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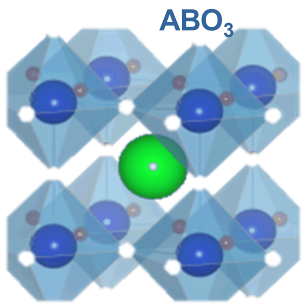

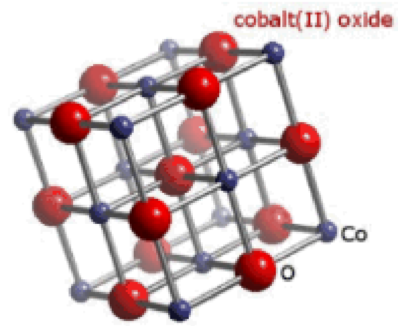

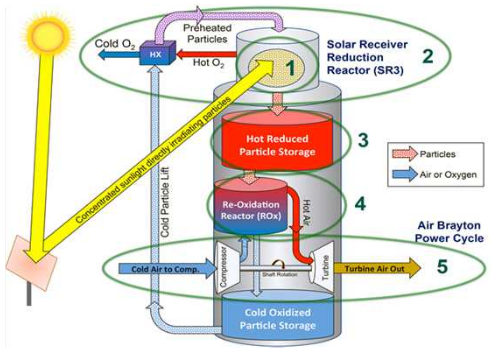

Metal Oxides with Ionic-Electronic Conductivity for Thermochemical Energy Storage

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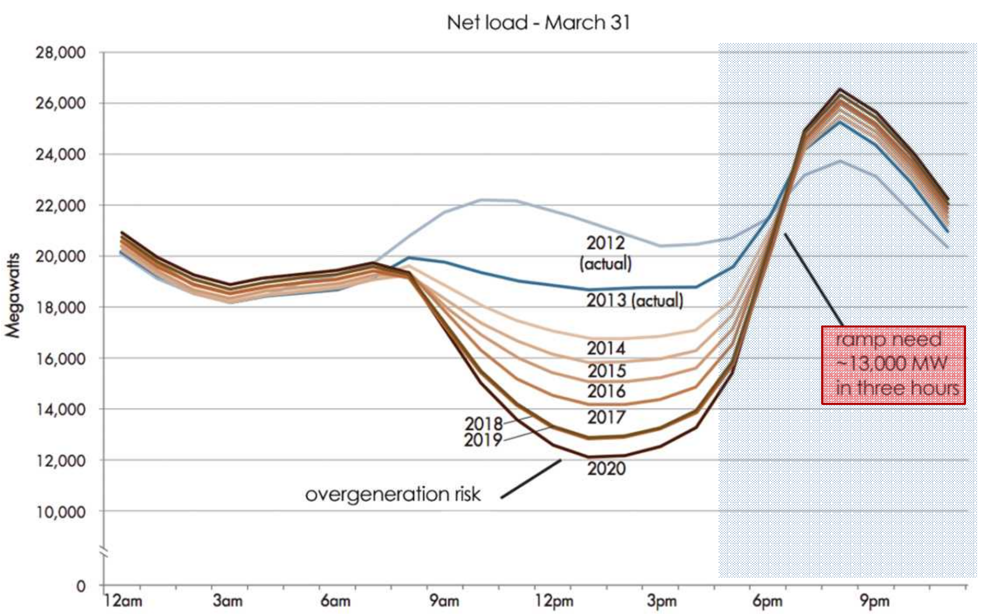
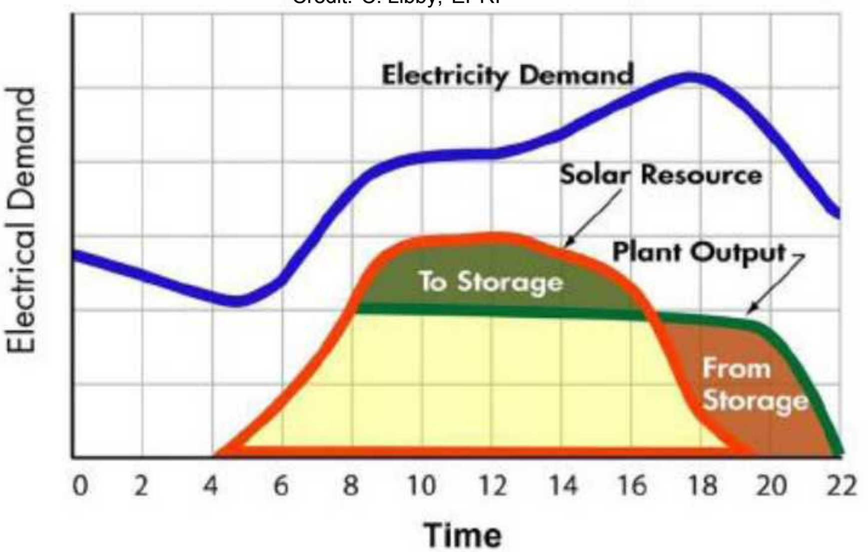
Storage is critical for market penetration of solar energy into the grid

