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Maximizing Efficiency in Two-Step Solar-Thermochermical Fuel Production

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Sandia National Laboratories

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Outline

- **Materials role and requirements in two-step cycles**
- **Key efficiency drivers**
- **Reactor design for low thermal reduction pressure**
- **Conclusions**

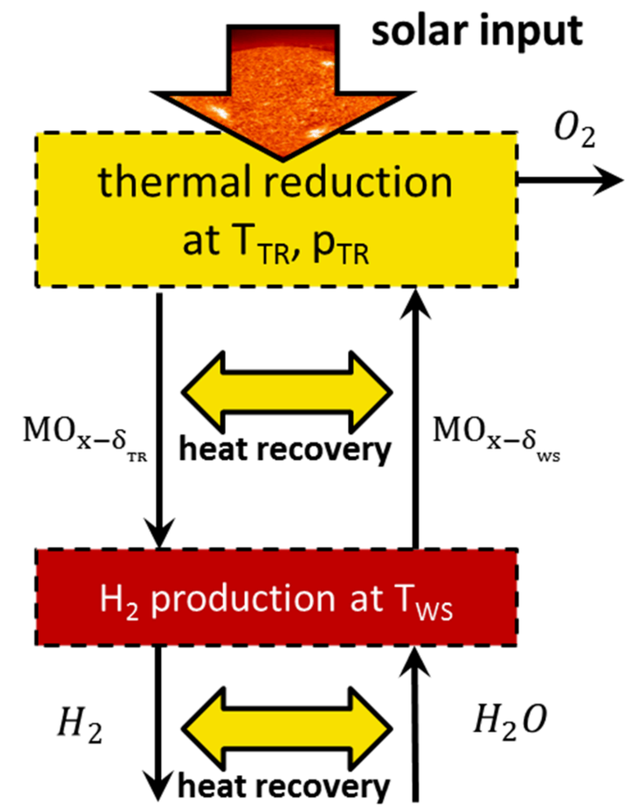
Two-Step Thermochemical Fuel Production

A theoretically simple process

$$\frac{1}{\delta_{TR}-\delta_{WS}} MO_{x-\delta_{WS}} \rightarrow \frac{1}{\delta_{TR}-\delta_{WS}} MO_{x-\delta_{TR}} + \frac{1}{2} O_2$$

$$\frac{1}{\delta_{TR}-\delta_{WS}} MO_{x-\delta_{TR}} + H_2O \rightarrow \frac{1}{\delta_{TR}-\delta_{WS}} MO_{x-\delta_{WS}} + H_2$$

$$H_2O \rightarrow H_2 + \frac{1}{2} O_2$$



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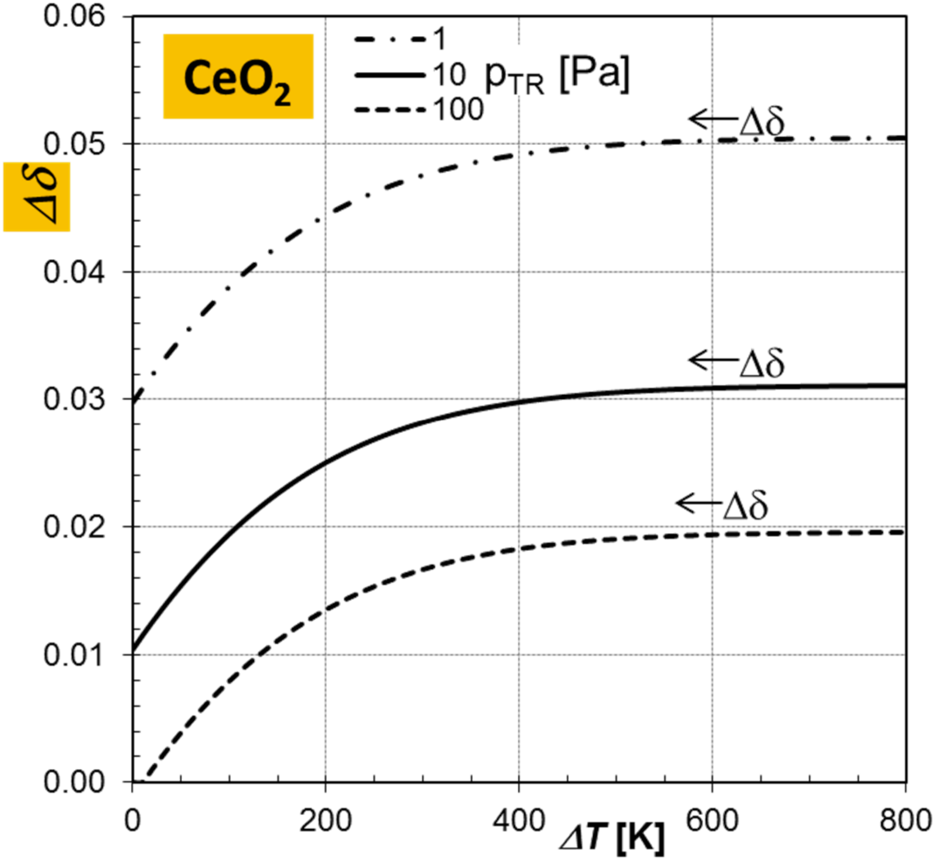
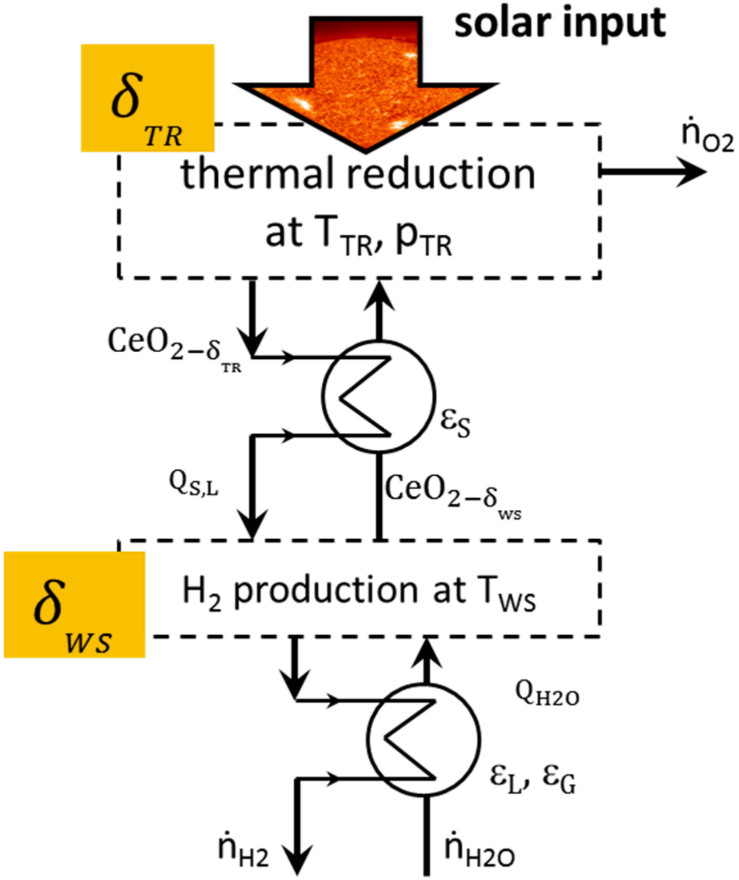
Key Material Requirements: Reactive Oxide

