Citation

Møller, K.T. and Williamson, K. and Buckley, C.E. and Paskevicius, M. 2020. Thermochemical energy storage properties of a barium based reactive carbonate composite. Journal of Materials Chemistry A. 8 (21): pp. 10935-10942. http://doi.org/10.1039/d0ta03671d

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Thermochemical Energy Storage Properties of a Barium Based Reactive Carbonate Composite

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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This study introduces a new concept of reactive carbonate composites (RCCs) for thermochemical energy storage, where a BaCO₃-BaSiO₃ mixture offers a successful thermodynamic destabilisation of BaCO₃ with moderate cyclic stability ~ 60 %, close to the theoretical maximum when considering unreactive impurities. This research presents an alternative to molten salt based energy storage technology that operates at higher temperature (850 °C) and hence maintains a higher Carnot efficiency at a competitive price level, enabling the development of a thermal energy storage system more favourable than state-of-the-art technology. Finally, the addition of catalytic quantities of CaCO₃ to the RCC significantly improves the reaction kinetics (one order of magnitude) through the formation of intermediate Ba_{2-x}Ca_xSiO₄ compounds, which are hypothesised to facilitate Ba²⁺ and O²⁻ mobility through induced crystal defects.

Introduction

Large-scale storage of renewable energy from solar or wind power is a prerequisite for covering base-load energy demand in the future as these energy sources are intermittent in their nature. Attention is often pointed towards hydrogen as an energy carrier, concentrated solar thermal power, or large-scale lithium battery facilities.^{1–5} However, cost is a major issue with these storage options. Concentrated solar thermal power (CSP) plants currently store energy using a KNO₃/NaNO₃ (60:40) molten salt, which has a low specific heat capacity of 1.53 kJ kg⁻ ¹ K⁻¹, *i.e.* a low energy density \leq 413 kJ kg⁻¹ when $\Delta T \leq$ 270 °C, and operates below 550 °C, which leads to a low Carnot efficiency when converting the heat back into electricity.⁶ Although, most research into metal carbonates is focused on CO2 sequestration,^{7,8} this class of materials have also been identified as promising for thermal energy storage due to their high enthalpy of formation and the low cost.^{1,6,9–12} The latter suggest to expand the application of thermal energy storage from CSP plants to a new technology defined as a thermal battery, where the energy input may be concentrated solar, industrial waste heat, energy from wind power, photovoltaics etc., which is stored and released through a chemical reaction.¹³ Witherite, the thermodynamically stable phase of BaCO₃, is industrially produced from naturally mined barite (BaSO₄) through the reaction with coke, also known as the 'black ash' process, and has a reasonable price of ~ \$494 USD per metric tonne.¹⁴ However, pristine BaCO₃ is thermally stable and decomposes at 1150 - 1400 °C,15 which is, perhaps, too high

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* E-mail: kasper.moller@curtin.edu.au; mark.paskevicius@gmail.com from an application point of view. Thus, thermodynamic destabilisation of the $BaCO_3$ is necessary. A recent study on:

 $\label{eq:Li2CO3(s) + Li2SiO3(s) \leftrightarrow Li4SiO4(s) + CO2(g) \ \Delta H_{700\ ^{\circ}C} = 109.0 \ \ kJ \\ mol^{-1} \ \ \textbf{(1)}$

suggests a destabilised metal carbonate as a thermochemical energy storage material operating at 700 °C,¹⁶ however, only 5 cycles were performed at low CO₂ pressure (< 0.4 bar). A disadvantage of this particular system is that Li is expensive (battery grade, 99.9%, Li₂CO₃ was on average \$17,000 USD per metric tonne in 2018, > 30 times the price of BaCO₃),¹⁷ and thus limits its utilisation in large-scale facilities. This study elaborates on the concept and introduces a new reactive carbonate composite (RCC). The incorporation of barium orthosilicate, BaSiO₃, improves the thermodynamics of BaCO₃ and thus enables the BaCO₃-BaSiO₃ system to operate in a suitable temperature range between 700 – 1000 °C as:

$$BaCO_3(s) + BaSiO_3(s) \leftrightarrow Ba_2SiO_4(s) + CO_2(g)$$
 (2)

