


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,<sup>a</sup> Kyle Hofstetter<sup>b</sup> and Stuart Licht  <sup>\*,abc</sup>

Beryllium carbonate has the highest capacity to bind and release the greenhouse gas CO<sub>2</sub> compared to amines, ionic liquids, CaCO<sub>3</sub> or Li<sub>2</sub>CO<sub>3</sub>. The thermodynamic equilibrium for CO<sub>2</sub> and BeO from BeCO<sub>3</sub> is calculated. TGA of BeCO<sub>3</sub> is used to determine the stepwise mechanism of its CO<sub>2</sub> release, and the low melting point Li/Sr/BeCO<sub>3</sub> is demonstrated.

## Introduction

Rising CO<sub>2</sub> levels are causing catastrophic climate change, and are an existential threat to the planet. Atmospheric CO<sub>2</sub> levels, stable at 235 (±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.<sup>1</sup> 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<sub>2</sub> sequestration, and CO<sub>2</sub> capture capacity is a measure of the extent of a chemical species binding of CO<sub>2</sub> for use in carbon sequestration chemistry. CO<sub>2</sub> capture capacity is quantified as mass or mole capacity of CO<sub>2</sub> per mass or mole of absorbent. In addition to the general need for effective CO<sub>2</sub> trapping materials to mitigate CO<sub>2</sub>-induced global warming and climate change, other examples of the need for lightest weight carbon capture materials for CO<sub>2</sub> air scrubbing, include those needed by submersibles, submarines, and spacecraft.<sup>2,3</sup>

Several recent reviews have focused on amines (and amino acids), calcium oxide (to calcium carbonate), and ionic liquids to bind and release CO<sub>2</sub>.<sup>4–9</sup> More recently, there has been a growing focus on nanomaterials, such as carbon nanomaterials,<sup>10–12</sup> and also on and lithium carbonate and mixed lithium/strontium carbonates<sup>13–16</sup> to capture CO<sub>2</sub> 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<sub>2</sub> captured.

CO<sub>2</sub> can be captured and stored by thermal cycling. In this case, dilute CO<sub>2</sub> 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,<sup>5,7</sup> or by chemical reactions, as occurs in the reaction of dissolved or solid calcium oxide with CO<sub>2</sub> to calcium carbonate, followed by high-temperature decomposition of calcium carbonate back to calcium oxide.<sup>8</sup> 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<sub>2</sub>. As an alternative to thermal cycling, the CO<sub>2</sub> capture can be accomplished by electrolysis (such as the electrochemical splitting of CO<sub>2</sub> to C and O<sub>2</sub>) to a product containing the captured CO<sub>2</sub>, such as the formation of Carbon NanoTubes (CNTs) from CO<sub>2</sub> in molten carbonates.<sup>17–20</sup> This latter CCUS process often occurs in a single step.

In Table 1, the capacity for CO<sub>2</sub> is compiled for common CO<sub>2</sub> absorbents (absorbents referring to both adsorbents, absorbents, and reactants). The capacity for CO<sub>2</sub> is presented in units of both mole CO<sub>2</sub>/mole absorbent and also in more typical units of kg CO<sub>2</sub> captured per kg absorbent in the last column. Pragmatic capacities for CO<sub>2</sub> 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<sub>2</sub> capture process.

Amines and amino acids have been widely studied both as absorbents, principally in the liquid phase, to absorb and release CO<sub>2</sub>, and as adsorbents principally affixed on membranes to adsorb and release CO<sub>2</sub>. As seen in Table 1, amines and amino acids have respective capacities for CO<sub>2</sub> of 0.19–0.37 or 0.27–0.35 kg CO<sub>2</sub> per kg (amine or amino acid). Ionic liquids have attained capacities of 0.07–0.09 kg CO<sub>2</sub> per kg. CaO/CaCO<sub>3</sub> has a capacity for CO<sub>2</sub> of 0.78 kg CO<sub>2</sub> (determined as of CaO + CO<sub>2</sub> → CaCO<sub>3</sub>

<sup>a</sup>C2CNT LLC, A4 188 Triple Diamond Blvd, North Venice, FL 34275, USA. E-mail: slicht@gwu.edu

