Electrochemical ammonia recovery and co-production of chemicals from manure wastewater

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Abstract

Livestock manure wastewater, containing high level of ammonia, is a major source of water contamination, posing serious threats to aquatic ecosystems. Because ammonia is an important nitrogen fertilizer, efficiently recovering ammonia from manure wastewater would have multiple sustainability gains from both the pollution control and the resource recovery perspectives. Here, we develop an electrochemical strategy to achieve this goal by using an ion-selective potassium nickel hexacyanoferrate (KNiHCF) electrode as a mediator. The KNiHCF electrode spontaneously oxidizes organic matter and uptakes ammonium ions (NH_4^+) and potassium ions (K^+) in manure wastewater with a nutrient selectivity of ~100%. Subsequently, nitrogen- and potassium-rich fertilizers are produced alongside the electrosynthesis of H_2 (green fuel) or H_2O_2 (disinfectant) while regenerating the KNiHCF electrode. The preliminary techno-economic analysis indicates that the proposed strategy has notable economic potential and environmental benefits. This work provides a powerful strategy for efficient nutrient (NH_4^+ and K^+) recovery and decentralized fertilizer and chemical production from manure wastewater, paving the way to sustainable agriculture.

Introduction

Livestock systems provide humans with protein-rich foods, but they are increasingly under pressure to become environmentally sustainable[1]. Many environmental issues[2] stem from managing livestock manure wastewater, a mixture of animal feces, urine, and other system by-products (e.g., waste feed, wash waters). In 2017, 296 billion pounds of livestock manure were generated in the U.S., equivalent in weight to the municipal wastewater produced by two-thirds of the U.S. population[3]. In the current manure management process, manure is simply stored and spread to nearby cropland as a fertilizer to reuse the nutrients. However, manure constituents[4], including nutrients, pathogens, and organic matter, can be lost to the environment during such manure treatment process, therefore it causes nuisance odors, degrades both surface and groundwater quality[5], contributes to climate change[6, 7], thus creating many environmental and human health issues[8]. To address these issues, manure processing systems capable of recovering embedded nutrients in a more manageable form with an increased nutrient density and value need to be developed[9, 10]. Although manure separation systems[11] and microbiological processes[12] are increasingly used for manure treatment, these systems are usually cost- and energy-intensive and have poor separation selectivity for the desired nutrients[13]. In comparison, electrochemical processes[14] driven by renewable electricity could be promising for distributed small-scale nutrient recovery and, especially, selective recovery of ammonia from manure wastewater.

Electrochemical ammonia recovery from wastewater has been focused on membrane-based processes using ion-exchange membranes[15, 16], such as bioelectrochemical systems[17, 18], electrochemical stripping[19], and electrodialysis[20]. The separation of ammonia is usually achieved by the diffusion and migration of ammonium (NH_4^+) ions across the cation-exchange membrane, and subsequently, the transported NH_4^+ ions can be further concentrated and recovered as valuable products[21]. All of these ammonia recovery processes must take place in complete electrochemical reaction cycles. However, the cathodic and anodic half-reactions in these electrochemical processes are not directly involved in the ammonia recovery processes. Instead, they are usually "sacrificial" reactions that decompose the electrolytes or microbial oxidation of the organic matter to provide the electric potential gradient to drive the migration of NH_4^+ ions and maintain the charge and ion balance[22]. Furthermore, the use of ion-exchange membranes increases the cost and complexity of the electrochemical devices. Recently, battery electrodes based on intercalation chemistry have been used for selective ion recovery from domestic wastewater that contains other cations in membrane processes[23-27]. If the currently paired half-reactions in such electrochemical ammonium or other nutrient ion recovery processes could be replaced with the production of value-added chemicals, the process efficiency and sustainability would improve. Therefore, integrating nutrient ion recovery from manure wastewater and electrochemical synthesis in a membrane-free fashion is attractive.

Here, we present a new approach for simultaneous ammonium recovery from manure wastewater and electrochemical synthesis of H_2 or H_2O_2 using an ion-selective redox material as a mediator. We identify potassium nickel hexacyanoferrate (KNiHCF) with high NH_4^+ (and K^+) selectivity, suitable redox potential, and excellent stability for spontaneous NH_4^+ (and K^+) uptake in manure wastewater, which can be conveniently driven by the oxidation of organic matter in manure wastewater. The electrochemical NH_4^+ release is paired with the electrosynthesis of H_2 or H_2O_2 with high Faradic efficiency without ion-exchange membranes. Such rational design enables the demonstration of integrated nutrient ion recovery and electrosynthesis system and co-production of fertilizers and value-added chemicals from manure wastewater using the KNiHCF electrode, air, electricity.

Results

Design of the ammonium recovery and electrosynthesis system

The integrated system for ammonia recovery and electrosynthesis includes the NH_4^+ (K^+) uptake, fertilizer production, electrosynthesis, and wastewater treatment processes (Fig. 1). The key is using solid-state redox materials that can selectively transport NH_4^+ ions and enable the electrochemical co-production of value-added chemicals in the other half-reactions without using membranes yet with no product crossover. We call these materials redox reservoirs (RRs)[28] because RRs allow temporary storage of electrons and ions and redirect them for different electrochemical half-reactions. Such RR strategy have been utilized for decoupled water splitting[29-31] and co-production of chemicals that are incompatible in the membrane processes, such as hydrogen peroxide (H_2O_2) and sodium persulfate[28] or hypochlorite[32]. In addition, proton-selective RR can selectively transport protons to achieve sustained electrochemical productions[33]. Exploring redox materials with high NH_4^+ selectivity may not only selectively recover NH_4^+ (K^+) nutrients from manure wastewater but also enable the simultaneous co-production of chemicals in a membrane-free fashion.

As illustrated in Fig. 1, the spontaneous oxidation of organic matter present in manure wastewater by the oxidized RR (RR^{ox}) drives the NH_4^+ (K^+) uptake process concurrent with the reduction of RR to the reduced RR (RR^{red}). Then, the RR electrode is transferred to different electrochemical cells to pair with cathodic H_2 or H_2O_2 production, while the oxidation of RR releases NH_4^+ (K^+). The NH_4^+-selective RR can reversibly uptake and release NH_4^+ (K^+) during redox cycles and maintains the charge balance in different cells, thus achieving effective NH_4^+ recovery. Drying the recovered solutions yields NH_4^+-rich fertilizers. Moreover, since relatively concentrated K_2SO_4 solution is used as the supporting electrolyte for H_2O_2 production, manure wastewater disinfected by the produced H_2O_2 can be concentrated/dried to recycle K^+-rich salts as electrolytes or fertilizers (potash).

The manure wastewater prepared from cow feces and urine is a weakly alkaline suspension (pH~9) and contains different inorganic ions (NH_4^+, Na^+, K^+, etc.), organic species, and solid particles (Supplementary Figs, 1-6, and Table 1). Given its complicated chemical compositions, the challenges of NH_4^+ recovery lie in the competing uptake of other cations present in manure wastewater, such as Na^+, and the stability of the RR material. Therefore, the ideal RR material should meet several criteria: high NH_4^+ selectivity, suitable redox potential, excellent (electro)chemical stability in manure wastewater, fast redox kinetics, and high capacity.

