The regulation of mass transfer across membranes is central to a wide spectrum of applications. Despite numerous examples of stimuli-responsive membranes for liquid-phase species, this goal remains elusive for gaseous molecules. We describe a previously unexplored gas gating mechanism driven by reversible electrochemical metal deposition/dissolution on a conductive membrane, which can continuously modulate the interfacial gas permeability over two orders of magnitude with high efficiency and short response time. The gating mechanism involves neither moving parts nor dead volume and can therefore enable various engineering processes. An electrochemically mediated carbon dioxide concentrator demonstrates proof of concept by integrating the gating membranes with redox-active sorbents, where gating effectively prevented the cross-talk between feed and product gas streams for high-efficiency, directional carbon dioxide pumping. We anticipate our concept of dynamically regulating transport at gas-liquid interfaces to broadly inspire systems in fields of gas separation, miniaturized devices, multiphase reactors, and beyond.

INTRODUCTION
The design of stimuli-responsive membranes capable of regulating substance transport at the nanoscale is a subject of intense research, motivated by the broad potential impact on science and technology (1–5). To date, a wide variety of functional membranes have been investigated with tunable permeability/selectivity of species in the liquid phase (solvents, ions, and dissolved organic molecules) (1–3). However, the control of gas molecule transport at gas-liquid interfaces remains largely unexplored (6, 7), mainly due to the smaller sizes and greater diffusivities of both free and dissolved gas molecules, as well as the spontaneous interfacial mass transfer necessary to establish vapor-liquid equilibrium (8, 9). Nevertheless, the ability to modulate transport behavior dynamically at a gas-liquid interface is crucial to a wide spectrum of emerging energy, biomedical, and chemical engineering applications, including fluidic control in miniaturized devices (10), gas-involved chemical reactions (11, 12), controlled gas exchange (13), and directional gas pumping (14).

Nearly all the reported micro/nanoscale gas gating mechanisms are confined to the field of microelectromechanical systems (MEMS), which usually involve mechanical moving parts coupled to magnetic, electric, pneumatic, or thermal actuation methods (10). However, such designs often inevitably introduce dead volume to the system and are challenging to realize low leakage rates, which can severely compromise the effectiveness of gas gating (15). Moreover, MEMS-based gas valves may also suffer from laborious and expensive fabrication, mechanical instability, and high energy consumption, hindering their compatibility with large-scale applications. On the other hand, membrane-based systems for controllable gas transport have only been demonstrated very recently using liquid-infused microporous membranes, where gases can only permeate through the membrane on deformation of the pore-filling gating liquid meniscus above a specific pressure threshold (6, 7, 16–20). Despite being a major breakthrough, the realization of continuous permeability adjustment in liquid-infused membranes may not be straightforward (7). Therefore, the development of smart gating membranes with dynamic and reversible control over gas transport behavior is still in its infancy, making research effort in this direction critically needed.

Here, we propose a new strategy to continuously and dynamically modulate gas transfer at a gas-liquid interface, based on reversible electrochemical metal deposition/dissolution (zinc, Zn) on conductive porous membranes at the gas-liquid interface. The high-porosity, low-tortuosity membrane ensured rapid gas transport at the gas-electrolyte interface in the open state (Fig. 1A). Through detailed study on the relationship between electrolyte formulation and the electrochemical nucleation behavior, highly reversible cycling of metallic Zn (>99% Coulombic efficiency [CE]) can be realized with excellent kinetics and deposition homogeneity. As a result, a compact and uniform layer of Zn nanocrystals can be formed on the membrane with minimum deposition capacity, affording an effective gas barrier within at most a few minutes (Fig. 1B). By adjusting the amount of electrodeposited metal, a continuous-state tuning of gas permeability can be achieved for the first time, with values spanning over two orders of magnitude. The reported gating mechanism requires much lower power input compared to conventional designs for fluid control and does not require continuous energy input to maintain the operational state. Moreover, this electrochemically mediated gas gating approach neither involves mechanical moving parts nor introduces dead volume between switching. Such configurational advantages are particularly desirable in processes such as membrane-based gas separation, which can offer higher efficiency, easier operation, and a smaller footprint compared to conventional batch processes (21).

