



Electrified release of pure CO₂ from postcapture liquid: A two-stage system lowers the total energy cost

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Electrified carbon capture and release holds promise in carbon management; but it is constrained by high energy demand. Here, we studied two candidate systems for electrochemical CO₂ release from a direct air capture (DAC) postcapture liquid: The first, a hydrogen loop cell, is electricity-efficient, but its evolved CO₂ is mixed with H₂, introducing a 3 to 4 GJ/tonCO₂ additional energy separation cost. The second system, a solid-state metal oxide redox couple (proton sponge), avoids the gas separation challenge but is stable only in the bicarbonate and not the highly alkaline regime. These considerations led us to examine a two-stage system: An efficient hydrogen loop would first downshift the pH from 13.5 to 9; and a second metal oxide would be used to release CO₂ from bicarbonate. We report an electrified process that provides the release of a pure CO₂ stream from a post-DAC liquid with a measured total energy of ~4.5 GJ/tonCO₂: 2.4 GJ from the H₂ looping stage and 2.1 GJ from the MnO₂-based stage—substantially lower than the >=10 GJ/tonCO₂ required by pH-swing methods such as bipolar membrane electrodialysis. We conclude with a generalized analysis of how staged pH downshifting reduces the overall Nernst voltage penalty and facilitates energy-efficient CO₂ release.

electrified CO₂ capture | pH swing | direct air capture | CO₂ capture and release

Direct air capture (DAC) seeks to reduce legacy CO₂ emission and contribute thereby to tackling a key contributor to global warming (1, 2). DAC is enabled by solid sorbents such as amine-functionalized resin and porous materials; and by using liquid sorbents such as caustic alkali (2–4). The liquid sorbent approach is seeing significant work at scale: (5, 6) Occidental's Permian Basin *Stratos* facility will have an annual capture of 500,000 t of CO₂ per year (7).

In a typical caustic alkali–based approach, CO₂ from air is contacted with (for example) a high-molarity KOH solution, captured into the carbonate form, and then separated from the aqueous phase as calcium carbonate (4). However, in order to release high-purity CO₂ and regenerate the capture solution, it is necessary to implement a high-temperature, energy-intensive thermal process, and this entails a high energy cost (*SI Appendix, Fig. S1 and Supplementary Note 1*) (4, 8). Here, the minimum thermodynamic energy is 4 GJ/tonCO₂, and the actual energy consumption 6 to 8 GJ/tonCO₂ (8, 9). Because it is a high-temperature process (>900 °C), supplying the needed energy typically requires a combustible fuel, such as the use of natural gas, and its associated CO₂ emissions and energy demand diminish the *net* carbon benefit (10, 11).

Electrochemical pH swing instead provides CO₂ release by acidifying the postcapture liquid while simultaneously regenerating hydroxide in a separate stream (12–16). The pH gradient sets a lower bound on the full cell voltage, and to transition from strongly basic postcapture liquid (pH ~13.5, selected to ensure good capture kinetics) to an acidified solution capable of good release kinetics (pH 4) requires at least 3 GJ/tonCO₂. In experimentally implemented systems such as the bipolar membrane electrodialysis (BPMED) system (Fig. 1A), when a pH ~13.5 liquid is the feed, an actual ~22 GJ/tonCO₂ is often seen (16).

This higher-than-thermodynamically mandated energy consumption stems from extra energy required for water dissociation; ohmic losses in flow systems that employ multiple channels; and the low charge efficiency of CO₂ release (16–18). Recent studies have identified a roadmap to ~8 GJ/tonCO₂ for BPMED but have noted that achieving further reductions may be challenging (19).

Results and Discussion

Our experimental work began by studying electrochemical H₂ looping system to release CO₂ from the postcapture solution (20–22).

Significance

Electrochemical methods that directly release CO₂ from direct-air-capture liquids offer a promising route toward low-carbon industrial cycles but are often hindered by high energy demand and complex gas separation. We report a two-stage electrified release process that first employs a hydrogen-loop cell to partially acidify the alkaline post capture liquid, followed by a solid-state metal-oxide stage that releases pure CO₂. This combined strategy lowers the total energy consumption to ~4.5 GJ/tCO₂, less than half that of conventional electrochemical pH-swing methods. The approach establishes a general framework that couples hydrogen recycling with redox-mediated proton transfer for energy-efficient, continuous, and separable CO₂ recovery from direct-air-capture media.

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The authors declare no competing interest.

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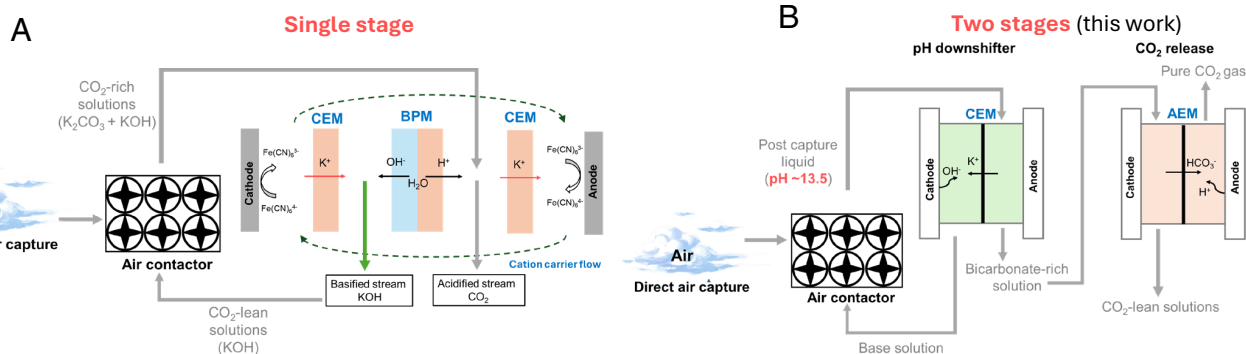


Fig. 1. (A) Schematic of a single cell of BPMED system for CO₂ release. (B) Schematic of the two-step electrified CO₂ release process developed in this work. In the first stage, the H₂ looping system converts the postcapture solution from an initial pH of 13.5 to a bicarbonate-rich solution with a pH of ~9. This bicarbonate-rich liquid is then fed into the CO₂ release cell, where pure CO₂ gas is released in a crossover-based manner.

