2 (equivalent to $103.6 \text{ mg L}^{-1} \text{ Pb}^{2+}$) solution using a CORRTST CS310H electrochemical workstation (Wuhan, China) with a three-electrode system. An active material-decorated carbon cloth ($1 \times 2 \text{ cm}^2$, effective area, $1 \times 1 \text{ cm}^2$) was used as the working electrode, with a platinum sheet electrode ($1 \times 1 \text{ cm}^2$) and a saturated Ag/AgCl (3 M KCl) electrode as the counter and reference electrodes, respectively. The working electrode was prepared by repeatedly grinding a mixture of 80% active material, 10% acetylene black, and 10% polyvinylidene fluoride (PVDF) with a small amount of 1-methyl-2-pyrrolidone (NMP) into a slurry and loading it on a sulfonated carbon cloth ($1 \text{ cm} \times 1 \text{ cm}$, 0.33 mm thick). Finally, the electrodes to be tested were dried overnight at 85°C under vacuum to remove NMP, and the amount of active substance loaded on each piece of carbon cloth was 1–2 mg. More details on electrochemical characterizations are presented in Supplementary Text

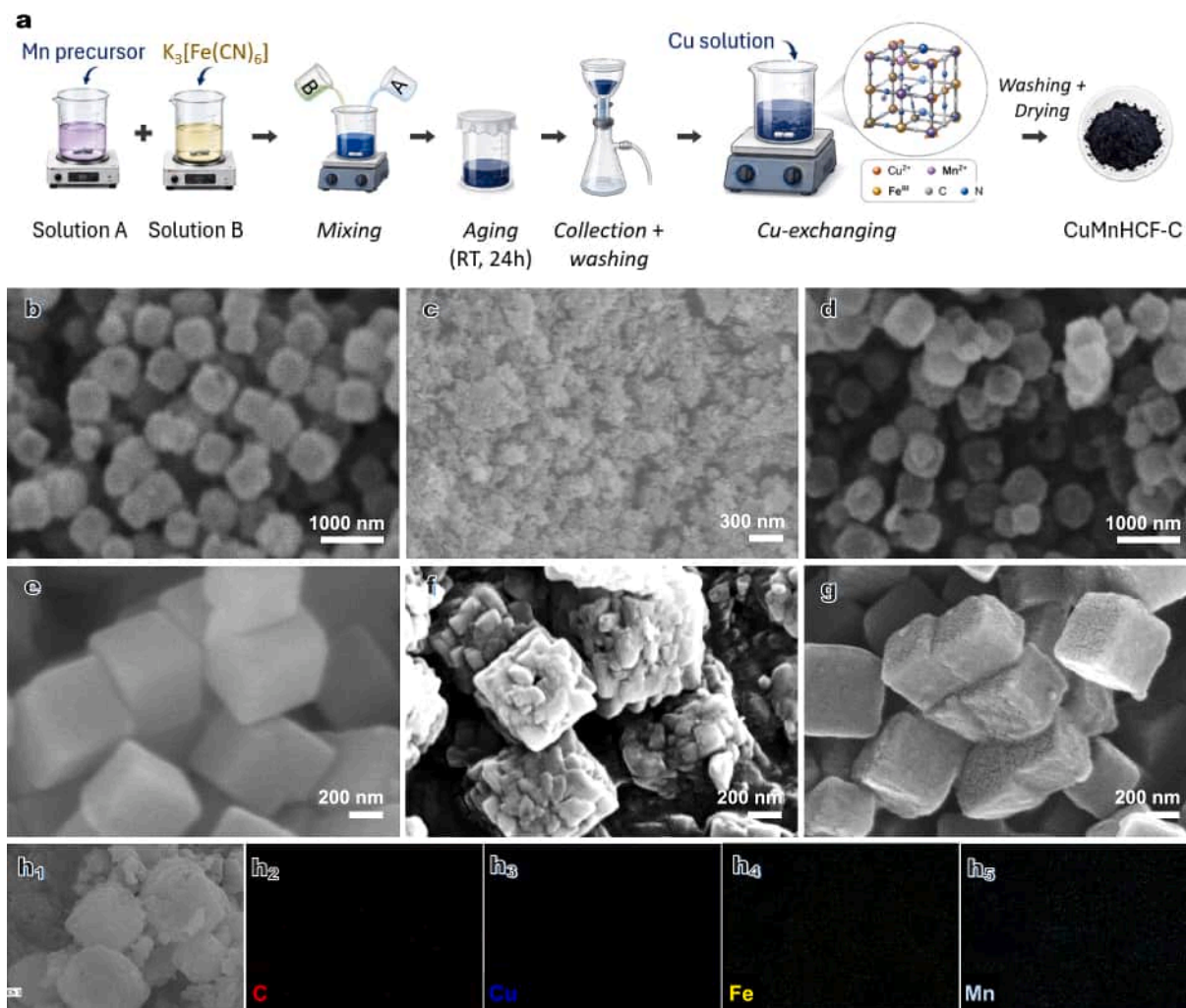


Fig. 1. (a) Schematic illustration of the preparation of typical PBA (e.g., CuMnHCF-C), (b–g) FE-SEM images of the as-prepared (b) Cu_{0.6}Ni_{0.4}HCF-C, (c) Cu_{0.6}Ni_{0.4}HCF-NB, (d) Cu_{0.6}Ni_{0.4}HCF-NF, (e) CuMnHCF-C, (f) CuMnHCF-NB, and (g) CuMnHCF-NF, and (h) SEM images and the corresponding EDX element mapping of CuMnHCF-NF showing the uniform distribution of C, Cu, Fe and Mn (h₂ – h₅).

S2.

2.3. Capacitive deionization test

Following the same procedure for fabricating the working electrodes, the PBA/sCC electrodes for CDI were fabricated in a size of $5 \times 5 \text{ cm}^2$ (more details are given in Text S3). The desalination experiment was performed in a homemade RCDI platform (Fig. S1, Supplementary data) containing a custom-built cell of a symmetric configuration of electrodes (Fig. S2). The cell was operated in batch mode and under constant voltage conditions for all the desalination tests. A total of 30 mL of Pb²⁺ solution ($100\text{--}1000 \text{ mg L}^{-1}$) was consecutively circulated between the RCDI cell (inside volume $\sim 5 \text{ mL}$) and the Pb²⁺ solution reservoir at a flow rate of 40 mL min^{-1} . The conductivity of the effluent was successively monitored by a DDSJ-308A conductivity meter (INESA Scientific Instrument Co., Shanghai, China) and used to calculate the Pb²⁺ concentration (Fig. S3). To examine the selectivity of electrodes, synthetic binary solutions of Pb²⁺/Na⁺ and ternary solutions of Pb²⁺/Ca²⁺/Mg²⁺ with varying molar ratios were employed. The concentration of each ion before and after RCDI operations was determined by an Optima 8300 (PerkinElmer, USA) inductively coupled plasma optical emission spectroscopy (ICP-OES). More details on the electrode-mass-normalized Pb²⁺ adsorption capacity (Γ) and Pb²⁺ selectivity coefficient (β) are given in Text S3.

