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High-Capacity and High-Stability Electrochemical CO₂ Capture Cell with Coupled Electricity Storage

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Abstract

We report an electrochemical cell for CO₂ capture based on pH swing cycles driven through proton-coupled electron transfer of a newly developed phenazine, 2,2'-(phenazine-1,8-diyl)bis(ethane-1-sulfonate) (**1,8-ESP**), which exhibits high aqueous solubility, > 1.35 M, over pH range 0.00–14.90. The system operates with a high capture capacity of 0.86–1.41 mol/L, a low energetic cost of 36.4–55.2 kJ/mol, and an extremely low capacity fade rate of < 0.01%/day, depending on organic concentration. The system charge-discharge cycle provides an electrical energy storage function that can be run efficiently only for storage when called for by electricity market conditions. These results demonstrate the great potential of electrochemically-driven pH swing cycles based on proton-coupled electron transfer of redox-active organics for CO₂ capture.

Introduction

The global average temperature today is more than 1 °C warmer compared to the pre-industrial revolution time.¹ Greenhouse gas emission is the primary driver for climate change, where the accumulated CO₂ emission from fossil fuel consumption is the major source, and leads to global warming, ocean acidification, and other severe environmental problems.²⁻³ In addition to the rapid displacement of fossil energy by clean energy,⁴ CO₂ capture, whether from a point source such as a fossil fuel or biomass combustion power plant⁵⁻⁷ or directly from air,⁸⁻⁹ is important because fossil fuel combustion is going to remain significant for a long time, and hard-to-abate emissions will still exist even if the electricity sector is fully decarbonized. To keep the global temperature rise under 1.5 °C by 2100, significant progress needs to be achieved in efficient large-scale CO₂ capture techniques.¹⁰

Considerable research and development efforts have been made to develop CO₂ capture methods with low energy consumption, fast capture rate, and high capture capacity (mol_{CO2} per liter of solvent). Amine scrubbing has been utilized at an industrial scale for post-combustion CO₂ capture from point sources.¹¹ Whereas the energy cost of amine scrubbing can be low, i.e. ~80 kJ mol_{CO2}⁻¹ for advanced solvent systems, serious problems including material degradation, toxicity, and corrosivity are concerning.¹² Another commercialized technology is to directly absorb CO₂ from air with a strong alkaline solution (pH >14) to form carbonates in a high-surface-area contactor.^{2, 13} However, this process is challenging as the thermal energy required to subsequently release CO₂ from solid carbonate precipitates is very high (264–396 kJ mol_{CO2}⁻¹). Other methods such as solid amine and amino-acid based direct air capture have been developed and have exhibited lower thermal energetic cost, but material decomposition may lead to high operational cost.¹⁴⁻¹⁶ Electrochemically mediated CO₂ capture may provide a lower-cost, more environmentally benign, and less energy-intensive approach that could be operated at ambient temperature and pressure without relying on external thermal energy.¹⁷⁻²⁰ CO₂ capture based on electrochemically induced pH swing, where CO₂ can be absorbed at high pH and released at low pH, is a promising electrochemical carbon capture method because of its low energetic cost and high applicable current density.²¹ Such a pH swing can be driven electrochemically through proton-coupled electron transfer (PCET) of organic molecules, i.e. upon electrochemical reduction and oxidation, the molecules undergoing PCET reactions uptake and release protons, leading to pH decrease and increase, respectively, in the aqueous solution.²²⁻²⁶ Leveraging the high tunability of redox-active organic molecules, electrolytes with desirable redox potential, high solubility, long lifetime, and low cost may be realized.²⁷ Recently a proof-of-concept point source (10%) CO₂ separation system based on 3,3'-(phenazine-2,3-diylbis(oxy))bis(propene-1-sulfonate) (**DSPZ**) as the PCET carrier was shown to require a low energy cost of 61.3 kJ mol_{CO2}⁻¹ at 20 mA cm⁻², and results extrapolated to 121 kJ mol_{CO2}⁻¹ for 0.4 mbar capture.²²⁻²³ Nevertheless, the development of PCET molecules with improved aqueous solubility is necessary to enhance the CO₂ capture capacity. Additionally, although various electrochemical CO₂ capture methods are reported, few have investigated the operational lifetime and stability of CO₂ capture materials.²⁸⁻²⁹

Here we report a high-capacity and high-stability electrochemical CO₂ capture system with coupled electricity storage. This system, based on an aqueous flow cell, employs a newly developed highly-soluble molecule sodium 2,2'-(phenazine-1,8-diyl)bis(ethane-1-sulfonate) (**1,8-ESP**) that demonstrates advantageous properties for both carbon capture and energy storage applications. **Figure 1** shows a schematic illustration of the integrated CO₂ capture-release and energy storage-delivery system with **1,8-ESP**. In the charging process paired with ferrocyanide on the positive side (**Figure 1a**), **1,8-ESP** on the negative side undergoes a two-electron reduction process and its reduced form rapidly consumes two protons from H₂O, increasing the pH and total alkalinity (TA) in solution; we call this the deacidification process. The CO₂-containing gas reacts with OH⁻ to form dissolved inorganic carbon (DIC), completing the CO₂ absorption and energy storage half-cycle. During discharging (**Figure 1b**), reduced **1,8-ESP** is oxidized, and it releases protons into the solution; we call this the acidification process. The pH and TA of the electrolyte decrease, resulting in pure CO₂ outgassing. During this half-cycle, electrical energy delivery and pure CO₂ gas release occur simultaneously. Thus the capital requirements could be shared without further cost investments while concurrently

providing storage services for the electrical grid, which must deal with increasing contributions from intermittent renewable power sources. Electricity price arbitrage in an electricity market is profitable only a small fraction of the time;³⁰ hence the dedication of the integrated system to CO₂ capture during periods when arbitrage is unprofitable could lead to significantly improved economics over those of comparable systems for either application alone.

In the present work, the electrochemical and physicochemical properties of **1,8-ESP** are studied, showing that the molecule exhibits remarkable redox activity and high solubility in any pH from acid to base, making it ideal as an agent to induce pH swing for CO₂ capture. We report the results of a detailed investigation of CO₂ capture capacity, energetic cost, capture rate, and stability for electrolytes with 0.1, 0.5 and 0.8 M **1,8-ESP**. We find that the energetic cost can be as low as 36.4 kJ mol_{CO₂}⁻¹ and the CO₂ capacity can be as high as 1.41 mol_{CO₂} L⁻¹. We demonstrate the operational stability of the carbon capture flow cell during 220 cycles of operation over 18 days with no detectable material decomposition, illustrating the great potential of **1,8-ESP** for a robust CO₂ capture system. Additionally, the cell exhibits excellent charge-discharge performance as a pure energy storage system when isolated from CO₂.

