Thermochemical and

Fundamental and High Throughput Advances in Electrochemical Energy Technologies

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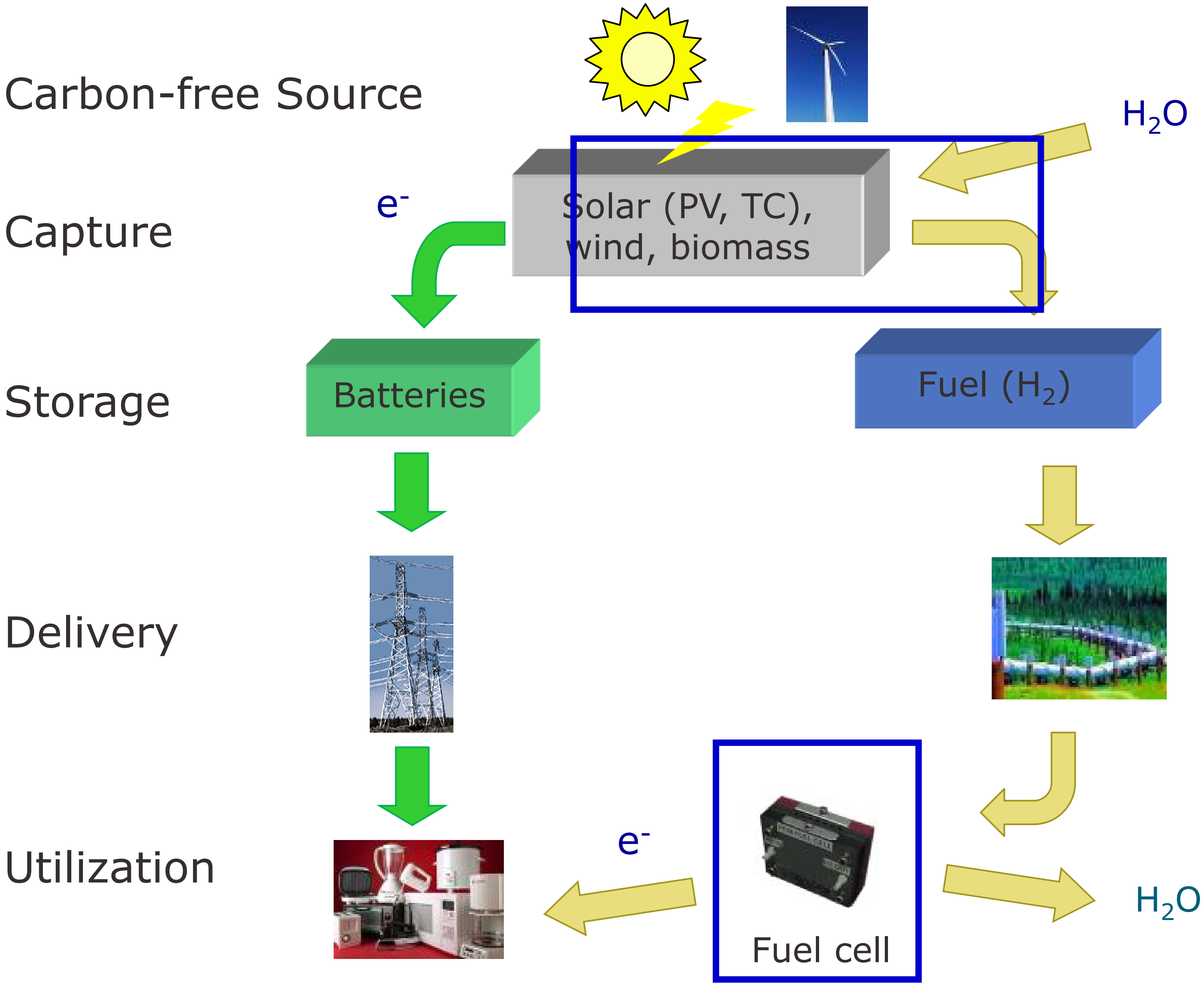
Sustainable Energy Cycle

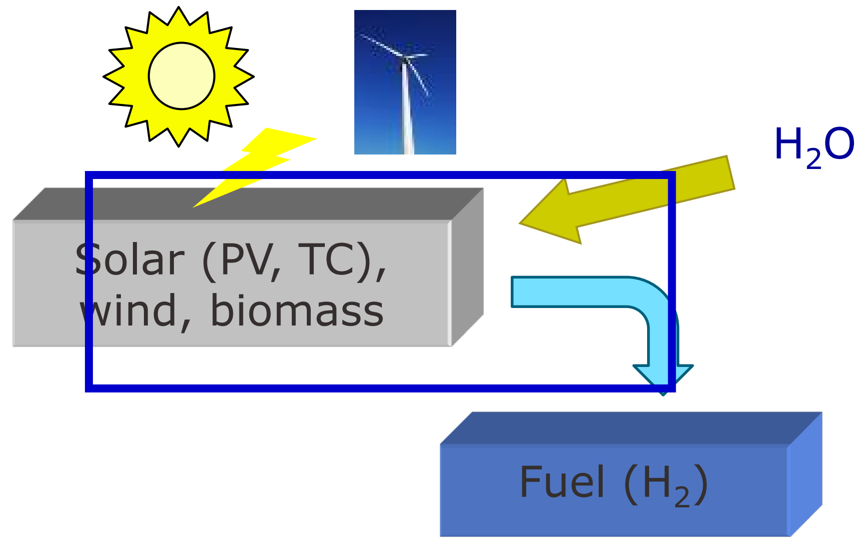


Sustainable Energy Cycle

Carbon-free Source

Capture

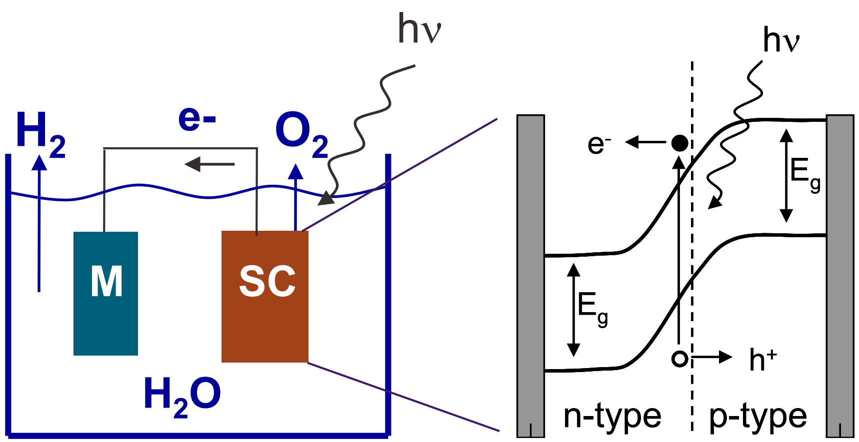
Storage



Solar-Driven Fuel Production

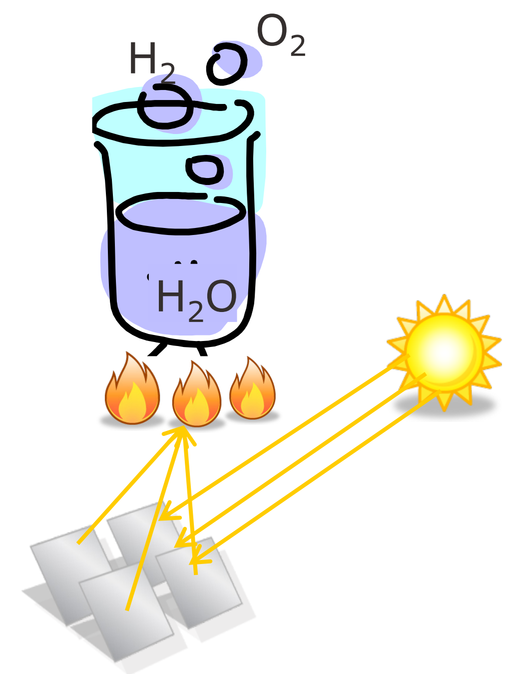
$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2 \qquad CO_2 \rightarrow CO + \tfrac{1}{2}O_2$$

- Photochemical Dissociation



  - Utilizes (only) select wavelengths
  - Material corrosion
  - Requires precious metal catalyst

