Nickel-Based Membrane Electrodes Enable High-Rate Electrochemical Ammonia Recovery

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Supporting Information

ABSTRACT: Wastewater contains significant amounts of nitrogen that can be recovered and valorized as fertilizers and chemicals. This study presents a new membrane electrode coupled with microbial electrolysis that demonstrates very efficient ammonia recovery from synthetic centrate. The process utilizes the electrical potential across electrodes to drive NH_4^+ ions toward the hydrophilic nickel top layer on a gas-stripping membrane cathode, which takes advantage of surface pH increase to realize spontaneous NH_3 separation and recovery using the membrane electrode structure. Compared with a control configuration with conventionally separated electrode and hydrophobic membrane, the integrated membrane electrode showed 40% higher $\text{NH}_3\text{--N}$ recovery rate ($36.2 \pm 1.2 \text{ gNH}_3\text{--N/m}^2/\text{d}$) and 11% higher current density. The energy consumption was $1.61 \pm 0.03 \text{ kWh/kgNH}_3\text{--N}$, which was 20% lower than the control and 70–90% more efficient than competing electrochemical nitrogen recovery processes ($5\text{--}12 \text{ kWh/kgNH}_3\text{--N}$). Besides, the negative potential on membrane electrode repelled negatively charged organics and microbes thus reduced fouling. In addition to describing the system's performance, we explored the underlying mechanisms governing the reactions, which confirmed the viability of this process for efficient wastewater–ammonia recovery. Furthermore, the nickel-based membrane electrode showed excellent water entry pressure ($\sim 41 \text{ kPa}$) without leakage, which was much higher than that of PTFE/PDMS-based cathodes ($\sim 1.8 \text{ kPa}$). The membrane electrode also showed superb flexibility (180° bend) and can be easily fabricated at low cost ($<20 \text{ \$/m}^2$).

1. INTRODUCTION

Ammonia (NH_3) is an essential nutrient for global food production and the second most common synthetic chemical in the world.¹ Ammonia is produced using the energy-intensive Haber–Bosch process ($\sim 14 \text{ kWh/kgNH}_3\text{--N}$), which accounts for 1–2% of global energy consumption and $\sim 1.6\%$ of global CO_2 emissions.² However, due to incomplete consumption and waste generation, significant amounts of ammonia and other nitrogen compounds end up in wastewater. This accounts for $\sim 30\%$ of total nitrogen fertilizers.^{3,4} Such high nitrogen loading not only adds treatment pressure and costs to the wastewater infrastructure,⁵ it also leads to eutrophication and other environmental problems.^{6,7} Current mainstream treatment processes such as Anammox and nitrification/denitrification do not recover nitrogen in a useful form, instead converting nitrogen (ammonium and/or nitrate) to N_2 , which consumes energy ($\sim 12.5 \text{ kWh/kgNH}_3\text{--N}$) and potentially releases greenhouse gas (i.e., N_2O) to the atmosphere.^{2,8} Moreover, the energy-intensive nutrient removal processes contribute to greenhouse gas emission of 0.9 kg CO_2

per cubic meter of treated wastewater.^{2,9} Thus, recovering such nutrients can be a promising strategy to benefit fertilizer and food production, as well as greatly reduce the energy and carbon footprint of the nitrogen cycle.^{2,10}

A promising waste stream for nutrient recovery in wastewater treatment is the centrate produced during centrifugal sludge dewatering.⁵ The centrate is nutrient-rich and contains high concentrations of ammonia nitrogen ($>1100 \text{ mgNH}_3\text{--N/L}$), total Kjeldahl nitrogen (TKN, $>1300 \text{ mgN/L}$), orthophosphate ($>200 \text{ mgPO}_4\text{--P/L}$), and organics (up to 2000 mg/L).¹¹ Generally, wastewater treatment plants recycle centrate back to the primary treatment units. However, the small volume of centrate ($<1\%$ total volume) can contribute up to 30% of nutrient loading, as well as elevated energy demand and pipe scaling (from struvite), which leads to an increase in

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the environmental footprint of mainstream treatment facilities.^{12,13} Therefore, direct ammonia recovery from centrate represents a good opportunity for wastewater nutrient recovery.