The H₂ looping system uses a cathodic hydrogen evolution reaction (HER) coupled with an anodic hydrogen oxidation reaction (HOR) (Fig. 2A). In this setup, H₂ is oxidized at the anode to acidify a solution—which is conveyed in a flow cell—leading to the release of CO₂. The electric field drives K⁺ to migrate across the CEM to the cathode, where it is reunited with OH⁻ produced via the HER. The H₂ generated at the cathode is recirculated to the anode to enable continuous operation. In this way, the H₂ looping system releases CO₂ at the anode and regenerates KOH at the cathode.

The cell voltage of the pH-downshifter depends on the anolyte composition. With a fixed catholyte of 1 M KOH, decreasing the anolyte pH from 13.5 (the typical outlet of air contactor, 0.32 M KOH + 1.34 M K₂CO₃) to 12 (1.5 M K₂CO₃) and further to 8.5 (3 M KHCO₃) results in a progressive increase in cell voltage from 0.35 V to 0.7 V at 25 mA cm⁻². An analysis of the components making up the cell voltage (Fig. 2B) shows that the Nernst loss from the pH gradient (ΔpH) is the largest contributor. The ohmic losses (quantified by electrochemical impedance spectroscopy (EIS); SI Appendix, Fig. S2 and Supplementary Note 2) and the

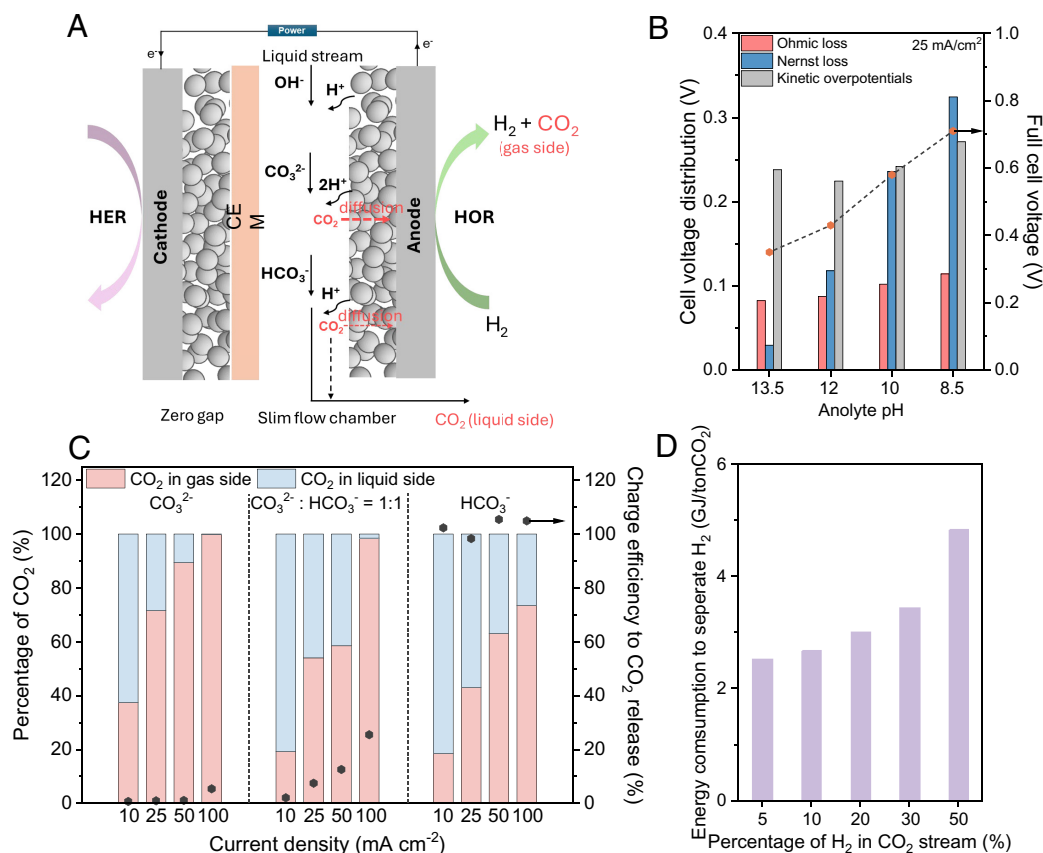


Fig. 2. Design and optimization of the H₂ looping system for CO₂ release. (A) Schematic illustration of the H₂ looping system in a slim flow cell configuration. (B) Distribution of cell voltage components (left Y-axis) and full cell voltage (right Y-axis) as a function of anolyte pH at 25 mA/cm². The anolytes with pH values of 13.5, 12, 10, and 8.5 correspond to 0.32 M KOH + 1.34 M K₂CO₃, 1.5 M K₂CO₃, 0.75 M K₂CO₃ + 1.5 M KHCO₃, and 3 M KHCO₃, respectively. (C) Percentage of CO₂ in the output stream (left Y-axis) and charge efficiency for CO₂ release (right Y-axis) at varying current densities and anolyte compositions. CO₂ in both the gas-side stream (transporting through the gas diffusion layer and mixed with H₂) and the liquid-side compartment (collected in the headspace of the gas-tight liquid chamber) is quantified via GC. (D) Energy consumption (GJ/tonCO₂) required for H₂ separation from the H₂/CO₂ mixed gas stream.

kinetic overpotentials (estimated as the cell voltage minus the Nernstian and ohmic contributions) are comparatively minor (23).

We quantified the fraction of HOR-derived charge used for CO₂ release (Fig. 2C, right y-axis). The charge efficiency for CO₂ release (CE_{CO₂}) was calculated from the amount of evolved CO₂ measured using gas chromatography (GC), together with the stoichiometric proton requirement for CO₂ liberation: 2 H⁺ per CO₂ for CO₃²⁻, 1.5 H⁺ per CO₂ for a 1:1 CO₃²⁻/HCO₃⁻ mixture, and 1 H⁺ per CO₂ for HCO₃⁻. When pH > 10 (CO₃²⁻/HCO₃⁻ > 1), CE_{CO₂} remains <25% across the 10 to 100 mA cm⁻² range, indicating that most HOR-derived charge is consumed by pH downshift rather than CO₂ release.

