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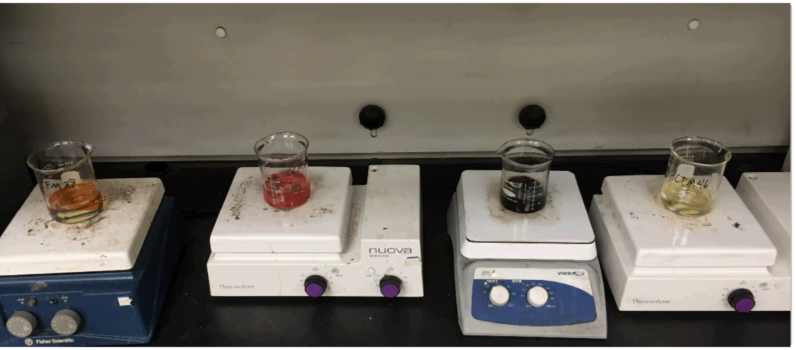
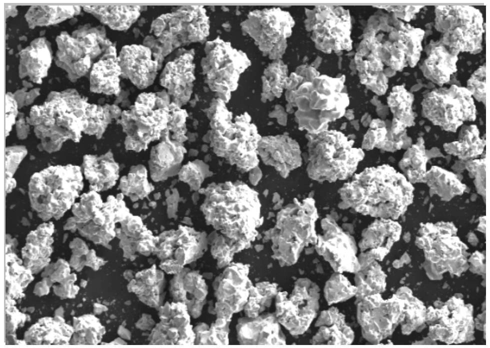


ABO_3 (A=La, Ba, Sr, K; B=Co, Mn, Fe) Perovskites for Thermochemical Energy Storage

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Presented by Subhash Shinde

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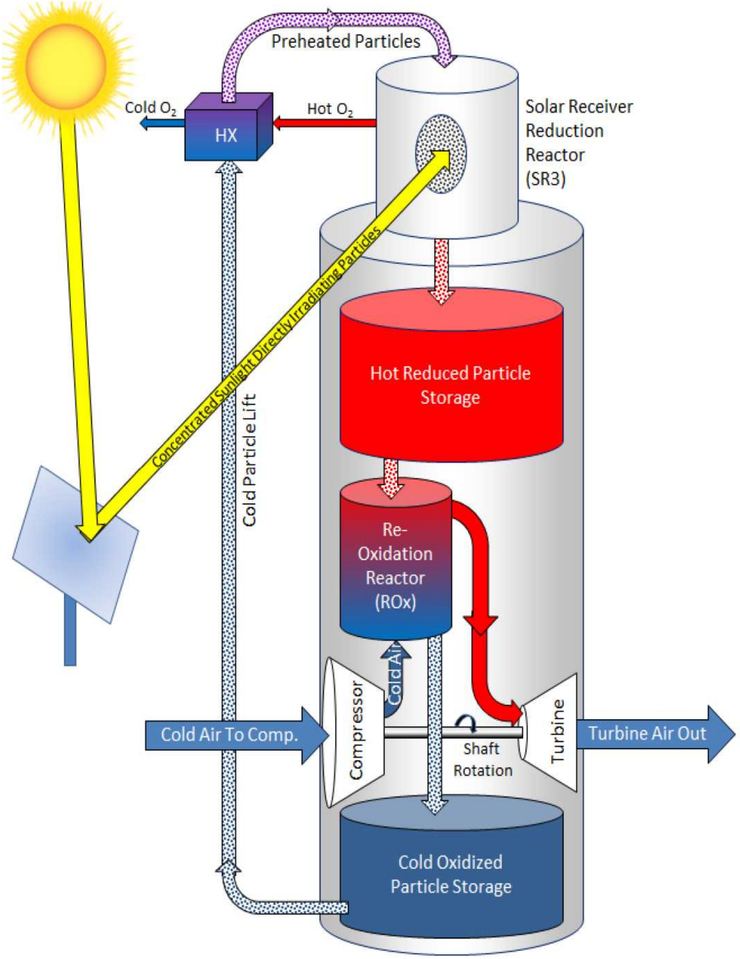
Thermal storage can be improved by harnessing chemical reactions

- Current molten-salt storage systems are limited
  - Sensible-only storage, low storage densities
  - Salt decomposition limits turbine operating temperatures
- Solid-particle thermochemical energy storage (TCES) offers many advantages
  - Ability store both sensible and redox reaction enthalpy, resulting in high storage densities
  - Increased storage temperatures potentially supports the use of high-efficiency power cycles
    - Air Brayton inlet ≥ 1200 °C
  - Direct irradiation of thermal storage media
  - Re-oxidation reaction can take place directly off compressor outlet



Materials must be designed to support the operating parameters of new power cycles

- Many Air-Brayton turbines are designed to operate at ≥ 1200 °C
- Such temperatures are problematic for existing TCES materials
- Mixed Ionic-Electronic Conducting (MIEC) Perovskites oxides offer a solution for increased storage temperatures
  - $ABO_3 \leftrightarrow ABO_{3-\delta} + \delta/2\ O_2(g)$
  - Continuous reduction reaction allows storage/extraction of heat at high temperatures

