


Cite this: *RSC Adv.*, 2024, **14**, 40133

Received 30th October 2024
Accepted 16th December 2024

DOI: 10.1039/d4ra07753a
rsc.li/rsc-advances

Beryllium carbonate: a model compound for highest capacity carbon sequestration chemistry†

Gad Licht,^a Kyle Hofstetter^b and Stuart Licht  ^{*abc}

Beryllium carbonate has the highest capacity to bind and release the greenhouse gas CO_2 compared to amines, ionic liquids, CaCO_3 or Li_2CO_3 . The thermodynamic equilibrium for CO_2 and BeO from BeCO_3 is calculated. TGA of BeCO_3 is used to determine the stepwise mechanism of its CO_2 release, and the low melting point Li/Sr/BeCO_3 is demonstrated.

Introduction

Rising CO_2 levels are causing catastrophic climate change, and are an existential threat to the planet. Atmospheric CO_2 levels, stable at $235 (\pm 50)$ ppm for several hundred thousand years prior to the industrial revolution, have nearly doubled to 424 ppm and continue to rise rapidly. The effects of climate change include an increasing probability of a mass species extinction event.¹ The ongoing toll on humanity and the planet's habitats are increasingly evident; on a personal note, the first and third authors of this study have just experienced ground zero of two "once in a millennium rainfall events" (Hurricanes Helene and Milton) in a period of two weeks, while the middle author is subject to increasingly frequent forest fires.

A principal path to mitigate climate change is CO_2 sequestration, and CO_2 capture capacity is a measure of the extent of a chemical species binding of CO_2 for use in carbon sequestration chemistry. CO_2 capture capacity is quantified as mass or mole capacity of CO_2 per mass or mole of absorbent. In addition to the general need for effective CO_2 trapping materials to mitigate CO_2 -induced global warming and climate change, other examples of the need for lightest weight carbon capture materials for CO_2 air scrubbing, include those needed by submersibles, submarines, and spacecraft.^{2,3}

Several recent reviews have focused on amines (and amino acids), calcium oxide (to calcium carbonate), and ionic liquids to bind and release CO_2 .^{4–9} More recently, there has been a growing focus on nanomaterials, such as carbon nanomaterials,^{10–12} and also on and lithium carbonate and mixed lithium/strontium carbonates^{13–16} to capture CO_2 has emerged. Table 1 summarizes common absorbents including amines, ionic liquids, calcium oxide (to calcium carbonate), and

more recently, lithium oxide (to lithium carbonate). In this study, beryllium carbonate is introduced as a model compound, establishing a baseline for among the highest capacities of CO_2 captured.

CO_2 can be captured and stored by thermal cycling. In this case, dilute CO_2 is generally introduced at a lower temperature and released in a concentrated form at a higher temperature. Thermal cycling can comprise adsorption chemistry, as generally occurs with various amine carbon capture chemistries,^{5,7} or by chemical reactions, as occurs in the reaction of dissolved or solid calcium oxide with CO_2 to calcium carbonate, followed by high-temperature decomposition of calcium carbonate back to calcium oxide.⁸ Thermal cycling is often accompanied by pressurization and also by different subsequent processes to sequester (Carbon Capture and Storage, CCS) or chemically convert (Carbon Capture Utilization and Storage, CCUS) the captured concentrated CO_2 . As an alternative to thermal cycling, the CO_2 capture can be accomplished by electrolysis (such as the electrochemical splitting of CO_2 to C and O_2) to a product containing the captured CO_2 , such as the formation of Carbon NanoTubes (CNTs) from CO_2 in molten carbonates.^{17–20} This latter CCUS process often occurs in a single step.

In Table 1, the capacity for CO_2 is compiled for common CO_2 absorbents (absorbents referring to both adsorbents, absorbents, and reactants). The capacity for CO_2 is presented in units of both mole CO_2 /mole absorbent and also in more typical units of kg CO_2 captured per kg absorbent in the last column. Pragmatic capacities for CO_2 will be lower than those compiled when a matrix (such as an inert membrane or solvent stabilizer) is required as an additional mass component in the CO_2 capture process.

Amines and amino acids have been widely studied both as absorbents, principally in the liquid phase, to absorb and release CO_2 , and as adsorbents principally affixed on membranes to adsorb and release CO_2 . As seen in Table 1, amines and amino acids have respective capacities for CO_2 of 0.19–0.37 or 0.27–0.35 kg CO_2 per kg (amine or amino acid). Ionic liquids have attained capacities of 0.07–0.09 kg CO_2 per kg. CaO/CaCO_3 has a capacity for CO_2 of 0.78 kg CO_2 (determined as of $\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$

^aC2CNT LLC, A4 188 Triple Diamond Blvd, North Venice, FL 34275, USA. E-mail: slicht@gwu.edu
^bCarbon Corp., 1035 26 St NE, Calgary, AB T2A 6K8, Canada

[†]Dept. of Chemistry, George Washington University, Washington DC 20052, USA

[†] Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4ra07753a>


Table 1 The high capacity for CO₂ of beryllium oxide as beryllium carbonate compared to other absorbents

