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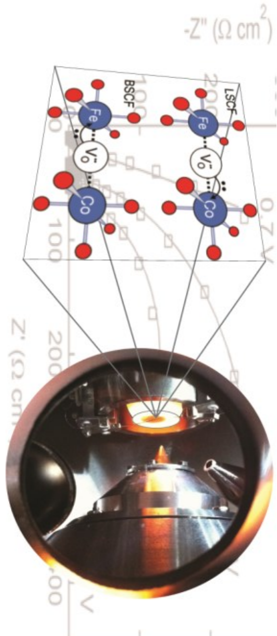

Operando spectroscopy: Insights into chemical and electrochemical activity of oxides used for energy conversion

Anthony H. McDaniel

Sandia National Labs

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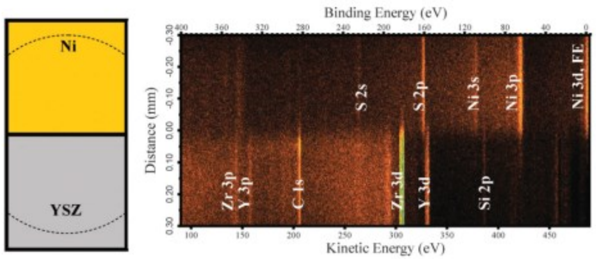
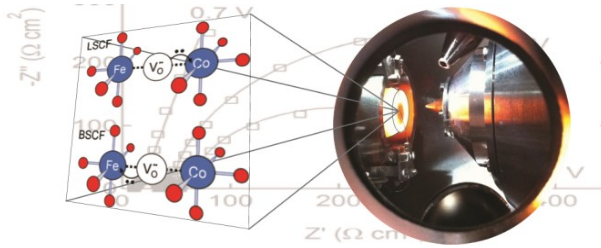
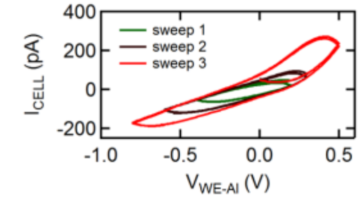
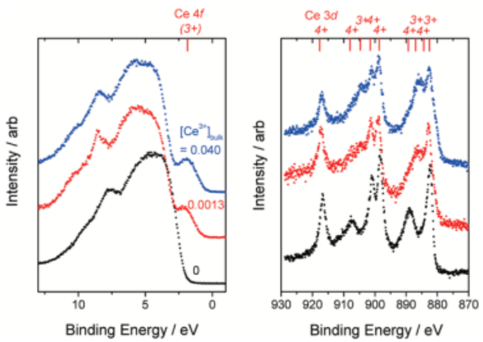
- ALS BL 9.3.2
  - Zhi Liu
  - Michael Grass
- ALS BL 5.3.2
  - David Kilcoyne

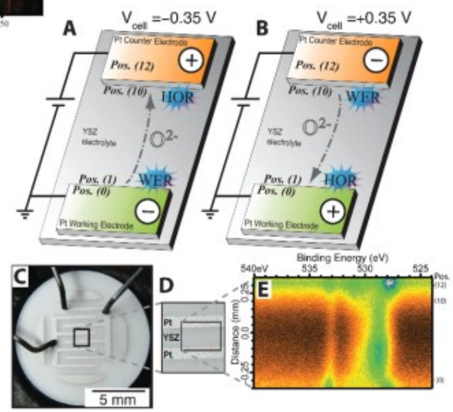
Operando measurements on energy materials using soft x-rays.

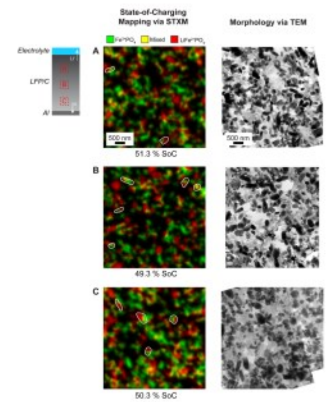


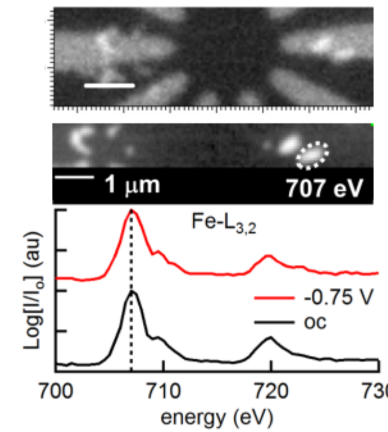












El Gabaly, F. et al. Oxidation Stages of Ni Electrodes in Solid Oxide Fuel Cell Environments, *Phys. Chem. Chem. Phys.* **15**, 8334 (2013).

