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Journal Name

Regeneration mechanisms of high-lithium content zirconates as CO$_2$ capture sorbents: experimental measurements and theoretical investigations

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By combining TGA and XRD measurements with theoretical calculations of the capture of CO$_2$ by lithium-rich zirconates (Li$_8$ZrO$_6$ and Li$_6$Zr$_2$O$_7$), it has been demonstrated that the primary regeneration product during absorption/desorption cycling is in the form of Li$_2$ZrO$_3$. During absorption/desorption cycles, lithium-rich zirconates will be consumed and will not be regenerated. This result indicates that among known lithium zirconates, Li$_2$ZrO$_3$ is the best sorbent for CO$_2$ capture.

Nowadays, the fossil fuels are the main energy source for the world's economy. One consequence of the use of these carbon based fossil fuels is emission of huge quantities of CO$_2$ into the atmosphere which results in environmental climate change.[1-3] In order to solve this environmental problem and to stop emission, the CO$_2$ must be captured and sequestered underground.[4-7] During the past few decades, many efforts have been devoted to the development of new technologies for CO$_2$ capture, sequestration, and utilization in order to improve energy efficiency.[8, 9] Among these technologies, capture is the area for which effective sorbent materials must be developed. Inorganic sorbents typically capture CO$_2$ through the reversible formation of carbonates. Recent experimental investigations found that alkali metal silicates and zirconates are good candidates as solid sorbents for CO$_2$ capture in terms of large CO$_2$ sorption capacity, infinite CO$_2$/N$_2$ or CO$_2$/H$_2$ selectivity, good reversibility, and high operating temperatures.[10-16] Among them, Li$_4$SiO$_4$ and Li$_2$ZrO$_3$ have been extensively investigated both experimentally and theoretically.[14, 17-23]

In both lithium silicates and lithium zirconates, there exist lithium-poor compounds, in which the Li$_2$O/SiO$_2$ or Li$_2$O/ZrO$_2$ ratio is less than 1.0, such as Li$_2$Si$_2$O$_5$, Li$_2$Si$_3$O$_7$, Li$_4$Zr$_3$O$_8$, and the lithium-rich compounds (in which the Li$_2$O/SiO$_2$ > 1.0 or Li$_2$O/ZrO$_2$ > 1.0), such as Li$_4$SiO$_4$, Li$_8$SiO$_6$, Li$_6$Zr$_2$O$_7$, Li$_8$ZrO$_6$, *etc*.[20, 22-24] For lithium silicates, previous studies already proved that lithium-poor silicates are not good candidates as CO$_2$ sorbents due to slow kinetics and low turnover temperature.[15, 17, 18, 23, 25-29] As for Li$_2$SiO$_3$, experimental results showed the kinetics of its CO$_2$ capture reaction are also too slow, and hence it is not a good candidate for a CO$_2$ capture technology.[23, 27] Although Li$_8$SiO$_6$ can absorb CO$_2$ over a wide range

of temperatures, in order to reach maximum CO$_2$ capture capacity, the capture should operate under different temperature ranges which increases the energetic and operating costs.[23, 25, 30, 31] Therefore, Li$_4$SiO$_4$ is a better choice among available known lithium silicates.

