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# Ionization controls for biomineralization-inspired CO<sub>2</sub> chemical looping at constant room temperature

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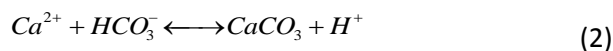
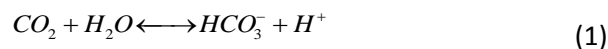
Living organisms such as corals can do CO<sub>2</sub> looping efficiently via biomineralization under ambient conditions. Inspired by this natural process, we establish a solution system of calcium acetate-ethanol-water (Ca(Ac)<sub>2</sub>-C<sub>2</sub>H<sub>5</sub>OH-H<sub>2</sub>O) for CO<sub>2</sub> chemical looping at constant room temperature. The CO<sub>2</sub> capture is achieved by its reaction with Ca(Ac)<sub>2</sub> to form calcium carbonate (CaCO<sub>3</sub>) mineral and HAc in the binary solvent with high C<sub>2</sub>H<sub>5</sub>OH content. However, an increasing of H<sub>2</sub>O content in the system triggers acetic acid (HAc) induced CaCO<sub>3</sub> dissolution to release CO<sub>2</sub>. The system can be recovered for CO<sub>2</sub> capture readily by a replenishment of C<sub>2</sub>H<sub>5</sub>OH. This biomimetic mineralization-based CO<sub>2</sub> capture/release is controlled by the ionization state of electrolytes, which is precisely regulated in the C<sub>2</sub>H<sub>5</sub>OH-H<sub>2</sub>O binary solvent. Our attempt highlights the fundamental principle of solution chemistry in reaction controls and provides a bioinspired strategy for CO<sub>2</sub> capture/release with very low cost and easy availability.

## Introduction

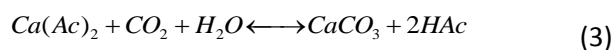
The sharply rising level of atmospheric CO<sub>2</sub> has already implicated in climate changes, threatening global ecologies and economies significantly.<sup>1,2</sup> New materials such as ionic liquids (ILs)<sup>3-5</sup>, zeolites<sup>6</sup>, carbonaceous adsorbents<sup>7</sup>, and metal-organic frameworks (MOFs)<sup>8</sup>, etc., have been developed for CO<sub>2</sub> capture with a regeneration ability. A key to these material-based CO<sub>2</sub> capture/release controls is the temperature swing regeneration.<sup>9-11</sup> At low temperature (typically, room temperature), the adsorbent materials are able to capture CO<sub>2</sub> and at high temperature (typically, 80 °C), the adsorbed CO<sub>2</sub> can be released from the materials.<sup>12,13</sup> Adsorption enthalpy is of particularly importance to develop the materials for CO<sub>2</sub> capture/release.<sup>14,15</sup> Low adsorption enthalpy leads to slow adsorption kinetics of CO<sub>2</sub> capture but high one affords great energy consumption for regeneration.<sup>16</sup> Moreover, the regeneration process needs extra energy consumption. For example, the heat capacities of ILs are usually more than 400 J/K/mol<sup>17,18</sup> so that the temperature rising from 25 °C to 80 °C needs >22 kJ/mol. An approach for CO<sub>2</sub> capture/release at constant room temperature can make the regeneration more readily to save energy but it is a great challenge.<sup>19</sup>

In nature, biomineralization is an important bioinorganic process for CO<sub>2</sub> capture/release and it takes place under ambient conditions. For instance, corals use CO<sub>2</sub> as a source of carbonate to generate CaCO<sub>3</sub>.<sup>20</sup> This biomineralization is well

controlled by microenvironments in living organisms:<sup>21</sup> (i) hydration of CO<sub>2</sub> is catalyzed by enzymes such as carbonic anhydrase (eq. 1); (ii) hydron (H<sup>+</sup>) is separated from bicarbonate (HCO<sub>3</sub><sup>-</sup>) by enzymes/membranes to keep solution pH; (iii) under physiological conditions, HCO<sub>3</sub><sup>-</sup> ions meet calcium ions (Ca<sup>2+</sup>) to generate CaCO<sub>3</sub> (eq. 2).<sup>22</sup> Thus, CO<sub>2</sub> can be efficiently solidified in the form of coral biomineral. The biological dissolution of CaCO<sub>3</sub> to release CO<sub>2</sub> is performed by secreting acids from the other functional enzymes,<sup>23</sup> which produce acidic microenvironment to reverse eqs. 1 and 2.



