Supplementary information

for

Optimising Thermochemical Energy Storage: A Comprehensive Analysis of $CaCO_3$ composites with $CaSiO_3$, $CaTiO_3$, and $CaZrO_3$

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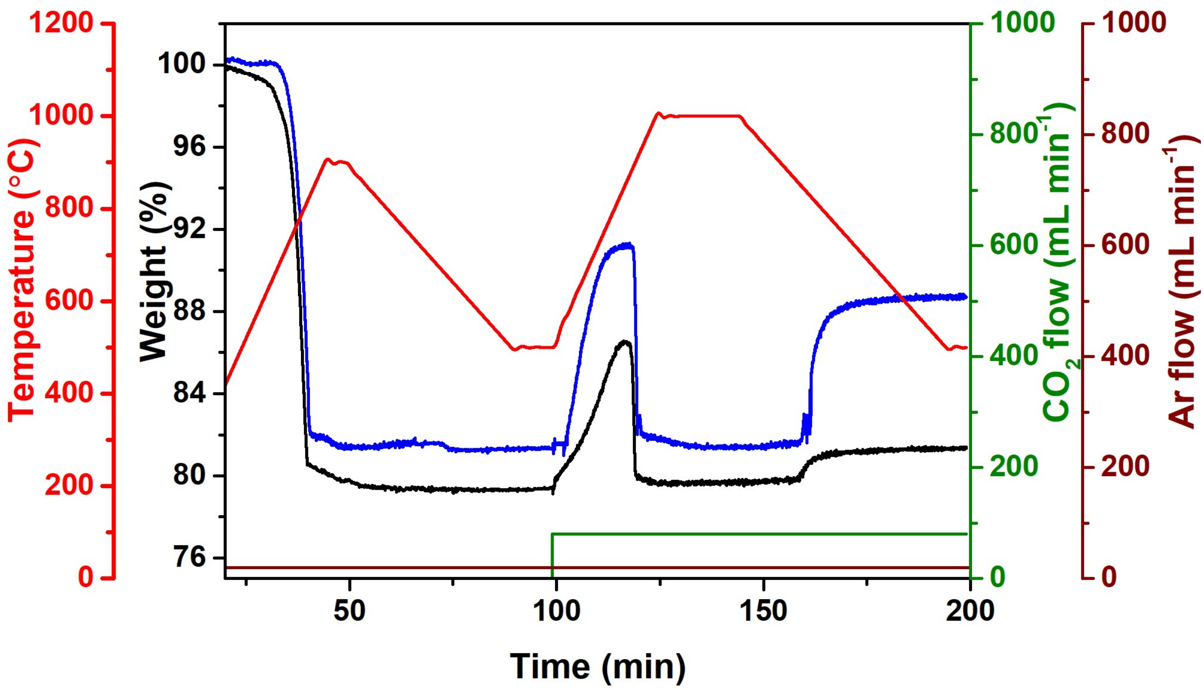

Fig. S1. TGA for $CaCO_3$-$CaSiO_3$ (black line) and $CaCO_3$-$CaTiO_3$ (blue line) under argon (brown line) and CO_2 atmosphere (green line).