However, in the case of lithium zirconates, it is still unclear which lithium zirconate is the best choice for CO$_2$ capture.[15, 32, 33] Nakagawa and Ohashi[14, 19] first reported that Li$_2$ZrO$_3$ powder reacts immediately with ambient CO$_2$ in the temperature range of 450 ºC to 550 ºC and the products decompose reversibly to Li$_2$ZrO$_3$ and CO$_2$ at temperatures above 650 ºC. Ida *et al*[12, 34] pointed out that the rate of the CO$_2$ sorption on pure Li$_2$ZrO$_3$ is controlled by the diffusion of CO$_2$ in the solid Li$_2$CO$_3$ shell, whereas Xiong *et al*[35] revealed that it is the size of the aggregated Li$_2$ZrO$_3$ that controls the CO$_2$ sorption rate. Pfeiffer *et al*[36] reported that hexa-lithium zirconate (Li$_6$Zr$_2$O$_7$) absorbed four times more CO$_2$ than Li$_2$ZrO$_3$, and its CO$_2$ sorption rate is faster than Li$_2$ZrO$_3$ at short times, but they became similar after long time runs. Yin *et al*[37, 38] compared the CO$_2$ adsorption properties of Li$_6$Zr$_2$O$_7$ with Li$_2$ZrO$_3$ in a low CO$_2$ concentration stream, and found that the CO$_2$ capture capacity of Li$_6$Zr$_2$O$_7$ could reach 86.7% and was gradually reduced in multi-cycle tests at 750 ºC, while the CO$_2$ capture capacity of Li$_2$ZrO$_3$ only preserved to 3.5% as the partial pressure of CO$_2$ decreases from 1.0 to 0.1 bars. They also found that the Li$_8$ZrO$_6$ first reacted with CO$_2$ to form Li$_6$Zr$_2$O$_7$ through 2Li$_8$ZrO$_6$ + 5CO$_2$ ↔ 5Li$_2$CO$_3$ + Li$_6$Zr$_2$O$_7$, then, the Li$_6$Zr$_2$O$_7$ continues to react with CO$_2$. Later, by a method of three-step calcinations, they synthesized high-purity Li$_8$ZrO$_6$ and characterized its CO$_2$ capture properties which involve phase transitions Li$_8$ZrO$_8$ → Li$_6$Zr$_2$O$_7$ → Li$_2$ZrO$_3$ → ZrO$_2$.[39]

Just as we do not know the ideal zirconate for CO$_2$ capture, the mechanisms of these CO$_2$ capture reactions by lithium zirconates are also not clear. From a qualitative point of view, some researchers proposed a double shell model to describe the mechanism of CO$_2$ sorption by Li$_2$ZrO$_3$.[12, 34, 40] They found that in order to continue to form Li$_2$CO$_3$, the lithium has to migrate through the Li$_2$CO$_3$ shell with the rate of the CO$_2$ absorption controlled by the diffusion of CO$_2$ into the solid lithium carbonate shell[12, 34] and the aggregate size controlled by the Li$_2$ZrO$_3$ bulk.[35] Yin *et al*.[37-39] pointed out that during the CO$_2$ adsorption process, the Li$_8$ZrO$_6$ first produce Li$_6$Zr$_2$O$_7$ and then Li$_2$ZrO$_3$. However, there is a dispute as to whether Li$_6$Zr$_2$O$_7$ and Li$_8$ZrO$_6$ can be regenerated during multiple CO$_2$ adsorption-desorption cycles. In Yin *et al*.'s studies,[37-39] although they claimed that the Li$_6$Zr$_2$O$_6$ and Li$_8$ZrO$_6$ could be

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regenerated, their results showed that with multiple cycles of CO_2 adsorption-desorption, the CO_2 capture capacities decreased to 45% due to Li_2O sublimation and particle sintering. Pfeiffer and Bosch [36] found that after the first absorption cycle the $Li_6Zr_2O_7$ does not regenerate during CO_2 desorption. With an *ab initio* thermodynamic approach, we calculated the thermodynamic properties of reactions of M_2ZrO_3 (M=Li, Na, K), $Li_6Zr_2O_7$ and Li_8ZrO_6 capturing CO_2 and concluded that the lithium-rich zirconates only can be regenerated at higher temperatures.[20, 21, 24] In order to fully address issues such as sorbent regeneration, here, we performed further experimental measurements and a detailed theoretical analysis.

By combining first-principles density functional theory with lattice phonon dynamics simulations, we calculated the thermodynamic properties of solids involved in the study, and in turn obtained the free energy changes and enthalpy changes of CO_2 capture reactions versus temperature and CO_2 pressure. The calculated thermodynamic properties of several lithium zirconates versus temperature and CO_2 pressure changes were further used to evaluate the equilibrium properties for the CO_2 adsorption/desorption cycles. Table 1 lists the calculated thermodynamic properties of CO_2 capture reactions by lithium zirconates.[20, 24]

Table 1. The weight percentage (wt. %) of CO_2 capture and the thermodynamic properties (ΔH, ΔG) at T=300K of the CO_2 capture reactions by lithium zirconates. The turnover temperatures (T_1 and T_2) of these CO_2 capture reactions under the conditions of pre-combustion (P_{CO2}=20 bar) and post-combustion (P_{CO2}=0.1 bar) are also listed. [20, 24]