<sup>b</sup>Carbon Corp, 1035 26 St NE, Calgary, AB T2A 6K8, Canada

<sup>c</sup>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 CO<sub>2</sub> of beryllium oxide as beryllium carbonate compared to other absorbents

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

from the 44.01 g per mol FW of CO<sub>2</sub> to the 56.08 g per mol FW of CaO). The lighter molecular weight Li<sub>2</sub>O/Li<sub>2</sub>CO<sub>3</sub> has a capacity for CO<sub>2</sub> of 1.47 kg CO<sub>2</sub>. In order of increasing CO<sub>2</sub> capacities, the absorbents are ionic liquids < amino acids & amines < CaO (to CaCO<sub>3</sub>) < Li<sub>2</sub>O (to Li<sub>2</sub>CO<sub>3</sub>).

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 CO<sub>2</sub> (1.83 kg CO<sub>2</sub> per kg BeO → BeCO<sub>3</sub>). Beryllium carbonate is also as an example of a melting point decrease facilitator by addition of BeCO<sub>3</sub> to binary Li/SrCO<sub>3</sub> electrolyte to become the substantially lower melting point ternary Li/Sr/BeCO<sub>3</sub>. 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 CO<sub>2</sub> release can then be achieved using a lower thermal energy input.

## Results and discussion

### Phase changes & CO<sub>2</sub> equilibria of alkali & alkali earth carbonates

As summarized in Table 2, the melting point of beryllium carbonate (mp 54 °C), Be<sub>2</sub>CO<sub>3</sub>, 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 Li<sub>2</sub>CO<sub>3</sub> is reported from 700 °C to 728 °C.<sup>22–28</sup> Furthermore, the CO<sub>2</sub> 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 CO<sub>2</sub>, and we also note that many properties, including melting points, of species related to CO<sub>2</sub> 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<sub>x</sub>Na<sub>y</sub>K<sub>z</sub>CO<sub>3</sub> 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 BeCO<sub>3</sub>, by 343 °C.

The extent to which an alkali or alkali earth carbonates retains CO<sub>2</sub> is given by:

$$\text{MCO}_3 \rightleftharpoons \text{CO}_2(\text{gas}) + \text{MO} \quad (\text{M} = \text{Be, Mg, Li}_2, \text{Na}_2, \text{etc.}) \quad (1)$$

$$K = p_{\text{CO}_2} a_{\text{MO}}/a_{\text{MCO}_3}; \quad K(T) = e^{-\Delta G(T)/RT} \quad (2)$$



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

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

<sup>a</sup> Li<sub>2</sub>CO<sub>3</sub> decomposition is more rapid under argon than under air.<sup>15</sup>

An extensive literature search did not reveal phase diagrams or equilibria for beryllium carbonate. We've calculated the BeCO<sub>3</sub>/BeO + CO<sub>2</sub> equilibrium from the available enthalpy and entropy of the constituent species.<sup>29</sup>

Fig. 1 presents a comparison of the carbonate/oxide equilibrium constant for binding and releasing of CO<sub>2</sub> 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 CO<sub>2</sub> activity domain, the carbonate salt will spontaneously form from CO<sub>2</sub> and the salt's oxide. Above any Fig. 1 equilibrium curve, the low CO<sub>2</sub> 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 MgCO<sub>3</sub> decomposes at 350 °C, releasing bound CO<sub>2</sub>, and as seen is the second largest (other than BeCO<sub>3</sub>) 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°.