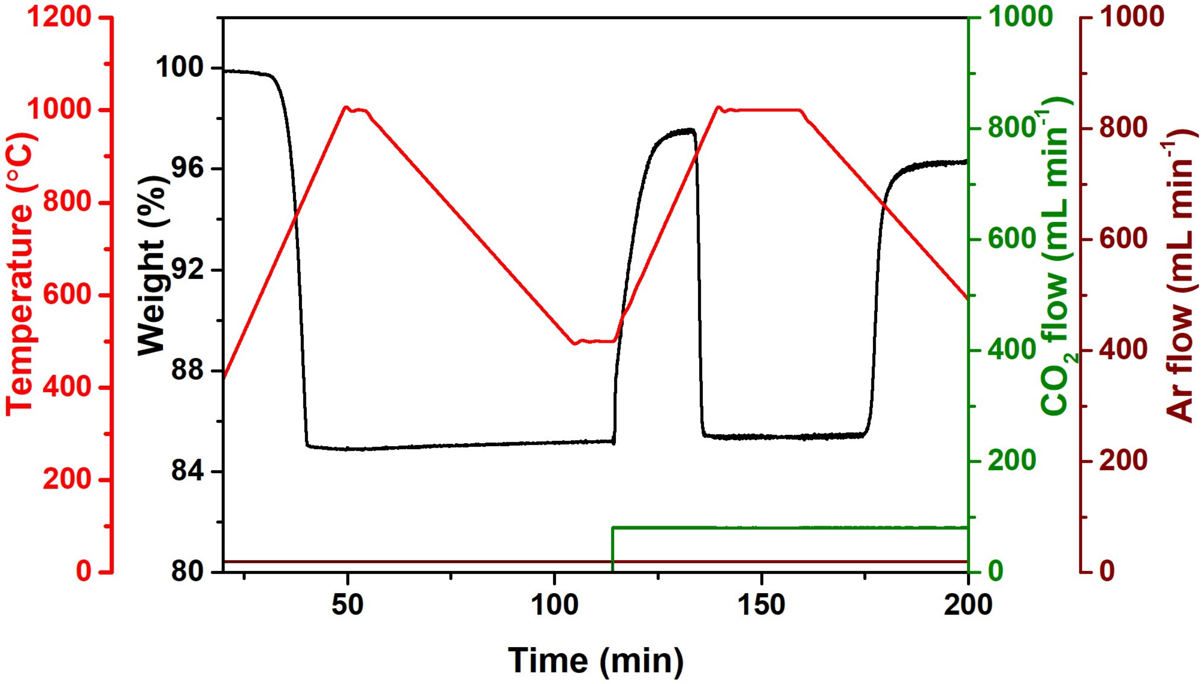

Fig. S2. TGA for $CaCO_3$-$CaZrO_3$ under argon and CO_2 atmosphere.

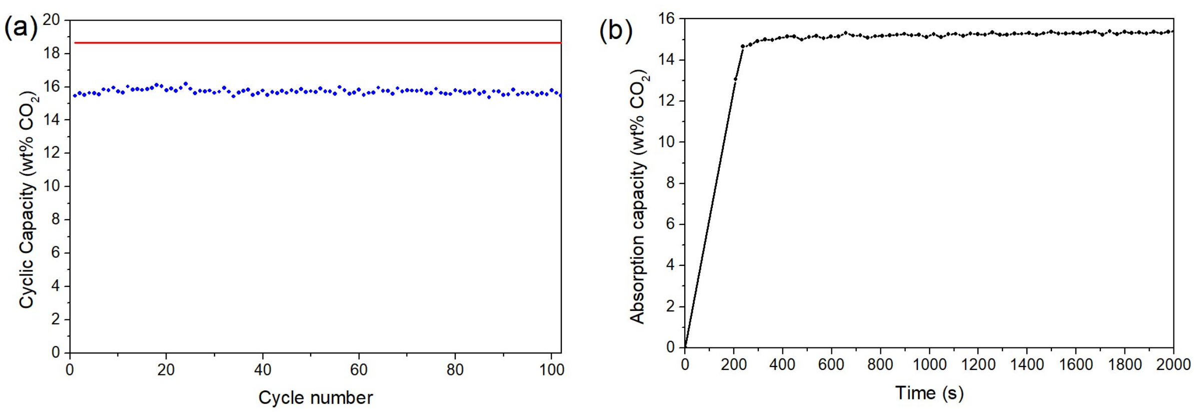

Fig. S3. CO_2 cycling of $CaCO_3$-$CaTiO_3$ on a manometric Sieverts apparatus. (a) Carbon dioxide sorption capacity (blue) over 102 cycles relative to the theoretical maximum sorption capacity (red). (b) CO_2 absorption kinetics on cycle 102. Temperature = 752 °C; Absorption pressure = 5.45 bar; Desorption pressure = dynamic vacuum.

