

Electrochemical Carbon Dioxide Capture and Release with a Redox-Active Amine

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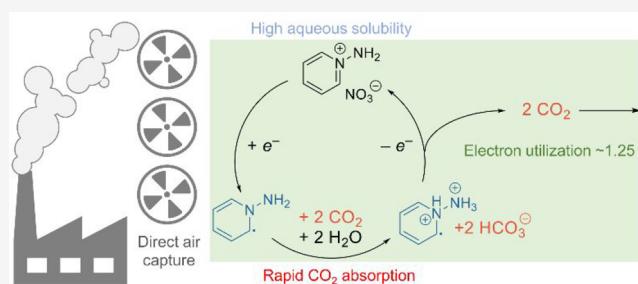
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ABSTRACT: Anthropogenic carbon dioxide (CO_2) emission from the combustion of fossil fuels is a major contributor to global climate change and ocean acidification. The implementation of carbon capture and storage technologies has been proposed to mitigate the buildup of this greenhouse gas in the atmosphere. Among these technologies, direct air capture is regarded as a plausible CO_2 removal tool whereby net negative emissions can be achieved. However, the separation of CO_2 from air is particularly challenging due to the ultradilute concentration of CO_2 in the presence of high concentrations of dioxygen and water. Here, we report a robust electrochemical redox-active amine system demonstrating a high electron utilization (i.e., mole of CO_2 per mole of electrons) of up to 1.25 with the capture of two CO_2 molecules per amine in an aqueous solution with a work of 101 kJ_e per moles of CO_2 . The capture of CO_2 directly from ambient air as the feed gas presented an electron utilization of 0.78.



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INTRODUCTION

It is essential that the accumulation of CO_2 in the atmosphere be constrained to slow global warming, as increasing ambient levels of this gas are recognized to be the primary factor behind undesirable climate pattern changes.^{1–3} Carbon capture and storage (CCS) technologies have received considerable attention from the scientific community for the effective minimization of CO_2 emissions to the environment, but more recently, direct air capture (DAC) has been given serious consideration as a “negative carbon emission” technology for the reduction of the atmospheric concentration of CO_2 .⁴ While conventional CO_2 capture technologies generally target CO_2 concentrations in the range 5–20% typical of emissions from stationary sources such as power plants and large industrial processes,⁵ CO_2 emissions from dispersed and mobile sources can be mitigated by capturing this greenhouse gas directly from the atmosphere, which currently contains about 412 ppm (~0.04%) of CO_2 ⁶ in the presence of high concentrations of dioxygen (21%) and water (0.2–4%). Effective technologies for addressing the global climate change problem via DAC must, therefore, be stable toward these species to maintain high CO_2 capture performance.

The most advanced technologies for CO_2 capture involve thermal cycles in which an aqueous alkanolamine absorbent, e.g., monoethanolamine (MEA), selectively captures CO_2 from impure gas streams, and this process is then followed by a thermal stripping operation in which pure CO_2 is released and the absorbent is regenerated (Figure 1a).⁷ However, despite their widespread use, current thermal-based capture technologies face challenges, including high energy requirements.⁸

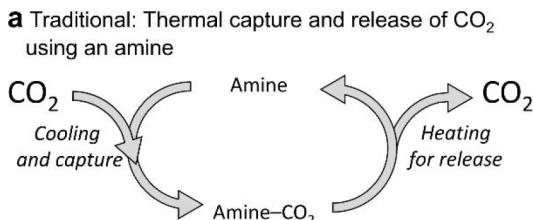
Several electrochemical approaches⁹ for the capture and release of CO_2 as possible alternatives to the benchmark thermal amine capture processes have been explored using organic redox-active compounds such as quinone derivatives,^{10–14} bipyridine,¹⁵ and disulfide¹⁶ and electrochemically mediated amine regeneration (EMAR) methods^{17,18} that employ a metal (e.g., copper) to displace the CO_2 from the amine. The major benefits of electrochemical methods over conventional thermal processes are the potentially lower energy consumption and the plug-and-play nature of their operation. However, disadvantages such as requiring pricey ionic liquid or volatile organic solvents, significant reactivities to dioxygen or water, and repetitive polarity switches (in the case of EMAR system) have prevented broader applications of electrochemical approaches to CO_2 mitigation. Furthermore, a limited number of studies of electrochemical capture and release of CO_2 from ultradilute CO_2 streams are available to date.^{10,13,16}