Electrochemical behaviors of NH_4^+-selective redox materials

Because the Stokes radius and desolvation energy barrier of NH_4^+ are smaller than those of common metal ions (e.g., Na^+, K^+, Ca^{2+}, Mg^{2+})[34, 35], the (de)intercalation of NH_4^+ should be intrinsically faster than other cations. Redox materials with large ionic channels[36] that can form non-ionic H-bonding with charge carriers[37, 38] may selectively accelerate the NH_4^+ migration over other cations. Following such general guidelines, we choose Ni and Cu-based Prussian Blue analogs (PBAs) with open-framework structures (Fig. 2a) because they are known as stable aqueous battery materials[39, 40] and show promise for NH_4^+ intercalation from aqueous solutions[23, 24].

We used co-precipitation methods to synthesize PBAs with different morphologies (see Methods), including KNiHCF nanoparticles (Fig. 2b), sodium nickel hexacyanoferrate microcubes (NaNiHCF, Supplementary Fig. 7a), and copper hexacyanoferrate nanoparticles (CuHCF, Supplementary Fig. 7b). Powder X-ray diffraction (PXRD) patterns of the KNiHCF and CuHCF samples (Supplementary Fig. 8) display the characteristic (200), (220), and (400) diffraction peaks that match well with the standard pattern of the cubic PBA phase (JCPDS No. 52-1907). In comparison, the NaNiHCF sample has the rhombohedral structure (Supplementary Fig. 8). Thermogravimetry analyses (TGA, Supplementary Fig. 9) and inductively coupled plasma optical emission spectroscopy (ICP-OES, Supplementary Table 2) revealed the water content and element compositions in these samples, respectively, to determine the exact chemical formulas of the KNiHCF, NaNiHCF, and CuHCF samples to be $K_{0.1}Ni_{1.5}[Fe(CN)_6] \cdot 6.7\ H_2O$, $Na_{2.1}Ni[Fe(CN)_6] \cdot 2.1\ H_2O$, and $K_{0.06}Cu_{1.5}[Fe(CN)_6] \cdot 5.5\ H_2O$, respectively.

We first evaluated the cycling stability of these PBA electrodes in manure wastewater. The CuHCF electrode showed near zero capacity from cyclic voltammograms (CV) and galvanostatic charge-discharge (GCD) tests and possible dissolution from PXRD (Supplementary Fig. 10). We further measured the NaNiHCF and KNiHCF electrodes since they were reported to be more pH-tolerant than the CuHCF electrode[41]. The NaNiHCF electrode with pre-intercalated Na^+ showed obvious capacity decay at 2 C rate in weakly alkaline solutions (Supplementary Fig. 11). Here, 1 C rate is 65 mA g^{-1} based on the theoretical capacity. The observed capacity decay of the redox materials is likely caused by two primary factors: structure collapse related to pH and incompatibility with the components in manure wastewater (Supplementary Fig. 11). The GCD tests of the KNiHCF electrode at 2 C rate confirmed its long-term cycling stability in various solutions and even manure wastewater (Fig. 2c, Supplementary Fig. 12, and Table 3).

Based on these results, we chose KNiHCF as the model RR material and studied its cation intercalation properties. CV profiles of the KNiHCF electrode in 1 M NaCl, KCl, and NH_4Cl solutions at 1 mV s^{-1} (Fig. 2d) showed reversible redox chemistry with intercalation potentials of NH_4^+, K^+, and Na^+ at ~0.686 V, ~0.678 V, and ~0.566 V versus standard hydrogen electrode (SHE), respectively. Based on the Nernst equation, such differences in thermodynamic driving forces (~0.120 V for NH_4^+/ Na^+ and ~0.08 V for NH_4^+/ K^+) mean that NH_4^+ intercalation is theoretically preferred when the molar ratio of NH_4^+/ Na^+ (or K^+) is greater than 9×10^{-3} (or 0.7) (Supplementary Note 1)[42]. Therefore, the KNiHCF electrode should selectively intercalate NH_4^+ in manure and common municipal wastewater given their compositions (Fig. 2e and Supplementary Table 4). The KNiHCF electrode showed similar CV profiles and rate capabilities in synthetic wastewater (sww, 0.50 M NH_4Cl + 0.183 M $KHCO_3$ + 0.146 M $NaHCO_3$), manure wastewater, and 1 M

NH_4Cl solution (Supplementary Figs. 13-15), suggesting possibly dominated NH_4^+ (de)intercalation in these solutions. Moreover, the KNiHCF electrode with 100 % state-of-charge (SOC) was spontaneously reduced to ~0 % SOC after 24 hours, likely by the organic matter present in manure wastewater (Fig. 2f). In comparison, the KNiHCF electrode retained 70.5 % SOC after 48-hour self-reduction in synthetic wastewater (Fig. 2f and Supplementary Fig. 16). Since the reduction of RR requires cation intercalation to balance the charge, these results suggest that the KNiHCF RR can spontaneously and selectively uptake NH_4^+ ions from manure wastewater.

NH_4^+ recovery from synthetic manure wastewater

We first studied the NH_4^+ recovery in synthetic wastewater using an integrated electrochemical system that includes an anodic cell ($Cell_{anodic}$) for NH_4^+ uptake from synthetic wastewater, a cathodic cell ($Cell_{cathodic}$) for NH_4^+ release in 0.1 M Li_2SO_4 solution (pH~1.3), and a KNiHCF RR electrode with a specific capacity (charge) of 186 C g^{-1} (Fig. 3a). Here, $Cell_{anodic}$ or $Cell_{cathodic}$ is named based on electrocatalytic half-reactions, not the oxidation/reduction of the RR. In $Cell_{anodic}$, the reduction of RR accompanied with the NH_4^+ uptake was paired with OER at the Pt anode (Fig. 3b, red region). In $Cell_{cathodic}$, the oxidation of RR released NH_4^+ to complete one recovery cycle, which was paired with HER at the Pt cathode (Fig. 3b, blue region). The ion or nutrient (NH_4^+ and K^+) selectivity and the Faradaic efficiency (FE) of the cations were calculated based on the concentrations of cations that were analyzed by ion chromatography (Methods).