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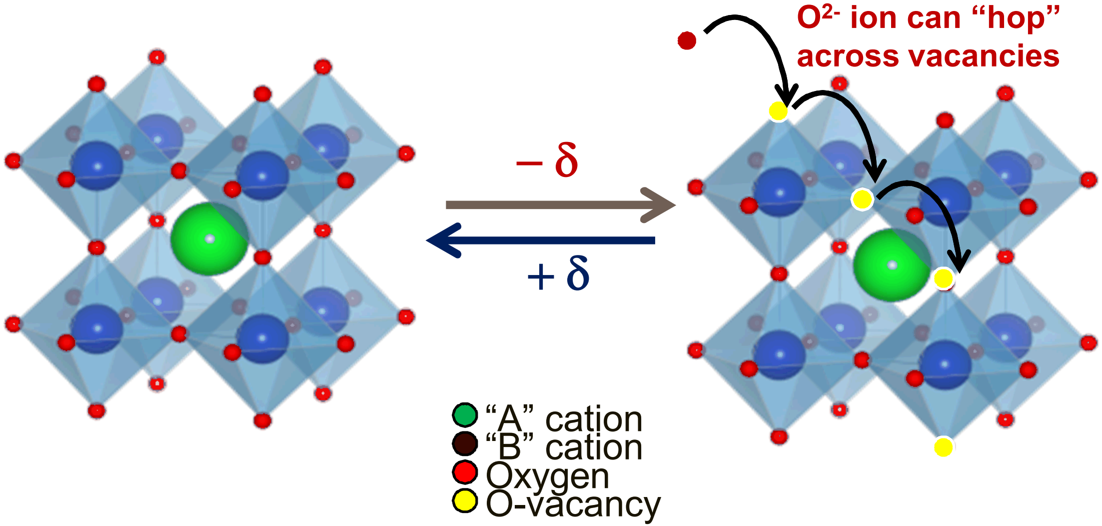
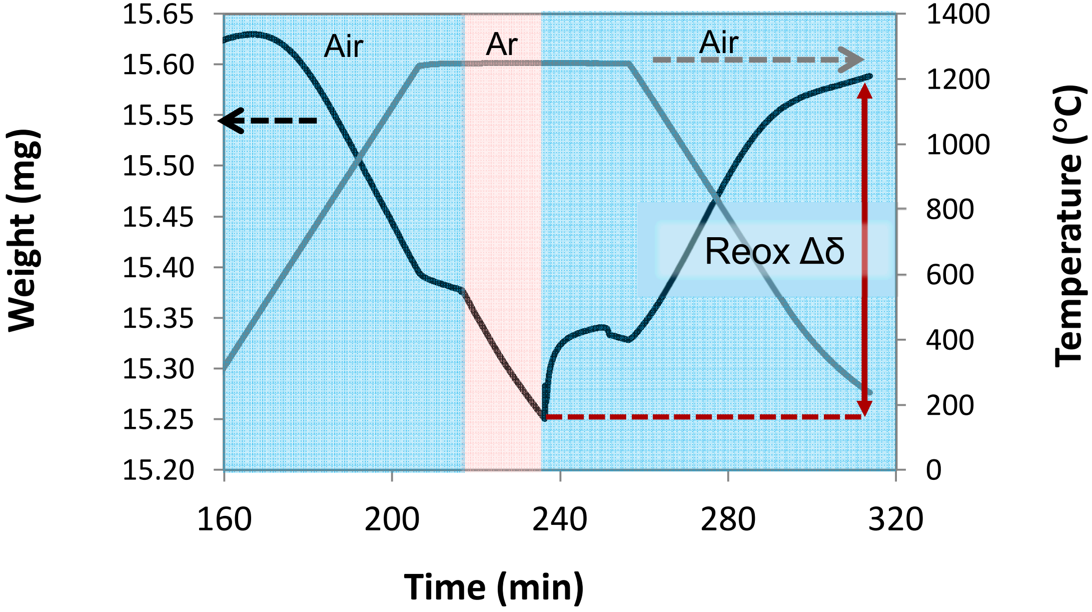
- No crystallographic phase change occurs during redox
- Vacancies facilitate oxide ion transport
- Redox activity continuous over variety of T and pO_2



Materials synthesis plan

- Start with known redox active perovskite: $La_xSr_{1-x}Co_yMn_{1-y}O_{3-\delta}$ (LSCM)
- Modify promising compositions by A- and B-site cation substitution
  - A = K, Ba, La Sr; B = Fe, Co, Mn
- Initial non-equilibrium thermogravimetric analysis (TGA) used to screen multiple compositions, identify candidates

Mass change measured as a function of temperature and pO_2



- Reduction occurs during heating to 1250 °C
  - Further reduction observed in argon
- Reoxidation is measured upon switching back to air and cooling to ~200 °C

LSCF/ LSCM families most promising

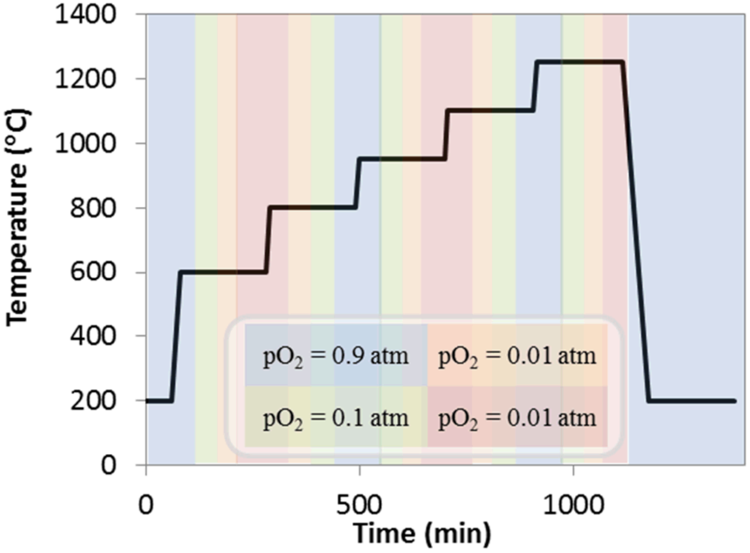
Material Composition	Crystallographic Phase	Reduction Onset (°C)	Reoxidation Δδ
LSCM1991	Tetragonal	432	0.32
LSCM1982	Tetragonal	438	0.31
LSCM1973	Tetragonal	431	0.28
LSCM2891	Tetragonal	425	0.33
LSCM2882	Tetragonal	256	0.28
LSCM2873	Tetragonal	395	0.31
LSCM3791	Cubic	343	0.39
LSCM3782	Cubic	359	0.36
LSCM3773	Cubic	358	0.31
LSCM4664	Cubic	334	0.24
LSCM7337	Rhombohedral	772	0.01
LSCM8228	Rhombohedral	932	-0.01
LSCM8237	Rhombohedral	972	0.00
LSCM9119	Orthorhombic	825	0.02
LSCM9128	Orthorhombic	834	0.00
LSCM9137	Orthorhombic	901	-0.01