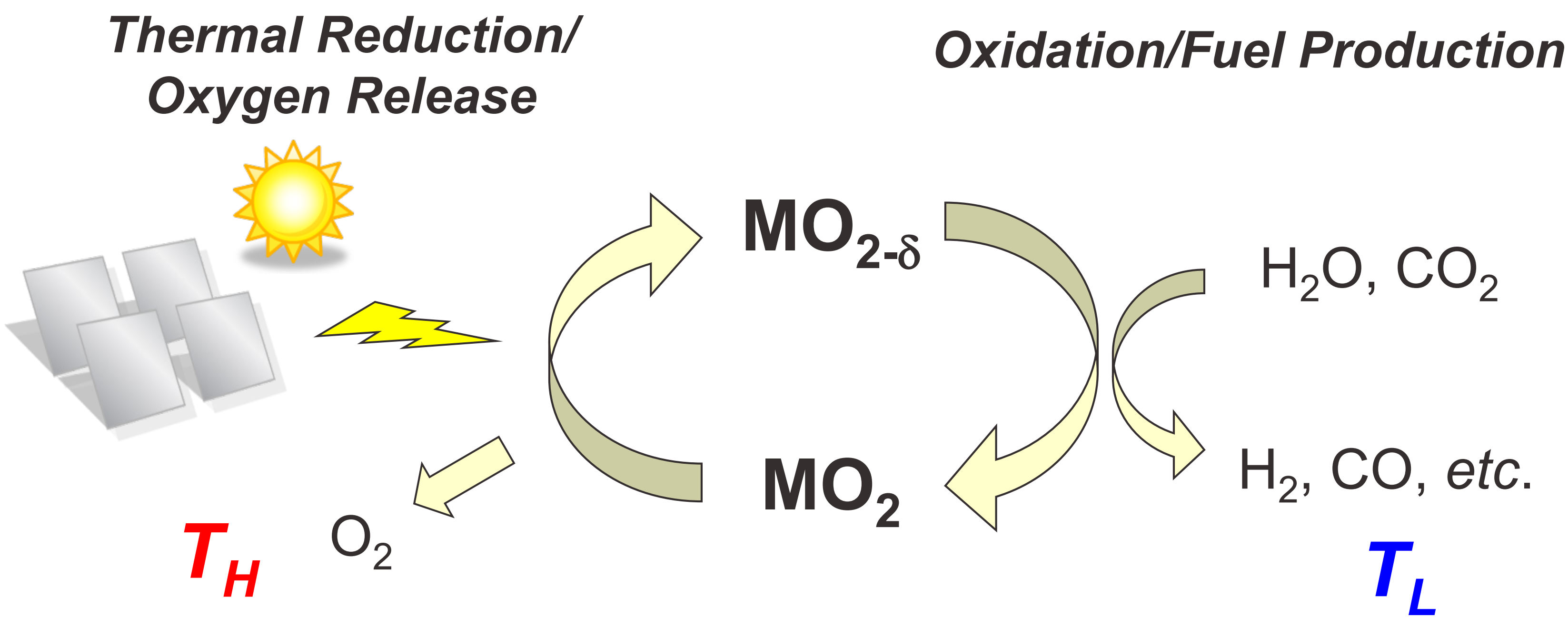
- Thermolysis



  - Reaction at > 4,000 °C
  - Requires gas separation

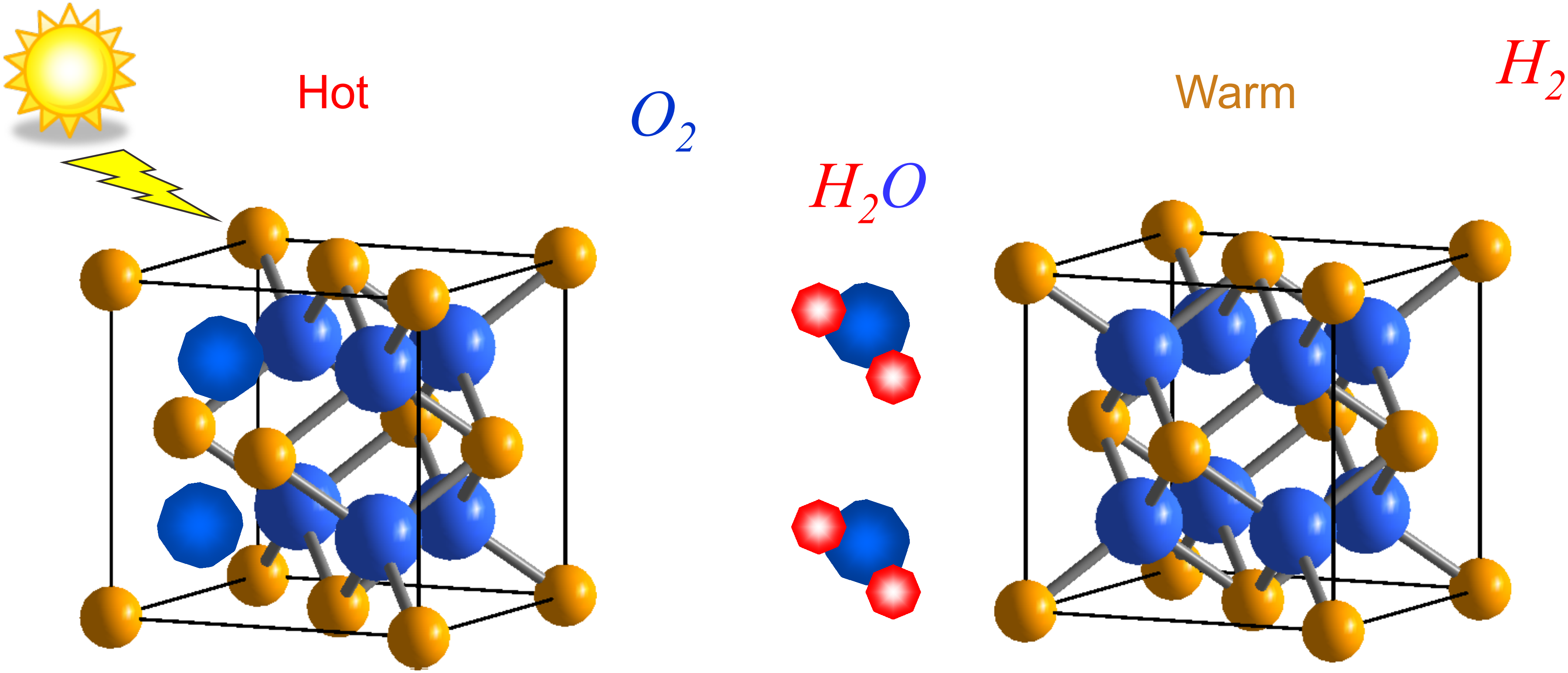
Solar-Driven Fuel Production

Two-step thermochemical process using non-stoichiometric oxides



Ideal candidate: ceria, or $CeO_{2-\delta}$

Cerium Dioxide as the Reaction Medium



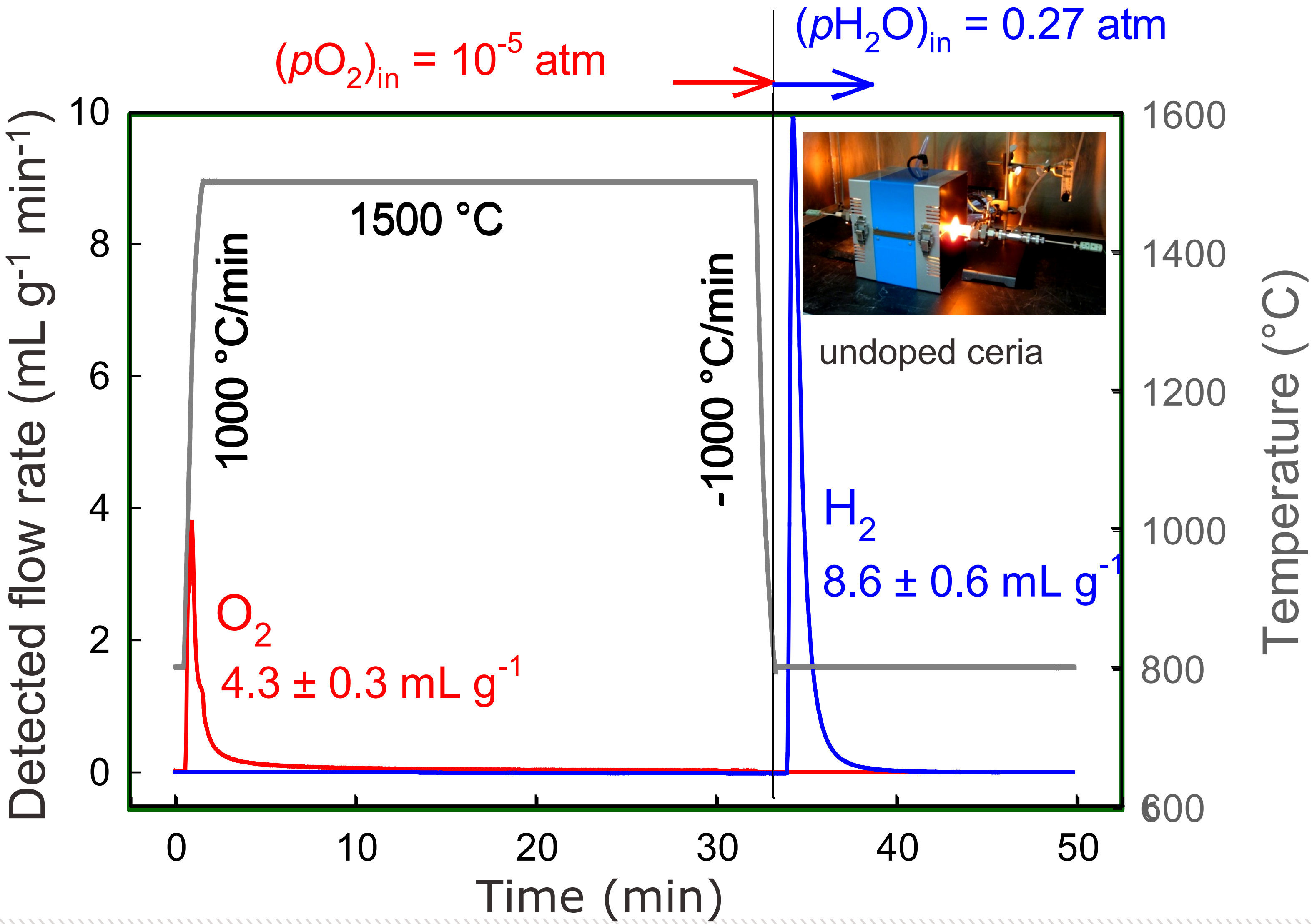
$$CeO_2 \rightarrow CeO_{2-\delta} + \delta/2\, O_2$$