- Without storage, solar electricity is generated when least needed
- Shifting solar electricity generation to period of peak demand would have large implications on grid integration
- Decrease Levelized Cost of Electricity (LCOE) through better sizing/usage of power block

Credit: California Independent System Operator Corporation



Credit: C. Libby, EPRI

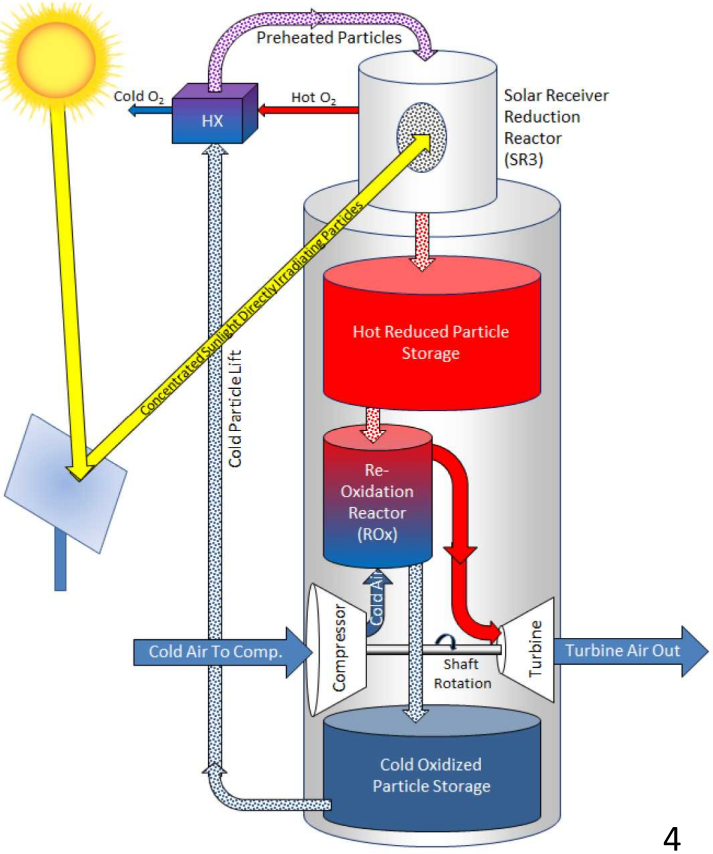


Storage: Why thermal?

- Mechanical
  - Flywheels, compressed air, hydrostatic
    - ✓ High capacities (large scale)
    - × Typically suffer from low efficiencies
- Electronic
  - Li-ion batteries
    - ✓ High efficiencies
    - × Expensive materials, limited charge/discharge rates
  - Supercapacitors
    - ✓ Fast charge/discharge rates
    - × Low energy densities
- Thermal
    - ✓ High efficiency
    - × Temperatures high to support new power cycles (~1200 °C)
      - ❖ ***Materials development crucial to feasibility of thermal storage at such temperatures***

Concentrating solar power (CSP) has unique ability to harness thermal storage

- Solar energy used to heat storage media, drive thermal engine
- Current molten-salt storage systems are limited
  - Sensible-only storage, low energy storage densities
  - Salt decomposition limits turbine operating temperatures (~ 600 °C, max.)
- Redox particle-based systems offer advantages
  - High storage densities *via* (sensible + reaction) enthalpy
    - Thermochemical energy storage (TCES)
  - Cycle not limited by low decomposition temperatures
  - Direct irradiation of thermal storage media
  - Re-oxidation reaction directly off compressor outlet, favorably shifting thermodynamics



Materials requirements driven by Air-Brayton operating parameters

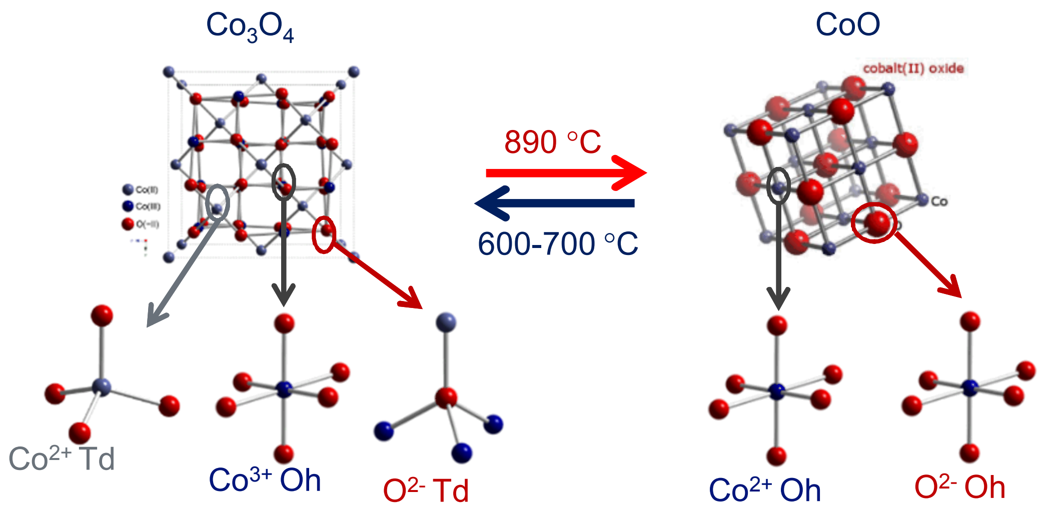
- High-efficiency Air-Brayton turbines are designed to operate at ~1200 °C
- Such temperatures are problematic for existing oxide TCES materials

