Development of High-Performance Prussian Blue Analogue (PBA) Electrodes for Ammonium Ion Recovery from Wastewater

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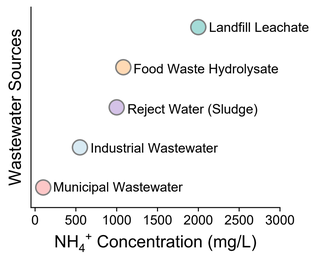
Motivation

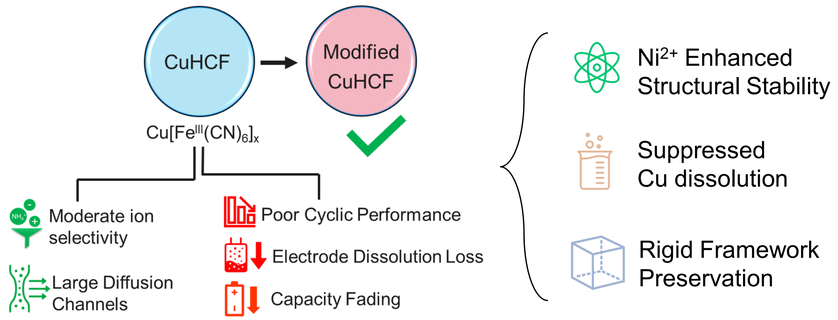
Aquatic Ecosystem Impact: Wastewater (WW) contains 100–2000 mg/L of NH_4^+.

Resource Recovery Potential: ~13.4% of total N-fertilizer consumption worldwide.

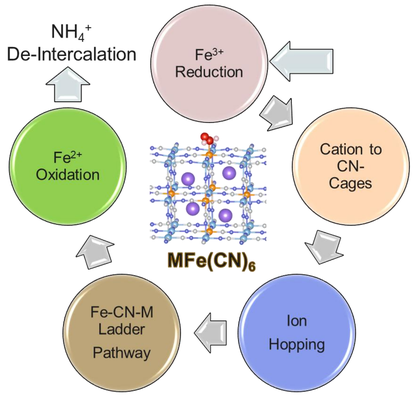
Carbon Emission Reduction: H-B process generates ~ 2.8 tons of CO_2/ton of NH_3.



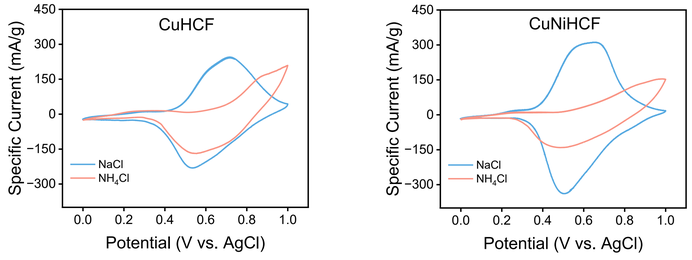
Hypothesis



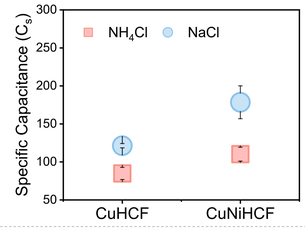
Intercalation Mechanism



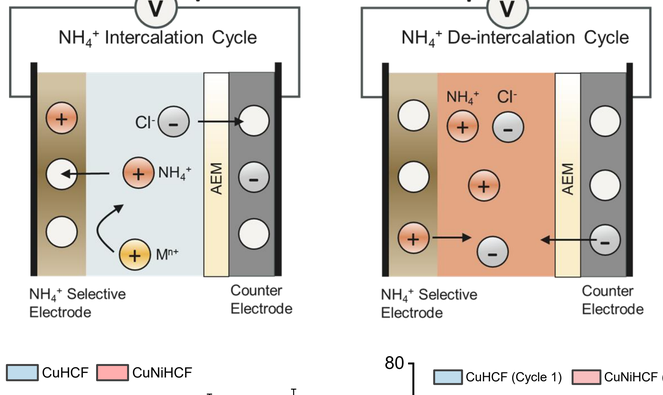
$$M[Fe^{III}(CN)_6]_x + x(NH_4^+ + e^-) \leftrightarrow (NH_4)_xM[Fe^{II}(CN)_6]_x$$

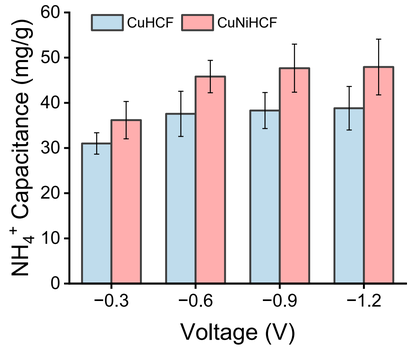


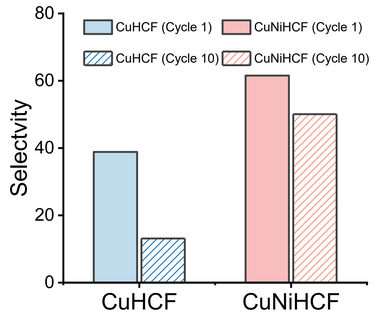
Intercalating Ions		NH_4^+	Na^+
Hydrated Radius (Å)		3.31	3.58
De-Hydration Energy (KJ/mol)		307	409
Intercalation Potential (V vs. AgCl)	CuHCF	0.54	0.54
	CuNiHCF	0.47	0.50