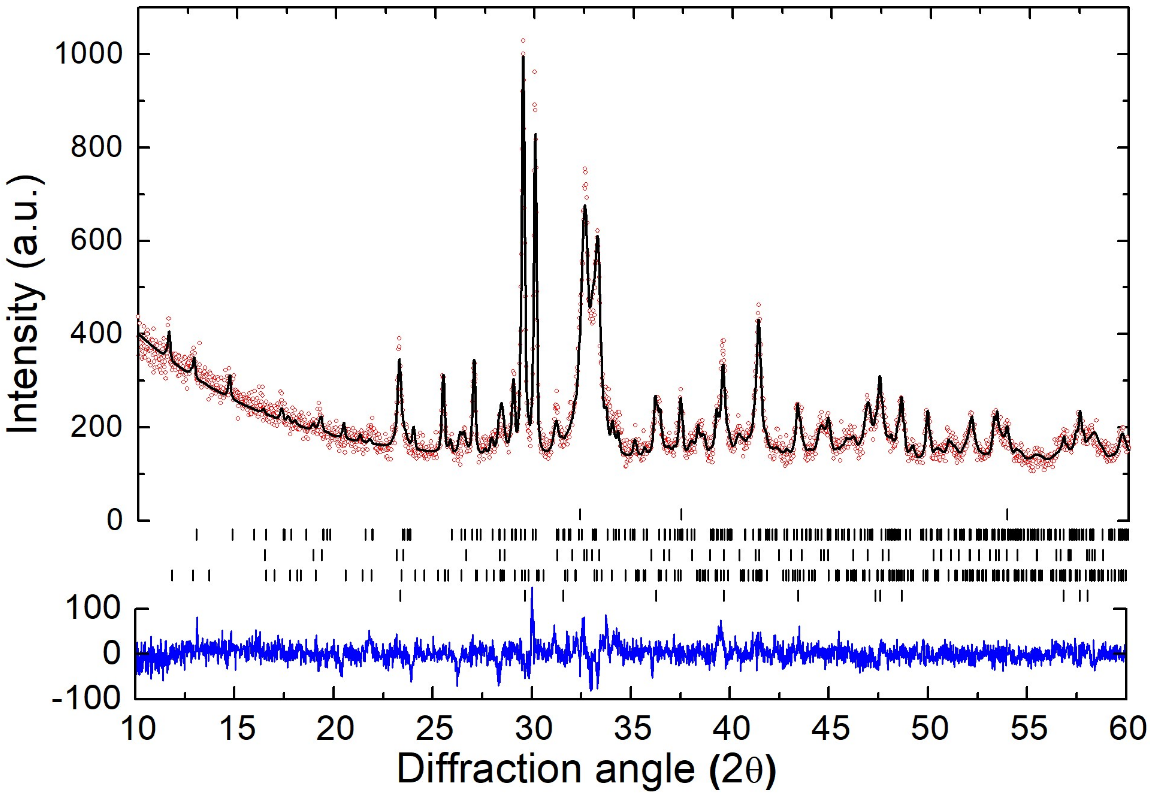

Fig. S4. Room temperature SR-XRD pattern and Rietveld refinement plot of $CaCO_3$-$CaSiO_3$ after CO_2 cycling (14 cycles, final stage: absorption). *Rwp* = 8.9 %. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $CaCO_3$ (16.1(3) wt%), $CaSiO_3$ (25.1(4) wt%), Ca_2SiO_4 (46.6(5) wt%), $Ca_5(SiO_4)_2CO_3$ (10.1(4) wt%) and CaO (2.2(1) wt%), bottom to top respectively. λ = Cu $K\alpha_{1,2}$ radiation.