Chueh, W. C. *et al.* Intercalation Pathway in Many-Particle $LiFePO_4$ Electrode Revealed by Nanoscale State-of-Charge Mapping. *Nano Letters* **13**, 866–872 (2013).

Chueh, W. C. *et al.* Highly Enhanced Concentration and Stability of Reactive Ce^{3+} on Doped CeO_2 Surface Revealed In Operando. *Chem. Mat.* 120507111054001 (2012).

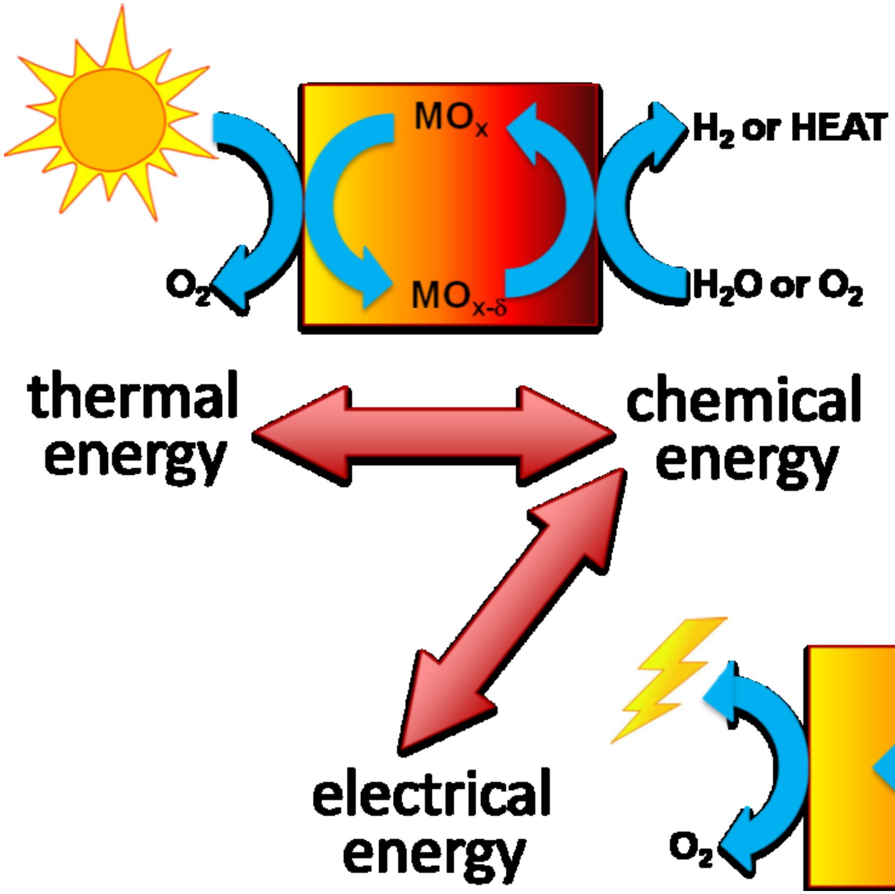
El Gabaly, F. *et al.* Electrochemical Intermediate Species and Reaction Pathway in H_2 Oxidation on Solid Electrolytes. *Chem. Comm.* **48**, 8338 (2012).

El Gabaly, F. *et al.* Measuring Individual Overpotentials in an Operating Solid-Oxide Electrochemical Cell. *Phys. Chem. Chem. Phys.* **12**, 12138 (2010).

Outline.

- Motivation.
- Summarize efforts to build soft x-ray user platforms for operando studies.
  - Electrochemical methods
  - Ambient pressure photoemission (APXPS)
  - X-ray absorption (NEXAFS)
- Examples.
  - Thermal redox of iron oxide
  - Electrochemical reduction of O_2 on a perovskite cathode
- Challenges and plea to theoreticians.