How much CeO_2 per mole H_2?

$\delta_{TR} - \delta_{WS} = \Delta\delta$ T_{TR}=1773K





The reversible oxygen capacity can be very low!

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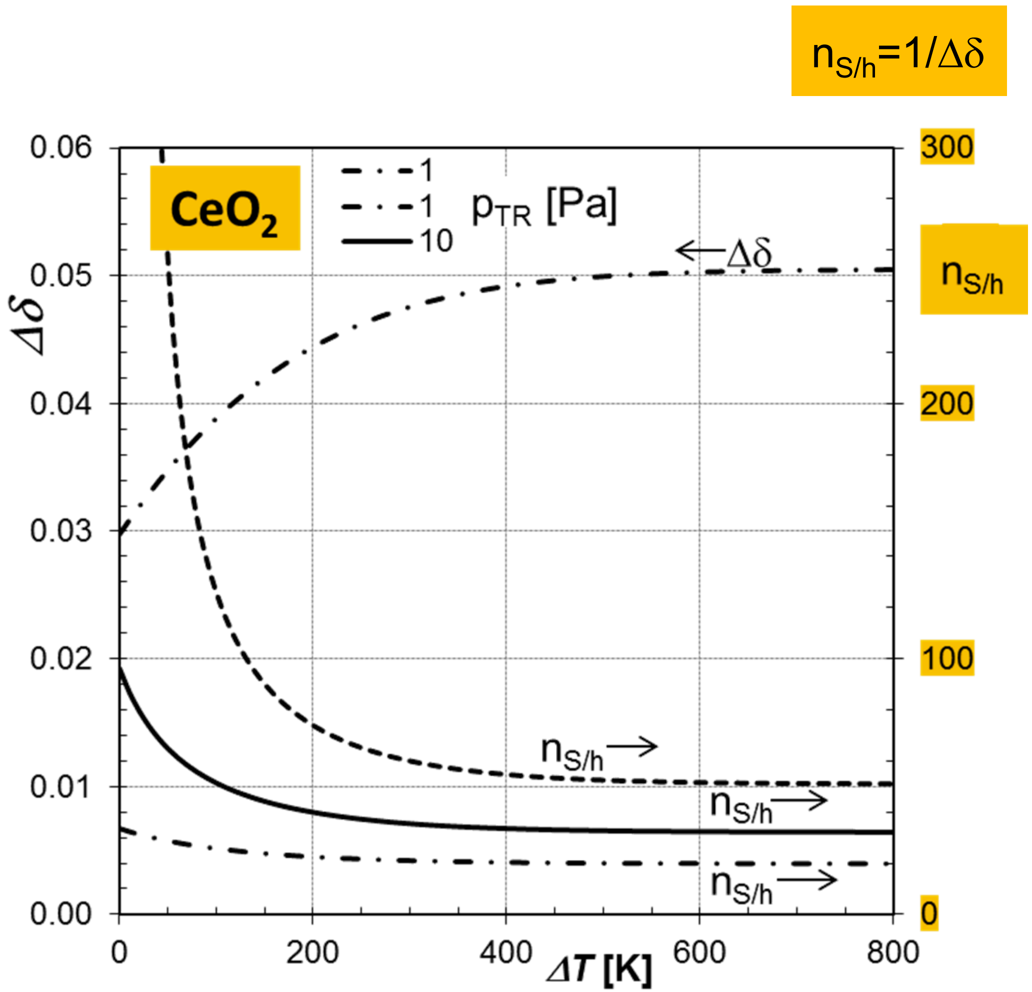

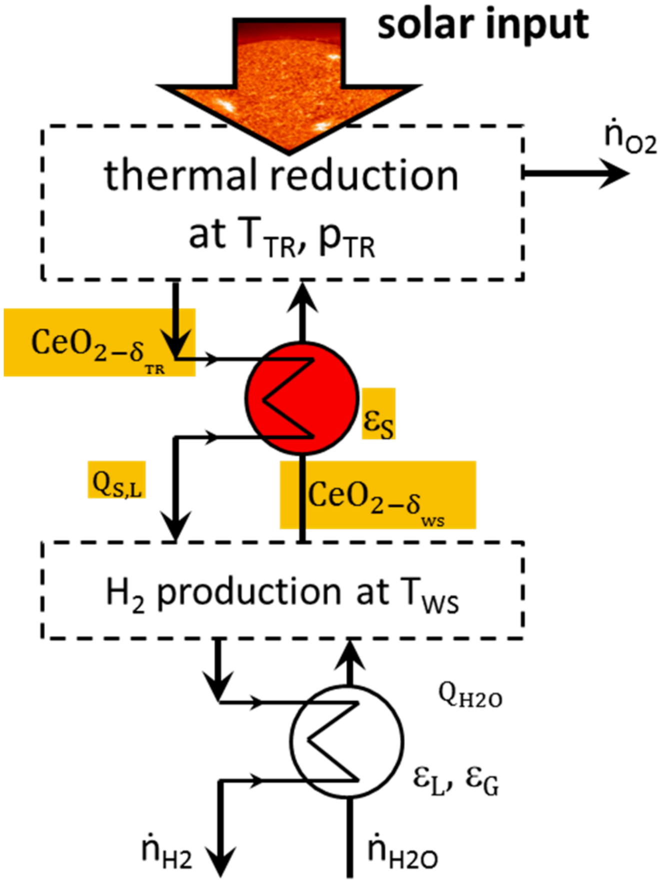

A low reversible oxygen capacity leads to a very high oxide/H_2 ratio and excessive oxide mass flow and heat recovery requirements