Therefore, there is a broad and emerging need for the development of efficient reversible electrochemical redox cycles that enable the capture of CO_2 from ultradilute gas streams, ideally, through direct air capture, and that operate under a wide range of dioxygen and humidity levels. Robust, stable, and

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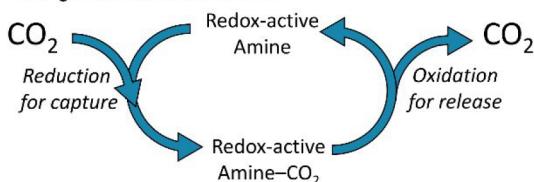
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- Water miscible
- Fast absorption of CO₂
- Work of 141–242 kJ/mole of CO₂

b This work: Electrochemical capture and release of CO₂ using a redox-active amine



- Aqueous media with high solubility
- Comparable CO₂ absorption rate to amines
- Work of 101 kJ_e/mole of CO₂
- Direct air capture

Figure 1. Reversible electrochemical process for capture and release of CO₂. (a) Traditional thermal-swing for CO₂ capture and release using an aqueous amine solution. The available electrical energy from thermal energies of 141–242 kJ is 35–61 kJ_e. (b) Reversible electrochemical capture and release of CO₂ using a redox-active amine.

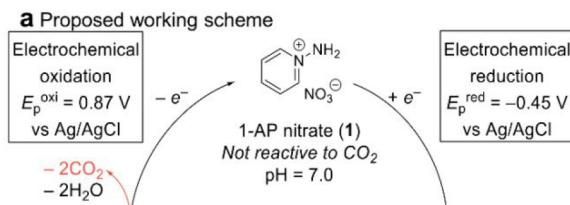
electrochemically reversible redox cycles involving an organic radical are of great importance not only to CCS applications⁹ but also to photochemistry,¹⁹ catalysis,²⁰ synthesis,²¹ materials science,²² redox flow batteries,²³ spintronics,²⁴ and biology.²⁵

Stable pyridinyl radicals have been discovered²⁶ but have not been explored as much as redox switches, in contrast to bipyridine, which has been one of the most popular redox switches in many areas of research.²⁷ In 1998, Monk and Hodgkinson reported that the 1-aminopyridinium (1-AP) cation could generate a stable, uncharged, radical species under acidic conditions by electrochemical reduction.²⁸ However, further electrochemical studies have not been carried out to any great extent. We hypothesized that electrochemical control of the nucleophilicity of the 1-AP cation and its 1-aminopyridinyl (1-APyl) radical in an aqueous solution should enable the reversible electrochemical capture and release of CO₂.

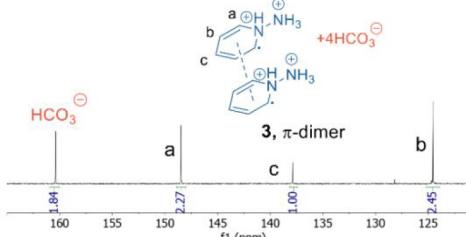
Here, we report a unique and robust electrochemical capture and release of CO₂ by employing 1-AP nitrate as a redox-active amine absorbent in an aqueous solution (Figure 1b). This reversible electrochemical redox-active amine cycle was demonstrated to show CO₂ capture and release with electron utilization (i.e., mole of CO₂ per mole of electrons) during CO₂ release of up to 1.25 over a wide range of CO₂ concentrations and, in particular, from ambient air. High aqueous solubilities (up to 13.3 M) of 1-AP nitrate should allow for a large cyclic capacity for CO₂.

RESULTS AND DISCUSSION

The prospective working scheme for electrochemical capture and release of CO₂ using 1-AP nitrate as a redox-active amine is depicted in Figure 2a. The reducible precursor, 1-AP nitrate (1), which is not reactive to CO₂ in the neutral pH aqueous solution



b Quantitative ¹³C-NMR of 3



c Cyclic voltammetry

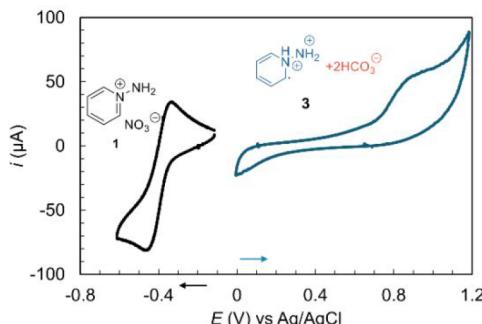


Figure 2. (a) Proposed working scheme for reversible electrochemical capture and release of CO₂ using the 1-AP nitrate (1) redox cycle. (b) Quantitative ¹³C NMR spectra of 1-APyl-bicarbonate 3 solution. (c) Cyclic voltammetry of 20 mM 1-AP nitrate (1, black curve) and 20 mM 1-APyl-bicarbonate 3 solutions (blue curve) in water with 0.1 M potassium nitrate as a supporting electrolyte at room temperature, bubbled with nitrogen, with a platinum working electrode, at a scan rate of 20 mV/s. Potentials were recorded versus Ag/AgCl as a reference electrode.