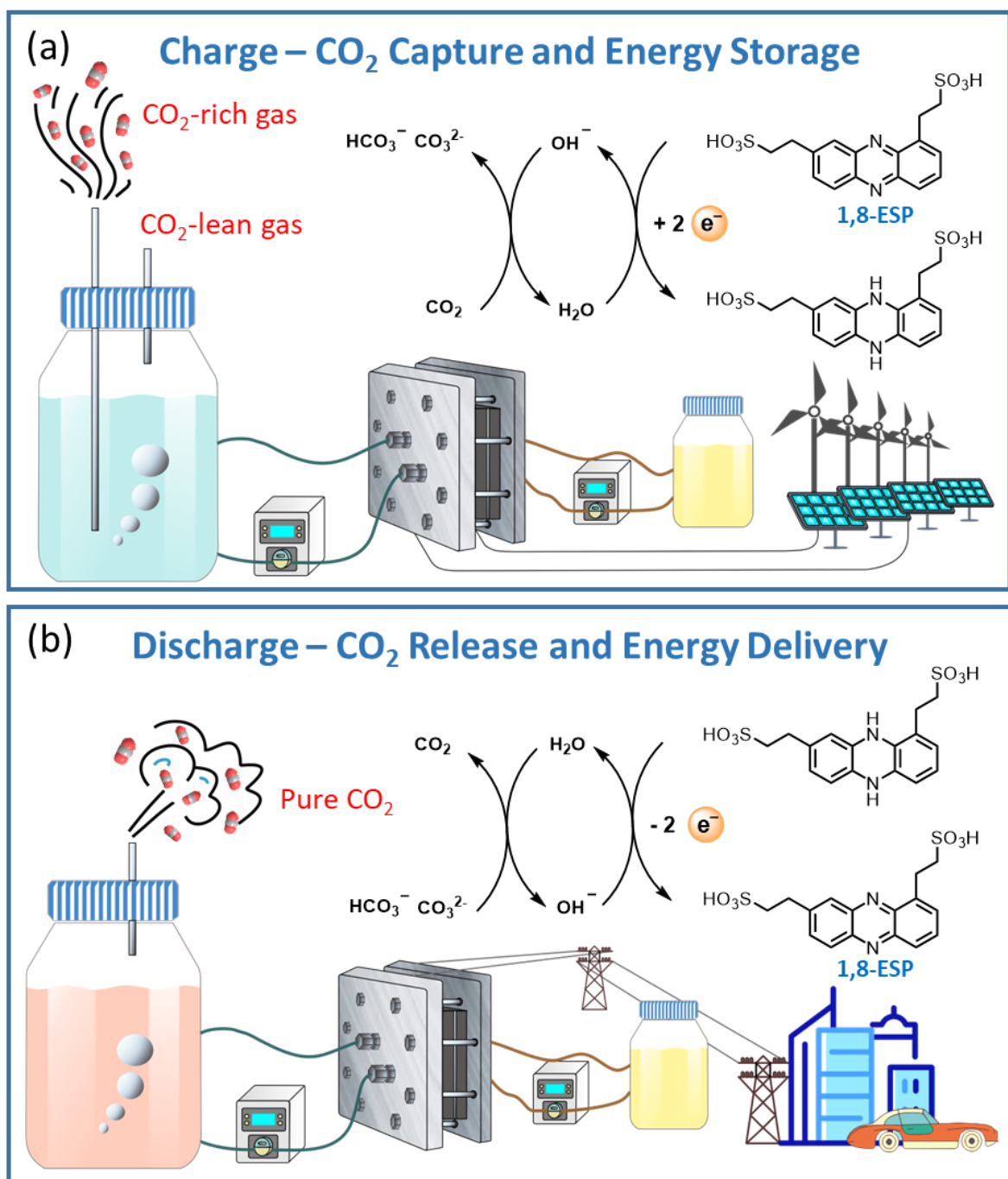


Figure 1. Illustration of CO₂ capture-release and energy storage-delivery cycle associated with cell charge and discharge process. (a) CO₂ capture and Energy storage process. (b) CO₂ release and Energy delivery process.

Results and Discussion

ESP isomers with substituents at different positions of the phenazine core (**1,8-ESP**, **2,7-ESP**, **1,6-ESP**) were synthesized (**Scheme S1**) and characterized by nuclear magnetic resonance (NMR) and high-resolution mass spectrometry (HRMS). The solubilities of these isomers (**Figure S12-18** and **Table S1**) were studied by UV-vis spectroscopy analysis. The unsymmetrically substituted **1,8-ESP** exhibits higher solubility than symmetrically substituted **2,7-ESP** and **1,6-ESP**; this shows the same trend as the theoretical study of solvation energies through DFT calculations (**Table S3**). Thus we set out to investigate **1,8-ESP** further for use as

a CO₂ capture agent due to its high solubility which enables high volumetric CO₂ capture capacity. **1,8-ESP** exhibits a solubility of 1.40 M in 1.0 M KCl, corresponding to a theoretical CO₂ separation capacity ($\Delta\text{DIC}_{3\rightarrow 1}$)²³ of 2.35 mol_{CO₂} L⁻¹ and 1.48 mol_{CO₂} L⁻¹ at inlet CO₂ partial pressures of 100 mbar and 0.4 mbar CO₂(g), which are the CO₂ concentration of flue gas from a typical coal power plant and atmospheric CO₂, respectively. This high solubility (1.40 M) also means a theoretical volumetric electrical discharge capacity of 75.0 Ah L⁻¹ for energy storage. Besides being soluble in pH neutral solution, **1,8-ESP** shows an even higher solubility of 1.60 M in 1.0 M H₂SO₄, 1.95 M in 1.0 M KOH and 2.06 M in 2.0 M KOH, minimizing the possibility of precipitation during the pH swing for CO₂ capture (**Figure 2a and Table 1**). The solubility of **1,8-ESP** is also explored in the presence of DIC. In a solution of 1.0 M TA that is saturated with 0.4 mbar CO₂ in air, i.e. 0.436 M K₂CO₃ and 0.128 M KHCO₃, **1,8-ESP** remains highly soluble (1.35 M), indicating its compatibility with DIC.

1,8-ESP possesses quasi-reversible redox electrochemical properties in a wide range of pH buffer solutions through cyclic voltammetry (CV) studies (**Figure 2b**). As shown in the Pourbaix diagram of **1,8-ESP** (**Figure 2c**), the linear relationship between pH and potential, with a slope of -58.1 mV pH⁻¹ suggests that the molecule undergoes a two-proton/two-electron process in the pH frame within the experiment. Note that **1,8-ESP** participates in 2H⁺, 2e⁻ PCET up to at least pH 14.90, suggesting a high capacity for CO₂ capture. To evaluate its redox reaction kinetics in solutions with different electrolytes, rotating disk electrode (RDE) experiments were carried out to analyze its diffusion coefficient (*D*) and electron-transfer rate constant (*k*₀) (**Figure S4-S9**). The calculated diffusion coefficients and electron-transfer rate constants according to the Tafel plots are reported in **Table 1**.