1400-1600 °C

$$\delta H_2O + CeO_{2-\delta} \rightarrow \delta H_2 + CeO_2$$

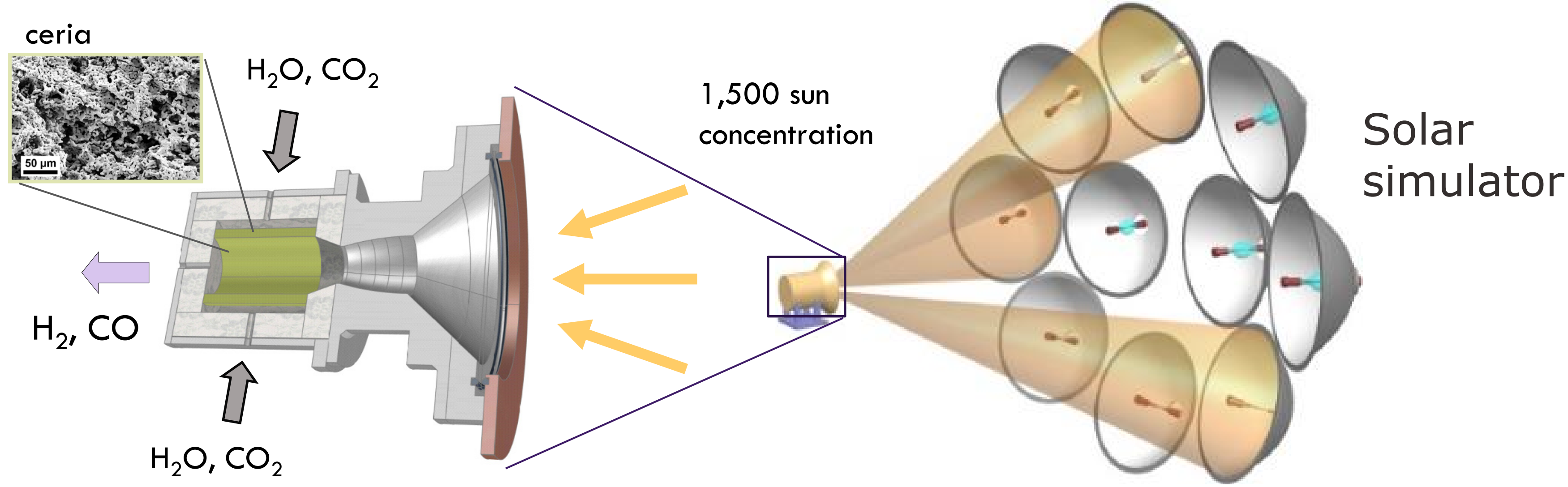
800-1600 °C

Experimental Demonstration

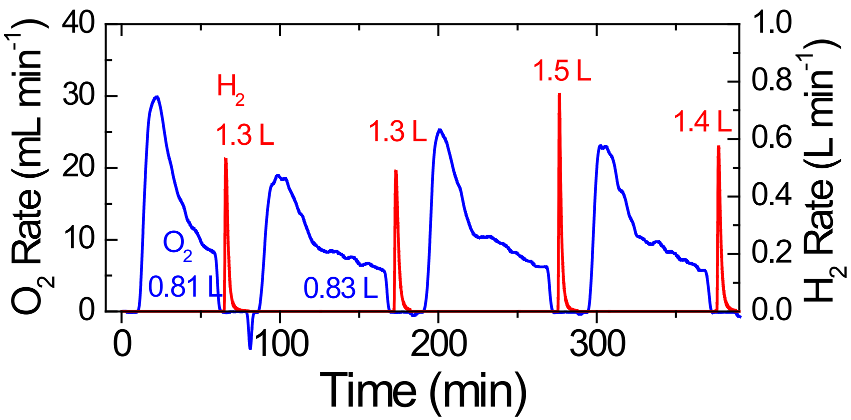


Chueh & Haile, *Phil. Trans. R. Soc.* **368**, 3269-3294 (2010).