due to the positive charge in the pyridinium ring, can be reduced electrochemically by one-electron transfer to provide a room-temperature electron-rich 1-APyl radical 2. The 1-APyl radical 2, stabilized by the formation of a diamagnetic π-dimer,²⁶ forms a basic solution (pH = 13.5). As CO₂ is introduced, the 1-APyl radical 2 solution captures CO₂ to produce two bicarbonate molecules per 1-APyl radical 2, the mechanism of which is supported by the quantitative ¹³C NMR spectrum (Figure 2b). Then, the 1-APyl-bicarbonate 3 solution can be oxidized electrochemically to reproduce 1-AP nitrate (1) and release free CO₂ to close the redox-cycle. Isolation of the activated compounds 2 and 3 by extraction with organic solvents was not successful and led to rapid decomposition to provide 4,4'-bipyridine. These results indicate that water plays an important role in stabilizing the radical species, and aqueous conditions are

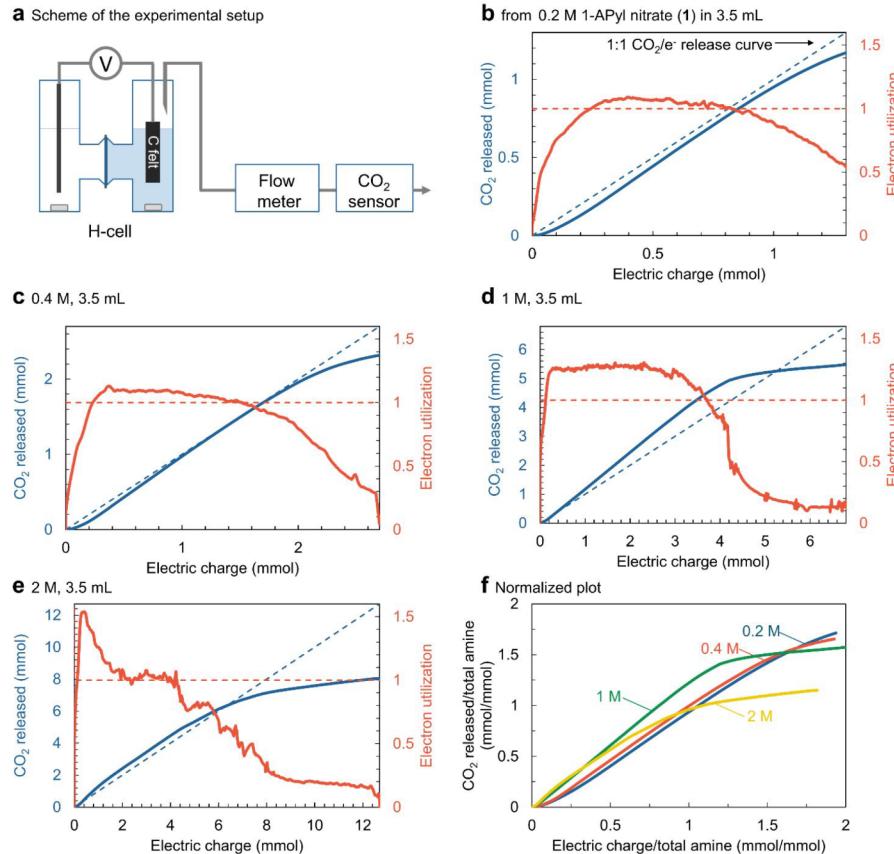


Figure 3. Electrochemical release of CO₂. (a) Schematic of the experimental setup for CO₂ release. The electrochemical H-cell containing 1-APyl-bicarbonate **3** solution to be oxidized by a constant current at room temperature was connected to the gas flow meter and an FT-IR CO₂ sensor. (b) Solution of 3.5 mL of 1-APyl-bicarbonate **3** prepared from 0.2 M 1-AP nitrate (**1**) solution was oxidized by a constant current of 50 mA. The amount of released CO₂ (blue curve) and electron utilization (red curve) are shown versus electric charge. (c) Solution of 3.5 mL of 0.4 M by 100 mA. (d) Solution of 3.5 mL of 1 M by 100 mA. (e) Solution of 3.5 mL of 2 M by 200 mA. (f) CO₂ release profiles of CO₂ (mmol) normalized by total amine amount (mmol) versus the electric charge (mmol) normalized by total amine amount (mmol) of 0.2, 0.4, 1, and 2 M solutions.