1,8-ESP has an extremely low permeability of 1.24×10⁻¹⁵ cm² s⁻¹ across a cation exchange membrane (Nafion NC700), suggesting a negligible crossover rate during cell operation (**Figure S19**). We attribute this to the large molecular structure and the deprotonated sulfonic acids with negative charges that repel **1,8-ESP** molecules from the negatively charged membrane surface.³¹⁻³² Another desirable property of absorption solution during CO₂ capture is a high surface tension of the solution. High surface tension helps to decrease foaming, which is a common problem in electrochemically mediated carbon capture.³³⁻³⁴ **1,8-ESP** solution possesses a higher surface tension than does water, and foaming is significantly suppressed during the cycling of **1,8-ESP** (**Figure 2d and Figure S20-21**). Compared to the previously reported molecule **DSPZ**, **1,8-ESP** exhibits a higher solubility and less foaming in solution, making it more attractive for electrochemical CO₂ separation (**Figure 2c, d and Figure S20-21**).

Table 1 Summary of the electrochemical and physicochemical properties of **1,8-ESP**.

1,8-ESP ^a	E _{1/2} vs. SHE (V) ^b	Solubility (mol L ⁻¹)	D (cm ² s ⁻¹) ^c	k ₀ (cm s ⁻¹) ^d
1.0 M KOH	-0.503	1.95	2.78×10 ⁻⁵	1.15×10 ⁻³
2.0 M KOH	-0.590	2.06	2.52×10 ⁻⁵	1.97×10 ⁻³
1.0 M KCl	-0.390	1.40	3.25×10 ⁻⁵	8.65×10 ⁻⁴
1.0 M KCl ^e	-0.370	1.35	2.46×10 ⁻⁵	1.24×10 ⁻⁴
1.0 M H ₂ SO ₄	0.393 (0.118) ^f	1.60	1.10×10 ⁻⁵ (3.10×10 ⁻⁵) ^f	4.25×10 ⁻⁵ (4.92×10 ⁻⁵) ^f

^aMeasured at room temperature. ^bRedox potential. ^cDiffusion coefficient. ^dElectron transfer rate constant. ^eWith 0.436 M K₂CO₃ and 0.128 M KHCO₃ (1.0 M KOH saturated with 0.4 mbar CO₂). ^fThe reduction of **1,8-ESP** in

1.0 M H_2SO_4 exhibits a two-step process (**Figure 2b** and **Figure S8**). The value in the parentheses is for the second step.

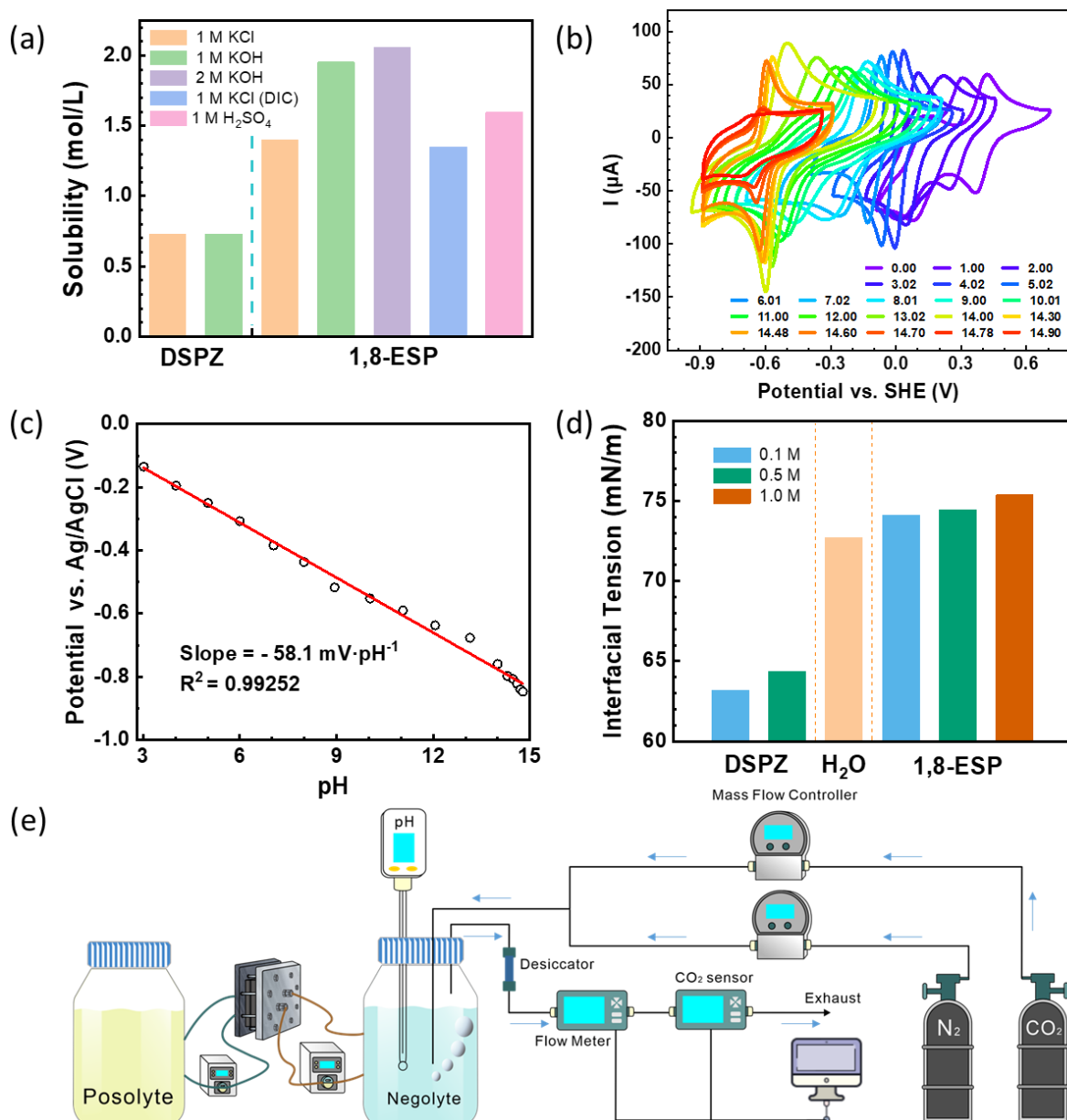


Figure 2. (a) Solubility of **1,8-ESP** and **DSPZ** in different electrolytes. (b) CV curves of **1,8-ESP** in different pH buffer solutions with 1.0 M KCl. (c) Pourbaix diagram of **1,8-ESP**. (d) Interfacial tension of **1,8-ESP**, H_2O and **DSPZ** with different concentrations at 20 °C. (e) Scheme of $\text{Fe}(\text{CN})_6$ (posolyte) | **1,8-ESP** (negolyte) flow cell for CO_2 capture/release experiments. The blue arrows indicate gas flow.