Metal oxides are in important class of energy conversion materials.

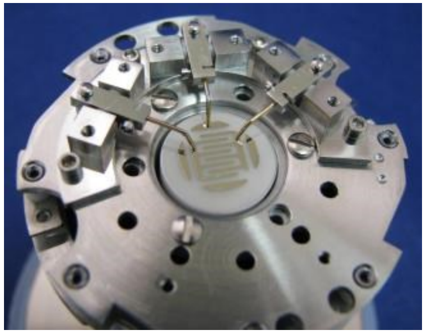


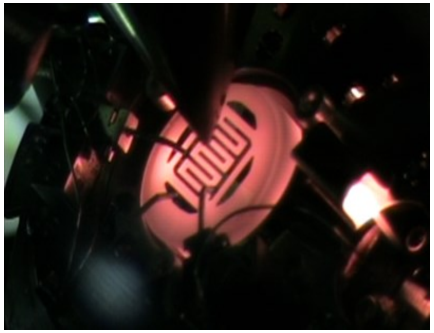
Knowledge gaps:

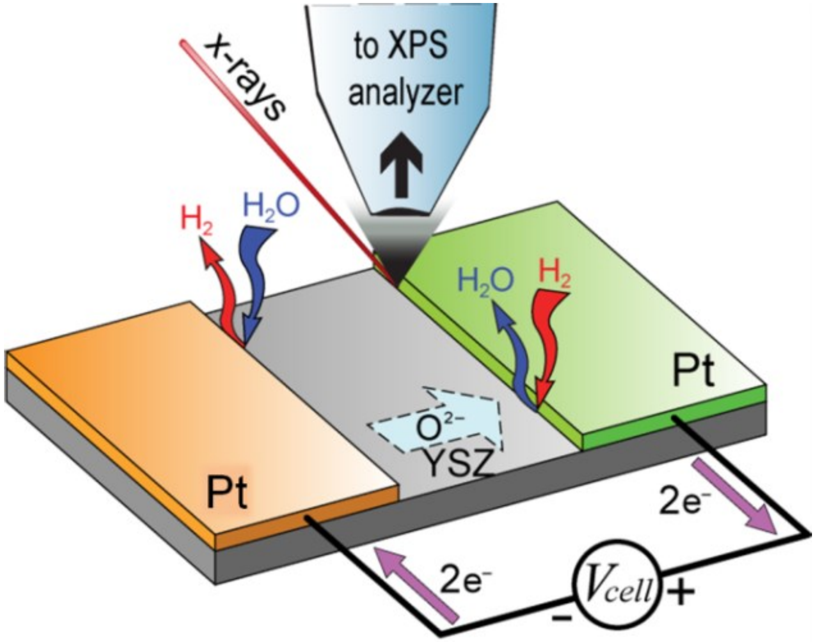
- What is the chemical state of the reactive surface?
- What are the rate limiting processes?
- How does the surface differ from bulk?

One environment configuration.

- Surface states.
  - Core level XPS
  - VB photoemission
  - XAS partial electron yield
  - Local potential
- Macroscopic behavior.
  - Impedance spectroscopy
  - Potential steps/sweeps
  - Reaction rates
- Electrolytic half-cell.