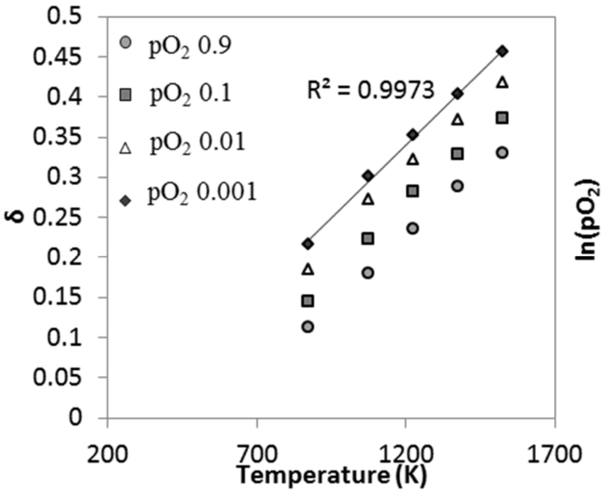
Material Composition	Crystallographic Phase	Reduction Onset (°C)	Reoxidation Δδ
LSCF1991	Cubic	406	0.31
LSCF1982	Cubic	394	0.37
LSCF1973	Cubic	372	0.36
LSCF2891	Cubic	369	0.38
LSCF2882	Cubic	357	0.38
LSCF2873	Cubic	366	0.38
LSCF2828	Cubic	340	0.35
LSCF3791	Cubic	352	0.38
LSCF3773	Cubic	348	0.40
LSCF4691	Cubic	342	0.35
LSCF4682	Cubic	332	0.36
LSCF4673	Cubic	336	0.35
LSCF4646	Cubic	349	0.30
LSCF4664	Rhombohedral	342	0.32
LSCF5555	Rhombohedral	500	0.29
LSCF6446	Rhombohedral	609	0.22
LSCF7337	Rhombohedral	736	0.19
LSCF8228	Rhombohedral	926	0.06
LSCF8237	Rhombohedral	886	0.08
LSCF9128	Rhombohedral	1005	0.01
LSCF9137	Rhombohedral	970	0.03

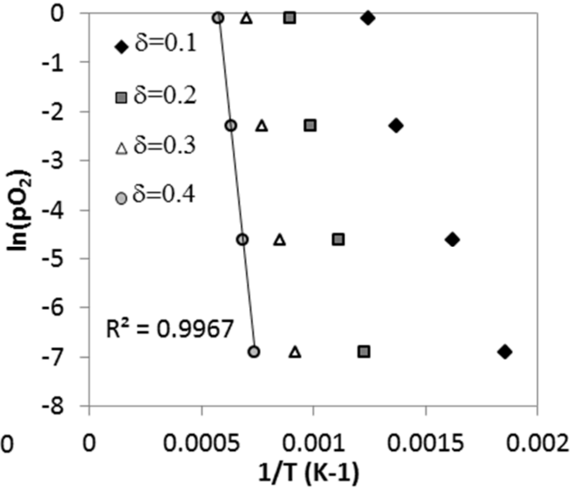
Materials with highest capacity (δ) studied in equilibrium TGA experiment

High-resolution equilibrium TGA used to estimate thermodynamic parameters

- Thermodynamic parameters extracted by van't Hoff approach:
  - $$\ln(pO_2) = 2\frac{-\Delta G_{rxn}}{RT} = 2\left(\frac{1}{T}\cdot\frac{-\Delta H_{rxn}}{R} + \frac{\Delta S_{rxn}}{R}\right)$$
  - Enthalpy determined by slope, entropy by intercept for each value of δ

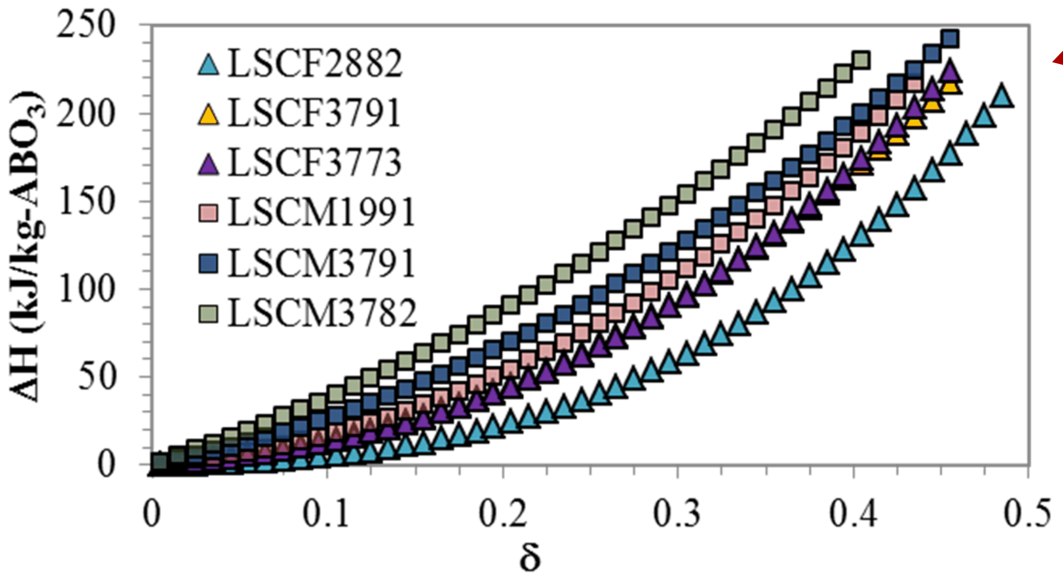






Reaction energy stored is a function of reaction enthalpy and redox capacity

- Reduction enthalpies indicate a balance between capacity (δ) and enthalpy (ΔH) must be found
- Material with highest measured δ has lowest total (integrated) reaction enthalpy, but material with lowest δ did not have highest total reaction enthalpy