Reaction	absorbing CO_2 Wt.%	ΔH (kJ/mol)	ΔG (kJ/mol)	T_1 (K)	T_2 (K)
$\frac{1}{4}Li_8ZrO_6 + CO_2 \leftrightarrow Li_2CO_3 + \frac{1}{4}ZrO_2$	72.50	-200.76	-151.60	1460	1090
$\frac{2}{5}Li_8ZrO_6 + CO_2 \leftrightarrow Li_2CO_3 + \frac{1}{5}Li_6Zr_2O_7$	45.31	-220.04	-172.55	>1500	1250
$\frac{1}{3}Li_6Zr_2O_7 + CO_2 \leftrightarrow Li_2CO_3 + \frac{2}{3}ZrO_2$	39.28	-169.50	-117.56	1140	880
$Li_6Zr_2O_7 + CO_2 \leftrightarrow Li_2CO_3 + 2Li_2ZrO_3$	13.09	-191.37	-145.00	1500	1110
$Li_2ZrO_3 + CO_2 \leftrightarrow Li_2CO_3 + ZrO_2$	28.75	-158.56	-103.85	1000	780

From Table 1, one can see that it is thermodynamically favorable for Li-rich zirconates (Li_8ZrO_6, $Li_6Zr_2O_7$) and Li_2ZrO_3 to react with CO_2 to form Li_2CO_3 and release a large amount of heat. For Li-rich zirconates, they may react with CO_2 to form an intermediate lithium zirconate, like $Li_8ZrO_6 \rightarrow Li_6Zr_2O_7 \rightarrow Li_2ZrO_3 \rightarrow ZrO_2$. Obviously, all of these lithium zirconates can completely react with CO_2 to form the final products Li_2CO_3 and ZrO_2, as already proved both by experimental measurements[12, 14, 15, 19, 32, 34-39] and theoretical calculations.[16, 20, 21, 24, 41]

However, as a good CO_2 sorbent, it should not only be easy for the material to absorb CO_2 in the first half cycle but also easy to release CO_2 and regenerate the sorbent in the second half cycle. Table 1 shows that much more energy will be needed to reverse these reactions, particularly, for those Li-rich zirconates. In order to investigate and verify the regenerability of the Li-rich zirconates, the following experimental measurements and theoretical analysis were performed.
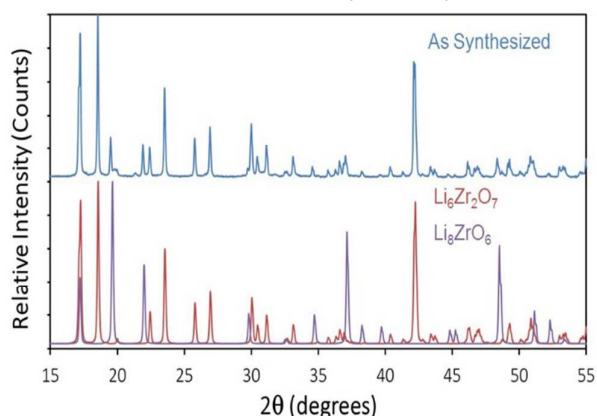

Figure 1. Powder X-ray diffraction of the Li-rich zirconate sample before capturing CO_2.

In this study, the Li-rich zirconate samples containing both $Li_6Zr_2O_7$ and Li_8ZrO_6 were prepared using a high temperature,

solid-state synthetic method. The samples were characterized using powder X-ray diffraction (XRD), as shown in Fig. 1. It should be pointed out that the Li-rich zirconates are meta-stable phases and therefore the synthetic conditions must be carefully tuned in order to prevent synthesis of the most thermodynamically stable phase, Li_2ZrO_3. As one can see from Fig. 1, the sample solely contains a mixture of Li-rich $Li_6Zr_2O_7$ and Li_8ZrO_6, without Li_2ZrO_3 or ZrO_2 in the sample.