To highlight the versatility of our gating approach, an electrochemical carbon dioxide (CO₂) separation device is demonstrated by sandwiching a redox-active CO₂ sorbent electrode between two gating membranes (Fig. 1, C and D), with the two electrochemical circuits (gating and CO₂ capture/release) sharing the same electrolyte. In this novel setup, Zn shuttling between the gating membranes can open one gate while simultaneously closing the other, and quinone-based CO₂ carriers, which are immobilized on a conductive porous substrate, can reversibly bind/release CO₂ in their reduced/oxidized form, respectively (14, 22–24). During capture, the
RESULTS AND DISCUSSION

Design rationale for the electrochemically mediated gas gating membrane

Vacuum-deposited metal thin films have been known to impart outstanding gas barrier properties to polymeric substrates and are extensively used today in applications ranging from food packaging to microelectronics (30). Therefore, the concept of dynamically modulating membrane gas permeability via reversible metal deposition/dissolution is highly feasible, provided important design criteria need to be fulfilled.

First, a high-porosity membrane is desirable for rapid gas transport in the open state, while the pore size should be small to minimize the amount of metal plating needed to achieve full pore blockage. Such material requirements make anodic aluminum oxide (AAO) an ideal candidate, as it exhibits well-defined one-directional channels with high pore density and a narrow pore size distribution (~100 nm in our case; Fig. 2, A and C). Other membranes such as porous battery separators and track-etched membranes can also be considered. A gold (Au) thin film (100 nm) was thermally evaporated for gating metal deposition on one side of the AAO to render it electrically conductive (Fig. 2, B and D, and fig. S1).

Second, the gating metallic species needs to have satisfactory deposition/dissolution kinetics for fast gating response. Redox couples such as Li+/Li0, Na+/Na0, Mg2+/Mg0, and Zn2+/Zn0 generally fall into this category and are therefore being actively pursued as anodes for rechargeable batteries (31). However, metallic Li, Na, and Mg are plagued with high (electro)chemical reactivity due to their low redox potentials (fig. S2), making them incompatible to interface with gaseous environments (31, 32). Zn is uniquely positioned for gas gating applications with advantageous features of good air stability, low cost, and environmental benignity (33).
It is worth noting that if the gating membrane were to be coupled with another electrochemical process sharing the same electrolyte, then the redox potential of that process should be more positive than that of Zn$^{2+}$/Zn$^0$ to avoid interference by Zn$^{2+}$ in the electrolyte. This is valid for the quinone-based CO$_2$ capture/release process demonstrated in this study, as can be seen from the cyclic voltammetry (CV) scans in Fig. 2E. The electrochemistry of the quinone electrode will be discussed in greater detail in a later section. The potential of Zn$^{2+}$/Zn$^0$ falls more negative than most of the practically relevant gas-involved electrochemical processes, such as electrochemically mediated gas capture (23, 24, 34) and organic electrosynthesis (35, 36), rendering our gas gating membrane widely applicable.

Third, homogeneous electrodeposition with high reversibility is another prerequisite for effective gas gating. Aqueous Zn chemistry commonly used in battery research unfortunately suffers from low efficiency (<50% in typical alkaline solution) and dendritic deposition morphology (33). Therefore, a non-aqueous electrolyte needs to be used, which has rarely been studied in literature (37).