To investigate the relationship between nutrient selectivity and NH_4^+ removal, we conducted a five-cycle recovery process, where the full recovery process cycle (Fig. 3a) was applied to the same batch of synthetic wastewater five times and the recovered ions were released in a new 0.1 M Li_2SO_4 solution for each cycle (Methods, Supplementary Figs. 17 and 18). During cycles 1 to 3, the NH_4^+ removal increased nearly linearly from 0 to 81 % and the Na^+ concentration ($[Na^+]$) in synthetic wastewater showed no apparent changes (Fig. 3c, top panel). The nutrient selectivity of ~97 % indicated that the KNiHCF electrode preferred the intercalation of NH_4^+ and K^+ over Na^+ (Fig. 3c, bottom panel). During cycles 4 and 5, the NH_4^+ removal approached ~100 %, but the nutrient selectivity decreased to 54 % because limited concentrations of nutrient ions remained in synthetic wastewater (Fig. 3c, top panel). Over five cycles, the FE of three cations decreased from 111 ± 5 % to 66 ± 6 % (Supplementary Fig. 19a), which might result from the competing proton intercalation due to decreasing pH from OER. The NH_4^+ / Na^+ selectivity of

6~14 and NH_4^+ / K^+ selectivity of 1.4 (Supplementary Fig. 19b) confirmed the thermodynamically favorable NH_4^+ recovery. The KNiHCF electrode recovered 64 % of NH_4^+ ions originally in synthetic wastewater, 18 % of NH_4^+ ions were transfer loss because of the inevitable residual solution on the electrode during electrode transfer, and NH_4^+ loss was 18 % (Fig. 3d). This NH_4^+ loss could result from the possible redox reactions between active chlorine and NH_4^+ during the NH_4^+ uptake process (Supplementary Fig. 20). We also conducted a three-cycle recovery process in synthetic wastewater to confirm the ion selectivity and cycling stability of RR (Supplementary Figs. 21-24). Since current electrochemical oxidation reactions may cause NH_4^+ loss, developing a mild oxidation process to pair with the reduction of RR will help to maintain the NH_4^+ balance and achieve a more efficient recovery.

NH_4^+ recovery from manure wastewater

We further investigated NH_4^+ recovery from manure wastewater using a two-step recovery process (Fig. 4a) that includes spontaneous NH_4^+ uptake in manure wastewater and electrochemical NH_4^+ recovery in 0.1 M Li_2SO_4 solution (pH~2). When NH_4^+ were intercalated into the KNiHCF RR electrode, the electrode was reduced spontaneously by the oxidation of organic matter in manure wastewater (Fig. 4b, red region). Then NH_4^+ was released during the RR oxidation, which is paired with HER at the Pt electrode to finish one recovery cycle (Fig. 4b, blue region).

We studied how NH_4^+ recovery in manure wastewater was influenced by the capacity of the RR electrode (Supplementary Fig. 25) and then conducted three parallel recovery processes, noted as run 1, 2, and 3, using a KNiHCF electrode with a capacity twice the minimal charges to recover NH_4^+ ions from manure wastewater. Each run was one recovery cycle that included spontaneous NH_4^+ uptake and electrochemical NH_4^+ recovery. For a typical recovery run, the $[NH_4^+]$, $[K^+]$, and $[Na^+]$ in manure wastewater were reduced by ~344, 69, and 35 mM, respectively (Fig. 4c, top panel). The NH_4^+ removal in manure wastewater was 66~68 % for each run (Fig. 4c, top panel). The nutrient selectivity was 93~98 % in the recovered solutions (Fig. 4c, bottom panel). The NH_4^+ / Na^+ selectivity of 6~7 and NH_4^+ / K^+ selectivity of ~1.3 (Supplementary Fig. 26) were similar to those achieved in synthetic wastewater. Unlike the case of NH_4^+ recovery in synthetic wastewater (Fig. 3d), there was nearly zero NH_4^+ loss in manure wastewater because the electrochemical oxidation process was replaced with the spontaneous oxidation of organic matter.

On average, 68 % NH_4^+ ions were recovered and 32 % NH_4^+ were left in manure wastewater after this one cycle (Fig. 4d and Supplementary Fig. 27), where the latter could be used as the feedstock for the next-cycle recovery process.

Chemical oxygen demand (COD), the amount of oxygen needed to oxidize the organic matter to carbon dioxide, was measured to quantify the amount of organic matter in manure wastewater. The COD decreased from 24.04 ± 0.4 g L^{-1} to $15.5{\sim}16.6 \pm 0.4$ g L^{-1} (a COD removal of 31 %~35 %) during each run (Fig. 4e), confirming the spontaneous oxidation of organic matter in manure wastewater by the RR. Cyclic voltammograms of different electrodes in synthetic and manure wastewater (Supplementary Figs. 28 and 29) and the self-reduction behaviors of the KNiHCF electrode in synthetic wastewater with model organic molecules (Supplementary Fig. 29c) showed that the oxidized KNiHCF electrode with a high potential enabled the oxidation of organic matter driven by their potential difference. Moreover, Coulombic efficiency (CE), defined as the ratio of the charges passing through the RR (C_{RR}) to the charges needed for COD removal (C_{COD}), is used to evaluate the efficiency of organic-to-electricity over the recovery processes (Supplementary Note 2). The CE of ~30 % for each run (Supplementary Figs. 30 and 31) might result from the complicated bio-related processes in manure wastewater. Also, since more organic matter is available for oxidation than the ammonium ions available to recover in manure wastewater (Supplementary Fig. 25 and Note 2), we could achieve ~93% COD removal using the KNiHCF electrode in a 4-cycle NH_4^+ uptake from the same manure wastewater by adding $(NH_4)_2SO_4$ salt to maintain the NH_4^+ concentration (Supplementary Fig. 32). Furthermore, the KNiHCF electrode showed long-term stability and retained 90.1% of its original NH_4^+-uptake capacity after 50 runs (Fig. 4f, Supplementary Fig. 33 and Table 5). The surface uptake and release rates using the KNiHCF electrode were 0.0071 mmol cm^{-2} h^{-1} and 0.093 mmol cm^{-2} h^{-1} (Supplementary Fig. 34), comparable to the values reported for membrane-based (bio)electrochemical systems[19, 43]. These results indicate the KNiHCF electrode's excellent performance in recovering NH_4^+ from manure wastewater.

Simultaneous NH_4^+ recovery and electrochemical synthesis

The NH_4^+ recovery could be paired with the electrochemical H_2 production (Supplementary Fig. 35 and Note 3) or two-electron oxygen reduction reaction (2e$^-$ ORR) to produce H_2O_2 (Fig. 5a), a common oxidant and disinfectant that can be used for wastewater treatment[44, 45]. We chose

Fe-decorated carbon nanotube (Fe-CNT) as the electrocatalyst for H_2O_2 production because of its good electrochemical activity and stability in neutral and alkaline solutions[46]. Given the high reactivity and intrinsic instability of H_2O_2, we optimized the supporting electrolytes and electrochemical configurations for H_2O_2 production (Supplementary Figs. 37-39 and Table 7). Because many crops (such as tomatoes and potatoes) are chloride-sensitive[47], we chose K_2SO_4 (sulfate of potash) as the supporting electrolyte. The Fe-CNT electrode in O_2-saturated 0.5 M K_2SO_4 solution delivered a high current density of 49 mA cm^{-2} at −0.10 V versus reversible hydrogen electrode (RHE), with the FE above 90 % in the potential range of 0.00 to 0.20 V versus RHE (Fig. 5b). With such optimizations, we achieved the accumulation of H_2O_2 up to 3.3 g L^{-1} with a FE of 82 % (Fig. 5c and Supplementary Fig. 40). Because KNiHCF could decompose H_2O_2 (Supplementary Figs. 41 and 42), a divided electrochemical cell needs to be used to co-produce H_2O_2 and fertilizer.