Next, we explored the energetic cost of the CO_2 absorption/release cycle. **Figure 2e** shows the schematic of the carbon capture flow cell and the hardware for providing the gas mixture and analyzing the exhaust. The upstream gas composition in the negolyte headspace was controlled by CO_2 and N_2 mass flow controllers (MFCs). Downstream of the negolyte reservoir, the gas was dried with a desiccator and the total gas flow rate and CO_2 partial pressure were measured using a digital flow meter and a CO_2 sensor, respectively. A pH probe immersed in the negolyte solution reported the temporal evolution of the pH, which enabled the tracking of

TA and dissolved inorganic carbon DIC in real time. **Figure 3** shows a single electrochemical carbon capture cycle using 0.5 M **1,8-ESP** in the negolyte. In this cycle, pure CO₂ was separated from a mixture of 10% CO₂ and 90% N₂ through a deacidification+CO₂ absorption process followed by acidification+CO₂ outgassing process. When a positive 20 mA cm⁻² current was applied at $t = 2$ hr (**Figure 3a**), charging the cell, the electrochemically induced deacidification process began, and so did CO₂ absorption, as indicated by the decreased downstream CO₂ partial pressure (**Figure 3e**) and gas flow rate (**Figure 3f**). The deacidification process lasted from $t = 2$ hr until $t = 4.5$ hr when the voltage reached the programmed cutoff value of 1.4 V (**Figure 3b**). During deacidification, TA increased linearly as an effect of galvanostatic charging whereas the pH, although still increasing because of increasing hydroxide concentration, was buffered by the absorbed CO₂ and the subsequently formed carbonate and bicarbonate. Had there not been any CO₂ presence in the feed gas stream, the pH would have reached 14 at the end of deacidification. CO₂ absorption continued to occur until $t = 12$ hr, as indicated by the fact that both downstream flow rate (**Figure 3f**) and $p\text{CO}_2$ (**Figure 3e**) took that long to return to baseline. The flat regions in voltage (**Figure 3b**) and pH (**Figure 3d**) in between $t = 12$ to 13 hr also suggest the absorption reaction was in a steady-state regime.

The acidification+CO₂ outgassing process started at $t = 15$ hr, when a negative 20 mA cm⁻² current was applied (**Figure 3a**). Unlike the deacidification+CO₂ absorption process where the electrochemical reaction outpaced the chemical reaction significantly, the acidification and CO₂ outgassing had almost the same duration ($t = 15$ to 17.3 hr). This difference suggests that the deacidification+CO₂ absorption process is rate-limited by CO₂ absorption and the acidification+CO₂ outgassing process is rate-limited by the acidification rate, which is controlled by the current density. In this particular half-cycle, the CO₂ outgassing rate was 2.2 mL min⁻¹ (14 mL min⁻¹ – 11.8 mL min⁻¹ baseline).

