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Supporting Information for:

Ionization controls for biomineralization-inspired CO_2 chemical looping at constant room temperature

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1. Figures

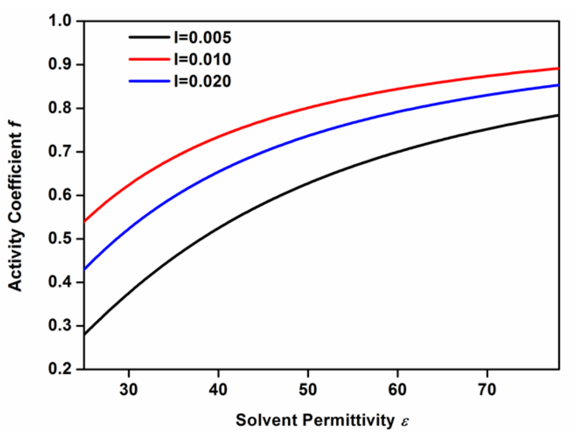

Figure S1. Relationship between activity coefficient $f_{\pm}$ and ε. The results were calculated from eqs. 5-7 (T = 298 K, N_A=6.02×10^{23}, k=1.38×10^{-16} erg/K, e=4.8024×10^{-10} esu, a =10^{-1} nm, $z_+ = z_- = 1$). The figure demonstrates that solvent permittivity reducing was followed by activity coefficient decrease.

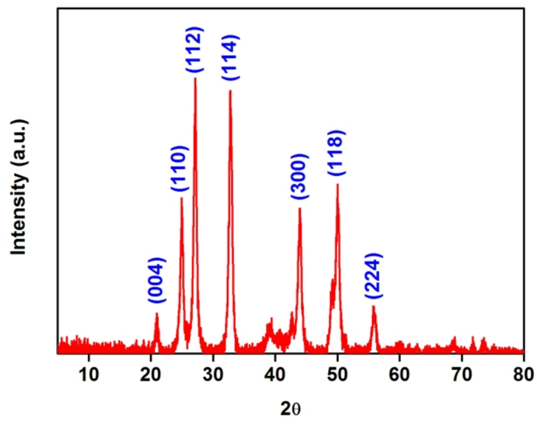

Figure S2. XRD pattern of the resulted precipitates during the CO_2 capture. It shows that the solid is vaterite.

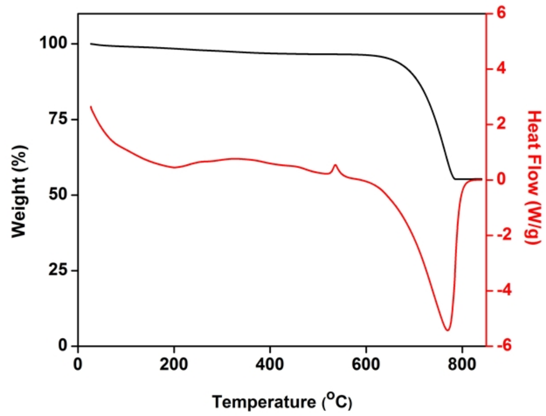

Figure S3. TGA of the resulted precipitates during the CO_2 capture. It confirms that the vaterite do not contain either water or ethanol.

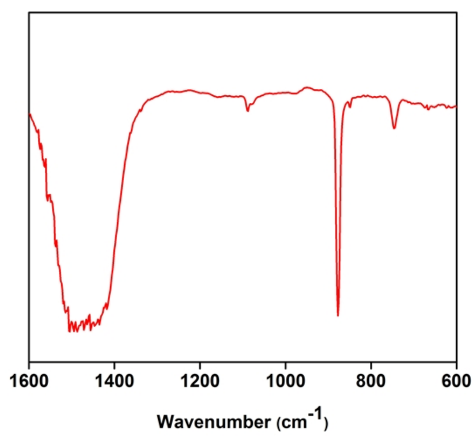

Figure S4. FT-IR of the resulted precipitates during the CO_2 capture. It confirms that the solid is pure vaterite.

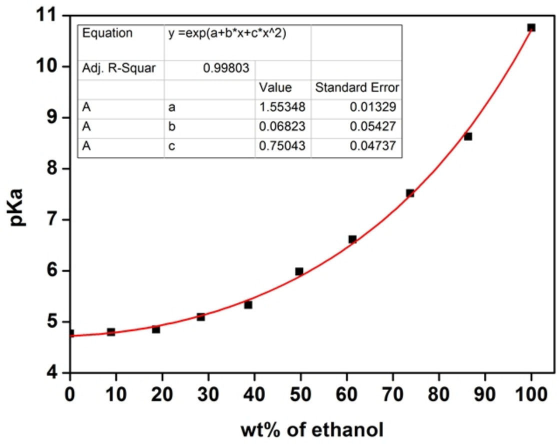

Figure S5. Calculated pK_a values of HAc in the binary solvent (line), which fits the experimental data (solid squares) well.[1]

