

Urine power cell with ammonium-intercalating electrodes: A novel approach to urine valorization coupled with CO₂ capture

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Abstract

This study introduces a novel approach for maximizing the valorization of human urine by coupling CO₂ capture and salinity gradient energy (SGE) harvesting using NH₄⁺-intercalating electrodes. Hydrolyzed urine (HU), rich in NH₄⁺ and widely available, is a promising resource for energy recovery through NH₄⁺ concentration gradients. Selective NH₄⁺-intercalating Prussian blue analogues (PBAs), such as copper hexacyanoferrate (CuHCF) and nickel hexacyanoferrate (NiHCF), are effective active materials for such electrodes. However, the alkaline pH of HU (around 9) caused structural and functional degradation of the PBAs, with CuHCF suffering over 90% loss in capacitance and NiHCF exhibiting a smaller but notable reduction of approximately 13%. This instability under alkaline conditions restricted the applicability of these PBA electrodes in HU. To address this limitation, HU was not used directly; instead, it was first utilized as a CO₂ absorbent to yield spent HU (SU) with neutral pH and elevated conductivity, which enabled the PBAs, particularly NiHCF, to preserve their structural integrity. Developed in this study, the urine-ammonium power cell (UPC) with NiHCF electrodes achieved stable power generation using SU and freshwater (1 g L⁻¹ NaCl) as the salinity gradient pair, with peak and average power densities of 1.6 and 0.3 W m⁻², respectively. This system presents the first successful demonstration of direct electricity generation from NH₄⁺ gradients using PBA electrodes, extending their application to real-world waste streams. While further development is necessary, the findings highlight the feasibility of the sequential valorization of human urine (and potentially other NH₄⁺-rich waste streams), first as an alternative CO₂ absorbent and then as a feedstock for SGE recovery. The proposed approach opens a new avenue for coupling waste-to-energy conversion with carbon mitigation and water pollution reduction, advancing a circular economy.

Main text

Human urine is a significant and problematic waste stream that contributes over 80% of the total nitrogen load in municipal wastewater, despite accounting for less than 1% of the volume.^{1,2} The high nitrogen content of urine results from the release of substantial amounts of ammonia (>8,000 mg N L⁻¹) through the natural hydrolysis of urea ((NH₂)₂CO + H₂O → 2NH₃ + CO₂) by ubiquitous ureolytic bacteria.^{3,4} Nitrogen removal is an essential yet costly process in municipal wastewater treatment, as improper management can cause eutrophication of water bodies, resulting in severe environmental impacts.⁵ Accordingly, there is growing scientific and societal interest in separating and valorizing urine at the source for more sustainable wastewater management.

Hydrolyzed human urine, with its high ammonium content, exhibits high salinity comparable to seawater (approximately 50 mS cm⁻¹)⁶ and significantly higher conductivity (30–50 mS cm⁻¹) than most wastewaters (1–2 mS cm⁻¹).⁷⁻⁹ These characteristics make it a promising source for the electrochemical recovery of salinity gradient energy (SGE) when coupled with low-salinity streams. Extensive research has been conducted on SGE recovery as sustainable energy source, primarily utilizing

the sodium ion concentration differences between seawater and freshwater.¹⁰ It is estimated that approximately 1 TW of power could be harvested globally from salinity gradients along coastal areas,¹¹ potentially supplying about 31% of the total electricity generated worldwide in 2022 (28,510 TWh).¹²

Several technologies, including pressure retarded osmosis (PRO), reverse electrodialysis (RED), and capacitive mixing (CapMix), have been developed for extracting SGE. PRO utilizes osmotic pressure across semi-permeable membranes that permit water to pass through while rejecting ions to generate pressure, which is subsequently used to produce electricity by driving a turbine. Although the process is simple and straightforward, practical application of PRO is limited by inherent challenges such as low energy availability and irreversible energy loss.^{10, 13} RED relies on the Donnan potential across multiple pairs of ion exchange membranes (IEMs) for energy harvesting. This technology directly converts ionic flux along concentration gradients into electrical energy without intermediate steps.¹⁴ However, the practicability of RED is compromised by several factors, including high membrane cost (typically >\$200 m⁻¹),¹⁵ low thermodynamic efficiency, and system complexity.^{16, 17} CapMix, a more recent alternative, directly captures SGE through controlled mixing by alternately exposing capacitive electrodes to solutions with different salinities for cyclic charging and discharging.¹⁸ However, its power density remains lower compared to RED and PRO, primarily due to the limited electrode capacity and insufficient ion exchange processes.^{17, 18} Despite ongoing efforts, none of these technologies have yet reached industrial viability.

By combining the Donnan potential across IEMs and the electrode potential of ion intercalating electrodes in a concentration flow cell, a previous study achieved a remarkably high power density (peak = 12.6 W m⁻²-membrane; average = 3.8 W m⁻²) using a pair of synthetic seawater and freshwater.¹⁰ This hybrid approach, generating power by simultaneously utilizing Donnan and electrode potentials, presents advanced possibilities for efficient SGE harvesting. The study used copper hexacyanoferrate (CuHCF) as the active material for the electrodes. Prussian blue analogues (PBAs), such as CuHCF and nickel hexacyanoferrate (NiHCF), have open framework crystal structures with large interstitial sites for ion intercalation,¹⁹ enabling efficient power extraction from the Na⁺ concentration difference between seawater and freshwater using PBA electrodes.¹⁰ It is notable that PBAs can accommodate various cations, including Li⁺, Na⁺, K⁺, and NH₄⁺, in aqueous solutions,¹⁹ and selectively interact with specific ions via faradaic reactions under electrochemical conditions.²⁰ This characteristic suggests the potential of PBA electrodes for efficient energy harvesting from concentration gradients of different ions beyond Na⁺. Specifically, NH₄⁺, the predominant cation in hydrolyzed urine (HU),³ can be a promising target ion for SGE recovery using PBA electrodes, given its common and abundant presence in the environment and the high selectivity of PBAs for NH₄⁺ over other common cations, such as Na⁺ and K⁺.²⁰ However, this potential has never been explored, although several recent studies have shown selective concentration and removal of NH₄⁺ using PBA electrodes, particularly CuHCF electrodes, with external energy input.²⁰⁻²²

This study investigates the promising yet unexplored potential of directly harvesting renewable energy as electricity from NH_4^+ gradients, using HU as the high-salinity solution. A concentration flow cell design with co-current feeding of high- and low-salinity solutions, separated by an anion exchange membrane (AEM), was employed.^{10, 23} Two PBA electrodes, one placed in each channel, capture NH_4^+ from the NH_4^+ -rich stream and release it into the NH_4^+ -poor stream, with the feed streams alternated between the channels after each cycle to regenerate the electrodes. This process enables continuous electricity generation through the circuit connecting the electrodes, providing an advantage as a sustainable power source. A critical concern when fueling electrochemical cells with PBA electrodes using HU is its alkaline pH of around 9.³ PBAs are typically most stable under mildly acidic conditions and vulnerable to alkaline pH, which can lead to degradation of electrode performance due to the dissolution of structural metals.²⁴ Significant loss of structural integrity in PBA electrodes, particularly CuHCF electrodes, under alkaline conditions has been well documented.^{10, 20, 24}

As an innovative solution, we suggest using HU first as an alternative solvent for CO_2 capture and then utilizing the spent HU (SU) for SGE recovery with PBA electrodes (**Fig. 1**). Effective CO_2 removal from biogas using HU has been demonstrated in our previous studies.^{3, 25} The absorption of CO_2 not only lowers the pH of SU (<8) but also increases its conductivity, thereby significantly improving its suitability for use in electrochemical systems compared to HU.²⁵ To test this concept, we compared synthetic HU and SU for energy recovery from NH_4^+ gradients against freshwater in the concentration flow cells, equipped with either CuHCF or NiHCF electrodes as representative PBA electrodes. Both electrode types demonstrated better and more stable performance when utilizing SU, with the NiHCF-electrode cell showing particularly promising results. This study presents a new and viable approach to sustainable energy extraction from urine, uniquely combining SGE harvesting with biogas upgrading (or CO_2 capture). This innovative strategy not only maximizes the utilization of urine but also extends the applications of PBA electrodes.