Microenvironmental pH plays a key role in biomineralization-based CO<sub>2</sub> looping,<sup>21-23</sup> which is precisely regulated by enzymes and membranes in living systems.<sup>22-24</sup> Unfortunately, this biological intelligence is unrealistic in chemical practices at present. Alternatively, we develop a feasible and costless method for a pH switch by ionization control in binary solvent. Such a strategy can achieve a biomineralization-like CO<sub>2</sub> looping at constant room temperature by using Ca(Ac)<sub>2</sub> as eq. 3.



It shows that a reaction of  $\text{Ca}(\text{Ac})_2$  with  $\text{CO}_2$  can produce  $\text{CaCO}_3$  and  $\text{HAc}$ . However, the formation of  $\text{CaCO}_3$  in the presence of  $\text{HAc}$  is unfavorable in aqueous solutions:  $\text{HAc}$  is a typical acid which can release abundant  $\text{H}^+$  (eq. 4) to dissolve  $\text{CaCO}_3$ .



Fortunately, we note that ionization of  $\text{HAc}$  (eq. 4) in some organic solvents can be significantly inhibited. Thus, the solution pH can be maintained at relatively high level for  $\text{CaCO}_3$  formation without an involvement of biological enzyme and membrane. In this hypothesis, the ionization control of electrolytes is a key to switch eq. 3. Besides temperature, solution chemistry shows that electrolyte ionization is also affected by solution ion strength ( $I$ ) and solvent permittivity ( $\epsilon$ ). Debye-Hückel theory demonstrates that the activity coefficient of electrolyte can be described by eq. 5,

$$\lg f_{\pm} = -\frac{A|z_+z_-|\sqrt{I}}{1 + Ba\sqrt{I}} \quad (5)$$

where,  $f_{\pm}$  is activity coefficient;  $z$ , valence states of electrolyte;  $a$ , constant. The parameters of  $A$  and  $B$  can be adjusted by  $\epsilon$ ,

$$A = \frac{1}{2.303} \left( \frac{2\pi N_A}{1000} \right)^{1/2} \left( \frac{e^2}{\epsilon kT} \right)^{3/2} \quad (6)$$

$$B = 10^{-7} \left( \frac{8\pi N_A e^2}{1000 \epsilon kT} \right)^{1/2} \quad (7)$$

in which,  $T$  is temperature;  $k$ , Boltzmann constant;  $N_A$ , Avogadro constant. Eqs. 5-7 indicate that solvents with low permittivity can result in low activity coefficient of electrolytes to inhibit electrolyte ionizations.<sup>25</sup> (Fig. S1) Particularly, it means that an inhibition of  $\text{H}^+$  releasing from  $\text{HAc}$  in a solvent with low permittivity may stabilize  $\text{CaCO}_3$  to promote eq. 3. But how can we regulate solvent permittivity? The answer is binary solvent since its permittivity depends upon the component ratio. For example, ethanol and water are the most common solvents in chemical studies and their  $\epsilon$  values are 78.5 and 24.5, respectively. Accordingly,  $\epsilon$  of  $\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$  mixture can be adjusted within the range of 24.5-78.5. In this article, we demonstrated that an appropriately established  $\text{Ca}(\text{Ac})_2$  solution using  $\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$  binary solvent could mimic biomineralization cycle to achieving  $\text{CO}_2$  chemical looping at constant room temperature (Fig. 1).