In this study, propylene carbonate (PC) was selected as the electrolyte solvent due to its wide electrochemical stability window and low volatility (26). We first studied the Zn plating morphology on Au-coated aluminum foil using 0.5 M zinc bis(trifluoromethanesulfonyl)imide (ZnTFSI$_2$) in PC. However, as seen from the scanning electron microscopy (SEM) images, Zn grew into large aggregates that only sparsely covered the substrate (fig. S3), which stands in stark contrast to the continuous thin film obtained in an aqueous electrolyte (fig. S4). This highly localized deposition behavior might be attributed to the relatively large interfacial energy between metallic Zn and PC. According to the classical nucleation theory, the Gibbs energy for nucleation is the sum of the bulk and the interfacial free
respectively (Fig. 3B). Thus, even a low deposition capacity of 0.1 mAh N_2 was passed via a mass flow controller (MFC) over one side of the AAO membrane obtained in PC electrolyte with 10% EG additive at a high current density of 3 mA cm^{-2} for 10 min. A compact Zn film consisting of uniform, crystalline Zn polyhedrons can be observed, and the homogeneity persisted over the whole deposition area (fig. S5). A side-view SEM image indicates a tight coverage of the Zn film on the surface of AAO (Fig. 2I and fig. S6). The thickness of the film at a deposition capacity of 0.5 mAh cm^{-2} was ~650 nm, which agrees well with the theoretical value of a dense Zn layer (655 nm). The dense deposition morphology is highly desirable for effective gas gating. The Zn cycling CE, which is defined as the ratio between dissolution and deposition capacity, is also critical for reversible gas gating. Unprecedented CE can be achieved using our PC-based electrolyte, with a value of 99.3% at a high current of 3 mA cm^{-2} (fig. S7).

**Ex situ testing of the electrochemically mediated gating membrane**

One distinct advantage of the electrochemically mediated gating mechanism is its ability to modulate the membrane permeability continuously. This feature has been observed previously in membranes gated with redox-active polymers, which are particularly useful for flux control in the liquid phase (39, 40). Here, a denser Zn film and more complete pore coverage can be observed with increasing deposition capacity, which, in turn, result in decreasing permeability (fig. S8). To verify the capability of continuous-state tuning, membranes with different amounts of Zn deposited were first evaluated ex situ in both the liquid and gas phase.

Liquid-phase diffusion experiments were conducted in an H cell configuration using methyl orange dye as a tracker. Methyl orange (1 mM) and pure water were separated by the membranes, and aliquots were taken from the permeate chamber to determine the crossover concentration via ultraviolet-visible (UV-vis) spectroscopy (fig. S9). As can be seen from Fig. 3A and fig. S10, the dye can diffuse rapidly through the membrane in its open state (pristine AAO), while the crossover rate decreased gradually with increasing Zn capacity until the color change was barely visible over 24 hours for the 0.5 mAh cm^{-2} Zn gated membrane. Quantitatively, the crossover concentration after 24 hours was 297 μM for pristine AAO, but was 28.7, 5.6, and 1.1 μM for 0.1, 0.3, and 0.5 mAh cm^{-2} Zn gated AAO, respectively (Fig. 3B). Thus, even a low deposition capacity of 0.1 mAh cm^{-2} (2-min deposition at 3 mA cm^{-2} current) can already slow down the dye diffusion by an order of magnitude, and 0.5 mAh cm^{-2} Zn effectively afforded a 300× reduction in membrane permeability.

Gas-phase gating, which is more demanding on the compactness of the gating metal layer, was also studied ex situ using CO_2 permeation as an example. In this experimental setup, 15% CO_2 (balance N_2) was passed via a mass flow controller (MFC) over one side of the membrane, and the permeated CO_2 was swept by pure N_2 toward an in-line gas analyzer to accurately determine the concentration (Fig. 3C). A detailed configuration of the gas cell is provided as fig. S11. As expected, the permeation flux for all membranes increased with increasing flow rate difference between the CO_2 feed and N_2 sweep streams, which corresponds to a higher transmembrane pressure (Fig. 3D and fig. S12). Consistent with liquid-phase experiments, the gas permeability of the membrane also decreased continuously with increasing Zn deposition under all flow conditions tested. Noticeably, no CO_2 permeation can be detected for 0.5 mAh cm^{-2} Zn gated AAO unless subjected to an extreme transmembrane pressure [200 standard cubic centimeters per minute (sccm) feed and 5 sccm sweep], which also translates into a two orders of magnitude reduction in gas permeability compared to the open-state membrane. The success of the above ex situ experiments in both the liquid and gas phase strongly demonstrates the effectiveness and wide tunability of our electrochemically mediated gating membrane.