Effects of electrolyte pH on electrode behavior

Before their use in energy extraction from urine, CuHCF and NiHCF electrodes were assessed for structural and functional stability over a pH range of 4.9 to 9.7 through cyclic voltammetry (CV). A 560 mM NH_4Cl solution, with a total ammonia nitrogen (TAN) concentration comparable to that of HU (**Table S1, ES†**), was used as the electrolyte. Both electrodes demonstrated a decrease in electrochemical activity with increasing electrolyte pH, but the patterns of change differed. The CuHCF electrode exhibited similar CV profiles with clear oxidation and reduction peaks within the pH range of 4.9 to 8.2; however, these peaks markedly declined at pH 8.7 and nearly disappeared at pH 9.2 and 9.7 (**Fig. 2a**). Correspondingly, the specific capacitance, which remained steady between 75 and 85 F g^{-1} at pH 4.9–8.2, dropped to 53 F g^{-1} at pH 8.7 (a 38% reduction compared to pH 8.2) and further fell to 16 F g^{-1} or less at pH 9.2 or above ($\geq 85\%$ reduction compared to pH 8.2) (**Fig. 2b**). These results were attributed to the collapse of the electrode material due to the dissolution of structural Fe and particularly Cu,

indicating a crucial impact of electrolyte pH on the structural stability and performance of CuHCF electrodes.²⁴ The strong negative linear relationships between the specific capacitance and the leached concentrations of Fe and Cu ($R^2 \geq 0.90$) further support this conclusion (**Fig. S1a, ESIt**). Consistent with this, the initially colorless electrolyte solution turned reddish-green at pH 8.2 with the dissolution of the metals and became increasingly greenish from pH 8.7 and with greater dissolution of Cu (**Fig. 2c**).

In contrast, the NiHCF electrode exhibited a gradual decreased in specific capacitance along with increasing dissolution of Ni as the electrolyte pH increased, particularly after reaching pH 8.2 (**Figs. 2d and 2e**). The specific capacitance at pH 9.7 (51 F g^{-1}) was reduced by approximately 30% compared to that at pH 7.7 (73 F g^{-1}). Correspondingly, the concentrations of leached metals, especially Fe, were significantly lower than those in the CuHCF electrode, with no visible changes in the electrolyte color (**Fig. 2f**). The dissolution of Fe was negligible across the tested pH range, except at pH 9.7, where a still very low level of Fe (1.0 mg L^{-1}) was detected in the electrolyte. Accordingly, the leached concentration of Fe did not correlate with the specific capacitance, whereas that of Ni showed a very strong negative linear relationship with the specific capacitance ($R^2 = 0.96$) (**Fig. S1b, ESIt**).

The higher specific capacitance of the CuHCF compared to the NiHCF electrode under stable conditions up to pH 8.2 can be attributed to the presence of dual redox couples, $\text{Cu}^{2+}/\text{Cu}^{3+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$, for ion intercalation in CuHCF, whereas NiHCF contains only a single redox couple, $\text{Fe}^{2+}/\text{Fe}^{3+}$.²⁶ However, this increased involvement of redox couples in CuHCF also renders it more susceptible to structural degradation under alkaline conditions.²⁷ Consequently, above pH 8.2, the NiHCF electrode demonstrated superior structural integrity and specific capacitance ($50.5\text{--}65.3 \text{ F g}^{-1}$) compared to the CuHCF electrode ($13.4\text{--}52.9 \text{ F g}^{-1}$) (**Figs. 2b and 2e**). These results highlight the difficulties in applying these PBA electrodes in concentration gradient cells with alkaline HU (approximately pH 9) as a feed, particularly for the CuHCF electrode. While future advancements in electrode material design may overcome these limitations, finding a sustainable way to adjust the pH of HU could offer a more immediate and practical solution. To this end, we propose utilizing SU, with a neutralized pH less than 8 due to CO_2 absorption during use in biogas upgrading,²⁵ instead of HU. The subsequent subsections discuss a series of experiments to investigate this unexplored potential.

Electrode behavior in HU versus SU electrolytes

The stability tests through CV were conducted on CuHCF and NiHCF electrodes, using synthetic HU (pH 9.0) and SU (pH 7.6) as the electrolytes (**Table S2, ESIt**). When tested with a 560 mM NH_4Cl solution (pH 4.9) as a reference, the CuHCF electrode maintained stable CV profiles over three repeated cycles, exhibiting a higher specific capacitance (132 F g^{-1}) compared to the NiHCF electrode (76 F g^{-1}) (**Figs. 3 and S2, ESIt**). However, when the electrolyte was changed to HU, the CV curve of the CuHCF electrode became flat with no apparent redox peaks (specific capacitance $< 10 \text{ F g}^{-1}$) (**Fig. S2, ESIt**). This substantial loss of charge storage capacity reflects the highly susceptible nature of the CuHCF lattice structure to alkaline pH.^{24, 27} While the NiHCF electrode showed significantly greater stability in alkaline

HU, it also experienced a 13% reduction in capacitance. Correspondingly, the dissolution of structural metals in HU was notably more pronounced in the CuHCF electrode than in the NiHCF electrode (**Fig. S2, ESIt**). These results indicate that exposure to HU can severely impair the structure and function of both electrodes, particularly the CuHCF electrode, consistent with the observations in Subsection 2.1.

Following the CV tests using HU, the electrodes were returned to the same NH_4Cl solution used for the reference CV profiles to examine their restoration potential. The CuHCF electrode showed no appreciable recovery of redox peaks across three consecutive CV cycles (**Fig. 3a**). The NiHCF electrode also did not achieve a meaningful restoration of charge storage capacity, with its specific capacitance remaining comparable to the compromised levels observed in the CV tests with HU (**Figs. 3b and S2, ESIt**). Consequently, the direct use of alkaline HU as a feed for SGE harvesting systems with CuHCF or NiHCF electrodes is not feasible due to the degradation of the electrodes' structural integrity and, therefore, their function.

To address the challenges posed by the alkaline pH of HU, the CuHCF and NiHCF electrodes were further tested with synthetic SU, which was prepared by saturating HU with CO_2 until pH stabilization. The resulting SU had an increased inorganic carbon concentration with a neutralized pH of 7.6 (**Table S2, ESIt**). Notably, both electrodes, particularly the NiHCF electrode, experienced significantly reduced structural and functional degradation compared to the tests with HU (**Figs. 4 and S3, ESIt**). Interestingly, the CuHCF electrode lost approximately half of its specific capacitance during the first CV cycle in SU (57 F g^{-1}), which decreased further over the subsequent two cycles (33 F g^{-1}). This result indicates that repeated or long-term exposure to SU, despite its neutralized pH, can degrade the structure and function of CuHCF as an electrode material. This finding contrasts with the observation from the tests using NH_4Cl solutions with varying pH, where no significant degradation was recorded up to pH 8.2 (**Fig. 2a**). Given the apparent recovery of charge storage capacity during the subsequent restoration test cycles using NH_4Cl solution (pH 4.9) (up to 94 F g^{-1}), the hindered activation of ion intercalation,²⁸ in addition to the irreversible structural degradation, likely contributed significantly to the electrode's reduced functionality in SU.^{29, 30}

In contrast, the NiHCF electrode maintained identical CV profiles with clear redox peaks over the repeated CV cycles in SU (**Fig. 4b**), with its specific capacitance remaining close to the reference value measured in NH_4Cl solution (pH 4.9) before exposure to SU. The specific capacitance recorded with SU was consistently 85 F g^{-1} , significantly higher than that observed with HU (67 F g^{-1}) (**Figs. S2 and S3, ESIt**). Consistently, the dissolution of structural metals was significantly reduced in SU compared to HU. Notably, over the subsequent restoration test cycles in NH_4Cl solution (pH 4.9), the specific capacitance increased to 91 F g^{-1} , only less than 6% below the reference value. The results from the CV tests using HU and SU collectively reconfirmed the detrimental impact of alkaline pH on the structural and functional stability of both CuHCF and NiHCF electrodes, further highlighting that CuHCF is particularly unsuitable for use with HU or SU. Meanwhile, NiHCF showed markedly superior structural integrity compared to CuHCF in both HU and SU, with marginal functional degradation, especially when SU was used as the

electrolyte. Consequently, considering the system's stability and robustness, the NiHCF electrode/SU combination was selected as the optimal candidate for developing a concentration flow cell to harvest SGE from urine, which we have termed urine-ammonium power cell (UPC).