- State-of-the-art cobalt oxide redox couple:

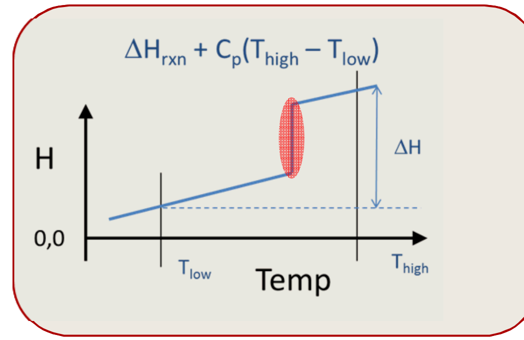
$$2Co_3O_4 + \Delta \leftrightarrow 6CoO + O_{2(g)} \quad \Delta H_{theoretical} = 844\ kJ/kg\ Co_3O_4$$

  - High theoretical ΔH occurring at one discrete transition
  - Reduction/oxidation in air occurs near 885 °C
  - Kinetics are slow at low temperatures
  - Cobalt is expensive

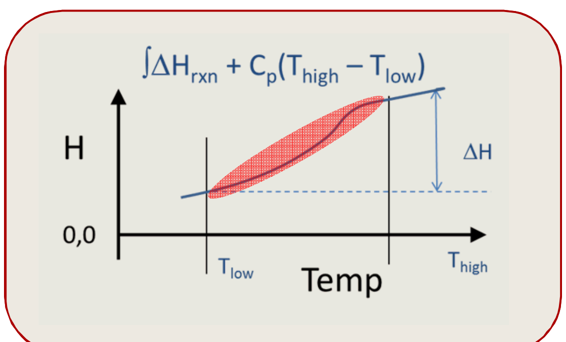
Cobalt oxide *vs.* Perovskites (ABO_3)

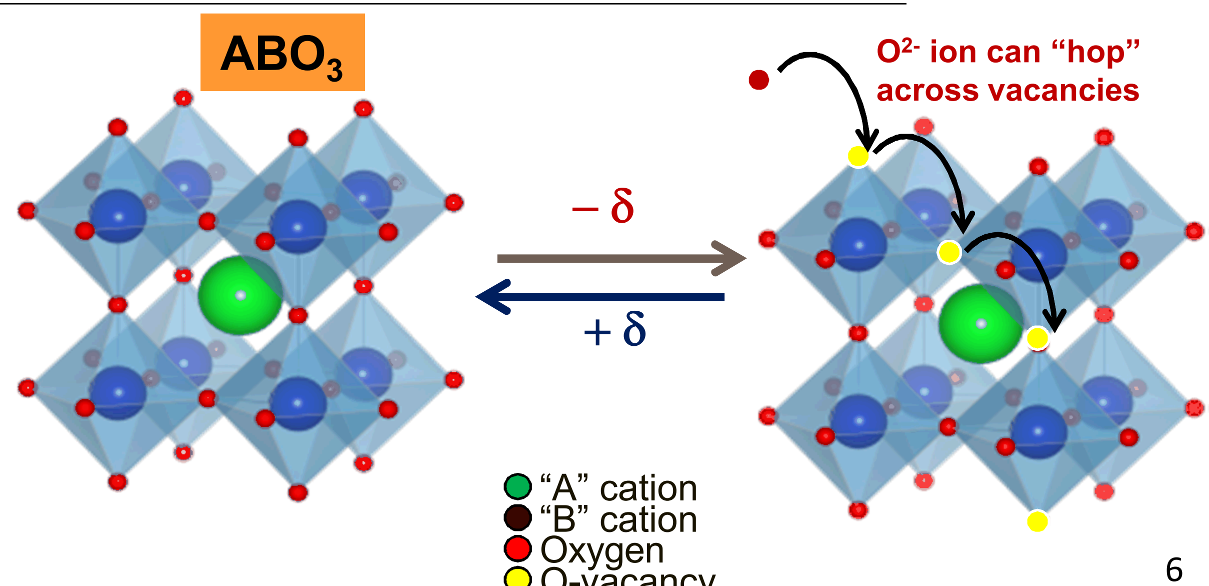


- Energetic phase change
- No O^{2-} transport
- Oxidation exotherm typically recovered at lower temperature than reduction



- No phase change occurs
- Vacancies facilitate O^{2-} transport
- Redox activity continuous over variety of T and pO_2





Perovskites offer a solution to increasing turbine inlet temperatures to ≥ 1200 °C