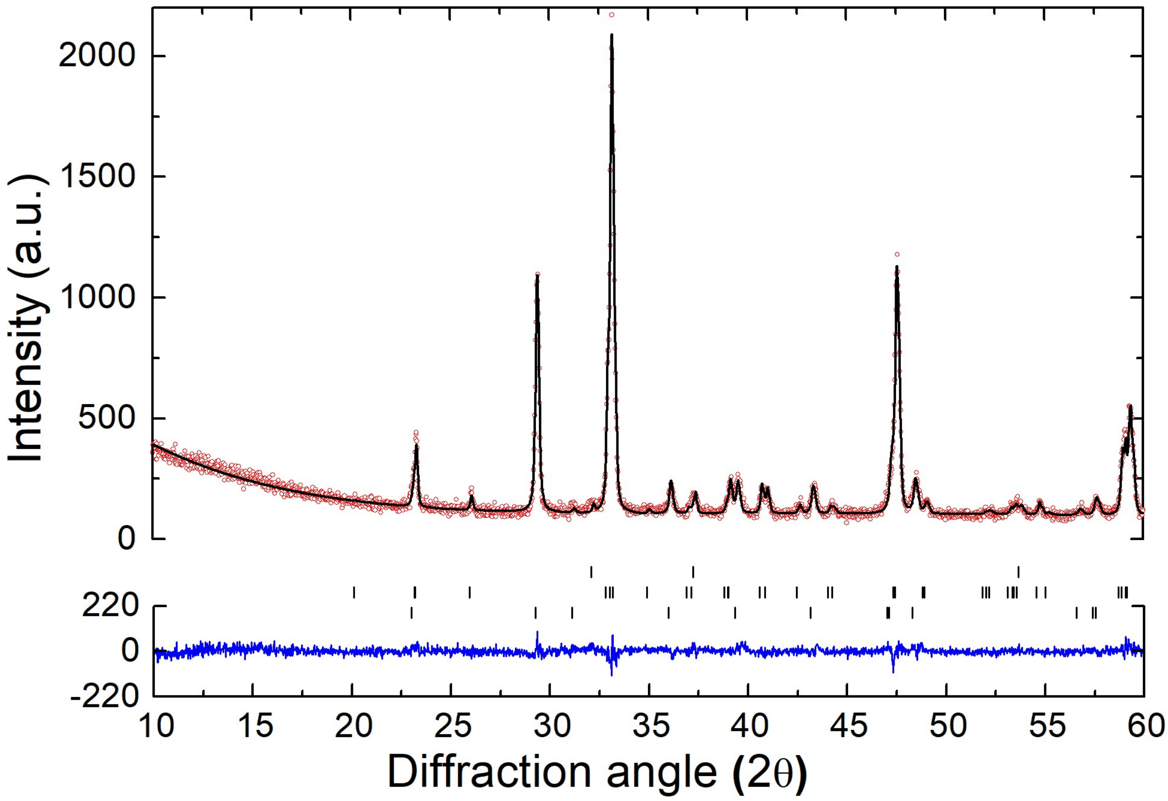

Figure S5. Room temperature SR-XRD pattern and Rietveld refinement plot of $CaCO_3$-$CaZrO_3$ after CO_2 cycling (100 cycles, final stage: absorption). *Rwp* = 7.7%. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $CaCO_3$ (30.8(3) wt%), $CaTiO_3$ (68.0(3) wt%), and CaO (1.14(8) wt%), bottom to top respectively. λ = Cu K$\alpha_{1,2}$ radiation.