We then analyzed the flow of H₂ in the H₂ looping system, focusing on the extent to which it remains mixed in with the (desirably pure) CO₂ stream. CO₂ evolution may occur near the HOR catalyst surface, in which case CO₂ will be collected at the outlet of the gas chamber; or CO₂ evolution can occur in the bulk anolyte, in which case CO₂ is collected in the headspace of the anolyte reservoir, and from here a small fraction redissolves into the high-pH anolyte (Fig. 2A and C). At higher current densities, CO₂ will evolve near the catalyst, diffuse through the gas diffusion layer and be carried out by the leftover H₂ stream (Fig. 2C), resulting in a mixed CO₂ and H₂ stream. This then requires an additional separation step to obtain a CO₂ stream ready for injection. A simulation of pressure-swing-adsorption gas separation (Fig. 2D and SI Appendix, Supplementary Note 3) shows that when 5% H₂ is mixed with CO₂, the energy required for separation is ~2.5 GJ/tonCO₂. This energy demand increases to ~4.8 GJ/tonCO₂ if the H₂ content rises to 50%. With an average CE_{CO₂} of 20% and a cell voltage of 0.6 V, the total energy consumption for CO₂ release, including separation, reaches ~10 GJ/tonCO₂.

We noted that solid-state CO₂ release approaches, based on a metal oxide redox couple (proton sponge), avoid the gas separation challenge. Specifically, nonnoble metal oxides such as MnO_x exhibit high redox reversibility and good stability under mildly alkaline to near neutral pH conditions. The electric field and ion-selective membrane drive bicarbonate transport to the electrode surface, where local acidification enables pure CO₂ release.

However, since these show limited stability under strongly alkaline conditions (viz. Pourbaix diagram) (24), we considered these as candidates for release CO₂ from a bicarbonate electrolyte.

Coprecipitated manganese (MnO_x/OH) (SI Appendix, Fig. S3 and Supplementary Note 4) was used as both cathode and anode in a membrane electrode assembly (MEA) configuration. An anion exchange membrane (AEM) facilitated anion transport between the

electrodes. KHCO₃ electrolyte was circulated on one side of the cell (referred to as the liquid side), while the opposite side was continuously flushed with a carrier gas stream (referred to as the gas side).

This system leverages a proton-coupled electron-transfer (PCET) redox reaction involving H⁺ insertion and deinsertion to/from MnO₂ (Fig. 3A) (25–27). During the CO₂ release process, which occurs under oxidative conditions, the reaction MnOOH → MnO₂ + H⁺ + e⁻ occurs, i.e., H⁺ deinsertion occurs within the anode, and HCO₃⁻ ions cross-over from the cathode to the anode, where these bicarbonate anions combine with H⁺ to form gaseous CO₂, which evolves from the system. To recharge this electrode for its later reuse in an additional release stage, we switch the potential to reductive conditions, converting MnO₂ back to MnOOH via proton insertion, MnO₂ + H⁺ + e⁻ → MnOOH.

This CO₂ release system operates without reliance on H₂ gas as a reactant, and the liquid–gas MEA configuration enables the release of pure, dry CO₂ from the anode side. The zero-gap design reduces ohmic losses.

We optimized CO₂ release conditions from KHCO₃ (SI Appendix, Fig. S4 and Supplementary Note 5), and we also carried out control experiments using inert electrodes and Na₂SO₄ electrolyte, finding that CO₂ that we collected originated from bicarbonate and did require the redox of MnO₂ couples (SI Appendix, Figs. S5 and S6 and Supplementary Notes 6 and 7).

When we used a proton-insertion potential of -0.2 V, we found that a deinsertion potential of +0.4 V delivered a CE_{CO₂} of ~40% and minimized total energy consumption to 3.0 GJ/tonCO₂. Tuning of both insertion and deinsertion potentials (SI Appendix, Figs. S7–S10 and Supplementary Note 8) to -0.4 V and +0.4 V, and optimizing the duration of each redox step (SI Appendix, Figs. S11 and S12 and Supplementary Note 9), enabled stable CO₂ release over 125 h at 30 mA cm⁻², with an energy consumption of 1.9 to 2.5 GJ/tonCO₂ and an average CE_{CO₂} of ~80% (Fig. 3B and C and SI Appendix, Fig. S15 and Table S4). The “missing” is attributed to background-ion crossover (e.g., OH⁻, CO₃²⁻, and K⁺), backdiffusion of CO₂ into the liquid chamber, and kinetic limitations in MnO₂ (i.e., restricted electron transport into the MnO₂ interior that slows the phase transition) (25).

This electrified CO₂ release energy cost is similar to, though slightly less than, that in a recently reported HER-HOR system that leverages a porous solid electrolyte; (21) and is lower than that in an oxygen evolution and oxygen reduction reaction (OER–ORR)-paired system (SI Appendix, Fig. S16 and Supplementary Note 11) (28).

Summarizing: Each subsystem, when employed on its own, fails to achieve high energy efficiency: The H₂ looping approach

