# $CO_2$ Scrubbing with Novel Lithium Zirconate Sorbents

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## Introduction

Electric power generated from the combustion of fossil fuels is accountable for over one-third of the global annual $CO_2$ emissions. Large stationary sources are, therefore, considered credible targets for carbon sequestration. For this reason, the successful implementation of practical and cost effective $CO_2$ separation and capture technologies are projected to have a major impact on mitigating environmental problems posed by $CO_2$ emissions.

Existing commercial operations for removing $CO_2$ from flue gas make use of chemical absorption with various amine solvents. Inherent deficiencies associated with this process include low $CO_2$ loadings and significant energy requirements for $CO_2$ release. Alternative technologies for $CO_2$ capture are considered necessary.

One promising technology with the potential for significant development employs dry scrubbing with regenerable sorbents.[1-9] These processes are cyclical since the sorbent can successfully remove the gaseous component, be regenerated, and in this step yield a concentrated stream of $CO_2$, and then reused. Advanced processes based on dry regenerable sorbents may offer attractive benefits over existing solvent-based practices.

Lithium zirconate ($Li_2ZrO_3$), with its favorable $CO_2$ sorption characteristics, is considered a promising material for $CO_2$ removal at high temperature. The chemical reaction for $CO_2$ capture using $Li_2ZrO_3$ is illustrated below. The forward reaction pathway depicts absorption of $CO_2$, whereas regeneration is expressed as the reverse reaction path.

$$Li_2ZrO_3\ (s) + CO_2\ (g) \Leftrightarrow Li_2CO_3\ (s) + ZrO_2\ (s) \qquad [1]$$

Nakagawa and Ohashi[1,2] observed $Li_2ZrO_3$ powder reacts immediately with $CO_2$ in the temperature range of 450° to 590°C. Ohashi and Nakagawa[3] also report the addition of potassium carbonate to $Li_2ZrO_3$ significantly influences its kinetic rate and increases its $CO_2$ capture capacity. They conclude this acceleration results from the formation of a $Li_2CO_3$-$K_2CO_3$ eutectic encapsulating a solid $ZrO_2$ core. Lin and Ida[5,6] confirm these observations and offer a comprehensive double-shell model describing the mechanism for $CO_2$ sorption/desorption on pure and potassium-doped $Li_2ZrO_3$ sorbents.

In this study, we examined the influence of potassium carbonate and other alkaline carbonate eutectic agents for enhancing the direct carbonation of $Li_2ZrO_3$. Improvement in the $CO_2$ sorption rate is important for its practical application in design and development of dry, regenerable sorbent materials for $CO_2$ capture under operating conditions prevailing in Integrated Gasification Combined Cycle (IGCC) processes.

## Experimental

High purity $Li_2ZrO_3$ procured from Aldrich Chemical Co. was used as the primary substrate. Thermogravimetric Analysis (TGA) with a microelectronic recording balance system (Cahn TG-131) was employed to examine the $CO_2$ sorption properties of pure and molten salt-containing $Li_2ZrO_3$ powders. A gas cylinder supplied $CO_2$ of stock gas grade (99.99%) to the TGA apparatus. Sample temperature was measured and controlled with a type K thermocouple located directly below the suspended sample pan. Approximately 100 mg of $Li_2ZrO_3$ was charged into a platinum sample pan for testing. For molten salt-containing $Li_2ZrO_3$ samples, 20% by weight of carbonate (or halide) salt was physically admixed with 100 mg $Li_2ZrO_3$ prior to placing the sample into the TGA instrument. **Table 1** shows the composition and eutectic temperatures of the molten salt-containing $Li_2ZrO_3$ samples.

**Table 1. Composition and eutectic temperatures of molten salt-containing $Li_2ZrO_3$ sorbent materials**

| Sample ID | Molten salt composition (mol%) | Eutectic Temp (°C)[a] |
|---|---|---|
| B1 | $K_2CO_3$ 38% $Li_2CO_3$ 62% | 488 |
| B2 | $K_2CO_3$ 57.3% $Li_2CO_3$ 42.7% | 498 |
| B3 | $Na_2CO_3$ 48% $Li_2CO_3$ 52% | 500 |
| B4 | KF 38% $Li_2CO_3$ 62% | n/a |
| B5 | $K_2CO_3$ 57% $MgCO_3$ 43% | 460 |
| T1 | $K_2CO_3$ 26.8% $Na_2CO_3$ 30.6% $Li_2CO_3$ 42.5% | 393 |

[a] Physical Properties Data Compilations Relevant to Energy Storage.
1. Molten Salts: Eutectic Data, U.S. Dept. of Commerce, March 1978

Prior to $CO_2$ sorption, each sample was pre-conditioned and dried in nitrogen by elevating the temperature (at 10°/min) to 500°C and holding for 30 minutes. Upon completion of this step, the surrounding stream of $N_2$ gas was switched to pure $CO_2$ while maintaining a flow rate of 140cc/min. $CO_2$ sorption testing was conducted at 500°C. The change in sample weight with time was recorded during absorption, upon which the experimental conversion of $Li_2ZrO_3$ to $Li_2CO_3$ was calculated. Regeneration of the $Li_2ZrO_3$ samples was performed by switching the feed gas back to $N_2$ after raising the temperature to 800°C.