We demonstrated simultaneous NH_4^+ (K^+) recovery and electrochemical H_2O_2 production in a two-compartment H-cell separated by a microporous glass frit (Fig. 5a) that allows the transport of major ions (e.g., K^+ and SO_4^{2-} in K_2SO_4 solution) to maintain the charge balance. After the spontaneous NH_4^+ uptake from manure wastewater, three parallel one-cycle processes of NH_4^+ recovery and H_2O_2 production using a KNiHCF electrode were conducted, as Run 1, 2, and 3. Over the three runs, COD removal was between 28 % to 30 % (Supplementary Fig. 43a), and the corresponding CE (C_{RR}/C_{COD}) was about ~ 30 %, consistent with the results above (Supplementary Figs. 43b). After this one-cycle recovery process, 52 ± 6 % NH_4^+ were recovered from and 41 ± 4 % NH_4^+ were left in manure wastewater (Fig. 5d) with a total NH_4^+ balance of 93 ± 10 %. No NH_4^+ and Na^+ were detected in the H_2O_2 chamber throughout the recovery processes, but [K^+] increased in the H_2O_2 chamber and decreased in the RR chamber (Supplementary Fig. 44), indicating that K^+ was the major cation crossing the glass frit. These runs produced H_2O_2 up to 2772 ppm with a FE of 91 % and released NH_4^+ up to 3187 ppm (177 mM) with a NH_4^+ removal of 59 % (Fig. 5e and Supplementary Fig. 45). The PXRD pattern of the salts recovered from the electrolyte in the RR chamber (Fig. 5f) matched with those of $(NH_4)_3H(SO_4)_2$, $(NH_4)_{0.1}K_{1.896}SO_4$, and K_2SO_4 (JCPDS No. 72-0354) well, confirming the production of K^+ and NH_4^+ fertilizers. We also conducted two consecutive cycles of NH_4^+ recovery and H_2O_2 production to achieve a more complete NH_4^+ recovery of 84 % and COD removal of 56 % (Fig. 5e and Supplementary Fig. 46). The KNiHCF electrode retained 96 % of the capacity after the above recovery processes

(Supplementary Fig. 47), showing good stability in these complex solutions. Furthermore, we can use the H_2O_2 solution co-produced during the NH_4^+ recovery processes to disinfect the manure wastewater and then recycle K^+-rich salts from such treated wastewater, which can be used as electrolytes or fertilizers.

NH_3 emissions and preliminary techno-economic analysis

One of the main advantages of the ammonia recovery process in terms of environmental sustainability is the reduction of NH_3 emissions from manure management, especially considering that livestock operations are the main source of NH_3 emissions globally[1, 2, 13]. We used process-based models (Supplementary Note 4 and Tables 7 and 8) to estimate NH_3 emissions from manure in a 1,000-lactating cow dairy farm (with and without anaerobic digestion), collecting, storing, and land-applying manure and the reduction in NH_3 emissions using the ammonia recovery process developed herein. Our proposed process could reduce NH_3 emissions by up to 70% compared to the business-as-usual scenarios (Fig. 6a, Supplementary Fig. 48, and Table 9). Moreover, we performed a preliminary economic analysis to quantify the economic benefits of using this technology in a modeled 1,000-cow dairy farm (Supplementary Notes. 5 and 6). When only considering the values of the produced chemicals and the major material and electricity costs in both their high and low price limits, the proposed process shows a potential to be profitable up to about US $ 200k per year for this modeled farm (Fig. 6b, Tables 10 to 16). The largest revenue and cost come from the produced KOH based on NH_4^+ and K^+-salt recovery and K_2SO_4 salt used as the electrolyte, respectively. The annual revenues from the produced $(NH_4)_2SO_4$, H_2O_2 and KOH (K^+ from manure) are ~$ 260k in the high case, high enough to cover the cost of RR materials and electricity. Fluctuating electricity costs from location-dependent varying market prices dominate the annual costs difference when comparing the low and high cases (Supplementary Table 15 and Fig. 51). The breakdown of various revenues in Fig. 6b also shows that the simultaneous production of valuable H_2O_2 and the recovery of both ammonia and potassium from the manure wastewater substantially contribute to the overall profitability. Note that this preliminary economic analysis did not consider the environmental and health benefits due to the reduction of ammonia emission.

Discussion

Efficient manure management and nutrient recovery are crucial to developing a more sustainable livestock system. Using an ion-selective redox material, we developed an electrochemical process for simultaneous ammonia recovery and electrochemical synthesis by integrating spontaneous NH_4^+ (K^+) uptake from manure wastewater, fertilizer production, and co-production of H_2 or H_2O_2. The new conceptual strategy can open new opportunities for electrochemical nutrient recovery from a variety of wastewater sources (including municipal wastewater and sewage sludge) and on-demand distributed electrochemical manufacturing with high recovery efficiency and low energy cost.

Recovering ammonia from manure wastewater has multiple sustainability gains from pollution control and resource recovery perspectives. Our results and preliminary analyses show that the new integrated strategy could improve the sustainability of livestock systems by upgrading the manure processing systems to reduce environmental impacts while improving the economic profitability of agricultural systems. Recovering ammonia from livestock manure can not only directly mitigates ammonia emissions compared to the direct application of manure in cropland, but also improve nitrogen use efficiency and minimize ammonia loss during fertilizer storage after recovery. Furthermore, the new integrated strategy could achieve distributed co-production of locally useful valuable chemicals, such as H_2O_2 disinfectant, that improves the economics of rural communities.

Although in the current lab-scale proof-of-concept experiments solution dilution sometimes occurs, further scale-up, device engineering, and optimization of operation conditions to minimize the volume of the recovered solution can achieve the concentration of nutrients and further reduce the energy cost for potential separation. Developing NH_4^+-selective redox materials with higher capacity, better stability, and lower cost, and reducing the electricity cost by participating in dynamic electricity markets with lower prices would further reduce the cost and increase the revenues of this process. Understanding the spontaneous oxidation process of organic matter in manure wastewater by the redox materials and optimizing the system design are crucial steps to improve the system's performance further. Since livestock manure wastewater can vary significantly depending on locations, animal type, diet, seasonal variations, farm size, etc., refined process design based on the compositions and characteristics of livestock manure could be important for further improving the system efficiency.

Methods

Chemicals. All chemicals were used as purchased without further purification. Sodium citrate dihydrate (ACS reagent grade) was purchased from ICN Biomedicals Inc. Carbon black (Super P Conductive, 99.0+ %) and carbon black (acetylene, 99.9+ %) were purchased from Alfa Aesar. TUBALL BATT NMP 0.4 % (a mixture of single-wall carbon nanotubes, 0.4 wt %; polyvinylidene fluoride, 2 wt %; N-methyl-2-pyrrolidone, > 96.7 wt %) was purchased from OCSiAl. Other chemicals were purchased from Sigma Aldrich. Titanium mesh (150 mesh, with a thickness of ~ 230 μm) was purchased from HeBei ChaoChuang Metal Mesh Co., Ltd (available through Alibaba.com). Deionized nanopure water (18.2 MΩ·cm) from ThermoScientific Barnstead water purification systems was used for all experiments.