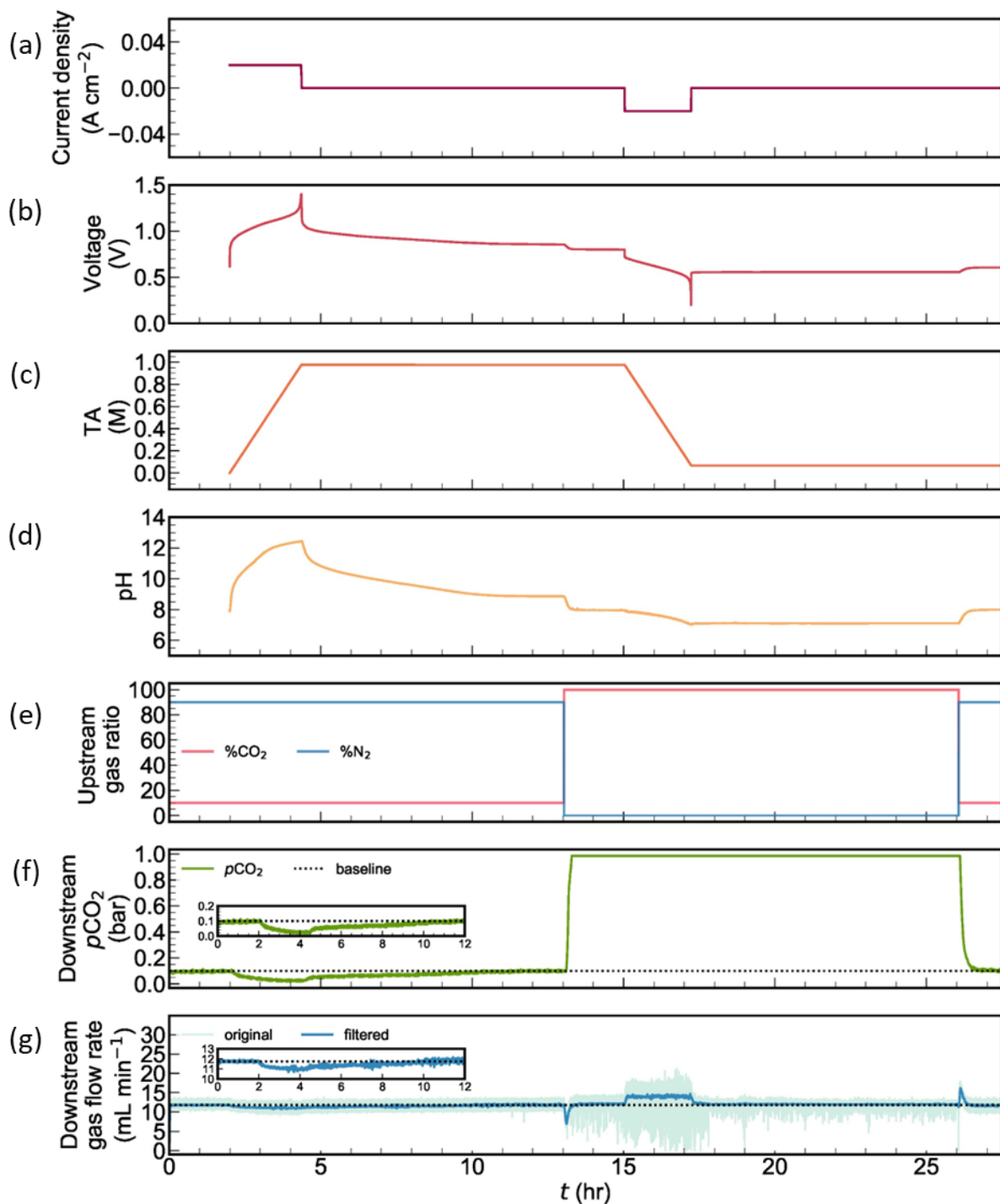


Figure 3. A CO₂ concentrating cycle with inlet pressure $p_1 = 0.1$ bar and exit pressure $p_3 = 1$ bar using a **1,8-ESP**-based flow cell at 20 mA cm^{-2} . Electrolytes comprised 10 mL 0.5 M **1,8-ESP** in 1.0 M KCl (negolyte, capacity-limiting) and 35 mL 0.3 M $\text{K}_4\text{Fe}(\text{CN})_6$ and 0.1 M $\text{K}_3\text{Fe}(\text{CN})_6$ in 1.0 M KCl (posolyte, non-capacity limiting). (a) Current density. (b) Voltage. (c) Total alkalinity. (d) pH of the negolyte. (e) N₂ and CO₂ percentage in the upstream source gas, controlled by mass flow controllers. (f) Downstream CO₂ partial pressure. The baseline indicates $p\text{CO}_2 = 0.1$ bar. Inset: Zoomed-in view of downstream CO₂ partial pressure in between $0 < t < 12$ hr, where CO₂ capture takes place. (g) Downstream total gas flow rate; the baseline is 11.8 mL min^{-1} . Inset: Zoomed-in view of downstream gas flow rate (filtered with a Savitzky-Golay filter.³⁵ The integrals of the filtered and the unfiltered data are the same) in between $0 < t < 12$ hr, where CO₂ capture takes place.

The effective amount of separated CO₂ could be calculated by integrating the difference between flow rate and the baseline (**Figure 3g**) over the CO₂ capture or outgassing region, and then subtracting the net amount captured and released in the transients during gas changes (e.g.

$t = 13$ to 13.3 hr and $t = 26$ to 26.3 hr).²³ In this cycle, 8.4 mmol or — assuming, throughout this paper, standard conditions of $T = 293$ K, $p = 1$ bar and ideal gas behavior — 202 mL of CO_2 was separated from a 10% inlet and concentrated to a 100% exit. The work input during deacidification was 917 J, calculated from integrating the product of current (**Figure 3a**) and voltage (**Figure 3b**) in between $t = 2$ hr and $t = 4.5$ hr. Similarly, the work returned during acidification was 479 J. Therefore, the overall cycle work was 438 J and the CO_2 molar cycle work was $52 \text{ kJ mol}_{\text{CO}_2}^{-1}$, which is obtained through dividing the cycle work by the effective amount of separated CO_2 . This value is modest compared with commercial amine scrubbing processes,³⁶ and is lower than that of the **DSPZ** cell, $61.3 \text{ kJ mol}_{\text{CO}_2}^{-1}$, at the same current density.²³

In addition to the molar energetic cost, the rate of capture and outgassing also affects the cost of the process at scale. In this cycle, the maximum CO_2 flow into the solution during capture was $0.7 \text{ mL}_{\text{CO}_2} \text{ min}^{-1}$ or $0.07 \text{ mL}_{\text{CO}_2} \text{ min}^{-1}$ per mL of solution and the max CO_2 outflow during outgassing was $1.8 \text{ mL}_{\text{CO}_2} \text{ min}^{-1}$ or $0.18 \text{ mL}_{\text{CO}_2} \text{ min}^{-1}$ per mL of solution. Conditions that influence the rate and optimization methods are discussed later in the text.

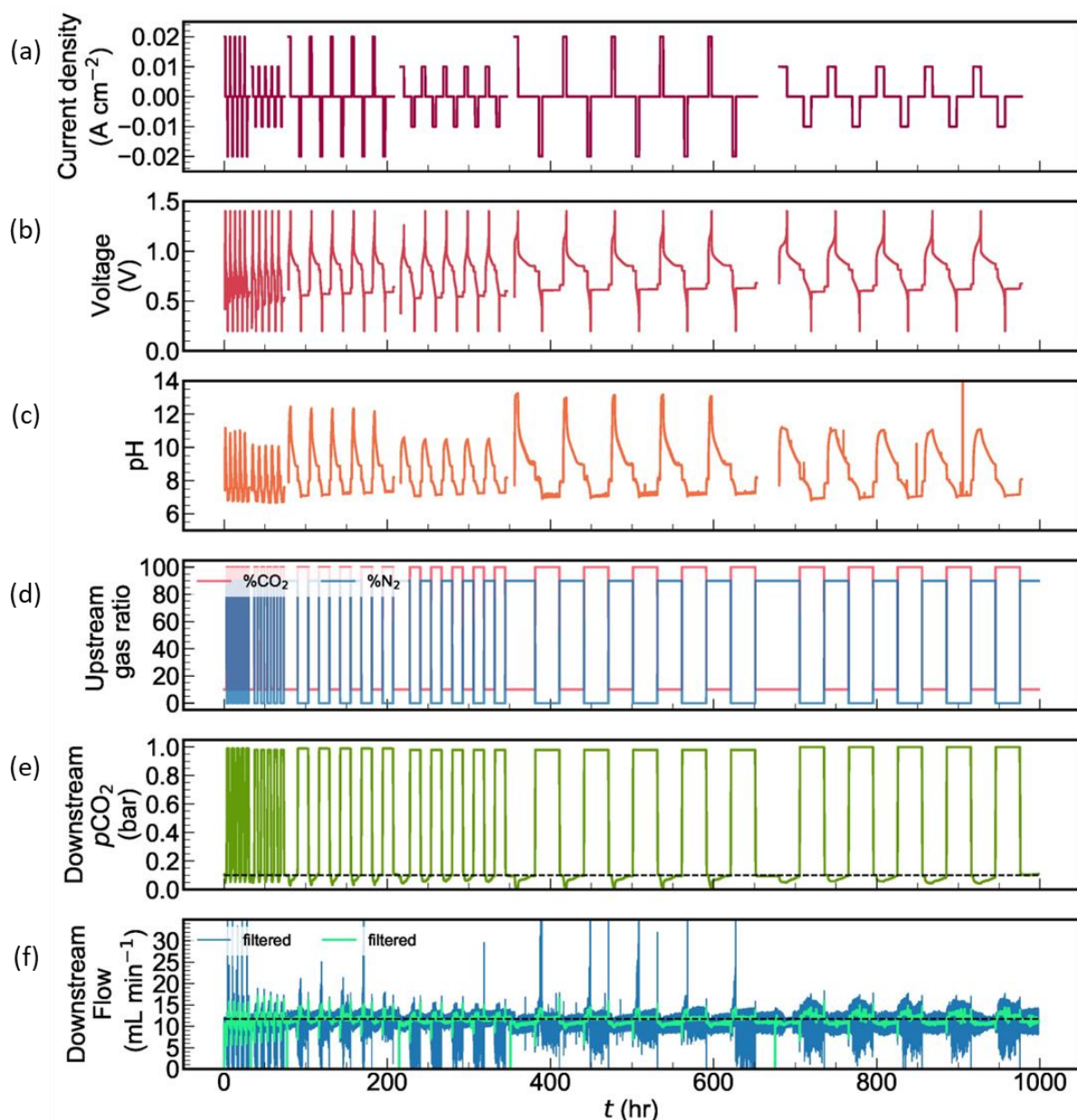


Figure 4. Thirty CO_2 concentrating cycles with the following conditions (5 cycles at each condition): 20 mA cm^{-2} 0.1 M **1,8-ESP**, 10 mA cm^{-2} 0.1 M **1,8-ESP**, 20 mA cm^{-2} 0.5 M **1,8-ESP**, 10 mA cm^{-2} 0.5 M **1,8-ESP**, 20 mA cm^{-2} 0.8 M **1,8-ESP**, 10 mA cm^{-2} 0.8 M **1,8-ESP**. The same cell as **Figure 3** was employed. (a) Current density. (b) Voltage. (c) pH of the negolyte. (d) N_2 and CO_2 percentage in the upstream source gas, controlled by mass flow controllers; total pressure 1.0 bar. (e) Downstream CO_2 partial pressure. (f) Downstream total gas flow rate.