Li<sub>2</sub>CO<sub>3</sub>/Li<sub>2</sub>O was introduced as among the highest CO<sub>2</sub>-capture materials, as delineated in the next to last row of Table 1, with a storage capacity of 1.47 kg CO<sub>2</sub> per kg Li<sub>2</sub>O. Under argon, Li<sub>2</sub>CO<sub>3</sub> entirely dissociates to CO<sub>2</sub> + Li<sub>2</sub>O. Specifically, at a TGA rate of 5° min<sup>-1</sup> under 1 atm of argon Li<sub>2</sub>CO<sub>3</sub> dissociation starts around the lithium carbonate melting point of 723 °C, and is 98% complete to Li<sub>2</sub>O by 900 °C, and under 1 atm of pure CO<sub>2</sub> also starts at 723 °C, but the dissociation is less than 10% complete by 900 °C.<sup>15</sup> However, under even small partial pressures of CO<sub>2</sub>, such as the 426 ppm (and rising) of atmospheric CO<sub>2</sub>, Li<sub>2</sub>CO<sub>3</sub> only fractionally dissociates to CO<sub>2</sub>, attaining 0.3 molal concentration Li<sub>2</sub>O per kg molten Li<sub>2</sub>CO<sub>3</sub> at 750 °C.<sup>36</sup> This high capacity was experimentally realized in the form of the electrolytic splitting of CO<sub>2</sub> in molten Li<sub>2</sub>CO<sub>3</sub> to graphene nanocarbons.<sup>40–49</sup> The small concentration of dissolved Li<sub>2</sub>O in molten Li<sub>2</sub>CO<sub>3</sub> under air is sufficient to support high CO<sub>2</sub> splitting electrochemical current and continuous renewal of the molten Li<sub>2</sub>CO<sub>3</sub> electrolyte with CO<sub>2</sub>.<sup>50</sup>

The relationship between melting and decomposition temperatures for carbonates is complex. Beryllium carbonate has respective melting and decomposition points of BeCO<sub>3</sub> ( $M_p = 54$  °C and  $D_p = 100$  °C),<sup>21</sup> lithium carbonate Li<sub>2</sub>CO<sub>3</sub> ( $M_p = 723$  °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 SrCO<sub>3</sub> ( $M_p = D_p = 1494$  °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% SrCO<sub>3</sub> is miscible in 750 °C molten Li<sub>2</sub>CO<sub>3</sub>.<sup>13</sup>

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,

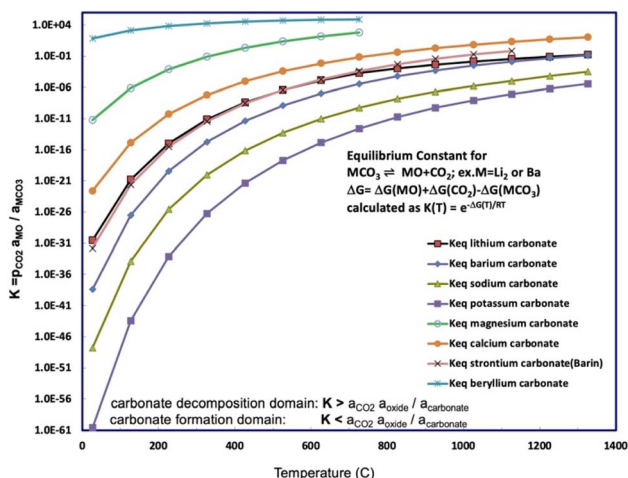


Fig. 1 Equilibrium constant for CO<sub>2</sub> release calculated for beryllium carbonate and compared to a range of alkali and alkali earth carbonates. The equilibrium constants as a function of temperature for strontium, lithium, sodium, potassium, and barium carbonate. The equilibrium constants are 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.<sup>29,36–39</sup>

while the formal  $\text{Li}_2\text{CO}_3$  decomposition point in Table 2 is  $\sim 1300$ , substantial decomposition has already occurred at  $750^\circ\text{C}$  with release of  $\text{CO}_2$  and the resultant  $\text{Li}_2\text{O}$  forming as a dissolved salt within the molten  $\text{Li}_2\text{CO}_3$ .<sup>36</sup> 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 $\text{CO}_2$ 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  $\text{CO}_2$  and beryllium oxide:



In accord with eqn (3),  $\text{BeCO}_3$  (FW  $69.02 \text{ g mol}^{-1}$ ) stores  $44.01 \text{ g mol}^{-1} \text{ CO}_2/\text{BeO}$  (FW  $25.01 \text{ g mol}^{-1}$ ) =  $1.83 \text{ kg CO}_2$  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  $\text{CO}_2$  of any of the alkali earth or alkali carbonates, and will begin to release  $\text{CO}_2$  near ambient temperatures. At room temperature, beryllium carbonate (solid  $\text{BeCO}_3$ ) is often stored under a blanket of  $\text{CO}_2$  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  $\text{CO}_2$  storable per kg oxide).