Air stripping, ion exchange, and membrane processes have been used for ammonia recovery from wastewater.^{14–17}

However, these technologies suffer from high energy demand and/or require large quantities of chemicals for regeneration.^{2,18} Moreover, many of these technologies have low selectivity. Besides, ammonium, phosphate, and other non-nutrient ions (e.g., Na^+ , Cl^-) are also recovered and mixed with ammonium, which downgrades product quality, reduces efficiency^{13,19–23} and leads to scaling (e.g., struvite).^{21,22,24}

In this regard, electrochemical processes carry a good advantage for product selection by utilizing low-cost electrons to realize phase separation.^{10,20,25–28} In an electrochemical system, the

electrolysis of water produces hydroxide ions on the cathode.^{29,30} By separating the anode and cathode using an ion exchange membrane (IEM), the high pH in the cathode chamber can drive the conversion of ammonium ion (NH_4^+) to ammonia (NH_3), which can be recovered using air stripping or gas-permeable hydrophobic membranes.^{13,19,31} On the basis

of this hypothesis, Kuntke et al. first achieved ammonia recovery ($3.29 \text{ gNH}_3\text{-N/m}^2/\text{d}$) from a membrane electrode assembly (MEA) air cathode in a microbial fuel cell (MFC) via gas diffusion.¹⁹ Though the air cathode was fabricated at low

cost, such gas diffusion structure was generally thick ($>1 \text{ mm}$) with low flexibility, and it could not withhold high water pressure ($<30 \text{ kPa}$),^{32–34} greatly limiting the potential for

scale-up. Soon afterward, a gas-permeable hydrophobic tubular membrane was employed into the catholyte of a microbial electrolysis cell (MEC) for ammonia recovery.²⁶ This

integration not only achieved high rate ammonia recovery ($19 \text{ gNH}_3\text{-N/m}^2/\text{d}$) but also greatly reduced system complexity. Similar configurations with separated electrode

and membrane were also adopted in abiotic electrochemical systems for ammonia recovery from urine with good results.^{28,35,36} However, in these processes with separated

electrode and membrane, the diffusion and/or migration of NH_3/OH^- from the cathode surface to the bulk for further recovery was reported as a major rate limiting process, which also governs cathodic potential losses.^{30,37}

In this study, we developed a highly efficient membrane electrode for active ammonia recovery from synthetic centrate. The membrane electrode consisted of a hydrophilic thin-film nickel layer deposited on a hydrophobic polypropylene (PP)

support layer. The central hypothesis is that by taking advantage of the electric potential across the anode and cathode during microbial electrolysis,²⁹ NH_4^+ ions are driven

toward the hydrophilic nickel top layer on the cathode, and the localized high pH on the cathode surface drives the conversion of NH_4^+ to NH_3 , which can be readily volatilized and harvested through the membrane, enabling high-efficiency recovery.^{29,30,38} The novelty of this process comes from several

aspects: this integration utilizes the in situ local pH change on the electrode surface, which reduces the loss of OH^-/NH_3 to the bulk solution and thus boosts the ammonia recovery rate.

Reciprocally, ammonia recovery on the electrode surface prevents the OH^-/NH_3 accumulation, and hence reduces surface pH and the overpotential that subsequently boosts current production.³⁰ In addition to ammonia recovery, the

applied negative potential on the membrane electrode repels negatively charged foulants and mitigates membrane foul-

ing.^{39–41} More importantly, the hydrophobic support of the membrane electrode prevents the permeation of any other ions, thus guaranteeing high purity ammonia in the recovery solution. Furthermore, the membrane electrode can be easily fabricated at a low cost. To the best of our knowledge, this is the first report of a flexible membrane electrode for ammonia recovery. In addition to demonstrating the performance of the system in terms of ammonia recovery, the underlying mechanisms governing the reactions are illustrated.

2. MATERIALS AND METHODS

2.1. Materials and Chemicals. A commercial hydrophobic polypropylene (PP) membrane ($0.22\text{-}\mu\text{m}$, Tisch Scientific, North Bend, OH) was used as the membrane support in this study. Polyvinylidene fluoride (PVDF) and multiwall carbon nanotubes (MWCNTs, outer diameter: $8\text{--}15 \text{ nm}$, length: $10\text{--}50 \mu\text{m}$) were purchased from Alfa Aesar (Haverhill, MA) and CheapTubes (Brattleboro, VT), respectively. All the chemicals were ACS grade and purchased from Fisher Scientific (Waltham, MA). All working solutions were prepared using Milli-Q water ($18.2 \text{ M}\Omega\cdot\text{cm}$) throughout the study unless otherwise stated.