Synthesis of KNiHCF. Potassium nickel hexacyanoferrate (KNiHCF) was synthesized using a modified co-precipitation method[39]. Typically, 80 mL of 40 mM $Ni(NO_3)_2$ solution and 80 mL of 20 mM $K_3Fe(CN)_6$ solution were added dropwise into 40 mL H_2O under vigorous stirring. The solution was stirred for 6 h at 70 °C to yield a dark-orange precipitate. Then the precipitate was centrifuged, rinsed with deionized water multiple times, and dried in a vacuum oven at 60 ºC overnight.

Synthesis of NaNiHCF. Sodium nickel hexacyanoferrate (NaNiHCF) was synthesized using a co-precipitation method[28]. Typically, 100 mL of 0.1 M $NiCl_2$ and 1 M sodium citrate dihydrate solution and 100 mL of 0.1 M $Na_4Fe(CN)_6$ solution were added dropwise to 100 mL H_2O under vigorous stirring. The molar ratio between Ni^{2+} and citrate was 1:10. The solution was then stirred for 24 h at 80 ºC to yield a light-green precipitate. This precipitate was centrifuged, rinsed with deionized water multiple times, and dried in a vacuum oven at 60 ºC overnight.

Synthesis of CuHCF. Copper hexacyanoferrate (CuHCF) was synthesized using a modified co-precipitation method[48]. Typically, 40 mL of 0.2 M $CuSO_4$ solution was added dropwise into 40 mL of 0.1 M $K_3Fe(CN)_6$ solution under vigorous stirring at room temperature. After 6 h of reaction, the olive-green precipitate was centrifuged, rinsed with deionized water multiple times, and dried in a vacuum oven at 60 ºC overnight.

Synthesis of Fe-CNT catalyst. The synthesis of Fe-CNT catalyst followed a reported impregnation and reduction method[32]. In a typical synthesis, a 7.5 mM iron nitrate solution was first prepared by dissolving 30.3 mg $Fe(NO_3)_3 \cdot 9H_2O$ into 10 mL nanopure water. Next, the carbon nanotube (CNT) suspension was prepared by mixing 50 mg MWCNT (724769, > 95 % carbon from Sigma Aldrich) with 20 mL of ethanol via sonication for 1 h until a well-dispersed suspension was achieved. Then 200 μL of 7.5 mM Fe^{3+} solution was added dropwise into the CNT suspension under sonication for 30 min. Then the solvent was removed using a rotary evaporator, and the as-prepared material was dried in a vacuum oven at 60 °C for 20 min to evaporate the residual solvent further. Finally, the dried $Fe(NO_3)_3$/CNT powder was heated in a tube furnace to 600 °C within 20 min under a gas flow of 100 sccm Ar (UHP, Airgas) and a pressure of 1 Torr and kept at the same temperature for another 40 min before cooling down to room temperature.

Materials characterizations. Powder X-ray diffraction (PXRD) patterns of the KNiHCF, NaNiHCF, and CuHCF samples were collected using a Bruker D8 Advance X-ray diffractometer equipped with Cu-Kα radiation. The size and morphology of the samples were characterized using a scanning electron microscope (SEM, Zeiss SUPRA 55VP) equipped with an energy-dispersive X-ray spectroscopy (EDS) detector. An inductively coupled plasma-optical emission spectrometer (ICP-OES, Agilent 5110) was utilized to determine the compositions of K, Na, Cu, Ni, and Fe elements. Thermogravimetric analysis (TGA, TA Q500) was used to determine the water content in various samples.

Fabrication and electrochemical tests of the RR electrodes. The RR electrodes were prepared via a conventional slurry-casting method using TUBALL BATT NMP 0.4% (0.4 wt % SWCNT, 2 wt % polyvinylidene fluoride, > 96.7 wt % N-Methyl-2-pyrrolidone), super P conductive carbon, and the active materials. Typically, 70 wt % active materials and 18 wt % Super P carbon black were grounded for 30 min using a high-energy ball mill (Mixer/Mill 8000M, Horiba). Then the mixtures were added into TUBALL BATT NMP 0.4% that provided 2 wt % SWCNT and 10 wt % polyvinylidene fluoride for the electrode slurry (SWCNT and PVDF both from TUBALL BATT NMP 0.4%). The slurry was stirred at 700 r.p.m. overnight at room temperature and then cast onto titanium mesh current collectors (150 mesh, with a thickness of ~ 230 μm). The titanium mesh was held in place by two PTFE (polytetrafluoroethylene) plates on both sides of the mesh and a clamp to secure the plates. The slurry was cast onto one side of the Ti mesh and subsequently onto the other side using stainless steel spatulas. The prepared electrodes were dried in a vacuum oven at 60 °C for 12 h to remove the residual solvent. The areal mass loading ranged from 5 to 24 mg cm^{-2}.

The electrochemical performance of the RR electrode was characterized in a three-electrode cell, with a Pt wire counter electrode and a saturated calomel electrode (SCE) as the reference electrode in various solutions (1 M NH_4Cl, 1 M KCl, 1 M NaCl, synthetic wastewater, and manure wastewater). Synthetic wastewater (0.50 M NH_4Cl + 0.183 M $KHCO_3$ + 0.146 M $NaHCO_3$) was prepared based on the chemical compositions of manure wastewater (Supplementary Fig. 2 and Table 1). Maure wastewater with a pH of ~7 was prepared by acidifying manure wastewater (pH~9) using 3 M H_2SO_4. Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) tests of the RR electrodes were recorded on a Bio-Logic VMP-3 multichannel potentiostat. The galvanostatic cycling was performed at 2 C rate for stability characterization and the rates of 1 C to 1000 C for the kinetics characterization, where 1 C is defined as 65 mA g^{-1} based on the theoretical capacity of as-synthesized materials. For studying the self-reduction behaviors, two KNiHCF RR electrodes with similar mass loading (~80 mg) were oxidized to 0.9 V vs. SCE in synthetic wastewater and transferred to two beaker-type cells containing 80 mL of either manure or synthetic wastewater. The potentials of the RR electrodes were monitored using a Bio-Logic SP-200 potentiostat.

Preparation of manure wastewater. Cow feces and urine were collected from the campus dairy cattle center at UW-Madison and stored in the cold room at 4 °C before use. To prepare manure wastewater, the feces and urine were mixed with a mass ratio of 1:9 with trace carbon black under stirring (e.g., 20 g feces, 180 g urine, and ~10 mg carbon black for a typical preparation). Since this solid-liquid mixture could not pass the filter membrane with a pore size smaller than 10 μm even when a vacuum system was used, centrifugation would be the proper method to separate the solids with large particle sizes. Here, trace carbon black was added to the mixture of cow urine and feces to achieve solid-liquid separation because it could work as the coagulation reagent and be easily separated from manure wastewater after centrifugation. After centrifugation at 8694 g (9000 r.p.m) for 15 min at 4 °C (50 g of the mixture in each centrifuge tube), the brownish supernatant with some suspended particles was used as manure wastewater without further filtration throughout this study. The precipitate with a brownish-yellow color was formed gradually during the storage of manure wastewater (as shown in Supplementary Fig. 1), but the precipitate was not used in the study.