Thermodynamically,  $\text{BeCO}_3$  is the carbonate best suited to initiate storage and release of  $\text{CO}_2$  at low temperatures.  $\text{BeCO}_3$  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,<sup>51</sup> and it and its oxide, particularly in powder form, is carcinogenic. However, the storage of  $\text{CO}_2$  by  $\text{BeCO}_3$  serves as a model for among the highest carbon storage capacity materials and lowest mass  $\text{CO}_2$  scrubbers.

### The stepwise mechanism of beryllium carbonate $\text{CO}_2$ storage

Eqn (1) only provides a thermodynamic overview of a carbonate's capability to release  $\text{CO}_2$ . The individual steps in the process of the binding of  $\text{CO}_2$  into beryllium carbonate are investigated here by ThermoGravimetric Analysis, TGA.

Fig. 2 presents the TGA results of beryllium carbonate conducted from  $30^\circ\text{C}$ , with a  $5^\circ\text{C}$  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  $730^\circ\text{C}$  or (2)  $100\% \text{ N}_2$  shown in the blue curve from  $30^\circ\text{C}$  to  $1000^\circ\text{C}$ . In the figure, the downward trend in the mass is seen to start at approximately, the cited<sup>21</sup>  $54^\circ\text{C}$  melting of  $\text{BeCO}_3$ . The equivalence of the curves with or without an atmosphere containing  $\text{O}_2$  provides primary evidence that  $\text{O}_2$  is neither evolved nor absorbed by beryllium carbonate during the TGA, and that species in equilibrium with  $\text{O}_2$ , including oxides, peroxides, and superoxides, those species are not participants in reactions related to the TGA temperature sweep.

In Fig. 2 above  $54^\circ\text{C}$ ,  $\text{BeCO}_3$  rapidly evolves  $\text{CO}_2$  upon melting (at increasing temperature, the release of  $\text{CO}_2$  from

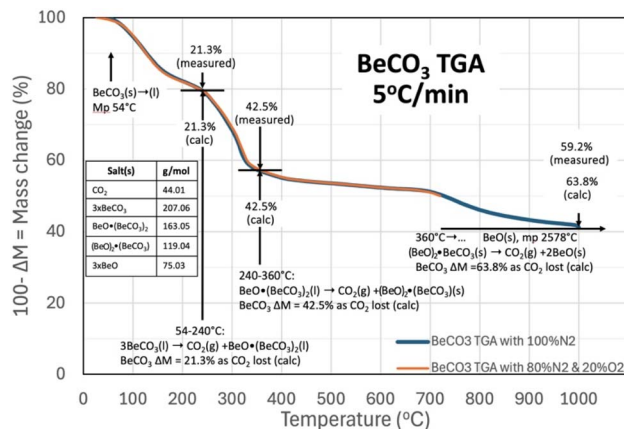
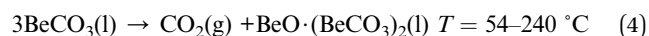


Fig. 2 TGA analysis of beryllium carbonate. The TGA is conducted from  $30^\circ\text{C}$  with a  $5^\circ\text{C}$  increase per minute in either (1)  $80\% \text{ N}_2/20\% \text{ O}_2$  (from  $30^\circ\text{C}$  to  $730^\circ\text{C}$ ) or (2)  $100\% \text{ N}_2$  (from  $30^\circ\text{C}$  to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

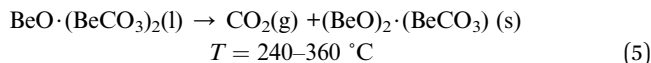
$\text{BeCO}_3$  is an exergonic, spontaneous reaction). Released gases diffuse more slowly through a solid than through a liquid.<sup>52</sup> Salts evolving  $\text{CO}_2$  from the liquid, as opposed to from the solid form, facilitate the rapid release of  $\text{CO}_2$ . For example, comparing liquid and solid  $\text{CO}_2$  amine sorbents, solid gas reactions require much higher minimum work,<sup>53</sup> and the concurrent observed increased rate of mass loss acts as an indicator that the salt has melted. In solid salts that can release  $\text{CO}_2$  by decomposition,  $\text{CO}_2$  release is constrained by surface depletion and by the slow diffusion of  $\text{CO}_2$  to the solid surface. Whereas, in the molten state, the liquid surface is continuously replenished, sustaining facile  $\text{CO}_2$  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  $\text{CO}_2$  mass loss is then determined by calculating mass consistent changes of the equivalent calcinated beryllium oxide and  $\text{BeCO}_3$  salts.

