

Enhanced Cobalt Ion Removal Using Copper Hexacyanoferrate Electrodes in Capacitive Deionization

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1. Introduction

Cobalt (Co) poses significant environmental and health risks due to its widespread industrial use and radioactive nature. Traditional methods for removing cobalt from wastewater include chemical precipitation, electro dialysis, ion-exchange, and adsorption, among others. Recently, capacitive deionization (CDI) has gained attention as an energy-efficient method for ion removal [1]. However, conventional carbon-based CDI systems face issues of reduced charge efficiency and removal capacity due to co-ion repulsion [2]. The study explores the use of Prussian blue analogs (PBAs) in asymmetric CDI cells, which show promise in enhancing ion removal and charge efficiency. The research focuses on a CuHCF electrode material for effective cobalt ion removal, examining its structural properties and electrochemical performance. The findings suggest that integrating PBA electrode materials into CDI systems could significantly improve the technology for cobalt ion removal and recovery from wastewater.

2. Experimental

2.1 Preparation of CuHCF

CuHCF nanoparticles were synthesized using a coprecipitation method. $K_3[Fe(CN)_6]$ (20 mM; Sigma-Aldrich) was added to deionized (DI) water (100 mL), and then 30 mM $CuNO_3 \cdot 3H_2O$ (Sigma-Aldrich) dissolved in DI water was slowly added to the above mixture. The prepared solution was aged for 18 h, washed three times with DI water, and collected by centrifugation at 4000 rpm. The final products were dried at 70 °C under vacuum overnight. An electrode slurry was prepared by mixing 80 wt. % CuHCF, 10 wt.% super-P carbon black, and 10 wt.% polymer binder (polyvinylidene fluoride, PVdF) in *N*-methyl-2-pyrrolidone (NMP) solution. The slurry was pasted onto a graphite sheet and vacuum-dried at 100 °C for 24 h.

2.2 Structural characterization

The crystal structures of the samples were characterized by X-ray diffractometry (XRD, X-pert PRO MRD, Philips) with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$, at 40 kV and 30 mA). The measurements were carried out from 10° to 60° in 2θ at a scan rate of 0.01° min^{-1} .

2.3 Electrochemical test and cell setup

Electrochemical tests of the samples were performed using a conventional three-electrode cell in aqueous 0.5 M $CoNO_4$ solution. The system comprised a platinum rod as the counter electrode and a saturated Ag/AgCl (3 M KCl) electrode as the reference electrode. Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) were performed using a potentiostat (WPG100; WonA Tech Co., Korea).

3. Result and discussion

The electrochemical characteristics of the CuHCF were investigated using CV, GCD measurement. In the CV curve, two pairs of pronounced peaks associated with redox reactions were observed. These peaks of CuHCF can be attributed to the redox reactions of low-spin Fe adjacent to the C atom ($Fe^{LS}-C$) and the redox reactions of Cu^{2+} and/or high-spin Fe connected to the N atom ($Fe^{HS}-N$). Further, the profiles of the CuHCF exhibited distinct voltage plateaus depending on the position of the CV redox peaks. The symmetrical profiles indicate the high electrochemical reversibility of CuHCF. The specific capacitance values derived from the GCD profiles at current densities of 0.2, 0.3, 0.5, 1.0, and 2.0 $A g^{-1}$ were 214.2, 169.1, 122.7, 80.0, and 65.5 $F g^{-1}$, respectively.

To investigate the structural evolution of CuHCF during the Co^{2+} insertion/extraction process, XRD was implemented and illustrated at different charge and discharge states (Fig. 4(a) and (b)). The crystal volume

of CuHCF changes reversibly with the Co^{2+} insertion/extraction process. At the beginning of discharge, Co^{2+} is inserted into CuHCF, which leads to slight changes in the (200), (220), and (400) diffraction peaks (Fig. 4(b)) and a shift to higher angles. During the charging process, the diffraction peaks return to their original states, indicating a reversible structural change. Fig. 2(c) displays the lattice parameter at the corresponding voltage states. In addition, Fig. 2(d) presents the composition ratio of Cu and Fe at each valence state, based on the deconvolution of Cu 2p and Fe 2p spectra at various states, as determined by XPS analysis. After discharging to 0.7 V, the ratios of Fe^{3+} to Fe^{2+} and Cu^{2+} to Cu^+ were similar to the pristine state. After full discharge to 0 V, Fe^{2+} and Cu^+ increased to 80.3% and 61.5%, respectively, confirming the reduction of $\text{Fe}^{3+}\text{-C}$ to $\text{Fe}^{2+}\text{-C}$. Interestingly, Cu also participates in the redox reaction. After fully discharging from 0 V to 0.72 V and then to 1.1 V, the Fe^{2+} and Cu^+ ratios were 11.0% and 55.2%, respectively, indicating a reversible extraction process of Co^{2+} . These changes in the Fe 2p and Cu 2p regions provide strong evidence for the electrochemical redox reaction involving the insertion/extraction of Co^{2+} .