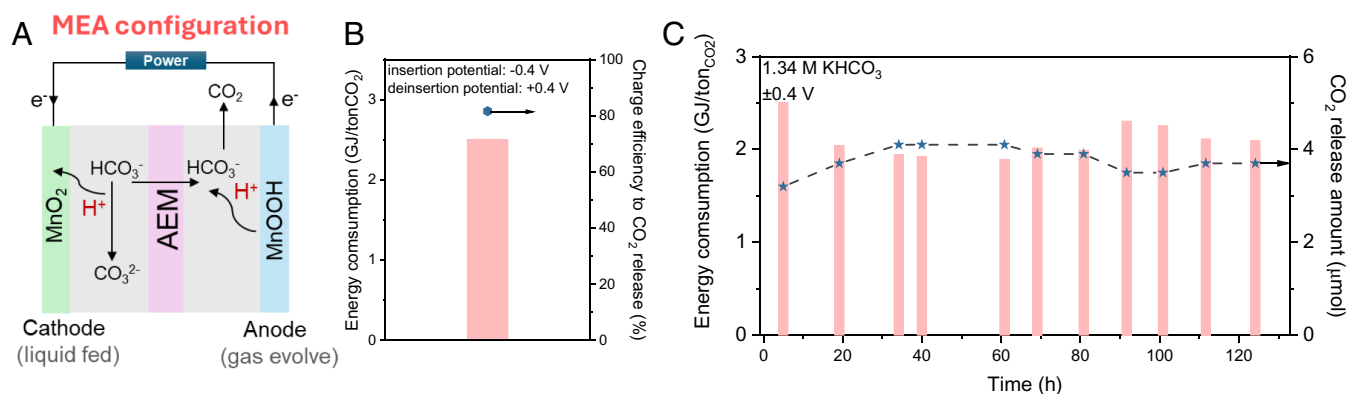


Fig. 3. Design and optimization of the MnO₂-based CO₂ release system. (A) A MnO₂-based system under CO₂ release conditions, with CO₂ released at the anode. (B) Energy consumption (left Y-axis) and charge efficiency to CO₂ release (right Y-axis) at proton insertion and deinsertion potentials of ±0.4 V and current density of 30 mA/cm² at the optimized conditions. (C) Energy consumption (left Y-axis) and CO₂ release amount (right Y-axis) using a pure KHCO₃ solution fed to the cathode under ±0.4 V and ±30 mA/cm² conditions over 125 h continuous operations.

is ineffective for direct CO₂ release under alkaline conditions and suffers from separation challenges; and the MnO₂ approach is unstable in strongly alkaline solutions but is effective in CO₂ release in bicarbonate-rich media. It appeared to us though that, when formed into a judiciously chosen cascade, the approaches might be sequenced to achieve compelling energetics.

We therefore implemented a two-stage system. Now optimizing the H₂ looping system for downshift to the pH of bicarbonate, we ran the system at 25 mA cm⁻², and continuously monitored anolyte pH, charge efficiency in pH downshift (CE_{pH}), and cell voltage, all this over a continuous 16 h of operation (Fig. 4A–C). The cell voltage progressively increased from 0.4 V to 0.75 V, and once we reached final pH ~9, the system had achieved complete neutralization of OH⁻ and had converted 95% of carbonate to bicarbonate, with an average CE_{pH} of 80% and an electrical energy input of 2.4 GJ/tonCO₂ (SI Appendix, Supplementary Note 12). KOH regeneration on the catholyte closely followed the charge transfer stoichiometry (ICP measurements of K⁺ concentration and pH probe analysis of OH⁻ concentration, SI Appendix, Fig. S17 and Supplementary Note 12). The progressive increase in cell voltage is attributed to i) an increasing ΔpH between the anolyte and catholyte, which raises the Nernst loss, and ii) declining ionic conductivity (OH⁻ > CO₃²⁻ > HCO₃⁻), which increases the ohmic loss during operation.

We used a second stage based on MnO₂ for CO₂ release (Fig. 4A), measuring a total energy consumption—the sum of that in each of the two stages—equal to 2.4 GJ/tonCO₂ from the pH

downshift added to 2.1 GJ/tonCO₂ from the CO₂-release electrolyzer (Fig. 4D and SI Appendix, Supplementary Notes 12–14).

From a fundamental/best-case-thermodynamic perspective, each one-stage pH swing system (BPMED, MnO₂-based cell, and H₂-looping system) is governed by the pH gradient with the associated Nernst term ($V = 0.059 \times \Delta\text{pH}$). Experimentally, the single-step H₂-looping process requires ~10 GJ t⁻¹ CO₂, a figure that includes a H₂/CO₂ separation cost of 3 to 5 GJ t⁻¹ CO₂, which is higher than that of the two-stage process.

In the CO₂-release cell, carbon (as KHCO₃) is released and removed as CO₂, yielding a more alkaline and CO₂-lean solution. This solution is then recycled to the air contactor to capture additional CO₂ from air. In an example mass balance (SI Appendix, Fig. S19, Table S9, and Supplementary Note 15), we consider the case in which 0.67 mol of CO₂ is captured. This is converted to 0.67 mol of CO₃²⁻, which adds to the preexisting 0.67 mol of CO₃²⁻, for a total of 1.34 mol of CO₃²⁻. During the pH-downshift step, this 1.34 mol of CO₃²⁻ is converted to 1.34 mol of HCO₃⁻. In the CO₂-release step, we let 0.67 mol of CO₂ be released to the gas phase, and the remaining 0.67 mol of HCO₃⁻ is converted back to 0.67 mol of CO₃²⁻ via pH increase in the CO₂-release cell. This regenerated 0.67 mol of CO₃²⁻ then enters the cathode of the pH-downshifter, combines with KOH, and is ultimately recycled back to the CO₂-capture vessel.

To understand how to reduce the electricity requirements for electrified CO₂ release, we reviewed the origins of the Nernst potential shift, and how it determines the minimum energy