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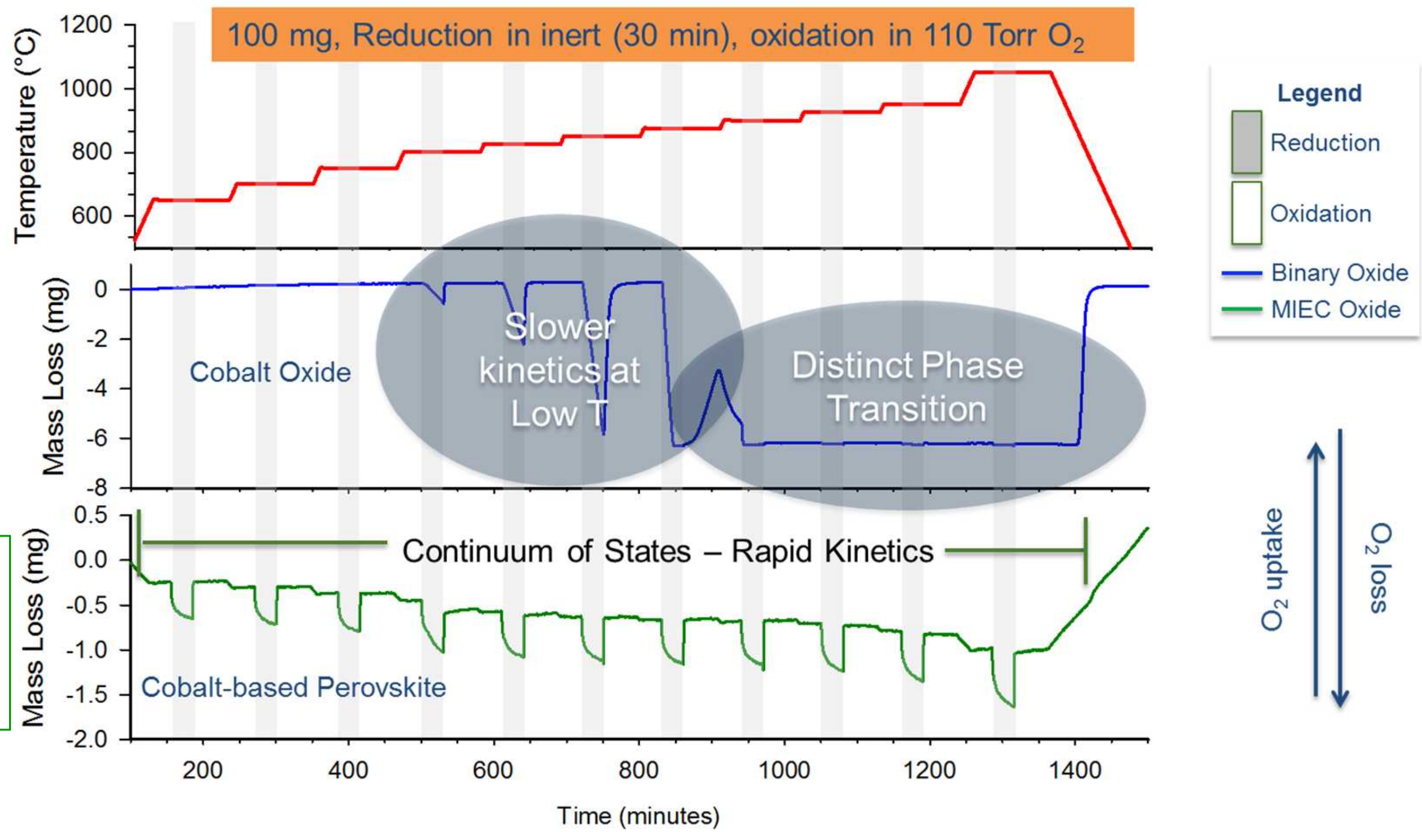
- Continuous reduction behavior as opposed to discrete reaction