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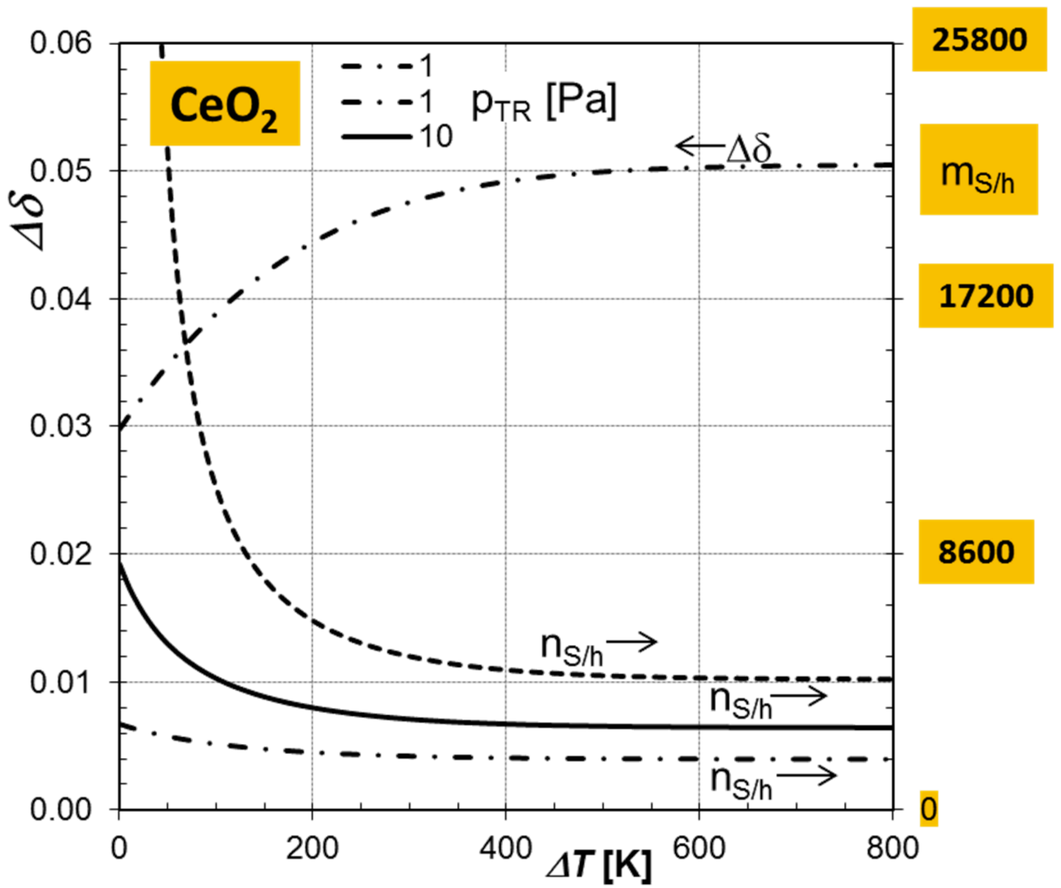