essential to maintain its capture properties. The stability of similar kinds of radical species in an aqueous system has been reported.^{28,29}

Cyclic voltammetry (CV) was conducted to probe the mechanism of this process, as depicted in Figure 2c. One electron reduction of 1-AP nitrate (**1**, black curve) in water at a concentration of 20 mM under a nitrogen atmosphere shows a quasi-reversible wave with a reductive peak potential at -0.45 V vs Ag/AgCl and an oxidative peak potential at -0.32 V vs Ag/AgCl, which indicates that the 1-APyl radical **2** is stable in water at room temperature. The electrochemical reversibility of the 1-AP cation strongly suggests that a radical pathway is operative in the capture and release of CO₂ by the 1-AP redox cycle. The one-electron oxidation of the 1-APyl-bicarbonate **3** solution (blue curve) represents an irreversible anodic peak at 0.87 V vs Ag/AgCl, which is consistent with our proposed mechanism of immediate CO₂ release when 1-APyl-bicarbonate **3** is oxidized. Notably, neither disproportionation³⁰ nor reduction of CO₂ by the 1-APyl radical³¹ was observed under the current conditions.

A bench-scale setup using an electrochemical H-cell was constructed and tested for the capture and release of CO₂ (Figure 3a). The system was equipped with an anion exchange membrane separating two 5 mL reaction chambers, carbon felt as a working electrode, and a stainless steel wire electrode for an arbitrary reaction in the counter chamber. The reaction mixture containing 0.2 M 1-AP nitrate (**1**, 1 mmol) in water (5 mL) in

the presence of 1 M potassium nitrate as a supporting electrolyte was reduced by a constant current of 50 mA for 62 min (equal to 1.9 mmol of electrons) to provide the full conversion of the starting material to its radical with 53% Faradaic efficiency. Then, pure CO₂ was bubbled into the solution for 10 min to complete the saturation of the electrochemically generated 1-APyl radical **2** solution. The output gas flow from the resulting 1-APyl-bicarbonate **3** solution (3.5 mL) upon anodic oxidation was quantified and qualified by a CO₂ flow meter and an FT-IR CO₂ sensor, respectively. The electron utilization (ϵ_{CO_2}) during CO₂ release on oxidation represents the ratio between the moles of CO₂ released and the moles of electrons transferred (eq 1):

$$\epsilon_{\text{CO}_2} = n_{\text{CO}_2} / n_{\text{electrons}} \quad (1)$$

Plots of the amount of released CO₂ by electrochemical oxidation versus electric charge in 1-APyl-bicarbonate **3** solutions prepared from 0.2, 0.4, 1, and 2 M 1-AP nitrate (**1**) solutions are displayed in Figure 3b–e. The experimental CO₂ output from the 0.2 M solution showed a steeper slope than the 1:1 CO₂/electron capture curve, corresponding to an electron utilization of up to 1.08 (Figure 3b). Although higher concentration solutions provided steeper slopes at the beginning of the process, the output CO₂ flow rate decreased rather rapidly as the reaction proceeded (Figure 3c–e). Satisfactorily, a stable electron utilization of 1.25 was observed with the 1 M 1-AP nitrate (**1**) solution under the current conditions (Figure 3d).

Figure 3f summarizes and compares the results for the different concentration solutions in terms of the moles of CO₂ released per electric charge transferred, both normalized by the moles of amine in solution. It is clear that at higher amine concentrations there is a more sluggish release of CO₂ during the later stages of the oxidation process, which may be related to pH swing effects. Combining the voltage difference (1.32 V) between the peak potentials from the CV measurements with the electrochemical electron utilization (up to 1.25) during CO₂ release, we estimated that the minimum system energy requirement with full utilization of the amine capacity would be 101 kJ_e per mole of CO₂. This energy demand can be reduced significantly to bring it in line with the 40–80 kJ_e/mol (~140–240 kJ/mol thermal) required for the benchmark MEA process³² by only partially regenerating the amines to give a working capacity that is less (e.g., ~50%) than the total capacity.¹⁰ The solutions of 1-AP cation with different counteranions such as perchlorate and tetrafluoroborate provided comparable CO₂ output results (see the Supporting Information). We chose the nitrate salt to further evaluate the system due to its better electron utilization during CO₂ release as well as better conductivity in an aqueous solution.³³

