Supporting Information

"Relationships between the elemental composition of electrolytes and the Supercapacitive Swing Adsorption of CO₂"

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Section S1. SSA electrode, module and operation.

The SSA electrodes were prepared using the method reported in our previous publication.^{1,2} Briefly, BPL 4x6 carbon (Calgon), conductive carbon black (VXCMAX22, Cabot Corporation), gluten (Hodgson Mill, food grade) and polytetrafluoroethylene (PTFE, 60% dispersion in H₂O, Sigma-Aldrich) with a mass ratio of 80:5:10:5 were dispersed in ethanol by sonication, and stirred at 65 °C for 2 hours. The mixture was then heated to 80 °C to evaporate the ethanol until becoming a dough. The dough was pressed using a pasta machine into flat sheets of 0.6-0.7 mm thickness. Two 7 cm × 7 cm sheets were cut, dried, and used as electrodes.

The SSA module used a radial gas flow design as reported in our previous work.² A schematic diagram of an SSA module is shown in Figure S1. Two mirror-polished titanium grade 7 plates (Tricor Metals., *3* and *8* in Figure S1) with 13 cm \times 13 cm \times 1 cm size served as mechanical support and current collector for the module. The gas flowed in a radial pattern from the gas inlet port (*1* in Figure S1) in the center through the carbon cloth to the outlet (*2* in Figure S1) in the periphery of the upper plate. Both gas ports were of 1 mm diameter and connected to 1/8" diameter stainless steel tubing via Swagelok connectors. The entire module was held together by 13 set screws fed through 13 holes near the edge of each titanium plate.



Figure S1. An SSA gas separation module, cross-sectional view. 1. Gas inlet. 2. Gas outlet.
3. Upper plate. 4. Carbon cloth. 5. Negative electrode (made of BPL 4x6 carbon, conductive carbon black, gluten and polytetrafluoroethylene with a mass ratio of 80:5:10:5).
6. Separator. 7. Positive electrode (made of BPL 4x6 carbon, conductive carbon black, gluten and polytetrafluoroethylene with a mass ratio of 80:5:10:5).
8. Bottom plate. 9. Gasket.

One electrode was soaked in the electrolyte solution for 2 h, and used as positive electrode (7 in Figure S1). The other electrode was not soaked in the electrolyte and used as negative electrode (5 in Figure S1). A filter paper (Whatman Grade 2, GE Healthcare Life Sciences) with 8 cm \times 8 cm size was wetted by the same electrolyte solution and used as a separator between the two electrodes (6 in Figure S1). A 9 cm \times 9 cm EPDM rubber sheet (1/16", McMaster-Carr, 9 in Figure S1) with an 8 cm \times 8 cm opening was placed between the upper and bottom plates and served as gasket. The sandwich made of the two electrodes and the separator was placed in the opening area of the gasket with the positive electrode being in contact with the bottom plate. A 7.5 cm \times 7.5 cm sized carbon cloth (AvCarb 1071 HCB, 4 in Figure S1) was placed between the negative electrode and the upper plate, and acted as gas diffusion layer. The upper and bottom plates were then clamped together by electrically insulated set screws. These screws were tightened evenly to 20 in.lb using a torque wrench.

A flow scheme for the SSA module in operation is shown in Figure S3. The SSA module was fed by a $15\% \text{ CO}_2/85\% \text{ N}_2$ gas mixture serving as a flue gas simulant. Before entering the SSA module, the gas mixture was moistened by bubbling it through the electrolyte solution (2 in Figure S3). A mass flow controller (Alicat MC-10SCCM-D/5M, 3 in Figure S3) was used to control the gas flow rate at 1 sccm. The effluent gas was dried in a custommade drying tube (Swagelok, 5 in Figure S3), and then analyzed by a CO₂ analyzer (Quantek Instrument, Model 906, 6 in Figure S3).

The SSA module was electrically controlled and monitored using a potentiostat (Gamry Reference 3000, 7 in Figure S3) in a two-electrode configuration. The negative electrode was defined as the working electrode, while the positive electrode served as counter and reference electrode.



Figure S2. A scheme for the operation of an SSA module in gas flow-through mode. 1.
Gas cylinder containing a 15% CO₂/85% N₂ gas mixture. 2. Bubbling moistener
containing 1 M NaCl solution. 3. Mass flow controller. 4. SSA module. 5. Drying tube. 6.
CO₂ analyzer. 7. Potentiostat.

Section S2. SSA performance metrics.

The SSA energetic metrics were calculated from voltage curves, and include the electric resistance (R, Ω .cm²), the specific capacitance (C, F.g⁻¹), the Coulombic efficiency (η_c , %), the energy efficiency (η_e , %), and the energy loss (ΔE , J).

The electrical resistance of the SSA module was determined using voltage drop method³ as

$$R = \frac{V_{Pstat} - V_{drop}}{I} \quad , \tag{S1}$$

where V_{Pstat} (V) is the voltage at potentiostatic step (either 0 or -1 V), V_{drop} (V) is the voltage at the very beginning of the galvanostatic charge or discharge step, and I (A) is the constant current (50 mA in this study).

The specific capacitance was calculated from the galvanostatic charge curve using⁴

$$C = \frac{4 \cdot l \cdot t_g}{m \cdot \Delta U} \quad , \tag{S2}$$

where t_g (s) is the galvanostatic charge duration, m (g) is the total mass of activated carbon in the two electrodes, and ΔU (V) is the change in cell voltage. Note that only the galvanostatic charge steps contribute to the specific capacitance. The holding steps, if any, do not affect the *C* value due to either I = 0 (in open circuit step) or $\Delta U = 0$ (in potentiostatic step).