CO_2 capture experiments were conducted using thermogravimetric analysis (TGA). Approximately 25 mg of the Li-rich zirconate sample was heated in flowing CO_2 with two heating/cooling cycles to investigate regeneration of the sorbent, Figure 2.
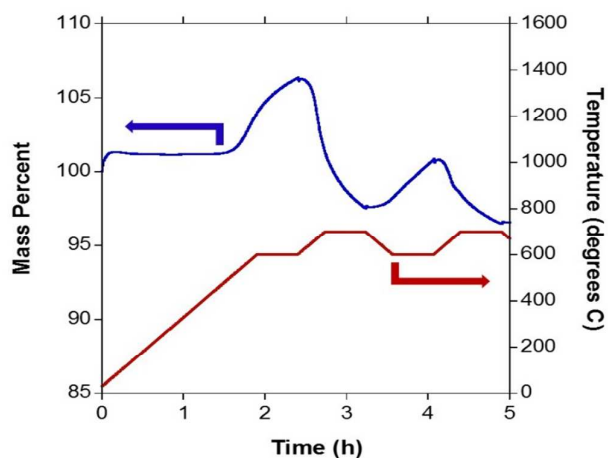

Figure 2. Thermogravimetric analysis measurements of Li-rich zirconates capturing CO_2.

The sample was observed to absorb approximately 4.9 mass percent CO_2 beginning around 500 °C. The sample was then heated further resulting in a loss of mass which continued until the sample mass dropped below the starting value. This is potentially due to the conversion of a portion of the Li-rich

zirconate to Li_2ZrO_3. Upon cooling the sample again absorbed CO_2. During the second cycle, the sample absorbed approximately 3.1 mass percent CO_2, 1.8 percent less than during the first cycle. This result is also consistent with the conversion of Li-rich zirconate to Li_2ZrO_3.
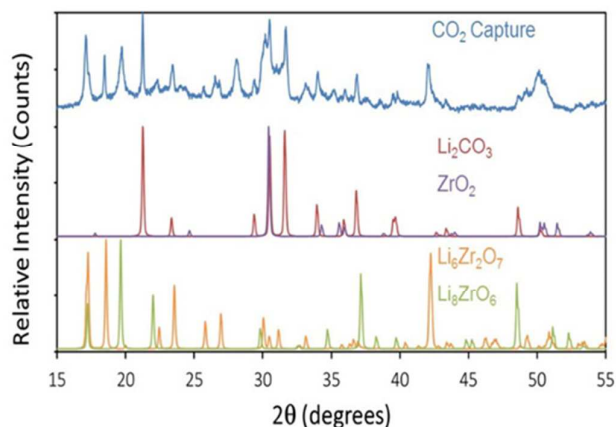

Figure 3. Powder X-ray diffraction of the Li-rich zirconate after capture CO_2. During first couple cycles, some Li-rich zirconate was left and has not yet reacted with CO_2. After multiple cycles, all Li-rich zirconates will be converted to Li_2CO_3 and ZrO_2.

In order to confirm that the mass increase was due to the absorption of CO_2, a sample was heated to 650 °C under flowing CO_2. The sample was then rapidly cooled to room temperature under flowing CO_2 before being removed from the TGA, ground, and analyzed using powder X-ray diffraction, Figure 3. Analysis of the powder diffraction pattern shows that while not completely reacted, a portion of the Li-rich zirconate sample reacted with CO_2 to form Li_2CO_3 and ZrO_2. Incomplete reaction was most likely due to the TGA program being relatively short which did not provide the sample with enough time to complete the conversion to Li_2CO_3. It can be predicted that with a longer reaction time, the unreacted Li-rich sample could be fully reacted with CO_2 to form Li_2CO_3.

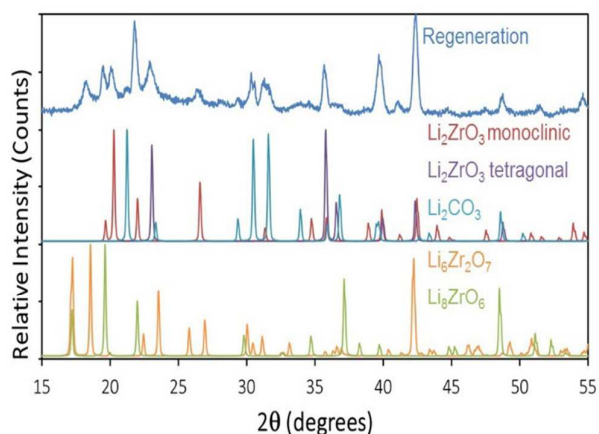**Figure 4.** Powder X-ray diffraction of the sample after regeneration. Since the sample does not fully consumed yet, the amounts of Li_8ZrO_6 and $Li_6Zr_2O_7$ are the same as shown in Fig. 3 which means during regeneration, no more Li_8ZrO_6 and

$Li_6Zr_2O_7$ were regenerated.