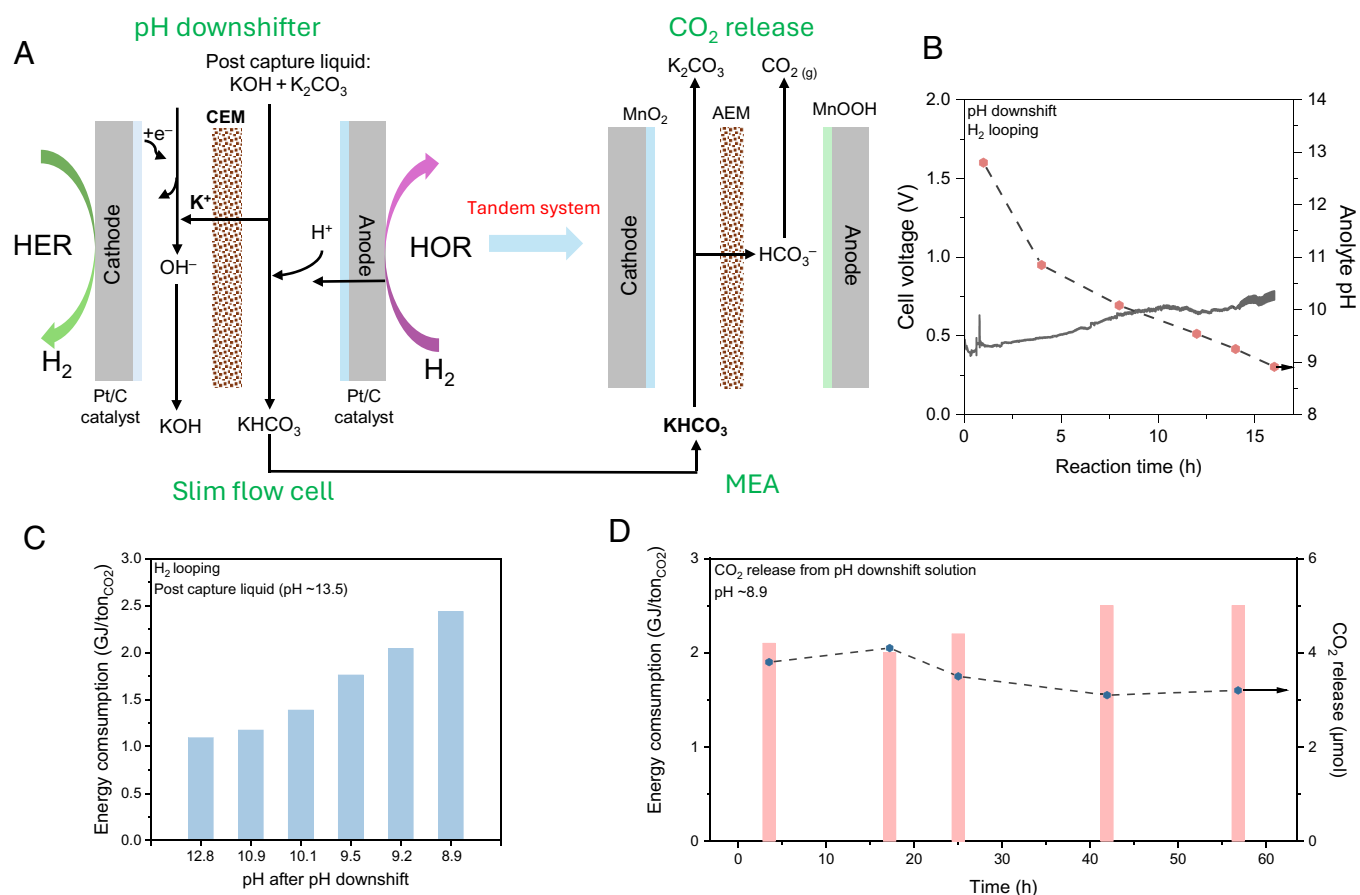


Fig. 4. H₂ looping system for pH downshift coupled with MnO₂-based system for CO₂ release. (A) An electrified tandem system for CO₂ release, comprising a H₂ looping system for pH downshifting and a MnO₂-based crossover system for CO₂ release. (B) Cell voltage (left Y-axis) and anolyte pH (right Y-axis) as a function of reaction time during 16 h of operation in the H₂ looping system at 25 mA/cm². The feed solution is a simulated postcapture liquid (0.32 M KOH + 1.34 M K₂CO₃). (C) Energy consumption for pH downshifting to various levels using the H₂ looping system. (D) Energy consumption and CO₂ release amount from the MnO₂-based system, using the feed solution (pH ~ 8.9) obtained from the first-stage pH downshift.

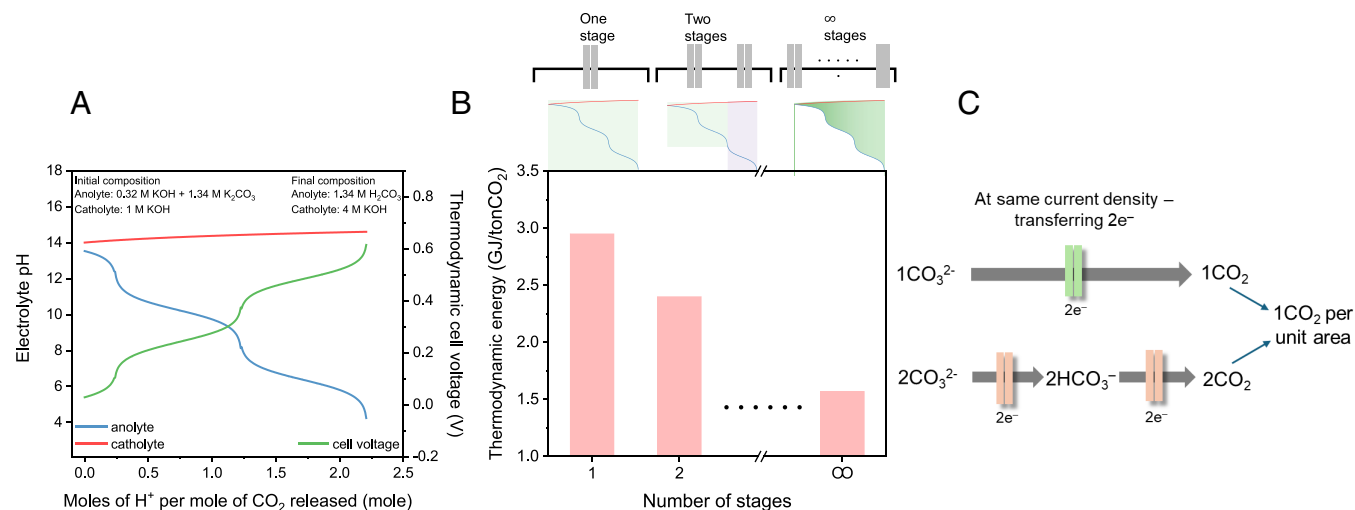


Fig. 5. Energetic analysis of CO_2 release technologies. (A) pH titration curve and corresponding thermodynamic cell voltage for converting $\text{CO}_3^{2-}/\text{OH}^-$ -rich postcapture liquid to H_2CO_3 via H^+ addition. The catholyte is postcapture liquid (pH ~ 13.5 , containing 0.32 M KOH + 1.34 M K_2CO_3); the anolyte is 1 M KOH. (B) We assume the one-stage case corresponds to CO_2 release under a constant $\Delta\text{pH} = 10.4$. The two-stage case uses the end-of-operation voltage for the first-stage pH downshift (i.e., the maximum ΔpH /Nernst loss in stage 1), followed by CO_2 release. The infinite-stage represents continuous pH downshift followed by CO_2 release, where ΔpH (Nernst loss) varies gradually as the bulk pH evolves. (C) Schematic illustration of the stoichiometric electron requirement, normalized per mole of CO_2 released and per unit electrode area, comparing single-stage and two-stage systems for CO_2 release from carbonate solutions.