## Results and Discussion

### $\text{CO}_2$ chemical looping in $\text{Ca}(\text{Ac})_2-\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$ system

Due to the postcombustion flue gas always contains 10%  $\text{CO}_2$ , we used the mixed gas (1 atm) consisted of 10%  $\text{CO}_2$  and 90%  $\text{N}_2$  in the experiments. When the  $\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$  binary solvent contained 51.1 wt%  $\text{C}_2\text{H}_5\text{OH}$ , the introduced  $\text{CO}_2$  gas could

react with 0.08 M  $\text{Ca}(\text{Ac})_2$  to produce  $\text{CaCO}_3$  (Fig. 1 Capture Process and Fig. S2-4). During the capture process, the originally transparent  $\text{Ca}(\text{Ac})_2-\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$  solution became turbid. The resulted solid phase was identified as vaterite, confirming the forward reaction of eq. 3.

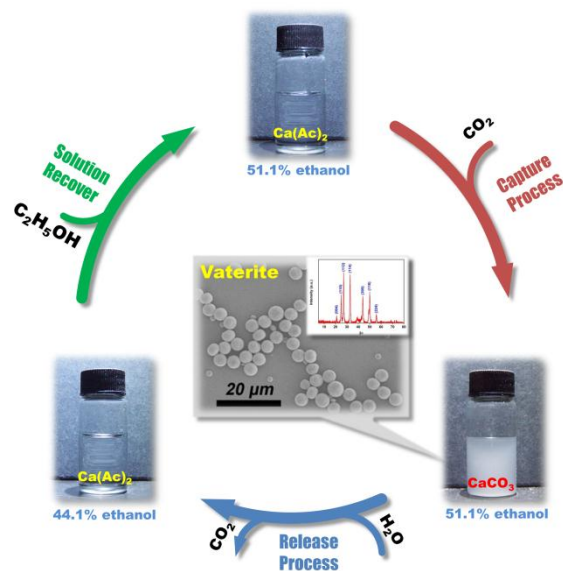


Figure 1. Controlling ionization as a “switch” for  $\text{CO}_2$  chemical looping in  $\text{Ca}(\text{Ac})_2-\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$  system at constant room temperature. 0.1 atm  $\text{CO}_2$  with 0.9 atm  $\text{N}_2$  are bubbled into the binary solvent containing 51.1 wt %  $\text{C}_2\text{H}_5\text{OH}$  and 0.08 M  $\text{Ca}(\text{Ac})_2$ .  $\text{Ca}(\text{Ac})_2$  interacts with  $\text{CO}_2$  to form  $\text{CaCO}_3$  (vaterite). The resulted  $\text{CaCO}_3$  can be dissolved to release  $\text{CO}_2$  by decreasing  $\text{C}_2\text{H}_5\text{OH}$  content to 44.1 wt %. After a complement of  $\text{C}_2\text{H}_5\text{OH}$  content to 51.1 wt%, the system is recovered for  $\text{CO}_2$  capture.

Although the precipitation was accompanied by  $\text{HAc}$  formation, the resulted  $\text{CaCO}_3$  was stable against dissolution in the presence of  $\text{HAc}$ . A reasonable explanation was that, the solution was insufficiently acidic due to the inhibited ionization state of  $\text{HAc}$  in  $\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$ . However, the inhibition degree was sensitive to  $\text{C}_2\text{H}_5\text{OH}$  content in the binary solvents. If  $\text{C}_2\text{H}_5\text{OH}$  content was reduced to 44.1 wt% by water addition, the precipitated  $\text{CaCO}_3$  could be demineralized spontaneously to release  $\text{CO}_2$  (Fig. 1 Release Process) and the system return to the transparent state, following the reversed reaction of eq. 3. It should be mentioned that the solubility of  $\text{CaCO}_3$  in neutral water only contribute to less than 2%, which could be regardless in this acid-resulted dissolution system (see details in supporting information). At this stage, the  $\text{Ca}(\text{Ac})_2-\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$  could not adsorb  $\text{CO}_2$  any more. However, the system recovery for  $\text{CO}_2$  capture could be reached by a reimbursement of  $\text{C}_2\text{H}_5\text{OH}$  content to 51.1 wt% (Fig. 1 Solution Recover). It should be mentioned that this looping could be generally available by replacing ethanol to other organic solvents with lower permittivity (Table S1), indicating a general validity of solvent permittivity controls in the mineralization-based  $\text{CO}_2$  looping.