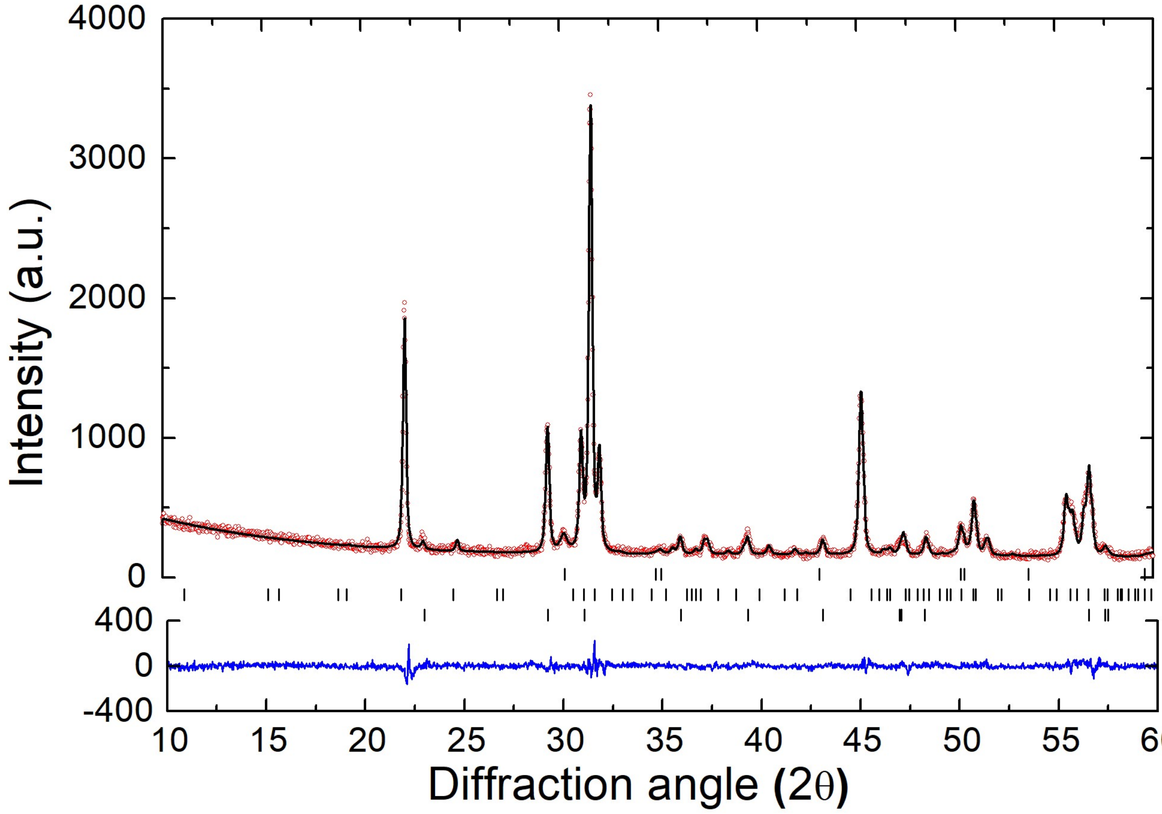

Figure S6. Room temperature SR-XRD pattern and Rietveld refinement plot of $CaCO_3$-$CaZrO_3$ after CO_2 cycling (100 cycles, final stage: absorption). *Rwp* = 7.7%. Experimental data as red circles, calculated diffraction pattern as black line and the difference plot in blue. Tick marks show positions for: $CaCO_3$ (29.2(3) wt%), $CaZrO_3$ (67.8(3) wt%), and ZrO_2 (3.0(2) wt%), bottom to top respectively. λ = Cu K$\alpha_{1,2}$ radiation.

	Molten salt (40NaNO$_3$:60KNO$_3$)	$SrCO_3 + SrSiO_3 \rightleftharpoons Sr_2SiO_4 + CO_2$	$BaCO_3 + BaSiO_3 \rightleftharpoons Ba_2SiO_4 + CO_2$	$CaCO_3 \rightleftharpoons CaO+CO_2$ (20 wt% Al$_2$O$_3$)	$CaCO_3 + CaSiO_3 \rightleftharpoons Ca_2SiO_4 + CO_2$	$CaCO_3 + CaTiO_3 \rightleftharpoons CaO + CaTiO_3 + CO_2$	$CaCO_3 + CaZrO_3 \rightleftharpoons CaO + CaZrO_3 + CO_2$
Enthalpy Δ*H* (kJ mol^{-1})	39.0	155.8	126.9	172	111[a]	169[b]	152[a]
Density (g cm^{-3})	2.17	3.75[c]	4.4[c]	2.89	2.77[c,d]	3.51[c,d]	3.59[c,d]
CO$_2$ Capacity (wt%)	-	14.13	10.71	16.1	20.35	18.56	15.75
Gravimetric Energy Density (kJ kg^{-1})	413	500	309	782	513	716	544
Gravimetric Energy Density (kWh kg^{-1})	0.115	0.14	0.09	0.22	0.14	0.20	0.16
Volumetric Energy Density (MJ m^{-3})	895	1876	1359	2260	1422	2513	1953
Volumetric Energy Density (kWh m^{-3})	249	521	378	628	394	698	542
Operating Temperature (°C)	290 – 565	700	850	900	750	750	750
Operating CO$_2$ Pressure (bar)	-	0.1 - 6.0	5 – 25	1	0.1-1	0.1-1	0.1-1
Theoretical Carnot Efficiency (%)[e]	46	69	73	74	70	70	70
Estimated Practical Efficiency (%)[e]	27	44	48	49	46	46	46
Mass Required (tonnes)[f]	11.6	5.8	8.7	3.4	5.5	4.0	5.2
Volume Required (m^3)[f]	5.3	1.6	2.0	1.2	2.0	1.1	1.4
Materials Cost (\$ tonne^{-1})	630	1,060	1,090	84.3	260	2,200	4,664
Total Materials Cost Required (\$)[f]	7,297	6,185	9,471	283	1,434	8,697	24,264
Material cost (US\$ per kWh$_{th}$)	5.7	7.6	12.7	0.4	1.8	11.1	30.9

