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High temperature thermochemical energy storage based on calcination–carbonation chemical looping reactions

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Concentrated solar power (CSP) is a promising source of clean electricity, however storage systems are essential to address the disparity between time-dependent solar availability and electricity demand. Thermochemical Energy Storage (TCES) based on metal carbonate/oxide calcination-carbonation chemical looping is a low cost, high energy storage density alternative to commercial molten salt storage systems.

Carbonate Looping Thermochemical Energy Storage

Process is based on metal oxide calcination carbonation chemical looping (cyclic process):

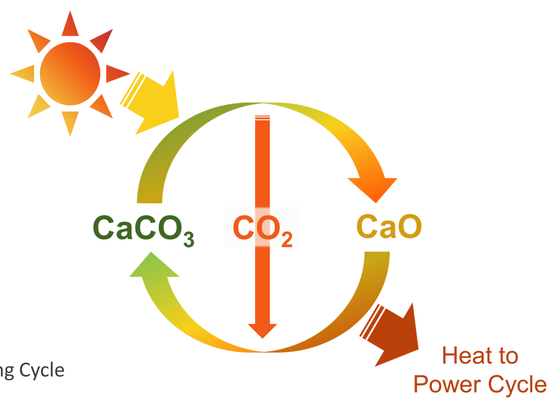

Figure 1: Calcium Looping Cycle

Decomposition/calcination (driven by solar thermal power) absorbs energy:
XCO_3 + heat → XO + CO_2 (X = alkaline earth metal)

Recombination/carbonation releases energy:
XO + CO_2 → XCO_3 + heat

If reaction is completely reversible, thermal energy can be recovered completely by recombination

Advantages and opportunities for carbonate looping TCES

- ✓ High storage energy densities → 692 vs 232 kWh_{th}/m^3 for solar salts (Edwards & Materić, 2012)
- ✓ Potentially lower corrosiveness → solids (XCO_3 and XO)
- ✓ Relatively low cost materials
- ✓ Reduced storage tank and receiver size and construction cost
- x Higher complexity → solid particle receiver
- x Requires gas storage (CO_2)
- x Higher temperatures → higher re-radiation losses

Material synthesis

Pechini method uses $Ca(NO_3)_2$ and $Sr(NO_3)_2$ nitrate as precursors in a citric acid solution. Ethylene glycol is added to form a resin, which is then dried out in an oven and calcined in a tube furnace (Jana et al., 2010).

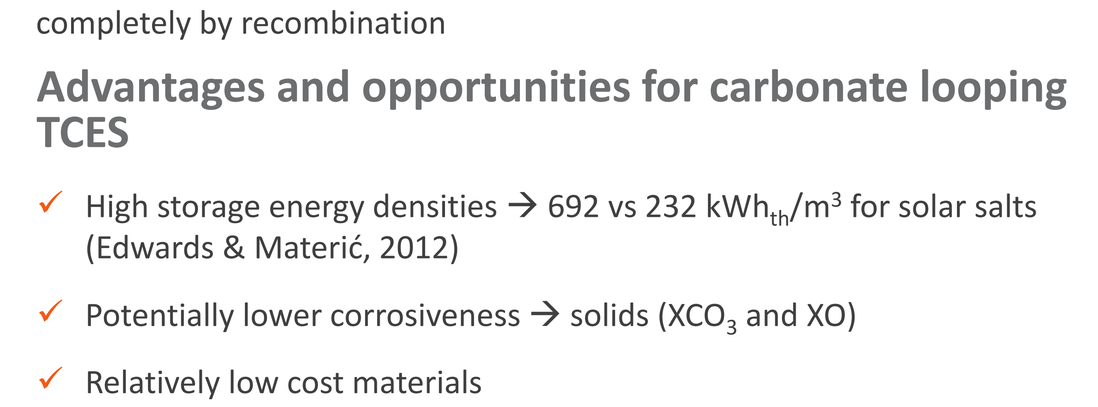

Figure 2: TGA mass change curves for synthesised $Ca_{0.95}Sr_{0.05}O$. Left: Carbonation at 750°C shows 69.2% conversion compared to theoretical conversion of CaO (only 49.0% conversion achieved with commercial $CaCO_3$). Right: Calcination at 900°C followed by second carbonation at 750°C. The second carbonation conversion achieves 53.7% of the theoretical value.