As seen in Fig. 2, molten  $\text{BeCO}_3$  evolves  $\text{CO}_2$  to become  $\text{BeO} \cdot (\text{BeCO}_3)_2$  from  $\sim 54^\circ\text{C}$  to  $240^\circ\text{C}$ , 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  $\text{CO}_2$  is evolved from  $3 \text{ BeCO}_3$  to become  $\text{BeO} \cdot (\text{BeCO}_3)_2$ , and the rapid mass loss indicative of facile  $\text{CO}_2$  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:

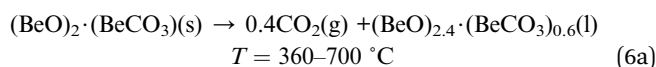


At increasing temperature, the molten  $\text{BeO} \cdot (\text{BeCO}_3)_2$  then evolves  $\text{CO}_2$  to become  $(\text{BeO})_2 \cdot \text{BeCO}_3$  (FW  $119.04$ ) from  $240^\circ\text{C}$  to  $360^\circ\text{C}$ ; again, as determined by the equivalence of both the observed and the calculated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

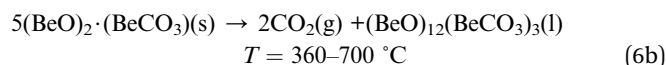




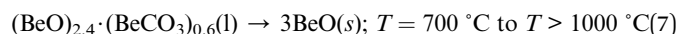
From 360 °C to ~700 °C, there is an observed slow, steady rate of CO<sub>2</sub> evolution as the mass loss observed in Fig. 2 increases to 50.9% from the original BeCO<sub>3</sub>. The slow rate of CO<sub>2</sub> evolution is evidence that the eqn (5) product may be solid, and the additional (50.9–42.5%)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



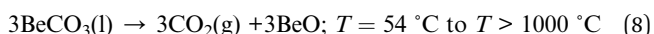
Equivalent to integral molecular values of:



Above 700 °C, the observed rate of mass loss and CO<sub>2</sub> 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)<sub>12</sub>(BeCO<sub>3</sub>)<sub>3</sub>(l) is a generalization of the total equivalence of BeO and BeCO<sub>3</sub> in the product, and it is likely that this consists of a solid BeO (mp 2578 °C) in a liquid phase of mixed BeO<sub>x</sub>/BeCO<sub>3</sub>. This product then evolves CO<sub>2</sub> to become BeO(s) from ~700 °C onward. As the end product of the beryllium carbonate CO<sub>2</sub> 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% CO<sub>2</sub> mass loss from BeCO<sub>3</sub>. 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% CO<sub>2</sub> mass loss from BeCO<sub>3</sub>:



For an overall reaction of:



The thermal release of CO<sub>2</sub> from BeCO<sub>3</sub> does not result in the formation of powdered BeO, which can be toxic, but rather initially forms BeO<sub>y</sub>·(BeCO<sub>3</sub>)<sub>y</sub>, and then at highest levels of CO<sub>2</sub> 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 CO<sub>2</sub> by heating BeCO<sub>3</sub> 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 CO<sub>2</sub> by beryllium oxide and beryllium oxide/carbonate intermediates is energetically favored by the reverse process of cooling or pressurizing under CO<sub>2</sub> beryllium oxide and beryllium oxide/carbonate intermediates and stores CO<sub>2</sub>. Beryllium oxide is stable, and this stability to reaction can be overcome by

introducing kinetic facilitation to increase the rate of CO<sub>2</sub> uptake by cooling and/or with pressurized CO<sub>2</sub>.