Chemical absorbent/product	Acronym	Formula	Formula weight, g mol ⁻¹	CO ₂ storage mechanism	Capacity for CO ₂ , mol CO ₂ /mol absorbent	Source, reference	Capacity for CO ₂ , kg CO ₂ per kg absorbent
1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide	[Bmim] [Tf ₂ N]	C ₁₀ H ₁₅ F ₆ N ₃ O ₄ S ₂	419.37	Ionic liquid	0.68	7	0.07
1-Aminopropyl-3-methylimidazolium tetraborafluorate/various products	APMim [BF ₄]	C ₇ H ₁₄ N ₃ BF ₄	227.01	Ionic liquid	0.34	7	0.07
1-Butyl-3-methylimidazolium hexafluorophosphate/various products	[Bmim] [PF ₆]	C ₈ H ₁₅ F ₆ N ₂ P	284.186	Ionic liquid	0.51	7	0.08
1-Butyl-3-methylimidazolium tetrafluoroborate/various products	[Bmim] [BF ₄]	C ₈ H ₁₅ BF ₄ N ₂	226.03	Ionic liquid	0.44	7	0.09
Taurine to protonated acid, HCO ₃ ⁻ or carbamate		C ₂ H ₇ NO ₃ S	125.14	Amino acid	0.7	7	0.25
Proline to protonated acid, HCO ₃ ⁻ or carbamate		C ₅ H ₉ NO ₂	115.132	Amino acid	0.7	7	0.27
Glycine to protonated acid, HCO ₃ ⁻ or carbamate		C ₂ H ₅ NO ₂	75.067	Amino acid	0.6	7	0.35
Monoethanolamine to RNHCOO ⁻	MEA	C ₅ H ₁₃ NO ₂	61.08	Amine	0.5	7	0.36
Diethanolamine to RNHCOO ⁻	DEA	C ₄ H ₁₁ NO ₂	105.14	Amine	0.5	7	0.21
Methyldiethanolamine to ""	MDEA	C ₅ H ₁₃ NO ₂	119.164	Amine	1	7	0.37
Diethylethanolamine to ""	DEAE	C ₆ H ₁₅ NO	117.192	Amine	0.5	7	0.19
Calcium oxide to carbonate		CaO	56.08	CaO + CO ₂ → CaCO ₃	1	9	0.78
Lithium oxide to carbonate		Li ₂ O	29.88	Li ₂ O + CO ₂ → Li ₂ CO ₃	1	16	1.47
Beryllium oxide to carbonate		BeO	24.01	BeO + CO ₂ → BeCO ₃	1	This study	1.83

from the 44.01 g per mol FW of CO₂ to the 56.08 g per mol FW of CaO). The lighter molecular weight Li₂O/Li₂CO₃ has a capacity for CO₂ of 1.47 kg CO₂. In order of increasing CO₂ capacities, the absorbents are ionic liquids < amino acids & amines < CaO (to CaCO₃) < Li₂O (to Li₂CO₃).

In this study, beryllium carbonate, with the lowest melting points of inorganic carbonates, is introduced as a model compound establishing a baseline for maintaining the highest capacities for CO₂ (1.83 kg CO₂ per kg BeO → BeCO₃). Beryllium carbonate is also as an example of a melting point decrease facilitator by addition of BeCO₃ to binary Li/SrCO₃ electrolyte to become the substantially lower melting point ternary Li/Sr/BeCO₃. Binary mixtures typically melt at lower temperatures than pure components because the presence of different molecules disrupts the crystal lattice, weakening intermolecular forces and reducing the energy needed to melt, and in this case CO₂ release can then be achieved using a lower thermal energy input.

Results and discussion

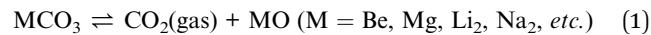
Phase changes & CO₂ equilibria of alkali & alkali earth carbonates

As summarized in Table 2, the melting point of beryllium carbonate (mp 54 °C), Be₂CO₃, is low in the extreme compared

to that of the other alkali earth or alkali carbonates, or compared to their binary or tertiary carbonate mixtures. It should be noted that reported values of carbonate melting points exhibit a considerable range of 10 °C or more. For example, in 7 studies, the melting point of Li₂CO₃ is reported from 700 °C to 728 °C.²²⁻²⁸ Furthermore, the CO₂ concentration in the atmosphere has increased by 35% since the first of these reports appeared (in 1957). The stability of lithium carbonate increases under 1 atm of CO₂, and we also note that many properties, including melting points, of species related to CO₂ equilibrium will need to be reevaluated due to the rapidly increasing atmospheric concentration of this greenhouse gas.

Alkali carbonate binary mix eutectics have lower melting points. The lowest melting alkali carbonate is generally considered to be the Li_xNa_yK_zCO₃ with a melting point of 397 °C (at $\sim x = 0.47$, $y = 0.62$, $z = 0.5$), still considerably higher than the melting point of BeCO₃, by 343 °C.

The extent to which an alkali or alkali earth carbonates retains CO₂ is given by:



$$K = p_{CO_2} a_{MO} / a_{MCO_3}; K(T) = e^{-\Delta G(T)/RT} \quad (2)$$



Table 2 Melting point of alkali and alkali earth carbonates and their eutectic mixtures

Carbonate	Melting point (°C)	Decomposition point (°C)	Ref.
Be ₂ CO ₃	54	~100	21
Li ₂ CO ₃ , Na ₂ CO ₃ or K ₂ CO ₃	723, 851 or 891	~1300 ^a (Li ₂ CO ₃)	30
BaCO ₃	810	~1360	31 and 32
MgCO ₃	—	~350	32
CaCO ₃	—	~850	31 and 32
SrCO ₃	1494	1494	13
Li ₂ /BaCO ₃ ; 55/45 mol%	609		31 and 34
K ₂ CO ₃ /MgCO ₃ ; 57/43 mol%	460		35
Li ₂ /K ₂ CO ₃ ; 62/38 mol%	498		35
Na ₂ /K ₂ CO ₃ ; 56/44 mol%	710		35
Li ₂ /Na ₂ /K ₂ CO ₃ ; 43.5/31.5/25 mol%	397		35
Li ₂ /Sr ₂ CO ₃ ; 60/40 wt%	680		13
Be/Sr/Li ₂ CO ₃ ; 33/33/33 wt%	480		This study

^a Li₂CO₃ decomposition is more rapid under argon than under air.¹⁵

An extensive literature search did not reveal phase diagrams or equilibria for beryllium carbonate. We've calculated the BeCO₃/BeO + CO₂ equilibrium from the available enthalpy and entropy of the constituent species.²⁹

Fig. 1 presents a comparison of the carbonate/oxide equilibrium constant for binding and releasing of CO₂ by beryllium carbonate compared to those for alkali, or other alkali earth carbonates as a function of temperature. Below any of the Fig. 1 equilibrium presented curves, that is, in the high CO₂ activity domain, the carbonate salt will spontaneously form from CO₂ and the salt's oxide. Above any Fig. 1 equilibrium curve, the low CO₂ activity domain ($a_{\text{CO}_2} a_{\text{oxide}} / a_{\text{carbonate}} < K$), the carbonate salt will spontaneously decompose. For example, as noted in Table 2, solid MgCO₃ decomposes at 350 °C, releasing bound CO₂, and as seen is the second largest (other than BeCO₃) of the eqn

(2) carbonate/oxide equilibrium constants. The high industrial carbon footprint conversion process of limestone to lime or cement depends on the solid state decomposition of calcium carbonate, such as aragonite, which occurs at ~850°.