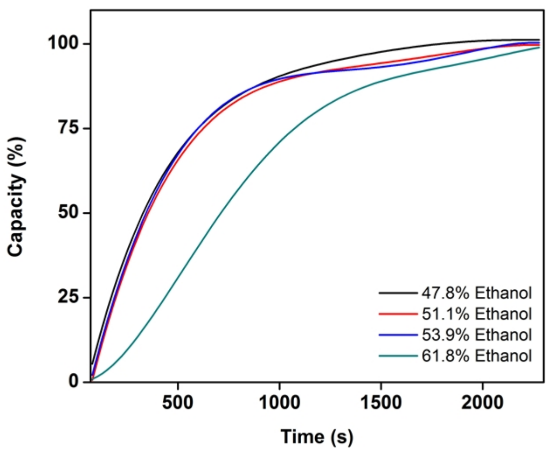

Figure S6. CO_2 absorption kinetics in $Ca(Ac)_2$-C_2H_5OH-H_2O. The $Ca(Ac)_2$ concentration was fixed at 0.08 M.

2. Tables

Table S1. CO_2 capture in different organic/water binary solvent.

Organic solvent	ε_i [a]	ε_{eff} [b]	Reactivity[c]
Water	78.5	78.5	No
Glycerol	46.5	55.1	No
1,2-Ethanediol	41.4	51.2	No
Methanol	33.0	44.7	Yes
Ethanol	24.5	37.9	Yes
Tetraethylene glycol	20.4	34.6	Yes
Tetrahydrofurfuryl alcohol	13.5	28.9	Yes
Diethylene glycol dimethylether	7.2	23.6	Yes

[a] ε_i, permittivity of pure organic solvent.
[b] ε_{eff}, permittivity of binary solvent.
[c] Reactivity means whether CO_2 can be captured by the system containing 0.05 M $Ca(Ac)_2$ in the binary solvent containing 70% (v/v) organic solvent.

It is better to choose a solvent with low permittivity, low vapor pressure, high boiling point, low viscosity, unreactive and miscible with water, and low toxicity is necessary for CO_2 capture in industry.

Table S2. Fitting of HAc K_a in C_2H_5OH-H_2O binary solvent.[a]

wt % of ethanol	Slope	Intercept	r^2
0	2.60E-08	8.17E-07	0.9996
9	1.17E-08	-3.35E-07	0.9981
19	4.69E-09	-1.03E-06	0.9999
28	1.85E-09	-6.39E-07	0.9997
39	8.78E-10	-1.76E-06	0.9811
50	2.01E-10	-1.94E-07	0.9987
61	5.70E-11	-8.06E-08	0.9980
74	1.10E-11	-1.00E-07	0.9984
86	1.21E-12	-3.06E-08	0.9984
100	1.82E-14	-9.58E-10	0.9018

[a] Raw data were measured in C_2H_5OH-H_2O binary solvent containing different concentrations of HAc. The result of each fitting was calculated and shown in Figure S4. r^2, goodness of fit.

Table S3. Data of ionization degree and pH in Figure 2.

wt% of ethanol	Concentration of HAc (mmol/L)	pH	Ionization degree (%)
0.0	25.00	3.2	2.7
9.4	25.00	3.2	2.5
19.1	25.00	3.3	2.2
28.9	25.00	3.4	1.7
38.7	25.00	3.5	1.3
48.4	25.00	3.7	0.8
58.2	25.00	4.0	0.4
68.0	25.00	4.3	0.2
77.7	25.00	4.7	0.1
87.5	25.00	5.3	0.0
97.3	25.00	5.9	0.0
0.0	12.50	3.3	3.8
9.4	12.50	3.4	3.5
19.1	12.50	3.4	3.0
28.9	12.50	3.5	2.4
38.7	12.50	3.7	1.8
48.4	12.50	3.9	1.1
58.2	12.50	4.1	0.6
68.0	12.50	4.5	0.3
77.7	12.50	4.9	0.1
87.5	12.50	5.4	0.0
97.3	12.50	6.1	0.0
0.0	6.24	3.5	5.3
9.4	6.24	3.5	4.9
19.1	6.24	3.6	4.3
28.9	6.24	3.7	3.4
38.7	6.24	3.8	2.5
48.4	6.24	4.0	1.6
58.2	6.24	4.3	0.9
68.0	6.24	4.6	0.4
77.7	6.24	5.1	0.1
87.5	6.24	5.6	0.0
97.3	6.24	6.2	0.0
0.0	3.12	3.6	7.4
9.4	3.12	3.7	6.8
19.1	3.12	3.7	6.0
28.9	3.12	3.8	4.8
38.7	3.12	4.0	3.5
48.4	3.12	4.2	2.2
58.2	3.12	4.4	1.2
68.0	3.12	4.8	0.5
77.7	3.12	5.2	0.2