Future studies can probe the likelihood that the reverse beryllium oxide reaction with CO<sub>2</sub> to beryllium carbonate can be facilitated by means including: (i) bubbling CO<sub>2</sub> through the various molten (liquid phase) stages of beryllium oxide and its beryllium oxide/carbonate intermediates or forming a liquid aerosol combined with CO<sub>2</sub>, (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 CO<sub>2</sub>, (iii) introducing the CO<sub>2</sub> by mixing with a combined solid and liquid phase (slush) of beryllium oxide/carbonate intermediates, (iv) or a multistep reaction to incorporate CO<sub>2</sub> into beryllium oxide such as, but not limited to, the (iva) the facile reaction of CO<sub>2</sub> 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 BeCO<sub>3</sub>.

### Beryllium-induced carbonate electrolyte melting point decrease

Li<sub>2</sub>CO<sub>3</sub> is expensive due its relative scarcity and due to its increasing demand as a primary resource for EVs, but is useful for CO<sub>2</sub> removal and its electrolytic transformation to graphene nanocarbons.<sup>16</sup> There is less demand for SrCO<sub>3</sub> and its derivative salts, such as SrO, are also much more abundant, and an order of magnitude less expensive than Li<sub>2</sub>CO<sub>3</sub>.<sup>13,51</sup> We had demonstrated that molten Li<sub>2</sub>CO<sub>3</sub> based electrolytes are effective for CO<sub>2</sub> carbon capture by the electrolytic splitting of CO<sub>2</sub>. Interestingly, we recently found that the replacement of the majority of the Li<sub>2</sub>CO<sub>3</sub> by SrCO<sub>3</sub> and SrO is also effective. The low-Li<sub>2</sub>CO<sub>3</sub> electrolytes based on SrCO<sub>3</sub> are substantially less expensive than comparable Li<sub>2</sub>CO<sub>3</sub>-based electrolytes, and are useful for splitting and transforming CO<sub>2</sub> to stable graphene nanocarbons including CNTs and carbon nano-onions (ESI†).<sup>13</sup> The use of an electrolyte that is a binary mixture (for example, Sr/Li carbonate or SrO/Li<sub>2</sub>CO<sub>3</sub>) that can provide a low melting point electrolyte that facilitates transition metal nucleated growth from CO<sub>2</sub> of nanographene carbon allotropes is preferred.<sup>13,16,40,42,47</sup> Low-Li<sub>2</sub>CO<sub>3</sub> 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 CO<sub>2</sub>.<sup>13,40,41</sup>

Pure SrCO<sub>3</sub> has a high melting point of 1194 °C, and in accord with Table 2 does not decompose until temperatures ≫ 1000 °C. As previously noted and as measured by TGA, the rapid decomposition of pure Li<sub>2</sub>CO<sub>3</sub> commences near the 723 °C melting under conditions of no CO<sub>2</sub> (argon) up through pure CO<sub>2</sub>.<sup>15</sup> A binary SrCO<sub>3</sub>/Li<sub>2</sub>CO<sub>3</sub> mix has a melting point of 690–790 °C. The melting point increases as the weight percent of SrCO<sub>3</sub> in the binary mix increases from 40 to 65%. The eutectic containing 40 wt% SrCO<sub>3</sub> melts at 690 °C, while the binary 50% SrCO<sub>3</sub> mix melts at 695 °C (ESI†). Fig. 3 demonstrates that this binary mix melting point is substantially decreased by the inclusion of



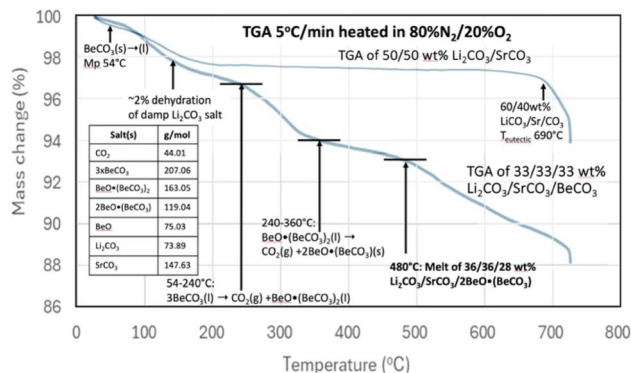


Fig. 3 TGA analysis of 50/50 wt% Li<sub>2</sub>CO<sub>3</sub>/SrCO<sub>3</sub> compared to 33.3/33.3/33.3 wt% Li<sub>2</sub>CO<sub>3</sub>/SrCO<sub>3</sub>/BeCO<sub>3</sub>. The TGA is conducted from 30 °C to 730 °C with a 5 °C min<sup>-1</sup> temperature increase per minute in 80% N<sub>2</sub>/20% O<sub>2</sub>.