3. Results and discussions

3.1. Characterizations of the as-prepared PBAs

As specified in Text S1, the composition and microstructure of tri-metallic Cu-based PBAs were regulated by tailoring the ratio of the metal precursors and post-synthetic chemical etching. Depending on the post-synthetic treatment, the as-prepared Cu-based PBAs are denoted with suffixes like -C, -NB, and -NF, respectively, to represent the cubic, nanobox, and nanoframe-structured PBAs with similar composition. The as-prepared Cu-based PBAs were observed to be nanosized with characteristic cubes ranging from ten to several hundred nanometers (Fig. 1b–g). Note that all the post-synthetic samples (i.e., Cu_{0.6}Ni_{0.4}HCF-NB, Cu_{0.6}Ni_{0.4}HCF-NF, CuMnHCF-NB, CuMnHCF-NF) are characterized by rough and/or concave surfaces derived from the chemical etching, which corresponds well with literature reports [40,42]. This morphological evolution has been explicitly discussed elsewhere [31,42,43], and we therefore focus on detectable changes in elemental and phase compositions. EDX element mapping revealed that the major metals are uniformly distributed over the surface of PBAs (Fig. 1h). X-ray crystallography analysis indicated that the XRD patterns of all Cu-based PBAs match the standard PDF card (PDF #86–0501) of nickel iron cyanide hydrate (Fig. 2b), confirming the successful preparation of such face-centered-cubic PBAs (Fig. 2a) [44]. Note that the major characteristic

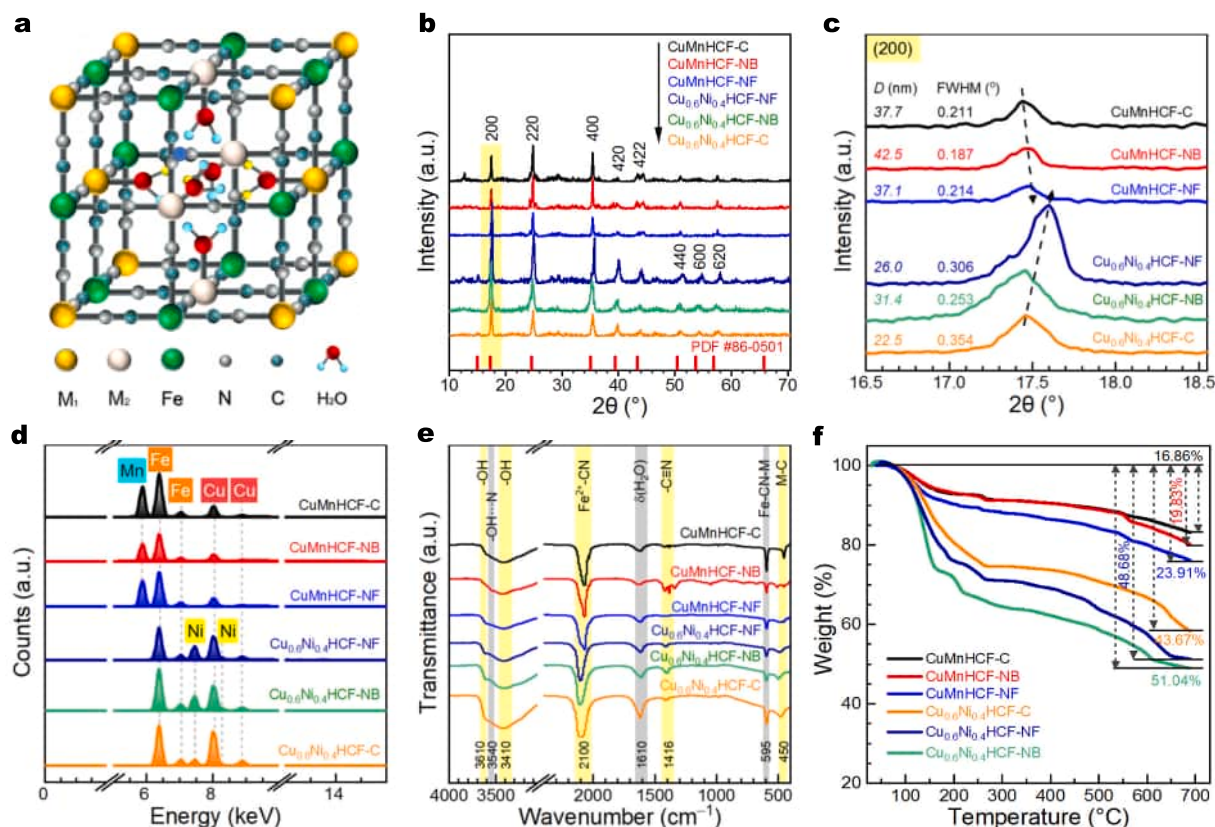


Fig. 2. Physical characterizations of the as-prepared Cu-based PBAs. (a) Schematic structure of the trimetallic PBAs, (b) XRD full patterns, (c) enlarged XRD patterns of the (200) planes, (d) XRF spectra, (e) FTIR spectra, and (f) TG curves.

plane (200) slightly shifted to higher 2θ directions upon post-synthetic treatments (Fig. 2c), implying the minor expansion of the lattice size of the PBA frameworks according to Bragg's law [45]. Calculations using the Scherrer Formula revealed that the grain sizes (D) are approximately 37.7, 42.5, and 37.1 nm for CuMnHCF-C, CuMnHCF-NB, and CuMnHCF-NF, respectively (Fig. 2c). A similar trend was also repeated in the case of Cu_{0.6}Ni_{0.4}HCF (Fig. 2c). The post-synthesis-induced changes in lattice and grain sizes may have varying impacts on their capacities for electrochemical Pb²⁺ capture.

XRF analysis also confirmed the ternary metal composition of these as-prepared Cu-based PBAs — co-occurring of Cu, Fe, and Mn in CuMnHCF, and Cu, Fe, and Ni within the CuNiHCF (Fig. 2d). Semi-quantitative XRF analysis demonstrated that apart from Cu_{0.6}Ni_{0.4}HCF-NB, the Cu/Ni ratios of other Cu_{0.6}Ni_{0.4}HCF samples are approximately 0.6:0.4 (cf. 0.58:0.42 for Cu_{0.6}Ni_{0.4}HCF-C, and 0.57:0.43 for Cu_{0.6}Ni_{0.4}HCF-NF, and 0.83:0.17 for Cu_{0.6}Ni_{0.4}HCF-NB). In the case of CuMnHCF, the Cu/Mn ratios are kept nearly constant, 0.1:0.9 (cf. 0.11:0.89 for CuMnHCF-C, 0.14:0.86 for CuMnHCF-NB, and 0.1:0.9 for CuMnHCF-NF), indicating that the elemental composition of the material was not changed so much by post-synthetic etching with tannic acid (Text S1). This difference may be attributed to the inherent ability of different Cu-based PBAs to resist acid etching [40]. Moreover, FTIR spectra also confirmed the PBA structure (Fig. 2e), with bands at 2100, 1610, and 3410 cm⁻¹ assignable to the stretching vibration of Fe²⁺-CN, and the bending and stretching vibrations of O—H in coordinated water [39]. Thermogravimetric analysis (TGA) revealed that the fractions of both weakly adsorbed and coordinated water within these Cu-based PBAs, as measured at approximately 260 °C, ranged from 9.06 wt% to 35.05 wt% (Fig. S4), which is consistent with previous reports [39,46]. Note that the fractions of water content (adsorbed and coordinated) and total weight loss upon heating to 700 °C of the CuMnHCF are far below those of the Cu_{0.6}Ni_{0.4}HCF samples (Fig. 2f), indicating that the latter set

of PBAs demonstrates poor structural stability that may affect their electrochemical properties for Pb²⁺ capture.