Obviously, the mass loss observed above 695 °C in the TGA is due to the Li_2CO_3 and ZrO_2 reacting to release CO_2 and form Li_2ZrO_3. This process was again probed using X-ray diffraction. In this case the sample was heated to 850 °C and then cooled under flowing N_2. After returning to room temperature, the sample was ground and a powder diffraction pattern was collected as shown in Fig. 4. The pattern shows a mixture of phases including monoclinic Li_2ZrO_3, tetragonal Li_2ZrO_3, Li_2CO_3, and ZrO_2. Notably absent are either of the Li-rich phases $Li_6Zr_2O_7$ and Li_8ZrO_6, indicating that high temperature regeneration of the zirconate leads to the generation of the most thermodynamically stable phase, Li_2ZrO_3. Observation of Li_2CO_3, and ZrO_2 were likely due to insufficient time allowed for the sample to completely convert back to Li_2ZrO_3.

Figure 5 shows the calculated relationships among the CO_2 pressure, temperature, and Gibbs free energy change of reactions of the sorbents' regenerations to release CO_2. From the calculated data, [16, 20, 21, 24, 41] a regeneration scheme can be created. Figure 6 shows the schematic thermodynamic profile of the regeneration reactions as well as the solid conversion paths.

From Figure 5 and Table 1, one can see that at post-combustion conditions with P_{CO2}=0.1 bar, all studied lithium zirconates can absorb CO_2 up to relatively high temperature range because the capture reactions are exothermic process. At T=780 K, the ΔG of reaction $Li_2CO_3+ZrO_2=Li_2ZrO_3+CO_2$ becomes zero. Above this T, this reaction starts to go forward which will regenerate the Li_2ZrO_3 sorbent and release CO_2. For other sorbent regenerating reactions, their ΔG values are still greater than zero and continue to absorb CO_2 up to even higher T as a result of high turnover temperatures as shown in Table 1. These results are in good agreement with the experimentally measured data in Figures 2 and 3.
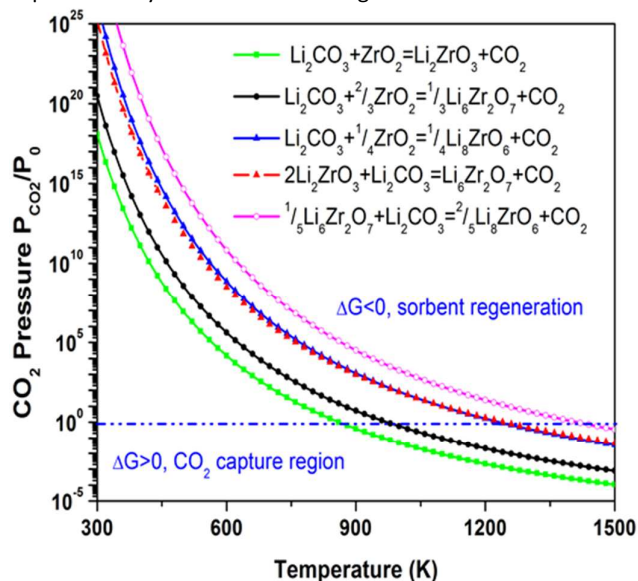

Figure 5. The calculated relationships of free energy (ΔG), regeneration temperature, and CO_2 pressure (plotted in logarithm scale) of the possible reactions of sorbent regenerations. Only ΔG=0 curves are shown explicitly. For each reaction, above its ΔG=0 curve, ΔG<0 to regenerate sorbent and release CO_2, whereas below the ΔG=0 curve, ΔG>0 curve, which means the sorbent absorbs CO_2 to form Li_2CO_3 and ZrO_2.