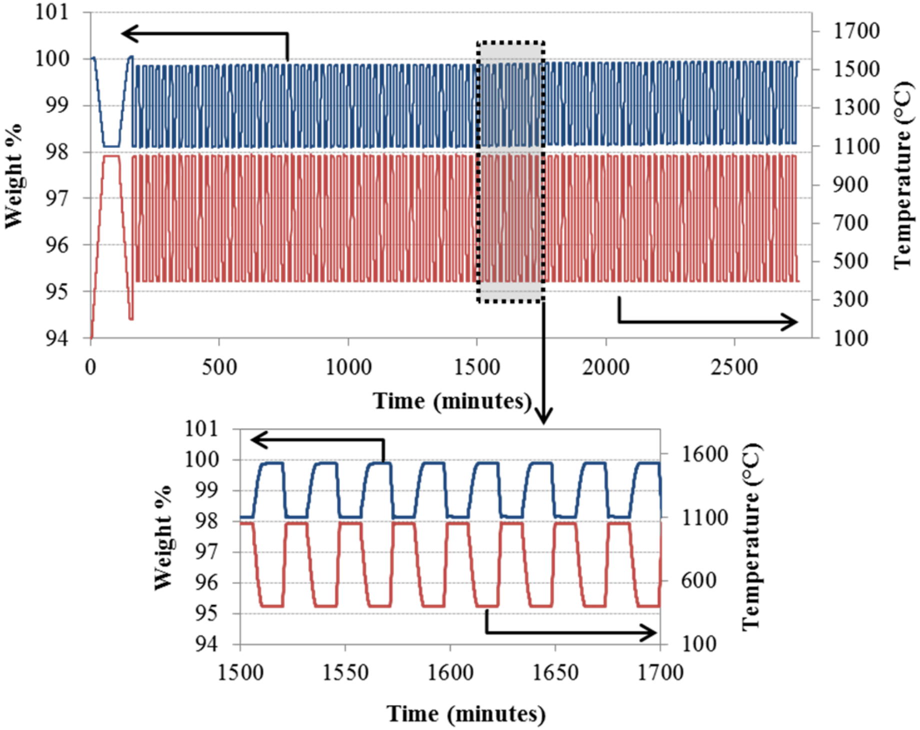


Maximum integrated enthalpy at 1250 °C, pO_2 = 0.01 atm

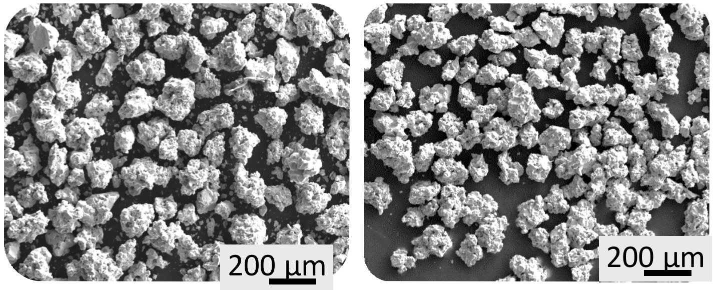
Characterization of cyclic stability

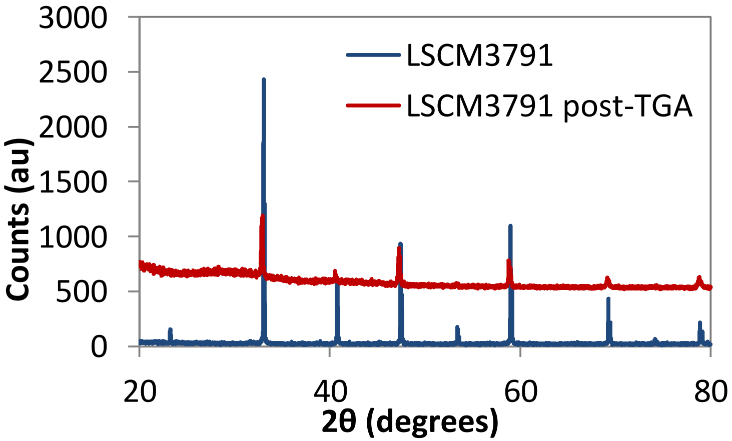
- Multi-cycle TGA used to measure cyclic repeatability and stability
  - Particles heated to 1050 °C, cooled to 400 °C for 100 cycles
- Scanning electron microscopy shows no change in morphology
- XRD shows no change in crystal phase