Chemical characterization of manure wastewater. Manure wastewater was used without further treatment, and its pH value was determined to be 9.0-9.2 using the Orion 810 BNUWP ROSS Ultra pH meter. The concentrations of various cations ([NH_4^+], [K^+], and [Na^+]) and anions in the manure wastewater and recovered samples were analyzed using ICS-1100 (cations) and Dionex ICS-2100 (anions) ion chromatography (IC) systems equipped with conductivity detectors, respectively. Typically, cation analysis was performed using a Dionex™ IonPac™ CS12A IC column with 7.5 mM methanesulfonic acid (MSA) solution as the mobile phase at 1.5 mL min^{-1}. The current of the suppressor was 33 mA. Anion analysis was performed using a Dionex™ IonPac™ AG/AS-14 column with 3.5 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ solution as the mobile phase at 1.2 mL min^{-1}. The current of the suppressor was 24 mA. The standard cation solutions were prepared by dissolving NaCl, LiCl, KCl, and NH_4Cl in nanopure water. The standard anion solutions were prepared by dissolving NaF, NaBr, NaCl, $NaNO_2$, $NaNO_3$, NaH_2PO_4, and Na_2SO_4. The standard acetate solution was prepared by dissolving only sodium acetate without other salts in nanopure water because of F^- and acetate coelution. All samples were diluted and filtrated using 0.45 μm syringe filters before analysis.

Total nitrogen (TN) in manure wastewater was analyzed using the total nitrogen reagent set from Hach (Total Nitrogen Reagent Set, HR, TNT, product# 2714100). Total phosphate in manure wastewater was analyzed using the total phosphate reagent set from Hach (High Range Total Phosphate Reagent Set, product# 2767245). Total carbon, organic carbon, and inorganic carbon in manure wastewater were analyzed using a Sievers M5310C total organic carbon analyzer after proper dilution and filtration. Chemical oxygen demand (COD) of manure wastewater was analyzed using the COD reagent set from Hach [TNTplus Vial Test, HR (20-1,500 mg/L COD), product# 2415925].

NH_4^+ recovery from synthetic wastewater. Two electrochemical cells, the NH_4^+-uptake cell ($Cell_{anodic}$) containing 25 mL synthetic wastewater and the NH_4^+-release cell ($Cell_{cathodic}$) with 25 mL 0.1 M Li_2SO_4 solution (pH ~1.3), were used to recover NH_4^+ from synthetic wastewater. The KNiHCF RR electrodes with the size of 4 ×4 cm^2 and a total capacity of 294 C (a total active material loading of ~1.600 g) were prepared as described above and used as the working electrode in both cells. In $Cell_{anodic}$, a Pt wire electrode and a SCE were used as the counter electrode and reference electrode. In addition, about 1 g $CaCO_3$ was added to the electrochemical cell to stabilize the pH. The NH_4^+-uptake process was conducted under a current of 45 mA. In $Cell_{cathodic}$, a Pt wire electrode and a SCE were used as the counter electrode and reference electrode. The NH_4^+-release process using KNiHCF RR electrodes was measured under a constant current of 30 mA.

Typically, one NH_4^+ recovery cycle included the NH_4^+ uptake from wastewater and the NH_4^+ release in Li_2SO_4 solution. For the five-cycle recovery process, the cations in the same 25 mL synthetic wastewater were recovered five times, and the recovered ions were collected in a new 0.1 M Li_2SO_4 solution for each cycle. The RR electrodes were oxidized to 0.9 V vs. SCE (RR^{ox}) in synthetic wastewater to de-intercalate cations before the NH_4^+ recovery processes. In $Cell_{anodic}$, the reduction of RR^{ox} to RR^{red} is accompanied by cation intercalation, which was paired with OER at the Pt anode. After the NH_4^+ uptake, the RR electrode was washed with nanopure water and 0.1 M Li_2SO_4 solution to remove the residual electrolyte, then moved to $Cell_{cathodic}$. In $Cell_{cathodic}$, the oxidation of RR released intercalated cations until 0.9 V vs. SCE, which was paired with HER at the Pt cathode. During these recovery processes, the capacity of the RR electrode was controlled by the potential and capacity restrictions to ensure the RR electrode was operated within the desired potential windows. For the three-cycle NH_4^+ recovery process, $Cell_{anodic}$ contained 16 mL synthetic wastewater and $Cell_{cathodic}$ contained 18 mL 0.1 M Li_2SO_4 solution (pH ~1.3). Other electrochemical configurations and operations were the same as those for the five-cycle recovery process.

The concentrations of cations in synthetic wastewater and recovered solutions after each recovery cycle were measured by IC following the above procedures. Based on the concentrations of cations, the ion selectivity between different cations, nutrient ($NH_4^+ + K^+$) selectivity, and Faradaic efficiency (FE) were calculated according to the following equations:

$$\text{Ion selectivity (M/N)} = \frac{[\mathrm{M}]_{\mathrm{recovered}} / [\mathrm{N}]_{\mathrm{recovered}}}{[\mathrm{M}]_{\mathrm{initial}} / [\mathrm{N}]_{\mathrm{initial}}} \tag{1}$$

$$\text{Nutrient } (\mathrm{NH_4^+} + \mathrm{K^+}) \text{ selectivity} = \frac{[\mathrm{NH_4^+}]_{\mathrm{recovered}} + [\mathrm{K^+}]_{\mathrm{recovered}}}{[\mathrm{NH_4^+}]_{\mathrm{recovered}} + [\mathrm{K^+}]_{\mathrm{recovered}} + [\mathrm{Na^+}]_{\mathrm{recovered}}} \tag{2}$$

$$\text{FE (\%)} = \frac{\text{Q based on recovered cations}}{\mathrm{Q_{RR}}} \times 100 \tag{3}$$

where the $[\mathrm{M}]_{\mathrm{recovered}}$ and $[\mathrm{N}]_{\mathrm{recovered}}$ were the concentrations of M and N cations in the recovered solutions, the $[\mathrm{M}]_{\mathrm{initial}}$ and $[\mathrm{N}]_{\mathrm{initial}}$ were the concentrations of M and N cations in synthetic wastewater, $[\mathrm{NH_4^+}]_{\mathrm{recovered}} + [\mathrm{K^+}]_{\mathrm{recovered}} + [\mathrm{Na^+}]_{\mathrm{recovered}}$ were the concentrations of NH_4^+, K^+, and Na^+ in the recovered solutions, and Q_{RR} was the charge passing through the RR electrode in the recovery processes.