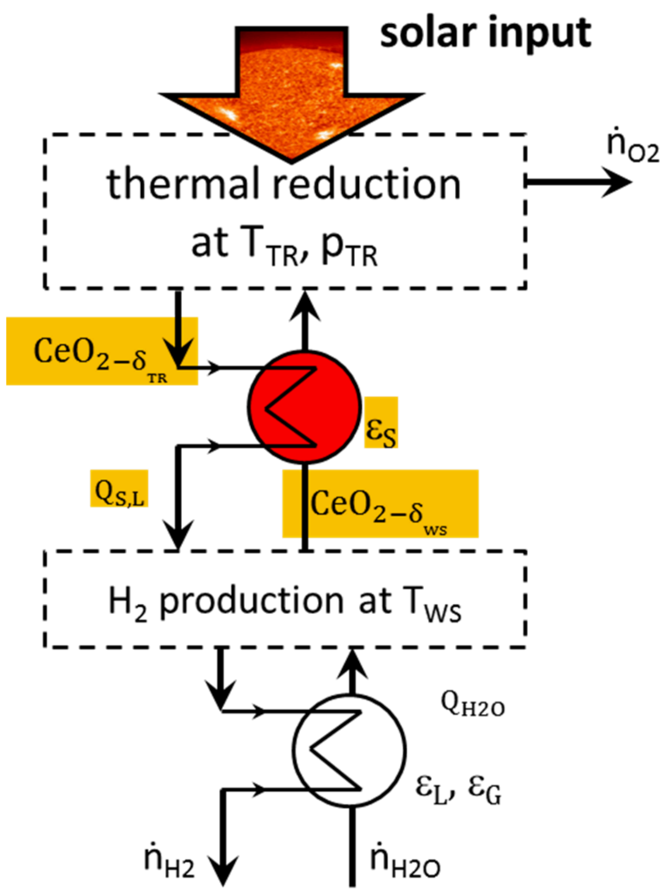

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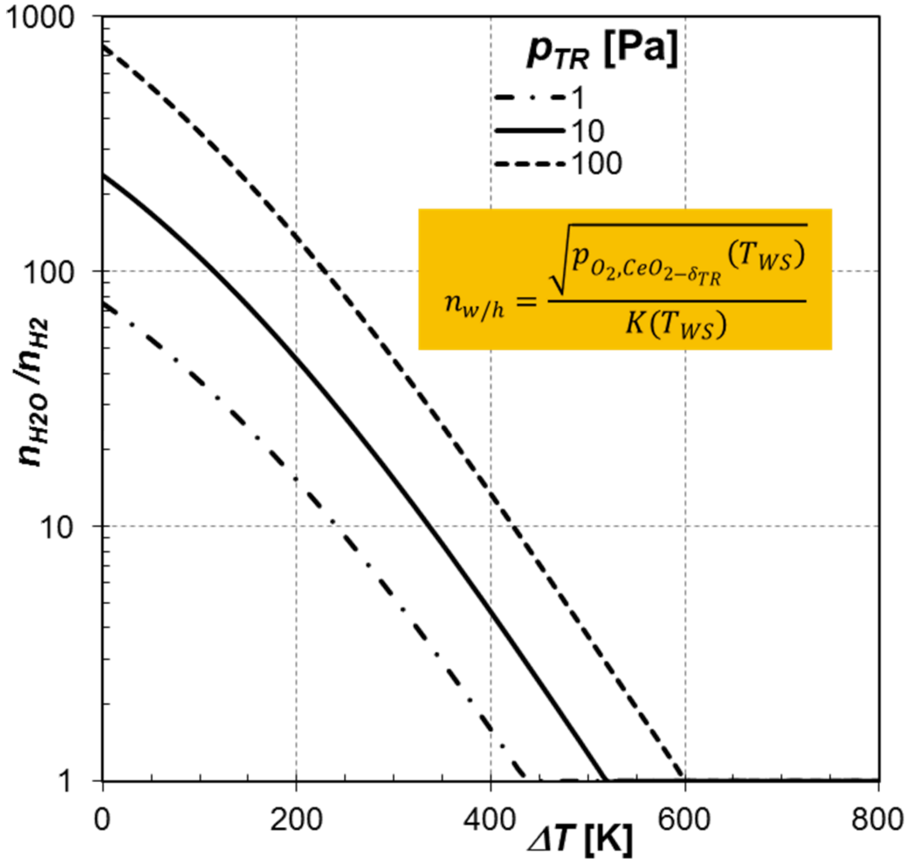
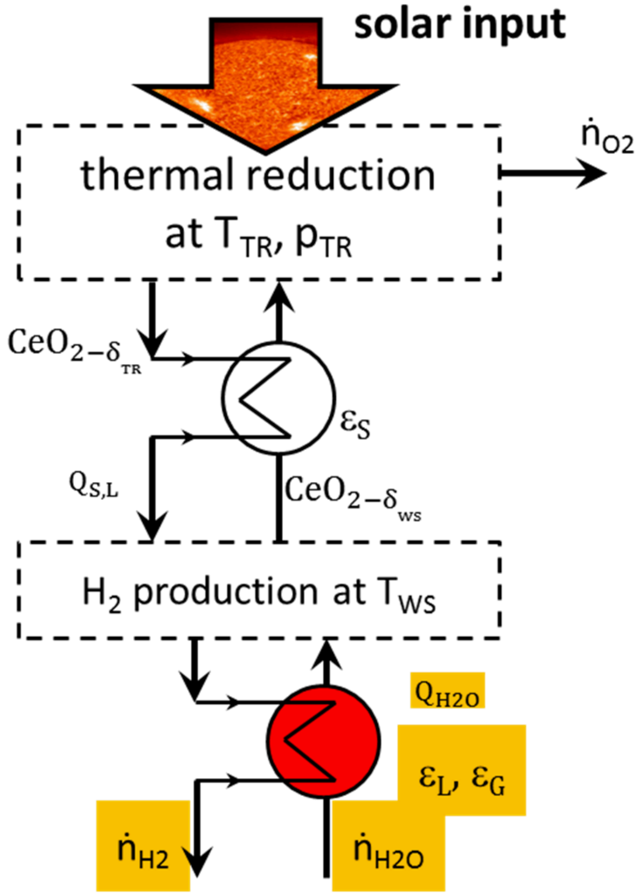
Key Material Requirements: Steam

How much steam per mole H_2?





Low ΔT or high reduction pressure leads to a high steam/H_2 ratio

Reactor Efficiency: An all Inclusive Measure

$$\eta_R = \frac{\dot{n}_{H_2} HHV_{H_2}}{\dot{Q}_A}$$

$$\dot{Q}_{TH} = A\dot{Q}_A - P_{rad}$$

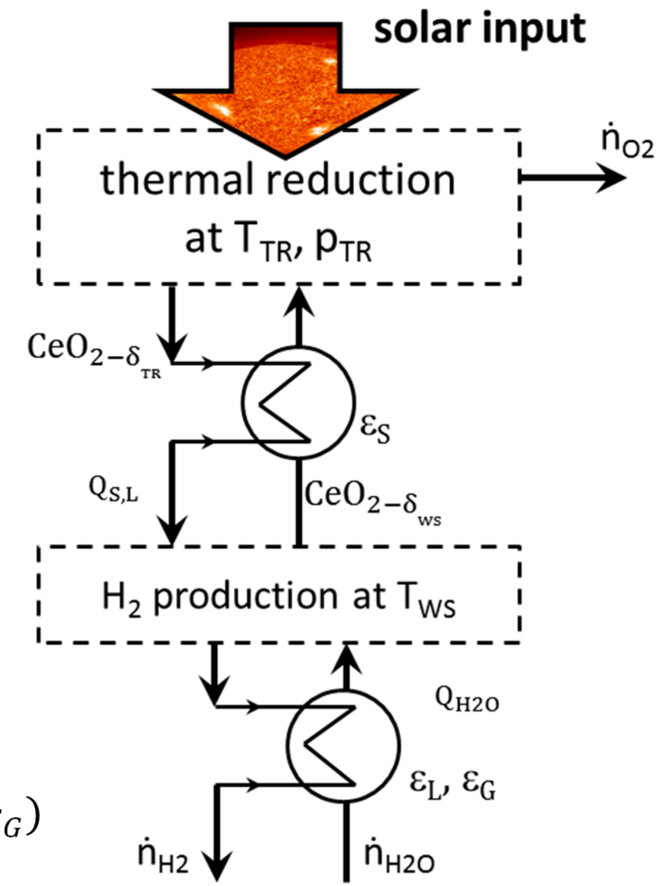
$$Q_{mol} = Q_{TR} + Q_S + Q_{AUX}$$

$$\dot{n}_{H_2} = \frac{\dot{Q}_{TH}}{Q_{mol}}$$

$$Q_{AUX} = \left(Q_{H_2O} + Q_{pump} + Q_{mech} + Q_{sep}\right) - \left(Q_{ROX} + Q_{S,L} + Q_{O_2}\right)$$