Urine-ammonium power cell: energy harvesting from urine

Two-chamber UPCs equipped with NiHCF electrodes (NiHCF-UPCs) were tested using HU or SU as the high-salinity stream (HS) and synthetic freshwater (FW, $1 \text{ g L}^{-1} \text{ NaCl}$) as the low-salinity stream (LS). The HS and LS were fed co-currently into their respective chambers, with the streams being switched between chambers each time the cell voltage dropped below the cutoff of 15 mV (i.e., saturation of the HS-side electrode) for continuous power generation (**Fig. 5**). This switching process alternates the electrodes between capturing and releasing charges, enabling continuous electricity generation with alternating directions.^{10, 23} NiHCF-UPC demonstrated efficient and stable harvesting of SGE between SU and FW over repeated cycles of operation (**Figs. 6a and 6b**). In contrast, as anticipated, when CuHCF electrodes were used, the SGE harvesting efficiency from both SU and HU dropped sharply after the first cycle and continued to decline over subsequent cycles (**Fig. S4, ESIt**). A control test using a 560 mM NH_4Cl solution (pH 4.9) as HS maintained consistent harvesting of SGE over multiple cycles (**Fig. S5, ESIt**), further confirming that CuHCF is not a suitable PBA candidate for SGE recovery from human urine.

NiHCF-UPC using the SU/FW pair achieved maximum average and peak power densities (PDs) of approximately 0.3 and 1.6 W m^{-2} , respectively, at an external resistance of 25Ω . These values were substantially higher than those obtained with the HU/FW pair (approximately 0.05 and 0.20 W m^{-2}) (**Figs. 6c and 6d**), corresponding to more than 10-fold and 5-fold differences, respectively (**Figs. 6b and 6d**). Notably, these differences significantly exceeded the approximately 1.4-fold difference in the specific capacitance of the NiHCF electrode observed in CV tests using HU and SU as electrolytes (**Figs. S2 and S3, ESIt**). This discrepancy can be attributed to the different experimental setups: continuous flow in UPCs versus closed batch in CV tests. In closed batch setups, metals leached from electrodes accumulate in the electrolyte, reducing further metal dissolution.^{24, 31} Meanwhile, in flow cells, regional overpotential can cause local pH fluctuations near the electrode surface,^{18, 32, 33} destabilizing PBA electrode structures. With its higher bicarbonate alkalinity (**Table S2, ESIt**), SU as HS offers an advantage over HU in reducing this pH instability.³⁴

In NiHCF-UPC fed with SU as HS, average PD remained fairly consistent across external resistances ranging from 5 to 50Ω , whereas peak PD varied significantly (**Fig. 6b**). This behavior is likely due to the low cutoff voltage of 15 mV, which extended cycle times and reduced the influence of peak voltage. Operation tests at an external resistance of 25Ω , where the highest peak PD was observed, revealed that diluting SU as HS led to a reduction in PD (**Fig. 7a**). At 2-fold and 10-fold dilutions with deionized water (DI), average PD decreased from 0.3 W m^{-2} with undiluted SU to 0.2 and 0.1 W m^{-2} , respectively, while peak PD fell from 1.6 to 1.1 and 0.44 W m^{-2} . These results align with the principle that greater ion concentration gradient between HS and LS generates higher cell voltage due to increased electrode and

Donnan potentials.¹⁰ Correspondingly, the open circuit voltage (OCV) measured for the diluted SU/FW pairs decreased with increasing dilution factors (**Fig. 7b**). Notably, consistent with the PD profiles, the reduction in OCV was not directly proportional to the dilution, decreasing from 0.5 V with undiluted SU to 0.25 V with 10-fold diluted SU. Despite the decrease in energy recovery per cycle with dilution, total energy recovery per unit volume of undiluted SU consumed increased by 1.6-fold ($1.3 \pm 0.1 \text{ kJm}^{-3}$) and 3.9-fold ($3.1 \pm 0.2 \text{ kJm}^{-3}$) at 2-fold and 10-fold dilutions, respectively (**Table S3, ESIt**). These findings suggest that energy recovery could be maximized through optimal dilution of SU as HS, although additional studies are required to optimize operating parameters such as cutoff voltage and cycle time.

The OCV for the SU/DI pair was approximately 0.8 V, which was significantly greater than the 0.5 V recorded for the SU/FW pair, while replacing FW with 10-fold diluted SU as LS reduced it to 0.3V (**Fig. 7c**). This observation reflects the different ion concentration gradients between HS and LS in the tests. Notably, despite the highest OCV, using DI as LS resulted in the lowest average and peak PDs (0.08 and 0.66 W m^{-2}) due to its poor conductivity (0.055 mS cm^{-1} or $18.2 \text{ M}\Omega\cdot\text{cm}$), increasing internal resistance (**Fig. 7a**). LS conductivity has been identified as a major factor influencing internal resistance and, consequently, the total resistance of the system, during SGE extraction between NaCl solutions using CuHCF electrodes.²³ Therefore, to maximize energy recovery from SU using UPC, it is important to select an LS with an appropriate ionic strength—low enough to yield a high OCV against HS but sufficient to ensure conductivity for efficient charge transfer.

Implications and outlook

To the best of the authors' knowledge, this is the first study to successfully demonstrate energy harvesting from NH_4^+ gradients using PBA electrodes, despite their known specific selectivity for NH_4^+ over other cations.^{22, 35-37} NH_4^+ -rich waste streams, including HU explored in this study, are generally alkaline, and electrode instability due to the dissolution of structural metals under alkaline conditions is the most critical issue limiting the application of PBA electrodes in SGE harvesting from such streams. We showed that this issue can be resolved by neutralizing HU through CO_2 absorption during its use in biogas upgrading, which also increases the conductivity of the resulting SU (**Table S2, ESIt**). These improved properties of SU enabled its effective and stable utilization as the HS, in combination with FW as the LS, in NiHCF-UPC for continuous power generation.

By combining SGE harvesting and biogas upgrading with urine, this innovative approach delivers multifaceted benefits. We have previously demonstrated that one liter of HU can upgrade more than ten liters of biogas to biomethane (95% CH_4 , v/v), with a CO_2 absorption capacity of $0.41\text{--}0.53 \text{ mol CO}_2 \text{ mol}^{-1}\text{-NH}_4^+$.³ This capacity is close to the theoretical value of $0.5 \text{ mol CO}_2 \text{ mol}^{-1}\text{-NH}_4^+$ for HU, where two moles of NH_3 are released along with one mole of CO_2 during the hydrolysis of urea, leaving one mole of NH_4^+ to be effective for CO_2 absorption. Alkanolamines, commonly used as CO_2 absorbents for industrial-scale biogas upgrading, exhibit similar CO_2 absorption capacities.³⁸ Replacing alkanolamines

(€1.9 kg⁻¹-monoethanolamine) with HU could eliminate the absorbent cost of approximately €1 m⁻³-CO₂ removed, assuming a CO₂ absorption capacity of 0.5 mol CO₂ mol⁻¹-amine and a 90% regeneration rate.^{39, 40} Europe currently produces 6.4 billion cubic meters of biomethane annually from 1,548 plants, with an average plant capacity of 468 m³-biomethane h⁻¹ and a corresponding CO₂ removal rate of 273 m³ h⁻¹, assuming CH₄ contents (v/v) of 60% in raw biogas and 95% in upgraded biomethane.⁴¹ Therefore, one average-size biomethane plant could save approximately 2.4 million euros annually by using HU as an alternative CO₂ absorbent.