The CO₂ absorption dynamics under different conditions are displayed in Figure 4. The changes in flow rate and concentration of CO₂ were monitored by a CO₂ flow meter and an FT-IR CO₂ sensor, respectively. The 1 mL 1-APyl radical **2** solution prepared from 0.2 M 1-AP nitrate (**1**) solution was equilibrated with 4, 15, and 100% CO₂ inlet gas streams (balanced by nitrogen) and showed a constant capacity regardless of the concentration of CO₂ (Figure 4a). In smaller-scale CO₂ absorption experiments using 1 mL of the 0.04 M solution (Figure 4b), the same equilibrium CO₂ capacity was attained within a reasonable equilibration time for both the 1 and 4% CO₂ inlet streams (Figure 4b). In Figure 4c, the CO₂ absorption curves for the 1, 4, 15, and 100% CO₂ inlet gas streams superimpose to show a constant capacity of 1.94 mol of CO₂ per mole of amine, with similar equilibration dynamics in terms of the volume of CO₂ introduced to the cell (mL) normalized by the total amine amount (mmol), which indicates a consistent behavior for CO₂ capture regardless of the feed CO₂ concentration over the range of 1–100% (Figure 4c). Notably, the 1-APyl radical **2** solution showed a CO₂ absorption rate comparable to that of ethylenediamine (EDA) and monoethanolamine (MEA), commonly used amines in thermal processes (Figure 4d). The capacity of the electrochemical CO₂ release process is 12.4 mmol/g 1-AP nitrate. For comparison, the aqueous amine industrial capture process has an uptake efficiency of ca. 8 mmol/g.³⁴

The reversible capture and release of CO₂ was tested over five cycles to evaluate the robustness of the 1-AP nitrate redox cycle (Figure 5). The cyclic stability was evaluated with a 0.8 mmol amine solution and restricted to operate at 80% of the full capacity of the cell in order to minimize undesired side reactions. The gas output and CO₂ fraction were monitored to show reproducible and stable capture and release of CO₂ during five cycles under the applied current conditions. The gas release rate was steady at 0.75 mL/min, consistent with the release of one mole of CO₂ per mole electrons transferred under steady current flow in each cycle.

We next sought to expand the use of the 1-AP nitrate redox cycle to the direct capture of CO₂ from ambient air (Figure 6). The 1-APyl radical **2** solution (3.5 mL) was prepared by first reducing a 0.2 M 1-AP nitrate (**1**) solution and then bubbling