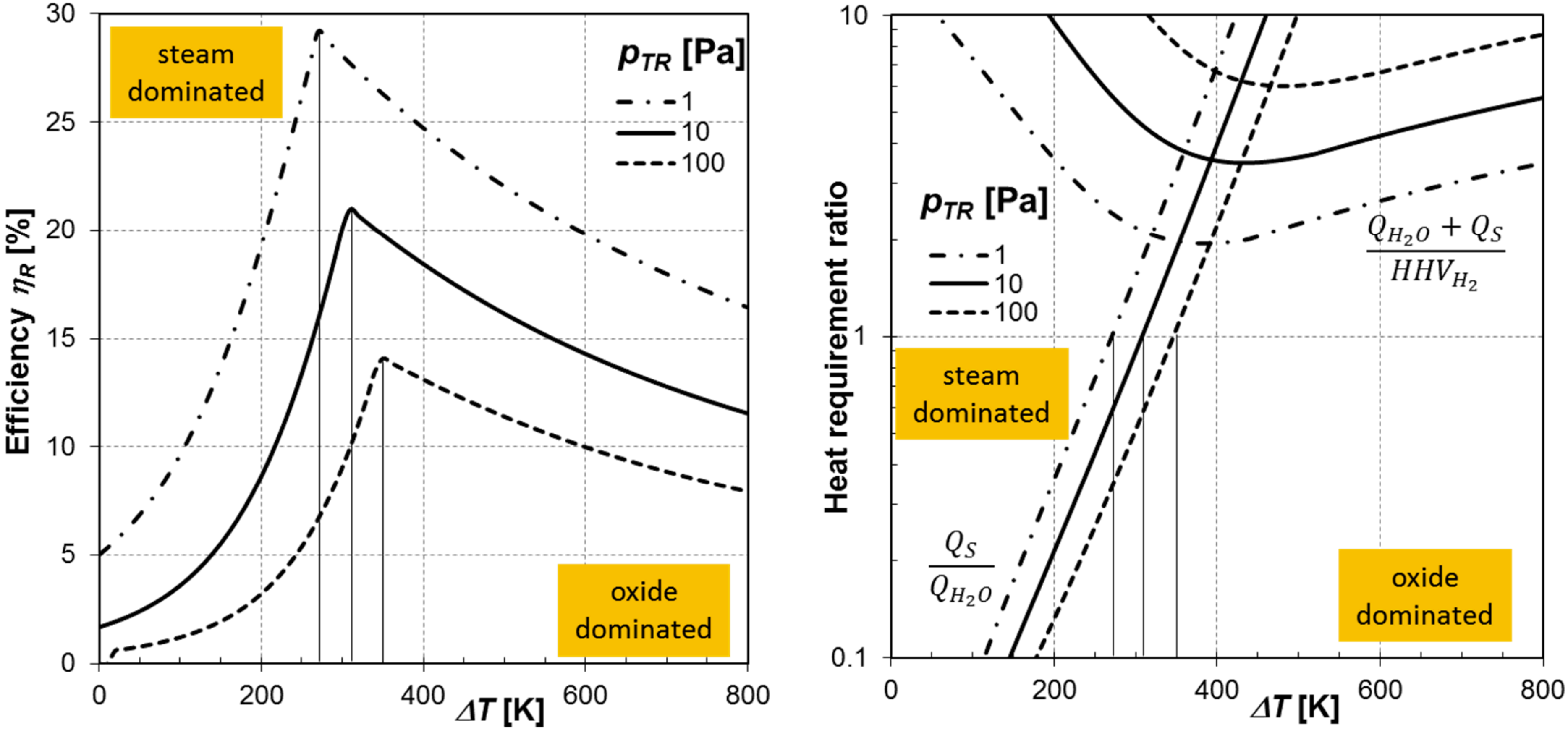
$$Q_S = \frac{C_{p,S}}{\Delta\delta}\Delta T(1-\varepsilon_S)$$

$$Q_{H_2O} = n_{w/h}[C_{p,L}\left(T_{bp} - T_0\right)(1-\varepsilon_L) + \Delta H_{vp}(1-\varepsilon_G) + C_{p,G}\left(T_{WS} - T_{bp}\right)(1-\varepsilon_G) + Q_{pump,vp}]$$