demand for CO_2 release in a single-stage system, i.e., in a cell that implements the full pH shift in one device, this compared to a multistage system. This analysis provides guidelines for the design of pH-swing-based CO_2 release systems.

Our analysis is based on a postcapture liquid with a pH of ~ 13.5 , consisting of 0.32 M KOH and 1.34 M K_2CO_3 , as determined from mass balance considerations (*SI Appendix, Fig. S19, Table S9, and Supplementary Note 15*) (4). In a single-stage pH-swing system, using BPMED as a representative example, the pH ~ 13.5 solution serves as the anolyte for CO_2 release, while 1 M KOH is used as the catholyte to regenerate the alkaline sorbent (Fig. 5A, titration curve). In the anolyte, protons first neutralize the free OH^- , after which carbonate species are protonated to release CO_2 (15, 22).

Specifically, neutralizing 0.32 mols OH^- requires an equivalent amount of H^+ , and converting 1.34 mols CO_3^{2-} to CO_2 requires 2.68 mols of H^+ per mol of CO_2 . As a result, a total of $(0.32 + 1.34 \times 2)/1.34 = 2.2$ mols of protons—and, equivalently, 2.2 mols of electrons—are needed to release 1 mol of CO_2 from the postcapture solution. In the catholyte, OH^- is regenerated, further increasing the alkalinity of the 1 M KOH solution, although the resulting pH rise is modest. The thermodynamic voltage originates from the pH gradient, as described by the Nernst equation: $V = 0.059 \times \Delta\text{pH}$. With a catholyte pH of 14.6 and an anolyte pH of 4.2 at the CO_2 release conditions, the pH difference is 10.4, corresponding to a Nernst voltage of 0.61 V.

To represent pictorially the energy requirement, we visualize (Fig. 5A and B) the area of a rectangle with base width 2.2 electrons per mole of CO_2 and height 0.61. For a single-stage CO_2 release process, assuming a sustained ΔpH of 10.4 in a single pass condition, a full cell voltage of 0.61 V must be applied across the entire 2.2 e^- required per mole of CO_2 released, yielding a thermodynamic energy requirement of 3 GJ $\text{t}^{-1} \text{CO}_2$.

This pictorial analysis suggests that the overall energetics can be enhanced by dividing the 2.2-electron process into two stages and infinite stages (Fig. 5B and *SI Appendix, Supplementary Note 17*). For the two-stage CO_2 -release system, we treat the process as two sequential pH excursions. In stage 1, we use the end-of-operation voltage for the pH-downshift step (i.e., the maximum ΔpH and thus the maximum Nernst loss in stage 1), corresponding to

$1.2 e^- \times 0.43 \text{ eV}$, or 1.1 GJ $\text{t}^{-1} \text{CO}_2$. In stage 2, the resulting bicarbonate solution is further acidified to pH 4.2 (H_2CO_3) to enable CO_2 release, corresponding to $1.0 e^- \times 0.61 \text{ eV}$, or 1.3 GJ $\text{t}^{-1} \text{CO}_2$. Together, the thermodynamic minimum for the two-stage approach is 2.4 GJ $\text{t}^{-1} \text{CO}_2$.

For an infinite-stage CO_2 -release process, the postcapture liquid is continuously recirculated and its pH is progressively downshifted to pH ≈ 4.2 (where H_2CO_3 dominates) to enable CO_2 release; accordingly, the ΔpH , and thus the associated Nernst loss, varies continuously as the solution composition evolves. The thermodynamic minimum energy is therefore given by the integral of the required potential over the entire pH excursion (i.e., the full right-hand side of the titration curve), yielding 1.6 GJ $\text{t}^{-1} \text{CO}_2$.

It is worth noting that implementing two (or more) CO_2 -release stages within a single device does not change the stoichiometric electron requirement normalized per mole of CO_2 released and per unit electrode area (Fig. 5C). For example, in a 1 cm^2 device, releasing 1 mol of CO_2 from CO_3^{2-} requires 2 mol of H^+ , i.e., 2 mol e^- per mol CO_2 per cm^2 (assuming 100% charge utilization). Dividing the process into two stages— $\text{CO}_3^{2-} \rightarrow \text{HCO}_3^-$ (1 mol e^-) followed by $\text{HCO}_3^- \rightarrow \text{CO}_2$ (1 mol e^-)—still totals 2 mol e^- per mol CO_2 per cm^2 , the same as the one-stage case, indicating the same CO_2 productivity per unit electrode area. If the two-stage process is implemented in two separate physical cells, the associated capital costs (e.g., membranes, electrodes, current collectors, and balance-of-plant hardware) would need to be evaluated in full.

Materials and Methods

Materials. Manganese(II) chloride (Sigma-Aldrich, $\geq 99\%$), sodium hydroxide (puriss, 98 to 100.5%), ammonium fluoride (Sigma-Aldrich, $\geq 99.99\%$), potassium hydroxide (ACS reagent, $\geq 85\%$), potassium carbonate (ACS reagent, $\geq 99.0\%$), potassium bicarbonate (puriss, 99.5 to 101.0%), methanol (Sigma-Aldrich, $\geq 99.8\%$), and ethanol (Sigma-Aldrich, $\geq 99.5\%$) were purchased from Sigma-Aldrich. Freudenberg H23, Freudenberg H23C3, carbon black Vulcan XC 72R, and Piperion membrane AEM (80 μm) were purchased from Fuel Cell Store. Nafion® perfluorinated resin solution (D520) and Nafion 117 membrane were purchased from Ion power. The Gaseous N_2 (UHP) was purchased from Airgas. Ultrapure water (18.2 M Ω from MilliQ) was used to prepare all the material synthesis solutions and electrolytes.