Li₂CO₃/Li₂O was introduced as among the highest CO₂-capture materials, as delineated in the next to last row of Table 1, with a storage capacity of 1.47 kg CO₂ per kg Li₂O. Under argon, Li₂CO₃ entirely dissociates to CO₂ + Li₂O. Specifically, at a TGA rate of 5° min⁻¹ under 1 atm of argon Li₂CO₃ dissociation starts around the lithium carbonate melting point of 723 °C, and is 98% complete to Li₂O by 900 °C, and under 1 atm of pure CO₂ also starts at 723 °C, but the dissociation is less than 10% complete by 900 °C.¹⁵ However, under even small partial pressures of CO₂, such as the 426 ppm (and rising) of atmospheric CO₂, Li₂CO₃ only fractionally dissociates to CO₂, attaining 0.3 molal concentration Li₂O per kg molten Li₂CO₃ at 750 °C.³⁶ This high capacity was experimentally realized in the form of the electrolytic splitting of CO₂ in molten Li₂CO₃ to graphene nanocarbons.⁴⁰⁻⁴⁹ The small concentration of dissolved Li₂O in molten Li₂CO₃ under air is sufficient to support high CO₂ splitting electrochemical current and continuous renewal of the molten Li₂CO₃ electrolyte with CO₂.⁵⁰

The relationship between melting and decomposition temperatures for carbonates is complex. Beryllium carbonate has respective melting and decomposition points of BeCO₃ ($M_p = 54$ °C and $D_p = 100$ °C),²¹ lithium carbonate Li₂CO₃ ($M_p = 723$ °C and $D_p = 1300$ °C), while as seen in Table 2, solid calcium and barium carbonate do not melt nor sublime, but rather decompose directly to calcium or barium oxide and carbon dioxide, finally, strontium carbonate has equivalent, but very high melting and decomposition points SrCO₃ ($M_p = D_p = 1494$ °C). For binary and ternary mixtures, all the higher melting point carbonates are observed to be highly soluble in lithium carbonate. For example, over 60 wt% SrCO₃ is miscible in 750 °C molten Li₂CO₃.¹³

The temperature at which individual carbonates do, or do not, melt is observable and reproducible to within a few degrees. However, the decomposition point is much less distinct, occurring over hundreds of degrees. For example,

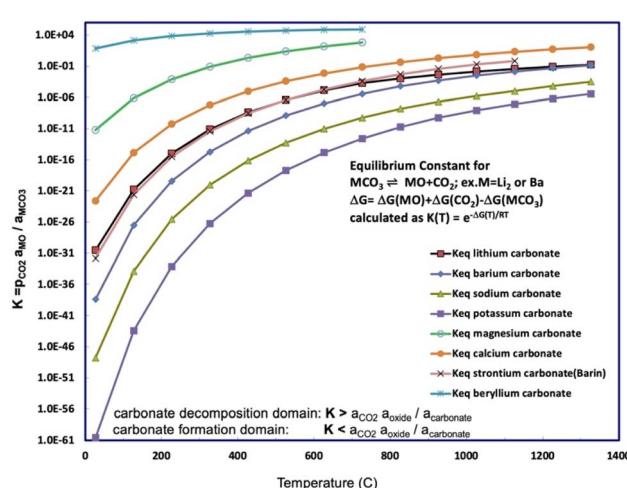


Fig. 1 Equilibrium constant for CO₂ release calculated for beryllium carbonate and compared to a range of alkali and alkali earth carbonates. The equilibrium constants as a function of temperature for strontium, lithium, sodium, potassium, and barium carbonate. The equilibrium constants are calculated from the free energy according to eqn (5). The free energy is calculated from the metal carbonate, metal oxide, and carbon dioxide enthalpies and entropies.^{29,36-39}



while the formal Li_2CO_3 decomposition point in Table 2 is ~ 1300 , substantial decomposition has already occurred at 750°C with release of CO_2 and the resultant Li_2O forming as a dissolved salt within the molten Li_2CO_3 .³⁶ Hence, this study focuses on the more precise melting point, rather than the broad range of observable decomposition point temperatures.

Beryllium carbonate as an ultra-high CO_2 storage material

When modeled as a specific example of eqn (1), beryllium carbonate is a high-capacity carbon capture storage material. Carbon dioxide is stored in beryllium carbonate and is released in the reaction to CO_2 and beryllium oxide:



In accord with eqn (3), BeCO_3 (FW 69.02 g mol^{-1}) stores $44.01 \text{ g mol}^{-1} \text{ CO}_2/\text{BeO}$ (FW 25.01 g mol^{-1}) = 1.83 kg CO_2 per kg $\text{BeO} \rightarrow \text{BeCO}_3$, as included in Table 1. As seen in Fig. 1, beryllium carbonate provides the largest of the equilibrium constants to release CO_2 of any of the alkali earth or alkali carbonates, and will begin to release CO_2 near ambient temperatures. At room temperature, beryllium carbonate (solid BeCO_3) is often stored under a blanket of CO_2 gas to prevent its decomposition. Beryllium oxide is the lightest weight oxide (other than water), and lithium and beryllium oxide have among the highest carbon capture storage capacities (as moles CO_2 storable per kg oxide).

Thermodynamically, BeCO_3 is the carbonate best suited to initiate storage and release of CO_2 at low temperatures. BeCO_3 is less prevalent as a salt than calcium, lithium, or strontium carbonate. Be is only the 48th most abundant element in the earth's upper crust,⁵¹ and it and its oxide, particularly in powder form, is carcinogenic. However, the storage of CO_2 by BeCO_3 serves as a model for among the highest carbon storage capacity materials and lowest mass CO_2 scrubbers.

The stepwise mechanism of beryllium carbonate CO_2 storage

Eqn (1) only provides a thermodynamic overview of a carbonate's capability to release CO_2 . The individual steps in the process of the binding of CO_2 into beryllium carbonate are investigated here by ThermoGravimetric Analysis, TGA.