[a] This work, DSC data. [b]This work, PCI data. [c]Intrinsic density. [d]Applies to the mixture. [e]Lower temperature of 30°C. [f]To generate 360 kWh of electrical energy. The conversion of thermochemical energy (E_{th}) to electrical energy (E_e) is $E_e = e_p \times E_{th}$, where e_p is the estimated practical efficiency. Assuming 100 % cycling capacity, except $CaCO_3 \rightleftharpoons CaO+CO_2$ (20 wt% Al$_2$O$_3$) which assumes 45.7 % as in ref. [2]

Table S1 Comparison of thermochemical properties, system variables, and cost parameters for select energy storage materials.[1-6]

Assumptions for Cost Analysis:

- According to the assumptions listed in Lazard's Levelised Cost of Storage Analysis, the useful plant lifetime is a span of 20 years to 40 years.[7]
- Equipment for system – 1 x compressor, 2 x intercoolers, 2 x turbine, electrical heater, 1 x CO_2 storage vessel, 1 x thermocline vessel
- Additional costs include feedstock and maintenance.
- Cost of electricity is 0.1$/kWh.[8]
- Cost of solar PV per kW is $750 USD, and is included in CAPEX.[9]
- System costs are calculated using Cost of Individual Equipment – Chemical Process Equipment.[10]

Table S2 CAPEX costs associated with plant.[7]

Component	**Cost ($USD)**
Compressor	15,007.50
Heat Exchanger	14,532
Turbine	575.15
Pressure Vessel	1,811.90
Thermocline Vessel	4,079.50
Stirling Engine Cost	14,000
Reactor Vessel	1,427.40
Heater Cost	2,102
Cost of CO_2	150
Cost of Solar PV	78,240
Insulation	2,800
Balance of Plant	4,600
Initial Investment of Plant	7,920
Total	**145,818.05**

Table S3 OPEX Costs associated with plant.[7]

System	Power Consumption (kW)	Cost (USD)
CO_2 compressor	8.82	$ 10.58
Heater	75.00	$ 90.00
Intercooler Charging	16.00	$ 19.20
Intercooler Discharging	4.50	$ 5.40
	Total 12 Hours	$ 125.18
	Total Yearly	$ 45,692.16
	Total Plant Lifetime 40 Years	**$ 1,827,686.40**
	Total Plant Lifetime 20 Years	**$ 913,843.20**

Total Energy Produced (kWh) 40 Years	5,256,000
Total Energy Produced (kWh) 20 Years	2,628,000

Table S4 OPEX Costs associated with each energy storage material.[7]

System Operational Costs	**Cost USD**	
Service Cost	$	864.00
Operation and Maintenance Cost in 1st Year	$	158.40
$CaTiO_3$	$	8,697.00
Total OPEX 40 Years	$	390,323.00
Total OPEX 20 Years	$	194,896.35
$CaZrO_3$	$	24,264.00
Total OPEX 40 Years	$	1,013,003.00
Total OPEX 20 Years	$	506,236.35
$CaSiO_3$	$	1,434.00
Total OPEX 40 Years	$	99,803.00

Total OPEX 20 Years	$ 49,636.35

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