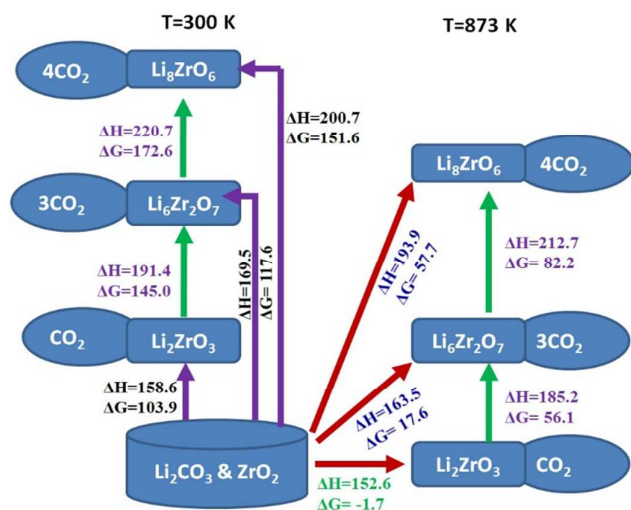**COMMUNICATION**

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Figure 6. The schematic of thermodynamic properties (ΔH and ΔG in unit of kJ/mol) evolution of sorbent regenerations at two temperatures. All the reactions and data are normalized to per one mole of CO_2.

To regenerate sorbents, as shown in Figures 5 and 6, external energy inputs are needed to increase temperatures. As one can see that when the temperature is increased above 780 K, the Li_2CO_3 and ZrO_2 first will react to form Li_2ZrO_3 and release CO_2. In order to obtain $Li_6Zr_2O_7$ and Li_8ZrO_6, the Li_2ZrO_3 should further react with Li_2CO_3 by reactions $2Li_2ZrO_3 + Li_2CO_3 \leftrightarrow Li_6Zr_2O_7 + CO_2$ and $^1/_5Li_6Zr_2O_7 + Li_2CO_3 \leftrightarrow ^2/_5Li_8ZrO_6 + CO_2$. Obviously, these reactions are also endothermic and need an additional energy input to drive the reactions forward. The requirement of additional energy input for regeneration is not optimal for CO_2 capture technology. As shown in Figure 6, at T=873 K (600 °C), only the $Li_2CO_3 + ZrO_2 \leftrightarrow Li_2ZrO_3 + CO_2$ reaction can happen with ΔG=-1.7 kJ/mol. To further convert $Li_2ZrO_3 \rightarrow Li_6Zr_2O_7 \rightarrow Li_8ZrO_6$, additional energies (185.2 and 212.7 kJ/mol at T=873 K) are required, which make the regeneration of Li-rich zirconates energetically unfeasible. Such conclusions are supported by the experimental measurements (Figures 3 and 4) and available reports in the literatures.[12, 34-39]

In this study, by combining experimental thermogravimetric analysis and powder X-ray diffraction measurements with first-principles density functional theory and lattice thermodynamics calculations on cycles of lithium-rich zirconates (Li_8ZrO_6 and $Li_6Zr_2O_7$) capturing CO_2, we investigated the regenerability of these lithium-rich zirconates. The obtained results confirmed that the Li_8ZrO_6 and $Li_6Zr_2O_7$ can absorb CO_2 to form Li_2CO_3 and ZrO_2. However, these sorbents are difficult to regenerate. Instead, the regenerated zirconate is in the form of Li_2ZrO_3. Although initially Li_8ZrO_6 and $Li_6Zr_2O_7$ possess higher capture capacity in comparison with Li_2ZrO_3, during multiple absorption/desorption cycles, these lithium-rich zirconates will be consumed completely and not regenerated. Therefore, as CO_2 sorbents, among all known lithium-rich and lithium-poor zirconates, these lithium-rich zirconates don't have advantage and Li_2ZrO_3 is the best sorbent for CO_2 capture.