Fig. 2 presents the TGA results of beryllium carbonate conducted from 30°C , with a 5°C temperature increase per minute, and in atmospheres of either (1) $80\% \text{ N}_2/20\% \text{ O}_2$ gas mix shown in the orange curve from 30 to 730°C or (2) $100\% \text{ N}_2$ shown in the blue curve from 30°C to 1000°C . In the figure, the downward trend in the mass is seen to start at approximately, the cited²¹ 54°C melting of BeCO_3 . The equivalence of the curves with or without an atmosphere containing O_2 provides primary evidence that O_2 is neither evolved nor absorbed by beryllium carbonate during the TGA, and that species in equilibrium with O_2 , including oxides, peroxides, and superoxides, those species are not participants in reactions related to the TGA temperature sweep.

In Fig. 2 above 54°C , BeCO_3 rapidly evolves CO_2 upon melting (at increasing temperature, the release of CO_2 from

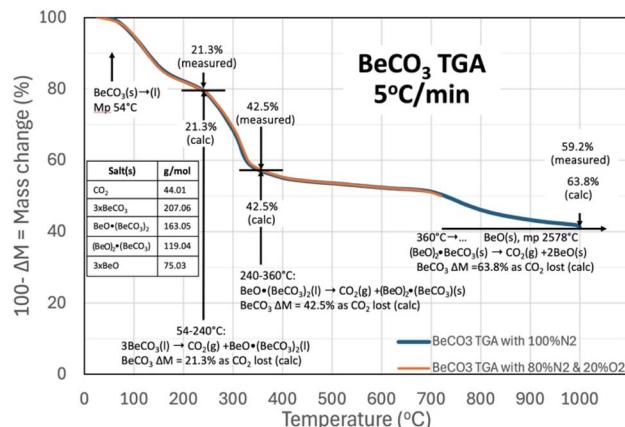


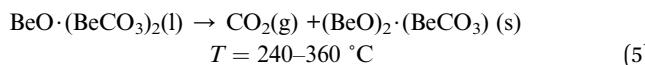
Fig. 2 TGA analysis of beryllium carbonate. The TGA is conducted from 30°C with a 5°C increase per minute in either (1) $80\% \text{ N}_2/20\% \text{ O}_2$ (from 30°C to 730°C) or (2) $100\% \text{ N}_2$ (from 30°C to 1000°C). Note, the observed TGA are identical (from 30°C to 730°C) in either the O_2 or pure N_2 environments.

BeCO_3 is an exergonic, spontaneous reaction). Released gases diffuse more slowly through a solid than through a liquid.⁵² Salts evolving CO_2 from the liquid, as opposed to from the solid form, facilitate the rapid release of CO_2 . For example, comparing liquid and solid CO_2 amine sorbents, solid gas reactions require much higher minimum work,⁵³ and the concurrent observed increased rate of mass loss acts as an indicator that the salt has melted. In solid salts that can release CO_2 by decomposition, CO_2 release is constrained by surface depletion and by the slow diffusion of CO_2 to the solid surface. Whereas, in the molten state, the liquid surface is continuously replenished, sustaining facile CO_2 access to the surface, and to the interior liquid bulk. In the figure, the mass loss and temperature are noted at the start of rapid mass declines with increasing temperature, and a mechanism of CO_2 mass loss is then determined by calculating mass consistent changes of the equivalent calcinated beryllium oxide and BeCO_3 salts.

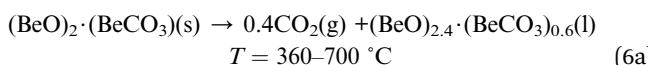
As seen in Fig. 2, molten BeCO_3 evolves CO_2 to become $\text{BeO}\cdot(\text{BeCO}_3)_2$ from $\sim 54^\circ\text{C}$ to 240°C , consistent with the equivalence of both the observed and the calculated mass loss as mass loss (of $\text{CO}_2/\text{mass BeCO}_3$) of 21.3% when one CO_2 is evolved from 3 BeCO_3 to become $\text{BeO}\cdot(\text{BeCO}_3)_2$, and the rapid mass loss indicative of facile CO_2 evolution from a liquid. In the future, several orders of magnitude larger than the TGA mg size samples would be useful to visually corroborate that this is in the liquid (l) phase at these temperatures:



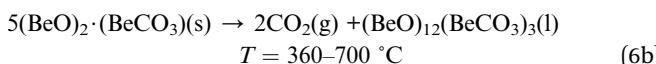
At increasing temperature, the molten $\text{BeO}\cdot(\text{BeCO}_3)_2$ then evolves CO_2 to become $(\text{BeO})_2\cdot\text{BeCO}_3$ (FW 119.04) from 240°C to 360°C ; again, as determined by the equivalence of both the observed and the calculated mass loss of 42.5% when 2CO_2 are evolved from 3BeCO_3 to become $\text{BeO}\cdot(\text{BeCO}_3)_2$, and once again the rapid mass loss indicative of facile CO_2 evolution from a liquid:



From 360 °C to ~700 °C, there is an observed slow, steady rate of CO₂ evolution as the mass loss observed in Fig. 2 increases to 50.9% from the original BeCO₃. The slow rate of CO₂ evolution is evidence that the eqn (5) product may be solid, and the additional (50.9–42.5%) 8.4% mass loss from 3BeCO₃ is evidence that the 2BeO·(BeCO₃) has evolved an additional 0.4 CO₂ over this temperature range with either a lower thermodynamic drive to release CO₂, or has reverted to the solid phase.