The Coulombic efficiency is calculated by

$$\eta_c = \frac{Q_c}{Q_d} \times 100\% \quad , \tag{S3}$$

where Q_c (C) and Q_d (C) are the total charge flowed into or out of the SSA module during charge and discharge process (galvanostatic charge/discharge step plus the following holding step if any), respectively.

The energy efficiency is calculated by

$$\eta_e = \frac{E_c}{E_d} \times 100\% \quad , \tag{S4}$$

where E_c (J) and E_d (J) are the total energy consumed or delivered by the SSA module during the charge and discharge process (galvanostatic charge/discharge step plus the following holding step if any), respectively.

The energy loss is calculated as

$$\Delta E = E_c - E_d \quad , \tag{S5}$$

Five adsorptive metrics were used to evaluate SSA performance. They are the adsorption capacity (AC, mol.kg⁻¹), the charge efficiency (A, dimensionless), the energy consumption (EC, kJ.mol⁻¹), the adsorption rate (AR, mol.kg⁻¹.s⁻¹), and the time-energy efficiency (TEE, mol.kJ⁻¹.s⁻¹).

The adsorption capacity indicates the CO₂ amount adsorbed per unit mass of carbon material, and is calculated as

$$AC = \frac{n_{a,CO2}}{m_{n,e}} , \qquad (S6)$$

where $m_{n.e}$ (kg) is the weight of activated carbon in the negative electrode, and $n_{a,CO2}$ (mol) is the amount of adsorbed CO₂. Our previous study has demonstrated the high selectivity of SSA effect for CO₂ over N₂.⁵ Therefore, $n_{a,CO2}$ can be calculated according to

$$n_{a,CO2} = \frac{P}{RT} (\int_0^t f_i dt - \int_0^t f_e dt),$$
 (S7)

where t (s) refers to the time of the total charge process, including the galvanostatic charge step and the following holding step if any; T (296 K) is the temperature, and R (8.314 J.mol⁻¹.K⁻¹) is the ideal gas constant; f_i and f_e (L.s⁻¹) are the flow rate of SSA influent (1.7 × 10⁻⁵ L.s⁻¹) and effluent gas, respectively. The SSA effluent flow rate is calculated as

$$f_e = \frac{100 - C_i}{100 - C_e} f_i \quad , \tag{S8}$$

where C_i and C_e (%) are CO₂ concentration in SSA influent (15%) and effluent gas, respectively. C_e was measured and recorded by the CO₂ analyzer (6 in Figure S2).

The charge efficiency is the ratio of adsorbed CO_2 over the charge stored in the electrodes during electrical charging, as

$$\Lambda = \frac{n_{a,CO_2}}{n_c} = \frac{n_{a,CO_2}}{Q_c} \times F \quad , \tag{S9}$$

where n_{a, CO_2} (mol) is the amount of adsorbed CO₂, n_c (mol) and Q_c (C) is the amount of capacitively stored charges, and *F* (96 485 C.mol⁻¹) is Faraday constant.

The energy consumption is defined as the energy consumed per unit of adsorbed CO_2 , and is calculated as

$$EC = \frac{\Delta E}{n_{a,CO2}} \quad . \tag{S10}$$

The CO_2 adsorption rate is the amount of CO_2 adsorbed per unit of carbon material mass and time, and is calculated as

$$AR = \frac{n_{a,CO2}}{m_{n,e} \times t} \quad , \tag{S11}$$

Time-energy efficiency refers to the adsorbed CO_2 amount per unit energy and time, and is calculated as

$$TEE = \frac{n_{a,CO2}}{\Delta E \times t} .$$
(S12)

Section S3. A representative cyclic voltammetry curve of SSA module.



Figure S3. A representative cyclic voltammetry curve of an SSA module using 1.0 M NaCl as electrolyte and feeding by $15\% \text{ CO}_2/85\% \text{ N}_2$ gas mixture. Scan rate: 1 mV.s⁻¹.

Section S4. Ion properties.

The ion electrical mobility (μ , m².V⁻¹.s⁻¹) is calculated from ion diffusion coefficient (D, m².s⁻¹) using Einstein relation:⁶

$$\mu = \frac{q}{kT}D, \qquad (S13)$$

where q (eV) is the charge of the ion, k (8.6×10⁻⁵ eV.K⁻¹) is Boltzmann constant, and T (298 K) is the temperature. The ion diffusion coefficient value is obtained from literature.⁶ The electrical mobility value of ions studied in this work is listed in Table S1.

Ionic potential is calculated as the charge of ion divided by its hydrated radius.^{7,8} The data for cation radius were obtained from literature.⁹

Ion	Electrical mobility (10 ⁻⁸ m ² .V ⁻¹ .s ⁻¹)	Hydrated ionic potential (eV.pm ⁻¹)
H^+	36.22	0.36
Li ⁺	4.01	0.26
Na ⁺	5.19	0.28
K^+	7.62	0.30
Mg^{2+}	5.49	0.47
F-	5.74	0.29
Cl-	7.90	0.30
Br⁻	8.09	0.30
HCO ₃ -	4.61	0.27
SO_4^{2-}	16.57	0.27
CO ₃ ²⁻	14.36	0.51

Table S1. Properties of ions studied in this work.

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