The feed solution was synthetic centrate¹³ that contained the following (mg/L): CH_3COONa , 2500; NaHCO_3 , 1500; NH_4Cl , 4000; KH_2PO_4 , 300; $\text{MgSO}_4\cdot 6\text{H}_2\text{O}$, 100; and CaCl_2 , 50. The total soluble chemical oxygen demand (COD), $\text{NH}_3\text{-N}$, $\text{PO}_4\text{-P}$, electrical conductivity, and pH of the synthetic centrate were $2000 \pm 20 \text{ mg/L}$, $1000 \pm 10 \text{ mg/L}$, $200 \pm 5 \text{ mg/L}$, $12.90 \pm 0.05 \text{ mS/cm}$, and 7.51 ± 0.05 , respectively.

2.2. Membrane Preparation and Characterization. The detailed preparation route of this membrane electrode can be seen in Figure S1. In brief, 0.5 g of PVDF and 1.0 g of MWCNT were dissolved/dispersed in 100 g of dimethylacetamide (DMAc) using a magnetic stirrer for 24 h. After 60 min of ultrasonication, the PVDF–MWCNT dispersion was sprayed uniformly over the PP membrane support followed by drying overnight in an oven at 50°C . The resulting nanocomposite electrically conductive (EC) CNT/PP membrane had MWCNT loadings of $0.29 \pm 0.04 \text{ mg/cm}^2$. To prepare the membrane electrode, electrodeposition was performed in a reactor with a porous Ni foam as the anode and the CNT/PP membrane as the cathode at a distance of 8 cm. The electrodeposition bath contained 150 mM $\text{NiSO}_4\cdot 7\text{H}_2\text{O}$, 25 mM $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$, and 500 mM H_3BO_3 (at pH 2.00 ± 0.05).⁴² A constant DC current of 0.2 A was applied on the electrodes for 24 h. The prepared membrane electrode was rinsed in deionized water to remove Ni salts and unbound Ni residues before drying overnight at 50°C . The resulting membrane electrode had a nickel loading of $7.36 \pm 0.10 \text{ mg/cm}^2$. The physical, electrochemical, and fouling properties of the membrane electrode were characterized using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), contact angle (CA) measurements, conductivity probe, and linear sweep voltammetry (LSV).^{38,39,43–47} Details of the measurements can be found in Supporting Information (SI).

2.3. Reactor and Operations. Experiments were carried out in an MEC reactor (Figure S2), with the electrodes separated by a piece of cation exchange membrane ($25.5 \text{ cm} \times 7.5 \text{ cm}$, CMI-7000, Membrane International, NJ). Diamond-shape polyester spacers were used in flow channels for separation and promoting mass transfer.^{45,46} The anode consisting of two carbon brushes (5 cm in diameter $\times$ 50

188 cm long) was inoculated with anaerobic sludge collected from
189 the Boulder Wastewater Treatment Plant and fed with the
190 synthetic centrate.