wt% of ethanol	Concentration of HAc (mmol/L)	pH	Ionization degree (%)
87.5	3.12	5.7	0.1
97.3	3.12	6.4	0.0
0.0	1.56	3.8	10.3
9.4	1.56	3.8	9.5
19.1	1.56	3.9	8.3
28.9	1.56	4.0	6.7
38.7	1.56	4.1	4.9
48.4	1.56	4.3	3.1
58.2	1.56	4.6	1.7
68.0	1.56	4.9	0.8
77.7	1.56	5.4	0.3
87.5	1.56	5.9	0.1
97.3	1.56	6.5	0.0
0.0	0.78	4.0	14.3
9.4	0.78	4.0	13.2
19.1	0.78	4.0	11.6
28.9	0.78	4.1	9.4
38.7	0.78	4.3	6.9
48.4	0.78	4.5	4.4
58.2	0.78	4.7	2.4
68.0	0.78	5.1	1.1
77.7	0.78	5.5	0.4
87.5	0.78	6.0	0.1
97.3	0.78	6.7	0.0
0.0	0.39	4.1	19.6
9.4	0.39	4.2	18.1
19.1	0.39	4.2	16.0
28.9	0.39	4.3	13.0
38.7	0.39	4.4	9.6
48.4	0.39	4.6	6.2
58.2	0.39	4.9	3.4
68.0	0.39	5.2	1.5
77.7	0.39	5.7	0.6
87.5	0.39	6.2	0.2
97.3	0.39	6.8	0.0
0.0	0.20	4.3	26.4
9.4	0.20	4.3	24.6
19.1	0.20	4.4	21.8
28.9	0.20	4.5	17.9
38.7	0.20	4.6	13.3
48.4	0.20	4.8	8.6
58.2	0.20	5.0	4.8
68.0	0.20	5.4	2.2

wt% of ethanol	Concentration of HAc (mmol/L)	pH	Ionization degree (%)
77.7	0.20	5.8	0.8
87.5	0.20	6.3	0.2
97.3	0.20	7.0	0.1
0.0	0.10	4.5	35.1
9.4	0.10	4.5	32.9
19.1	0.10	4.5	29.3
28.9	0.10	4.6	24.3
38.7	0.10	4.8	18.2
48.4	0.10	4.9	12.0
58.2	0.10	5.2	6.7
68.0	0.10	5.5	3.1
77.7	0.10	6.0	1.1
87.5	0.10	6.5	0.3
97.3	0.10	7.1	0.1

Table S4. Data of balance value in Figure 3

Concentration of $Ca(Ac)_2$ (mol/L)	Balance value (wt % of ethanol)	Concentration of $Ca(Ac)_2$ (mol/L)	Balance value (wt % of ethanol)
0.010	67.2	0.108	45.6
0.014	63.1	0.116	45.4
0.023	58.8	0.123	45.3
0.031	55.5	0.131	45.2
0.039	53.0	0.139	45.1
0.047	51.1	0.146	45.1
0.054	49.6	0.154	45.0
0.062	48.5	0.162	45.0
0.070	47.6	0.169	45.0
0.077	47.0	0.177	45.0
0.085	46.5	0.185	44.9
0.093	46.1	0.192	44.9
0.100	45.8	0.200	44.9

Table S5. Fitting of enthalpy change of reaction in C_2H_5OH-H_2O binary solvent.[a]

wt % of ethanol	slope	intercept	r^2
47.8	-3861.5	5.4192	0.9839
51.1	-2853.7	3.9259	0.9890
53.9	9083.9	-35.874	0.9958
58.4	4139.6	-19.401	0.9631
61.8	-3621.6	7.157	0.9306

[a] Raw data was measured from $Ca(Ac)_2$-C_2H_5OH-H_2O system containing 0.08 M $Ca(Ac)_2$. The result of each fitting was calculated and shown in Figure 3. r^2 represents the goodness of fit.

3. Discussion

Influence of solubility against acid dissolution. The solubility of $CaCO_3$ in water is 1.3×10^{-5} g/mL at 25 ^oC.[2,3] However, the amount of $CaCO_3$ dissolved by HAc is significantly higher. For example, about 5.3×10^{-4} g/mL $CaCO_3$ dissolved by changing 80 wt% of ethanol to 50 wt% with 0.05 M $Ca(Ac)_2$, which is 40 times higher than the solubility, indicating that the influence of solubility is regardless to the acid dissolution.

Reference

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