**In situ testing of the electrochemically mediated gas gating membrane**

In situ testing of the electrochemically mediated gating membrane was conducted to further verify its ability to reversibly and dynamically control gas transport at the gas-liquid interface. The setup was similar to that used for ex situ testing, but the membrane was coupled with a mesh counter electrode with predeposited Zn (Fig. 4A and fig. S13). In the open state, CO_2 can transport through the electrolyte-imbibed separator via dissolution-diffusion and outgas into the sweep stream. Figure 4B shows the sweep stream CO_2 concentration in response to gating (10-min deposition/dissolution at 3 mA cm^{-2}, with 10-min rest in between), where consistent gate on/off switching can be observed over 20 cycles. Looking at an individual cycle, the permeated CO_2 concentration kept decreasing with increasing Zn deposition until finally no crossover can be detected, followed by a gradual restoration of the open-state value with Zn dissolution (Fig. 4C). Note that the discrepancy between the onset of deposition/dissolution and the CO_2 signal response was due to system dispersion and the headspace volume of the flow chamber (fig. S14). Moreover, the in situ Zn cycling demonstrated an outstanding CE (averaged >99.5%; Fig. 4D) and stable voltage profiles (fig. S15), both providing strong evidence of the high reversibility of the gating membrane. The gating kinetics can be easily tuned by varying the cycling current while still maintaining a remarkable gating on/off ratio (Fig. 4E).

On the basis of the experimental data, the electrical energy required for complete on/off switching was calculated to be 518 mJ cm^{-2} (~0.144 mWh cm^{-2}) at a switching current of 3 mA cm^{-2}, which translates to an average power of 0.864 mW cm^{-2}. This energy/power input is orders of magnitude lower than those of conventional miniaturized valves involving mechanical actuation mechanisms (10). Moreover, unlike many other designs for fluid control, the electrochemically mediated gating membrane does not require continuous energy input to maintain its operational state, which further reduces the energy consumption.

**High-efficiency electrochemical CO_2 separation enabled by gas gating membranes**

To highlight the versatility of the gating approach, an electrochemical CO_2 concentrator is demonstrated here as a proof of concept, where the use of gas gating membranes enabled a new operating mode for gas separation by preventing the undesirable cross-talk.
between the dilute and concentrated gas streams as well as obviating the need for system blowdown between absorption and desorption required in conventional temperature and pressure swing processes. It is worth emphasizing that various additional form factors are possible to incorporate the electrochemical gas gating membrane in gas separation (fig. S16), and our reported gas gating mechanism can also create opportunities in many other applications.

The development of high-efficiency CO₂ separation technologies is crucial for greenhouse gas mitigation, and of value in the petroleum, chemical, and heavy industries, as well as in specialty applications such as life support in confined spaces (34, 41). One emerging strategy involves electrochemical cycles to capture/release CO₂, with quinones being a representative example (14, 22–24, 26). Electrochemically reduced quinones can bind to electrophilic CO₂ to form stable adducts, while the oxidation of the adducts regenerates the sorbents to release CO₂. A poly(1,4-anthraquinone) (PAQ)–carbon nanotube (CNT) composite was selected as the sorbent electrode (theoretical capacity, 260 mAh g⁻¹ or 9.7 mmol CO₂ g⁻¹) (42). This material has recently been used by our group to demonstrate electro-swing–based CO₂ separation in a cyclic reactor configuration (24). To facilitate liquid-phase CO₂ mass transfer, PAQ was cast on a porous carbon felt 50 μm in thickness and paired with a LiFePO₄ (LFP) counter electrode (the PAQ-LFP electrode pair is termed the “CO₂ cell” hereafter). As seen from the capture-release voltage profiles, polarization increases with increasing PAQ mass loading and/or cycling rates, together with decreased capacity (Fig. 5A). Therefore, 0.75 mg cm⁻² loading with 30-min capture/release (0.4 mA cm⁻² current) was identified as an optimal cycling condition, under which satisfactory carbon capture capacity can be used while preserving good electrochemical kinetics and stability (Fig. 5B).

To prevent the system from operating beyond the mass transfer limit, the limiting current density of the CO₂ cell was estimated based on the diffusion model described in Fig. 5C (method S1). The limiting current is defined as the current when steady-state CO₂ concentration reaches zero at the depth of the PAQ electrode. CO₂ (15%) was used in the calculation, which is the approximate concentration expected in many carbon capture applications (41). The limiting current decreases with decreasing gas pressure and/or increasing electrode thickness, with the value being ~2 mA cm⁻² for a 50-μm electrode under 1 atm pressure (Fig. 5D). Thus, the identified optimal PAQ cycling condition did not exceed the limiting current, yet was close enough to take sufficient advantage of kinetics. Operating slightly below the limiting current also allowed a smaller
gas-liquid contact area (size of the gating membrane) than the size of the CO₂ cell, which can reduce the gating energy consumption.