191 Different operations were tested in sequence in the same
192 reactor with the same anode,⁴⁷ and both anolyte and catholyte
193 were the synthetic centrate. Three runs with different cathodes
194 and working conditions were operated. For each run with the
195 same operating condition, 7–11 batch cycles were repeated. In
196 Run 1, a piece of fresh Ni foam was used as the cathode
197 without PP membrane or ammonia recovery (Figure S2C-1).
198 This was the baseline experiment in order to show the MEC
199 performance (i.e., current and H₂ production) without
200 ammonia recovery, which was used to compare with the
201 results in Run 2 and Run 3 regarding the effects of ammonia
202 recovery on current and energy production. In Run 2, a same
203 piece of fresh Ni foam was used as the cathode but equipped
204 with a PP membrane for ammonia recovery using an external
205 acid solution recirculating independently on the opposite of
206 the cathode for ammonium capture (Figure S2C-2). In
207 addition to being compared with Run 1, Run 2 was also
208 used to simulate the conventional configuration with separated
209 electrode and membrane for ammonia recovery^{10,26,27,35,36} for
210 further comparisons with Run 3 with the new membrane
211 electrode, where the electrode and membrane were integrated.
212 In Run 3, a similar operation was used as in Run 2, except the
213 membrane electrode was employed as the cathode with nickel
214 layer facing the catholyte and membrane layer facing the
215 ammonia recovery solution (Figure S2C-3). To evaluate the
216 effects of active ammonia recovery on overpotential of the
217 membrane electrode, an operation similar to that of Run 3
218 (named as Membrane Electrode without Ammonia Recovery)
219 was used, except the ammonia recovery chamber was
220 hydraulically connected to the cathode chamber (Figure
221 S2C-4). Schematics and detailed explanations of these
222 configurations can be found in Section S2 of the SI. During
223 operations, the anolyte and catholyte were recirculated
224 separately with their respected reservoirs, and the flow rate
225 was 650 mL/min. For Run 2 and 3 with ammonia extraction, a
226 peristaltic pump at 100 mL/min was used to circulate acid
227 solution (1% H₂SO₄) between the ammonia recovery chamber
228 and an external reservoir (1.0 L). The gas products including
229 H₂ and NH₃ were extracted into the acid solution for NH₃
230 adsorption into H₂SO₄ before collected in a 2.0-L bottle using
231 water displacement method. Solutions were replenished before
232 each batch. A voltage of 0.8 V was applied across the
233 electrodes, and the voltage across an external resistor (*R*, 1 Ω)
234 was measured every 10 min using a data acquisition system
235 (Keithley Instruments, Inc., Solon, OH).⁴⁸ The whole
236 experiment was operated at room temperature (22.0 ± 0.5
237 °C).

238 **2.4. Analysis.** All samples were filtered through 0.45-μm
239 cellulose membranes (Millipore) for COD, N, and P
240 measurements. COD was measured according to standard
241 methods described in detail by the American Public Health
242 Association.⁴⁹ NH₃-N (TNT 832/831/830) and PO₄-P
243 (TNT 846) were measured with HACH test tubes (HACH,
244 Loveland, CO). Gas samples were analyzed using a gas
245 chromatograph (8610C, SRI Instruments) for H₂ and CH₄. All
246 samples were collected and analyzed in triplicate.⁵⁰ The
247 ammonia recovery rate (gNH₃-N/m²/d) and specific energy
248 consumption (kWh/kgNH₃-N), cathodic H₂ recovery (*r*_{cat},
249 %), H₂ production rate (*Q*, m³-H₂/m³/d) and energy
250 efficiency relative to electrical input (*η*_E, %) were used to

evaluate ammonia recovery and energy production from the
MEC (Section S12–13 in SI).⁴⁷

3. RESULTS AND DISCUSSION

3.1. Membrane Electrode Characterization. Visual
images and SEM micrographs of the prepared membrane
electrode are shown in Figure S1, Figure 1, and Figure 5. XPS

Figure 1. (A) SEM micrographs (1: top surface; 2: cross section), (B) XPS (1: survey spectrum; 2: high-resolution scan spectra of Ni 2p), (C) XRD of the prepared membrane electrode, and (D) linear sweep voltammetry (LSV) curves of the different cathodes. Current density was normalized to cathode effective project area (7 cm²).

analysis of the cauliflower-like thin film on the membrane
electrode surface (Figure 1B2) revealed relatively high peaks
for Ni(0) (852.7 eV), Ni(2+)(OH)₂ (856 eV), and a weaker
peak of Ni(2+)O (854 eV), indicating that the nickel layer was
a mixture of metallic and oxidized Ni.⁵¹ The presence of
oxidized Ni on the membrane electrode was likely due to
partial oxidation by oxygen dissolved in the electrodeposition
bath or in air.⁴² The XRD pattern (Figure 1C) was consistent
with the typical profile of a nickel substrate with both
elemental and oxidized forms.⁴⁷ Moreover, the prepared
membrane electrode can be bent 180° with quick and natural
recovery, showing excellent flexibility compared to the
conventional nickel foam electrode, which was hardly
recovered after bent for only 30° (Figure S5).