BeCO<sub>3</sub> in a ternary mix. Specifically, Fig. 3 compares the TGA's of a binary mix 50/50 wt% Li<sub>2</sub>CO<sub>3</sub>/SrCO<sub>3</sub> to that of a ternary mix composed one-third by weight each in Li<sub>2</sub>CO<sub>3</sub>, SrCO<sub>3</sub>, BeCO<sub>3</sub>. The TGA starts from 30 °C, with a 5 °C min<sup>-1</sup> temperature increase, and under an 80% N<sub>2</sub>/20% O<sub>2</sub> gas mix.

For the TGA of the binary mix of 50/50 wt% Li<sub>2</sub>CO<sub>3</sub>/SrCO<sub>3</sub>, 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 Li<sub>2</sub>CO<sub>3</sub>/SrCO<sub>3</sub> mixture. Alternatively, in addition to the low-temperature drying, the 33.3/33.3/33.3 wt% Li<sub>2</sub>CO<sub>3</sub>/SrCO<sub>3</sub>/BeCO<sub>3</sub> ternary mix exhibits the hallmarks of pure BeCO<sub>3</sub> 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 Li<sub>2</sub>CO<sub>3</sub>/SrCO<sub>3</sub>/BeO(BeCO<sub>3</sub>)<sub>2</sub> and specifically of 36/36/28 wt% Li<sub>2</sub>CO<sub>3</sub>/SrCO<sub>3</sub>/BeO when taking into account the loss of CO<sub>2</sub> up to 480 °C from the original BeCO<sub>3</sub> 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<sub>2</sub> from an isolated alkali earth carbonate within the liquid.

The melting point observed for the Li<sub>2</sub>CO<sub>3</sub>/SrCO<sub>3</sub>/BeCO<sub>3</sub> ternary carbonate mix at 480 °C in Fig. 3 is 215 °C lower than the binary Li<sub>2</sub>CO<sub>3</sub>/SrCO<sub>3</sub> mix without the beryllium carbonate addition. Hence, inclusion of BeCO<sub>3</sub> can lower the melting point of conventional inorganic carbonates prepared without a mix of BeCO<sub>3</sub>.

## Experimental

### Thermodynamic carbonate/CO<sub>2</sub> equilibrium calculation

Enthalpies, entropies of species *i*, *i* = alkali and alkali earth carbonates, oxides, and CO<sub>2</sub> are from standard Barin, NIST (calculated from the available condensed phase thermochemistry data Shomate equations), and NASA data bases<sup>29–39</sup> 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<sub>2</sub> evolution, and phase change

BeCO<sub>3</sub>, 99+% purity, was from Chemsavers. Li<sub>2</sub>CO<sub>3</sub> was purchased at a battery grade >99.5%, and used as received. The Li<sub>2</sub>CO<sub>3</sub> had an analyzed composition of 99.8% (Li<sub>2</sub>CO<sub>3</sub>, Shanghai Seasongreen Chemical Co). The SrCO<sub>3</sub> used was 99.4% pure SrCO<sub>3</sub> (Shendong Zhi Chemical Co. Thermal) gravimetric analysis (TGA) was conducted using a PerkinElmer STA 6000 TGA/DSC TGA, under either pure N<sub>2</sub> or a mix of 80% N<sub>2</sub> and 20% O<sub>2</sub>. TGAs were conducted with 15 mg of sample using a temperature ramp of 5 °C min<sup>-1</sup> 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<sub>2</sub> was considered indicative that O<sub>2</sub> 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<sub>2</sub> in the atmosphere are driving catastrophic climate change, posing an existential threat to the planet. As CO<sub>2</sub> concentrations increase, they contribute to global warming, extreme weather events, and ecological disruptions. Addressing this challenge requires innovative solutions, one of which is CO<sub>2</sub> capture and sequestration.