3.2. Electrochemical properties of PBA/sCC electrodes

To distinguish the contribution of the PBA active phase from that of the carbonaceous substrate, sCC was deliberately employed as the reference electrode. Rather than pristine CC, sCC was selected because it represents the actual conductive substrate incorporated into the PBA electrodes and retains the surface functionalities introduced by sulfonation [47]. The electrochemical properties of these Cu-based PBA-integrated sCC electrodes are depicted in Figs. 3, S5–S7. Notably, all these PBA/sCC electrodes demonstrated typical CV profiles of Faradaic electrodes with characteristic redox peaks (Figs. 3, S5), while the sCC electrode exhibited a leaf-like shape, indicative of a typical pseudocapacitive behavior possibly induced by sulfonation [48]. In the voltage window between 0 and 1 V (vs Ag/AgCl), the Cu_{0.6}Ni_{0.4}HCF/sCC electrodes showed major redox peaks with $E_{1/2}$ at approximately 0.8 and 0.4 V (vs Ag/AgCl), in good agreement with previous reports [45]. In the case of CuMnHCF/sCC electrodes, the two pairs of redox peaks are likely assignable to Fe^{III}/Fe^{II} and Mn^{IV}/Mn^{III} [34], both of which significantly contributed to capacitive Pb²⁺ capture [8]. Besides, comparison of CV curve areas of these PBA/sCC electrodes at 5 mV s⁻¹ indicates that CuMnHCF-NF/sCC has the highest CV area, followed by CuMnHCF-NB/sCC, Cu_{0.6}Ni_{0.4}HCF-NF/sCC, and CuMnHCF-C/sCC. This trend also reflects the order of specific capacitance and thus the ion storage capacity of these electrodes under the same conditions. Moreover, b -value (i.e., the slope derived from the cyclic voltammogram at varying scan rates, see Fig. S5) analysis was used to deconvolute the charge storage kinetics of these PBA/sCC electrodes, with a diffusion-controlled intercalation process at $b \approx 0.5$ and surface-controlled capacitive behavior at $b \approx 1.0$ (Text S2) [49]. The b -values of these electrodes were within the range of

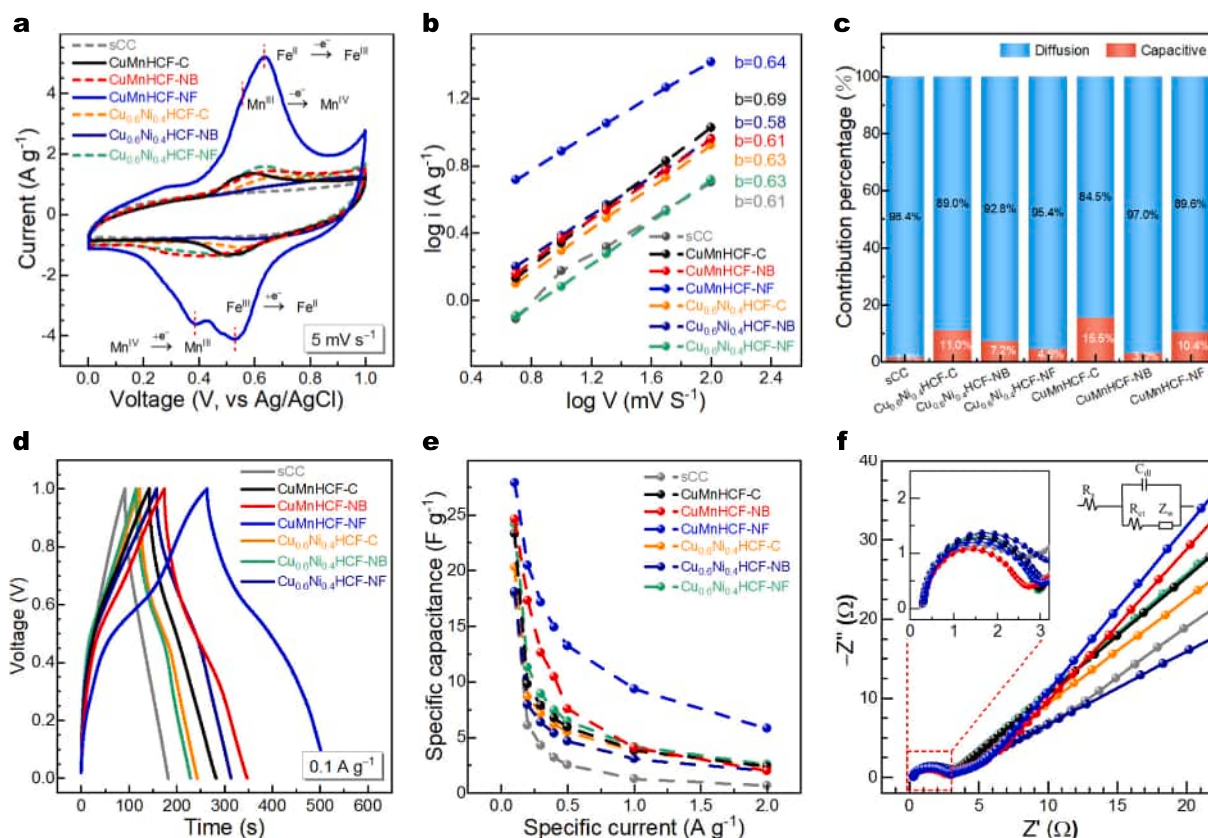


Fig. 3. Electrochemical characterizations of PBA/sCC electrodes. (a) CV curves at 5 mV s^{-1} in 1 M NaCl solution, (b) b -values of these electrodes derived from the slope of cathodic peak current to scan rate ($5\text{--}100 \text{ mV s}^{-1}$), (c) contribution percentage of diffusion- and capacitive-controlled capacitance at 5 mV s^{-1} , (d) GCD curves at 0.1 A g^{-1} in 1 M NaCl solution, (e) specific capacitances (C_s) at different specific currents, and (f) Nyquist plots of EIS and the fitting curves, the top-right inset is the equivalent circuit.