Includes all major energy requirements and losses

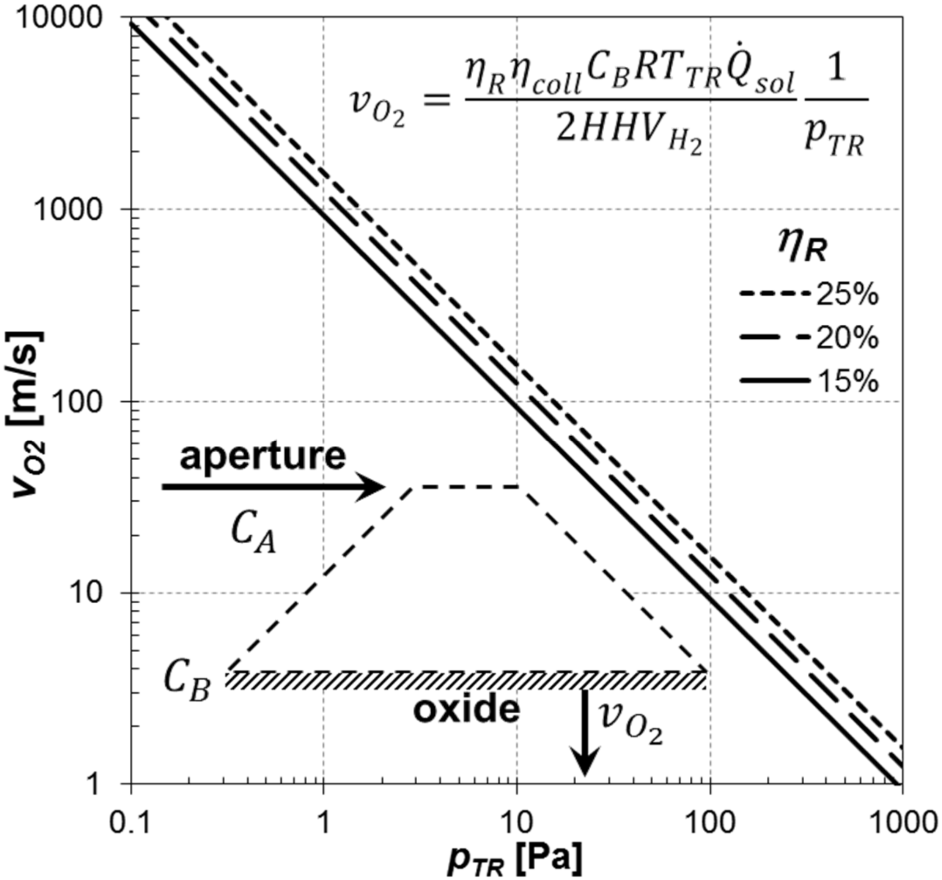
Maximizing Efficiency: Solid/Steam Heating Balance and a Low Reduction Pressure

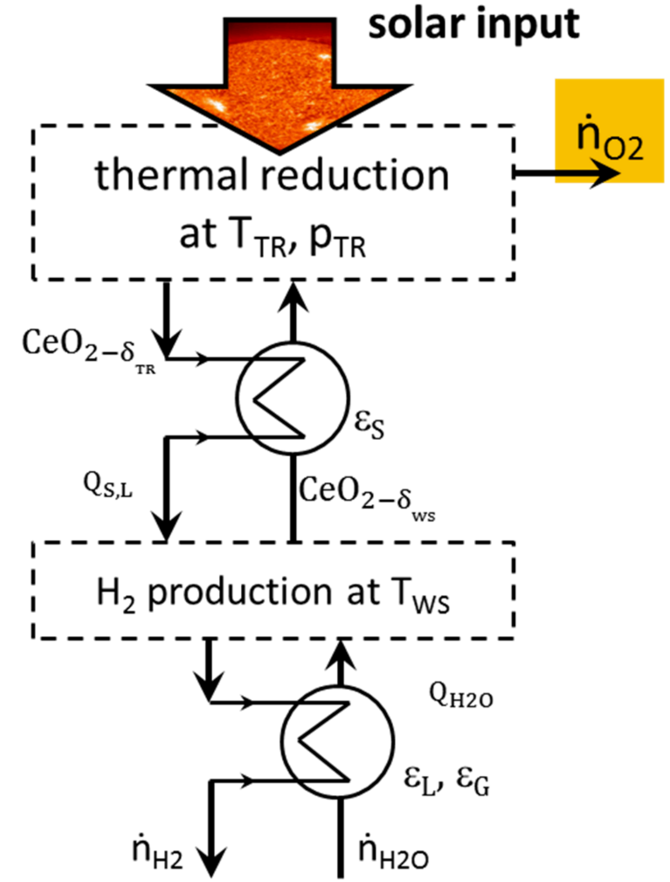


Efficiency is the highest when:

- **Oxide and steam heating loads are roughly equal**
- **Thermal reduction pressure is low**

O_2 Pressure Limits: Flow Volume and Speed





At low pressure required flow volumes and velocities are astronomical!

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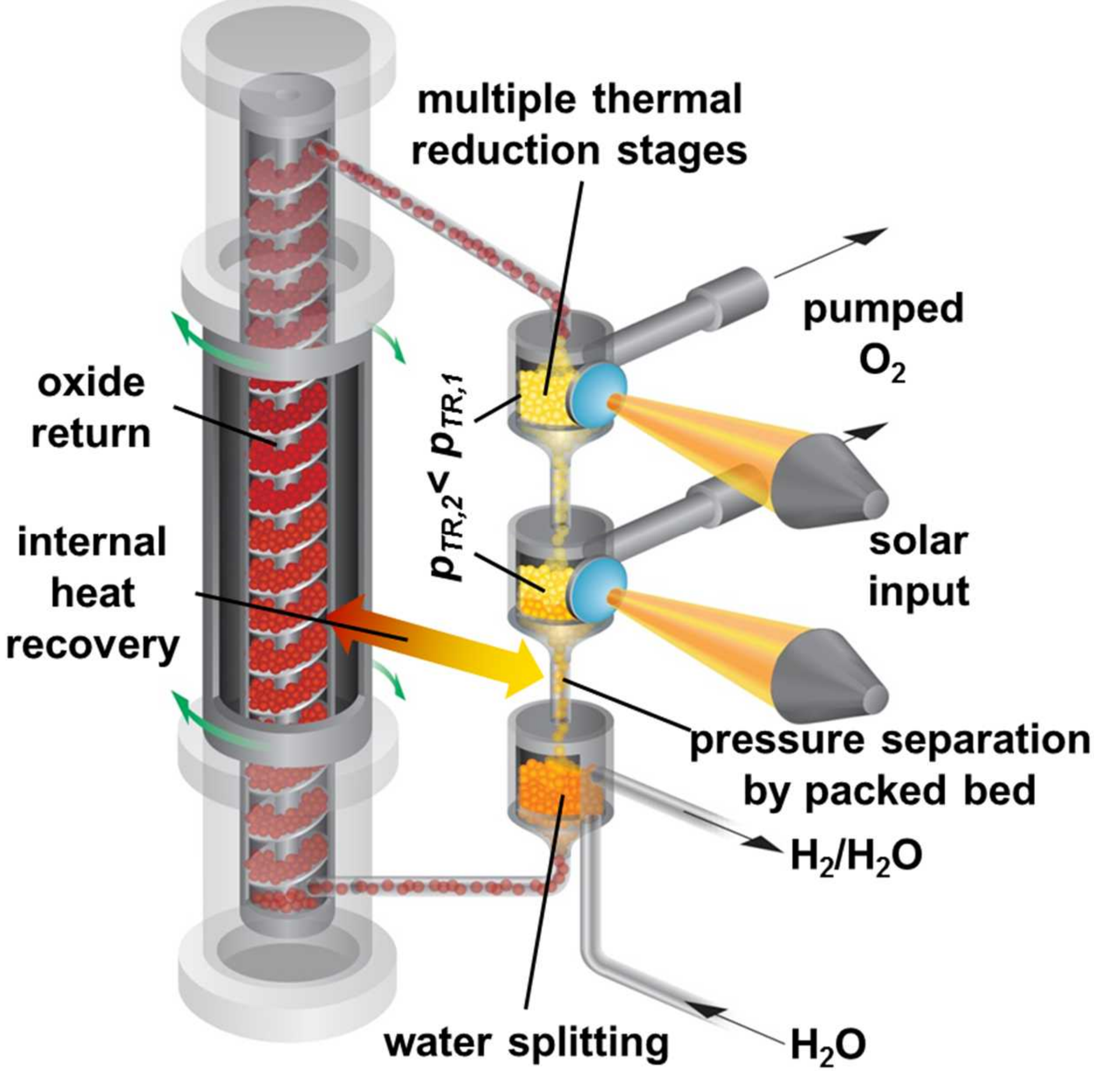
Staged Reduction Reactor for Low Pressure