The effect of current density and negolyte concentration on energy, capacity and capture/outgassing rate were explored next. **Figure 4** shows 30 electrochemical carbon separation cycles done under varying current densities and **1,8-ESP** concentrations. As the concentration of **1,8-ESP** increases, it takes longer to finish each cycle because of increased electron capacity and higher TA. Consequently, more CO_2 can be captured per unit volume, as shown in **Figure 5a**. With a 0.8 M **1,8-ESP** solution, a CO_2 capacity of close to $1.4 \text{ mol}_{\text{CO}_2} \text{ L}^{-1}$ or $1.8 \text{ mol}_{\text{CO}_2}$ per $\text{mol}_{1,8\text{-ESP}}$ is achieved. Such CO_2 loading per active material is comparable to the loading in amine scrubbing process, although the concentration of amines can be higher.³⁶⁻³⁷ Changing current densities does not change the capacity, but it has a significant impact on the CO_2 ingassing rate during deacidification+capture and outgassing rate during

acidification+desorption. The magnitude of both absorption flow and outgassing flow decreases as current density decreases (**Figure 5b**) because current density determines the rate of TA formation or consumption. The magnitude of peak absorption flow increases with **1,8-ESP** concentration because the rate of CO₂ absorption increases with hydroxide concentration,³⁸ which increases with **1,8-ESP** concentration. This trend is more obvious at the higher current density because more hydroxides can be accumulated due to the sluggish hydroxide-CO₂ reaction. In contrast, the max outgassing flow does not change significantly across the three concentrations because, unlike the absorption case, the rate of hydroxide consumption, i.e. current density, is the rate-limiting reaction in the acidification+desorption process. To increase overall productivity, i.e. CO₂ separation per unit time, it is essential to raise the CO₂ capture rate because it is significantly slower than the outgassing rate. One method is to use a contactor engineered for high gas-solution interaction surface area.¹³ Another approach is to incorporate promoters, which are molecules that enhance the CO₂ capture rate of caustic solutions.³⁹ Heating the solution may also increase the rate, although the capacity may be compromised.⁴⁰

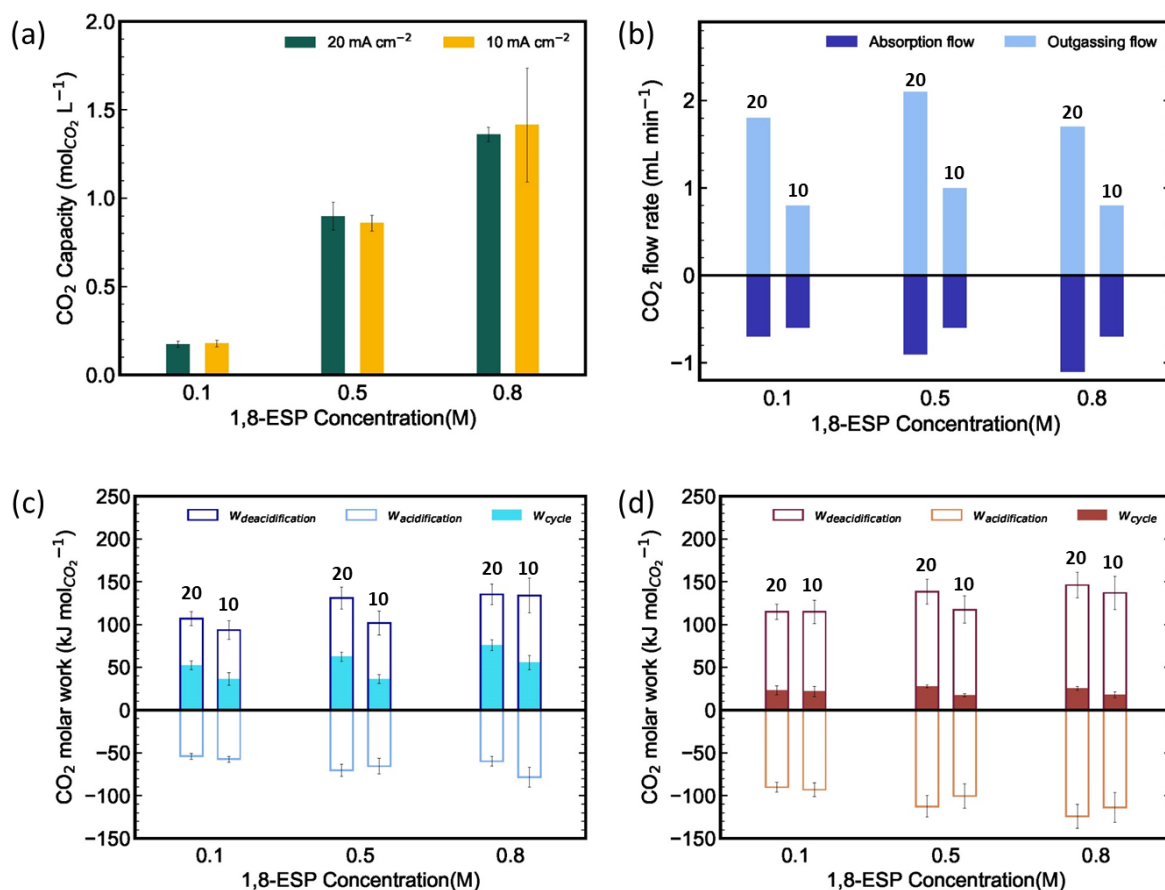


Figure 5. Bar-plots that summarize CO₂ separation performance at different **1,8-ESP** concentrations and current densities. The error bars represent standard deviation calculated over five cycles under each condition. (a) CO₂ capacity per liter solution. (b) Max CO₂ outgassing rate during acidification+desorption (positive) and max CO₂ ingassing rate during deacidification+absorption (negative). (c) CO₂ molar deacidification, acidification and cycle work obtained under alternating 10% CO₂/90% N₂ during deacidification and 100% CO₂ during acidification. (d) CO₂ molar deacidification, acidification and cycle work when the cell was cycled in a pure N₂ atmosphere.