0.58–0.69 (Fig. 3b), implying Pb^{2+} capture was implemented through both the intercalation and the capacitive processes, with intercalation being the dominant pathway [8,45]. This mechanism is also reflected by the quantitative capacitance contribution ratios (diffusion-controlled vs. capacitive-controlled, Figs. 3c and S6), which are dominated by diffusion (i.e., the intercalation process) for all these electrodes at a lower scan rate, with a higher capacitive contribution at a higher scan rate as expected (Fig. S6). This would be beneficial for pseudocapacitive Pb^{2+} storage.

GCD analysis shows that all PBA/sCC electrodes exhibited relatively symmetrical triangles in the GCD curves (Figs. 3d and S7a–g), suggesting a good charge-discharge reversibility of Pb^{2+} insertion/extraction within these electrodes and a high Coulombic efficiency [22,50]. Notably, the specific capacitance (C_s) calculated from the discharge duration of GCD curves beyond the iR drop (i.e., the voltage loss due to the internal resistance) decreased with increasing specific current (i) accordingly, with the CuMnHCF-NF and $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF}$ demonstrating higher C_s of 27.87 and 24.21 F g^{-1} at 0.1 A g^{-1} , respectively (Fig. 3e and Table S1). This implies that the nanoframe structures are likely to be attributed to their improved storage capacity for Pb^{2+} as compared to other counterparts, in good agreement with the above CV data (Fig. 3a). Note that the iR drops of these electrodes are also very low compared to previous reports [50,51]. For instance, the CuMnHCF-NF electrode demonstrated an iR of 12.4 mV at a specific current of 0.1 A g^{-1} (Fig. S7h), indicating that the CuMnHCF-NF electrode has the lowest internal resistance and excellent capacitive performance (Table S1).

To further explore the fundamental mechanism for the above CV and GCD results, EIS analysis was performed and depicted in Fig. 3f. The Nyquist plots are featured by two distinct regions—the semicircle-like high-frequency region and the linear low-frequency region (Fig. 3f). In

general, the diameters of these semicircles represent the charge transfer resistance (R_{ct}) corresponding to the redox reaction at the electrode/electrolyte interface, with a lower R_{ct} showing a higher redox rate [52]. The intercepts of these semicircles at the real axis (Z') refer to the equivalent series resistance (R_s) that is used to assess the conductivity of the electrode, whereas the slopes of the straight lines in low-frequency regions stand for the Warburg impedance (Z_w) that is attributed to the interfacial ion migration from the electrolyte to the electrode. Note that the R_{ct} values of these Cu-based PBA/sCC electrodes increase in the order of $\text{sCC} < \text{CuMnHCF-NF} < \text{CuMnHCF-NB} < \text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF} < \text{CuMnHCF-C} < \text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-C} < \text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NB}$ (Table S1), suggesting that CuMnHCF-NF, CuMnHCF-NB and $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF}$ demonstrated the best electron transfer performance during Pb^{2+} -involved redox reactions except the pristine sCC electrode. Likewise, the R_s values of these electrodes followed the same trend as R_{ct} , reflecting the intrinsic resistance of these electrodes, with CuMnHCF-NF, CuMnHCF-NB, and $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF}$ electrodes showing high conductivity among these electrodes. This observation is consistent with the above iR drop results (Table S1). Notably, the CuMnHCF-NF, CuMnHCF-NB, and $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF}$ electrodes also exhibited relatively large slopes as compared to their counterparts, demonstrating their high ion transport capacity and thus efficient CDI performance [50]. Collectively, the higher charge transfer rate, greater electronic conductivity, and ion migration rate of these hierarchical Cu-based PBA/sCC electrodes, particularly the CuMnHCF-NF, CuMnHCF-NB, and $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF}$, are believed to demonstrate enhanced Pb^{2+} capture capacities.

3.3. CDI performance for Pb^{2+} capture

The Pb^{2+} removal dynamics of these Cu-based PBA/sCC electrodes

were initially evaluated via a single charge-discharge cycle at 1.2 V using a 100 mg L⁻¹ Pb²⁺ feed solution. The real-time conductivity profiles exhibit distinct electrosorption, saturation, and desorption stages (Fig. 4a), confirming the reversible capture and release of Pb²⁺ ions during the charging and discharging stages. Correspondingly, all the capture capacities (Γ) normalized to the mass of PBA alone (Text S3) vs time plots are typically L-shaped (Fig. S8a), with an initial rapid increase in Γ followed by a plateau as the electrode reaches saturation equilibrium (~ 40 min), which is consistent with earlier reports [19,21,37]. Notably, the Γ values and removal efficiencies (%R) reveal a strong structural dependence (Fig. 4b). For instance, the CuMnHCF-NF and Cu_{0.6}Ni_{0.4}HCF-NF electrodes, featuring HCl-etched nanoframe structures, achieved the highest Γ values of 64.96 and 57.85 mg g⁻¹, respectively, and demonstrated near-complete adsorption efficiencies (up to 100%). This performance significantly surpasses that of their bulk (—C) and nanobox (—NB) counterparts, as well as the bare sCC substrate (21.86 mg g⁻¹). The enhanced capture capacity of both NF-structured electrodes aligns with the intrinsic electrochemical kinetics, where the highly accessible nanoframe provides shortened diffusion pathways for Pb²⁺ to rapidly occupy interstitial sites within the PBA lattice [31,53]. Besides, the relatively lower internal and charge transfer resistances of these electrodes (Table S1) also contributed to their higher Pb²⁺ capture capacities.

To comprehensively evaluate the trade-off between removal kinetics and total capture capacity, the corresponding salt adsorption rate (SAR) was plotted against Γ (Kim-Yoon plot, Fig. 4c). An ideal CDI electrode should simultaneously maximize both metrics, occupying the upper-right region of the plot [54]. The CuMnHCF-NF electrode distinctly outperforms all other samples, positioning itself at the top-right corner to indicate the optimal balance of rapid Pb²⁺ removal and high total

capacity. Similarly, within the Cu_{0.6}Ni_{0.4}HCF series, the -NF variant exhibits the highest SAR and Γ . This exceptional rate capability is directly attributed to the hierarchical nanoframe structure, which minimizes ionic diffusion resistance and facilitates the rapid occupation of available interstitial positions [31,53].