$$Co_3O_4 \downarrow 3CoO + \frac{1}{2} O_2$$

$$ABO_3 \downarrow ABO_{3-\delta} + \delta/2\ O_2$$



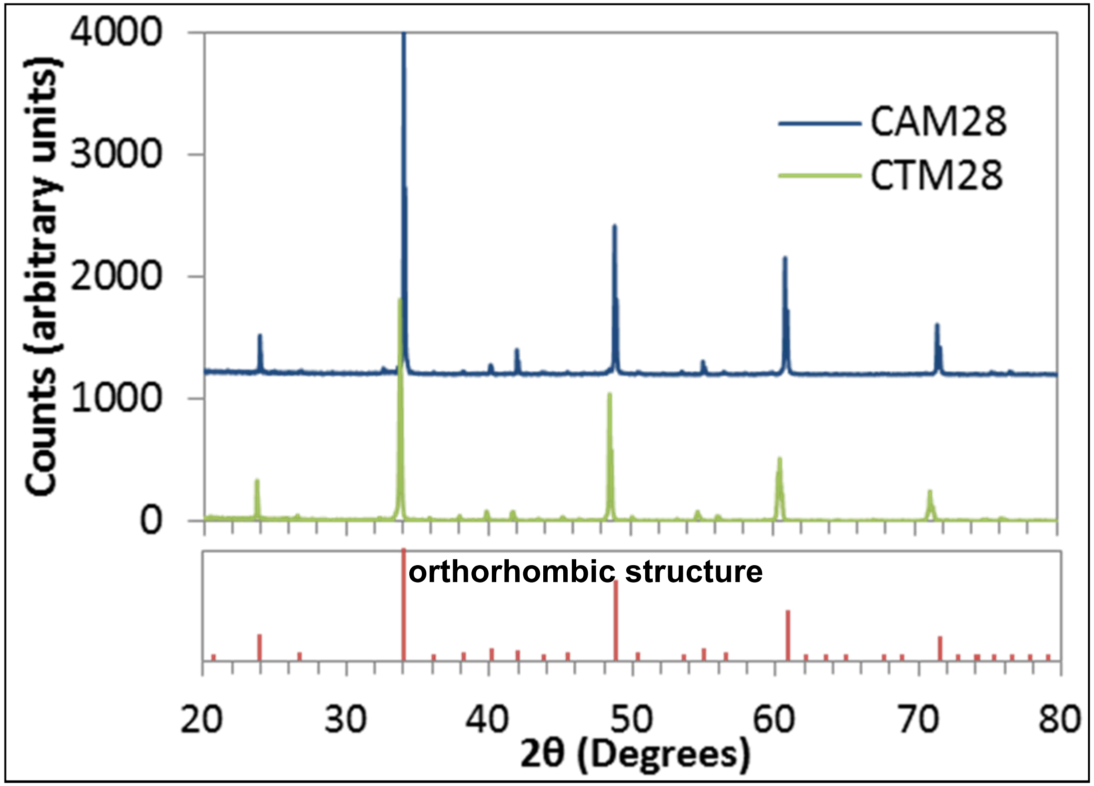
- Perovskites need to be engineered to increase capacity (mass loss) and reaction enthalpy

Perovskite compositions

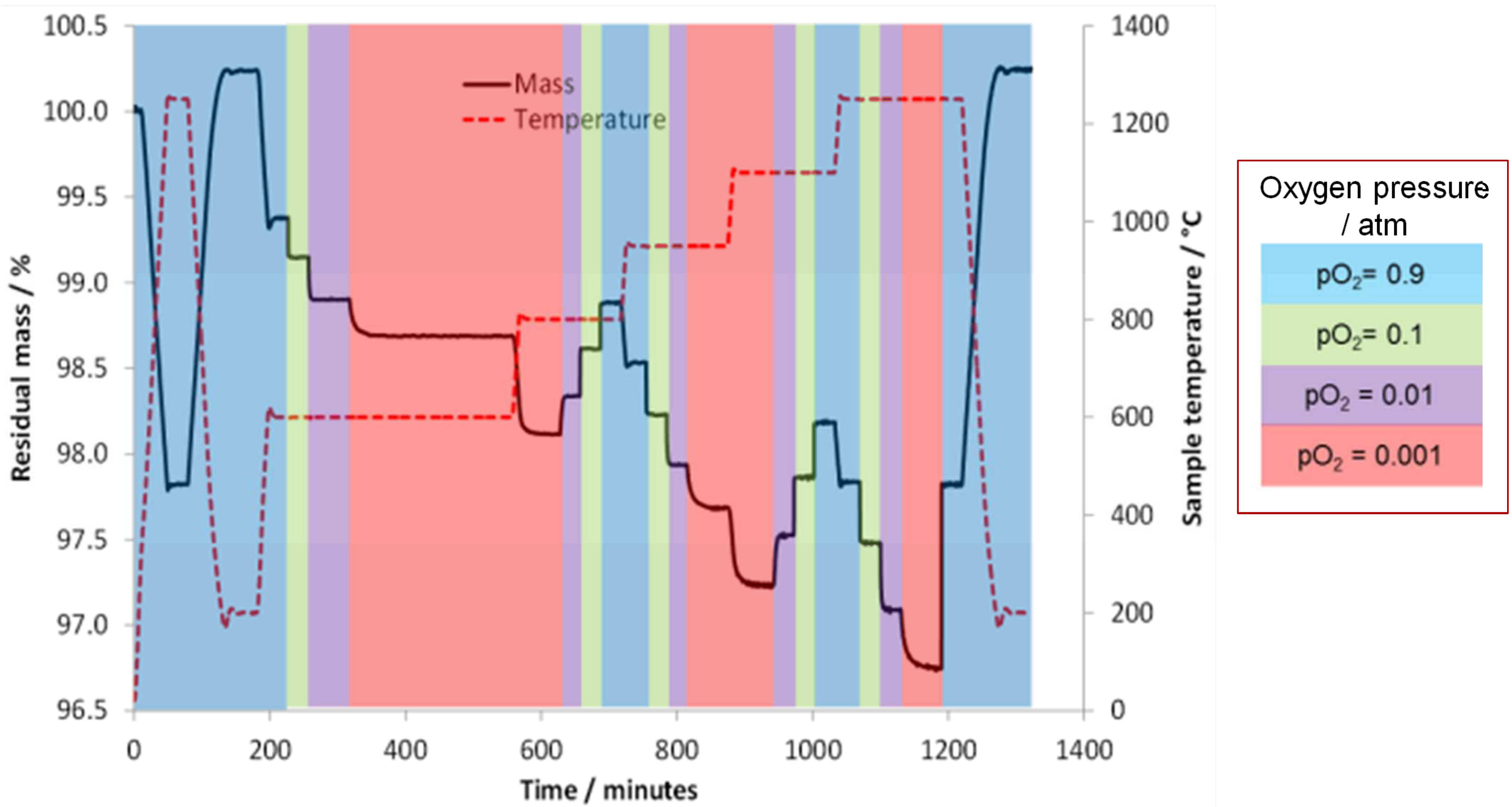
- $ABO_3 + H \leftrightarrow ABO_{3-\delta} + \delta/2\ O_{2(g)}$
  - Gas species dominates entropy term (largest # degrees-of-freedom)
- At equilibrium (onset of reduction) $\Delta G_{red} = 0 = \Delta H_{red} - T\ \Delta S_{red}$,
  - A change in reduction enthalpy necessitates a change in reduction temperature
- Previous studies focused on $La_xSr_{1-x}Co_yM_{1-y}O_{3-\delta}$, with M = Fe,Mn
  - High redox capacity (δ), but at low temperature (low reaction enthalpy)
- New materials aim to improve cost, reaction enthalpy:
  - Cost-effective, lightweight cations desired
  - A-site: Ca, B-site: Mn, Ti, Al