Performance: Operation, Capacity, and Selectivity

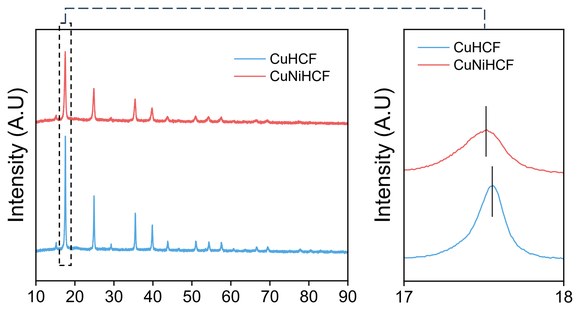




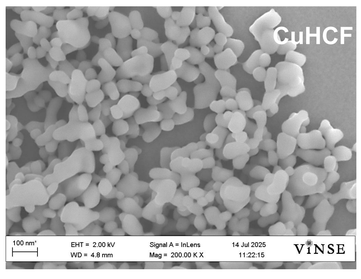


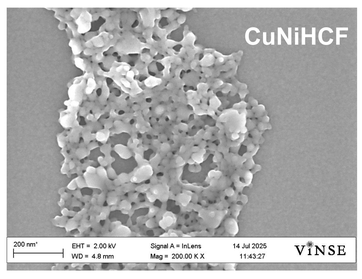
- $NH4^+$ capacitance shows voltage-dependent capacitance, with CuNiHCF outperforming pristine CuHCF across all voltages tested. Optimum -0.9 V.
- CuNiHCF outperformed the pristine CuHCF in terms of selectivity. In the first cycle, CuNiHCF demonstrates a 63% improvement in NH_4^+/Na^+ selectivity.
- After 10 cycles, CuNiHCF retains 81% of its initial selectivity. In stark contrast, CuHCF's selectivity retains only 32% of its original selectivity.

Characterization



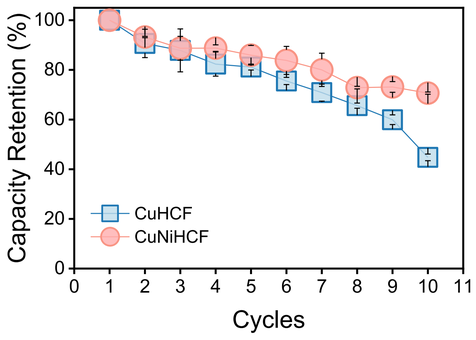
- d_{CuHCF}: 5.053 Å
- $d_{CuNiHCF}$:5.062 Å
- $V_{CuNiHCF}$ increases by 0.36%

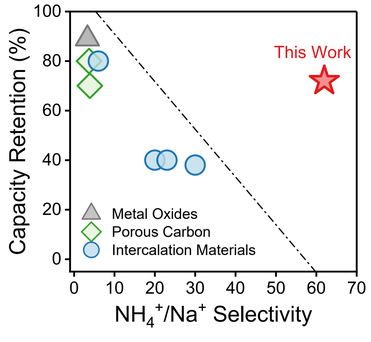


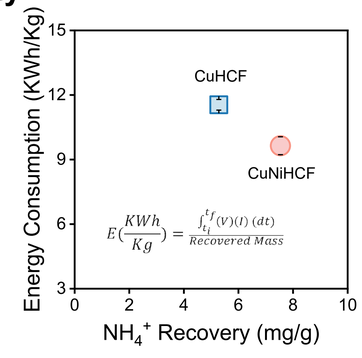


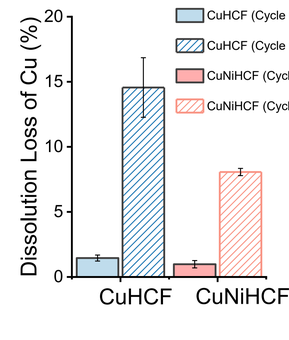
- Pristine CuHCF exhibits relatively uniform polyhedral particles ranging from 70-100 nanometers.
- The incorporation of Ni^{2+} in CuNiHCF produces a shift toward smaller particle sizes with increased agglomeration. This transformation occurs because metal incorporation fundamentally alters the nucleation and growth kinetics.

Performance: Stability









Conclusion

- We investigated the incorporation of Ni^{2+} into the CuHCF framework for NH_4^+ ion recovery from wastewater.
- Ni-modified electrodes outperformed the pristine ones in terms of capacitance, selectivity, and stability.
- Ni-modification solves the problem of Cu leaching and reduces energy consumption.
- Our proposed electrode outperforms in NH_4^+ recovery compared to other electrodes used in the literature.

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