Thermodynamics of the RCC BaCO₃-BaSiO₃ was evaluated using the software HSC Chemistry.¹⁸ The predicted temperature where the reaction has an equilibrium pressure of 1 bar ($T_{1 \text{ bar}}$) was determined to be 670 °C with $\Delta H_{670 \text{ °C}}$ = 151.9 kJ mol⁻¹ CO₂. However, an increased working temperature of 850 °C was selected, where the thermodynamic predictions are p_{eq} = 18.1 bar and $\Delta H_{850 \text{ °C}}$ = 126.9 kJ mol⁻¹ CO₂.

Experimental

Sample Preparation

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Table 1 Overview of samples discussed in this study.

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Sample	Compound 1	Compound 2	Compound 3	Molar ratio Compound 1:2:3	Mol% CaCO₃
S1	BaCO ₃	BaSiO₃ (Alfa Aesar)		1:1	0
S2	BaCO ₃	BaSiO₃ (Alfa Aesar)	CaCO ₃	1:1:0.052	2.5
S3	BaCO₃	BaSiO₃ (Alfa Aesar)	CaCO ₃	1:1:0.105	5
S4	BaCO ₃	BaSiO₃ (Alfa Aesar)	CaCO ₃	1:1:0.224	10
S5	BaCO₃	BaSiO ₃ (as-synthesised)	CaCO ₃	1:1:0.105	5

 $BaCO_3$ (Sigma-Aldrich, ACS reagent, $\geq 99\%$), CaCO₃ (Sigma-Aldrich, ReagentPlus), and $BaSiO_3$ (Alfa Aesar) were used aspurchased. $BaSiO_3$ was synthesised in the laboratory by heating a ball-milled 1:1.17 molar mixture of $BaCO_3$ and SiO_2 (Sigma-

Aldrich, 99.5%, nanopowder, 10-20 nm particle size) to 1000 $^\circ C$ for six hours in air.

Samples were prepared in various molar ratios, see Table 1, and were ball-milled in stainless steel milling vials with stainless steel balls (10 mm diameter, ball-to-powder mass ratio of 11:1) using an Across International Planetary Ball Mill (PQ-N04). A sequence of 20 min milling and a 1 min break, which is repeated three times to achieve an accumulated milling time of 1 hour, was applied.

Thermal Analysis

Differential scanning calorimetry and thermogravimetric analysis (DSC-TGA) was simultaneously performed on a Mettler Toledo DSC 1 instrument by heating ~15 - 25 mg of sample in an Al₂O₃ crucible from room temperature to 1200 °C under flowing Argon atmosphere (20 mL min⁻¹) at $\Delta T/\Delta t$ = 10, 20, or 30 °C min⁻¹. For comparison, CO₂ cycled samples were first absorbed and then analysed at three heating rates (as above) to construct Kissinger plots and determine their activation energy.

Sievert's measurements

Pressure cycling measurements were performed on a HyEnergy PCTpro E&E using a custom built SiC sample holder.¹⁹ Samples (typical mass ~ 2.4 g) were generally heated to 850 °C ($\Delta T/\Delta t$ ~ 4 °C min⁻¹) at $p(CO_2) \approx 1$ bar to avoid decomposition of the CaCO3 catalyst. The temperature was kept isothermal throughout the measurements and $\ensuremath{\text{CO}_2}$ pressure cycling was initiated between carbonation at $p(CO_2) \sim 21$ bar for 12 hours and decomposition at $p(CO_2) \sim 3$ bar for 12 hours. As reaction kinetics become faster with increasing cycle numbers, the carbonation/decomposition times were adjusted to 1, 3, or 6 hour(s). The samples were cycled from 20 - 35 carbonation and calcination cycles. At all times, the total gas volume used was 194.06 cm^3 (158.43 cm^3 reference volume and 35.63 cm^3 sample volume) and the non-ambient volume was determined to be between 13.8 to 15.5 cm³. All data was manually corrected from the PCTPro to include the correct volumes and compressibility factors for gaseous CO2.20 The cycling was ceased when the sample was in the absorbed state and cooled under a backpressure of CO₂. However, in some cases, samples were decomposed at 850 °C and analysed to determine the reaction decomposition products.