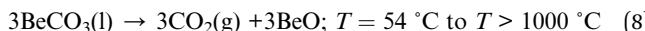
Equivalent to integral molecular values of:



Above 700 °C, the observed rate of mass loss and CO₂ evolution again increased, indicative that the product has once again entered a liquid phase as noted on the right side of eqn (6a). In eqn (6b) (BeO)₁₂(BeCO₃)₃(l) is a generalization of the total equivalence of BeO and BeCO₃ in the product, and it is likely that this consists of a solid BeO (mp 2578 °C) in a liquid phase of mixed BeO_x/BeCO₃. This product then evolves CO₂ to become BeO(s) from ~700 °C onward. As the end product of the beryllium carbonate CO₂ loss is a solid, high melting point BeO (mp 2578 °C), and by 1000 °C, the mass observed mass loss has reached 59.2% of the full, calculated 63.8% CO₂ mass loss from BeCO₃. Holding the TGA temperature at 1000 °C for 4 more hours resulted in a further mass loss of 1.2% to 60.4% of the full, calculated 63.8% CO₂ mass loss from BeCO₃:



For an overall reaction of:



The thermal release of CO₂ from BeCO₃ does not result in the formation of powdered BeO, which can be toxic, but rather initially forms BeO_y·(BeCO₃)_y, and then at highest levels of CO₂ release temperatures, forms BeO in the TGA as a sintered (solid) mass due to the high temperature of formation, rather than an easily dispersible and potentially toxic powder.

The kinetically and thermodynamic-driven release of CO₂ by heating BeCO₃ and beryllium oxide/carbonates intermediate compounds has been demonstrated, and will presumably similarly occur by alternatively reducing the pressure over those compounds, or by simultaneously heating and reducing the pressure of those compounds. Thermodynamically, the storage of CO₂ by beryllium oxide and beryllium oxide/carbonate intermediates is energetically favored by the reverse process of cooling or pressurizing under CO₂ beryllium oxide and beryllium oxide/carbonate intermediates and stores CO₂. Beryllium oxide is stable, and this stability to reaction can be overcome by

introducing kinetic facilitation to increase the rate of CO₂ uptake by cooling and/or with pressurized CO₂.

Future studies can probe the likelihood that the reverse beryllium oxide reaction with CO₂ to beryllium carbonate can be facilitated by means including: (i) bubbling CO₂ through the various molten (liquid phase) stages of beryllium oxide and its beryllium oxide/carbonate intermediates or forming a liquid aerosol combined with CO₂, (ii) increasing the surface area of the various solid phases stages of beryllium oxide and its beryllium oxide/carbonate intermediates such as by forming a powder, solid aerosol or fixing it to a high surface membrane or aerogel while combining with CO₂, (iii) introducing the CO₂ by mixing with a combined solid and liquid phase (slush) of beryllium oxide/carbonate intermediates, (iv) or a multistep reaction to incorporate CO₂ into beryllium oxide such as, but not limited to, the (iva) the facile reaction of CO₂ with ammonium compounds to form ammonium carbonates and the (ivb) reaction of beryllium oxide with sulfate compounds to form beryllium sulfates, followed by the (ivc) the facile reaction of ammonium carbonates and beryllium sulfates to form BeCO₃.

Beryllium-induced carbonate electrolyte melting point decrease

Li₂CO₃ is expensive due its relative scarcity and due to its increasing demand as a primary resource for EVs, but is useful for CO₂ removal and its electrolytic transformation to graphene nanocarbons.¹⁶ There is less demand for SrCO₃ and its derivative salts, such as SrO, are also much more abundant, and an order of magnitude less expensive than Li₂CO₃.^{13,51} We had demonstrated that molten Li₂CO₃ based electrolytes are effective for CO₂ carbon capture by the electrolytic splitting of CO₂. Interestingly, we recently found that the replacement of the majority of the Li₂CO₃ by SrCO₃ and SrO is also effective. The low-Li₂CO₃ electrolytes based on SrCO₃ are substantially less expensive than comparable Li₂CO₃-based electrolytes, and are useful for splitting and transforming CO₂ to stable graphene nanocarbons including CNTs and carbon nano-onions (ESI[†]).¹³ The use of an electrolyte that is a binary mixture (for example, Sr/Li carbonate or SrO/Li₂CO₃) that can provide a low melting point electrolyte that facilitates transition metal nucleated growth from CO₂ of nanographene carbon allotropes is preferred.^{13,16,40,42,47} Low-Li₂CO₃ electrolysis may be performed using a planar, rather than a coiled, and brass, rather than Monel, cathode without substantially affecting low-lithium CNT growth from CO₂.^{13,40,41}

Pure SrCO₃ has a high melting point of 1194 °C, and in accord with Table 2 does not decompose until temperatures $\gg 1000\text{ }^\circ\text{C}$. As previously noted and as measured by TGA, the rapid decomposition of pure Li₂CO₃ commences near the 723 °C melting under conditions of no CO₂ (argon) up through pure CO₂.¹⁵ A binary SrCO₃/Li₂CO₃ mix has a melting point of 690–790 °C. The melting point increases as the weight percent of SrCO₃ in the binary mix increases from 40 to 65%. The eutectic containing 40 wt% SrCO₃ melts at 690 °C, while the binary 50% SrCO₃ mix melts at 695 °C (ESI[†]). Fig. 3 demonstrates that this binary mix melting point is substantially decreased by the inclusion of



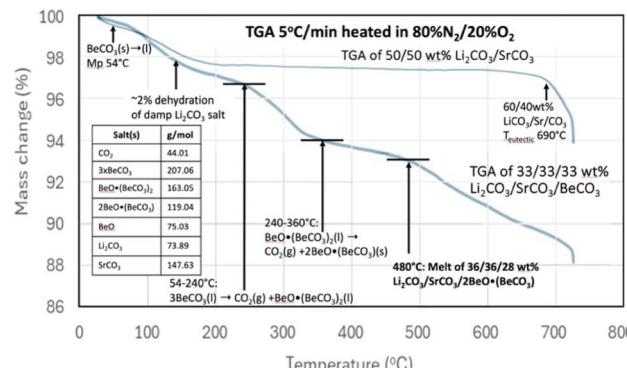


Fig. 3 TGA analysis of 50/50 wt% $\text{Li}_2\text{CO}_3/\text{SrCO}_3$ compared to 33.3/33.3 wt% $\text{Li}_2\text{CO}_3/\text{SrCO}_3/\text{BeCO}_3$. The TGA is conducted from 30 °C to 730 with a 5 °C increase per minute in 80% $\text{N}_2/20\% \text{O}_2$.

BeCO_3 in a ternary mix. Specifically, Fig. 3 compares the TGA's of a binary mix 50/50 wt% $\text{Li}_2\text{CO}_3/\text{SrCO}_3$ to that of a ternary mix composed one-third by weight each in Li_2CO_3 , SrCO_3 , BeCO_3 . The TGA starts from 30 °C, with a 5 °C min^{-1} temperature increase, and under an 80% $\text{N}_2/20\% \text{O}_2$ gas mix.