Despite the vast potential of urine as a renewable energy source, only a few studies have attempted to extract SGE from urine, particularly through RED⁴ and hybrid membrane distillation (MD)-RED.⁴² However, these studies yielded peak PDs of only 0.25–0.30 W m⁻² from synthetic HU using a similar single-pass configuration. In contrast, this study achieved a significantly higher peak PD of 1.6 W m⁻² from the SU/FW pair by applying a PBA electrode system. In addition, only one IEM was used for the system, whereas at least three IEMs were necessary per unit cell pair in a conventional RED system. Nevertheless, the extracted power from urine in this study (0.3 W m⁻² on average and 1.6 W m⁻² at peak) remains lower than that reported for NaCl solution pairs (0.4–3.8 W m⁻² average PD).^{10, 23, 26, 43, 44} One possible reason is the high concentration of various ionic species present in the tested SU (**Table S2, ESIf**), whereas most studies extracting SGE from seawater have employed simplified NaCl solution pairs for convenience, overlooking the influence of diverse organic and inorganic substances naturally present in seawater.^{10, 18, 23, 45-49}

Other factors contributing to the relatively low PD include suboptimal experimental parameters, such as low cutoff voltage, small electrode surface area, and single-pass flow configuration. Increasing the cutoff voltage can improve average PD by shortening cycle time and minimizing the adverse impact of voltage tailing.^{10, 18} However, an excessively high cutoff voltage hinders full discharging of PBAs prior to recharging, resulting in insufficient voltage buildup in subsequent cycles and disrupting continuous current generation via flow switching. Accordingly, while shorter cycle times increase energy extraction efficiency, a trade-off exists between energy efficiency and total energy recovery, highlighting the need for further research to optimize operating parameters. Moving forward, scaling up the experimental system and modifying the flow configuration—particularly by employing larger electrode areas⁵⁰ and a closed-loop flow setup⁴²—could improve the performance and feasibility of the newly developed UPC system. Although additional studies are required to refine system design and operation, this work represents a foundational step toward direct electricity generation from NH₄⁺-rich waste streams using PBA electrodes.

Conclusions

This study presents a novel waste-to-energy concept by integrating urine separation, CO₂ capture, and power generation using NH₄⁺-intercalating PBA electrodes. A key innovation enabling this integration is

the use of neutral NH_4^+ -rich SU as the HS for SGE recovery, which is produced after using HU as a CO_2 absorbent in processes such as biogas upgrading or flue gas treatment. The CO_2 -saturated SU, with its neutral pH and increased conductivity, significantly improved the structural and functional stability of PBA electrodes, which were severely compromised when exposed to alkaline HU. The developed flow cell-type UPC with NiHCF electrodes successfully demonstrated continuous electricity generation from SU via NH_4^+ concentration gradients. The NiHCF-UPC using the SU/FW pair achieved stable SGE recovery with peak and average PDs of 1.6 and 0.3 W m^{-2} , respectively, highlighting its potential as a sustainable power generation system. Beyond extending the applicability of PBA electrodes, coupling this approach with biogas upgrading offers significant additional economic and environmental benefits by enabling the dual valorization of human urine as both an alternative CO_2 absorbent and a renewable energy source. While substantial further research is required to improve energy efficiency and system scalability, this work provides a promising proof-of-concept for integrating CO_2 capture and sustainable energy recovery from urine.

Methods

Fabrication of PBA electrodes

CuHCF and NiHCF electrodes were prepared by co-precipitation followed by drop casting, as previously described.^{22, 24, 51} Equal volumes (100 mL) of 0.2 M $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ or $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich) and 0.1 M $\text{K}_3[\text{Fe}(\text{CN})_6]$ (J. T. Baker) were simultaneously introduced into 40 mL of DI at a flow rate of 0.5 mL min^{-1} under vigorous stirring. The resulting precipitates were collected and washed four times with DI by sequential resuspension and centrifugation at 7,800 g for 10 min. The washed precipitates were dried at 70°C for 2 h in a drying oven, followed by overnight drying in a vacuum oven at the same temperature. The obtained CuHCF and NiHCF were ground into fine powders using a mortar and pestle. A 250 mg portion of each was then mixed with 25 mg of carbon black (Vulcan XC72R, Cabot) and 25 mg of polyvinylidene fluoride (Kynar HSV 900, Arkema) in 3.5 mL of 1-methyl-2-pyrrolidinone (Sigma-Aldrich). A 0.5-mL aliquot of each mixed slurry was drop-cast onto a carbon cloth (1071HCB, AvCarb Material Solutions) with 3.4-cm diameter and a 3-cm effective diameter. The coated electrodes were dried at 70°C for 1 h in a drying oven and then overnight in a vacuum oven at the same temperature.

The surface and cross-sectional morphology of the fabricated CuHCF and NiHCF electrodes were analyzed by scanning electron microscopy (SEM; SU8220, Hitachi) (**Fig. S6, ESIt**). Elemental distribution was examined by energy-dispersive X-ray spectroscopy (EDS; EDAX Genesis APEX2, AMETEK) (**Fig. S7, ESIt**). The crystalline structures of the synthesized CuHCF and NiHCF were analyzed by high-power X-ray diffraction (XRD; D/MAX2500V/PC, Rigaku) over a 2θ range of 20° to 60°, with a step size of 0.02° ($\lambda = 1.54 \text{ \AA}$) (**Fig. S8, ESIt**).

Preparation of synthetic HU and SU

Synthetic HU was prepared with a TAN concentration of 560 mM and a pH of 9.0 (**Table S1, ESIt**).²⁵ SU was prepared by bubbling CO₂ gas into HU contained in a glass vessel with a 5-L working volume, using a peristaltic pump at a rate of 120 mL min⁻¹ until the pH stabilized. The dissolution of CO₂ in SU lowered the pH from 9.0 to 7.6 and increased the inorganic carbon concentration from 2.5 to 4.4 g L⁻¹, with no change in TAN concentration (**Table S2, ESIt**).

Evaluation of electrode stability across pH conditions

CV measurements were performed using a potentiostat (VSP, BioLogic) and a custom three-electrode electrochemical cell with a cubic exterior and cylindrical internal chamber (3-cm diameter × 4-cm length) (**Fig. S9, ESIt**). The setup consisted of a working electrode (CuHCF or NiHCF) on graphite foil as the current collector, a coiled Pt wire counter electrode (MW-1033, BASi), and an Ag/AgCl (3 M NaCl) reference electrode (MF-2052, BASi). To assess the effect of pH on the electrochemical performance of CuHCF and NiHCF, CV tests were conducted in 560 mM NH₄Cl electrolyte, with its pH adjusted from the initial value of 4.9 to 6.7, 7.2, 7.7, 8.2, 8.7, 9.2, and 9.7 by adding 10 N NaOH. For each pH condition, two CV cycles were recorded at a scan rate of 1 mV s⁻¹ over a potential range of 0–1 V after stabilization of the CV response through initial conditioning cycles. The CV curve from the second cycle is presented as representative, and the specific capacitance was reported as the average of the two cycles.

The same CV procedure was applied to evaluate the stability of CuHCF and NiHCF electrodes in HU and SU, with 560 mM NH₄Cl solution (pH 4.9) used as the control electrolyte. Three CV cycles were conducted for each electrolyte, and the representative specific capacitance was obtained by averaging the values from these cycles. To examine changes in the redox behavior of the electrodes, additional CV scans were conducted in the control electrolyte before and after each test. Specific capacitance (F g⁻¹) was calculated from the CV curves using the following equation:⁵²

$$\text{Specific capacitance} = \frac{\int I dV}{2m_e \Delta V v} \quad (3)$$

where I is the current (C s⁻¹), m_e is the mass of electroactive material (g), and ΔV is the voltage window (V), and v is the scan rate (V s⁻¹).

$$P = V_{cell}^2 / R_{ext} \quad (4)$$

Continuous operation of UPCs

CuHCF and NiHCF electrodes were pre-conditioned in 1 M NH₄Cl electrolyte (pH 4.6) using the same electrochemical cell employed in the CV tests described in the preceding subsection. The electrodes

underwent three CV cycles at a scan rate of 3 mV s^{-1} , with voltage ranges of 0.6–1.0 V for CuHCF and 0.3–0.7 V for NiHCF, selected based on their respective redox peak profiles. Subsequently, constant voltages corresponding to the lower and upper limits of the scanned range were applied for 5 min to induce NH_4^+ intercalation and de-intercalation: 0.6 V (intercalation) and 1.0 V (de-intercalation) for CuHCF, and 0.3 V (intercalation) and 0.7 V (de-intercalation) for NiHCF.