Synthesis of MnO_x/OH . The MnO_x/OH was prepared by coprecipitation method following reference paper (29).

Solution A (metal precursor): MnCl_2 15 mmol + NH_4F 40 mmol + DIW 30 mL
Solution B (precipitant): NaOH 40 g + DIW 520 mL

The solution A is prepared by the above recipe and kept under stirring for 10 min in the beaker to make a homogeneous solution. After 15 min of stirring, Solution B is dropped into the Solution A beaker dropwise. When the pH of Solution A becomes 8 and the color of the solution turns to light-brown color, the titration process is completed which is kept stirring for 24 h with covering the beaker by Parafilm. After 24 h, Solution A is washed with ethanol, DIW, and ethanol through centrifugation followed by drying it in a vacuum oven under 60 °C. The dried sample is named MnO_x/OH which is ground with a mortar to make a powder sample.

Electrode Preparation. Working and counterelectrodes were made by spray coating the material ink composed of MnO_x/OH and carbon black with a weight ratio of 10:1, 750 mg Nafion D520 and 18 mL solvent solution (Ethanol: Methanol: H_2O = 4 : 4 : 1). The ink was mixed in a sonicator overnight to get a homogeneous solution. The homogeneous solution was introduced on the hydrophilic gas diffusion electrode (Freudenberg H23) with a loading weight of around 10 mg/cm².

CO_2 Release Device Assembly. MnO_x/OH fabricated electrode papers were cut by 4 cm² and pressed onto an AEM, which worked as working and counterelectrode. Two pieces of silicone rubber gaskets (0.01 inch) with a 4 cm² square-shaped window were placed between the membrane-electrode-assembly (MEA) electrochemical cell and the titanium current collector plates. The electrolyte solution was circulating through the liquid side of the MEA system and the gas line was connected to the gas side of the MEA system.

pH Downshift Device Assembly. The pH-downshift cell is composed of two silicone rubber gaskets and the titanium current collector plates. Pt/C doped hydrophilic carbon paper (Freudenberg H23) and PtRu/KB600 doped hydrophobic carbon paper (Freudenberg H23C3) were loaded at the cathode and anode sides respectively. The two electrodes were separated by a cation exchange membrane (Nafion 212) and a slim flow channel where HOR and HER take place in the slim flow channel. At the anode side, hydrogen gas and high pH solution with $\text{KOH}/\text{K}_2\text{CO}_3$ flow into the cell and then post-pH downshift solution containing KHCO_3 comes out from the cell as a product. At the cathode side, hydrogen gas and KOH are produced by the HER process and the products come out from the cell as well. The pH values of product solutions were measured by a pH meter (Oakton PC450). K^+ concentration was quantified by inductively coupled plasma mass spectrometry (ICP-MS, Thermo Scientific iCap Q). Electrolyte samples were filtered (0.20 μm), acidified with 2% HNO_3 and diluted appropriately to keep total dissolved solids below 0.2%.

The evolved CO_2 was quantified by GC (Shimadzu2014) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) equipped with a Methanizer. The calibration curve was established by analyzing the standard calibration gases with different concentrations (10 to 10,000 ppm).

Accordingly, in a pure bicarbonate electrolyte, releasing 1 mol of CO_2 requires 1 mol of HOR-derived H^+ , whereas in a pure carbonate electrolyte, it requires 2 mol of HOR-derived H^+ . For a 1:1 $\text{CO}_3^{2-}/\text{HCO}_3^-$ mixture, we assume an average requirement of 1.5 mol H^+ per mol CO_2 .

The amount of released CO_2 was quantified by GC (Shimadzu2014) equipped with a Methanizer. CE_{CO_2} was then calculated as:

$$\text{CE}_{\text{CO}_2} = \frac{Q_{\text{CO}_2}}{Q_{\text{total}}} \times 100\%,$$

where Q_{CO_2} is the charge associated with the HOR-derived protons required to release the measured amount of CO_2 and Q_{total} is the total applied charge.

Electrochemical Measurement. The CO_2 release behavior was checked by a BioLogic VSP300 potentiostat with controlling electrochemical factors. Ultrahigh purity (UHP) nitrogen (N_2) or oxygen (O_2) gas was supplied to the system by a mass flow controller (Alicat Scientific). The concentration of CO_2 after the electrochemical device was measured by a CO_2 analyzer (T360M, Teledyne) which

requires continuous gas flow with a flow rate higher than a certain level. Therefore, N_2 flowed into the gas side of the electrochemical device with a flow rate of 20 sccm to deliver released CO_2 gas to the analyzer, and N_2 of 680 sccm was supplied to the outlet gas line of the electrochemical device to maintain the gas flow level as 700 mL/min entirely.

After loading the electrochemical device with sprayed electrodes and anion membrane, the electrolyte solution was circulated at the liquid side by a peristaltic pump with a 5 rpm. For the gas side, UHP N_2 was flowing continuously with a flow rate of 20 sccm. Before the CO_2 release process, electrodes were pretreated by a cyclic voltammetry (CV) program in the range of $-1.5\text{ V} - +1.5\text{ V}$ with a scan rate of 50 mV/s (pretreatment step). During the CV process, 0.5 M potassium hydroxide (KOH) circulated with 5 rpm at the liquid side and 20 sccm of UHP N_2 flowed into the gas side with 5 sccm of UHP O_2 which is similar to the volumetric ratios of N_2 and O_2 in ambient air without CO_2 to exclude the effect of CO_2 . After the redox material on the electrode was activated enough, KOH was replaced by the target electrolyte which contains potassium bicarbonate (KHCO_3) or potassium carbonate (K_2CO_3) with flowing N_2 gas only. With flowing N_2 gas to the electrochemical device and CO_2 analyzer simultaneously, the baseline for the CO_2 analyzer was acquired after at least 2 h by observing the stabilization of the CO_2 concentration level. Then, CO_2 -releasing behavior was recorded by applying specific potential and current under limited charge level change. The electrode was activated under negative potential (proton insertion step) and then CO_2 was released under positive potential (proton deinsertion step).