In-house Powder X-ray Diffraction

Powder X-ray diffraction data was collected in-house on a Bruker D8 Advance equipped with a Cu X-ray source (Cu K_{a1} radiation, $\lambda = 1.540593$ Å, Cu K_{a2} radiation, $\lambda = 1.544414$ Å) in flat-plate Bragg-Brentano geometry. Data were collected in the 2 θ range 5 – 80 ° on a Lynxeye PSD detector. The assynthesised BaSiO₃ was further investigated by adding a known 21.2 wt% NIST LaB₆ standard to quantify the amorphous fraction of the sample.

In Situ Synchrotron Radiation Powder X-ray Diffraction

In Situ time-resolved synchrotron radiation powder X-ray diffraction (SR-PXD) data were collected at the Australian Synchrotron, Melbourne, Australia using the Powder Diffraction (PD) beamline.²¹ The wavelength was $\lambda = 0.825018$ Å and data were collected on a Mythen microstrip detector in two different positions with a data acquisition time of 30 s in each position. Samples were packed in quartz capillaries (o.d. 0.7 mm, wall thickness 0.05 mm) and mounted in a custom gas fitting sealed with rubber rings, which was then connected to a gas manifold that provided vacuum or CO₂. During data acquisition, the samples were continuously oscillated over 90° to prevent preferred orientation of the particles. Finally, the samples were heated with a hot air blower at $\Delta T/\Delta t = 6$ °C min⁻¹. Diffraction patterns were quantitatively analysed using the Rietveld method in the software TOPAS (Bruker-AXS).

Scanning Electron Microscopy

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were conducted using a Zeiss Neon 40EsB equipped with a field emission gun. The SEM images were collected using an accelerating voltage of 5 kV, an aperture size of 30 μ m, and a working distance between 2.5 ~ 7 mm. SEM samples were prepared by embedding powdered samples in an epoxy resin that was polished using colloidal silica, which were then sputter coated with a 10 nm thick carbon layer.

Results & Discussion

Destabilisation of BaCO₃ utilising BaSiO₃

From TG-DSC data it is evident that BaCO₃ is destabilised by BaSiO₃, see Figure 1, where a mass loss (CO₂) is detected at lower temperatures. For both pristine BaCO₃ and the RCC, BaCO₃-BaSiO₃ (**S1**), a polymorphic phase transition is observed for BaCO₃ at ~ 815 °C from an orthorombic (space group *Pmcn*) to a trigonal structure (*R*3*m*),²² which has previously been



Figure 1 TG (upper) and DSC (lower) data comparing pristine BaCO₃ and the reactive carbonate composite BaCO₃-BaSiO₃ (**S1**). $\Delta T/\Delta t$ = 10 K min⁻¹, 20 mL argon flow.

reported to occur at ~ 750 °C and 805 °C.^{23–25} A second polymorphic phase transition is observed at ~ 974 °C from the trigonal to cubic structure (*Fm*-3*m*).^{24–26} The TG data reveal that pristine BaCO₃ decomposes above 1000 °C, whereas the RCC initiates decomposition at ~ 650 °C, releasing CO₂. Hence, the operational temperature of BaCO₃ becomes more favourable for applications when destabilised by BaSiO₃. Additional information is provided in Figures S1-S3.

