Computational Designing and Screening of Solid Materials for CO_2 Capture Technology

Yuhua Duan
National Energy Technology Laboratory, U. S. Department of Energy, Pittsburgh, PA 15236, USA

Research & Innovation Center — NATIONAL ENERGY TECHNOLOGY LABORATORY

Motivation

- **Due to the environmental issues that the world faces today, there are significant interests to develop materials capable to capture CO_2 with optimal performances.**
- **Solid materials are potential candidates for CO_2 sorbents. By combining the database mining with *ab initio* thermodynamic calculation, we implemented a novel theoretical methodology to screen solid sorbents from known material databank and to synthesize new materials with improved CO_2 capture capabilities for further experimental validations.**

Theoretical Methods

For the reaction of a solid to absorb CO_2([...] are optional):

$$solid\_sorbent + CO_2 \pm [H_2O] \rightarrow sorbent\_CO_2 + [solid]$$

The chemical potential ($\Delta\mu$) of the reaction can be calculated as:

$$\Delta\mu(T,P) = \Delta\mu^0(T) - RT(\ln P_{CO_2} \pm \ln P_{H_2O})$$

A. Intensive search for thermodynamic properties of solids from known databases and literatures. If all of them are known, obtain the better candidates by minimizing free energies based on operating conditions.

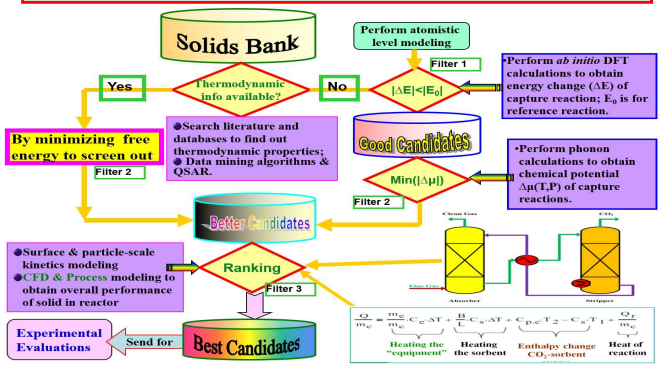
B. If their thermodynamic properties are unknown, calculate by

$$\Delta\mu^0(T) \approx \Delta E^{DFT} + \Delta E_{ZPE} + \Delta F_{PH}(T) - (G_{CO_2}(T) \pm G_{H_2O}(T))$$

Reaction Heat: $$\Delta H(T,P) = \Delta\mu(T,P) + T(\Delta S_{PH}(T,P) - S_{CO_2}(T,P) \mp S_{H_2O}(T,P))$$

where
- G_{CO2}, S_{CO2}, and G_{H2O} and S_{H2O} evaluated from statistical mechanics;
- ΔE^{DFT} are calculated by density functional theory;
- ΔE_{ZPE}, $\Delta S_{PH}(T)$ and $\Delta F_{PH}(T)$ evaluated through phonon dispersions.

High-Throughput Screening Methodology



Application to Alkali and Alkaline Metal Materials

- **21** reactions for alkali and alkaline metal oxides, hydroxides and bicarbonates capture CO_2;
- Set CaO as reference. After filter I, only **10** reactions left; After filter II, only **4** solids were selected which are in good agreement with experimental data. ↔ validation our method.

Best Candidates with Rank:
1. MgO
2. $NaHCO_3$/Na_2CO_3

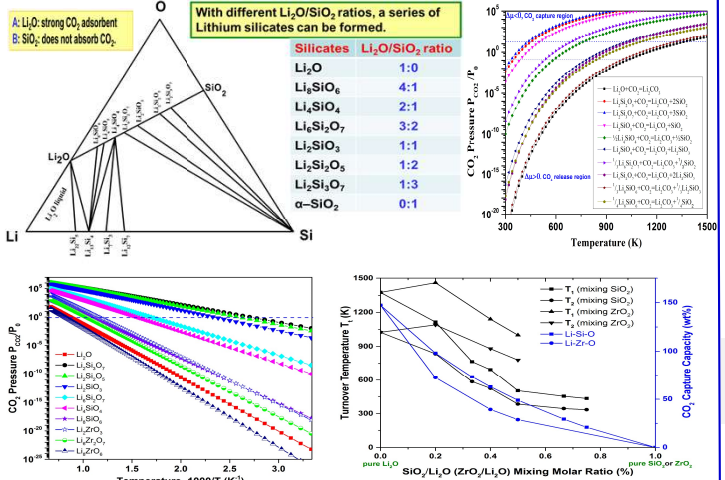
Synthesis New Sorbents to Fit Operation Needs

I. Mixture A/B Sorbents (T_A>T_B) using A capture CO_2 by decreasing T_A

A: Li_2O: strong CO_2 adsorbent
B: SiO_2: does not absorb CO_2.

With different Li_2O/SiO_2 ratios, a series of Lithium silicates can be formed.

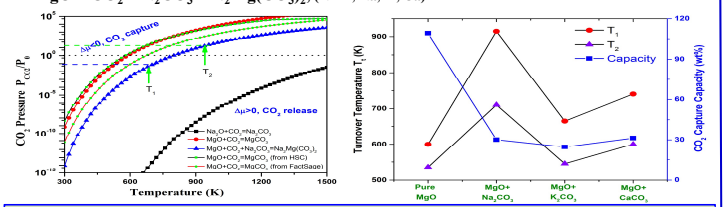
Silicates	Li_2O/SiO_2 ratio
Li_2O	1:0
Li_8SiO_6	4:1
Li_4SiO_4	2:1
$Li_6Si_2O_7$	3:2
Li_2SiO_3	1:1
$Li_2Si_2O_5$	1:2
$Li_2Si_3O_7$	1:3
α-SiO_2	0:1



- By mixing SiO_2/ZrO_2 (B) into Li_2O (A) to form lithium silicates (zirconates), the turn over T_t of the newly formed material is lower than T_A. By adjusting ratio of A and B, the T_t could be shifted into the range which a particular CO_2 capture technology needs.