Additionally, the Pb²⁺ extraction performance of the PBA/sCC electrodes is highly sensitive to operational parameters, specifically the feed concentration and applied voltage (Figs. 4d, e, and S8–S10). Increasing the feed Pb²⁺ concentration (100–1000 mg L⁻¹) intensifies the concentration gradient between the bulk electrolyte and the electrode surface. This promotes mass transfer, thereby accelerating the attainment of adsorption equilibrium and yielding higher Γ values (Figs. S8b–i, S9). Furthermore, as the cell voltage increases from 0.6 V to 1.2 V, the electrochemical driving force for Faradaic (redox) reactions is thus enhanced [50], resulting in a nearly linear increase in Γ (Figs. S10, S11). Notably, the Γ values exhibit an immediate and reversible response when switching between 1.2 V and 0.6 V (Figs. 4e and S10), underscoring the robust and dynamic controllability of the electrodes for lead removal. Across all tested voltages and concentrations, the Pb²⁺ capture capacity consistently follows the order: CuMnHCF-NF > Cu_{0.6}Ni_{0.4}HCF-NF > CuMnHCF-NB > CuMnHCF-C > Cu_{0.6}Ni_{0.4}HCF-C > Cu_{0.6}Ni_{0.4}HCF-NB > sCC, demonstrating that the enhanced performance arises not simply from a high-affinity material, but from the combined effects of CuMnHCF composition and the electrode architecture, with the hierarchical nanoframe architecture outperforming others (Fig. S8i). The Pb²⁺ separation performance of the present electrodes was benchmarked against representative electrochemical electrodes reported in the literature (Fig. 4f, Table S2). Because reported uptake capacities depend strongly on the initial Pb²⁺ concentration, applied voltage, electrode configuration, and operating time, the comparison considers

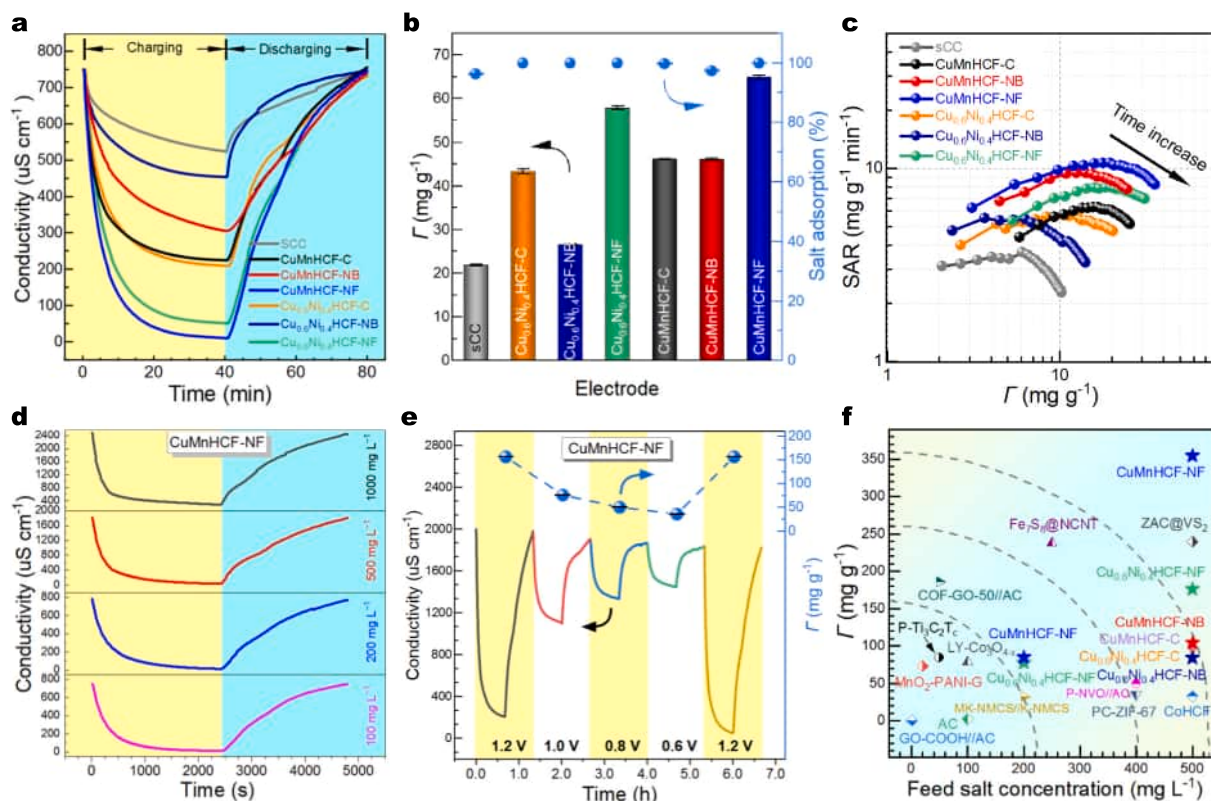


Fig. 4. (a) Plots of conductivity versus time in one charge-discharge operation of RCIDI cells with PBA/sCC electrodes in 100 mg L⁻¹ Pb²⁺ solution at 1.2 V, (b) Corresponding capacity (Γ) and removal efficiency (%R) of these electrodes in 100 mg L⁻¹ Pb²⁺ solution, (c) Kim-Yoon plots, (d-e) Plots of conductivity versus time of RCIDI cells with the CuMnHCF-NF electrode (d) with varying concentrations at 1.2 V and (e) at varying voltages in 500 mg L⁻¹ Pb²⁺ solution, (f) Comparison in Γ of various electrodes for Pb²⁺ capture from solutions via CDI. Note that the dotted lines are used for visual guidance, and that the electrode code can be found in Table S2.

not only electrode-mass-normalized uptake, but also SAR and Pb^{2+} removal efficiency (%R). It delivered an SAR of $10.65 \text{ mg g}^{-1} \text{ min}^{-1}$ and 99.9% Pb^{2+} removal, demonstrating that the high uptake was accompanied by rapid and effective Pb^{2+} separation by CuMnHCF-NF. Although COF-GO-50/AC exhibited a higher SAR ($19.83 \text{ mg g}^{-1} \text{ min}^{-1}$), its uptake was only 186.0 mg g^{-1} [55], highlighting the favorable balance between capacity and kinetics achieved by CuMnHCF-NF. Nevertheless, direct comparison of selectivity, regeneration stability, and energy consumption remains difficult because these parameters have not been consistently reported under standardized conditions in the literature. Accordingly, Table S2 is intended as a multidimensional performance benchmark rather than an absolute ranking of Pb^{2+} separation technologies.

Ultimately, the above analysis verifies that the structural tailoring of the CuMnHCF-NF electrode successfully translates its intrinsic electrochemical advantages into enhanced, high-throughput Pb^{2+} capture performance in CDI applications. However, the initial Pb^{2+} concentration of $100\text{--}500 \text{ mg L}^{-1}$ is higher than that encountered in many natural waters and treated industrial effluents, and the corresponding high Pb^{2+} capture performance therefore should not be interpreted as direct evidence of applicability to dilute environmental waters [55]. Further validation at environmentally relevant Pb^{2+} concentrations, particularly in the presence of competing ions and realistic wastewater matrices, is therefore necessary before practical deployment for dilute-water remediation can be established.