The CO₂ molar work cost of the carbon capture cycles (**Figure 5c**) is compared with that of the cycles performed under N₂ (**Figure 5d**). The latter represents the energy loss caused by internal cell dissipation, i.e. only ohmic, electron transfer and mass transport losses; it is evaluated by dividing the measured deacidification, acidification and cycle work in the absence

of CO₂ by the amount of captured CO₂ measured in the carbon capture cycle of the same current density and **1,8-ESP** concentration. The deacidification work of the cycles under CO₂ is lower than that of the CO₂-free cycles because CO₂ absorption decreases the negolyte pH, thereby decreasing the overall cell voltage. The same mechanism decreases the magnitude of the returned work during acidification in the cycles under CO₂. The average pH during deacidification is around 10.5 and 13.5 for CO₂ and N₂ cycling, respectively, whereas the average pH during acidification is around 7.5 and 13.5 respectively. The greater pH gap during acidification, caused by higher CO₂ partial pressure in the head space, causes a net increased cycle work. As the concentration of **1,8-ESP** increases, the pH gap in acidification increases, which leads to a positive correlation between **1,8-ESP** concentration and cycle work. Lower current density also leads to lower cycle work because of smaller cell losses. It is noteworthy that 36.4 kJ mol_{CO₂}⁻¹ CO₂, a remarkably low value, is achieved at both 0.1 and 0.5 M using 10 mA cm⁻² current density. **Table 2** summarizes the capture cell properties studied in this work. At low concentration only a minimal amount of capture work is needed to drive the system, but this comes at the cost of volumetric capture capacity and reaction rate. At high concentration, capture capacity can be an order of magnitude higher, and the rate is faster, but the molar cycle work increases: increased cell resistance is expected when the solution viscosity is high (**Table S2**).

Table 2 Summary of cell metrics at different **1,8-ESP** concentrations and current densities.

Concentration (M)	Current density (mA cm ⁻²)	Cycle work (kJ mol _{CO₂} ⁻¹)	Max absorption/desorption flow rate (mL min ⁻¹)	CO ₂ capture capacity (mol _{CO₂} L ⁻¹)	Discharge capacity (Ah L ⁻¹)	Capacity fade rate (%/day) ^a
0.1	20	52.4	-0.7 / 1.8	0.18	5.0	0.00
	10	36.4	-0.6 / 0.8	0.17		(0.00) ^b
0.5	20	62.5	-0.9 / 2.1	0.90	22.2	0.01
	10	36.4	-0.6 / 1.0	0.86		
0.8	20	75.9	-1.1 / 1.7	1.36	42.7	0.01
	10	55.2	-0.7 / 0.8	1.41		

^aUnder nitrogen atmosphere. ^bUnder pure CO₂ atmosphere.

Although various CO₂ capture methods with promising performance have been achieved, few studies have addressed the operational lifetime of such device, and the stability of CO₂ capture material remains a major challenge. We investigated the chemical stability of **1,8-ESP** carefully through elevated temperature chemical degradation studies. **1,8-ESP** solution at 45 °C was monitored by time-dependent NMR spectroscopy and no chemical decomposition is found over more than 100 days from the NMR spectra (**Figure 6a**). We attribute such high molecular stability to the chemically inert carbon linkage between the soluble functional groups (-SO₃H) and the phenazine core in the structure of **1,8-ESP**. It avoids the decomposition from nucleophilic substitution and hydrolysis of the molecule.^{31, 41} It has been observed in our previous work that the reduced state of phenazine derivatives tends to tautomerize and lose its reversible redox activities.⁴²⁻⁴³ The reduced state of **1,8-ESP** at 45 °C was compared with an internal standard, showing no degradation. DFT theoretical study corroborated the chemical stability of **1,8-ESP** in its reduced state whose standard free energy of tautomerization (ΔG) is calculated to be >45 kJ mol⁻¹ (**Table S3**), excluding the tautomerization pathway.

We investigated long term cycling stability of a **1,8-ESP** cell in 0.1 M by imposing 550 charge-discharge cycles over 16 days under nitrogen atmosphere. Cycles began with a

galvanostatic process at 20 mA cm^{-2} until voltage limits of 1.4 V on charging and 0.4 V on discharging were reached, followed by potentiostatic processes that lasted until the magnitude of the current density fell to 4 mA cm^{-2} . The cell exhibited no perceptible capacity fade, which is in agreement with the absence of chemical decomposition products detected after cycling by NMR (**Figure 6c** and **Figure S22**). Both of 0.5 M and 0.8 M **1,8-ESP** cells showed an extremely low fade rate²⁷ of around 0.01%/day during 14 days testing (**Figure S10** and **Table 2**) but, if this fade rate were to continue unchanged, it would be low enough for decadal implementation. The compatibility of **1,8-ESP** with CO_2 is also vital to the system lifetime as it has been reported that a significant number of molecules can bind with CO_2 and precipitate out from the solution⁴⁴ or enhance molecular decomposition.⁴⁵ The operational stability of the **1,8-ESP** carbon capture system was investigated with capture-release cycles with pure CO_2 (99.9%) as the feed gas (**Figure 6d**). During 220 cycles over 18 days, the voltage profiles reflecting the continuous CO_2 capture and release processes exhibited high reproducibility. No precipitation occurred and no chemical decomposition products were detected by NMR (**Figure S23**), indicating compatibility of **1,8-ESP** with CO_2 . The system stability is also exhibited in the retention of the discharge capacity: no discharge capacity decay was observed during cycling, suggesting excellent system stability.

Finally, we investigated the performance of the cell when it is isolated from CO_2 and operated as a pure energy storage system. In **Figure S11** we show the polarization and long-term cycling performance of a **1,8-ESP** cell with 2.0 M electron concentration, corresponding to a volumetric capacity of 54.0 Ah per liter of negolyte. The cell exhibited an average open-circuit voltage exceeding 1.1 V. When a current density at 20 mA cm^{-2} was applied in purely galvanostatic cycling, the coulombic efficiency was above 99.9% and the capacity utilization reached 92.6% with a round-trip energy efficiency of 78.5%. We first applied galvanostatic cycling for ~10 days with no obvious capacity fade being observed. This was then followed by a galvanostatic-potentiostatic cycling regimen which accesses almost all of the theoretical capacity (95%) for more than 180 days and found a low capacity fade rate of 0.008%/cycle (0.05%/day), demonstrating its excellent performance to be among those of state-of-the-art flow batteries.²⁷ The operator would have the flexibility of timing cell charging and discharging based on electricity prices with the added flexibility of either exposing the electrolyte to CO_2 for capture, or isolating the electrolyte from CO_2 in order to maximize instantaneous revenue from energy storage.