Cyclic energy capacity studies

The cyclic CO₂ storage stability is evaluated from the Sieverts experiments (see Figure 2). Sample **S1** maintains a steady ~ 40 - 45 % CO₂ capacity during 12-hour calcination/carbonation cycles. The low capacity is partly assigned to slow reaction kinetics during CO₂ release and absorption from the pristine BaSiO₃-BaCO₃ system, see Figures 3 and S4. Thus, an attempt to catalyse the CO₂ absorption and release was undertaken using CaCO₃, which shows excellent kinetics in its pure form.¹³ Previously, a solid-solution regime has been reported for Ca₁-



Figure 2 Comparison of the cyclic CO₂ storage capacity after calcination in each cycle. **S1** is the uncatalysed BaCO₃-BaSiO₃ while **S2-S4** are CaCO₃ catalysed with various amounts of CaCO₃, while **S5** is catalysed with 0.105 mol CaCO₃ and contains synthesised BaSiO₃. Calcination/carbonation times vary and are indicated in the following way: 2 hours (\blacktriangle); 3 hours (\blacklozenge); 5 hours (\diamondsuit); 6 hours (\circlearrowright); 12 hours (\blacklozenge).



Figure 3 Comparison of the reaction kinetics in the 15th desorption highlighting the positive effect of adding CaCO $_3$ to the system.

_xBa_xCO₃ above ~ 850 °C.²⁷ Thus, it was hypothesised that this solid solution could enhance the CO₂ and/or Ba²⁺ diffusion through the metal carbonate. Addition of 2.5 (S2) and 5 mol% (S3) CaCO₃ influences the cyclic capacity to a small extent (~ 45 % and ~ 37 % CO₂ capacity, respectively). However, the addition of a larger quantity, i.e. 10 mol%, of CaCO3 reduces the CO2 capacity to ~ 20 - 25 %. Sample S5 increases in capacity for the first 15 cycles before stabilising at \sim 60 % and thus proves superior to the other samples (see Figure 2). The absorption/desorption time was decreased to 5 hours as the sample reached a plateau within this time frame, see also Figure S4. Despite the reduction in time, the capacity increases along with reaction kinetics. Hence, an activation of the sample, possibly through the formation of Ba_{2-x}Ca_xSiO₄ (c.f. Powder Xray diffraction section) and homogenisation of the sample seem necessary.

Although the CO₂ capacity suffers from adding a large amount of CaCO₃ to the system, the reaction kinetics improve significantly (see Figure 3). The difference is apparent in the 15th desorption, where calcination is ~ 10 times faster in sample **S2** compared to the pristine RCC, sample **S1**, (~ 40 min compared to ~ 4.5 hours, respectively). Generally, the calcination reaction kinetics for samples **S2** through **S5** are more than doubled compared to sample **S1** (see Figure S4).

Powder X-ray diffraction

Powder X-ray diffraction (PXD) data indicate that the aspurchased BaSiO₃ (Alfa Aesar) contains multiple Ba-Si-O compositions (see Figure S5), since the as-milled samples (**S1**-**S4**) contain major fractions of, *e.g.* Ba₄Si₆O₁₆ (barium-poor). Hence, the decreased cyclic CO₂ capacity, which is close to half of that expected, is attributed to the fact that the commercial BaSiO₃ contains a large amount of impurities, which retards reaction (**2**). However, quantification of the amorphous fraction is not possible through Rietveld refinement as unidentified crystalline compounds are also present. Sample **S5**, containing the synthesised BaSiO₃, is a more homogenous mixture of BaCO₃ and BaSiO₃ and hence the cyclic capacity is superior (see Figures 2 and S6). However, impurities of Ba₄Si₆O₁₆ and an

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amorphous content (likely SiO₂) are still an issue (see Figure S6), and thus the BaSiO₃ content only amounts to 62.1 wt% of what is expected. Hence, the cyclic capacity of sample **S5** is theoretically decreased to 62.4 %, due to the lower amount of BaSiO₃ available for reaction (**2**), and thus proves that the sample's cyclic stability is close to the theoretical maximum when considering the unreactive impurities. The addition of small quantities of CaCO₃ does not influence the PXD pattern of the ball-milled samples due to overlapping Bragg reflections and the smaller X-ray scattering power of Ca²⁺ compared to Ba²⁺ (see Figure S5).