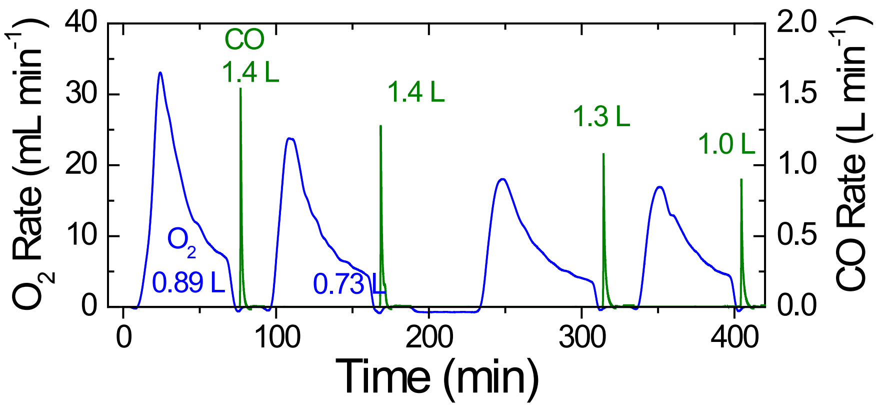
Reactor Proof of Principle



Splitting water

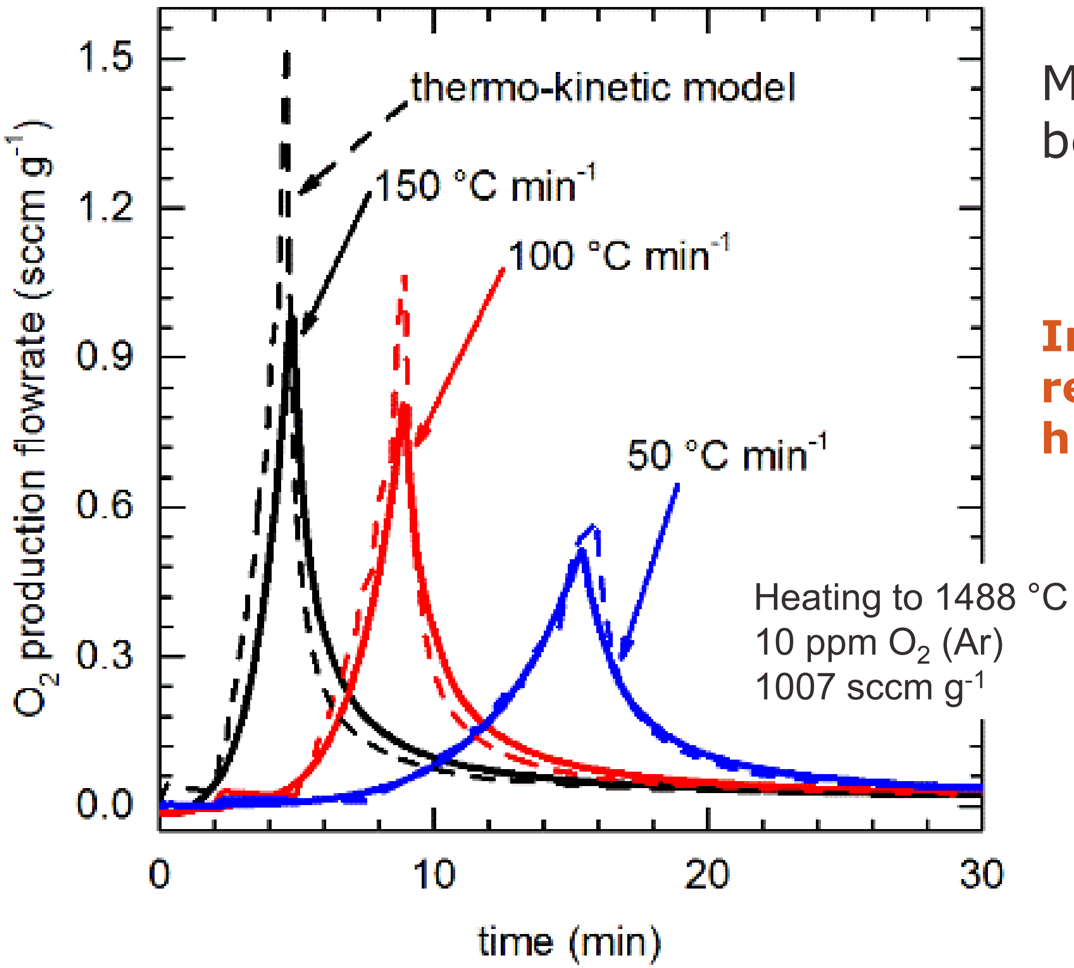


Splitting carbon dioxide



Chueh, …, Haile, Steinfeld, *Science* **330** (2010) 1797-1801

Predictable Gas Evolution Rates



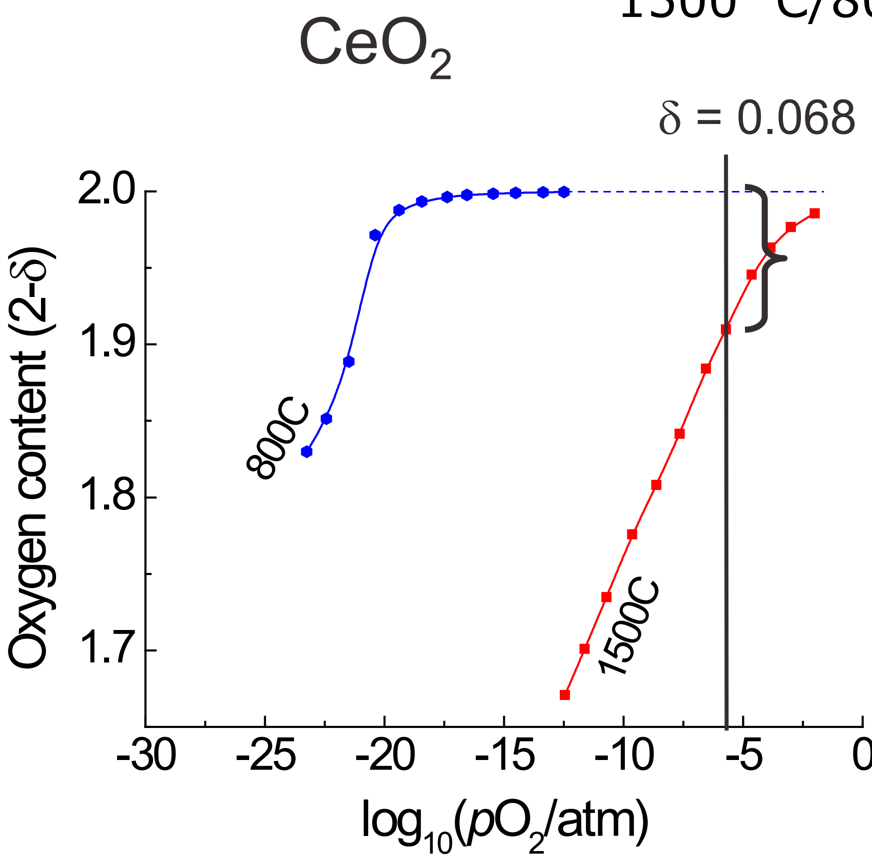
Model: quasi-equilibrium between solid and gas

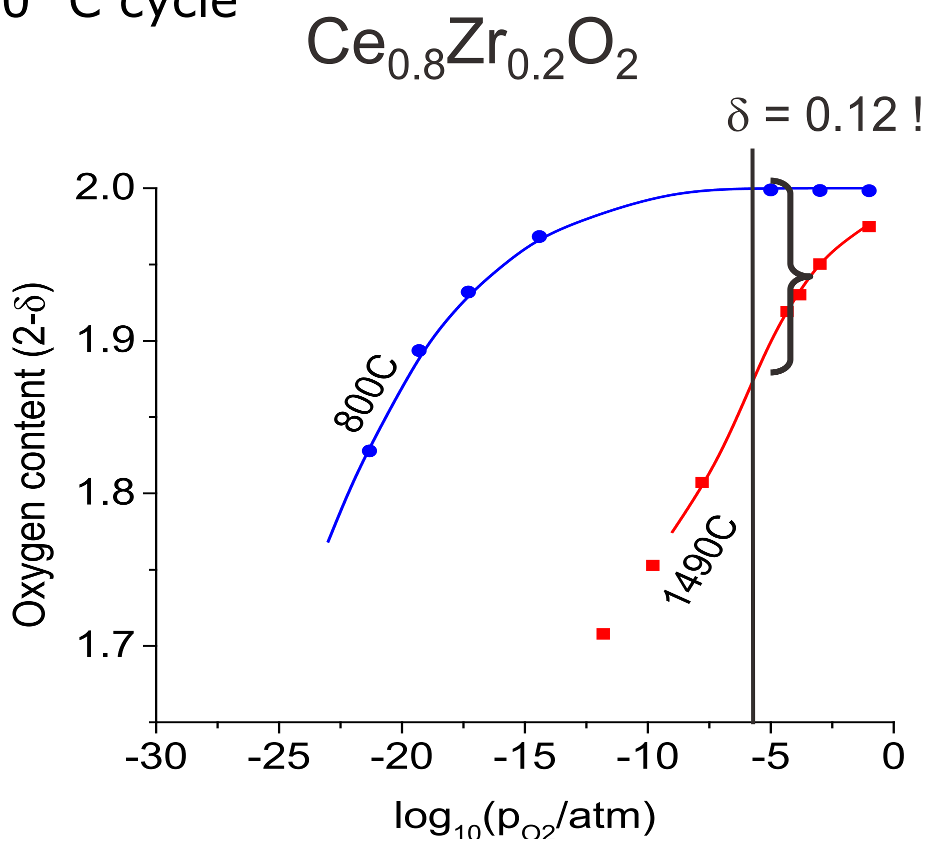
Implication: Surface reaction and diffusion at high T are "infinitely" fast

Davenport, …, Haile, *Int. J. Hydr. Energy* **330** (2017) 16932-16945

Better Materials: $Ce_{1-x}Zr_xO_{2-\delta}$

1500 °C/800 °C cycle



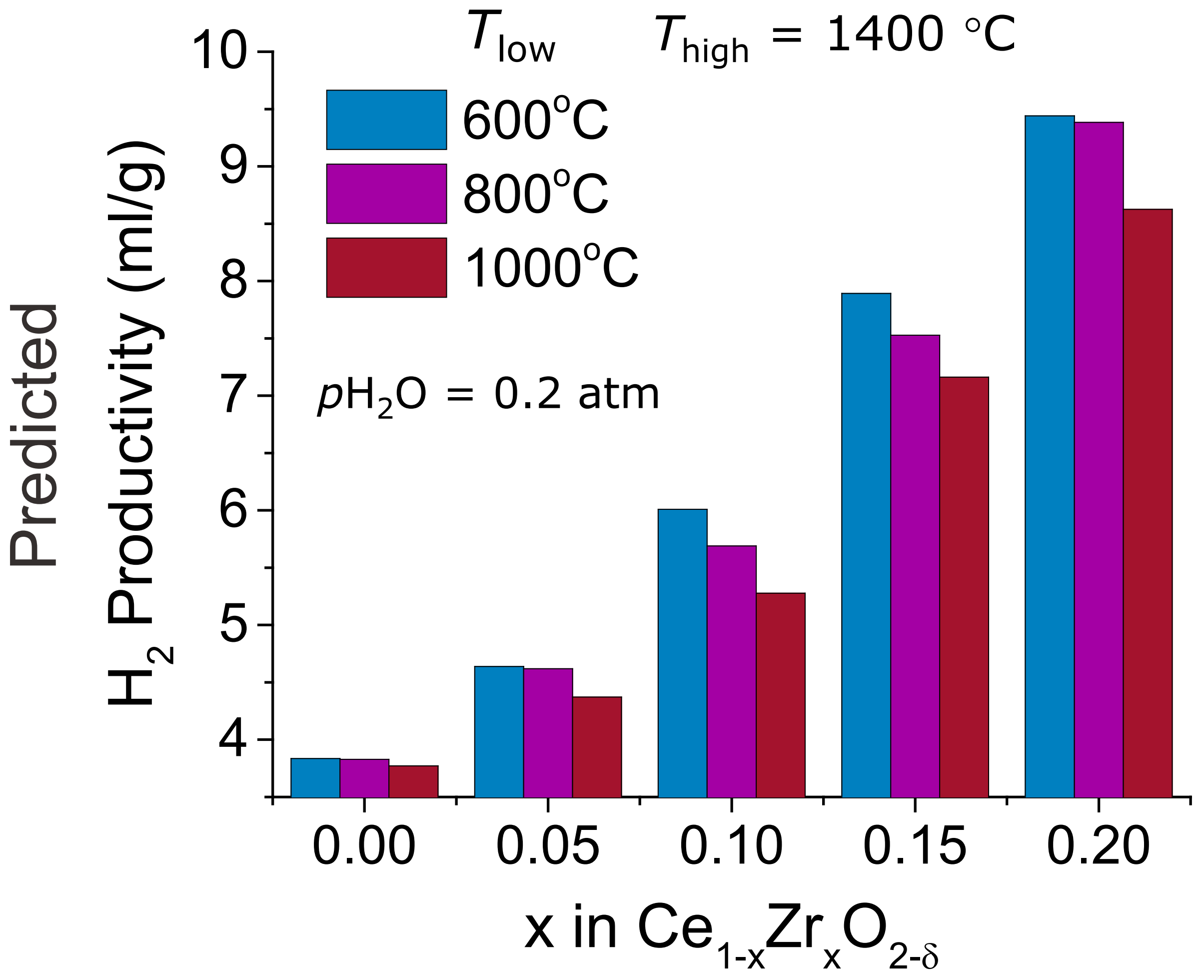


Fuel production per cycle: 8.6 → 15.2 mL H_2 g^{-1} oxide (!)