Synthesis and phase characterization

- Materials synthesized using an aqueous (Pechini) method
- X-ray diffraction used for phase identification
- Compositions:
  - CAM28 ($CaAl_{0.2}Mn_{0.8}O_{3-\delta}$)
  - CTM28 ($CaTi_{0.2}Mn_{0.8}O_{3-\delta}$)

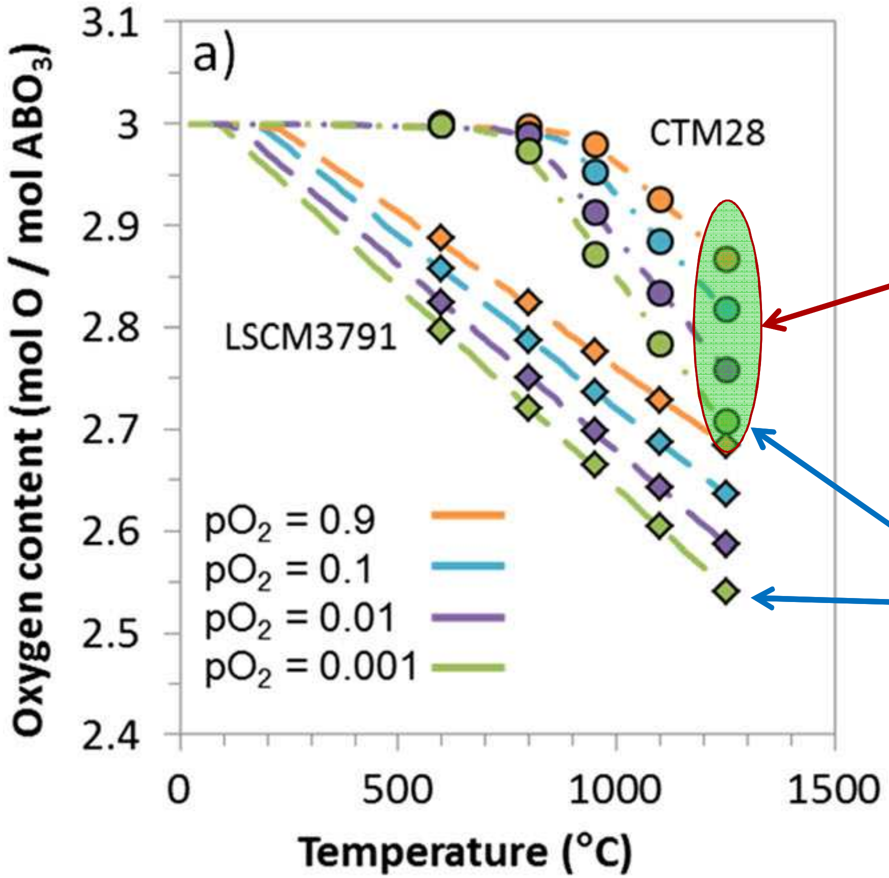


Thermogravimetric data acquired over range of temperatures and oxygen partial pressures