Notes and references

Experimental methods: In this work, the chemicals were used as obtained: (i) Lithium Carbonate, anhydrous, 99% Alfa Aesar; (ii) Zirconium(IV) Oxide, 99%, Sigma-Aldrich. Li-rich zirconates were synthesized from stoichiometric mixtures of Li_2CO_3, and ZrO_2. The mixtures were ground by hand for 10 minutes in an agate mortar and then transferred to an alumina crucible. The crucible was placed into a box furnace at 900 °C for 4 hours. The samples were rapidly cooled to room temperature and ground by hand for 10 minutes in an agate mortar prior to physical property measurements. Correct stoichiometry of the products was assured based on the ratio of the starting materials. A Panalytical X'Pert Pro diffractometer was used to collect powder diffraction patterns for the obtained samples. Scans were performed from 5 to 100 degrees 2-theta with a step size of 0.17 ° and a scan speed of 200 s/°. The patterns were analyzed using Panalytical's Highscore Plus to determine the compositions of samples in this study. Experimental CO_2 capture studies were conducted using thermogravimetric analysis (TGA). Data were collected on a Mettler Toledo differential scanning calorimeter (DSC) and TGA. For analysis, a sample of approximately 25 mg was placed into a platinum pan and heated under flowing CO_2 (75 ml/minute) from 30 °C to 600 °C at 5 °C/minute, followed by a dwell of 30 minutes at 600 °C, the sample was then heated to 700 °C under flowing N_2 (75 ml/minute) to facilitate regeneration, followed by a dwell of 30 minutes, then cooled under flowing CO_2 from 700 °C to 600 °C at 5 °C/minute. The sample was allowed to absorb CO_2 and then a second heating to 700 °C was performed with identical conditions.

Theoretical methods: The *ab initio* thermodynamic properties calculations were performed by combining first-principles density functional theory with lattice phonon dynamics simulations. The complete description of our computational methodology can be found in our previous publications.[20-24, 42-44] By calculating the thermodynamic properties of solids involved in the study, the free energy changes and enthalpy changes of CO_2 capture reactions versus temperature and CO_2 pressure can be obtained and were used to evaluate the equilibrium properties for the CO_2 adsorption/desorption cycles.

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1. R. S. Haszeldine, *Science*, 2009, **325**, 1647-1652.
2. J. D. Figueroa, T. Fout, S. Plasynski, H. McIlvried and R. D. Srivastava, *Int. J. Greenh. Gas Control*, 2008, **2**, 9-20.
3. B. Y. Li, Y. Duan, D. Luebke and B. Morreale, *Applied Energy*, 2013, **102**, 1439-1447.
4. N. MacDowell, N. Florin, A. Buchard, J. Hallett, A. Galindo, G. Jackson, C. S. Adjiman, C. K. Williams, N. Shah and P. Fennell, *Energ. Envirn. Sci.*, 2010, **3**, 1645-1669.