3.4. Recycling performance

The long-term cycling stability of the optimal CuMnHCF-NF and $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF}$ electrodes was evaluated over 40 consecutive

adsorption-desorption cycles under constant voltage conditions in $500 \text{ mg L}^{-1} \text{ Pb}^{2+}$ solutions (Figs. 5 and S12). Initially, the CuMnHCF-NF and $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF}$ electrodes exhibited high Γ values of 354.5 and 175.9 mg g^{-1} for Pb^{2+} ions, respectively. After 10 cycles, the capacities gracefully decreased to 290.6 and 166.4 mg g^{-1} , yielding Γ retention rates of 81.3% and 95.3% (Figs. 5a and S12a). Following 40 cycles, the overall capacity retention rates were maintained at 77.7% ($\Gamma = 277.4 \text{ mg g}^{-1}$) and 75.9% ($\Gamma = 132.4 \text{ mg g}^{-1}$). This marginal degradation is markedly greater to traditional MnO_2 -based or binary PBA electrodes [34,50], highlighting the robust structural durability of both trimetallic PBA frameworks. Concurrently, the real-time conductivity profiles demonstrate highly reversible ion capture and release; while the peak conductivity gradually decreased from ~ 950 to $\sim 700 \mu\text{S cm}^{-1}$ over 40 cycles, the fluctuation range between the peaks and troughs ($\sim 20 \mu\text{S cm}^{-1}$) remained stable. This observation indicates that the ion transport channels remain intact and the insertion/extraction reversibility is well-maintained, which is highly consistent with the observed Γ decay trend (Figs. 5a, S12a).

To elucidate the mechanisms underlying this capacity decay, three potential factors were generally considered: (i) structural degradation of the PBA lattice, which reduces ion storage sites; (ii) partial loss of copper/manganese species, decreasing the number of effective active sites; and (iii) a gradual increase in interfacial impedance due to repeated ion insertion/extraction, hindering ion transport [56]. To verify these structural and molecular hypotheses, the post-cycling CuMnHCF-NF and $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF}$ electrodes were characterized using XRD, XRF, and FTIR and compared with their pristine counterparts (Figs. 5c–e, S12b–d). Notably, all characteristic diffraction peaks of both PBAs showed a significant decrease in intensity after cycling for 40 cycles (cf. Figs. 5c, S12b), with a sharp PVDF peak derived from the PVDF binder

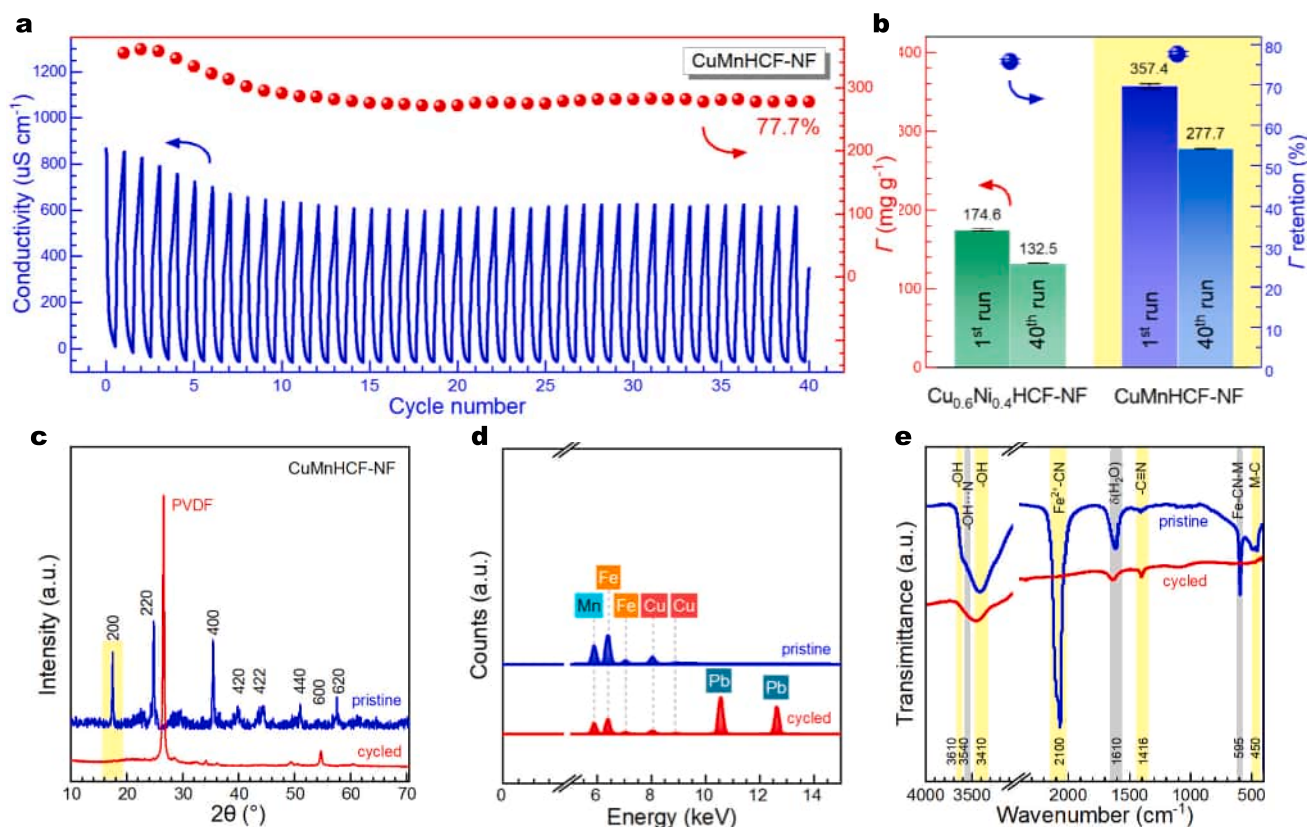


Fig. 5. (a) Cycling stability and Γ of CuMnHCF-NF electrode in 500 mg L^{-1} of Pb^{2+} solution applied in RCDD for 40 charge-discharge operations, (b) comparison of Γ and Γ retention (%) of the $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF}$ and CuMnHCF-NF electrodes, (c) XRD patterns, (d) XRF, and (e) FTIR spectra of the CuMnHCF-NF electrode before the 1st (pristine) and after the 40th cycle of operations (cycled). Note that the PVDF peak in panel c is derived from the PVDF binder used in the preparation of the PBA/SCC electrodes.

used for preparing PBA/sCC electrodes (Text S3). This indicates that both electrodes have undergone severe structural degradation during Pb^{2+} intercalation/deintercalation, with the $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF}$ electrode being a bit more stable, as evidenced by its retained weak peaks (Fig. S12b). This is also verified by the FTIR spectra, with the absence (Fig. 5e) or weakening of the Fe^{2+} -CN stretching bands at 2100 cm^{-1} (Fig. S12d). Complementing the XRD and FTIR data, XRF analysis revealed that the lattice Fe, Cu, and Mn/Ni elements showed a moderate decrease in intensity, along with two remarkable Pb peaks in the cycled electrodes (cf. Figs. 5d, S12c), indicating irreversible occupancy of specific lattice sites by Pb^{2+} ions, which accounts for the capacity decay observed in both electrodes (Figs. 5a, S12a). It should be noted that the above solid-phase characterization techniques do not directly quantify the concentrations of dissolved metal species from the Cu-based PBA electrodes in the effluent. Therefore, the extent of aqueous Cu, Mn, Ni, and Fe release cannot be quantitatively determined from the present

data. Quantitative ICP-OES/ICP-MS analysis and elemental mass-balance assessment will be necessary in future work to establish the magnitude of metal leaching and its implications for long-term environmental application. Besides, energy consumption and charge efficiency are important for evaluating the practical viability of our Cu-based PBA electrodes applied to RCDI, as parasitic reactions, irreversible ion trapping, and electrode degradation may reduce charge utilization during operation. These metrics should also be systematically investigated in future work through electrical energy and Faradaic charge balances.