Thermogravimetric Analysis = TGA

Equilibrium data taken from TGA experiments

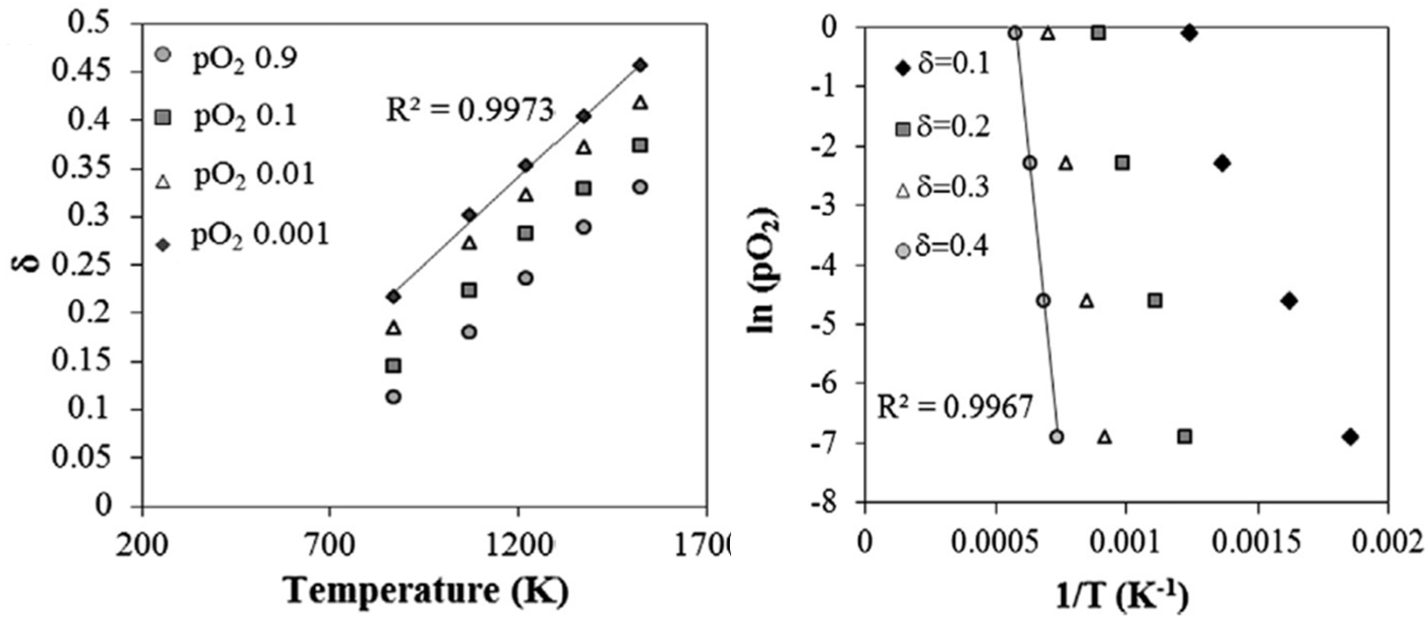


Large changes in oxygen stoichiometry even at 1250 °C by change in pO_2.

δ_{max}, observed at pO_2 = 0.001 atm, T = 1250 °C

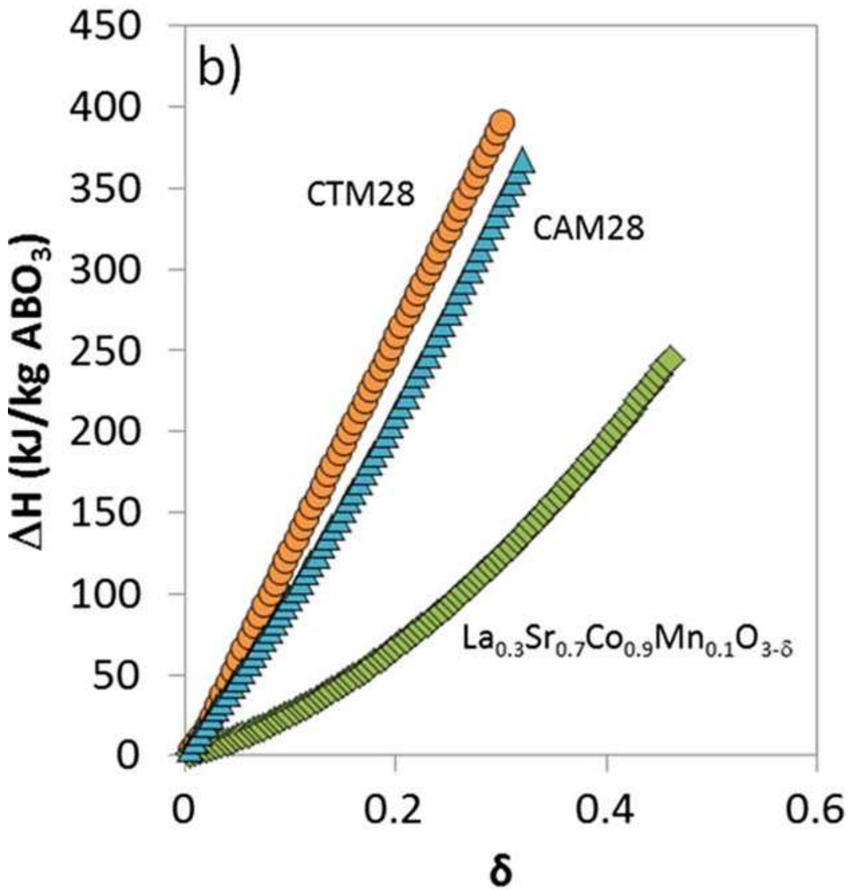
Equilibrium TGA data used to estimate thermodynamic parameters