When the CO₂ cell was tested by flowing CO₂ on one side and N₂ on the other, a cyclic fluctuation of the permeated CO₂ concentration can be observed (Fig. 5E). During capture, CO₂ in the electrolyte was being actively consumed, resulting in a reduction in permeation, and a distinct concentration spike can be observed when PAQ was being oxidized to release the captured CO₂ (Fig. 5F). This behavior was verified through a COMSOL transport modeling, where the simulation predictions match closely with the experimental results (Fig. 5F). Details on the simulation can be found in method S2.

Nevertheless, a substantial CO₂ permeation background existed [~4500 parts per million (ppm) for the cycle shown in Fig. 5F] when the CO₂ cell was operated without a gating mechanism, due to the spontaneous CO₂ diffusion down the concentration gradient. In real gas separation scenario, if the CO₂ cell has access to both the dilute feed stream and the concentrated product stream, CO₂ will have a much higher tendency to be released back into the feed unless a sufficient differential pressure is created across the cell, which is detrimental to the separation efficiency (14, 21). As a result, traditional gas separations using solid sorbents can only rely on batch processes, involving large-footprint columns, time- and energy-consuming system blowdown, and complex gas switching between different operating stages.

Integrating the CO₂ cell with our electrochemically mediated gas gating membranes offers an exciting opportunity to overcome the abovementioned barrier in separation efficiency. By sandwiching the CO₂ cell between two gating membranes in opposite on/off states (termed the “gating cell” hereafter), the system can only access one gas stream at a time to circumvent the undesirable cross-talk caused by chemical potential differences.

Figure 6A illustrates the configuration of the integrated CO₂ separation system, and detailed information is provided as fig. S17. The following design aspects were noted for high separation efficiency. (i) A “zero-gap” design was used, where the CO₂ cell and the gating cell were in tight contact without headspace or gas bubbles to avoid gas channeling (43). (ii) Minimum electrolyte was added such that the capture capacity of the CO₂ cell dominated over the physical CO₂ solubility in the electrolyte (method S3). (iii) The gating cell area (1 cm²) was smaller than the CO₂ cell (6.45 cm²) based on limiting current estimation to reduce gating energy consumption. (iv) The thickness of all components was reduced whenever possible to facilitate mass transfer. In real operation, the device would work by directionally pumping dilute CO₂ into a concentrated product. However, due to the limitation of our CO₂ detection method, an N₂ sweep was used in place of the product stream to monitor CO₂ capture/release with a gas sensor. The gating cell is defined as “closed”/“open.”
when the system is accessing the feed/sweep stream, respectively (Fig. 6B). Thus, under this testing condition, metrics defining high-efficiency separation include no CO$_2$ crossover with the gate closed and a high concentration spike during CO$_2$ release with the gate open.

Figure 6C shows the typical behavior of the integrated separation system. Pure CO$_2$ was used as feed first to maximize the measurement sensitivity. No crossover can be detected when the gate was closed, confirming that the system was accessing only the feed stream during electrochemical CO$_2$ capture (red segment). After capture, we opened the gate by shuttling Zn to the other side of the gating cell, during which a gradual permeation increase appeared due to CO$_2$ outgassing from the electrolyte (teal segment). Subsequently, a distinct concentration spike was observed when the CO$_2$ cell was electrochemically oxidized to release CO$_2$ from the quinones (blue segment). Last, the CO$_2$ signal decayed back to zero on closing of the gate, thus completing a capture-release cycle (yellow segment). Consistent behavior was observed over multiple cycles (fig. S18). If we qualitatively compare the system efficiency by the ratio between the magnitude of the concentration spike and the permeation background, the value is ~0.39 for the integrated system, while it is only ~0.19 without the gating mechanism. Moreover, by lowering the feed concentration to more practical values (20% CO$_2$),
transport to the product stream was dominated by the contribution from the CO\textsubscript{2} cell (Fig. 6D, contribution from the CO\textsubscript{2} cell is marked in blue and contribution from the physical solubility of the electrolyte is marked in teal). The results fulfilled our abovementioned metrics for high-efficiency separation. These phenomena were further validated using the corresponding COMSOL transport model simulation, where an excellent agreement with the experimental data was obtained (Fig. 6C, inset). The previous simulation model was adapted but with added gate closing/opening features, simulated as a temporal change in porosity that follows the gate closing/opening timing to reflect the zinc deposition/dissolution in the gating mechanism (method S2). The model allows the prediction of system performance at different gas compositions and operation parameters, paving the way for more comprehensive system-level modeling of such gas separation devices in the future.