### Ionization Controls

In order to confirm the ionization controls in the biomimetic CO<sub>2</sub> looping, we used HAc-C<sub>2</sub>H<sub>5</sub>OH-H<sub>2</sub>O to examine the profiles of electrolyte ionization, pH and permittivity at 25 °C (Fig. 2, Fig. S5, and Tables S2, S3). The results showed that an increasing of C<sub>2</sub>H<sub>5</sub>OH content in the binary solvent decreased the binary solvent permittivity (Fig. 2A, red solid line) and accordingly, the HAc ionization was inhibited (Fig. 2A, dash line). Thereby, pH of HAc-C<sub>2</sub>H<sub>5</sub>OH-H<sub>2</sub>O solutions was flexible due to the different C<sub>2</sub>H<sub>5</sub>OH:H<sub>2</sub>O ratio (Fig. 2B). For example, in the binary solvent containing 51.1 wt% C<sub>2</sub>H<sub>5</sub>OH, the ionization degree of 0.1 mM HAc was 10.3% and the solution pH was 5.0. If the C<sub>2</sub>H<sub>5</sub>OH content was reduced to 44.1 wt%, the ionization degree of 0.1 mM HAc was promoted to 14.7% and the solution became more acidic with a pH value of 4.8. Since the stability of CaCO<sub>3</sub> is critically sensitive to solution pH,<sup>26,27</sup> such a pH change was sufficient to switch CaCO<sub>3</sub> mineralization/demineralization.

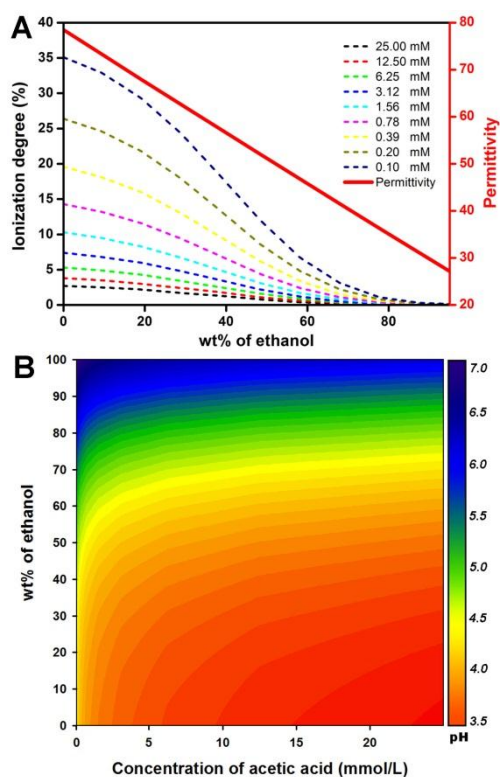


Figure 2. Diagram of C<sub>2</sub>H<sub>5</sub>OH content-permittivity-ionization-pH of HAc-C<sub>2</sub>H<sub>5</sub>OH-H<sub>2</sub>O at 25 °C. (A) solvent permittivity, red solid line; ionization degree at different concentration of HAc, dash line (B) pH distribution, different colour stand for different pH.

### Influence Factor for CO<sub>2</sub> Capture/Release

The mineralization ability of CaCO<sub>3</sub> in Ca(Ac)<sub>2</sub>-C<sub>2</sub>H<sub>5</sub>OH-H<sub>2</sub>O were in situ monitored by solution turbidity (320 nm) and precipitate mass (Fig. 3, Table S4). When C<sub>2</sub>H<sub>5</sub>OH content was less than 45% in the binary solvent, no mineralization occurred despite of Ca(Ac)<sub>2</sub> concentrations. It implied a relatively high ionization state of electrolytes in the solvent with  $\epsilon > 54$ , which could lead to CaCO<sub>3</sub> dissolution in the presence of HAc. The experiments using the other organic-water binary solvent

