

Selective removal of cesium ions with a copper hexacyanoferrate electrode in a capacitive deionization system

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1. Introduction

To restore the environment polluted by a serious accident in a nuclear facility to its original state, a technology capable of safe, effective, rapid, and accurate decontamination is required. In particular, in the case of large-scale nuclear accidents such as Chernobyl and Fukushima nuclear accidents, if not dealt with in an early stage, radioactive materials can spread widely and the large-scale disasters can occur. Among the radioactive nuclides, cesium (Cs) isotopes are one of the most dangerous nuclides due to their significantly hazardous effect on human health [1,2]. Radioactive Cs (especially, ¹³⁷Cs) exhibits high-energy gamma radiation with a long half-life (30 years) [3,4].

Since Cs⁺ ions are highly soluble in water, they spread easily in nature and cause severe environmental problems. In addition, Cs⁺ ions easily bioaccumulate in ecosystems due to their ability to displace Na⁺ and K⁺ ions in living organisms [5]. Hence, it is crucially important to capture Cs⁺ ions in an appropriate way from the radioactively contaminated water to minimize its radioactivity.

Electrode materials that selectively interact with specific ions by Faradic redox reactions or ion (de)intercalation provide an effective strategy for highly selective electrosorption of Cs⁺ from aqueous solution.

In this work, we investigated the Cs removal performance, by revealing the effect of applied voltage, concentration of initial Cs⁺ ions, and initial pH value, of copper hexacyanoferrate (CuHCF) electrode in an electrochemical system. In addition, to evaluate the selective Cs⁺ ion electrosorption property of the CuHCF electrode, we carried out an electrosorption test in a cation mixture solution containing Na⁺ and Sr²⁺ ions.

2. Methods and Results

2.1 Fabrication of CuHCF

CuHCF was prepared through a facile wet-chemical synthetic method. 100 mL deionized (DI) water of 30 mM CuNO₃·3H₂O and 100 mL DI water of 20 mM K₃[Fe(CN)₆] were mixed with vigorous stirring for 6 h. The obtained solution was aged for 18 h and then washed three times with DI water. The precipitates were

collected by centrifugation at 4000 rpm, and then dried for 24 h at 70 °C under vacuum conditions.

To study the crystal structure of CuHCF, powder X-ray diffraction (XRD) was conducted. Fig. 1 shows the XRD patterns of as-synthesized CuHCF. All diffractive peaks well match with a cubic structure (JCPDS No. 86-0513) without any other impurities. The scanning electron microscope (SEM) image inserted in Fig. 1 shows that the synthesized CuHCF has nanoparticle agglomerates in a granular morphology with diameters of about 50-100 nm. The nano-size ensured sufficient electrolyte contact area and shortened the transport distance of ions.

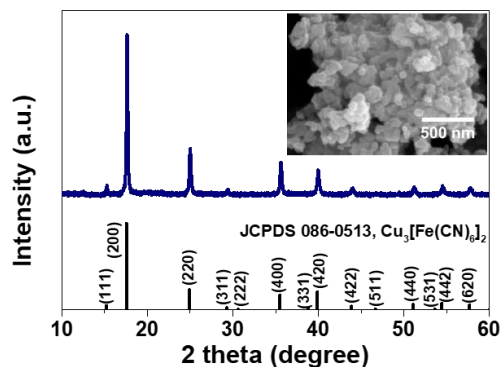


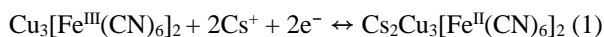
Fig. 1. XRD pattern of CuHCF powder (inset shows SEM image).

2.2 Redox reaction of the CuHCF electrode

CuHCF electrodes as cathode were prepared by mixing a slurry containing 80 wt.% active material (CuHCF), 10 wt.% super-P carbon black, 10 wt.% polymer binder (polyvinylidene fluoride, PVdF). The N-methyl-2-pyrrolidone (NMP) was used as a solvent in the mixture. The slurry was coated on a graphite sheet, and then dried in a vacuum oven at 100 °C for 24 h.