Panlener et al., *J Phys. Chem. Solids* (1975)

Hao & Haile *Chem. Mat.* (2014)

Equilibrium behavior of $Ce_{1-x}Zr_xO_2$



From measured thermodynamic properties

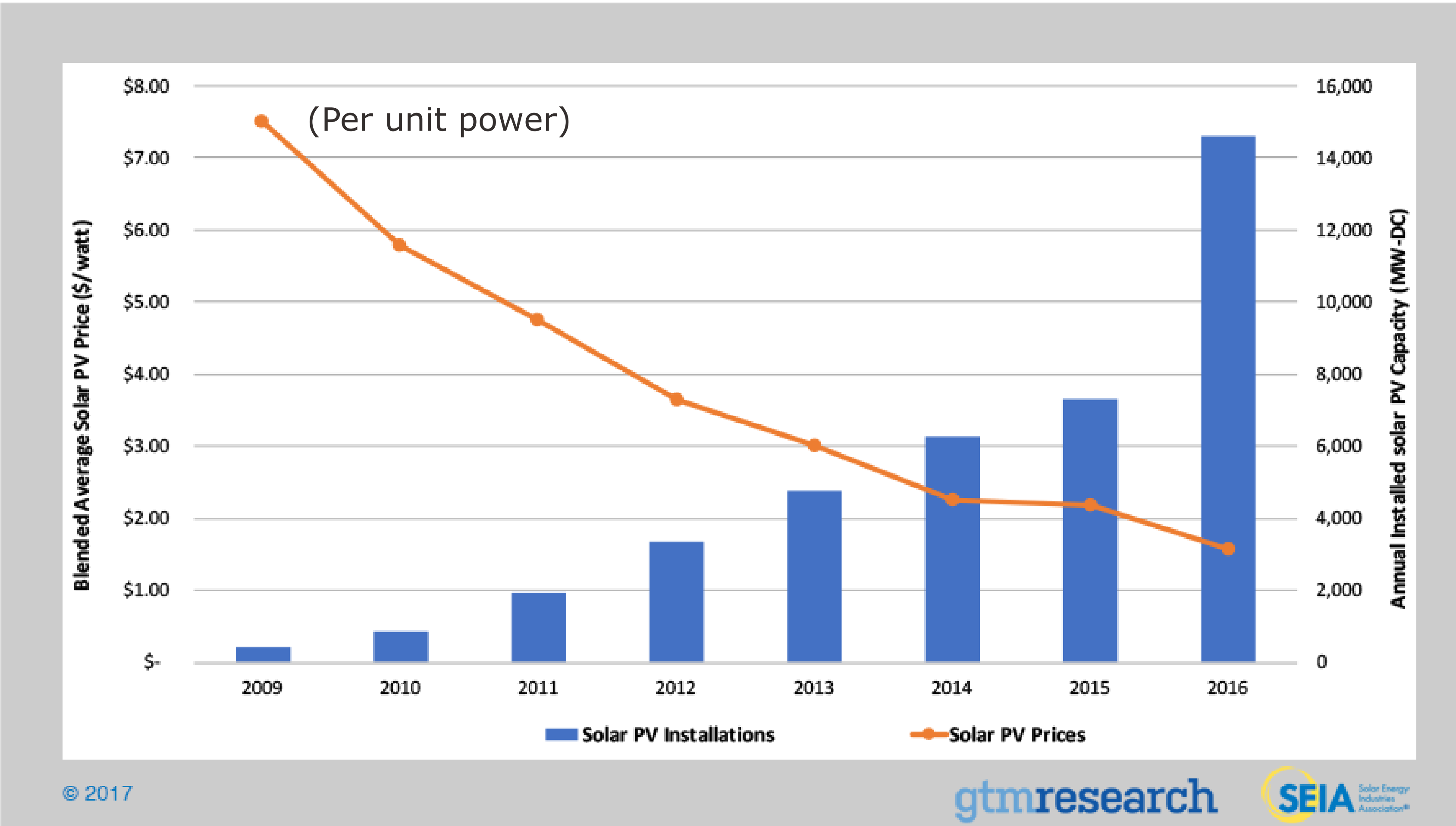
Motivates high throughput methods

Hao & Haile *Chem. Mat.* (2014)

Findings and Outlook

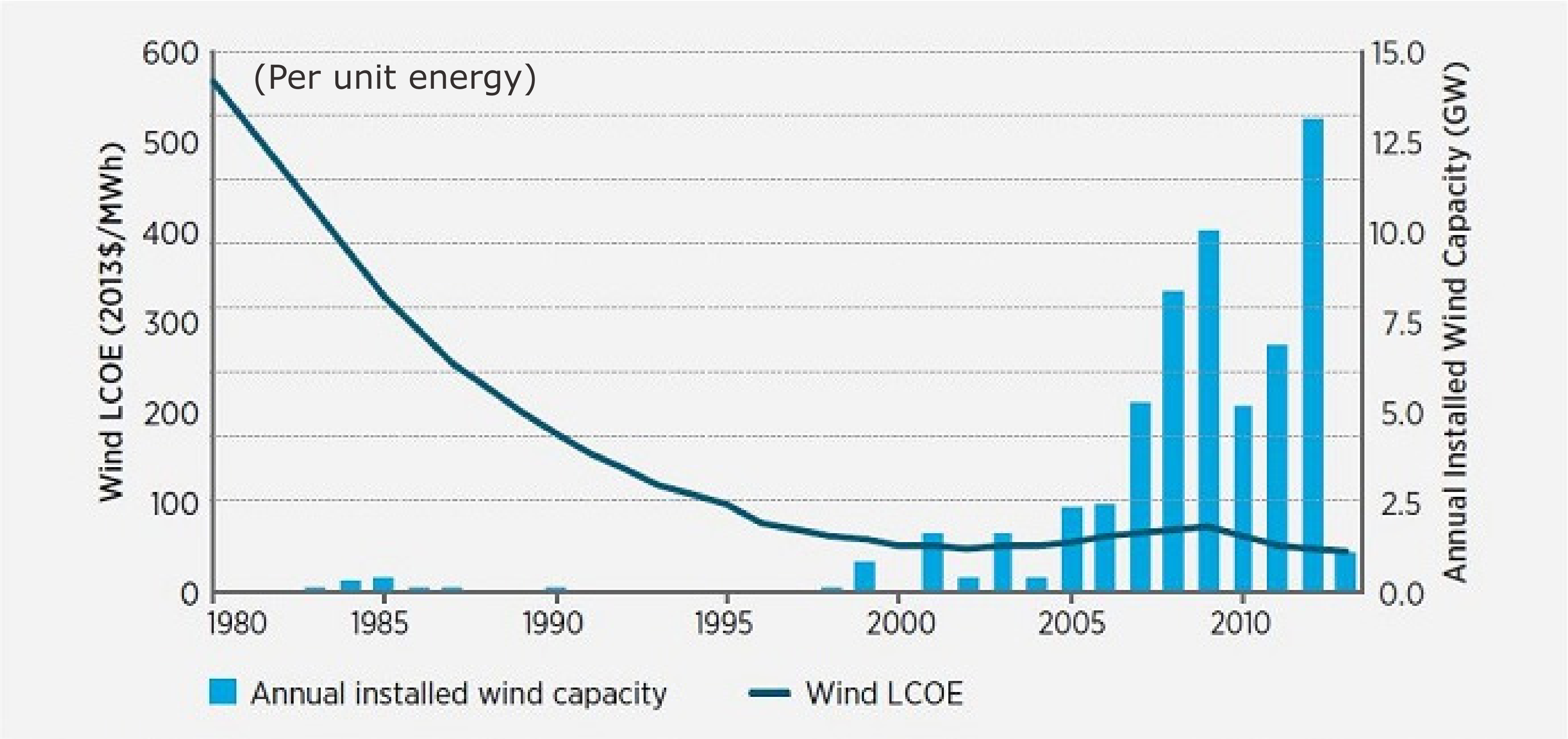
- Ceria is robust upon extended thermochemical cycling
- Surface reaction rate and bulk diffusion are extremely fast
  - Do not limit fuel production rates at high temp (~1000 °C)
- Modifying thermodynamic properties
  - Fuel per cycle ↑, for cycles taken to completion
- Fuel production rates limited by thermodynamics at high T
  - Modifying material to ↑ fuel per cycle, ↓ rate
- Thermodynamic conundrum!
  - Entropy change in MO_x limited to entropy of mixing
  - Pursue thermodynamic changes with *larger sources of entropy*