(Table S1) also showed that  $\epsilon$  of approximately 54 was a critical point for the CaCO<sub>3</sub> mineralization control. H<sub>2</sub>O has a  $\epsilon$  value of 78.5 and thereby, the reaction of CO<sub>2</sub> and Ca(Ac)<sub>2</sub> to form CaCO<sub>3</sub> and HAc cannot be performed; rather, it is a conventional understanding that CaCO<sub>3</sub> can be dissolved readily by HAc in aqueous solutions. However, this reaction balance could be broken by increasing C<sub>2</sub>H<sub>5</sub>OH content to > 45 wt% in C<sub>2</sub>H<sub>5</sub>OH-H<sub>2</sub>O solvents and in such a case, the concentration of Ca(Ac)<sub>2</sub> became the determining factor. In the solvent containing 48 wt% C<sub>2</sub>H<sub>5</sub>OH, the spontaneous precipitation occurred by gas bubbling into the system containing >0.065 M Ca(Ac)<sub>2</sub>, which could be used for CO<sub>2</sub> capture. In contrast, the solution kept in the transparent state without any precipitates if the Ca(Ac)<sub>2</sub> concentrations were <0.065 M. In Capture Area, the mineralization reaction was always enhanced significantly within a range of Ca(Ac)<sub>2</sub> concentrations of 0-0.08 M but this tendency was not so remarkable at >0.08 M. This phenomenon indicated 0.08 M Ca(Ac)<sub>2</sub> as an economical concentration with the optimal CO<sub>2</sub> capture ability in the system.

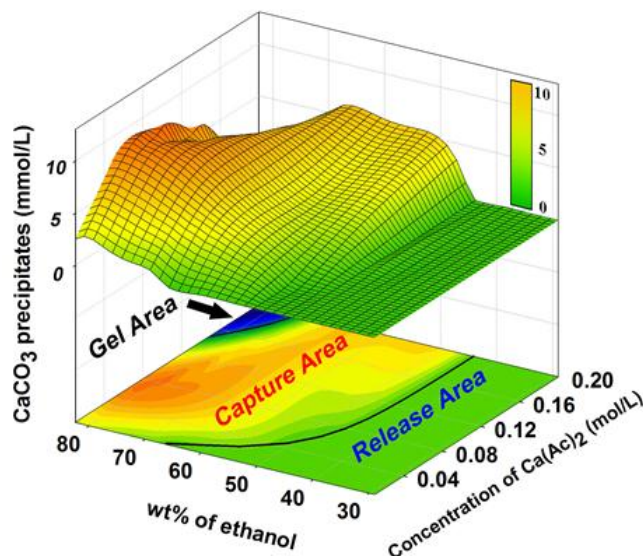


Figure 3. Phase diagram for CO<sub>2</sub> capture/release in Ca(Ac)<sub>2</sub>-C<sub>2</sub>H<sub>5</sub>OH-H<sub>2</sub>O system at 25 °C. The amounts of CaCO<sub>3</sub> precipitates represent the mineralization (or CO<sub>2</sub> capture) abilities. Capture Area stands for the formation of CaCO<sub>3</sub> in Ca(Ac)<sub>2</sub>-C<sub>2</sub>H<sub>5</sub>OH-H<sub>2</sub>O. In Release Area, the resulted CaCO<sub>3</sub> can be dissolved for CO<sub>2</sub> releasing.

C<sub>2</sub>H<sub>5</sub>OH content was another important determining factor when Ca(Ac)<sub>2</sub> concentration was fixed. For instance, the balance point for the control of eq. 3 was 46.9 wt% C<sub>2</sub>H<sub>5</sub>OH at Ca(Ac)<sub>2</sub> concentration of 0.08 M. The solvent with higher C<sub>2</sub>H<sub>5</sub>OH content triggered and promoted the mineralization process. Oppositely, the solvent with lower C<sub>2</sub>H<sub>5</sub>OH content induced CaCO<sub>3</sub> demineralization by HAc. The mineralization capacity or CO<sub>2</sub> capture in Ca(Ac)<sub>2</sub>-C<sub>2</sub>H<sub>5</sub>OH-H<sub>2</sub>O system could be mediated flexibly by C<sub>2</sub>H<sub>5</sub>OH content and Ca(Ac)<sub>2</sub> concentration. Generally, more Ca(Ac)<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>OH would facilitate the mineralization-based CO<sub>2</sub> capture but an coexistence of high Ca(Ac)<sub>2</sub> concentrations (>0.12 M) and