Incrementally pumping O_2 reduces the overall flow volume and velocity

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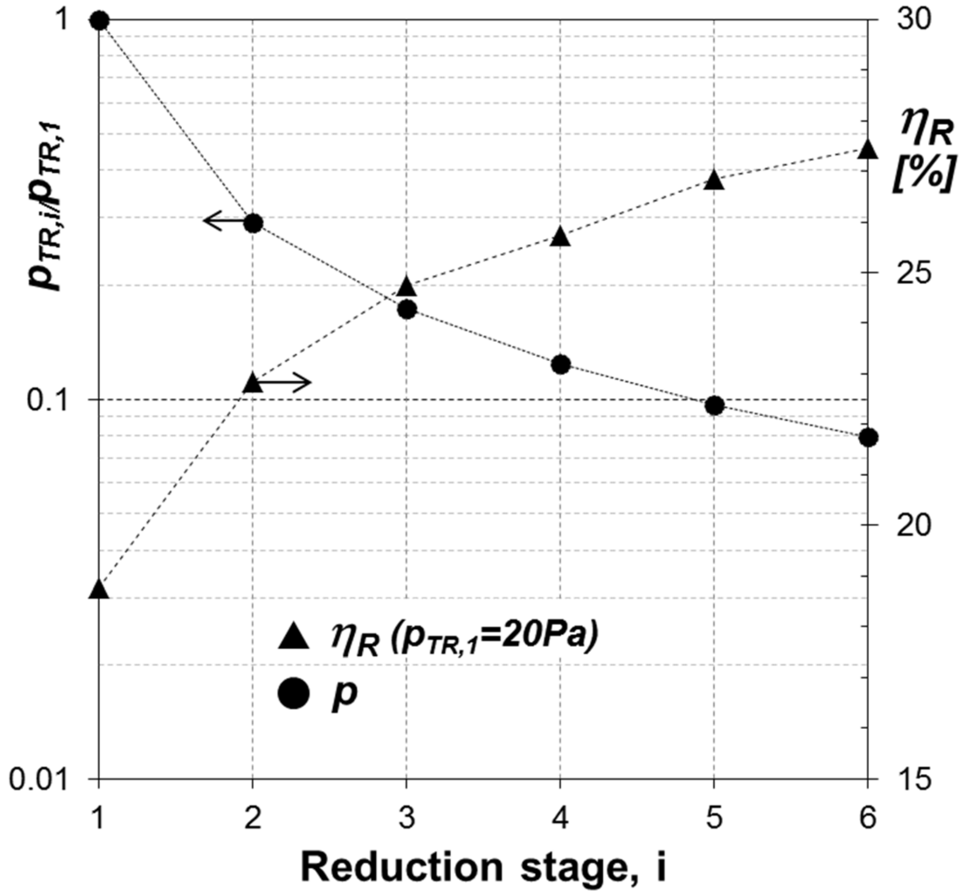
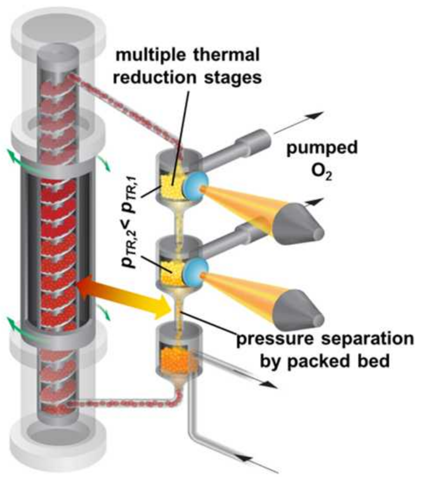
Staged Reduction for Low Pressure