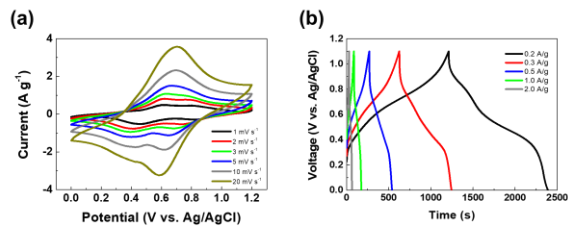


Fig. 1. (a) CV curves of CuHCF at different scan rates, (b) charge-discharge profiles of CuHCF at different current densities.

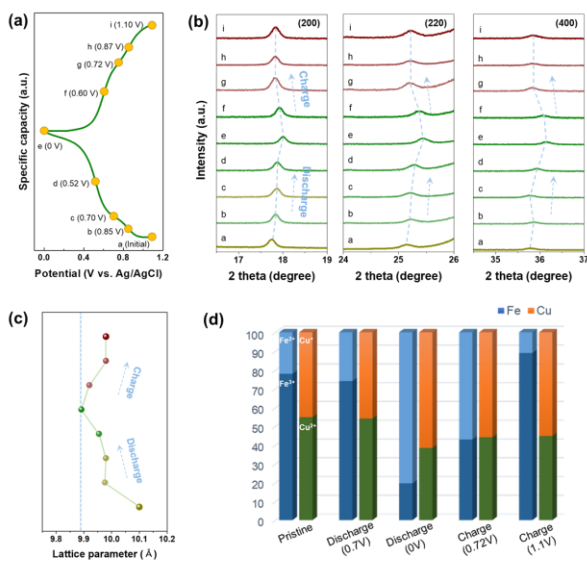


Fig. 2. Charge-discharge profiles of CuHCF at different depths, (b) *ex-situ* XRD patterns at selected state, (c) the refined lattice parameter of the corresponding voltage profile,

(d) composition ratios of Cu and Fe in each valence state based on deconvolution of Cu 2p and Fe 2p spectra.

Besides, the long-term cycling performance of CuHCF at a current density of 0.5 A g^{-1} is shown in Fig. 3. The first discharge capacity of 229.9 mAh g^{-1} is achieved with an initial coulombic efficiency of 99.7%. A discharge capacity of 150.5 mAh g^{-1} was achieved and the coulombic efficiency reached 99.9% after 300 cycles.

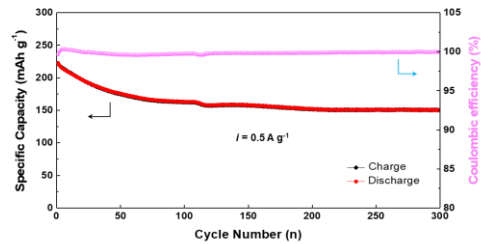


Fig. 3. Long-life cycling stability at the current density of 0.5 A g^{-1} over 300 charge/discharge cycles.

4. Conclusions

In this study, we explored the use of CuHCF as an electrode material for the removal of Co^{2+} ions from wastewater. The electrochemical characterization revealed that the CuHCF electrode exhibits pronounced redox peaks corresponding to the $\text{Fe}^{\text{LS}}\text{-C}$ and $\text{Fe}^{\text{HS}}\text{-N}$ redox reactions, as well as excellent electrochemical reversibility, as indicated by the symmetrical voltage profiles. The specific capacitance values were found to be substantial, with the highest recorded at 214.2 F g^{-1} at a current density of 0.2 A g^{-1} . Structural analysis through XRD demonstrated the reversible changes in the crystal structure of CuHCF during Co^{2+} insertion and extraction, which was further supported by XPS analysis showing the valence changes of Cu and Fe during the process. Additionally, the CuHCF electrode displayed good long-term cycling stability with a high coulombic efficiency over 300 cycles. These findings suggest that integrating CuHCF and similar Prussian blue analogs into CDI systems could significantly enhance the efficiency and effectiveness of cobalt ion removal and recovery, offering a promising approach for addressing environmental and health concerns associated with cobalt contamination in wastewater.

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