X-ray diffraction (XRD) characterization of the modified $Li_2ZrO_3$ samples after $CO_2$ sorption at 500°C was conducted using a PANalytical X'pert Pro powder diffractometer with a Cu X-ray source at 45 kV and 40 mA. The XRD patterns were recorded over a 2θ range of 8° to 70°. Phase identification was verified by comparison to the ICDD inorganic compound powder diffraction data base.

## Results and Discussion

**Figure 1** shows the $CO_2$ uptake of the Aldrich $Li_2ZrO_3$ powder at 500°C after the surrounding $N_2$ gas stream was switched to pure $CO_2$ ($P_{co2}$ = 1atm). The pure $Li_2ZrO_3$ sample shows a steady but very slow

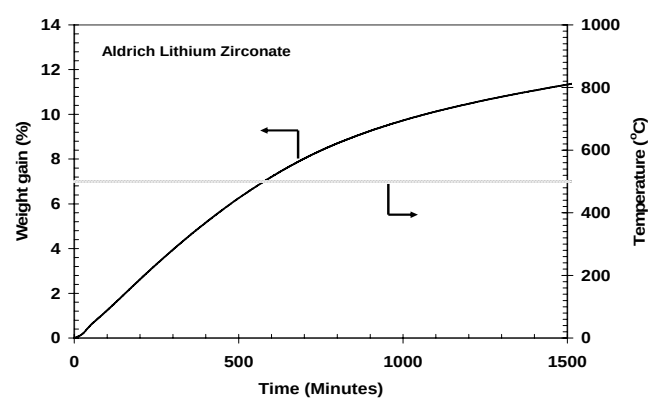


**Figure 1.** $CO_2$ sorption profile of Aldrich $Li_2ZrO_3$ powder at 500°C Initial sample weight: 100 mg $Li_2ZrO_3$ Gas flow rate: 140cc/min Total pressure: 1 atm

increase in sample weight upon $CO_2$ exposure. From this figure, pure $Li_2ZrO_3$ gained nearly 11 wt % $CO_2$ of its sample weight within 1500 minutes, which corresponds to a reaction yield of 38.3% based on equation 1. (Theoretical maximum uptake of $CO_2$ for pure $Li_2ZrO_3$ sample equals 28.7 wt %.) After completion of the first sorption step, the $Li_2ZrO_3$ sample was successfully regenerated at 800°C in nitrogen. These results were found in good agreement with values reported by Nakagawa and Ohashi,[1-3] Essaki[4] et al. and Lin.[5] XRD analyses identified $Li_2ZrO_3$, $Li_2CO_3$ and $ZrO_2$ as major crystalline phases after $CO_2$ exposure at 500°C.

The influence of molten salt mixtures of alkaline and alkaline earth carbonates on the rate of $CO_2$ sorption of the modified $Li_2ZrO_3$ powders at 500°C is illustrated in **Figure 2**. It should be noted that no attempt was made to optimize the dispersion of the molten salts onto the $Li_2ZrO_3$ powder. The majority of the binary eutectic containing $Li_2ZrO_3$ samples absorbed 11 to 13 wt % of $CO_2$ of the sample weight within 60 minutes. The potassium/lithium carbonate-containing $Li_2ZrO_3$ samples (designated *B1* and *B2*) have eutectic melting points of 488° and 498°C respectively. These samples show a much faster rate (25 times faster) of $CO_2$ uptake compared to the pure $Li_2ZrO_3$. The binary sodium/lithium carbonate doped $Li_2ZrO_3$ sample (*B3*) and ternary carbonate doped $Li_2ZrO_3$ sample (T1), consisting of sodium carbonate, potassium carbonate, and lithium carbonate, with a melting point of 393°C, produced comparable rates of $CO_2$ uptake as the potassium-containing *B1* and *B2* samples.

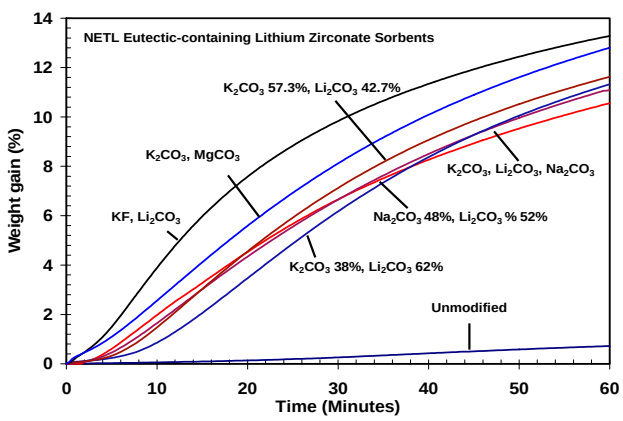


**Figure 2** Influence of eutectic additives on rate of $CO_2$ sorption for NETL promoted $Li_2ZrO_3$ sorbents. Reaction temperature: 500°C.