EIS measurements in the HER-HOR H_2 -looping system were performed under galvanostatic operation over a frequency range of 100 kHz to 100 mHz. The spectra were fitted using a modified Randles equivalent circuit (Inset of [SI Appendix, Fig. S2](#)), consisting of an ohmic resistance R in series with a parallel combination of a charge-transfer resistance R_{ct} and a constant phase element (CPE).

Mass Balance of Closed-System. Our tandem system, a combination of a hydrogen loop (H-loop) cell for pH downshift and electrified CO_2 release cell, aims for closed-system basically which can fulfill the entire circulation of electrolyte solution theoretically. 1) The CO_2 capture vessel was assumed to be filled with 3 M KOH first to capture CO_2 which contained KOH and K_2CO_3 . After capturing CO_2 , 2) the postcapture solution was transferred to the anode of the H-loop cell. At this point, at the anode, a HOR happened by supplying H_2 gas followed by conversion of H_2 to H^+ which reacted with KOH and K_2CO_3 to form KHCO_3 . As the next process, 3) the KHCO_3 solution was pumped into the liquid side of the CO_2 release cell. Then, 4) the gas-phase CO_2 was released from the KHCO_3 at the gas side of the CO_2 release cell, and OH^- was generated by forming CO_3^{2-} and increasing the pH of the solution at the liquid side. 5) Then, pH-increased solution notated was moved to the cathode of the H-loop cell where HER occurred with retrieving KOH and hydrogen gas again. The (7) post-HER solution containing KOH was fed to the CO_2 capture vessel to work as a CO_2 capturing solution, and 6) the balance of chemicals in the cathode and anode were supported by the transport of KOH from anode to cathode. (1) Back to the CO_2 capture vessel, the mol of captured CO_2 was also balanced by the (2) and (7) process finally. The simplified diagram of the whole process, chemical equations, and mole of each chemical at each process were revealed in [SI Appendix, Supplementary Note 15](#).

CO_2 Capture and Release Measurement. The amount of released CO_2 during the electrochemical test can be calculated by integration of the CO_2 flow rate peak corresponding to the proton insertion/deinsertion cycle. The baseline of each CO_2 peak was checked by observing the peak by matching it with the potential change. Baseline of each peak is determined at the point that potential change initiates for CO_2 release as a linear horizontal line. The CO_2 flow rate is defined by the following terms and equation (Eq. [S1](#)). Ideal gas law is applied to convert CO_2 concentration measured by a CO_2 analyzer into the CO_2 flow rate. The flow rate of total gas flowing to an analyzer containing released CO_2 and carrier N_2 gases (f_{total}) is measured by a CO_2 analyzer in the unit of L/min.

$c_{\text{CO}_2, \text{peak}}$ [ppm] CO_2 concentration of peak at each releasing point
 $c_{\text{CO}_2, \text{baseline}}$ [ppm] CO_2 concentration of peak at baseline point
 $f_{\text{total}, \text{V}}$ [ml/min] total gas flow rate measured by CO_2 analyzer

$f_{CO_2, mol}$ [mol/min] CO₂ molar flow rate measured by CO₂ analyzer after unit conversion

P_{total} [kPa] pressure measured by CO₂ analyzer

$$f_{CO_2, mol} \left[\frac{mol}{min} \right] = (c_{CO_2, measure} - c_{CO_2, baseline}) (\%) \times f_{total, V} \left[\frac{l}{min} \right] \times \frac{p_{total} (kPa)}{8.314 \left(\frac{kPa \cdot l}{mol \cdot K} \right) \cdot 293.15 (K)}, \quad [S1]$$

The charge efficiency (Eq. S2) and energy cost (Eq. S3) can be quantified by integrating charge ($Q_{release}$) and total cyclic energy (E_{cycle}) as a summation of energies consumed during the proton insertion step ($E_{H^+, d}$) and proton deinsertion ($E_{H^+, i}$) (CO₂ release) steps. The points at the beginning and end of the CO₂ release are notated as t_b and t_e , respectively.

$$\text{Charge efficiency } [\%] = \frac{\int_{t_b}^{t_e} f_{CO_2, mol} dt}{\int_{t_b}^{t_e} Q_{release} dt}, \quad [S2]$$

$$\text{Energy cost} \left[\frac{GJ}{ton_{CO_2}} \right] = \frac{\int_{t_b}^{t_e} E_{cycle} dt}{\int_{t_b}^{t_e} f_{CO_2, mol} dt \times 44.01 \frac{g}{mol}}. \quad [S3]$$

Materials Characterization. The X-ray diffraction (XRD) was implemented by STOE STADI hMP diffractometer using Mo or Ag K- α radiation ($\lambda_{Ag} = 0.056$ nm, $\lambda_{Mo} = 0.071$ nm) with a scan rate of 4°/min. X-ray photoelectron spectroscopy (XPS) spectra were collected by Thermo Scientific NEXSA G2 XPS spectrometer, equipped with an Al K alpha radiation source and electron flood-gun with a pressure of 8×10^{-8} mbar and a pass energy of 50 eV. All spectra were calibrated with the C 1 s peak at 284.8 eV and Mn 2p and O 1 s spectra were displayed to grasp the phases of Mn and O species. The surface area of the material was measured by the Brunauer–Emmett–Teller method through N₂-sorption at the adsorption temperature of -196 °C using a Micromeritics 3-flex instrument under relative pressure from 0.0 to 1.0. The surface of the prepared redox material was observed by scanning electron microscopy image acquired by JEOL JSM-7900FLV with energy-dispersive X-ray spectroscopy. The microscopy was operated under 15 kV to obtain images with a magnitude of $\times 30,000$.

Data, Materials, and Software Availability. Study data are included in the article and/or [SI Appendix](#).

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