To evaluate the electrochemical properties of the CuHCF electrode, we performed a cyclic voltammetry (CV) test with a three-electrode system using a 0.5 M CsNO₃ solution. A platinum rod and a saturated Ag/AgCl (3 M KCl) electrode were used as a counter and reference electrode, respectively. Fig. 2. Shows the CV curves 0.2 to 1.4 V at different scan rates of 0.5–10.0 mV s⁻¹. The anodic peak of 1.02 V observed at a

scan rate of 0.5 mV s^{-1} is the reduction of Fe^{3+} to Fe^{2+} , which is accompanied with intercalation of Cs^+ ions into the CuHCF structure to maintain charge neutrality. As a reverse scan, a cathodic peak at 1.08 V is observed, which is related to the de-intercalation of Cs^+ out of CuHCF. The corresponding reversible redox reaction during intercalation/de-intercalation of Cs^+ ions with CuHCF is proposed as follows:



ESIX (electrochemically switched ion exchange) is a combination of ion exchange and electrochemical reaction that provides a reversible reaction for selective adsorption/desorption of Cs^+ ions.

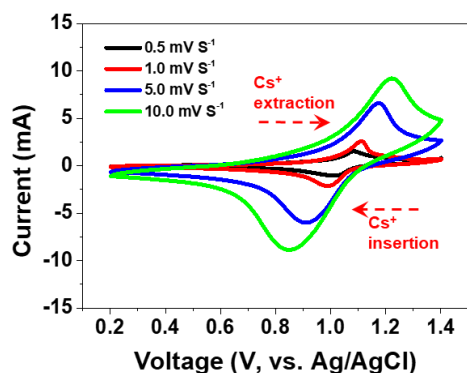


Fig. 2. CV curves of the CuHCF electrode at different scan rates.

2.3 Electrochemical Cs removal performance test

Electrochemical Cs removal experiments were performed by using a continuous water flow circulation system. The test system was constructed with a CuHCF cathode, a commercial activated carbon (AC, P-60, obtained from Kuraray Chemical Co. (Japan)) anode, in which an anion-exchange membrane (AEM, NEO-SEPTA ASE) placed adjacent. Each electrode pair was separated by a spacer (100 mesh, NBC PP) with a thickness $200 \mu\text{m}$ in order to prevent short-circuiting. Moreover, the spacer was also utilized as a flow channel for the influent water within the CDI cell. The performance of the CuHCF electrode was investigated under 100 mg-Cs L^{-1} in 200 mL feed solution with a constant flow rate (30 mL min^{-1}).

Fig. 3(a) shows the electroadsorption capacities and charge efficiencies at different voltages in a 100 mg L^{-1} concentration of the Cs^+ ions for the CuHCF electrode at $1.0, 1.2, 1.4,$ and 1.6 V applied voltage were $164, 201, 218,$ and 218 mg g^{-1} , respectively, and the corresponding charge efficiencies (Λ) were $0.36, 0.37, 0.33,$ and 0.23 , respectively. The increase in the electroadsorption capacities was because the reaction rate in the CuHCF electrode increased when a higher voltage

was applied. Whereas, the charge efficiency decreased at voltages higher than 1.2 V , which can be attributed to the higher leakage current during the electroadsorption process caused by side reactions (e.g., water electrolysis, oxidation of the electrode).

The influence of pH on the electroadsorption capacity of the CuHCF electrode is presented in Fig. 3(b). The results revealed an electroadsorption capacity of about 153 mg g^{-1} at pH 1.0 , and the electroadsorption capacity continuously increased with an increasing pH value to achieve about 218 mg g^{-1} at pH 5.6 . In acidic conditions, more H^+ ions were adsorbed on the surface of the CuHCF electrode, which reduced the electroadsorption performance of the Cs^+ ions. This result was possibly due to the shielding effect of electric potential [8].