10x pressure decrease possible with as few as 5 chambers

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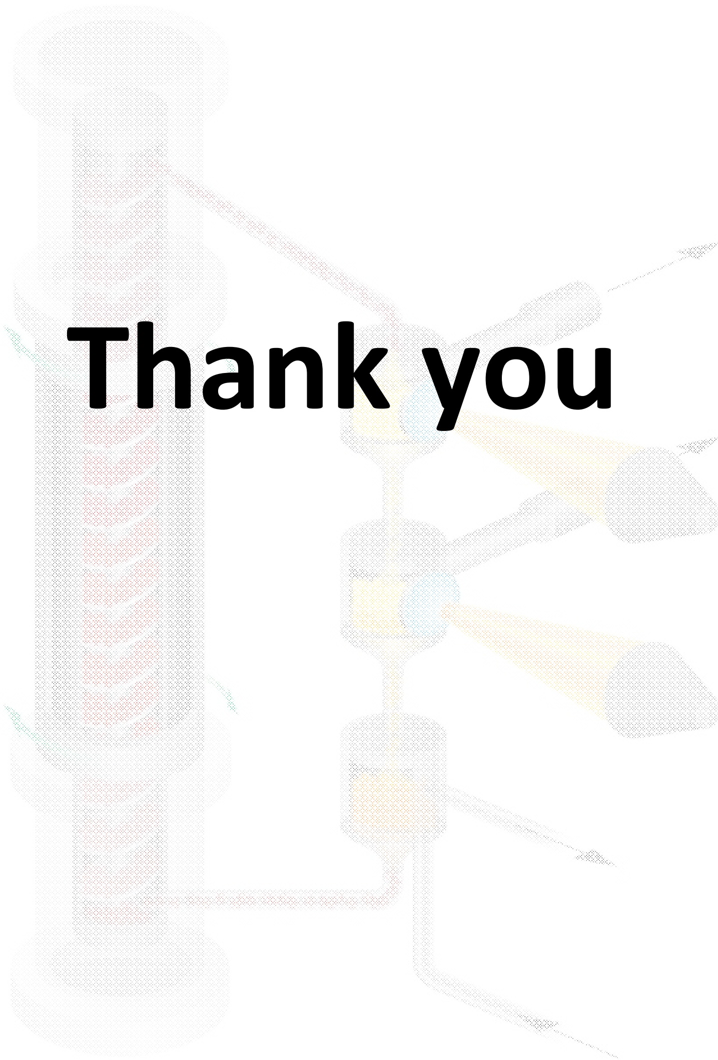
Conclusions

- Materials with low $\Delta\delta$ pose a mass flow challenge
- Optimal ΔT can be found to maximize efficiency
- Thermal reduction pressure limited by O_2 flow
- A >10x pressure decrease feasible in staged reduction
- Best results by combining ΔT_{opt}, staged pumping and advanced reactive oxides

Thank you



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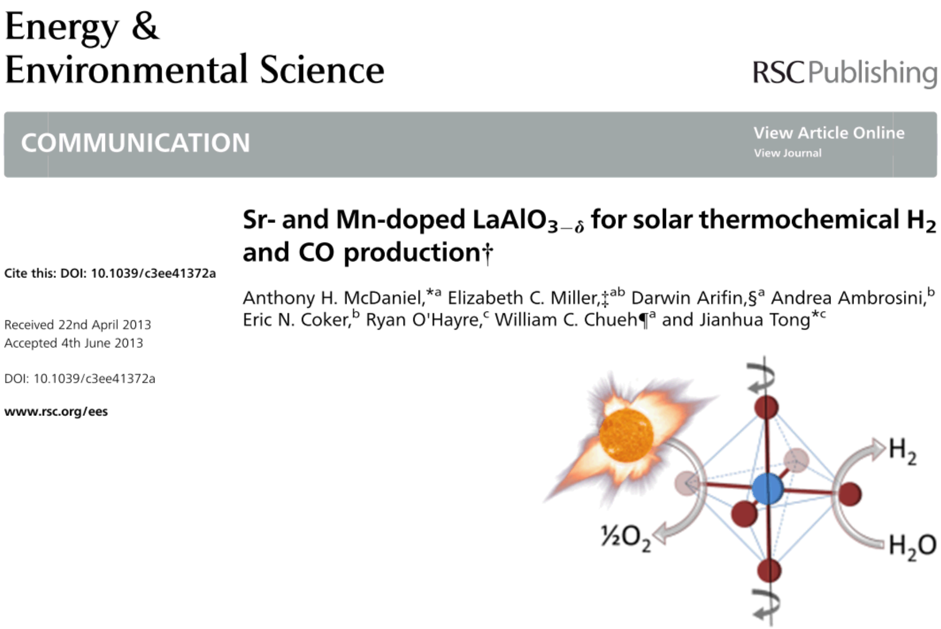
Next Generation Redox Active Materials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Sr- and Mn-doped $LaAlO_{3-\delta}$ for solar thermochemical H_2 and CO production†

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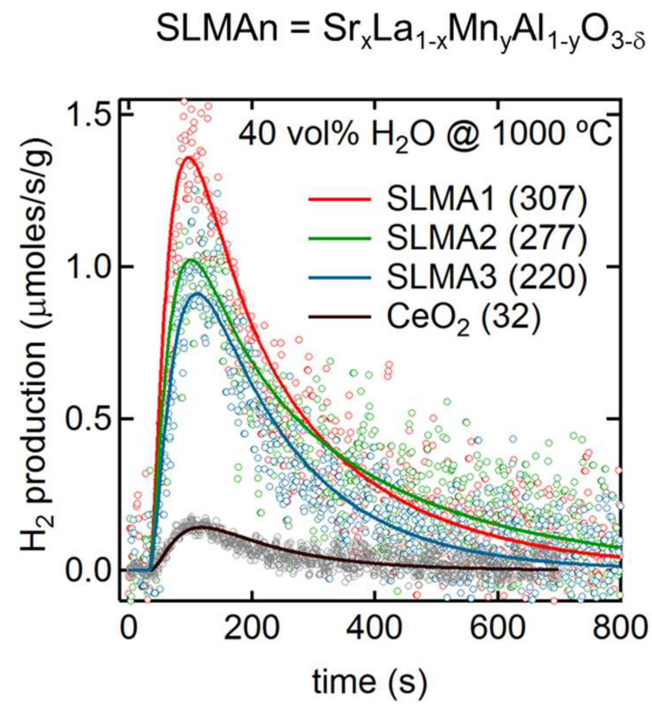
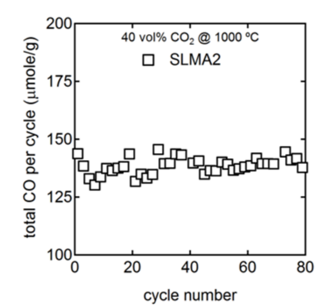
SLMAn = $Sr_xLa_{1-x}Mn_yAl_{1-y}O_{3-\delta}$



- Perovskite compounds split H_2O in a thermochemical cycle.
  - First of a kind observation, also demonstrated durability
- Kinetics benchmarked against CeO_2.
  - Similarly fast oxidation rates
- Make ~9× more H_2 than CeO_2 at T_{TR} = 1350 °C.



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