Solar Electricity Trends (US)



Solar Energy Industry Associates

Wind Electricity Trends (US)

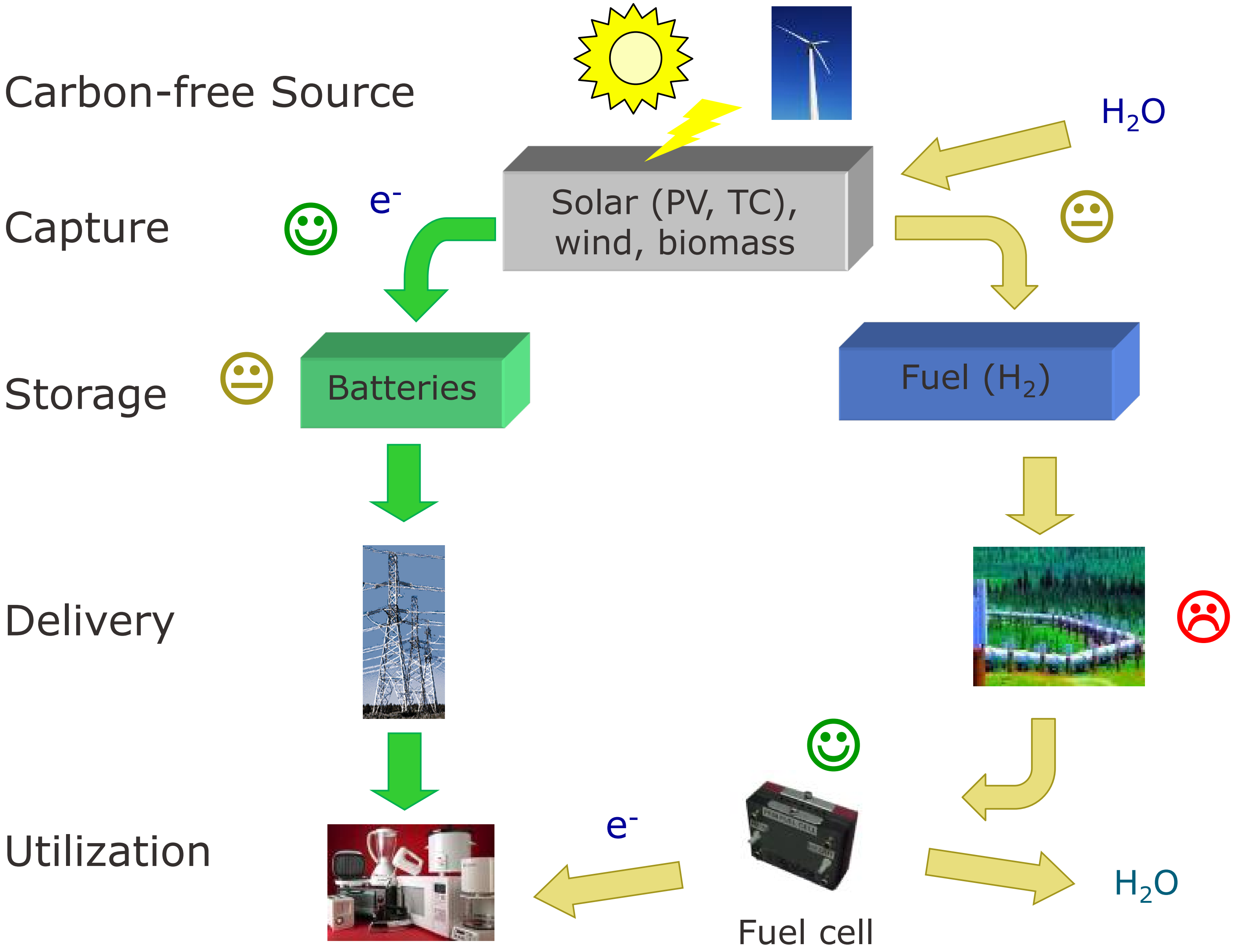


Note: In the *Wind Vision*, 'good to excellent sites' are those with average wind speeds of 7.5 meters per second (m/s) or higher at hub height. LCOE estimates exclude the PTC.

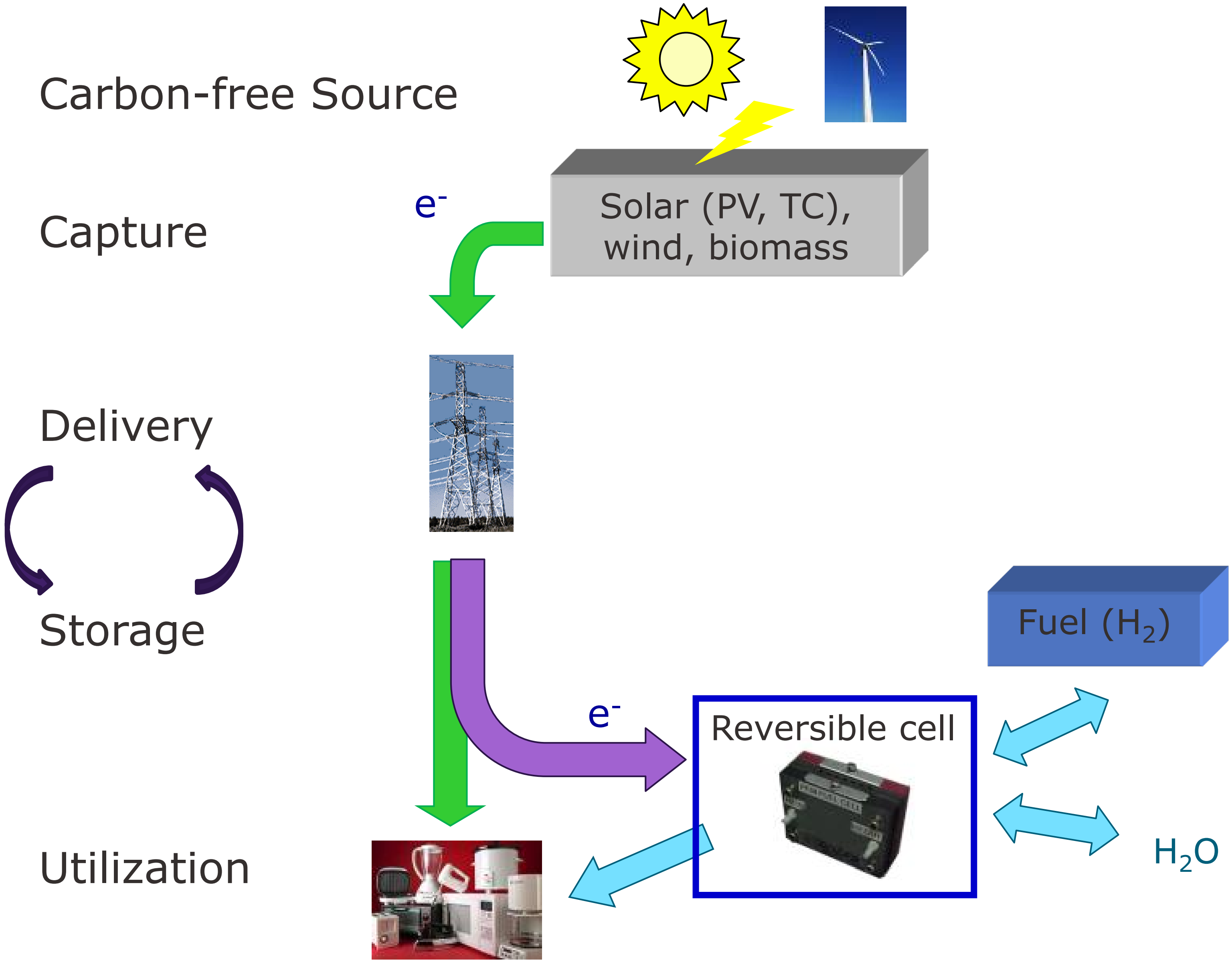
Source: Adapted from Lawrence Berkeley National Laboratory 2014 data [23]