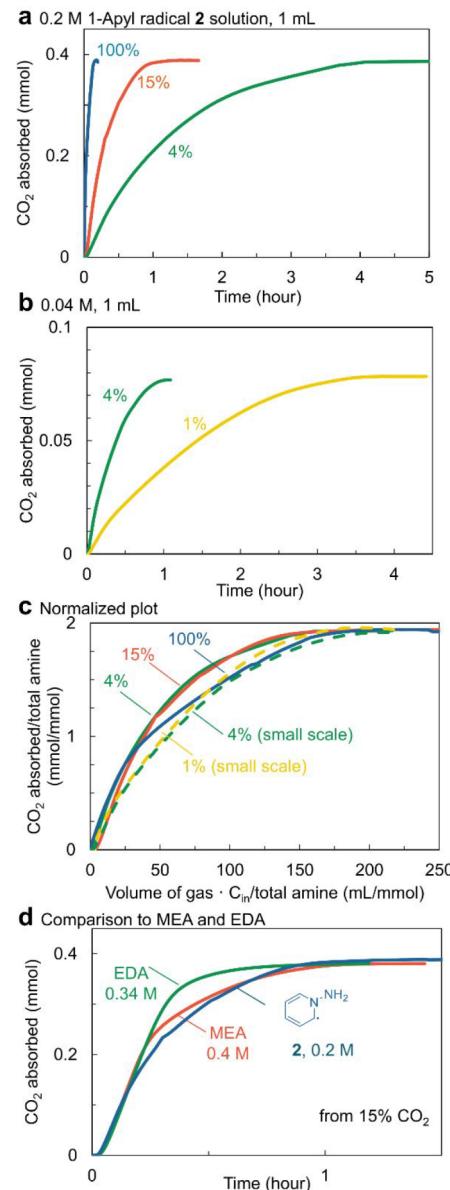


Figure 4. CO₂ absorption dynamics in 1-APyl radical **2** solutions. (a) CO₂ absorption profiles at CO₂ inlet gas stream concentrations of 4, 15, and 100%. A 0.2 M 1-APyl radical **2** solution in 1 mL of water was contacted with the gas at a flow rate of 3.3 mL/min at room temperature. (b) CO₂ absorption profiles for 1 and 4% CO₂ inlet gas streams at a smaller scale. One milliliter of 0.04 M 1-APyl radical **2** solution was contacted with the gas at a flow rate of 3.3 mL/min at room temperature. (c) Normalized CO₂ absorption profiles. (d) Comparison of the CO₂ absorption profile for 1-APyl radical **2** (0.2 M in 1 mL of water) to those for ethylenediamine (EDA, 0.34 M in 1 mL of water, 19% of dicarbamate formation was observed by ¹H NMR) and monoethanolamine (MEA, 0.4 M in 1 mL of water). A flow of 15% CO₂ concentration balanced by nitrogen was used.

the solution with nonpretreated air for 18 h at a flow rate of ca. 100 mL/min (Figure 6a). Electrochemical oxidation of the air-bubbled solution was carried out to evaluate the direct air capture efficiency. The system presented an electron utilization during CO₂ release of up to 0.78 with 36% cell capacity usage with the 0.2 M solution. Bubbling with air for an extended period of 4 days did not improve the results (see the Supporting Information), indicating that the solutions were saturated. Initial