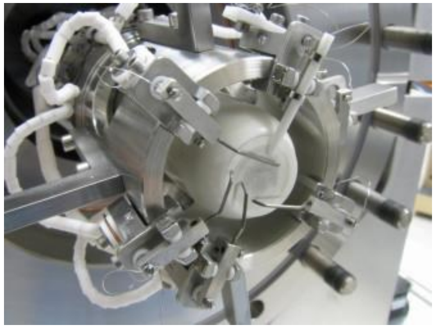


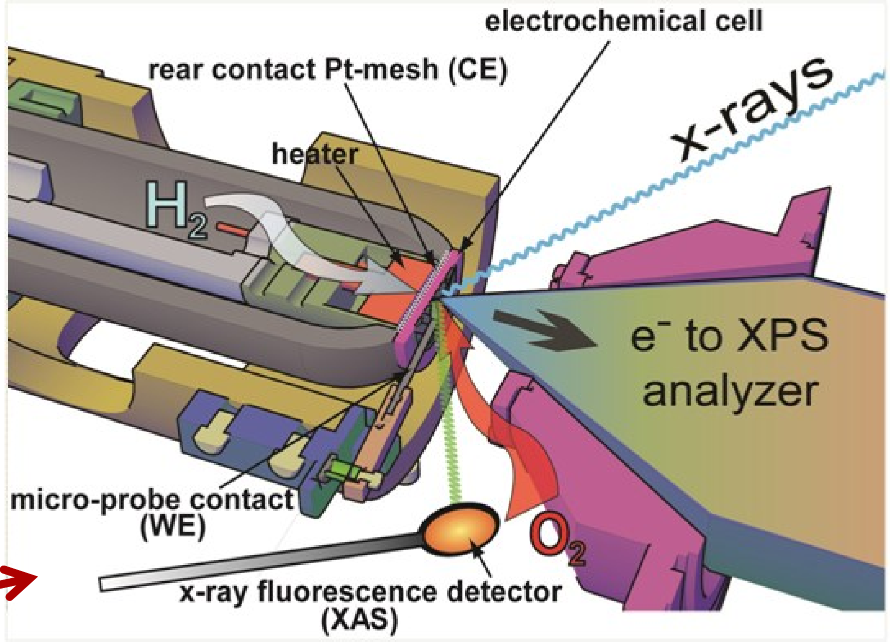


J. A. Whaley *et al.*, Note: Fixture for Characterizing Electrochemical Devices in-operando in Traditional Vacuum Systems, *Rev. Sci. Instrum.* **81**, 086104 (2010).

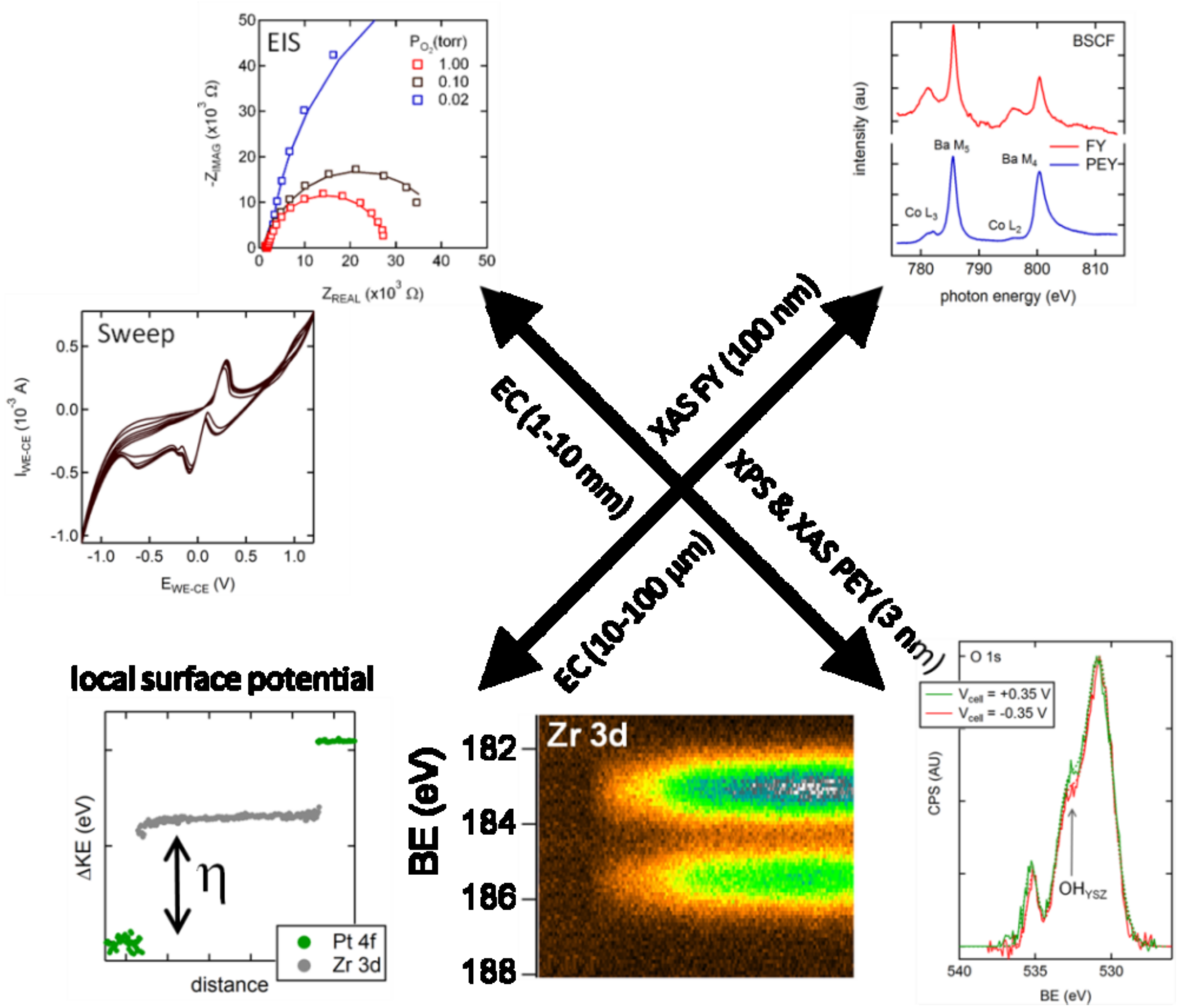
Two-environment configuration.