American Wind Energy Association

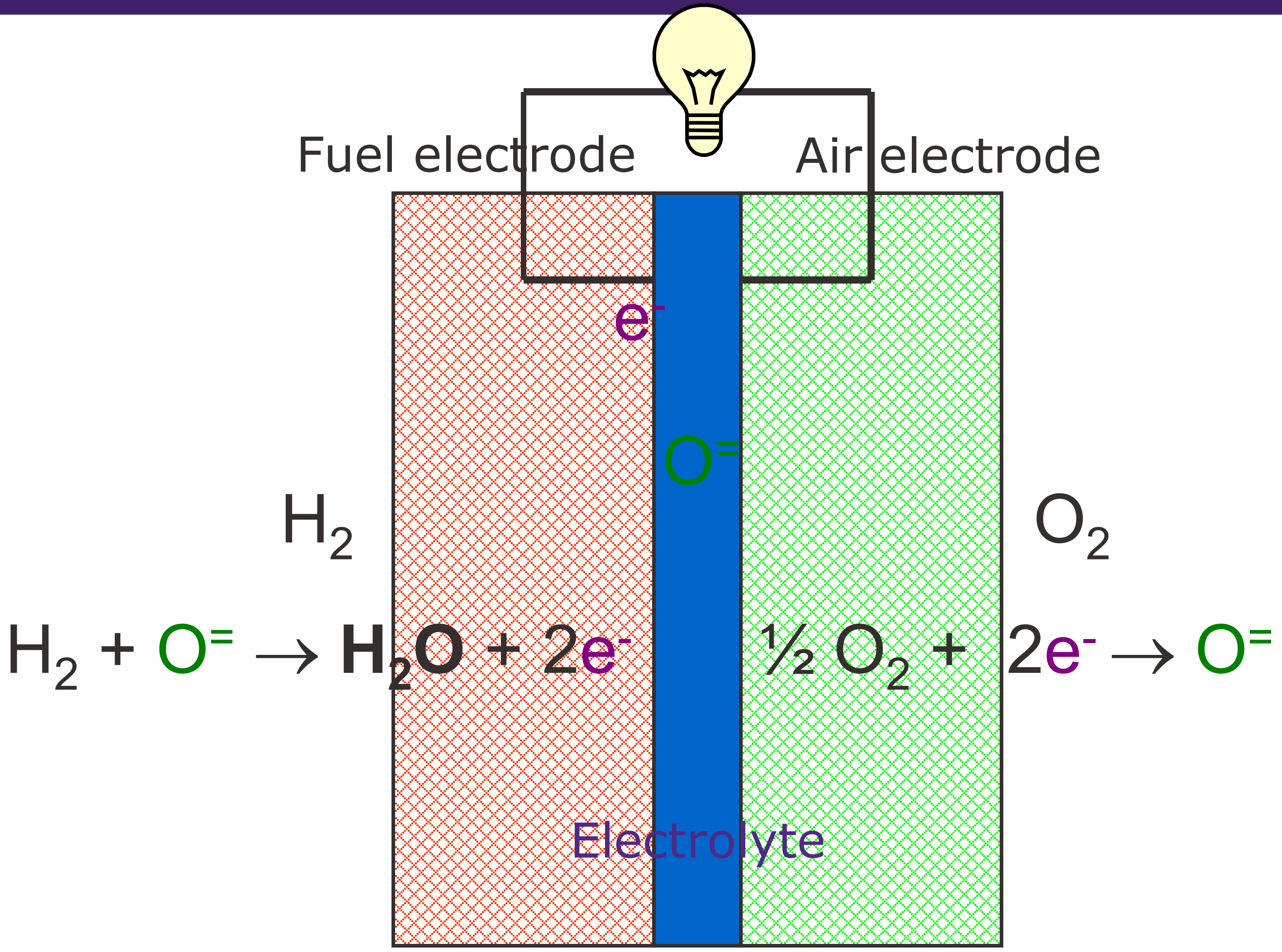
Sustainable Energy Cycle



Sustainable Energy Cycle



H_2/O_2 Reversible Electrochemical Cell



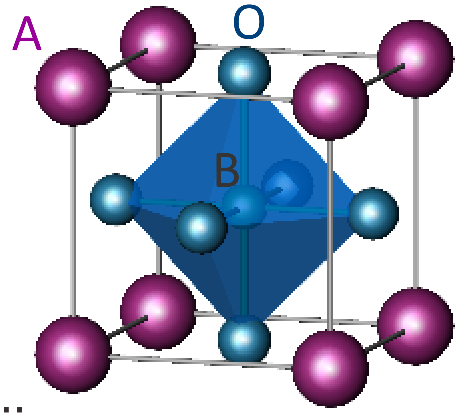
Overall: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

Oxygen Electroreduction / Evolution

reduction (electricity generation)

$$O_2 + 4e^- \rightleftarrows 2O^{2-}$$

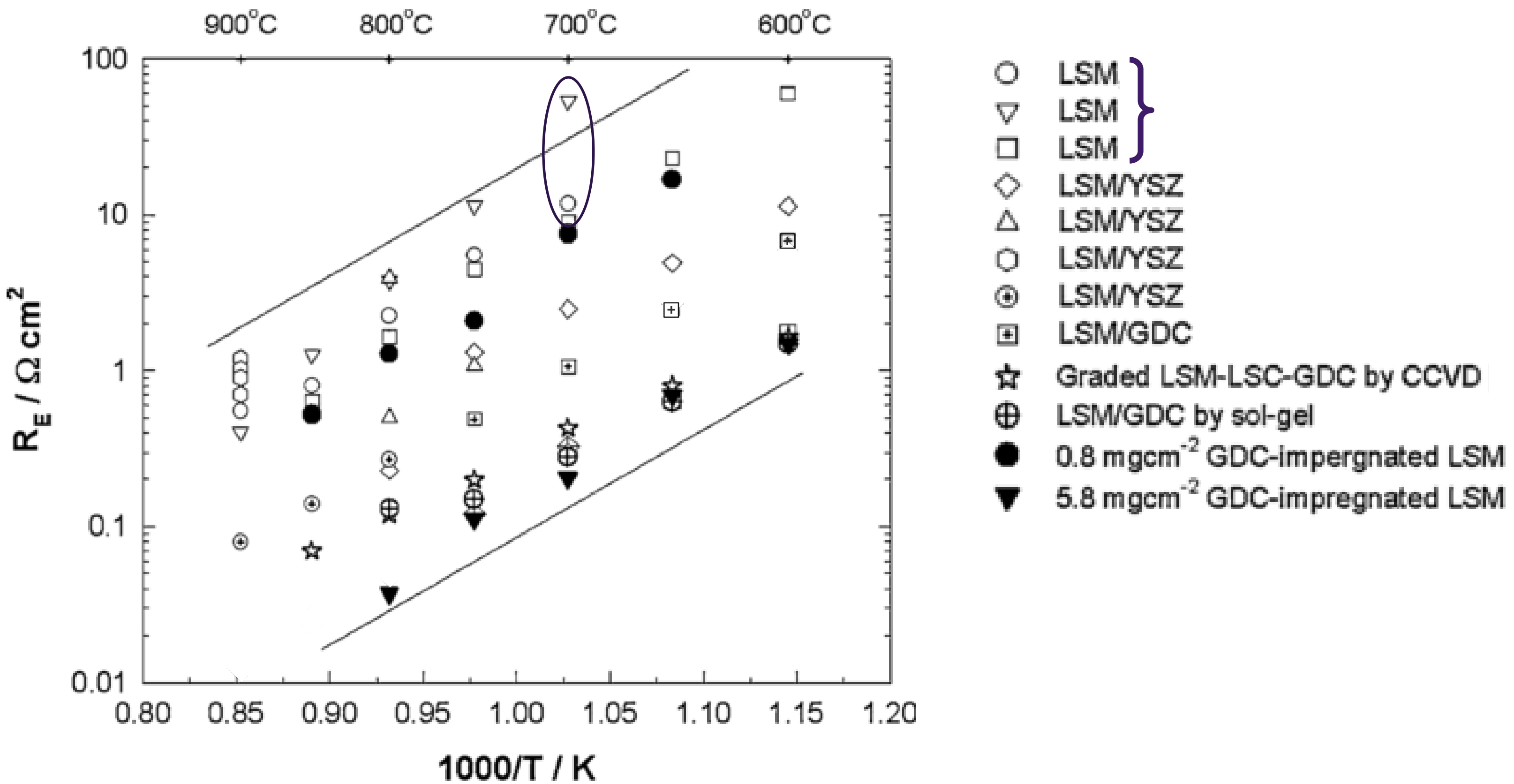
evolution (fuel generation)



- Typically, perovskite oxides: ABO_3
  - A = Ba, Sr, La, RE… ; B = Co, Fe, Mn, TM..
- ***Vast*** composition space
- Reaction pathway varies depending on
  - Material composition
  - Temperature
  - Environmental conditions (gas vs. liquid, concentration, pH)
- ***Vast*** parameter space