After CO₂ pressure cycling of BaCO₃-BaSiO₃ (**S1**) it is evident that reaction (**2**) is occurring through absorption and desorption of CO₂ (see Figure 4a). However, Bragg reflections from BaSiO₃ are still present after CO₂ absorption due to an incomplete reaction although an intensity decrease is observed due to consumption. The addition of CaCO₃ to the system proved to enhance reaction kinetics significantly during cyclic measurements. The increased kinetics are in-fact not assigned to the hypothesised Ca₁₋ $_xBa_xCO_3$,²⁷ but to the formation of Ba_{2-x}Ca_xSiO₄ that offers increased cation mobility of Ba²⁺ as the smaller Ca²⁺ cation introduces defects in the Ba₂SiO₄ crystal structure^{28,29} (see Figure 4b and reaction scheme (**3**)). The composition of Ba₂.



Figure 4 PXD data ($\lambda = 1.54056$ Å) of **A**: the cycled BaCO₃-BaSiO₃ (**S1**) in the CO₂ absorbed and desorbed state confirming the expected reaction (1) occurring and **B**: the cycled BaCO₃-BaSiO₃-0.052CaCO₃ (**S2**) in the CO₂ absorbed and desorbed state showing the influence of CaCO₃ on the system.



Figure 5 *In situ* SR-PXD data of BaCO₃-BaSiO₃ (**S1**) heated from room temperature to 935 °C ($\Delta T/\Delta t = 6$ °C min⁻¹; $\lambda = 0.825018$ Å, $p(CO_2) = 1$ bar). Colour code: BaCO₃ (Orange); BaCO₃-HT (dark green); BaSi₂O₅ (pink), BaSiO₃ (blue); Ba₅Si₈O₂₁ (red); Ba₄Si₆O₁₆ (green); Ba₂SiO₄ (purple). The dashed line represents the temperature profile.

 $_x$ Ca $_x$ SiO $_4$ varies depending on the absorbed or desorbed state of the sample and the loading level of CaCO₃. Higher loading of CaCO₃ leads to a higher fraction of Ba_{2-x}Ca $_x$ SiO₄ after cycling, probably due to an extended reaction between CaCO₃ and BaSiO₃, which may cause the significantly lower cyclic capacity observed in sample **S4**. The findings imply that CaCO₃ has reacted with BaSiO₃ to form Ca₂SiO₄, which is favourable according to thermodynamic calculations, see reaction scheme (**4**):¹⁸

 $(1-x)Ba_2SiO_4(s) + xCa_2SiO_4(s) \rightarrow Ba_{2-2x}Ca_{2x}SiO_4(s)$ (3)

 $2CaCO_3 (s) + BaSiO_3 (s) \rightarrow Ca_2SiO_4 (s) + BaCO_3 (s) + CO_2 (g) T_{1bar}$ = 450 °C $\Delta G_r \approx 0$ J/mol (4)

Reaction scheme (**4**) suggests that a higher loading of $BaSiO_3$ is necessary to increase the CO_2 cyclic capacity, as a part of the $BaSiO_3$ is consumed in this reaction and thus is not available for reaction with $BaCO_3$ to cycle through reaction scheme (**2**). This is further supported by TGA data on sample **S5** after 25 cycles and absorption, where two calcination steps are observed; the first from reaction (**2**) and the second from leftover $BaCO_3$ (see Figure S3).

Insight into the reaction mechanism using In situ powder X-ray diffraction

The *in situ* SR-PXD data of BaCO₃-BaSiO₃ (**S1**) supports the inhouse PXD, as the initial sample primarily contains witherite but also a range of Ba-Si-O compounds, *i.e.* BaSiO₃, BaSi₂O₅, Ba₄Si₆O₁₆, and Ba₅Si₈O₂₁ (see Figure 5). Upon heating, the witherite undergoes a first-order polymorphic transition into its high-temperature polymorph (space-group *R*-3*m*, BaCO₃-HT) between $T \sim 782$ and 835 °C. Simultaneously, Bragg reflections