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5. P. Markewitz, W. Kuckshinrichs, W. Leitner, J. Linssen, P. Zapp, R. Bongartz, A. Schreiber and T. E. Muller, *Energ. Environ. Sci.*, 2012, **5**, 7281-7305.
6. M. E. Boot-Handford, J. C. Abanades, E. J. Anthony, M. J. Blunt, S. Brandani, N. Mac Dowell, J. R. Fernandez, M. C. Ferrari, R. Gross, J. P. Hallett, R. S. Haszeldine, P. Heptonstall, A. Lyngfelt, Z. Makuch, E. Mangano, R. T. J. Porter, M. Pourkashanian, G. T. Rochelle, N. Shah, J. G. Yao and P. S. Fennell, *Energ. Environ. Sci.*, 2014, **7**, 130-189.
7. J. Y. Wang, L. Huang, R. Y. Yang, Z. Zhang, J. W. Wu, Y. S. Gao, Q. Wang, D. O'Hare and Z. Y. Zhong, *Energ. Environ. Sci.*, 2014, **7**, 3478-3518.
8. Q. Wang, J. Luo, Z. Zhong and A. Borgna, *Energ. Environ. Sci.*, 2011, **4**, 42-55.
9. G. T. Rochelle, *Science*, 2009, **325**, 1652-1654.
10. G. Pannocchia, M. Puccini, M. Seggiani and S. Vitolo, *Ind. Eng. Chem. Res.*, 2007, **46**, 6696-6706.
11. D. J. Fauth, E. A. Frommell, J. S. Hoffman, R. P. Reasbeck and H. W. Pennline, *Fuel Processing Technology*, 2005, **86**, 1503-1521.
12. J. Ida, R. T. Xiong and Y. S. Lin, *Sep. Purif. Technol.*, 2004, **36**, 41-51.
13. K. Essaki, K. Nakagawa and M. Kato, *J. Ceram. Soc. Jpn*, 2001, **109**, 829-833.
14. K. Nakagawa and T. Ohashi, *J. Electrochem. Soc.*, 1998, **145**, 1344-1346.
15. B. N. Nair, R. P. Burwood, V. J. Goh, K. Nakagawa and T. Yamaguchi, *Prog. Mater. Sci.*, 2009, **54**, 511-541.
16. Y. Duan, J. Lekse, X. Wang, B. Li, B. Alcántar-Vázquez, H. Pfeiffer and J. W. Halley, *Phys. Rev. Applied*, 2015, **3**, 044013.
17. M. Kato and K. Nakagawa, *J. Ceram. Soc. Jpn*, 2001, **109**, 911-914.
18. M. Kato, S. Yoshikawa and K. Nakagawa, *J. Mater. Sci. Lett.*, 2002, **21**, 485-487.
19. K. Nakagawa and T. Ohashi, *Electrochemistry*, 1999, **67**, 618-621.
20. Y. Duan, *J. Renewable Sustainable Energy*, 2011, **3**, 013102.
21. Y. Duan, *J. Renewable Sustainable Energy*, 2012, **4**, 013109.
22. Y. Duan and K. Parlinski, *Phys. Rev. B*, 2011, **84**, 104113.
23. Y. Duan, H. Pfeiffer, B. Li, I. C. Romero-Ibarra, D. C. Sorescu, D. R. Luebke and J. W. Halley, *Phys. Chem. Chem. Phys.*, 2013, **15**, 13538-13558.
24. Y. Duan, *Phys. Chem. Chem. Phys.*, 2013, **15**, 9752-9760.
25. F. Duran-Munoz, I. C. Romero-Ibarra and H. Pfeiffer, *J. Mater. Chem. A*, 2013, **1**, 3919-3925.
26. T. Okumura, K. Enomoto, N. Togashi and K. Oh-ishi, *J. Ceram. Soc. Jpn*, 2007, **115**, 491-497.
27. R. Rodriguez-Mosqueda and H. Pfeiffer, *J. Phys. Chem. A*, 2010, **114**, 4535-4541.
28. M. J. Venegas, E. Fregaso-Israel, R. Escamilla and H. Pfeiffer, *Ind. Eng. Chem. Re.s*, 2007, **46**, 2407-2412.
29. T. Yamaguchi, T. Niitsuma, B. N. Nair and K. Nakagawa, *J. Membr. Sci.*, 2007, **294**, 16-21.
30. C. Chen, J. Kim and W. S. Ahn, *Korean J. Chem. Eng.*, 2014, **31**, 1919-1934.
31. F. Vega, A. Sanna, B. Navarrete, M. M. Maroto-Valer and V. Cortes, *Greenh. Gases Sci. Technol.*, 2014, **4**, 707-733.
32. S. Wang, C. An and Q.-H. Zhang, *J. Mater. Chem. A*, 2013, **1**, 3540-3550.
33. A. Iwan, H. Stephenson, W. C. Ketchie and A. A. Lapkin, *Chem. Eng. J.*, 2009, **146**, 249-258.
34. J. Ida and Y. S. Lin, *Environ. Sci. Technol.*, 2003, **37**, 1999-2004.
35. R. Xiong, J. Ida and Y. S. Lin, *Chem. Eng. Sci.*, 2003, **58**, 4377-4385.
36. H. Pfeiffer and P. Bosch, *Chem. Mater.*, 2005, **17**, 1704-1710.
37. X. S. Yin, S. P. Li, Q. H. Zhang and J. G. Yu, *J. Am. Ceram. Soc.*, 2010, **93**, 2837-2842.
38. X. S. Yin, M. A. Song, Q. H. Zhang and J. G. Yu, *Ind. Eng. Chem. Res.*, 2010, **49**, 6593-6598.
39. X. S. Yin, Q. H. Zhang and J. G. Yu, *Inorg. Chem.*, 2011, **50**, 2844-2850.
40. K. Essaki, K. Nakagawa, M. Kato and H. Uemoto, *J. Chem. Eng. Jpn*, 2004, **37**, 772-777.
41. Y. Duan, *Sci. Lett.*, 2014, **3**, 56.
42. Y. Duan and D. C. Sorescu, *Phys. Rev. B*, 2009, **79**, 014301.
43. Y. Duan and D. C. Sorescu, *J. Chem. Phys.*, 2010, **133**, 074508.
44. Y. Duan, D. Luebke and H. W. Pennline, *Int. J. Clean Coal Energy*, 2012, **1**, 1-11.