For the TGA of the binary mix of 50/50 wt% $\text{Li}_2\text{CO}_3/\text{SrCO}_3$, a few percent weight loss is evident in Fig. 3 at low temperature as the damp material dries. Then the mass is moderately constant, decreasing slowly until a more rapid weight loss occurs around the 690 °C melting point observed for a $\text{Li}_2\text{CO}_3/\text{SrCO}_3$ mixture. Alternatively, in addition to the low-temperature drying, the 33.3/33.3/33.3 wt% $\text{Li}_2\text{CO}_3/\text{SrCO}_3/\text{BeCO}_3$ ternary mix exhibits the hallmarks of pure BeCO_3 up to a temperature of 360 °C that were seen in Fig. 2. However, in addition, another sharper decrease in mass loss is observed starting at 480 °C. These are attributed to the melting point of new lower melting ternary mixes of $\text{Li}_2\text{CO}_3/\text{SrCO}_3/\text{BeO}(\text{BeCO}_3)_2$ and specifically of 36/36/28 wt% $\text{Li}_2\text{CO}_3/\text{SrCO}_3/\text{BeO}$ when taking into account the loss of CO_2 up to 480 °C from the original BeCO_3 in the formation of BeO . Note, these wt% masses refer to the measured ratio of masses, as distributed through homogeneous speciation in the oxide dissolved in alkali earth carbonate melt, and not that there is a specific release of CO_2 from an isolated alkali earth carbonate within the liquid.

The melting point observed for the $\text{Li}_2\text{CO}_3/\text{SrCO}_3/\text{BeCO}_3$ ternary carbonate mix at 480 °C in Fig. 3 is 215 °C lower than the binary $\text{Li}_2\text{CO}_3/\text{SrCO}_3$ mix without the beryllium carbonate addition. Hence, inclusion of BeCO_3 can lower the melting point of conventional inorganic carbonates prepared without a mix of BeCO_3 .

Experimental

Thermodynamic carbonate/ CO_2 equilibrium calculation

Enthalpies, entropies of species i , $i =$ alkali and alkali earth carbonates, oxides, and CO_2 are from standard Barin, NIST (calculated from the available condensed phase thermochemistry data Shomate equations), and NASA data bases.^{29–39} At any given temperature, the free energy of species “ i ” was calculated as:

$$\Delta G_i(T) = \Delta H_i(T) - T\Delta S_i(T) \quad (9)$$

The free energy of equilibrium eqn (1) was then calculated as:

$$\Delta G_{\text{eqn (1)}}(T) = \Delta G_{\text{CO}_2}(T) + \Delta G_{\text{MCO}}(T) - \Delta G_{\text{MCO}_3}(T) \quad (10)$$

The eqn (1) equilibria constants for the various alkali and alkali earth carbonates were then calculated in accord with eqn (2).

TGA measurement, CO_2 evolution, and phase change

BeCO_3 , 99% purity, was from Chemsavers. Li_2CO_3 was purchased at a battery grade >99.5%, and used as received. The Li_2CO_3 had an analyzed composition of 99.8% (Li_2CO_3 , Shanghai Seasongreen Chemical Co). The SrCO_3 used was 99.4% pure SrCO_3 (Shendong Zhi Chemical Co. Thermal) gravimetric analysis (TGA) was conducted using a PerkinElmer STA 6000 TGA/DSC TGA, under either pure N_2 or a mix of 80% N_2 and 20% O_2 . TGAs were conducted with 15 mg of sample using a temperature ramp of 5 °C min^{-1} over the indicated temperature range. The daily reproducibility of known pure carbonate or graphene samples served as instrumental calibration, and any buildup of residual carbonate was removed by acid wash. In this study, the similarity of the measured mass change with or without the presence of O_2 was considered indicative that O_2 and related species were not participants in the mass loss sequence. TGA rapid mass loss was considered as gas evolved from the liquid phase, while a low rate of mass loss was considered an indicator of gas evolved from the solid phase as delineated in the text.

Conclusions

Rising levels of CO_2 in the atmosphere are driving catastrophic climate change, posing an existential threat to the planet. As CO_2 concentrations increase, they contribute to global warming, extreme weather events, and ecological disruptions. Addressing this challenge requires innovative solutions, one of which is CO_2 capture and sequestration.

The capacity for CO_2 is a crucial metric in assessing the effectiveness of various chemical species in absorbing, adsorbing or reacting CO_2 for sequestration purposes. This capacity is quantified as the amount of CO_2 (in kilograms) that can be captured per kilogram of the absorbent material. Common absorbents used in this field include amines, ionic liquids, and calcium oxide, which can transform into calcium carbonate. More recently, lithium oxide (Li_2O), which converts to lithium carbonate (Li_2CO_3), has gained attention as a potential absorbent.

In this study BeCO_3 has been introduced as a model compound due to its remarkably high CO_2 capture capacity. Although the practical application of beryllium is limited by its scarcity-ranking, as only the 48th most abundant element in the Earth's upper crust, it boasts a CO_2 capture capacity of 1.83 kg CO_2 per kg of BeO . This is significantly higher than that of other common absorbents: amines range from 0.19–0.37 kg CO_2 per kg, ionic liquids capture between 0.07 and 0.09 kg CO_2 per kg,



calcium carbonate (CaCO_3) with a capacity of 0.78 kg CO_2 per kg, and lithium carbonate (Li_2CO_3) that captures 1.47 kg CO_2 per kg Li_2O .

To better understand the thermodynamics involved, the equilibrium between CO_2 and beryllium oxide (BeO) derived from BeCO_3 has been calculated and compared to various alkali and alkaline earth carbonates. Thermogravimetric analysis (TGA) of BeCO_3 has also been conducted to elucidate the stepwise mechanism of CO_2 release, providing insights into how this process in a stepwise release of CO_2 at increasing different temperatures.