$C_2H_5OH$  content (>70 wt%) could result in gel phase (Fig. 3, Gel Area), which was unfavourable for  $CO_2$  absorption. Therefore, an appropriate selection of experimental conditions based upon Fig. 3 was of importance for the  $CO_2$  chemical looping. Moreover, the  $CO_2$  capture process by  $CaCO_3$  mineralization in  $Ca(Ac)_2$ - $C_2H_5OH$ - $H_2O$  was fast and typically, the mineralization could be almost completed within 12 min (Fig. S6).

### Enthalpy Change of Reaction and $CO_2$ Capacity

Furthermore, we confirmed that  $\Delta H$  of eq. 3 was also tuned efficiently by the binary solvent. Fig. 4 (Table S5) shows that  $\Delta H$  decreased from +31.7 kJ/mol to -75.5 kJ/mol when  $C_2H_5OH$  content was increased from 47.8 wt% to 53.9 wt%. The further increasing of  $C_2H_5OH$  content would lead to another increasing of  $\Delta H$ . This increasing was due to the strong binding effect between  $Ca(Ac)_2$  and  $C_2H_5OH$ , which finally resulted in gel phase formation. We noted that the maximum capacity for  $CO_2$  capture should be at  $C_2H_5OH$  content of 62 wt%. However, this high percentage of  $C_2H_5OH$  in solvent was not beneficial for  $CO_2$  chemical looping since more water and ethanol should be required for  $CO_2$  release and system recovery, respectively. Besides, the strong binding effect between  $Ca(Ac)_2$  and  $C_2H_5OH$  could retard the mineralization-involved absorption kinetic of  $CO_2$  (Fig. S6). In order to mediate eq. 3 more readily by  $\Delta H$  for an easy chemical looping, Fig. 4 shows that  $C_2H_5OH$  content between 48% and 54% was the most suitable range that could balance efficiency and economy.

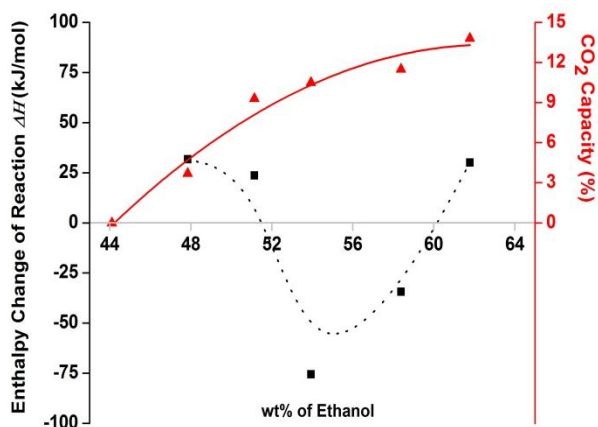


Figure 4. Enthalpy change of reaction ( $\Delta H$ , red) and  $CO_2$  capture capacity (black) in  $Ca(Ac)_2$ - $C_2H_5OH$ - $H_2O$  with different  $C_2H_5OH$  wt%. The  $Ca(Ac)_2$  concentration was fixed at 0.08 M.

### $CO_2$ Chemical Looping

Material regeneration is another key to  $CO_2$  chemical capture/release. In our case, the  $Ca(Ac)_2$  concentration in the system was decreased  $\sim 50\%$  after each cycle by the water and ethanol additions. Although the initial system contained high concentration of  $Ca(Ac)_2$ , 0.20 M, it still lost  $CO_2$  capture ability significantly after two cycles (Fig. 5 black). However, this problem could be appropriately solved by using  $Ca(Ac)_2$ - $C_2H_5OH$  instead of pure  $C_2H_5OH$  for the system recovery,

which could maintain  $Ca(Ac)_2$  concentration at a constant level for  $CO_2$  capture. This improved  $Ca(Ac)_2$ - $C_2H_5OH$ - $H_2O$  system with constant 0.08 M  $Ca(Ac)_2$  at capture stage exhibited perfect capacity and infinite regeneration ability for the  $CO_2$  chemical looping (Fig. 5 red).