On the basis of these images, the thickness of the CNT and
nickel thin film on the membrane electrode were determined
to be 15 ± 5 μm and 25 ± 5 μm, respectively. The sheet
resistivity and the corresponding electrical conductivity of the
CNT layer were 9.4 ± 1.3 × 10⁻⁴ Ω·m and 10.7 S/cm,
respectively, which were comparable to the results reported in
previous studies on CNT conductivity.^{38,52} The coated nickel
layer improved the electrical conductivity and reduced sheet
resistivity by 546 times, to 5871 S/cm and 1.7 ± 0.6 × 10⁻⁶
Ω·m, respectively. The membrane electrode showed excellent
electrochemical properties in hydrogen evolution reactions
(HER) (Figure 1D) with even more positive onset potential
than that of the nickel foam (-0.3 V vs -0.5 V).^{47,53} With the
decrease of the applied potential, the membrane electrode was

more effective in current increase than the nickel foam. At the cathodic potential of -0.8 V (vs standard hydrogen electrode (SHE)), the cathodic current of the membrane electrode was 25.5 A/m², which was higher than that of the nickel foam (18.0 A/m²), suggesting that the membrane electrode has lower overpotential and higher catalytic activity. Such advantage was likely attributed to the crystalline composition of the coated nickel layer (Figure 1B2), where Ni(OH)₂ has been widely reported as enhancing catalytic activities (i.e., better water dissociation).^{54,55} This was further supported by LSV curves of the nickel foam after electrolysis, which became rich in Ni(OH)₂ and showed improved HER performance (Figure S9B). Moreover, both the 2D structure and the gas permeability by the hydrophobic support played important role in higher performance, which facilitated gas separation on the cathode surface and reduced the overpotential.^{31,56}

3.2. Ammonia Recovery and Current Production.

Figure 2 shows the profiles of current production and rates of

Figure 2. Time-course changes of current and ammonia recovery rate in the reactor. There were 9 batches in Run 1 (Ni foam without NH₃ recovery) and Run 2 (Ni foam + PP membrane), and 7 batches in Run 3 (Ni decorated membrane electrode), with each batch lasting 12 h.

ammonia recovery during the different batch runs. A typical batch profile started with rising current in the first few hours due to the adaptation of the electroactive bacteria to the newly replenished solutions.^{17,57} Once reaching the peak, the current decreased gradually until the end of the batch. Run 1 and Run 2 showed no significant differences in the peak current (54.4 ± 2.3 mA in Run 1 vs 55.8 ± 1.9 mA in Run 2) during early cycles, which was presumably due to the similar substrate conditions (e.g., COD and pH) at the beginning of each run. However, over time, the catholyte pH in Run 1 (without ammonia recovery) increased significantly from 7.51 to 9.34 due to OH⁻ accumulation in the cathode chamber (Figure S10A). In response, the current dropped to 35.3 ± 2.9 mA at the end of the cycle. With ammonia recovery in Run 2, the catholyte pH was maintained below 8.36 and the end current was elevated to 44.9 ± 1.9 mA. The benefits of active ammonia recovery were even more significant when the membrane electrode was used in Run 3, during which the catholyte pH stabilized at around 8.06. Its peak and end currents were 60.9 ± 1.6 (~11% higher than those of Run 1 and Run 2) and 52.2 ± 1.8 mA (~48.3% higher than Run 1 and ~16.3% higher than Run 2), respectively. In addition, the current profiles positively correlated with ammonia recovery rate in Run 2 and Run 3, which was consistent with previous studies.^{10,25,28,58} The ammonia recovery rate and energy demand by the Ni-decorated membrane electrode in Run 3 were 36.2 ± 1.2 gNH₃-N/m²/d and 1.61 ± 0.03 kWh/kgNH₃-N, respectively, which were 40% faster (25.7 ± 1.2 gNH₃-N/m²/d) and 20% more energy efficient (1.93 ± 0.08 kWh/kgNH₃-N) than

those obtained in Run 2 with separated Ni foam and PP membrane. In turn, the resulting higher current in Run 3 corresponded with higher COD removal rates in the anode chamber (151 ± 8 mgCOD/L/d), compared to those in Run 2 (119 ± 20 mgCOD/L/d) and Run 1 (106 ± 24 mgCOD/L/d). Though the bioelectrochemical ammonia recovery rate using the membrane electrode in Run 3 (36.2 ± 1.2 gNH₃-N/m²/d) was an order of magnitude lower than the reported abiotic electrochemical systems (50 – 300 gNH₃-N/m²/d), the energy demand without considering H₂ production using the membrane electrode was up to 86% lower (1.61 ± 0.03 vs 5 – 12 kWh/kgNH₃-N).^{2,10,25,36,58} The membrane electrode in Run 3 also showed very high COD rejection (>99%) with the COD in the recovery solution maintained below 10 mg/L.