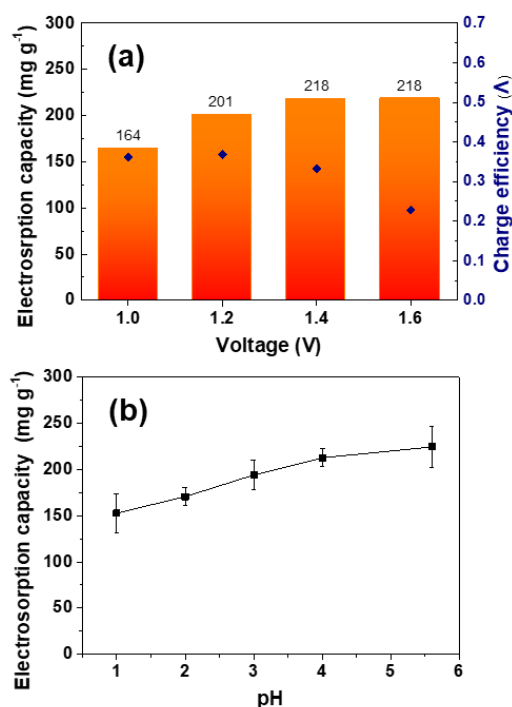


Fig. 3. (a) Electroadsorption capacity and charge efficiency of the CuHCF electrode at different applied voltage; (b) electroadsorption capacity of the CuHCF electrode at different pH values.

The cyclic performance is a key parameter for the reversibility of the Cs (de)intercalation reaction. Fig. 4 shows the conductivity of the electrolyte, which continuously flow through the electrochemical cell, and removal capacity during 10 cycles, performed by repeated adsorption/desorption ($1.4/-1.4 \text{ V}$) processes in a 100 mg-Cs L^{-1} solution. The removal capacity was gradually decreased, reaching approximately 158 mg g^{-1} at the 10th cycle. The results showed the reusable properties of CuHCF electrodes.

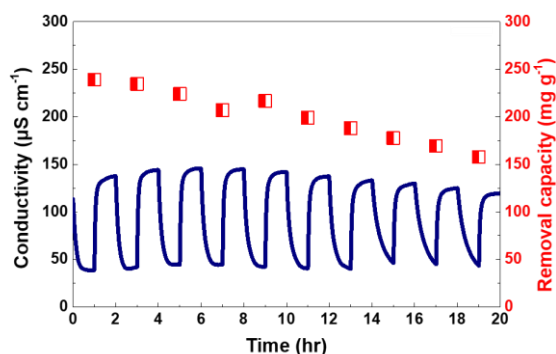


Fig. 4. Cyclic performance of CuHCF electrode at 1.4 V in a 100 mg-Ce L⁻¹ solution.

2.4 Selective electrosorption of Cs⁺ ions on the CuHCF electrode

Large volumes of radioactive liquid waste require special treatment prior to storage or discharge into environment. An efficient treatment concept is the removal of trace radionuclides from wastewater and should be selective only for those target ions.

To study the ion selectivity of the CuHCF electrode, the electrosorption performance was evaluated for the Cs⁺, Na⁺, and Sr²⁺ ions. As shown in Fig. 5, the electrosorption capacity in single ion solution for Cs⁺ (218.5 mg g⁻¹) was higher than that for Na⁺ (26.6 mg g⁻¹) and Sr²⁺ (77.1 mg g⁻¹) ions, suggesting high affinity of the CuHCF electrode to the Cs⁺ ions. The electrosorption capacity of each ion in mixed solution showed a consistent tendency with that of single solution, and the electrosorption followed Cs⁺ (162.0 mg g⁻¹) > Sr²⁺ (33.4 mg g⁻¹) > Na⁺ (10.7 mg g⁻¹). The order of hydration radii is known as Cs⁺ (3.29 Å) < Na⁺ (3.58 Å) < Sr²⁺ (4.12 Å), and Cs⁺ ions with small hydration radii migrating more readily in the lattice channels (Channel size ≈ 3.2 Å).