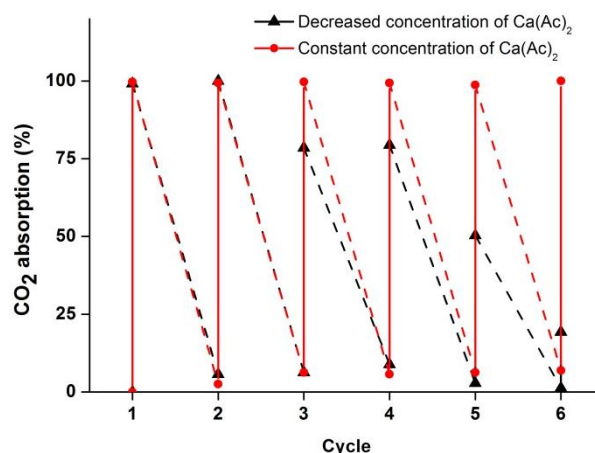


Figure 5. Six cycles of  $CO_2$  absorption and desorption in the binary solvent contained 53.9 wt% and 44.1 wt%  $C_2H_5OH$ , respectively. Black shows that the system with initial  $Ca(Ac)_2$  concentration of 0.20 M lost its  $CO_2$  capture ability by the water and ethanol additions. Red shows that the system with fixed 0.08 M  $Ca(Ac)_2$  concentration for  $CO_2$  capture could be infinitely regenerated with unchanged  $CO_2$  capture ability.

### Conclusions

The biomineralization-inspired  $CO_2$  chemical looping has prominent advantages: (i) the  $CO_2$  capture/ release is regulated easily by binary solvent at room temperature without temperature or pressure change; (ii) the materials,  $Ca(Ac)_2$ ,  $C_2H_5OH$ , and  $H_2O$  are featured by their low cost and easy availability; (iii) the biomimetic controls of  $CO_2$  using  $CaCO_3$  mineral phase is not only efficient but also environmentally friendly.

In nature, biomineralization of  $CaCO_3$ , especially by corals, provides an important pathway for  $CO_2$  biological looping. Specific enzymes, membranes and functional proteins are involved and complicated coordinated in this biological process to adjust solution specimens to achieve the controls for  $CO_2$  capture/release under ambient conditions. However, such an achievement can be dramatically simplified by ionization controls in binary solvent. The current study demonstrates an example about  $CaCO_3$  mineralization/demineralization controls by using solvent formula. More generally, this attempt highlights the fundamental principle of solution chemistry in regulations of electrolyte reactions, which may open up a new door for  $CO_2$  capture and sequestration technology for sustainable energy applications.

## Experimental

### Materials

Calcium acetate monohydrate ( $\text{Ca}(\text{Ac})_2 \cdot \text{H}_2\text{O}$ , 98%), acetic acid (HAc, 99.9%), and ethanol (99.8%) were purchased from Aladdin (China). All reagents were used without further purification.

### CO<sub>2</sub> capture reactions

The solutions with different  $\text{Ca}(\text{Ac})_2$  concentrations and ethanol contents were prepared by mixing the corresponding components. The CO<sub>2</sub> capture process was performed by bubbling the mixed gases (1 atm) containing 10% CO<sub>2</sub> and 90% N<sub>2</sub> into 4 mL solution at a rate 100 mL/min.

### Characterization of precipitates

The precipitates in solution were obtained by centrifugation (5400 rpm, 1-6P, Sigma, Germany). The solid samples were washed using 53.9 wt% ethanol for twice and dried in vacuum at 40 °C. XRD, TGA and FT-IR were used to characterize the precipitates and the results were shown in Fig. S2-S4.