II. Mixture A/B Sorbents (T_A>T_B) using B capture CO_2 by increasing T_B

$MgO + CO_2 + N_2CO_3 = N_2Mg(CO_3)_2$, (N=Li, Na, K, Ca)



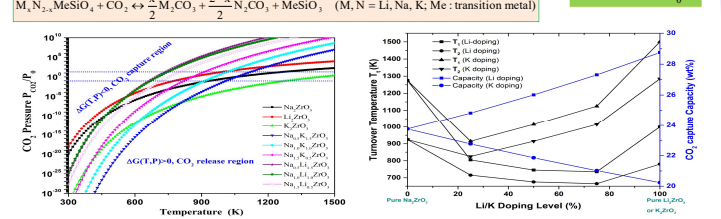
- By mixing alkali oxide (or carbonate) (A) into MgO (B), after capturing CO_2, the double salt is formed. Such CO_2 capture reaction has a higher T_t than T_B. By adjusting the type of A and the ratio of A/B, the T_t could be increased into the range to best fit the CO_2 capture technology needs.

III. Doped Solid Materials to Adjust Turn-over T_t

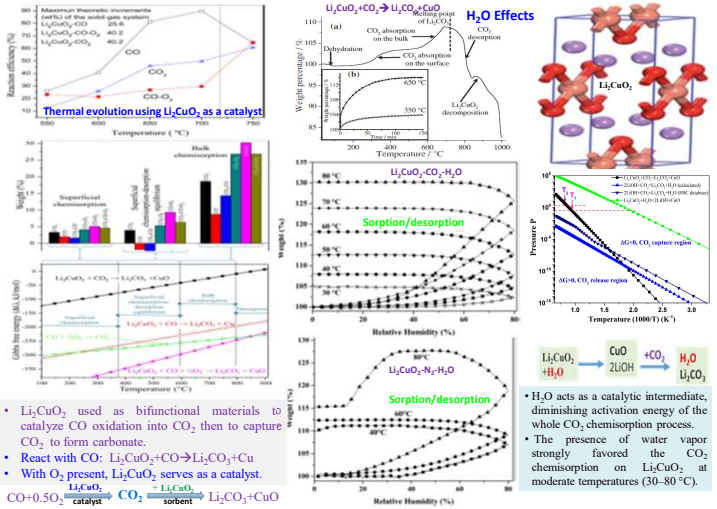
$$M_xN_{2-x}ZrO_3 + CO_2 \leftrightarrow \frac{x}{2}M_2CO_3 + \frac{2-x}{2}N_2CO_3 + ZrO_2 \qquad (M, N = Li, Na, K;\ x = 0, 0.5, 1, 1.5, 2)$$

$$M_xN_{2-x}MeSiO_4 + CO_2 \leftrightarrow \frac{x}{2}M_2CO_3 + \frac{2-x}{2}N_2CO_3 + MeSiO_3 \qquad (M, N = Li, Na, K;\ Me: transition\ metal)$$

$$T_t = \frac{\Delta\mu^0(T)}{R \ln \frac{P_{CO_2}}{P_0}}$$



Dual-functionality: CO Oxidation + CO_2 Capture



- Li_2CuO_2 used as bifunctional materials to catalyze CO oxidation into CO_2 then to capture CO_2 to form carbonate.
- React with CO: Li_2CuO_2+CO→Li_2CO_3+Cu
- With O_2 present, Li_2CuO_2 serves as a catalyst.

$$CO + 0.5O_2 \xrightarrow{Li_2CuO_2\ catalyst} CO_2 \xrightarrow{+\ Li_2CuO_2\ sorbent} Li_2CO_3 + CuO$$

Li_2CuO_2 + H_2O → CuO + 2LiOH —(+CO_2)→ H_2O + Li_2CO_3

- H_2O acts as a catalytic intermediate, diminishing activation energy of the whole CO_2 chemisorption process.
- The presence of water vapor strongly favored the CO_2 chemisorption on Li_2CuO_2 at moderate temperatures (30–80 °C).

Conclusions

- **Our theoretical approach can obtain similar results as experimental measurements and can be used to identify better candidates.**
- **The strength of our method is to screen complex sorbent materials for which their thermodynamic properties are not available.**
- **Hundreds of solid materials have been investigated. Now, we are continuing to work on screening of multi-components, substituted, doped, and mixed materials to search for good CO_2 sorbents.**
- **By mixing/doping different solids, we can theoretically synthesize new materials which may fit the industrial operating conditions with optimal CO_2 capture performance.**
- **Some solid sorbents possess dual-functions: oxidation CO and capture CO_2.**

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Acknowledgement

The author thanks Drs. D. C. Sorescu, B. Y. Li, X. F. Wang, K. L. Zhang, X. S. Li, D. King, B. Alcántar-Vazquez, H. Pfeiffer, P. Sanchez-Camacho, H. A. Lara-Garcia, E. Vera, J. Arturo Mendoza-Nieto, J. L. Chi, L. F. Zhao, Y. H. Xiao, F. Shi, W. Shi, B. Zhang, D. Luebke, H. W. Pennline, J. K. Johnson, K. Parlinski, J. W. Halley, P. Singh, D. Hopkinson, G. Richards, and M. Syamlal for fruitful discussions and collaborations.

Contact information: Tel. 412-386-5771, email: yuhua.duan@netl.doe.gov

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