The higher performance observed in Run 3 was believed to be associated with the mutual benefits caused by the active ammonia harvesting at the membrane electrode surface, which alleviated the accumulation of NH₃/OH⁻ and reduced cathode overpotential;^{27,59} this, in turn, led to a higher current density and ammonia recovery. According to the Nernst eq (Section S10 in SI), increasing pH by one unit can lead to an increase of overpotential by 59 mV. Therefore, the low catholyte pH in Run 3 might have reduced the apparent overpotential by 17.7 and 75.5 mV compared to Run 2 and Run 1, respectively. To further illustrate the effect of active ammonia recovery on the overpotential, the membrane electrode was operated with and without active ammonia recovery (Figure 3B). It was shown

Figure 3. (A) Mass balance of NH₃-N in the reactor during different runs; negative values mean mass loss; positive values mean mass gain; (B) time-course changes of cathode potential of the membrane electrode when operated with ammonia recovery (Run 3) and without ammonia recovery; (C) relating the current production to the NH₃-N loss in the anolyte; (D) relating current production to the overall NH₃-N recovery in Run 3. The current in C and D is the average current of one batch (12 h).

that the overpotential difference was 0.11 V, suggesting that at a same current density, the actual pH on the electrode surface with active ammonia recovery was 1.86 lower than that operated without ammonia recovery. It is interesting to note that the pH variance at the cathode surface was larger than that of the bulk (1.28, Figure S10A). This indicated that the pH difference between the cathode surface and bulk solution during ammonia recovery was comparatively lower than that without ammonia recovery. The reduced pH gradient was due

Figure 4. Conceptual diagram illustrating ammonia recovery mechanisms by the membrane electrode. Diffusion: Diffusion of H^+ and NH_4^+ from the bulk solution to the cathode surface due to electro-adsorption. Reaction: Production of H_2 , NH_3 , OH^- on the cathode surface by microbial electrolysis and high surface pH. Extraction: Convection or extraction of H_2 and NH_3 from the cathode surface via the hydrophobic layer of the membrane electrode.

to the active ammonia harvesting, which could effectively remove ammonia from the electrode surface thus altered the $\text{NH}_4^+/\text{NH}_3$ equilibrium and mitigated the accumulation of NH_3/OH^- on the electrode surface. The reduced pH on the electrode surface hence mitigated cathodic potential losses and might theoretically enhance the overall electrical efficiency by 8.8%.^{30,60}

3.3. Ammonia Mass Balance and Mechanism for Improved Recovery. Figure 3 shows the overall mass balance of the $\text{NH}_3\text{-N}$ present in different operating conditions. Although for all runs good mass balances were achieved, the $\text{NH}_3\text{-N}$ transport in different runs varied significantly. Driven by the current, NH_4^+ was continuously transported from the anolyte to the catholyte (Figure 3A) and the loss rate in the anolyte was positively correlated with the current in the reactor (Figure 3C). This is in agreement with our previous findings in microbial resource recovery, in which ion transport was determined by the current and by its relative abundance in the solution.²¹ For Run 1 without ammonia harvesting, most of the $\text{NH}_3\text{-N}$ loss in the anode chamber can be balanced with the $\text{NH}_3\text{-N}$ increase in the cathode chamber. However, up to 85 mg $\text{NH}_3\text{-N}$ overall loss from the system was observed, presumably due to the formation of struvite precipitate due to increased cathode pH;^{13,24} this is supported by the corresponding loss of $\text{PO}_4\text{-P}$ (Figure S9).

In contrast, when ammonia harvesting was applied in Run 2 and Run 3, $\text{NH}_3\text{-N}$ concentrations dropped in both the anolyte and catholyte. This simultaneous drop was due to the ammonia harvesting from the cathode to the recovery solution (Figure 3A). Overall, in Run 3, where the cathode chamber was equipped with the membrane electrode (on which NH_4^+ N was electro-adsorbed and pH was much higher than the bulk pH^{61,62}), the direct deprotonation and capture greatly enhanced ammonia recovery by 40% as compared to Run 2. Benefiting from the active ammonia recovery using the

membrane electrode, the local pH on the membrane electrode surface was lowered, which reduced the cathodic potential loss (Figure 3B) and enhanced current production (Figure 2). Moreover, the catholyte bulk pH was also maintained below 8.06 during Run 3 (Figure S10A), which mitigated ammonia/phosphate precipitation (Figure S11).