Continuous SGE harvesting experiments were conducted in a zero-gap concentration flow cell comprising two symmetric chambers with an open diameter of 3 cm, yielding an effective electrode surface area of approximately 7 cm^2 . The chambers were separated by an AEM (Selemion AMVN, Asahi Glass) positioned between the electrodes (**Fig 4**). Each chamber consisted of an end plate, a current collector (graphite foil), a CuHCF or NiHCF electrode, rubber gaskets, and a fabric spacer ($120\text{-}\mu\text{m}$ thick, Sefar nitex 03-200/54). HS (synthetic HU or SU) and LS (synthetic FW, $1 \text{ g L}^{-1} \text{ NaCl}$) were fed into the bottom of their respective chambers at a flow rate of 15 mL min^{-1} and discharged from the top, ensuring co-current flow in the two chambers. The flows were alternated between HS and LS whenever the monitored cell voltage dropped below the predetermined cutoff of 15 mV, indicating the completion of half a cycle (i.e., charging or discharging). All UPC operation tests were performed for at least three full cycles, with the results presented excluding the first cycle, which was considered a pre-stabilization step. An external resistance ranging from 5 to 50Ω was connected between the electrodes, and the generated power (P) was calculated using the following equation:

$$\text{Peak PD} = \frac{V_{peak}^2}{R_{ext} \cdot A} \quad (5)$$

$$\text{Average PD} = \frac{\int_{t_p}^{t_c} V_{cell}^2 dt}{R_{ext} \cdot A} \quad (6)$$

where V_{cell} is the measured cell voltage and R_{ext} is the applied external resistance.

PD was determined by normalizing the generated power with respect to the effective electrode surface area (approximately 7 cm^2). Peak and average PDs during a half cycle were calculated using the following equations:

where V_{peak} is the peak cell voltage observed during a half cycle, A is the effective electrode surface area, t_p is the time at which the peak cell voltage occurs, and t_{cutoff} is the time at which the cell voltage reaches the cutoff threshold of 15 mV.

To evaluate the effects of HS dilution on SGE recovery from SU/FW pairs, NiHCF-UPCs were operated in continuous mode with 2-fold, 5-fold, and 10-fold diluted SU as the HS, along with undiluted SU for comparison, following the procedure described earlier in this subsection. UPC performance was further

assessed using FW, 10-fold SU, and DI as LSs, with undiluted SU serving as the HS. Additionally, OCVs were measured for all tested HS/LS pairs using a potentiostat (VSP, BioLogic), with the HS and LS flows alternating at 2-min intervals under open-circuit conditions.

Analytical methods

Solution conductivity and pH were measured using an Orion DuraProbe 4-Electrode Conductivity Cell and an Orion Star A211 pH Benchtop Meter (Thermo Scientific), respectively. Anions and cations were quantified using two Dionex ICS-1100 ion chromatographs (Thermo Scientific), equipped with IonPac AS14 and IonPac CS12A columns for anion and cation analysis, respectively. Dissolved organic and inorganic carbon concentrations were determined using a TOC-VCPH analyzer (Shimadzu). Samples for ion chromatography and dissolved carbon analysis were filtered through a 0.22-mm pore-size syringe filter prior to measurement. Metal concentrations (Cu, Ni, and Fe) leached from the PBA electrodes were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES; 700-ES, Varian). Samples for ICP-OES were diluted with a 2% w/w HNO₃ solution, applying appropriate dilution factors depending on the metal concentrations and the detection limits. All analyses were conducted at least in duplicate.

Declarations

Author Contributions

Hanwoong Kim: Conceptualization, Validation, Formal analysis, Investigation, Visualization, Writing-original draft. **Woohyuk Shin:** Formal analysis, Investigation. **Moon Son:** Conceptualization, Validation, Methodology, Writing-review & editing, Supervision. **Changsoo Lee:** Conceptualization, Validation, Writing-review & editing, Supervision, Funding acquisition.

Data Availability

All data are available in the main text or the ESI† and are also available from the corresponding authors upon reasonable request.

Conflicts of Interest

There are no conflicts to declare.

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Figures

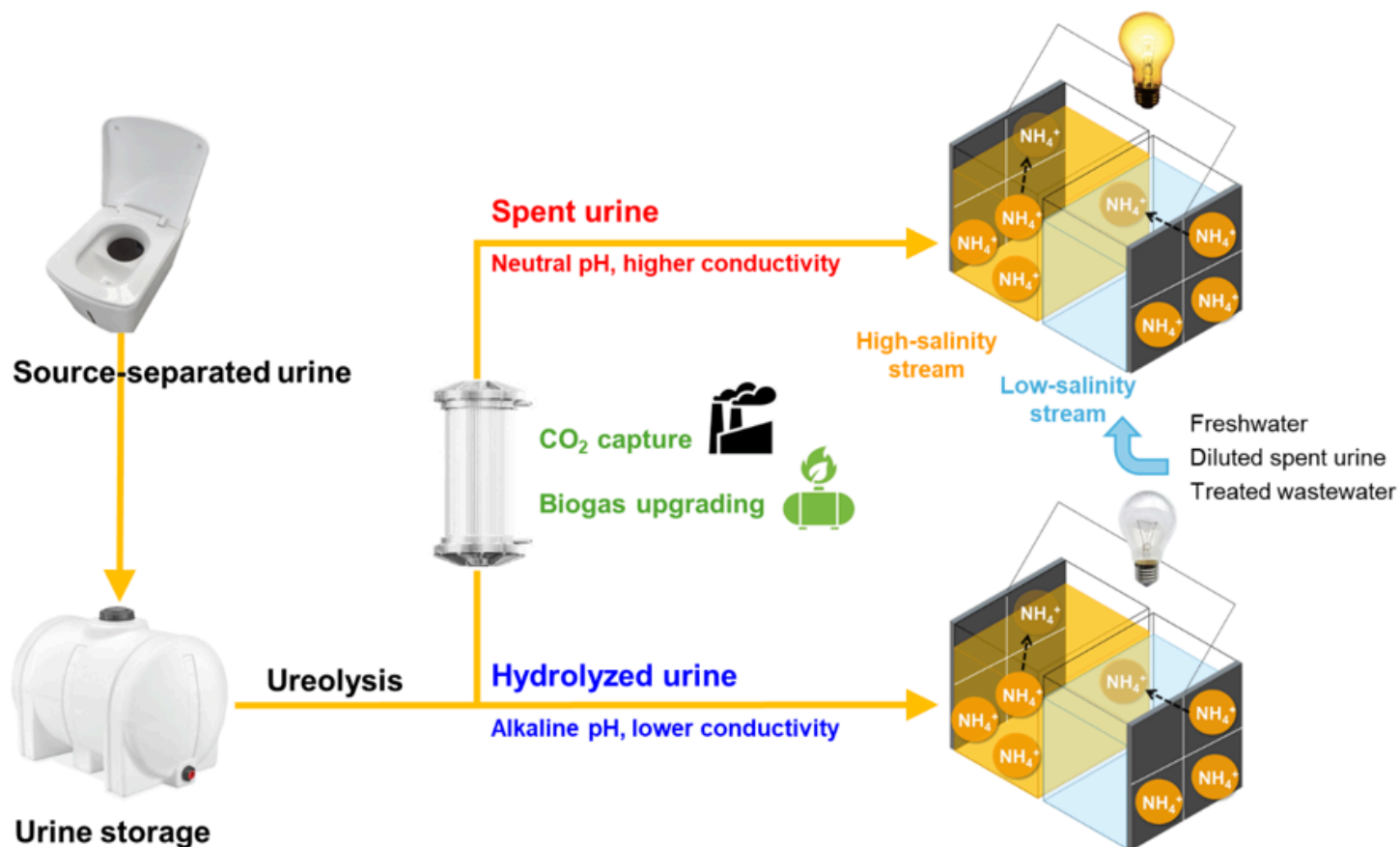


Figure 1

Conceptual illustration of an integrated system coupling CO₂ capture and energy generation from human urine. Source-separated urine undergoes ureolysis during storage, producing hydrolyzed urine (HU) characterized by high salinity and alkaline pH. Direct use of HU as a high-salinity stream is hindered by the instability of NH₄⁺-intercalating Prussian Blue Analogue electrodes under alkaline pH conditions. To resolve this issue, HU is first used as a CO₂ absorbent, which lowers its pH and increases conductivity. The resulting spent urine (SU) can support stable continuous electricity generation when paired with low-salinity streams such as freshwater, diluted SU, or treated wastewater. This innovative approach allows simultaneous carbon mitigation, reduction of water pollution, and energy recovery from an otherwise underutilized resource.