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Figure 6 Comparison of *in situ* SR-PXD (λ = 0.825018 Å) data of BaCO₃-BaSiO₃ (**S1**) and BaCO₃-BaSiO₃-0.224CaCO₃ (**S4**) at *T* = 850 °C and *p*(CO₂) = 1 bar. Markers: BaCO₃-HT (heart); CaCO₃ (open square), BaSi₂O₅ (open circle), BaSiO₃ (spades); Ba₅Si₈O₂₁ (clove); Ba₄Si₆O₁₆ (star); Ba₂SiO₄ (diamonds); Ba₂, Ca₂SiO₄ (four squares).

from the reaction product Ba_2SiO_4 appear at $T \sim 782$ °C. The Bragg reflections from BaCO₃-HT indicate that one, or more, unit cell axes expand while one or more contract as some reflections move towards lower angle and some towards higher angle, respectively. Bragg reflections from BaCO₃-HT disappear at $T \sim 940$ °C, however, the low temperature polymorph is not re-formed upon cooling, hence it is concluded that BaCO₃ is consumed in reaction 2. The slow and continuous formation of Ba_2SiO_4 at $T \sim 940$ °C supports the broad DSC signal previously observed over a wide temperature range as reaction kinetics are slow (see Figure 1). During cooling, the Ba₂SiO₄ undergoes thermal contraction. Similarly, in situ SR-PXD data of BaCO3-BaSiO₃-0.224CaCO₃ (S4) is presented in Figure S7, while the main difference at high temperature (850 °C) between samples **S1** and **S4** is highlighted in Figure 6. The presence of Ba_{2-x}Ca_xSiO₄ and a lower fraction of Ba₂SiO₄ in sample S4 is believed to be the reason for the major difference observed in reaction kinetics.

Influence on activation energy

The activation energy, E_a , was determined for the calcination (CO₂ release) of BaCO₃ in the as-milled and cycled samples of BaCO₃-BaSiO₃ (**S1**), BaCO₃-BaSiO₃-0.052CaCO₃ (**S2**), and BaCO₃-BaSiO₃-0.105CaCO₃ (**S5**) based on Kissinger's relation:

$$\ln[\beta/T_p^2] = -E_a/RT_p + A \tag{1}$$

here, β is the heating rate, T_p is the DSC peak temperature for calcination, E_a is the activation energy of calcination, R is the gas constant, and A is a reaction specific constant. The sample (**S1**) was thus calcinated at three different heating rates, *i.e.* $\Delta T/\Delta t = 10$, 20, and 30 K min⁻¹ (Figure 7a) and the peak endotherm temperature was determined to be 994, 1040, and 1065 °C, respectively. A Kissinger plot was constructed (Figure 7b), and the activation energy for calcination of the BaCO₃-BaSiO₃ composite (**S1**) was determined to 195 \pm 7 kJ mol⁻¹. In



Figure 7 Differential scanning calorimetry of (**A**) as-milled $BaCO_3$ - $BaSiO_3$ (**S1**, bold line) and the cycled **S1** sample (thin line) at three different heating rates to construct (**B**) the Kissinger plot of $BaCO_3$ - $BaSiO_3$. (**C**) the Kissinger plot of $BaCO_3$ - $BaSiO_3$ -0.052CaCO_3 (**S2**). The slope of the Kissinger plot makes it possible to extract the activation energy, E_a , of calcination.

comparison, the calcination activation energy of pristine BaCO₃ has been reported between 283 - 305 kJ mol⁻¹ (vacuum and Argon flow, respectively).^{24,30} Hence, a significant decrease in the decomposition activation energy is observed in the thermodynamically destabilised BaCO₃-BaSiO₃ composite. The activation energy was further determined for the BaCO₃-BaSiO₃ reactive carbonate composite after 35 cycles of calcination/carbonation and it is evident that the activation energy increases slightly to 210 ± 10 kJ mol⁻¹, which agrees well with the rather constant reaction kinetics observed throughout cycling (see Figure S4).

The opposite effect is observed for the CaCO₃ catalysed sample (**S2**), where an activation energy for the as-milled sample is determined to be 236 \pm 7 kJ mol⁻¹ (Figure 7c), which is slightly higher than that for the primary BaCO₃-BaSiO₃ composite (**S1**).