NH_4^+ recovery from manure wastewater using RR electrodes. The NH_4^+-uptake cell ($\mathrm{Cell_{N\text{-}uptake}}$) containing 2 mL manure wastewater and the NH_4^+-release cell ($\mathrm{Cell_{N\text{-}release}}$) with 10 mL 0.1 M Li_2SO_4 solution (pH ~2) were used to recover NH_4^+ from manure wastewater. The KNiHCF RR electrodes with a size of 2 ×2 cm^2 and a total capacity of 216 C (a total active material loading of ~1200 mg) were used in both cells. In $\mathrm{Cell_{N\text{-}uptake}}$, a SCE electrode was used as the reference electrode to monitor the potential of the RR electrode. In $\mathrm{Cell_{N\text{-}release}}$, a Pt wire electrode and a SCE were used as the counter electrode and reference electrode. The NH_4^+-release process using KNiHCF RR electrodes was measured under a constant current of 10 mA. COD removal was calculated according to the following equation to describe the consumption of organic matter over the NH_4^+ recovery process:

$$\text{COD removal (\%)} = \frac{[\mathrm{COD}]_{\mathrm{initial}} - [\mathrm{COD}]_{\mathrm{final}}}{[\mathrm{COD}]_{\mathrm{initial}}} \times 100\ \% \tag{4}$$

where $[\mathrm{COD}]_{\mathrm{initial}}$ and $[\mathrm{COD}]_{\mathrm{final}}$ are the amounts of COD in manure wastewater before and after recovery.

Three parallel recovery experiments were conducted, denoted as Run 1, Run 2, and Run 3. Typically, one NH_4^+ recovery run included the NH_4^+ uptake from manure wastewater and NH_4^+ release in Li_2SO_4 solution. Cations in 2 mL manure wastewater were recovered only once, and the recovered ions were collected in 0.1 M Li_2SO_4 solution for each run. The RR electrodes were oxidized to 0.9 V vs. SCE before use. For each run, in $\mathrm{Cell_{N\text{-}uptake}}$, the reduction of RR and NH_4^+ uptake occurred spontaneously. After a 24-h reduction process, the RR electrodes were washed with nanopure water and 0.1 M Li_2SO_4 solution to remove the residual electrolyte, then moved to $\mathrm{Cell_{N\text{-}release}}$. In $\mathrm{Cell_{N\text{-}release}}$, the oxidation of RR released intercalated cations until 0.9 V vs. SCE, which was paired with HER at the Pt cathode. During these recovery processes, the capacity of the RR electrode was controlled by the potential and capacity restrictions to ensure the RR electrode was operated within the desired potential windows. The concentrations of cations in manure wastewater and recovered solutions were measured by IC and the ion selectivity, nutrient selectivity, and FE were calculated based on the above equations. For the 50 recovery runs, each run included a 10-hour NH_4^+ uptake in manure wastewater and nearly 2-hour electrochemical NH_4^+ release. The COD removal and nutrient selectivity were analyzed every 5 runs.

NH_4^+ recovery from manure wastewater and H_2 production. NH_4^+ recovery and H_2 production were demonstrated in two cells, the NH_4^+-uptake cell ($Cell_{N\text{-uptake}}$) containing 10 mL manure wastewater and the H_2 cell ($Cell_{H_2}$) with 25 mL 0.1 M $(NH_4)_2SO_4$ solution (pH ~1.3). The KNiHCF RR electrodes with a size of 4 ×4 cm^2 and a total capacity of 892 C (a total active material loading of ~4.800 g) were used in both cells. The NH_4^+-release process using KNiHCF RR electrodes was measured under a constant current of 45 mA. The electrochemical configurations and operations were the same as those in "NH_4^+ recovery from manure wastewater", except using $(NH_4)_2SO_4$ solution rather than Li_2SO_4 solution. The concentrations of cations in manure wastewater and recovered solutions were measured by IC and the ion selectivity, nutrient selectivity, and FE were also calculated based on the above equations. Finally, the recovered solution was dried to acquire solid product powder, and the PXRD pattern of the sample was collected.

NH_4^+ recovery from manure wastewater and H_2O_2 production. NH_4^+ recovery and H_2O_2 production using the NH_4^+-selective RR electrodes were demonstrated in two cells, the NH_4^+-uptake cell ($Cell_{N\text{-uptake}}$) containing 10 mL manure wastewater and the H-cell ($Cell_{H_2O_2}$) with a glass frit (89057-758, ACE glass Incorporated, USA). In each chamber of the H-cell, 14 mL 0.5 M K_2SO_4 solution (pH ~7) was used. The KNiHCF RR electrodes with a size of 4 ×4 cm^2 and a total capacity of 892 C (a total active material loading of ~4.800 g) were used in both cells. In $Cell_{H_2O_2}$, two Fe-CNT electrodes (mass loading of each electrode around 1 mg) were used back-to-back as the working electrodes with a SCE reference electrode and the RR electrode as the counter electrode in the other chamber. The electrolyte solution was continuously bubbled with O_2 gas to ensure the O_2 saturation. The H_2O_2 production process using KNiHCF RR electrodes was measured under a constant current of 45 mA. Preparation of the Fe-CNT electrodes and electrochemical characterization of the H_2O_2 production are in Supplementary Methods.

The operations were the same as those in "NH_4^+ recovery from manure wastewater", except the H_2O_2 production occurred on the Fe-CNT electrode in this configuration. For the 2-cycle recovery process with H_2O_2 production, cations in 10 mL manure wastewater were recovered twice, and the recovered ions were collected in a new 14 mL 0.5 M K_2SO_4 solution for each cycle. The same KNiHCF RR electrodes in these 1-cycle recovery processes were used. The concentrations of cations in manure wastewater and recovered solutions, ion selectivity, nutrient selectivity, and FE were analyzed and calculated based on the above procedure and equations. The recovered solution in the RR chamber was dried to get solid product powder, and the PXRD pattern of the sample was collected.

The concentration of the produced H_2O_2 was measured following the procedures described above. Based on the product concentrations, the Faradaic efficiencies were calculated according to the following equations:

$$\mathrm{FE}(\%)_{H_2O_2} = \frac{\mathrm{Q\ for\ } H_2O_2 \mathrm{\ production}}{Q_{\mathrm{passing,\ RR}}} \times 100 = \frac{[H_2O_2] \times V \times 2 \times 96485}{Q_{\mathrm{passing,\ RR}}} \times 100 \qquad (5)$$

where V, $[H_2O_2]$, and the $Q_{\mathrm{passing,\ RR}}$ are the volume of the solution, the concentration of produced H_2O_2, and the charge passing through the RR electrode, respectively.

Data availability

The data that support the findings of this study are available from https://datadryad.org/stash/share/cFZs-SiOoCr9vc0Bket78q_6o33JBEuo9Qb_IOT3f30.

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Author contributions

R.W. and S.J. designed the experiments. R.W. carried out materials synthesis, materials characterization, electrochemical measurements, ammonium recovery and electrochemical production measurements, and analysis of manure wastewater with the help of K. Y.. K.Y. and M.Q. prepared manure wastewater. C. W. and F. B. conducted the techno-economic analysis. H.

A.V. and R. L. modeled the ammonia emission reductions. M.Q. and S.J. supervised the project. R.W., M. Q. and S.J. wrote the manuscript, and all the authors commented on it.

Additional information

Supplementary information is available for this paper in the online version of the paper.

Ethics declarations

Competing interests

A provisional patent based on this work has been filed by R. W. and S. J.. The remaining authors declare no competing interests.