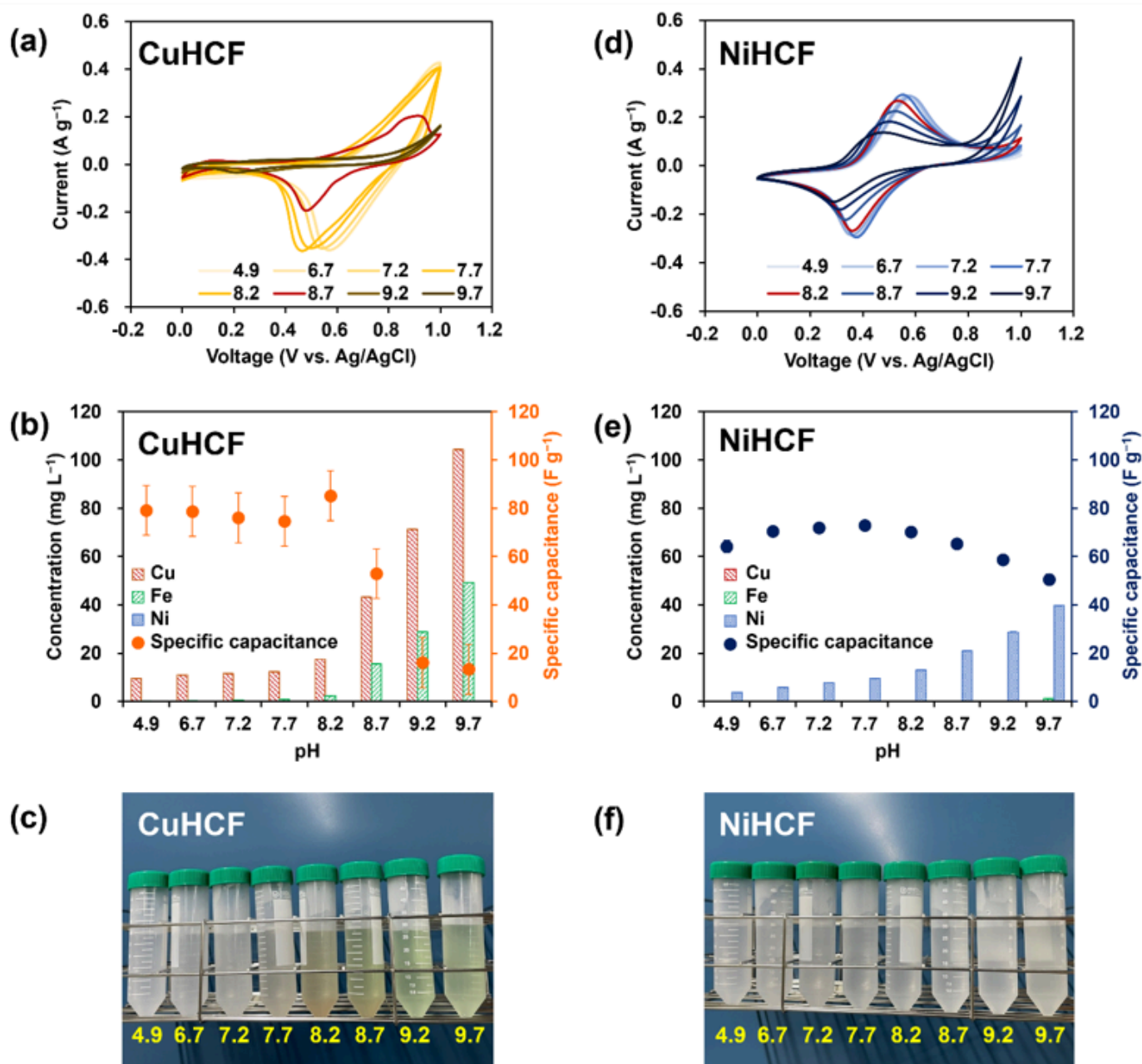


Figure 2

Stability assessment of CuHCF and NiHCF electrodes in 560 mM NH₄Cl solutions over a pH range from 4.9 to 9.7: (a, d) cyclic voltammety profiles; (b, e) leached metal concentrations (Cu, Fe, and Ni) and specific capacitance; and (c, f) photographs showing changes in electrolyte color.

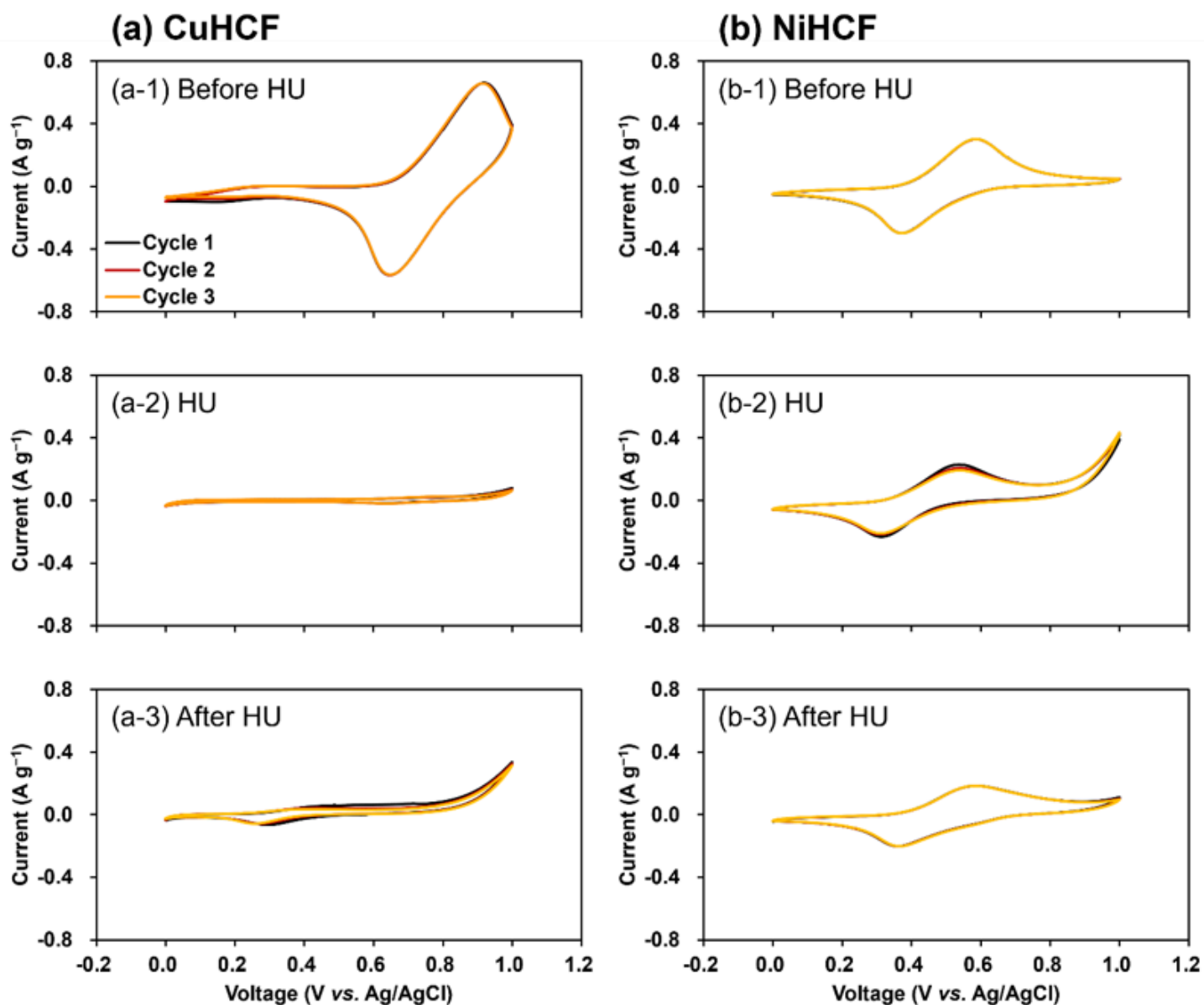


Figure 3

Cyclic voltammetry profiles of (a) CuHCF and (b) NiHCF electrodes evaluated in hydrolyzed urine (HU): (a-1, b-1) before HU exposure, measured in 560 mM NH_4Cl solution (pH 4.9); (a-2, b-2) measured in HU; and (a-3, b-3) after HU exposure, measured again in the same NH_4Cl solution.