The capacity for CO<sub>2</sub> is a crucial metric in assessing the effectiveness of various chemical species in absorbing, adsorbing or reacting CO<sub>2</sub> for sequestration purposes. This capacity is quantified as the amount of CO<sub>2</sub> (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<sub>2</sub>O), which converts to lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>), has gained attention as a potential absorbent.

In this study BeCO<sub>3</sub> has been introduced as a model compound due to its remarkably high CO<sub>2</sub> 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<sub>2</sub> capture capacity of 1.83 kg CO<sub>2</sub> per kg of BeO. This is significantly higher than that of other common absorbents: amines range from 0.19–0.37 kg CO<sub>2</sub> per kg, ionic liquids capture between 0.07 and 0.09 kg CO<sub>2</sub> per kg,



calcium carbonate ( $\text{CaCO}_3$ ) with a capacity of 0.78 kg  $\text{CO}_2$  per kg, and lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) that captures 1.47 kg  $\text{CO}_2$  per kg  $\text{Li}_2\text{O}$ .

To better understand the thermodynamics involved, the equilibrium between  $\text{CO}_2$  and beryllium oxide ( $\text{BeO}$ ) derived from  $\text{BeCO}_3$  has been calculated and compared to various alkali and alkaline earth carbonates. Thermogravimetric analysis (TGA) of  $\text{BeCO}_3$  has also been conducted to elucidate the stepwise mechanism of  $\text{CO}_2$  release, providing insights into how this process in a stepwise release of  $\text{CO}_2$  at increasing different temperatures.

Additionally, the influence of  $\text{BeCO}_3$  on the melting point of mixtures has been explored. A comparison of the binary carbonate system consisting of  $\text{Li}_2\text{CO}_3$  and strontium carbonate ( $\text{SrCO}_3$ ) with a ternary system that includes  $\text{BeCO}_3$  illustrates how the addition of  $\text{BeCO}_3$  can substantially depress the melting point.  $\text{BeCO}_3$  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  $\text{BeCO}_3$ , but also contributes to the broader understanding of  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CO}_2$  capture: A systematic review, *Fuel*, 2024, **358**, 130337.
- 9 S. Licht, Efficient solar-driven synthesis, carbon capture and desalinization, 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  $\text{CO}_2$  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  $\text{CO}_2$ , *Nano Lett.*, 2015, **15**, 6142–6148, DOI: [10.1021/jp9044644](https://doi.org/10.1021/jp9044644).
- 18 J. Ren and S. Licht, Tracking airborne  $\text{CO}_2$  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  $\text{CO}_2$ , *RSC Sustainability*, 2024, **2**, 2496–2504.





- 20 G. Licht, K. Hofstetter and S. Licht, Buckypaper made with carbon nanotubes derived from CO<sub>2</sub>, *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. Zablotskii, 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. Itkina 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. CO<sub>2</sub> Util.*, 2013, **2**, 303–312.
- 32 X. Wang, G. Licht, X. Liu and S. Licht, CO<sub>2</sub> 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 CO<sub>2</sub> by molten electrolysis into a wide controlled selection of carbon nanotubes, *J. CO<sub>2</sub> Util.*, 2017, **18**, 335–344.
- 34 P. Pasierb, R. Gajerski, M. Rokita and M. Rekas, Studies on the binary system Li<sub>2</sub>CO<sub>3</sub>–BaCO<sub>3</sub>, *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 CO<sub>2</sub>, *Catalysts*, 2022, **12**, 137.
- 41 X. Liu, G. Licht, X. Wang and S. Licht, Controlled Growth of Unusual Nanocarbon Allotropes by Molten Electrolysis of CO<sub>2</sub>, *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 CO<sub>2</sub>, *Mater. Today Chem.*, 2021, **22**, 100529.
- 43 X. Wang, G. Licht, X. Liu and S. Licht, One pot facile transformation of CO<sub>2</sub> 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 CO<sub>2</sub> 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. CO<sub>2</sub> Util.*, 2020, **236**, 288–294.
- 46 X. Wang, X. Liu, G. Licht and S. Licht, Calcium metaborate induced thin walled carbon nanotube syntheses from CO<sub>2</sub> 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. CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> by molten electrolysis into a wide controlled selection of carbon nanotubes, *J. CO<sub>2</sub> 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 CO<sub>2</sub> 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.