Collectively, this multi-modal characterization confirms that the structural degradation and partial loss of metal constituents of both trimetallic Cu-based PBA frameworks occurred during the cycling process, irreversibly impairing their long-term Pb^{2+} capture capacities for practical applications. Therefore, rational framework stabilization strategies, such as high-entropy transition metal substitution and surface

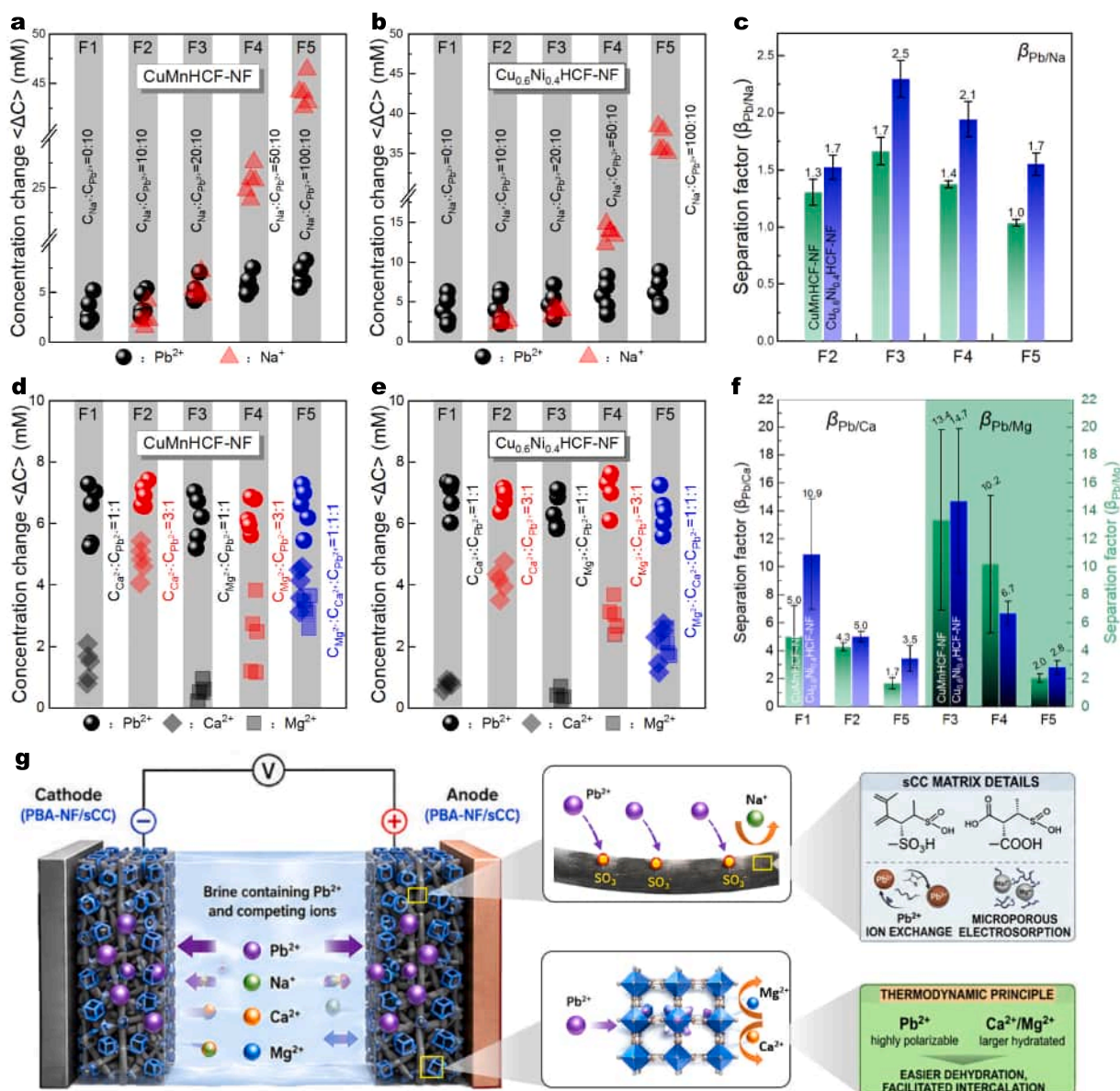


Fig. 6. (a, b) Cation average concentration changes (ΔC) in feed solutions (F1–F5) with varying $\text{Pb}^{2+}/\text{Na}^{+}$ ratios upon a half-cycle of RCDI operation with electrodes (a) CuMnHCF-NF, (b) $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF}$. (c) The corresponding separation factors of both electrodes toward Pb^{2+} over Na^{+} . (d, e) ΔC changes in feed solutions (F1–F5) with varying $\text{Pb}^{2+}/\text{Ca}^{2+}$ or $\text{Pb}^{2+}/\text{Mg}^{2+}$ ratios upon a half-cycle of RCDI operation with electrodes (d) CuMnHCF-NF, (e) $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF}$, (f) the corresponding separation factors of both electrodes toward Pb^{2+} over Ca^{2+} or Mg^{2+} , and (g) the possible sCC-driven and thermodynamic selectivity mechanisms for Pb^{2+} over Na^{+} and $\text{Ca}^{2+}/\text{Mg}^{2+}$ ions. Note that the balls, triangles, diamonds, and squares represent ΔC of Pb^{2+} , Na^{+} , Ca^{2+} , and Mg^{2+} after a half-cycle of RCDI operation.

coating [57,58], should be explored in future research to enable durable and long-term Pb^{2+} capture.