Figure Legends/Captions

Fig. 1 | Schematic illustration of the simultaneous ammonia recovery and electrochemical synthesis system using ammonium ion-selective redox reservoir (RR). The system includes the NH_4^+ (K^+) uptake, fertilizer production, electrochemical synthesis, and wastewater treatment processes. The NH_4^+ (K^+) uptake process and the RR reduction occur spontaneously, driven by the oxidation of organic matter in manure wastewater (brown cell). Then, the RR electrodes are transferred into electrochemical cells to release recovered NH_4^+ (K^+) and produce NH_4^+- and K^+-rich fertilizer when the RR is oxidized (blue cells). The oxidation of the RR electrode is paired with cathodic reactions, such as hydrogen evolution reaction (HER) and two-electron oxygen reduction reaction (2 e^- ORR), to produce H_2 or H_2O_2. The produced H_2O_2 solution that contains relatively concentrated K^+ could be used for wastewater disinfection. After NH_4^+ recovery and H_2O_2 disinfection, drying treated manure wastewater could recycle K^+-rich salts as electrolytes or fertilizers.

Fig. 2 | Structural and electrochemical characterizations of the KNiHCF material. a, Crystal structure of the KNiHCF, which has similar structure to CuHCF but different transition metal elements or intercalated cations. **b,** SEM image of the as-synthesized KNiHCF nanoparticle. **c,** Cycling stability of the KNiHCF electrode in various solutions at 2 C rate (130 mA g^{-1}): 1 M NaCl, 1 M KCl, 1 M NH_4Cl, synthetic manure wastewater (sww, 0.50 M NH_4Cl + 0.183 M $KHCO_3$ + 0.146 M $NaHCO_3$), and manure wastewater with a pH of ~7 or ~9. **d,** Cyclic voltammograms of the KNiHCF electrode in 1 M NaCl, 1 M KCl, and 1 M NH_4Cl solutions at 1 mV s^{-1}. **e,** Calculated intercalation potential difference between NH_4^+ and Na^+ (blue line) or K^+ (red line) at different molar ratios of NH_4^+ / Na^+ or K^+. The red dots show the actual molar ratios of NH_4^+ / Na^+ or K^+ in the manure wastewater studied herein. The red ellipse shows the representative molar ratios of NH_4^+ / Na^+ or K^+ in common municipal wastewater (details in Supplementary Table 4). **f,** Self-reduction behaviors of the KNiHCF electrode in synthetic and natural manure wastewater. The potential of the KNiHCF electrode was monitored when resting the electrode with 100 % state-of-charge (SOC) in these solutions.

Fig. 3 | NH_4^+ recovery from synthetic wastewater. a, Schematic illustration of the NH_4^+ recovery processes using the KNiHCF electrode from synthetic wastewater. Each recovery cycle includes two steps. In the first step, the NH_4^+ uptake into RR electrode is paired with OER at the Pt anode in synthetic wastewater (left cell). In the second step, the NH_4^+ release from RR electrode is paired with HER at the Pt cathode in 0.1 M Li_2SO_4 solution (pH ~1.3) (right cell). **b,** Chronopotentiometry profiles of the KNiHCF and Pt electrodes in the NH_4^+ uptake and release steps. **c,** Concentration changes and ion balance of NH_4^+, Na^+, and K^+ over the five-cycle recovery process from synthetic wastewater. Nearly 100 % NH_4^+ removal was achieved after the five-cycle recovery process. The nutrient (NH_4^+ + K^+) selectivity was ~100 % in the initial three cycles when the concentrations of nutrient ions were not too low compared to that of Na^+. **d,** NH_4^+ balance after the five-cycle recovery process. The corresponding data points in **c** and **d** are overlayed as dot plots. Data are presented as mean values +/- standard deviation with a n number of 3.

Fig. 4 | NH_4^+ recovery from manure wastewater. a, Schematic illustration of the NH_4^+ recovery process using the KNiHCF RR electrode from manure wastewater. Three parallel recovery experiment cycles were conducted on three manure wastewater samples (runs 1, 2, and 3). Each recovery run includes two steps: the NH_4^+ uptake and reduction of RR driven by the oxidation of organic matter in manure wastewater (left cell) and NH_4^+ release and oxidation of the RR paired with HER in 0.1 M Li_2SO_4 solution (pH ~2) (right cell). **b,** Potential of the KNiHCF RR electrode in the NH_4^+ uptake and release steps. **c,** Concentration changes and ion balance of NH_4^+, Na^+, and K^+ over the three recovery runs from manure wastewater. The nutrient selectivity is ~100 % over the three runs. **d,** NH_4^+ balance over the three runs. **e,** Initial COD and COD removal over the three NH_4^+ recovery runs. **f,** Capacity retention of RR, NH_4^+ removal, COD removal, and nutrient selectivity throughout 50 recovery runs from manure wastewater (the values are measured and presented every 5 runs). The corresponding data points in **c** are overlayed as dot plots. Data in **c**, **e**, and **f** are presented as mean values +/- standard deviation with a n number of 3.

Fig. 5 | Simultaneous NH_4^+ recovery and H_2O_2 production enabled by the KNiHCF RR. a, Schematic illustration of the electrochemical configuration for NH_4^+ release and H_2O_2 production in a two-compartment H-cell separated by a glass frit. **b,** Cyclic voltammograms of the Fe-CNT electrode in O_2-saturated 0.5 M K_2SO_4 solution at 10 mV s^{-1} and the corresponding potential-dependent Faradaic efficiency for H_2O_2 production. **c,** The accumulation of H_2O_2 in O_2-saturated 0.5 M K_2SO_4 solution in the H-cell at 45 mA during the process of NH_4^+ release. **d,** NH_4^+ balance over the one-cycle and two-cycle NH_4^+ recovery processes from manure wastewater. **e,** Concentrations of recovered NH_4^+ and produced H_2O_2, the Faradaic efficiency of H_2O_2 production and NH_4^+ removal over the one-cycle and two-cycle recovery processes. The current H_2O_2 production was 45 mA during all processes. **f,** PXRD pattern of the recovered salts dried from 5 mL recovered solution in the RR chamber (14 mL in total), in comparison with standard PXRDs of various compounds. Inset is the photograph of the recovered salts with a mass of 0.658 g in a 20 mL vial. Data in **d** are presented as mean values +/- standard deviation with a n number of 3.

Fig 6. | Reduction of daily ammonia (NH_3) emissions from manure with NH_4^+ recovery and the preliminary economic analysis at a modeled 1000-lactating cow dairy farm. a, Daily NH_3 emissions from manure at a modeled 1000-lactating cow dairy farm with and without NH_4^+ recovery. NH_3 emissions (kg/day for the farm) based on variations in manure land application methods (surface and injection), manure processing (no processing and anaerobic digestion (AD) and solid-liquid separation (SLS), and efficiency of NH_3 recovery using the NH_4^+-selective redox material. **b,** Annual revenues and costs from the preliminary economic analysis of a 1000-cow dairy farm. Calculated revenues and costs with high or low chemical and electricity prices for ammonia recovery from a 1000-cow dairy farm.

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