LSCM3791



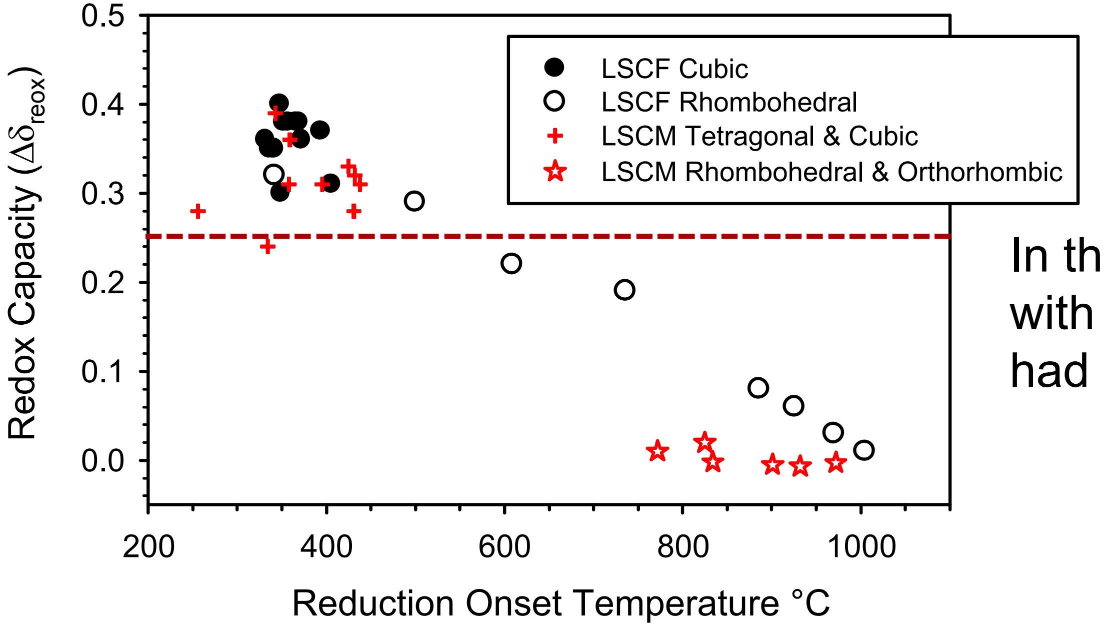
Before After





Relationship between enthalpy and reduction temperature

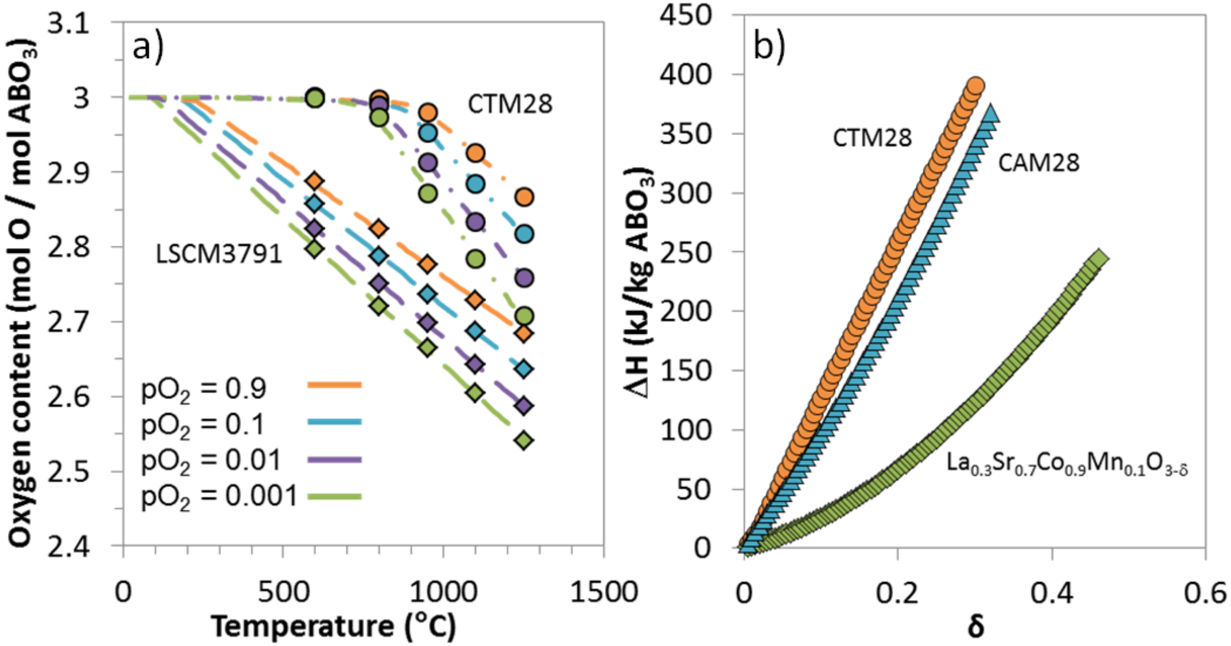
- $ABO_3 + \Delta H \leftrightarrow ABO_{3-\delta} + \delta/2\ O_{2(g)}$
  - Gas species dominates entropy term (largest # degrees-of-freedom)
  - ΔH between two solid compositions likely << entropy in diatomic gas particle
- $\Delta G_{red} = \Delta H_{red} - T\ \Delta s_{red}$, where $\Delta G_{red} = 0$ is the onset of reduction (equilibrium)
  - For two compositions at equilibrium with nearly equal entropy, a change in reduction enthalpy necessitates a change in reduction temperature



In the LSCX system, materials with high reduction temperatures had low redox capacity (δ < 0.25).