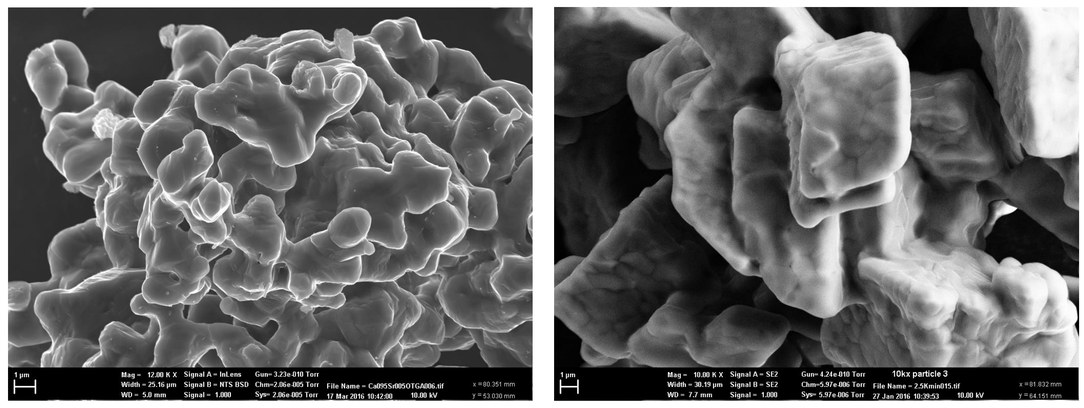

Figure 3: SEM microphotographs at 10K magnification. Left: Sample (synthesised $Ca_{0.95}Sr_{0.05}O$, calcined at 900°C) carbonated in TGA at 750°C. Right: Sample (commercial $CaCO_3$) calcined at 900°C and carbonated at 750°C in TGA. The synthesised oxide retains its smaller particle size after one cycle and shows reduced sintering.

Material performance analysis

Starting materials: commercial $CaCO_3$ and $SrCO_3$

Synthesised oxides and mixed oxides: CaO and $Ca_xSr_{1-x}O$ ($Ca_{0.95}Sr_{0.05}O$, $Ca_{0.75}Sr_{0.25}O$, $Ca_{0.5}Sr_{0.5}O$)

Seeking fast kinetics and maximum energy storage density in 100% CO_2 atmosphere

Evaluate structural cyclability of candidate materials as a function of cycle number

CHARACTERISATION PROCESS	APPARATUS	INFORMATION OBTAINED
Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)	SETSYS TGA (CSIRO Energy, Newcastle)	• Reaction kinetics of calcination and carbonation cycling • Kinetic parameters: activation energy, reaction rate • Thermodynamic parameters: enthalpy of reaction
X-ray diffraction (XRD)	XRD Panalytical (EMX, University of Newcastle)	• XRD characterization: atomic composition and crystallite size • In-situ (heating stage) XRD analysis: reaction kinetics, time evolution of crystallites
Scanning electron microscopy (SEM)	Zeiss FESEM (EMX, University of Newcastle)	• Images of microstructure before and after calcination and carbonation: indicates particle size and structure
Nitrogen adsorption/desorption	N_2 chemisorption (NIER, University of Newcastle)	• Gas adsorption isotherms: indicate specific surface area and porosity
Infrared spectroscopy	Fourier Transform Infrared Spectroscopy (University of Newcastle)	• Characteristic transmittance peaks at wavenumbers indicates presence of functional groups (such as oxides, hydroxides or carbonates)

Table 1: Material characterisation techniques and descriptions.

Challenges

Lack of prior art detailing kinetic modelling of carbonates in 100% CO_2 atmosphere

Reaction irreversibilities, incomplete conversion

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ACKNOWLEDGEMENTS

The Australian Solar Thermal Research Initiative (ASTRI) program is supported by the Australian Government, through the Australian Renewable Energy Agency (ARENA).

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