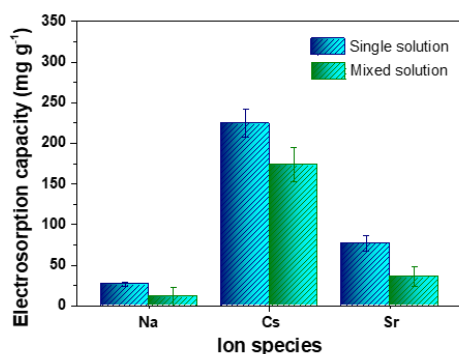


Fig. 5. Electrosorption capacity of the CuHCF electrode under single feed solution and mixed solution with a concentration of 100 mg L⁻¹.

3. Conclusions

We prepared highly crystalline nanoparticulate CuHCF using a facile co-precipitation method. CuHCF was used as a cathode material for electrochemical removal of Cs in an aqueous solution. The CuHCF electrode was expected to improve electrosorption performance and achieve the selective removal of Cs⁺ ions in cation mixtures. The electrosorption performance of the CuHCF electrode strongly depends on the applied voltage, the pH value of the initial feed solution. Our lab-scale tests confirmed that sustainable operation of CuHCF electrodes can be realized. Thus, the proposed electrochemical system with CuHCF is a promising candidate for the efficient removal Cs⁺ ions from wastewater.

REFERENCES

- [1] C. Loos-Neskovic, S. Ayrault, V. Badillo, B. Jimenez, E. Garnier, M. Fedoroff, D. J. Jones, and B. Merinov, Structure of copper-potassium hexacyanoferrate(II) and sorption mechanisms of cesium, *J. Solid State Chem.*, Vol. 177, pp. 1817–1828, 2004.
- [2] N.S. Fisher, K. Beaugelin-Seiller, T.G. Hinton, Z. Baumann, D.J. Madigan, and J. Garnier-Laplace, Evaluation of radiation doses and associated risk from the Fukushima nuclear accident to marine biota and human consumers of seafood, *Proc. Natl. Acad. Sci.*, Vol. 110, pp. 10670–10675, 2013.
- [3] F. Futagami, M. Soliman, K. Takamiya, S. Sekimoto, Y. Oki, T. Kubota, M. Konno, S. Mizuno, T. Ohtsuki, Isolation, characterization and source analysis of radiocaesium micro-particles in soil sample collected from vicinity of Fukushima Dai-ichi nuclear power plant, *J. Environ. Radio.*, Vol. 106388, pp. 223–224, 2020.
- [4] M.A. Waggoner, Radioactive decay of Cs¹³⁷, *Phys. Rev.*, Vol.82, pp. 906–909, 1951.
- [5] D. Rana, T. Matsuura, M.A. Kassim, and A.F. Ismail, Radioactive decontamination of water by membrane processes – a review, *Desalination*, Vol. 321, pp. 77–92, 2013.
- [6] J. Choi, H. Lee, and S. Hong, Capacitive deionization (CDI) integrated with monovalent cation selective membrane for producing divalent cation-rich solution, *Desalination*, Vol. 400, pp. 38–46, 2016.
- [7] F.A. AlMarzooqi, A.A. Al Ghaferi, I. Saadat, and N. Hilal, Application of Capacitive Deionisation in water desalination: A review, Vol. 342, pp. 3–15, 2014.
- [8] Y. Xu, H. Zhou, G. Wang, Y. Zhang, H. Zhang, and H. Zhao, Selective pseudocapacitive deionization of calcium ions in copper hexacyanoferrate, *Acs Appl. Mater. Interfaces*, Vol. 12, pp. 41437–41445, 2020.