Next generation:– doped calcium manganese oxides

- Cost
  - Large quantities needed for storage necessitates use of earth-abundant materials e.g., Ca, Ti, Al, Mn
- Performance
  - Higher reduction temperature resulting in higher enthalpy, even with lower capacity



Conclusions

- The $La_xSr_{1-x}Co_yM_{1-y}O_{3-\delta}$ (M=Mn,Fe) perovskites display many of the required characteristics required for high temperature TCES
  - Redox active above 1200 °C
  - Do not degrade when cycled
  - Stable in operating environment

- However, LSCM/LSCF are not optimal
  - Reduction extent is adequate, but reaction enthalpy is low
  - Reduction onset temperature has been identified as a key indicator of reaction enthalpy

- New compositions under development with increased reduction temperature and reaction enthalpy

Acknowledgements

- We are grateful to Bonnie McKenzie (Sandia National Laboratories) for conducting SEM and providing images, and to Dr. Peter Loutzenhiser (Georgia Institute of Technology) and Dr. Ellen Stechel (Arizona State University) for technical discussions.
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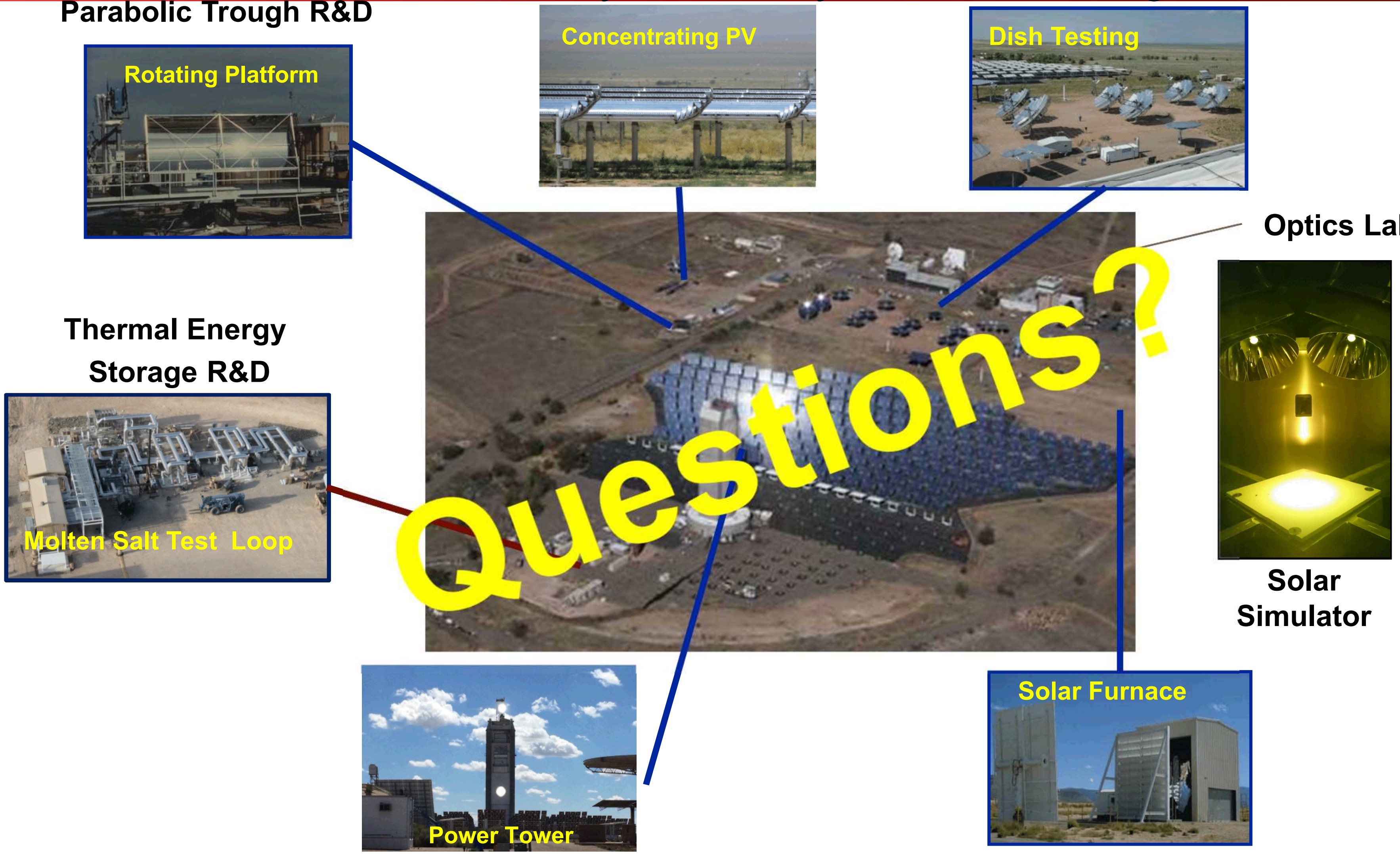


Parabolic Trough R&D

PV System Reliability

Dish Stirling R&D

Optics Lab

Thermal Energy Storage R&D

Solar Simulator

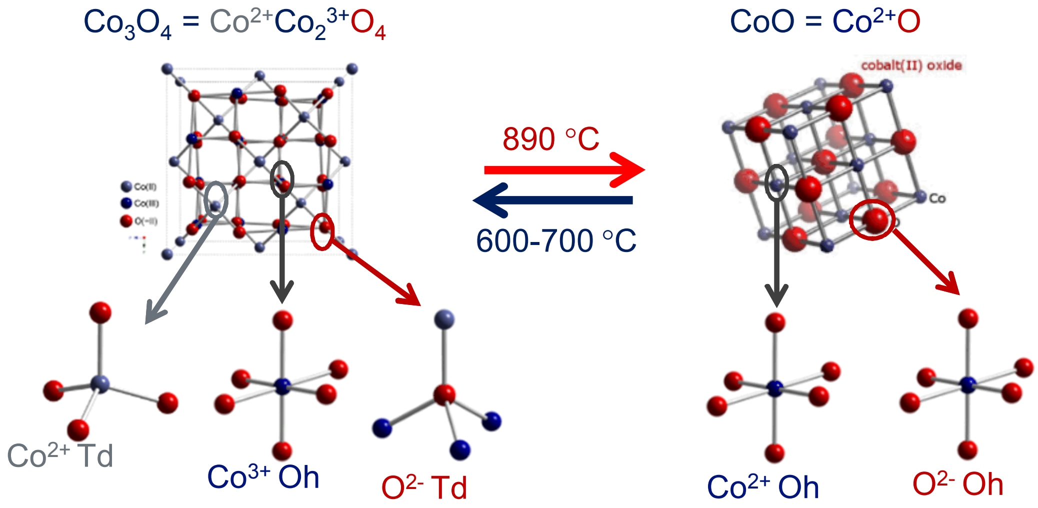
Receivers and Heliostats

Solar Fuels and Selective Absorbers

Questions?