### Ionization measurement in binary solvent

HAc (0-100 mM) in different C<sub>2</sub>H<sub>5</sub>OH-H<sub>2</sub>O binary solvent were prepared and the solutions were kept in 25 °C for 30 min. The solution conductivities were measured by a conductivity meter (DDSJ-308A, INESA Scientific Instrument, China). The limit molar conductivity and  $K_a$  of HAc were calculated using Walden's rules and eqs. 8 and 9<sup>28</sup>

$$K_a = \frac{c \times \alpha^2}{1 - \alpha} \quad (8)$$

$$c\Lambda_m = K_a (\Lambda_m^\infty)^2 \frac{1}{\Lambda_m} - K_a \Lambda_m^\infty \quad (9)$$

where,  $\alpha$  is degree of ionization;  $\Lambda_m$ , molar conductivity;  $\Lambda_m^\infty$ , limit molar conductivity.

### Phase diagram for CO<sub>2</sub> capture/release

$\text{Ca}(\text{Ac})_2$  (0-0.2 M) were added into different C<sub>2</sub>H<sub>5</sub>OH-H<sub>2</sub>O binary solvent. The mixed gases (10% CO<sub>2</sub> and 90% N<sub>2</sub>, 1 atm) were bubbled into the solution for 4 min. Then, the turbidity of the solution was *in situ* measured with UV spectrophotometer (T6, Puxi, China) at 320 nm. The turbidity above 0.3 always accompanied with significant precipitation process. The resulted precipitated were dried in vacuum at 40 °C for the mass measurement.

### Enthalpy change of reaction controls

By a preparation of 50 mL CO<sub>2</sub> capture solution, the mixed gases (10% CO<sub>2</sub>/90% N<sub>2</sub>, 1 atm) were bubbled into the solution (100 mL/min) at different temperature (10-45°C). The kinetic data for the CO<sub>2</sub> capture were shown in Fig. S6 and the CO<sub>2</sub> capture capacities were calculated. According to eq. 3 and van't Hoff equation (eq. 10),<sup>29</sup> we were able to get the equilibrium constant ( $K$ , eq. 11) and then the enthalpy change,  $\Delta H$  (eq. 12).  $[\text{Ca}(\text{Ac})_2]$  and  $[\text{HAc}]$  referred to the finally balanced concentrations of  $\text{Ca}(\text{Ac})_2$  and HAc neutral molecules, respectively, after the reaction at different temperature.

$$\frac{d \ln K}{dT} = \frac{\Delta_r H_m^\theta}{RT^2} \quad (10)$$

$$K = \frac{c[\text{HAc}]^2}{c[\text{Ca}(\text{Ac})_2] \times p[\text{CO}_2] \times c[\text{H}_2\text{O}]} \quad (11)$$

$$\begin{aligned} \ln K &= \ln \frac{c[\text{HAc}]^2}{c[\text{Ca}(\text{Ac})_2]} - \ln \frac{1}{p[\text{CO}_2] \times c[\text{H}_2\text{O}]} + A \\ &= \ln \frac{c[\text{HAc}]^2}{c[\text{Ca}(\text{Ac})_2]} + A' = -\frac{\Delta_r H_m^\theta}{RT} + A' \end{aligned} \quad (12)$$

in which,  $T$  is temperature;  $\Delta H_m^\theta$ , standard mole enthalpy change of reaction.

### CO<sub>2</sub> chemical looping

In the free-drift case of  $\text{Ca}(\text{Ac})_2$  concentrations, 53.9 wt % of ethanol was pre-prepared with 0.2 M  $\text{Ca}(\text{Ac})_2$ . The mixed gases (10% CO<sub>2</sub>/90% N<sub>2</sub>, 1 atm) were bubbled into the solution for 10 min and the turbidity was measured. Then water was added to adjust the wt % of ethanol to 44.1. After 30 min release, the turbidity was measured and ethanol was increased to 53.9 wt % by ethanol addition for next cycle. In the case of constant concentration of  $\text{Ca}(\text{Ac})_2$ , 53.9 wt % of ethanol was pre-prepared with 0.08 M  $\text{Ca}(\text{Ac})_2$ . In the recovery process, the ethanol addition was replaced by  $\text{Ca}(\text{Ac})_2$ -C<sub>2</sub>H<sub>5</sub>OH slurry for a replenishment of  $\text{Ca}(\text{Ac})_2$  concentration.

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### Notes and references

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