Additionally, the influence of BeCO_3 on the melting point of mixtures has been explored. A comparison of the binary carbonate system consisting of Li_2CO_3 and strontium carbonate (SrCO_3) with a ternary system that includes BeCO_3 illustrates how the addition of BeCO_3 can substantially depress the melting point. BeCO_3 has been presented as a model carbonate to advance the foundation of understanding of the requirements of maximum carbon sequestration. It should be emphasized that beryllium, beryllium carbonate and beryllium oxide are more toxic, less abundant and therefore less available and more expensive than previously studied lower sequestration capacity lithium, magnesium and calcium compounds. This research not only highlights the unique properties of BeCO_3 , but also contributes to the broader understanding of CO_2 capture technologies and their potential role in mitigating climate change.

Data availability

The data supporting this article have been included as part of the ESI.†

Author contributions

G. L. and S. L. designed the research; K. H., G. L. and S. L. performed the research and analysed the data; G. L. and S. L. wrote the paper.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are grateful to Emissions Reduction Alberta award IT0162473 for partial support of this research.

Notes and references

- 1 M. C. Urban, Accelerating extinction risk from climate change, *Science*, 2015, **348**, 571–573.
- 2 H. M. Baek, Possibility of service-regeneration of LiPH for submarines and improvements in CO_2 scrubbing performance in LiOH canisters, *JAMET*, 2022, **46**, 115–121.
- 3 S. Satayapal, T. Filburn, J. Trela and J. Strange, Performance and Properties of a Solid Amine Sorbent for Carbon Dioxide

Removal in Space Life Support Applications, *Energy Fuels*, 2001, **15**, 250–255.

- 4 C. F. Martín, M. G. Plaza, J. J. Pis, F. Rubiera, C. Pevida and T. A. Centeno, On the limits of CO_2 capture capacity of carbons, *Sep. Purif. Technol.*, 2010, **74**, 225–229.
- 5 J. Y. Lai, L. H. Ngu and S. S. Hashim, A review of CO_2 adsorbents performance for different carbon capture technology processes conditions, *Greenhouse Gases:Sci. Technol.*, 2021, **11**, 1076–1117.
- 6 E. Victor, K. Chukwuemeka, O. A. Blessing, I. C. Success, O. Chisom, E. B. Chukwuemeka and N. U. Christian, A Concise Review of Sorbent Materials for Carbon Dioxide Capture and Storage, *J. Mat. Sci. Res. Rev.*, 2022, **10**, 72–98.
- 7 S. Y. W. Chai, L. H. Ngu and B. S. How, Review of carbon capture adsorbents for CO_2 utilization, *Greenhouse Gases:Sci. Technol.*, 2022, **12**, 394–427.
- 8 Y. Tan, W. Liu, X. Zhang, W. Wei and S. Song, Conventional and optimized testing facilities of calcium looping process for CO_2 capture: A systematic review, *Fuel*, 2024, **358**, 130337.
- 9 S. Licht, Efficient solar-driven synthesis, carbon capture and desalination, *STEP*, *Adv. Mater.*, 2011, **23**, 5592–5612.
- 10 M. Firdaus, A. Desforges, A. R. Mohamed and B. Vigolo, Progress in adsorption capacity of nanomaterials for carbon dioxide capture: A comparative study, *J. Cleaner Prod.*, 2021, **328**, 129553.
- 11 Y. Deng, J. Li, Y. Mia and D. Izikowitz, A comparative review of performance of nanomaterials for Direct Air Capture, *Energy Rep.*, 2021, **7**, 3506–3516.
- 12 X. Wang, T. He, J. Hu and M. Liu, The progress of nanomaterials for carbon dioxide capture via the adsorption process, *Environ. Sci.:Nano*, 2021, **8**, 890–912.
- 13 G. Licht, K. Hofstetter and S. Licht, A new electrolyte for molten carbonate decarbonization, *Commun. Chem.*, 2024, **7**, 211.
- 14 Q. Zhu, Y. Zeng and Y. Zheng, Overview of CO_2 capture and electrolysis technology in molten salts: operational parameters and their effects, *Ind. Chem. Mater.*, 2023, **1**, 59.
- 15 L. Shi, T. Qu, D. Liu, Y. Deng, B. Yang, and Y. Dai, Process of Thermal Decomposition of Lithium Carbonate, in *Materials Processing Fundamentals*, J., Lee, S., Wagstaff, G., Lambotte, A., Allanore and F., Tesfaye, The Minerals, Metals & Materials Series, 2020.
- 16 J. Ren, A. Yu, P. Peng, M. Lefler, F.-F. Li and S. Licht, Recent advances in solar thermal electrochemical process (STEP) for carbon neutral products and high value nanocarbons, *Acc. Chem. Res.*, 2019, **52**, 3177–3187.
- 17 J. Ren, F.-F. Li, J. Lau, L. Gonzalez-Urbina and S. Licht, One-pot synthesis of carbon nanofibers from CO_2 , *Nano Lett.*, 2015, **15**, 6142–6148, DOI: [10.1021/jp9044644](https://doi.org/10.1021/jp9044644).
- 18 J. Ren and S. Licht, Tracking airborne CO_2 mitigation and low cost transformation into valuable carbon nanotubes, *Sci. Rep.*, 2016, **6**, 27760, DOI: [10.1038/srep27760](https://doi.org/10.1038/srep27760).
- 19 G. Licht, K. Hofstetter and S. Licht, Polymer composites with carbon nanotubes made from CO_2 , *RSC Sustainability*, 2024, **2**, 2496–2504.

20 G. Licht, K. Hofstetter and S. Licht, Buckypaper made with carbon nanotubes derived from CO₂, *RSC Adv.*, 2024, **14**, 27195–27197.

21 R. C. Ropp, *Encyclopedia of the Alkaline Earth Compounds*, Elsevier, Netherlands, pp. 359–360, 2013, ISBN 9780444595539.

22 *The Differential Thermal Investigations of Clays*, ed. T. L. Webb, H. Heystek and R. C. Mackenzie, Mineralogical Society, London, 1957, p.329.