SUPPLEMENTARY SLIDES

State of the Art MO vs. Perovskites



- Energetic crystallographic phase change at redox
- Structure not amenable to oxide ion transport
- Oxidation exotherm typically recovered at lower temperature than reduction

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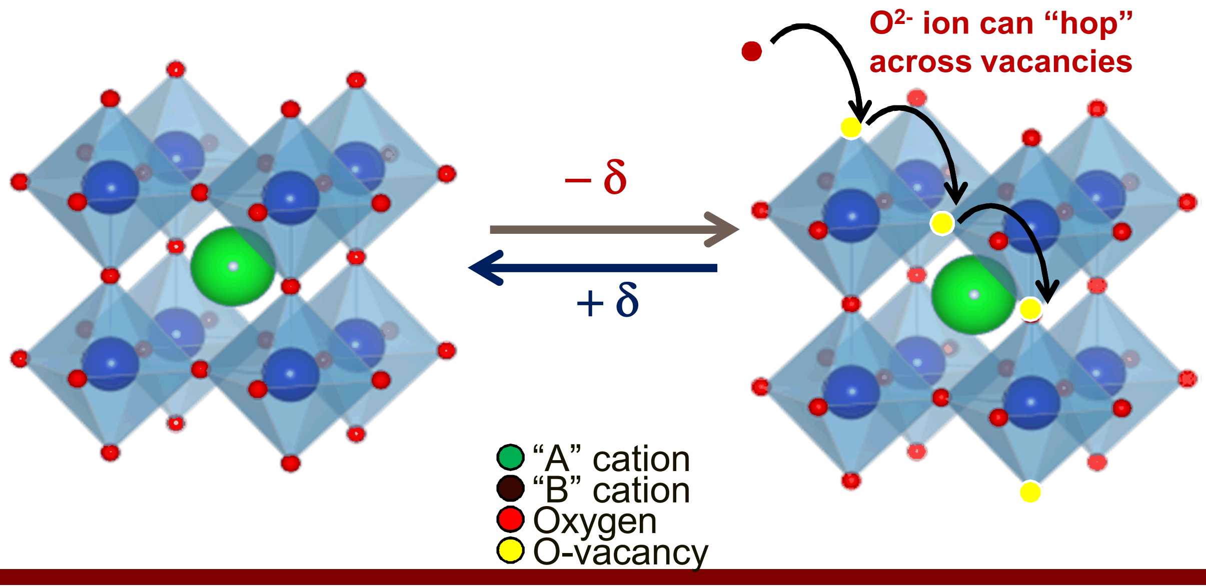
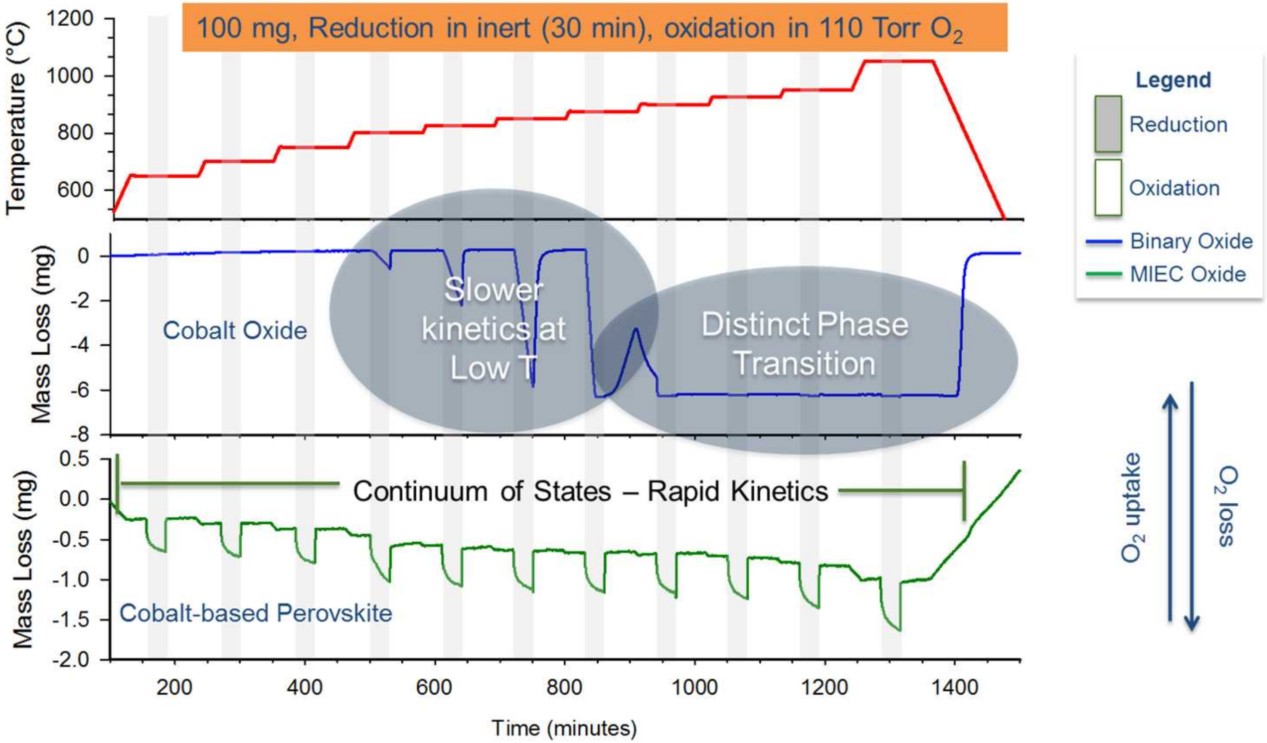
- No crystallographic phase change occurs during redox
- Vacancies facilitate oxide ion transport
- Redox activity continuous over variety of T and pO_2