Figure 8 SEM and EDS of a) sample S2 as-milled. The blue highlight marks a region rich in SiO₂ b) sample S2 after 34 cycles and absorbed and c) sample S5 after 25 cycles and absorbed. Element colour code: Ba : red; Si : green; O : purple.

It is hypothesised to be due to either a slight difference in particle size arising from ball-milling or the additional reaction of Ca²⁺ incorporation into the Ba₂SiO₄ structure. However, after the conducted cyclic measurements, the activation energy is eventually lowered to 158 ± 5 kJ mol⁻¹ after 34 cycles (see Figure 7c), which is lower than the uncatalysed sample and in agreement with the observed increase in reaction kinetics, see Figure S4. The DSC data for sample **S2** is presented in Figure S9.

Table 2 Cost comparison (USD) of materials for producing 1 TJ of electrical energy.

Sample morphology

The as-milled samples of BaCO₃-BaSiO₃(-CaCO₃, 2.5, 5, and 10 wt%; **S1-S4**, respectively) all reveal large particles are present (> 10 μ m), which are identified through EDS mapping to be Ba depleted and mainly contain Si and O, *i.e.* SiO₂ (see Figure 8a). The presence of large SiO₂ particles are still evident after CO₂ cycling of the samples, illustrated by sample **S2** in Figure 8b. Hence, this impurity, present in the commercial BaSiO₃, does not participate in the reaction and thus the low cyclic capacity

	Molten Salt	Li ₂ CO ₃ +Li ₂ SiO ₃ ≓ Li ₄ SiO ₄ + CO ₂	$BaCO_3+BaSiO_3 \rightleftarrows Ba_2SiO_4 + CO_2$			
	(40 NANO ₃ : 60 KNO ₃)					
Enthalpy Δ <i>H</i> (kJ/mol)	39.0	109.0	126.9			
Molar Mass (g/mol)	94.60	163.86	410.75			
Density (g/cm ³)	2.17	2.3 ^d	4.4 ^e			
CO ₂ Capacity (wt.%)	-	26.86	10.71			
Gravimetric Energy Density (kJ/kg)	413	665	309			
Volumetric Energy Density (MJ/m ³) ^a	895	1530	1359			
Operating Temperature Range (°C)	290-565	700	850			
Operating Pressure Range (bar)	-	0.1-0.8	5 - 25			
Carnot Efficiency (%) ^b	46	69	73			
Estimated Practical Efficiency (%)	27	44	48			
Mass Required (tonnes) ^c	9100	3401	6903			
Volume Required (m ³) ^{<i>c</i>}	4194	1479	1569			
Materials Cost (\$/tonne) ^{14,17,31}	630	17000 ^f	494 ^f			
Total Materials Cost Required (\$) ^c	5,730,000	57,800,000	3,410,000			
^a Based on crystalline data. ^b Lower temperature. ^c To generate 1 TJ of electrical energy. ^d Applies to Li ₄ SiO ₄ . ^e Applies to the mixture BaCO ₃ -						
BaSiO ₂ , JBased entirely on the cost of $M_{\nu}CO_2$, as this is also the starting reagent for synthesising $M_{\nu}SiO_3$.						

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of < 50 % is believed to be due to the discrepancy in molar ratio between $BaCO_3$ and $BaSiO_3$. The SiO_2 was not identified through PXD and is thus believed to be amorphous.

The BaCO₃-BaSiO₃(synthesised)-0.105CaCO₃ sample (**S5**) does not contain large SiO₂ particles, possibly due to the starting reagent being nanoparticle size, and thus the sample is more homogenous and leads to a higher energy capacity through increased reactivity. Generally, sintering seems not to be an issue, as seen in other carbonate systems,⁹ as the reverse reaction (reaction scheme (**2**)) ensures segregation of the reactants whilst maintaining a good surface contact. The asmilled sample **S5** has calcium and silicon rich regions (see Figure S10). However, after cycling and absorption, the elements are well distributed in the sample as evident from Figure 8c. This may also explain the stabilisation in reaction kinetics after cycling, once the sample morphology is uniform.