The realization of reversible, dynamic transport control at a gas-liquid interface uniquely enabled directional CO\textsubscript{2} pumping without the need for differential pressure. Combining units operating at opposite polarities can afford an effectively continuous CO\textsubscript{2} capture-release process (fig. S19). Compared to conventional batch processes, our membrane-based “zero-gap” CO\textsubscript{2} separation device can obviate the need for system blowdown between absorption and regeneration, simplify reactor design, improve energy efficiency, and reduce the footprint of separation units for process intensification (41). Moreover, this novel gas separation process will also open unprecedented opportunities for niche applications, such as life support systems in manned space/marine missions and electrochemical gas compression (28, 29).

Controlling transport behavior at gas-liquid interfaces is a largely under-researched topic, albeit being crucial for emerging technologies. In this work, we propose a novel gating mechanism capable of dynamically and continuously modulating gas transport at a gas-liquid interface, driven by electrochemical metal deposition/dissolution on conductive porous membranes in a rationally formulated electrolyte. The gas gating membrane can operate with low power consumption, and excellent on/off ratio, reversibility, kinetics, and tunability as verified by both ex situ and in situ testing. Moreover,
actuated only by electrochemistry, the gating membrane involves neither moving parts nor headspace, which is desirable for high gating efficiency and reliability. As a proof of concept, a compact, electrochemically mediated carbon dioxide separation device is achieved by sandwiching a redox-active CO$_2$ sorbent electrode between two gating membranes. The gating mechanism effectively minimized cross-talk between feed and product streams such that ideally the integrated device can directionally pump CO$_2$ against a concentration gradient without the need for differential pressure, making it versatile for diverse carbon capture applications. We anticipate that our concept of dynamically regulating mass transfer at gas-liquid interfaces will inspire applications in wide fields ranging from gas separations to miniaturized energy/medical devices to microscale gas-involved reactors and beyond.

MATERIALS AND METHODS

Materials

AAO membranes were purchased from Whatman (Anodisc 6809-6012, 25 mm diameter, 100 nm pore size) and rendered electrically conductive by depositing 100-nm Au on one side of the membrane via thermal evaporation. The electrolytes were prepared by dissolving the corresponding salts zinc bis(trifluoromethanesulfonyl)imide (Alfa Aesar), lithium bis(trifluoromethanesulfonyl)imide (Solvay), and/or tetrabutylammonium hexafluorophosphate (Sigma-Aldrich) in PC (anhydrous, 99.7%, Sigma-Aldrich), EG (anhydrous, 99.8%, Sigma-Aldrich), and/or dimethyl sulfoxide (Sigma-Aldrich). PC and EG were dried over molecular sieves (4 Å, Sigma-Aldrich) before use. Ferrocene and anthraquinone were purchased from Sigma-Aldrich.