Importantly, the ammonia recovery in Run 3 was directly correlated with the current, as shown in Figure 3D. This is likely because NH_4^+ ions served as proton shuttles during operation,^{17,22,62} in which NH_4^+ ions carried protons to the membrane electrode surface, and lost protons when they were converted to NH_3 . In this study, the NH_4^+ ions accounted for $36.9 \pm 0.7\%$ of all proton shuttles, which agreed with the findings from a previous study.⁶²

During MEC operation, the effective concentration ($C_{\text{effective},i}$) of a cation on the electrode surface can be determined using the Nernst–Planck equation.⁶³ Accordingly, NH_4^+ ions are pulled via diffusion and migration from the bulk solution and accumulate at the electrode–solution interface, where NH_4^+ concentration is higher than that in the bulk (Figure 4).⁶⁴ Because of water reduction during electrolysis on the MEC cathode, OH^- accumulates on the electrode surface, leading to localized pH increase and the deprotonation of NH_4^+ .^{29,30} Researchers previously employed hydrophobic membranes for ammonia recovery from the catholyte,^{26,35} but the diffusion and/or migration of NH_3/OH^- from the cathode surface to the bulk largely governed the cathodic potential losses thus current production, which may reduce the overall recovery performance.³⁰ Moreover, buffer ions (e.g., HCO_3^- and HPO_4^{2-}) can further reduce the efficiency by countering catholyte pH change^{30,37} and decreasing the ammonia fraction. In this study, we took advantage of the local pH increase on the membrane cathode surface to enable in situ NH_3 generation and separation, which mitigated overpotential and eliminated the transport limitation of

NH₃/OH[−] from the cathode surface to the bulk for further recovery.³⁰ This approach enhanced the local generation and consumption of OH[−] and promoted NH₄⁺ transport from the bulk toward the electrode to enable continuously high efficiency NH₃ harvesting (Figure 4). The active ammonia recovery also reduced the electrode–solution interface pH, which reduced the overpotential associated with electrolysis and enhanced current production.³⁰

In addition to ammonia, hydrogen gas was also recovered from the system. In Run 1 without ammonia recovery, the system was operated similarly to a traditional two-chamber MEC with a nickel foam cathode, so H₂ was stably produced at 0.15 ± 0.01 m³-H₂/m³/d with a cathode efficiency of 100 ± 7%. The cathodic efficiency was approximately 40% higher than our previously reported result in a single-chamber MEC.⁴⁷ It is interesting to note that ammonia recovery in Run 2 reduced H₂ production and cathode efficiency to 0.13 ± 0.02 m³-H₂/m³/d and 75 ± 9%, respectively, though the current was much higher as shown in Figure 2 and Table S3. However, with active ammonia recovery using the membrane electrode, Run 3 exhibited improved H₂ production rate (0.19 ± 0.01 m³-H₂/m³/d) and cathode efficiency (85 ± 2%) compared to Run 2. The variation of H₂ production is believed to be associated with ammonia recovery, thus pH and free ammonia in the catholyte, which can greatly affect the activities of hydrogen consumption microbes (e.g., sulfate-reducing bacteria and methanogens).^{65,66} Detailed discussions can be found in SI Section S13.

3.4. Low Fouling Behavior. Figure 5 shows the membrane surface in Run 2 and membrane electrode in Run

Figure 5. SEM images of the (A) PP membranes (1: pristine; 2: fouled) in Run 2 and (B) the membrane electrode (1: fouled; 2: after cleaning using 0.1% H₂SO₄ for 15 min) in Run 3.