23 A. D. Pelton, C. W. Bale and P. L. Lin, *Can. J. Chem.*, 1984, **62**, 457.

24 L. Barin, in *Thermochemical Data of Pure Substances*, VCH, Weinheim, 1989, pp.1–9.

25 N. N. Semenov, T. V. Zablotzkii, I. Sib and O. Akad, *Nauk SSSR*, 1962, **2**, 58.

26 E. I. Maslova, I. S. Lileev, I. Sib and O. Akad, *Nauk SSSR*, 1958, **1**, 63.

27 L. S. Itkinaa and N. M. Chaplygina, *Russ. J. Inorg. Chem.*, 1962, **7**, 1456.

28 Y. Otsubo and K. Yamaguchi, *J. Chem. Soc. Japan*, 1961, **82**, 557.

29 M. Leader, curator, NASA Glenn ThermoBuild thermodynamic database, <https://cearun.grc.nasa.gov/ThermoBuild/>; last accessed April 17, 2024.

30 S. Licht, B. Wang, S. Ghosh, H. Ayub, D. Jiang and J. Ganley, A new solar carbon capture process: STEP carbon capture, *J. Phys. Chem. Lett.*, 2010, **1**, 2363–2368.

31 S. Licht and B. C. B. Wang, STEP carbon capture: the barium advantage, *J. CO₂ Util.*, 2013, **2**, 303–312.

32 X. Wang, G. Licht, X. Liu and S. Licht, CO₂ utilization by electrolytic splitting to carbon nanotubes in non-lithiated, cost effective, molten carbonate electrolytes, *Adv. Sustainable Syst.*, 2022, **2022**, 2100481.

33 J. Ren, M. Johnson, R. Singhal and S. Licht, Transformation of the greenhouse gas CO₂ by molten electrolysis into a wide controlled selection of carbon nanotubes, *J. CO₂ Util.*, 2017, **18**, 335–344.

34 P. Pasierb, R. Gajerski, M. Rokita and M. Rekas, Studies on the binary system Li₂CO₃–BaCO₃, *Physica B*, 2001, **304**, 463–476.

35 S. Fangini and A. Masi, Molten carbonates for advanced and sustainable energy applications: Part 1, *Int. J. Hydrog. Energy*, 2016, **41**, 18739–19746.

36 J. Ren, J. Lau, M. Lefler and S. Licht, S. The minimum electrolytic energy needed to convert carbon dioxide to carbon by electrolysis in carbonate melts, *J. Phys. Chem. C*, 2015, **119**, 23342–23349.

37 P. J. Linstrom and G. Mallard, NIST Chemistry WebBook. NIST Standard Reference Database Number 69, 2001, National Institute of Standards and Technology, *J. Chem. Eng. Data*, 2001, **46**(5), 1059–1063.

38 J. Malcom and W. Chase, *NIST-JANAF Thermochemical Tables Fourth Ed.* Amer Chem Soc, Amer Inst Phys, Nat Inst Stand Tech, 1998, <http://webbook.nist.gov>, retrieved April 22, 2024.

39 L. Barin, *Thermochemical Data of Pure Substances. Part II*, VCH, 1989, pp. 1418–1427.

40 X. Liu, G. Licht and S. Licht, Controlled Transition Metal Nucleated Growth of Carbon Nanotubes by Molten Electrolysis of CO₂, *Catalysts*, 2022, **12**, 137.

41 X. Liu, G. Licht, X. Wang and S. Licht, Controlled Growth of Unusual Nanocarbon Allotropes by Molten Electrolysis of CO₂, *Catalysts*, 2022, **12**, 137.

42 X. Liu, G. Licht and S. Licht, The green synthesis of exceptional braided, helical carbon nanotubes and nanospiral platelets made directly from CO₂, *Mater. Today Chem.*, 2021, **22**, 100529.

43 X. Wang, G. Licht, X. Liu and S. Licht, One pot facile transformation of CO₂ to an unusual 3-D nan-scaffold morphology of carbon, *Sci. Rep.*, 2020, **10**, 21518.

44 X. Liu, J. Ren, G. Licht, X. Wang and S. Licht, Carbon nano-onions made directly from CO₂ by molten electrolysis for greenhouse gas mitigation, *Adv. Sustain. Syst.*, 2019, **3**, 1900056.

45 X. Liu, X. Wang, G. Licht and S. Licht, Transformation of the greenhouse gas carbon dioxide to graphene, *J. CO₂ Util.*, 2020, **236**, 288–294.

46 X. Wang, X. Liu, G. Licht and S. Licht, Calcium metaborate induced thin walled carbon nanotube syntheses from CO₂ by molten carbonate electrolysis, *Sci. Rep.*, 2020, **10**, 15146.

47 X. Wang, F. Sharif, X. Liu, G. Licht, M. Lefler and S. Licht, Magnetic carbon nanotubes: Carbide nucleated electrochemical growth of ferromagnetic CNTs, *J. CO₂ Util.*, 2020, **40**, 101218.

48 M. Johnson, J. Ren, M. Lefler, G. Licht, J. Vicini, X. Liu and S. Licht, Carbon nanotube wools made directly from CO₂ by molten electrolysis: Value driven pathways to carbon dioxide greenhouse gas mitigation, *Mater. Today Energy*, 2017, **5**, 230–236.

49 J. Ren, M. Johnson, R. Singhal and S. Licht, Transformation of the greenhouse gas CO₂ by molten electrolysis into a wide controlled selection of carbon nanotubes, *J. CO₂ Util.*, 2017, **18**, 335–344.

50 G. Licht, K. Hofstetter and S. Licht, Separation of Molten Electrolyte from the Graphene Nanocarbon Product Subsequent to Electrolytic CO₂ Capture, *Decarbon*, 2024, **4**, 100044.

51 Z. Hu and S. Gao, Upper crustal abundances of trace elements: A revision and update, *Chem. Geol.*, 2008, **253**, 205–221.

52 A. Kantzas, J. Bryan, S. Taheri, *Molecular Diffusion, Chapt. 3 in Fundamentals of Fluid Flow in Porous*, Media PERM, 2024, available at: <https://perminc.com/resources/fundamentals-of-fluid-flow-in-porous-media/chapter-3-molecular-diffusion/>.

53 H. S. Caram, R. Gupta, H. Thomann, F. Ni, S. C. Weston and M. Afeworki, A simple thermodynamic tool for assessing energy requirements for carbon capture using solid or liquid sorbents, *Int. J. Greenhouse Gas Control*, 2020, **97**, 102986.