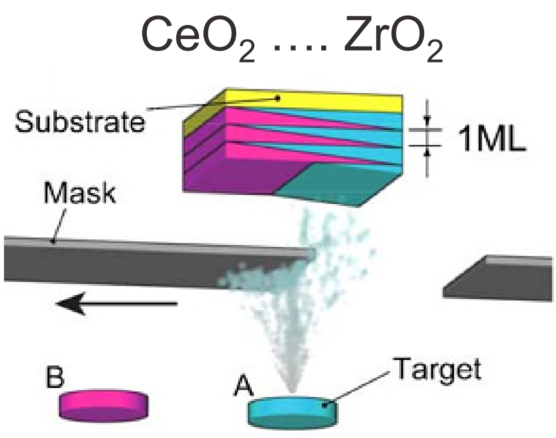
Range of Interfacial Resistance Values

Canonical cathode material: (La,Sr)MnO_3, LSM

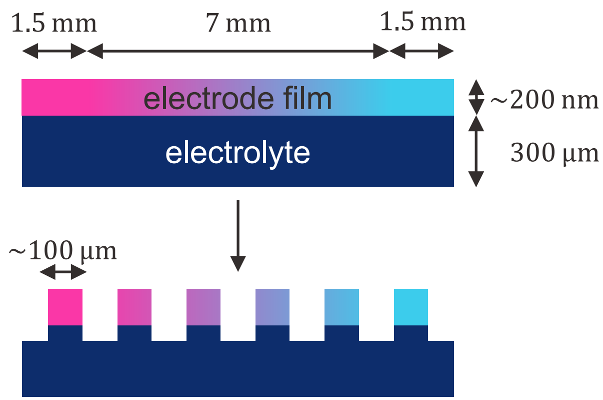


S. Jiang. *J. Mater. Sci.* **43**, 6799-6833 (2008)

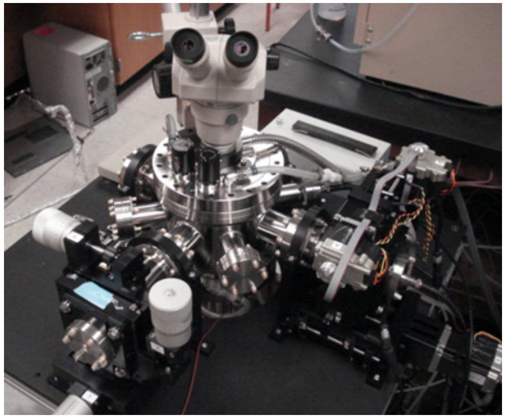
High-throughput methodology



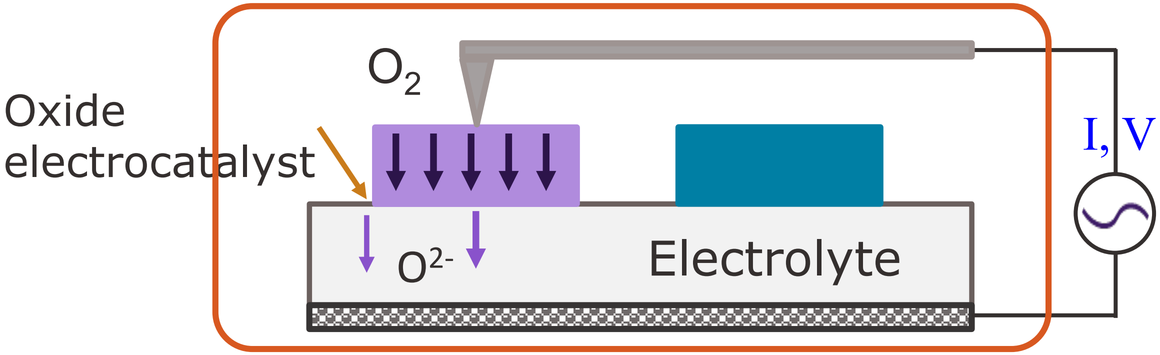
Gradient library

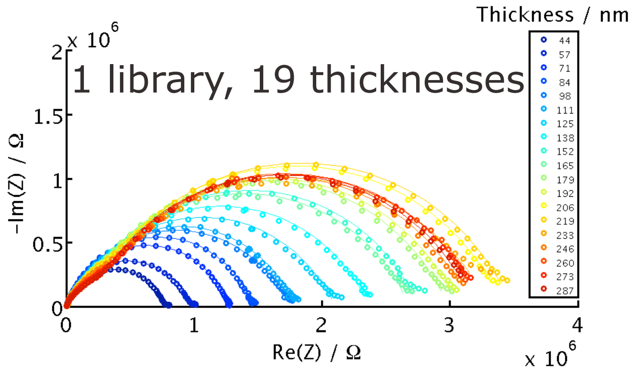


Photolithographic patterning



Environmental scanning electrical impedance probe



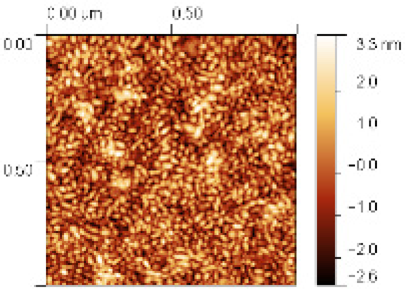


MRS Bull. **27**, 301-308 (2002)

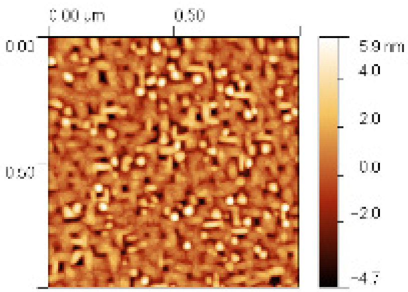
J. Mater. Chem. **A 3**, 19330-19345 (2015)

Example: $(La_{0.8}Sr_{0.2})MnO_3$

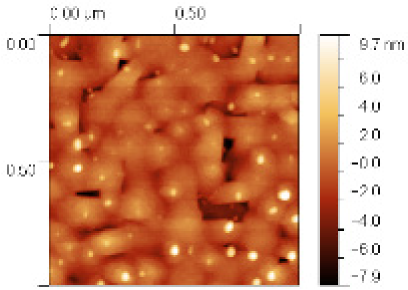
Growth temperature gradient $\Rightarrow$ microstructure / surface structure gradient



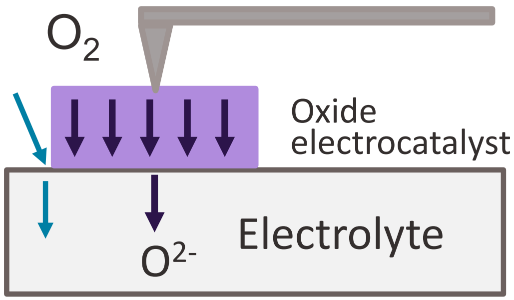
555˚C

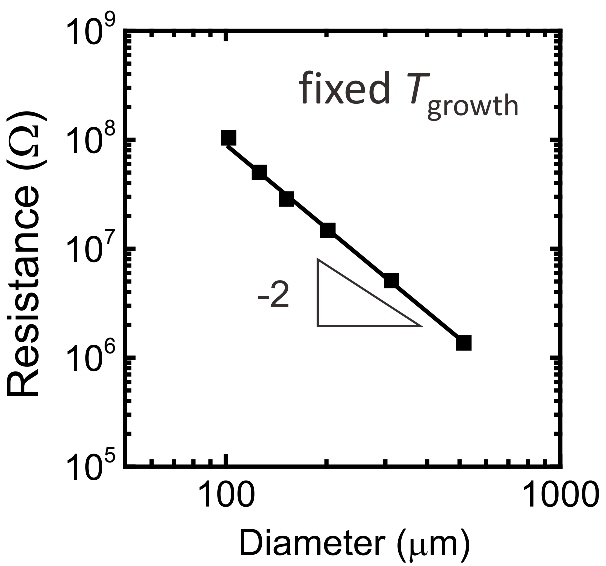


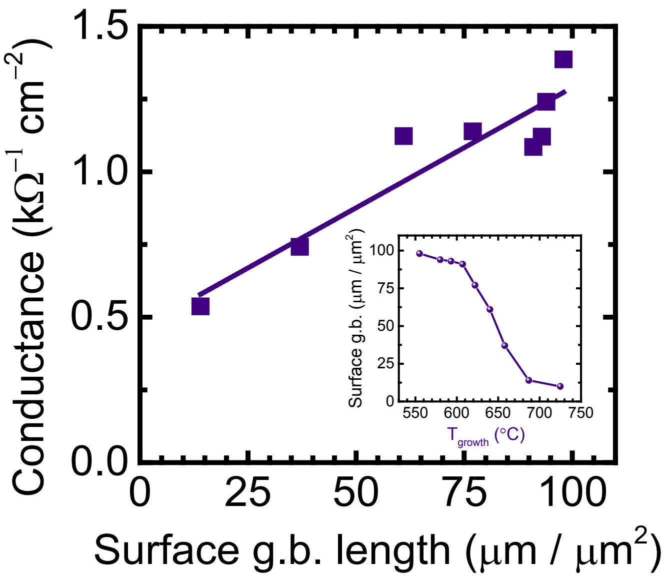
640˚C



725˚C







$$O_2 + 4e^- \rightleftarrows 2O^{2-}$$

Electrocatalysis enhanced at exposed grain boundaries!

J. Mater. Chem. **A 3**, 19330-19345 (2015)

Acknowledgments

- Key Researchers:
  - Dr. Tim Davenport
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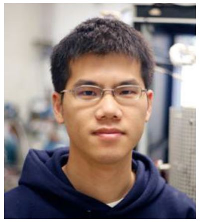
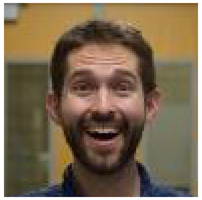
  - Dr. Rob Usiskin,
  - Soon-to-be Dr. Chris Kucharczyk



- Collaborators:
  - Aldo Steinfeld and team at ETH, Zurich
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  - ARPA-e HEATS Program
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- Research Group