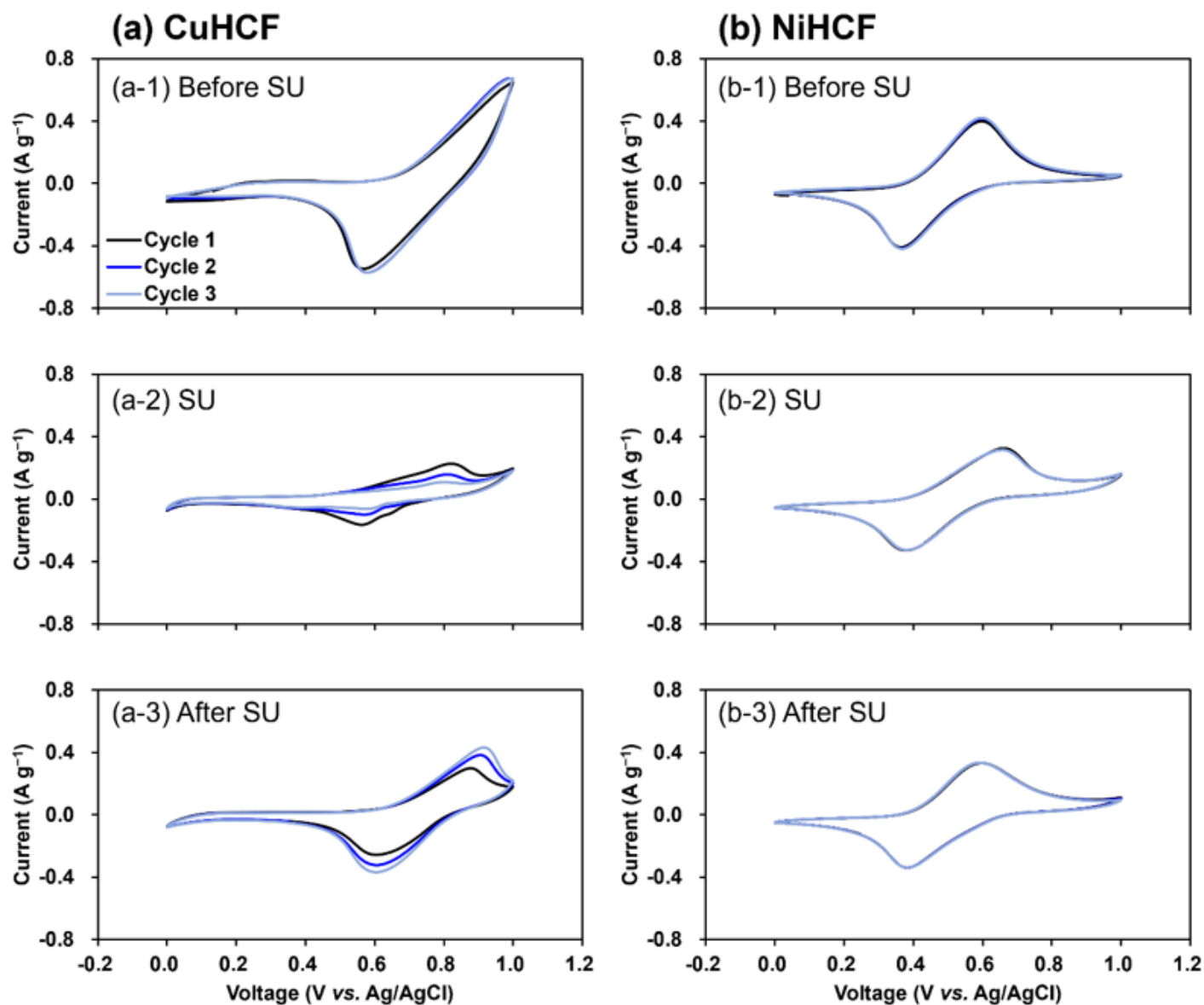


Figure 4

Cyclic voltammetry profiles of (a) CuHCF and (b) NiHCF electrodes evaluated in spent urine (SU): (a-1, b-1) before SU exposure, measured in 560 mM NH_4Cl solution (pH 4.9); (a-2, b-2) measured in SU; and (a-3, b-3) after SU exposure, measured again in the same NH_4Cl solution.

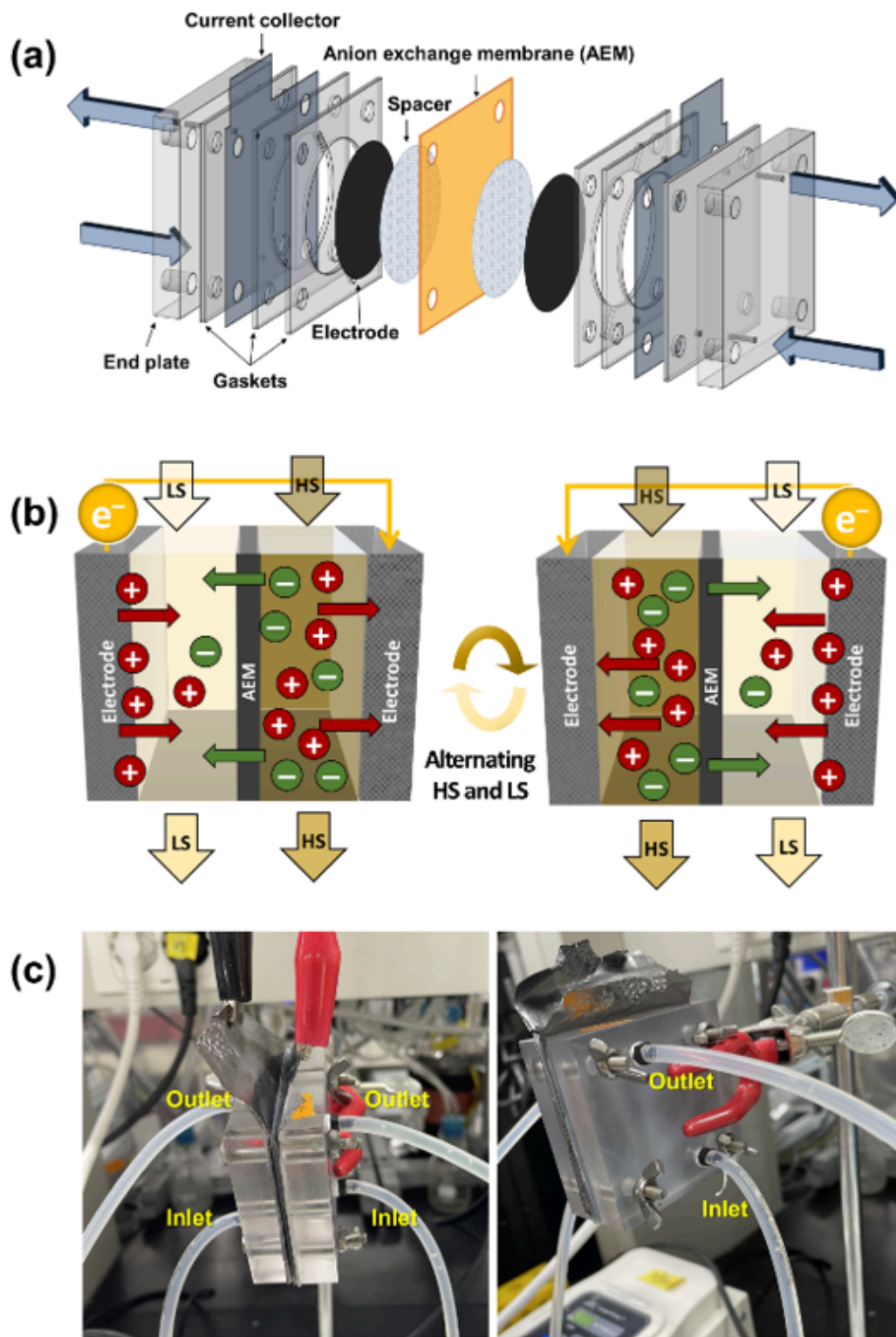


Figure 5

Configuration of urine-ammonium power cell (UPC): (a) exploded view of component assembly; (b) schematic of continuous operation with alternating high- and low-salinity streams (HS and LS); and (c) photographs of UPC in operation. Note that, otherwise noticed, NiHCF electrodes were selected as suitable electrodes.