3 following the ammonia harvesting experiments. The bare PP membrane used in Run 2 displayed a yellowish color (Figure S7C), and its SEM images with EDX analysis showed the presence of organic fouling with significant crystal deposition (Figure 5A). The deposited organics reduced the porosity of the PP membrane (Figure 5A-2),⁶⁷ which could reduce the ammonia recovery efficiency. A more severe issue on PP membrane in Run 2 can be membrane wetting, which can result from organic matter depositing inside the membrane's

pores.⁶⁸ This can result in the acid leaking and reduced gas separation. In contrast, the membrane electrode in Run 3 did not suffer from organic fouling (Figure 5B-1 and Figure S7A-2). This benefit may be a result of the negative potential on the membrane electrode during operation, which repelled the negatively charged organics and/or microbes.^{39,40} In addition, the electrodeposited nickel thin layer greatly reduced the roughness (~35 nm vs ~120 nm of the PP membrane, Figure S3) and hydrophobicity (CA: 21.4 ± 0.5°, Table S1) of the composite membrane electrode, both of which help mitigate organic fouling and biofouling.^{17,69} However, the membrane electrode did show inorganic scaling (Figure S7A-2 and Figure 5B-1), which, based on XPS analysis, was found to be similar to the composition of NH₄MgPO₄ (struvite)^{24,70} and/or Mg₃(PO₄)₂ or Ca₃(PO₄)₂^{71,72} (Figure S8A). This was believed to be attributed to the heterogeneous/surface crystallization on the electrode surface, which was exacerbated by the pH change due to electrolysis.^{70–72} During electrolysis, the negative potential can promote the formation of an electric double layer on the membrane surface.^{73,74} Though the double layer repels anions but also adsorbs cations (e.g., NH₄⁺ and Mg²⁺).⁷⁴ Even though it has benefits of antiorganic fouling and promoting ammonium transfer, the side effect is the increased pH due to OH[−] accumulation, which could promote crystallization.^{71,72} Fortunately, inorganic scaling did not significantly hinder the performance of the membrane electrode, with current production dropped from 61.2 to 56.5 mA (7.7%), and ammonia recovery decreased from 37.4 to 34.9 gNH₃-N/m²/d (6.8%), respectively, in 7 batches (Figure 2 and Figure 3A). Moreover, the deposited crystals only appeared on the membrane surface and were easily cleaned with 0.1% H₂SO₄ (Figure 5B-2, Figure S7A-3 and Figure S8A).

3.5. Implications and Outlook. The study demonstrated in both reaction mechanisms and lab scale experiments that the nickel-based membrane electrodes can achieve high rates of electrochemically driven ammonia recovery. The layered structure enabled both efficient catalysis on the hydrophilic side and gas separation on the hydrophobic side, and the negative potential and local OH[−] accumulation reduced fouling and facilitated ammonia generation. In addition to the data presented, we also found the membrane electrode endured higher water pressure (41.4 ± 0.4 kPa) than traditional air cathodes (~12 kPa for PVDF based cathode, and 0.18 ± 0.02 m for PTFE and PDMS based cathodes).³² The high water enter pressure was able to prevent gas channel flooding and grant the membrane electrode better scalability or modulation (SI Section S5). Furthermore, the membrane electrode was very thin (<250 Åm, Figure 1) and flexible (180° bend, Figure S5) and could be easily compiled into reactors, either in the form of flat sheet or spiral-wound. Additionally, the material cost of the membrane electrode (<20\$/m², SI Section S6) was only a small fraction of the commercial nickel foam (160\$/m²), and the fabrication process was easy and repeatable (SI Section S1). With many benefits discovered in this proof-of-concept study, more work can be done in optimizing the membrane electrode and improving system performance. Long-term studies using actual high ammonium substrates such as centrate, manure, or urine need to be investigated, and scaling up and system integration need to be performed. The process can also be optimized by modeling ammonia recovery and catholyte pH, all of which are key factors affecting ammonia and energy recovery.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b01349.

S1. Preparation Route of the Membrane Electrode; S2. Reactors and Configurations; S3. Surface Roughness; S4. Surface Hydrophobicity/hydrophilicity; S5. Water Entry Pressure and Flexibility; S6. Cost Analysis of the Membrane Electrode; S7. Membrane Electrode and Nickel Foam Before and After Electrolysis; S8. XPS Spectra of the Membrane Electrode Before and After Electrolysis; S9. LSV Scan of the Membrane Electrode Before and After Electrolysis; S10. Effect of Active Ammonia Harvest on Cathodic Potential; S11. Mass Balance of $\text{PO}_4\text{-P}$; S12. Ammonia Mass Balance Calculations; S13. Energy Production and Calculations. (PDF)

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