- Thermodynamic parameters extracted by van't Hoff approach:
  - $K = \frac{[ABO_{3-\delta}]^{1/\delta} \, pO_2^{1/2}}{[ABO_3]^{1/\delta}}$, assume ratio of solid activities is ≈unity
  - $\ln(pO_2) = 2\frac{-\Delta G_{rxn}}{RT} = 2\left(\frac{1}{T}\cdot\frac{-\Delta H_{rxn}}{R} + \frac{\Delta S_{rxn}}{R}\right)$
    - Enthalpy determined by slope, entropy by intercept for each value of δ



Enthalpies from van't Hoff are given for a specific oxygen non-stoichiometry

- Describe energy to remove a mole of O_2 at a specific δ

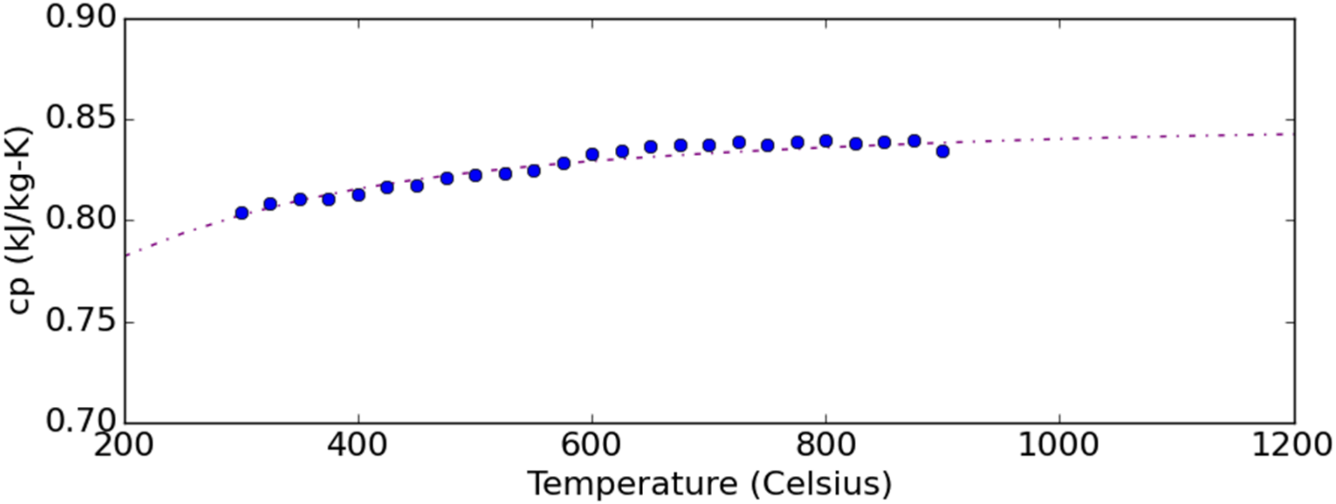


Material	Reduction onset (°C)	Maximum δ	Enthalpy at δ_{max} (kJ/kg)
LSCM3791	352	0.461	240 [a]
CTM28	901	0.293	390 [b]
CAM28	759	0.322	370 [b]

[a] S.M. Babiniec, et al., *Solar Energy*, **118**, 451–9, (2015).
[b] S.M. Babiniec, et al., *Int. J. Energy Res.*, **40**, 280–4, (2016).

Heat capacity as a function of temperature is needed to calculate sensible heat

- Einstein heat capacity model used to fit data for CAM28, converted to polynomial fit for ease of integration
  - CTM28 expected to be similar due to same structure and similar molecular weight



$$c_p = a_5 * T^5 + a_4 * T^4 + a_3 * T^3 + a_2 * T^2 + a_1 * T + a_0$$

	a_5	a_4	a_3	a_2	a_1	a_0
CAM28	8.066E-18	-7.169E-14	2.455E-10	-4.070E-7	3.346E-4	7.329E-1

$\Delta H_{sens} = \int_{T1}^{T2} C_p(T)dT$ = 871 kJ/kg between 200 and 1250 °C

$$\Delta H_{total} = \Delta H_{sens} + \Delta H_{reaction} = 871 + 370 = 1241\ kJ/kg$$

Discussion/Conclusions

- CAM28 shows high storage enthalpy
  - Sensible + reaction enthalpy is over 1000 kJ/kg
  - Increase in reduction temperature results in larger reaction enthalpy
    - CTM28 and CAM28 show an increase in reaction enthalpy of over 60% compared to the previously studied $La_{0.3}Sr_{0.7}Co_{0.9}Mn_{0.1}O_{3-\delta}$
  - The use of calcium in the A-site instead of lanthanum and strontium will result in significant cost savings

Acknowledgements

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