Characterizations

SEM images and energy-dispersive x-ray elemental mappings were taken with a Zeiss SUPRA 55-VP scanning electron microscope. Liquid-phase diffusion tests were carried out in 5-ml H cells (Adams & Chittenden Scientific Glass). The two chambers were separated by an AAO membrane with a 0.5-cm$^2$ effective area. Methyl orange & Chittenden Scientific Glass). The two chambers were separated by an AAO membrane with a 0.5-cm$^2$ effective area. Methyl orange

Electrochemical Zn cycling

All the electrochemical measurements were conducted using a VersaSTAT4 potentiostat (Princeton Applied Research). To do the Zn deposition morphology, either Au-coated AAO or Au-coated aluminum foil was used as the substrate. The deposition was carried out in a pouch cell configuration with glass fiber separator (MilliporeSigma) and Zn foil (0.25 mm thick, Thermo Fisher Scientific) counter electrode. Zn foil was polished progressively down to 7000 grit sandpaper before use. For the study of nucleation overpotential, Zn dust (<10 μm, Sigma-Aldrich) counter electrode was used, which was fabricated by mixing 80% Zn dust, 10% carbon black (Super P, MTI Corp.), and 10% polypyrrole fluoride (Sigma-Aldrich) in N-methylpyrrolidinone followed by slurry coating on aluminum foil.

Ex situ and in situ gas cell measurements

The gas-phase measurements were conducted using a house-machined device consisting of two gas flow chambers separated by the gating membrane, all held together with rubber gaskets and screws (detailed gas cell configuration shown as fig. S11). Membranes were mounted on brass holder discs using 5-min epoxy glue (Devcon). CO$_2$ of different concentrations flowed through one gas chamber, and N$_2$ sweep gas flowed through the other. The concentration of CO$_2$ in the N$_2$ stream was measured with an in-line CO$_2$ sensor (ExplorerR-W 20% CO$_2$ sensor). The sensor has a measurement range of 0 to 20% CO$_2$ and an accuracy of ±0.7 ppm. For in situ testing of the gas gating membrane, the membrane was coupled with a stainless steel mesh (316 stainless steel, 100 mesh, McMaster-Carr) counter electrode with pre-deposited Zn, and the two electrodes were separated by glass fiber separator.

Testing of the CO$_2$ cell

PAQ was synthesized following a previously reported procedure (44). To obtain the PAQ-CNT composite, PAQ was dissolved in chloroform (1 mg ml$^{-1}$) using a probe sonicator (Cole-Parmer Ultrasonic Processor, pulser mode: on 5 s–off 3 s, 60% amplitude). Subsequently, CNT was added into the solution (1 mg ml$^{-1}$) and the mixture was sonicated for another 20 min to afford a homogeneous dispersion. The PAQ-CNT ink was then drop-cast on 50-μm carbon felt (Fibre Glast Carbon Fiber Veil). The LFP counter electrode was prepared by mixing 95% LFP (MTI Corp.), 2.5% carbon black, and 2.5% polystyrene sulfonate in N-methylypyrrolidinorhodonidone followed by drop-casting on 50-μm carbon felt (mass loading, 8 mg cm$^{-2}$). The PAQ electrode and the LFP electrode were separated with a 25-μm polypropylene separator (Celgard 3501). The electrochemical cycling of the CO$_2$ cell was carried out using constant current followed by constant voltage until the current decays to 20% of the constant current cycling. The electrolyte used was 0.1 M LiTFSI + 0.5 M ZnTFSI in PC with 10% EG additive.

Testing of the integrated CO$_2$ separation system

Zn was predeposited on one of the AAO membranes (0.6 mAh cm$^{-2}$, 0.5 mAh cm$^{-2}$ Zn cycling capacity plus 20% extra to compensate Coulombic loss). The size of the PAQ electrode was 1 inch by 1 inch with an active material mass loading of 0.75 mg cm$^{-2}$. The size of the LFP electrode was 1 inch by 1 inch with an active material mass loading of 8 mg cm$^{-2}$. The AAO membranes and the electrodes were separated with 25-μm polypropylene separators and confined tightly using gaskets. CO$_2$ (100 or 20%) was used as the feed stream, and N$_2$ was used as a sweep stream for detection purpose. A complete capture and release cycle started with 30 min of CC-CV CO$_2$ capture with gate closed. Once the capture capacity was reached, the polarity of the gating cell was switched at 3 mA cm$^{-2}$ for 10 min, followed by 5-min rest. Subsequently, CO$_2$ was released from the PAQ electrode by 30 min of CC-CV oxidation, followed by 10-min rest. Last, the cycle was completed by switching the polarity of the gating cell again (3 mA cm$^{-2}$ for 10 min).

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/6/42/eabc1741/DC1

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