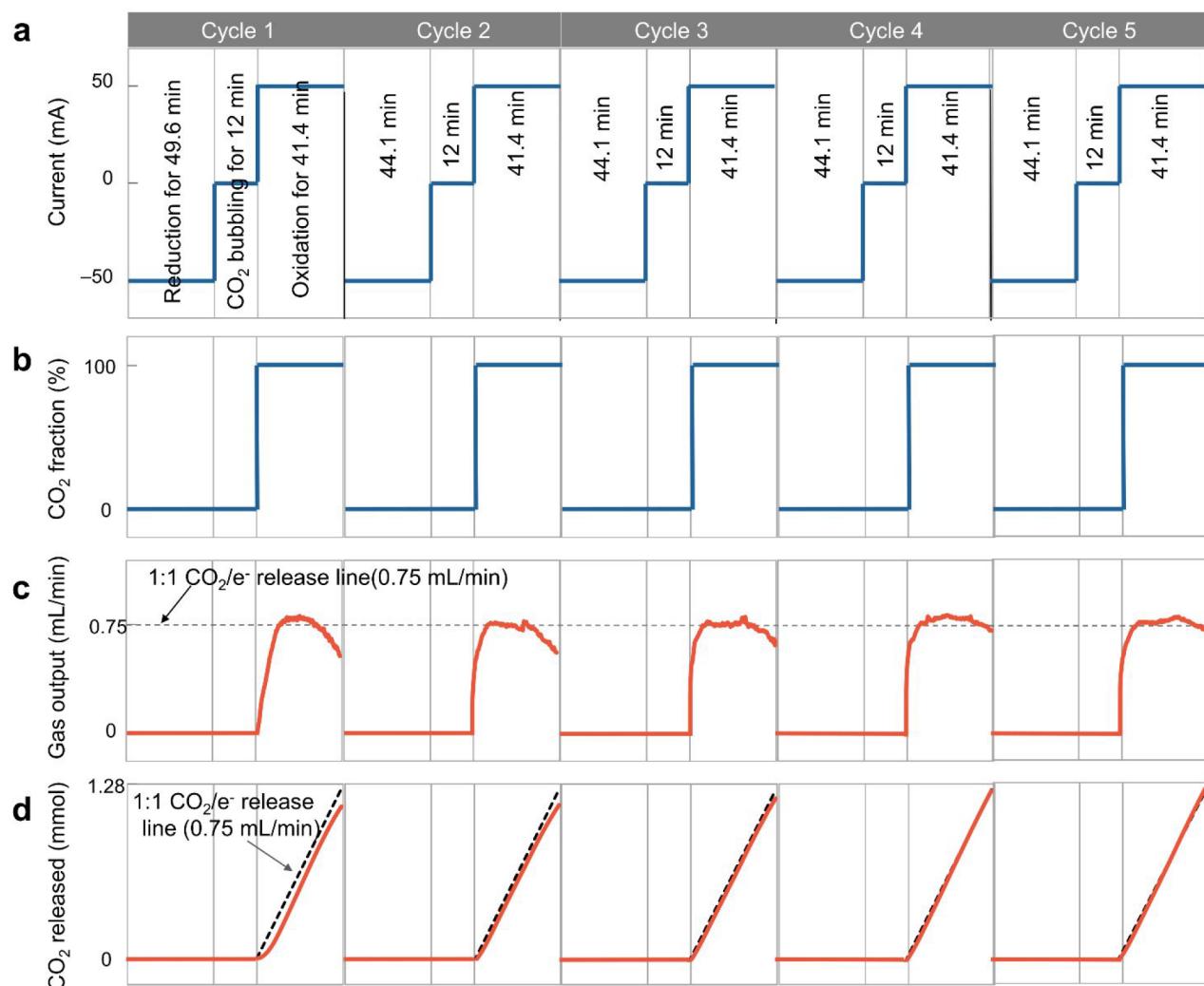


Figure 5. Cyclic stability of the electrochemical CO₂ capture and release by 1-AP nitrate (**1**) redox system for 5 cycles. (a) Constant current of −50 mA was applied for 49.6 min (1.54 mmol of electrons) for cycle 1 and 41.4 min (1.29 mmol of electrons) for cycles 2–5 to reduce the amine (0.2 M, 0.8 mmol in 4 mL of water), followed by bubbling of the solution with pure CO₂ for 12 min and the application of a constant current of 50 mA for the oxidation step for 44.1 min (1.37 mmol of electrons) for cycles 1–5. (b) CO₂ fraction, (c) gas output, and (d) amount of released CO₂.

CO₂ absorption rates from the ambient air were measured in 0.1, 0.2, and 0.4 M solutions of 1-APyl radical **2** (Figure 6b). The CO₂ absorption rate from the air was significantly lower in the 0.1 M solution than in the others, consistent with the incomplete saturation of the 1-APyl solutions despite a longer air contact time. Considering the electron utilization during CO₂ release and the potential difference obtained from the CV, direct air capture under the current conditions requires as little as 162 kJ_e per mole of CO₂, which is within range of 400 kJ/mol thermal (equivalent to 100 kJ_e/mol with a Carnot efficiency of 0.25), which is considered a target to be achieved by DAC technologies.³⁵

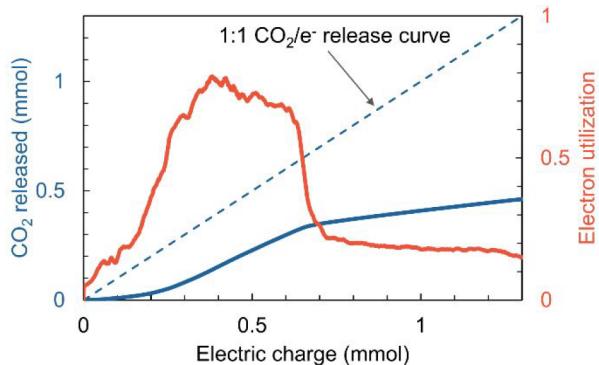
To test the stability of the 1-APyl radical in air, a set of experiments was carried out (Figure 6c). Exposure to pure dioxygen (10 mL/min) of the 1-APyl radical **2** solution (0.2 M, 5 mL) for 1 and 30 days (red curves) followed by saturation with pure CO₂ provided 6.6 and 46% decreases, respectively, of the capacity of the system compared to the output for the freshly CO₂-saturated solution (blue curve). The first control experiments conducted with the 1-APyl radical **2** solution (0.2 M, 5 mL) sealed under nitrogen and stored on the bench for 1 and 30 days (green curves), followed by bubbling with pure CO₂,

resulted in 7.2 and 22% decreases, respectively, in the capacity of the system. These results suggest that the 1-APyl radical **2** might decompose slowly over time and the exposure to dioxygen could accelerate decomposition under the applied current conditions. A second control experiment conducted with the 1-APyl radical **2** solution (0.2 M, 5 mL) bubbled with nitrogen (10 mL/min) for 30 days showed a 54% decrease in the capacity, which indicates that gas bubbling could lead to decomposition of the activated compound to 4,4'-bipyridine that was observed as a byproduct. Although further studies for the stability under the various conditions are warranted, operation in the presence of oxygen remains feasible.