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

- Continuous reduction behavior as opposed to discrete reaction
  - Perovskite $ABO_3 \leftrightarrow ABO_{3-\delta} + \delta/2\ O_2(g)$



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

Materials synthesis plan

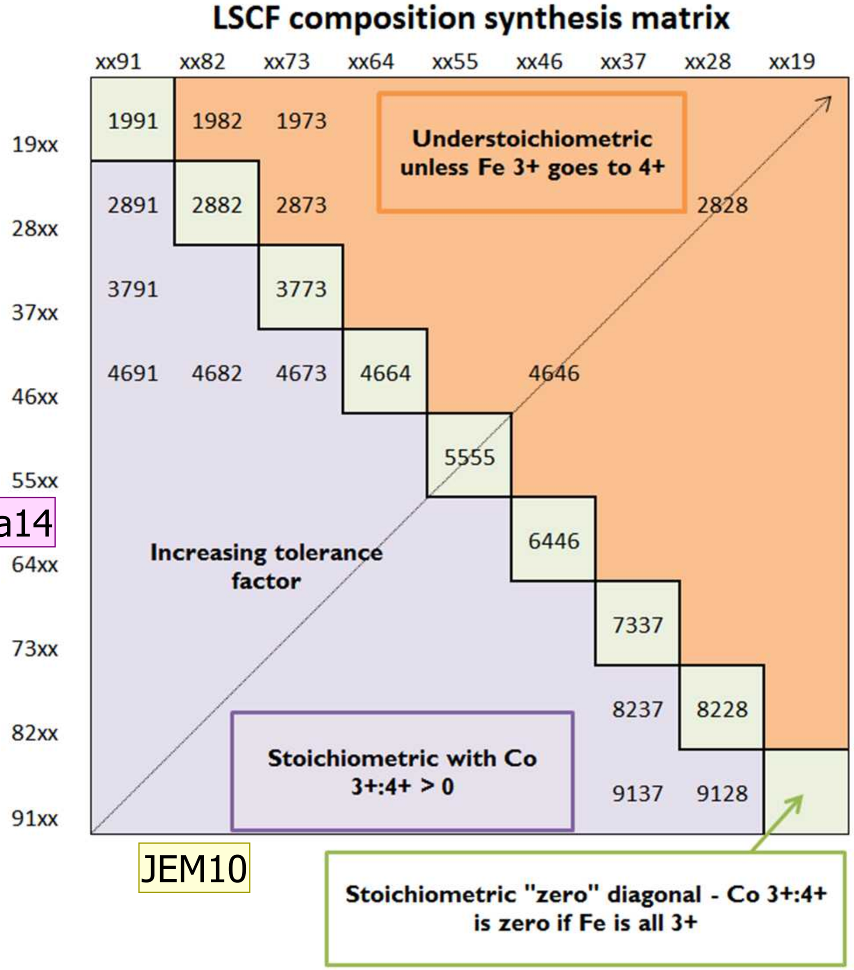
- Start with known redox active perovskite: $La_xSr_{1-x}Co_yMn_{1-y}O_{3-\delta}$ (LSCM)
- $La_{0.a}Sr_{0.b}Co_{0.c}Fe_{0.d}O_{3-\delta}$ = LSCFabcd
  - Example: $La_{0.3}Sr_{0.7}Co_{0.2}Mn_{0.8}O_{3-\delta}$ = LSCM3728
- Modify promising compositions with A- and B-site cations
  - A-site: Ba, K; B-site: **Fe**,Mn

SMB4 aa5

aa17

aa14

- Example: LSCF synthesis matrix
  - Focus~~ed~~ on compositions with highest reduction capacity
    - Diagonal, B-site fully at 4+
  - ~~Probed other regions of interest~~



LSCF composition synthesis matrix

	xx91	xx82	xx73	xx64	xx55	xx46	xx37	xx28	xx19
19xx	1991	1982	1973						
28xx	2891	2882	2873					2828	
37xx	3791		3773						
46xx	4691	4682	4673	4664		4646			
55xx					5555				
64xx						6446			
73xx							7337		
82xx							8237	8228	
91xx							9137	9128	

Understoichiometric unless Fe 3+ goes to 4+

Increasing tolerance factor

Stoichiometric with Co 3+:4+ > 0

Stoichiometric "zero" diagonal - Co 3+:4+ is zero if Fe is all 3+

JEM10

Slide 17

JEM10	Maybe make this more compact and bulletized James E. Miller, 9/23/2015
SMB4	Should we state here that the LSCM and B-site substituted LSCF were the most promising compositions, and just move on from Ba and K? It is hard to incorportate them without adding unnessecary slides and we can just reference the viewer to the manuscript. Babiniec, Sean Michael, 9/24/2015
aa5	We could. Limited tome--no need to dwell. Andrea Ambrosini, 9/24/2015
aa14	Don't keep this green. (Not sure if it was just for highlighting change purposes.) Andrea Ambrosini, 10/5/2015
aa17	Is there a reason Fe is bold? Andrea Ambrosini, 10/5/2015