Cost analysis

A cost comparison between the developed BaCO₃-based thermochemical energy storage material, the state-of-the-art molten salt and a previously suggested Li₂CO₃-based material is given in Table 2. Although the Li₂CO₃-Li₂SiO₃ system shows a good cyclability at ~ 100 % over 5 cycles at 700 °C, the expensive LiCO₃ makes the materials cost for producing a thermal energy storage system capable of storing 1 TJ_{e} \sim 10 times more expensive than molten salts. Thus, an energy storage system based on this material is unlikely to be commercial. Additionally, the high cyclic stability is attributed to melting of Li₂CO₃, which enhances CO₂ diffusivity, but also increases requirements for the materials container to avoid molten salt corrosivity, *i.e.* the engineering costs may also be increased. Contrary, the BaCO₃-BaSiO₃ system materials are ~ 40 % cheaper than molten salt while the footprint of the system is also reduced (~ 1/3), which makes it worth considering as a successor for current technology. The higher operating temperature (850 vs. 550 °C) and thus higher Carnot efficiency is favourable and makes the system compatible with the Rankine-Brayton combined cycle and Stirling engines for thermal to electrical energy conversion.³² Finally, abundance of the materials play a crucial role, *i.e.* BaCO₃ is widely available, whereas shortage of batteryquality lithium and other battery components, e.g. cobalt, may become an issue if large-scale thermal energy storage and electrical vehicles adopt lithium-ion batteries as their main storage system.^{17,33,34}

Conclusions

Thermodynamic destabilisation of BaCO₃ is achieved by addition of BaSiO₃, which promotes a chemical reaction on CO₂ release resulting in a lowering of the decomposition temperature of BaCO₃ by more than 350 °C. Hence, BaCO₃ is tailored for utilisation in thermal energy storage applications. The commercial sample of BaSiO₃ contains a large quantity of impurities, *e.g.* large particles of SiO₂, which hampers the cyclic energy storage capacity of the BaCO₃-BaSiO₃ system compared to the more pure, synthesised BaSiO₃, which provides the

highest energy capacity retention, *i.e.* ~ 60 %, which is very close to the theoretical maximum determined to be 62.4 %. The capacity may be improved by optimising the molar ratio of BaCO₃ to BaSiO₃ and CaCO₃ as the formation of Ca₂SiO₄ and eventually Ba2-xCaxSiO4 is evident, while unreacted SiO2 is also found in sample S5. Hence, BaSiO₃ and BaCO₃ are consumed, which leaves a discrepancy in molar ratio causing an energy capacity loss as the pristine BaCO₃ is thermodynamically too stable to calcine at the physical conditions applied here. Addition of CaCO₃ in various amounts, i.e. 2.5 - 10 mol%, significantly improves the reaction kinetics by up to 10 times, through the formation of Ba_{2-x}Ca_{2x}SiO₄ intermediates. However, addition of 10 mol% influences the energy capacity negatively. The possibility to significantly improve reaction kinetics by introducing a second metal carbonate is a new, interesting approach, which opens up new avenues for future research in this materials class for thermal energy storage. Finally, it is proven here that BaCO₃ is able to operate at 850 °C, which is suitable in combination with a Stirling engine. However, lowering the temperature to 670 °C where the equilibrium pressure is 1 bar makes it suitable to combine with commercially available steam turbines, and may thus be worth further investigation.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

KTM acknowledges the Independent Research Fund Denmark for an International Postdoctoral Grant (case-number: 8028-00009B). MP and CEB acknowledges the Australian Research Council for FT160100303 and LP150100730, respectively. CEB, MP, and KTM acknowledge the Global Innovation Linkage project for grant GIL73589. KW acknowledge the Australian Government for an Australian Government Research Training Program Scholarship. Part of this research was undertaken using the EM/XRD instrumentation (ARC LE0775553 and LE0775551) at the John de Laeter Centre, Curtin University. Dr. Nigel Chen-Tan and Anna Emenheiser are acknowledged for assistance with initial sample preparation and thermal stability analysis. ANSTO is acknowledged for providing access to the PD beamline at the Australian synchrotron, Melbourne, Australia.

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