3.5. Selectivity for Pb^{2+} ions

The selectivity of the CuMnHCF-NF and $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF}$ electrodes toward Pb^{2+} over monovalent Na^+ was systematically evaluated under constant voltage (1.2 V) across varying $\text{Pb}^{2+}/\text{Na}^+$ ratios (10,0 to 10:100 mM/mM). As shown in Fig. 6a, b, the change in concentration (ΔC) data of Pb^{2+} upon a half-cycle of RCDI operation (i.e., $\Delta C_{\text{Pb}} = C_{\text{Pb, initial}} - C_{\text{Pb, final}}$, positively correlated with the Pb^{2+} capture capacity) increased slightly with rising Na:Pb ratios (i.e., 0:10 for feed solution F1, 10:10 for F2, 20:10 for F3, 50:10 for F4, and 100:10 mM/mM for F5) for both electrodes, suggesting the preferential capture of Pb^{2+} over both electrodes in the presence of high concentrations Na^+ ions (cf. F4, F5). To quantify selectivity, the separation factors of Pb^{2+} over Na^+ ($\beta_{\text{Pb}/\text{Na}}$, defined as the ratio of the percent of Pb^{2+} captured to the percent of monovalent Na^+ removed simultaneously, Text S3) of both electrodes were calculated and depicted in Fig. 6c. Note that the $\beta_{\text{Pb}/\text{Na}}$ values for both electrodes show a trend of first increasing and then decreasing across the binary solutions from F2 to F5, with the maxima (i.e., 1.7 for CuMnHCF-NF vs 2.5 for $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF}$) occurring at F2 (Na:Pb = 20:10 mM/mM). Na^+ has a smaller hydrated radius and hydration free energy than Pb^{2+} , and thus a greater thermodynamic potential to be captured (Table S3). This preferential selectivity for Pb^{2+} is contrary to an earlier report for binary PBA (e.g., NiHCF) [31] and is fundamentally driven by the PBA redox mechanism, where the reduction of Fe^{III} to Fe^{II} facilitates Pb^{2+} insertion into the NF-structured frameworks with shorter diffusion pathways [53]. Moreover, the sCC appears to provide additional Pb^{2+} -interacting surface sites (e.g., $-\text{SO}_3\text{H}$, $-\text{COOH}$) as reported earlier [47,48], whereas the PBA framework contributes electrochemically driven Pb^{2+} storage.

To assess competitive interference from divalent ions with identical charge and similar hydrated radii, the electrodes were tested in binary ($\text{Pb}^{2+}/\text{Mg}^{2+}$ and $\text{Pb}^{2+}/\text{Ca}^{2+}$) and ternary ($\text{Pb}^{2+}/\text{Ca}^{2+}/\text{Mg}^{2+}$) solutions with varying ratios as detailed in Table S4. Notably, the ΔC values of Pb^{2+} fluctuated between 5 and 8 mM (Fig. 6d, e), regardless of the solutions of binary or ternary cations, while the ΔC values of other competing ions were restricted within the range of 1 to 5 mM, yielding high $\beta_{\text{Pb}/\text{Ca}}$ of 10.9, 5.0, and 3.5 for the $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF}$ electrode in solutions F1, F2, and F5, respectively (cf. 5.0, 4.3, and 1.7 for CuMnHCF-NF, Fig. 6f). In parallel, the $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF}$ electrode demonstrated an exceptional $\beta_{\text{Pb}/\text{Mg}}$ of 14.7 for Pb^{2+} in F3 with equimolar Pb^{2+} and Mg^{2+} ions (cf. 13.4 for Pb^{2+} on CuMnHCF-NF), demonstrating a notable selectivity toward Pb^{2+} over Mg^{2+} . Even when Mg^{2+} concentration was tripled (i.e., 30 mM, F4), both electrodes still showed $\beta_{\text{Pb}/\text{Mg}}$ as high as 10.2 and 6.7 for CuMnHCF-NF and $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF}$ electrodes, respectively (Fig. 6f). This pronounced selectivity is governed by thermodynamic distinctions among these divalent cations (Table S3). Specifically, Pb^{2+} has a lower hydration energy and a highly polarizable electron cloud compared to Ca^{2+} and Mg^{2+} , allowing it to more readily shed its hydration shell and intercalate into the PBA lattice [59]. Moreover, the lower hydration energy and small hydrated radius of Ca^{2+} compared to Mg^{2+} accounted for its relatively lower competition than that of Ca^{2+} , leading to greater selectivity for Pb^{2+} over Mg^{2+} ($\beta_{\text{Pb}/\text{Mg}} > \beta_{\text{Pb}/\text{Ca}}$) across these systems (Fig. 6f).

Synthesizing the selectivity data reveals that the $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF}$ electrode consistently outperforms the CuMnHCF-NF electrode across both monovalent and divalent competition scenarios (Fig. 6c, f). While both electrodes benefit from the NF architecture's efficient diffusion pathways and the sCC matrix's electrosorption for Pb^{2+} ions, their divergent selectivities are therefore likely attributed to intrinsic differences in lattice affinity (Fig. 6g). A possible explanation is that the CuMnHCF-NF framework possesses an inherently stronger affinity for competing ions (i.e., Na^+ , Ca^{2+} , and Mg^{2+}) relative to the $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF}$ framework, which in turn dilutes its Pb^{2+} selectivity,

despite maintaining a high absolute Pb^{2+} capture capacity. To verify this speculation, future research is needed based on density functional theory (DFT) or in-situ spectroscopy techniques. Nevertheless, the combination of the highly Pb^{2+} -selective $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF}$ and the adsorption capabilities of sCC establishes this composite electrode as a highly viable and robust candidate for targeted Pb^{2+} remediation in complex CDI matrices.

4. Conclusions

In summary, two sets of trimetallic Cu-based PBAs with cubic, nanobox, and nanoframe structures (CuMnHCF and $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF}$) integrated with sCC were successfully developed as robust electrodes for selective Pb^{2+} capture on an RCDI platform. The HCl-etched nanoframe architecture provides shortened ion diffusion pathways and mitigates structural strain, while the sCC matrix contributes high conductivity and supplementary active sites (e.g., $-\text{SO}_3\text{H}$, $-\text{COOH}$), collectively endowing the electrodes with improved redox activity and fast electron/ion transport. Consequently, the optimized nanoframe-structured CuMnHCF-NF and $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF/sCC}$ electrodes deliver an exceptional Pb^{2+} electrosorption capacity at 1.2 V (as high as 354.5 and 175.8 mg g^{-1} in 500 mg L^{-1} solutions), driven by a synergistic mechanism of Faradaic lattice intercalation and non-Faradaic electrosorption/ion-exchange, alongside excellent long-term cycling stability. Furthermore, this electrode exhibits pronounced selectivity for Pb^{2+} over competing monovalent (Na^+) and divalent (Ca^{2+} , Mg^{2+}) ions across varying concentration ratios (e.g., $\beta_{\text{Pb}/\text{Na}} = 2.5$, $\beta_{\text{Pb}/\text{Ca}} = 10.9$, $\beta_{\text{Pb}/\text{Mg}} = 14.7$ for $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF}$), which is fundamentally attributed to the lower hydration energy and higher polarizability of Pb^{2+} as well as the lattice properties of the tailored CuMnHCF-NF and $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{HCF-NF}$ frameworks. Although a high Pb^{2+} concentration of 100–500 mg L^{-1} was employed to evaluate the intrinsic Pb^{2+} capture capability of these electrodes, the applicability of the Cu-based RCDI system to dilute environmental waters remains to be established. Future studies should therefore investigate Pb^{2+} capture at environmentally relevant concentrations and in realistic water matrices containing competing ions, together with long-term cycling and energy-consumption assessments. Overall, this rational structural engineering of trimetallic Cu-based PBA nanoframes on functionalized carbon cloth supports effectively overcomes the inherent trade-offs among capacity, selectivity, and durability in CDI, offering a highly efficient material platform and mechanistic insights for targeted heavy metal remediation from complex aqueous environments.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The work was not funded.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2026.140341>.

Data availability

Data will be made available on request.

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