Presently, we expect **1,8-ESP** to be excellent for energy storage and for CO_2 capture from flue gas, which has a CO_2 concentration of order 10% and a relatively low O_2 concentration. However, although it is more stable than **DSPZ** against chemical oxidation by atmospheric O_2 , **1,8-ESP** still lacks sufficient stability to be useful for direct air capture (DAC) of CO_2 . This chemical oxidation by O_2 is reversible and so can be counteracted by, e.g., electrochemical reduction; however, the additional pulse of electrochemical reduction simultaneously oxidizes the posolyte, leading to a cell out-of-balance situation. Effective cell rebalancing can be accomplished and the original chemical compositions of both electrolytes restored by reverse polarization,²³ driving the oxygen evolution reaction; however, the loss of efficiency is currently too high for realistic applications in DAC. A high priority for future research is the development of molecules with the advantages of **1,8-ESP** but which also have sufficient

stability against O₂ to be deployed in DAC.⁴⁶ Another complementary approach is to develop additives that anodically shift the reduction potential of the redox active molecules.⁴⁷

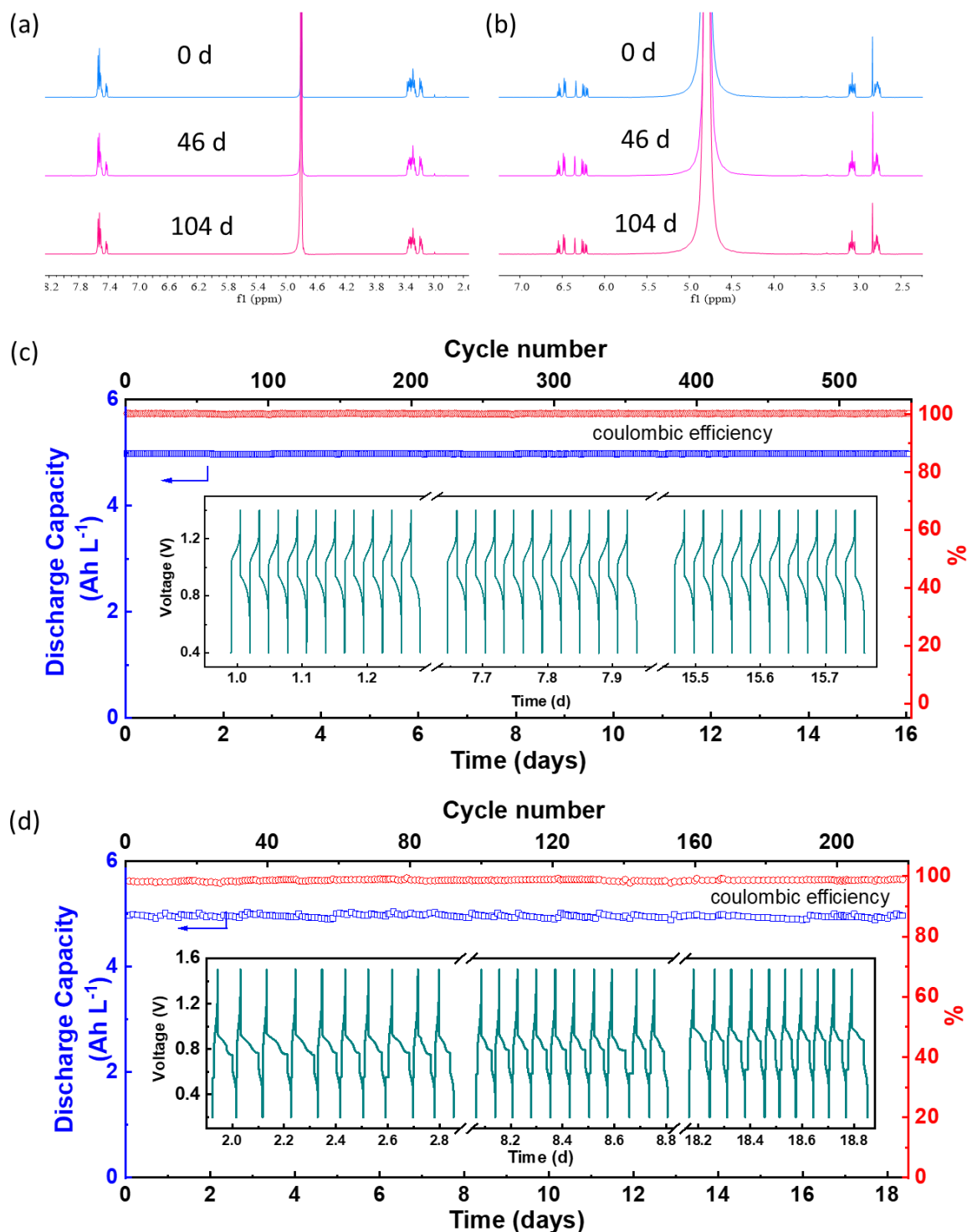


Figure 6. (a) Time-dependent ¹H NMR spectra of **1,8-ESP** (oxidized state) at 45 °C. (b) Time-dependent ¹H NMR spectra of the reduced state of **1,8-ESP** with 0.01 M NaCH₃SO₃ as the internal standard (2.83 ppm) at 45 °C. Galvanostatic-potentiostatic cycling performance of 0.1 M **1,8-ESP** full cell (c) under N₂ and (d) with CO₂ capture and release cycles. The red and blue symbols represent coulombic efficiency and discharged capacity respectively, and the inset shows representative voltage versus time curves. The cell is assembled with an NC700 membrane

and carbon cloths (ELAT-Hydrophilic) electrode. Negolyte: 7 mL 0.1 M **1,8-ESP** in 1.0 M KCl. Posolyte: 40 mL 0.1 M K₄Fe(CN)₆ and 0.02 M K₃Fe(CN)₆ in 1.0 M KCl solution.

Conclusion

In this work, an electrochemical CO₂ capture system with coupled electricity storage based on a **1,8-ESP** flow cell is developed and is demonstrated to possess high capacity, high stability, and low energetic cost. The newly developed molecule **1,8-ESP** shows excellent aqueous solubility, reversible electroactivity, fast kinetics, high chemical stability, and low permeation through membranes in cells. For CO₂ capture, the relationships between electrolyte concentration and volumetric capacity, energetic cost, and capture rate are established. The CO₂ capture system with 0.8 M **1,8-ESP** exhibits a volumetric CO₂ capture capacity of 1.4 mol_{CO₂} L⁻¹ with an energetic cost of 55.2 kJ mol_{CO₂}⁻¹ at 10 mA cm⁻²; results under these and other conditions are summarized in Table 2. The cell offers high performance as a pure energy storage device when isolated from CO₂, which enables the operator to increase revenue by operating purely for electricity price arbitrage when market conditions call for it, and implementing CO₂ capture at other times. A 220-cycle cell test with continuous CO₂ capture and release over 18 days left no evidence of chemical decomposition in the electrolyte; a 1200-cycle cell test for pure energy storage performance with a negolyte capacity of 54.0 Ah L⁻¹ over 180 days exhibited a low capacity fade rate of 0.05%/day. These results show that **1,8-ESP** can be the basis of a high-performance system for CO₂ capture, energy storage, or both.

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Data availability

All data generated or analyzed during this study are included in the published article and its Supplementary Information

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