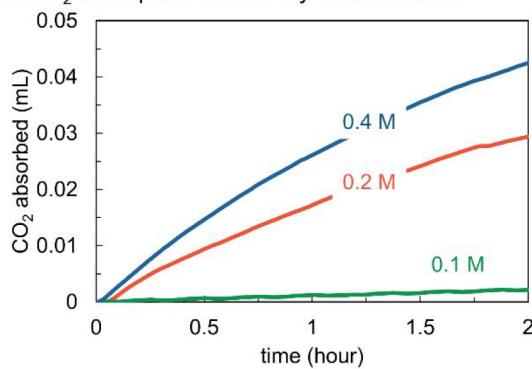
CONCLUSION

In conclusion, we demonstrated that the 1-AP nitrate redox cycle in an aqueous solution can be exploited for reversible electrochemical capture and release of CO₂ with an electron utilization during CO₂ release of up to 1.25. The 1-APyl radical solution exhibits a constant capacity for capture of CO₂ from inlet streams of concentration from 1 to 100%. The robustness of this system, demonstrated for 5 cycles with no significant loss in performance, coupled with the stability of the 1-APyl radical

a 0.2 M 1-APyl radical **2** bubbled by air for 18 h



b CO₂ absorption from air by concentration



c Stability test

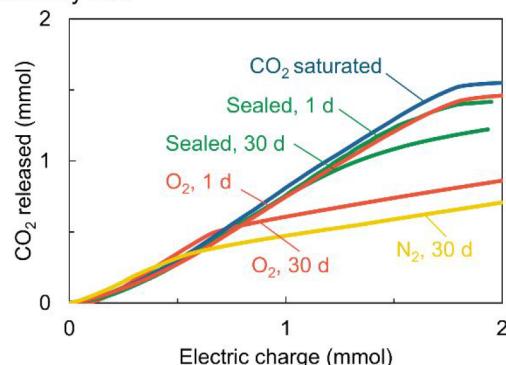


Figure 6. Direct air capture and stability test of 1-APyl radical **2** solution. (a) CO₂ released by electrochemical oxidation on application of a constant current of 50 mA to the 1-APyl radical **2** solution (0.2 M, 3.5 mL) that was bubbled with air for 18 h at a flow rate of ca. 100 mL/min. (b) CO₂ absorption profiles from air. 1-APyl radical **2** aqueous solutions (0.1, 0.2, and 0.4 M; 1 mL) were bubbled with air at a flow rate of 3.3 mL/min at room temperature. (c) Oxygen sensitivity test. The 1-APyl radical **2** solutions (0.2 M, 5 mL) were bubbled with dioxygen for 1 and 30 days (red curves) at a flow rate of 10 mL/min followed by contact with pure CO₂ for an additional 12 min. The 1-APyl radical **2** solutions were sealed under nitrogen for 1 and 30 days (green curves) followed by contact with pure CO₂ for 12 min for the control experiments. The solutions were electrochemically oxidized at a constant current of 50 mA, and the released CO₂ was monitored.

to dioxygen, augurs well for its application in direct air capture operations. While we anticipate that the 1-AP cation redox cycle will introduce new opportunities for CO₂ separation from air, this cycle can also be used effectively in large-scale separations applications to avoid the need for thermal regeneration of the amine solutions. Moreover, in contrast to other indirect

electrochemically mediated sorbent regeneration systems in which protons or metal ions released from an activated anode modulate the CO₂ binding to the sorbent,^{10,18,36,37} and which by their very nature necessitate cyclic operations, this direct redox couple enables continuous, stable operational opportunities. Process optimization and chemical modification of the 1-AP through the attachment of appropriate moieties that control the electron distribution, and hence the redox potentials, should lead to decreased energy expenditures and to a viable process for CO₂ capture from a wide range of sources using electricity from renewable resources.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.1c10656>.

Discussions of materials and instrumentation used, synthesis methods, procedures for electrochemical capture and release of CO₂, setup of redox-active amine system for CO₂ capture and release, energy calculation, evaluation of 1-aminopyridinium tetrafluoroborate and perchlorate, in situ pH measurements, and results from direct air capture for 4 days, figures of schematic illustrations and pictures of setup for CO₂ release experiment, and NMR spectra, and table of selected electrochemical carbon capture methods summary (PDF)

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Notes

The authors declare the following competing financial interest(s): H.S. and T.A.H. are inventors on a patent application related to this work filed by Massachusetts Institute of Technology (No.: 63/214,845; filed on June 25, 2021). All other authors declare that they have no competing interests.

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