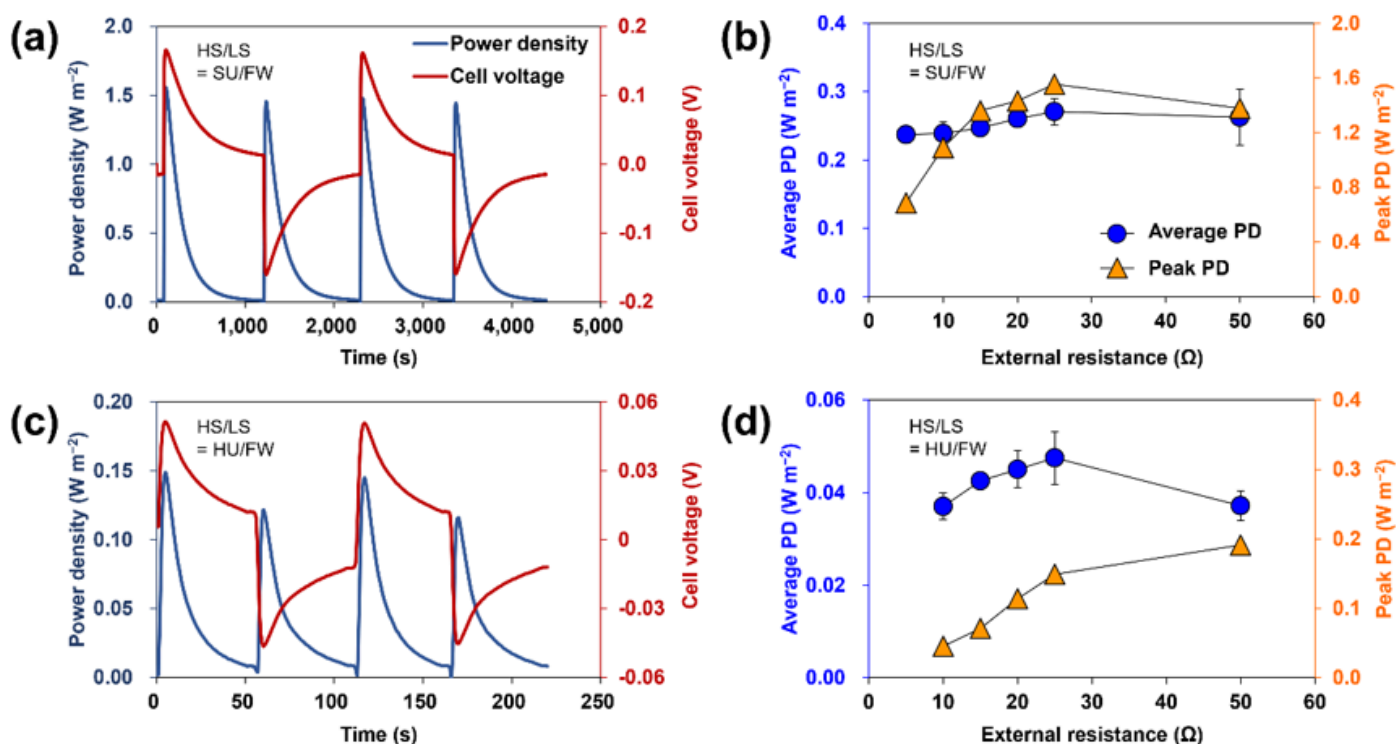


Figure 6

Power generation performance of urine-ammonium power cells operated with spent urine (SU) or hydrolyzed urine (HU) as high-salinity stream (HS) and freshwater (FW) as low-salinity stream (LS): (a, c) power density (PD) and cell voltage profiles at an external resistance of 25 Ω for SU and HU, respectively; and (b, d) average and peak PD profiles as a function of external resistance for SU and HU, respectively.

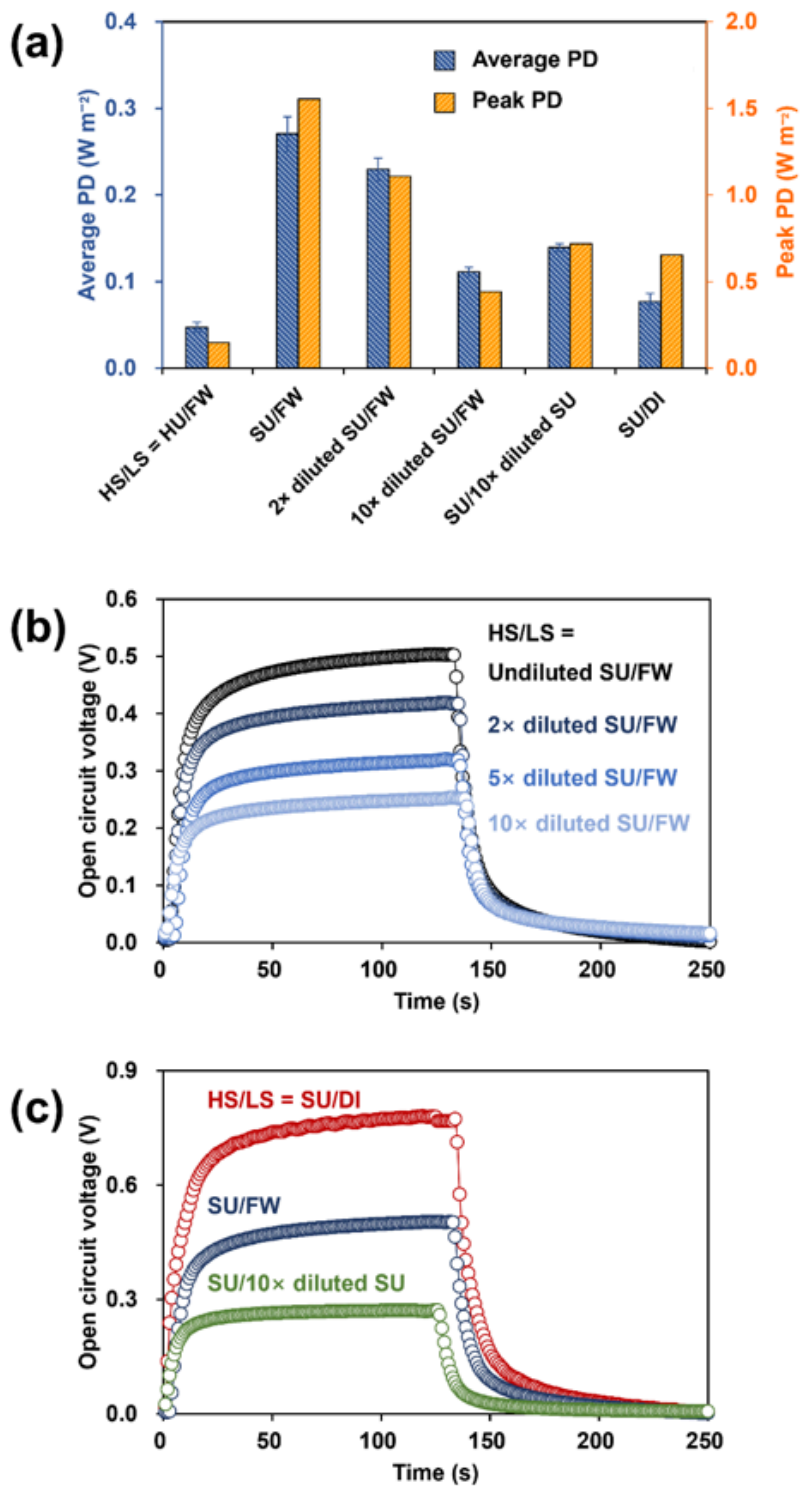


Figure 7

Power output and voltage characteristics of urine-ammonium power cells with spent urine (SU) in various high-/low-salinity stream (HS/LS) combinations: (a) average and peak power densities (PDs); (b) open circuit voltage (OCV) between diluted SU (undiluted to 10-fold diluted) and freshwater (FW); and (c) OCV between SU and different LSs, including deionized water (DI), FW, and 10-fold diluted SU.

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