The binary $K_2CO_3$-$MgCO_3$-containing $Li_2ZrO_3$ sample (*B5*) has a melting point of 460°C, which is nearly 40°C lower than previous binary carbonate $Li_2ZrO_3$ samples tested. The rate along with its capacity remained high over the entire sixty minutes under a 100% $CO_2$ flow. Sample *B5* absorbed over 12% of its sample weight, corresponding to 41.7% of its theoretical maximum. **Figure 3** shows a scanning electron micrograph of the spent $K_2CO_3$-$MgCO_3$-containing $Li_2ZrO_3$ sample after $CO_2$ sorption at 500°C. At this magnification, the single particle appears to be dense, non-porous in appearance. The mixed potassium halide/carbonate $Li_2ZrO_3$ sample (*B4*) gave the fastest rate (40 times faster) of $CO_2$ uptake compared to the unmodified $Li_2ZrO_3$ sample. Under IGCC applications, sorbent kinetics is anticipated to improve due to elevated $CO_2$ pressures. XRD analysis identified $Li_2CO_3$ and $ZrO_2$ as major phases upon rapid quenching of carbonated *B4* and *B5* samples in $CO_2$.

By TEM and EDX analysis, Ohashi and Nakagawa[3] report the existence of a potassium/lithium carbonate eutectic surrounding a solid $Li_2ZrO_3$ core. In the case of the pure $Li_2ZrO_3$ sample (without $K_2CO_3$ additive), formation of an impervious shell of $Li_2CO_3$ results on the outer surface of the unreactive $Li_2ZrO_3$ core. This observation suggests diffusion resistance of $CO_2$ through the solid $Li_2CO_3$ product layer is the rate-limiting step. In contrast, the potassium/lithium carbonate-containing $Li_2ZrO_3$ sample reacts with gaseous $CO_2$ at 500°C to form a molten liquid outer layer and a solid interior $ZrO_2$ shell. Therefore, the difference in $CO_2$ sorption rate can be partially contributed to the molten carbonate layer; $CO_2$ diffuses through the molten carbonate layer at a much faster rate.

Lin and Ida[5] describe a comprehensive double-shell model relating to the mechanism for $CO_2$ sorption on potassium-doped $Li_2ZrO_3$. They conclude after the formation of the molten potassium-lithium carbonate layer and $ZrO_2$ shell, the carbonation reaction will proceed by the diffusion of $Li^+$ and $O^{2-}$ ions through the $ZrO_2$ shell along with diffusion of $CO_2$ through the molten carbonate layer. Strategies for reducing the depth of the solid $Li_2CO_3$ and $ZrO_2$ shells formed during reaction should provide additional insight and improvement in sorbent performance.

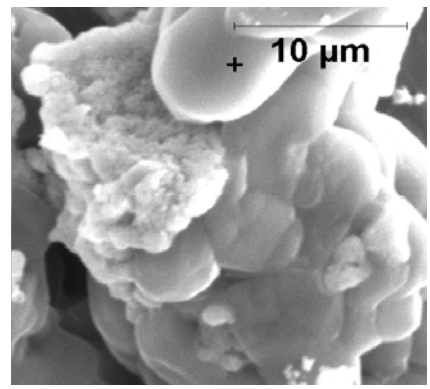


**Figure 3.** Scanning electron micrograph of $K_2CO_3$-$MgCO_3$ eutectic containing $Li_2ZrO_3$ sample (*B5*) after $CO_2$ sorption at 500°C.

## Conclusions

$CO_2$ sorption performances of alkaline and alkaline earth-containing $Li_2ZrO_3$ sorbent materials at 500°C show very favorable reaction kinetics for $CO_2$ capture in comparison to pure lithium zirconate. Future work will focus on the synthesis of molten salt-containing, nanocrystalline $Li_2ZrO_3$ samples along with $CO_2$ sorption testing using TGA and a fixed-bed reactor with mixtures of gases simulating fuel gas environments, such as that found in IGGC operations.

## References


1. Nakagawa, K.; Ohashi, T. *J. Electrochem. Soc.* **1998**, 45(4), 1344-1346
2. Nakagawa, K.; Ohashi, T. *J. Electrochemistry* **1999**, 67(6), 618-621.
3. Ohashi, T.; Nakagawa, K. *Mat.Res. Soc. Symp. Proc.* **1999**, 47, 249-254.
4. Essaki, K.; Nakagawa, K.; Kato, M. *J. of the Ceramic Society of Japan* **2001**, 109(10), 829-833.
5. Lin, Y.S.; Ida, J. *Environ. Sci. Technol.* **2003**, 37(9), 1999-2004.
6. Ida, J.; Xiong, R.; Lin, Y.S. *Sep. Pur. Technol.* **2003**, article in press.
7. Gupta, H.; Fan, L.S. *Ind. Eng. Chem. Res.* **2002**, 41(16), 4035-4042.
8. Fauth, D.J.; Hoffman, J.S.; Pennline, H.W. *Fuel Chemistry Division Preprints*, **2003**, 48(1), 169-170.
9. Pennline, H.W.; Hoffman, J.S. U.S. Patent No. 6,387,337, **2002**.