- Surface states.
  - Core level XPS
  - VB photoemission
  - XAS partial electron yield
  - Local potential
- Bulk states.
  - XAS fluorescent yield
- Macroscopic behavior.
  - Impedance spectroscopy
  - Potential steps/sweeps
  - Reaction rates
- Galvanic full-cell.

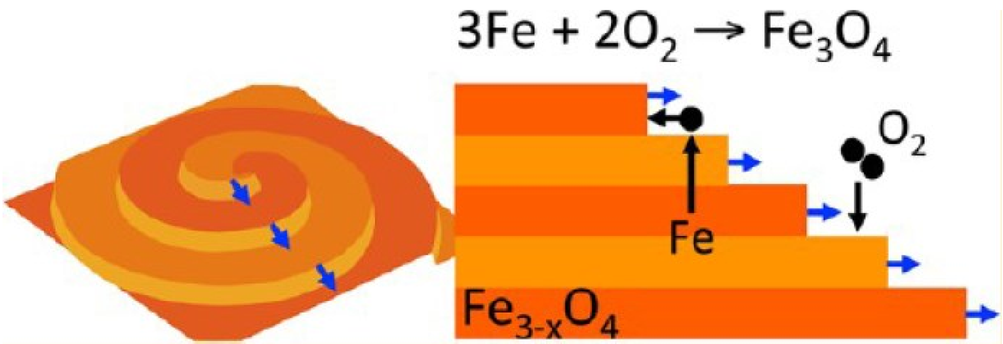




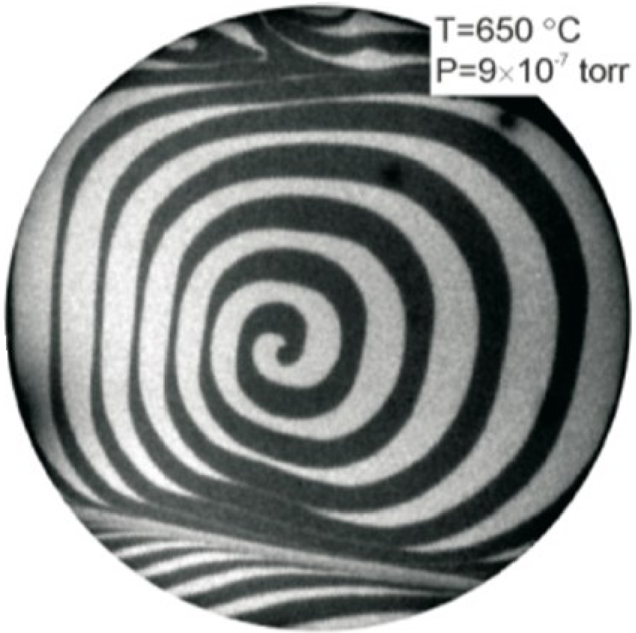
Suite of characterization tools available.



thermal energy ⟷ chemical energy



LEEM image



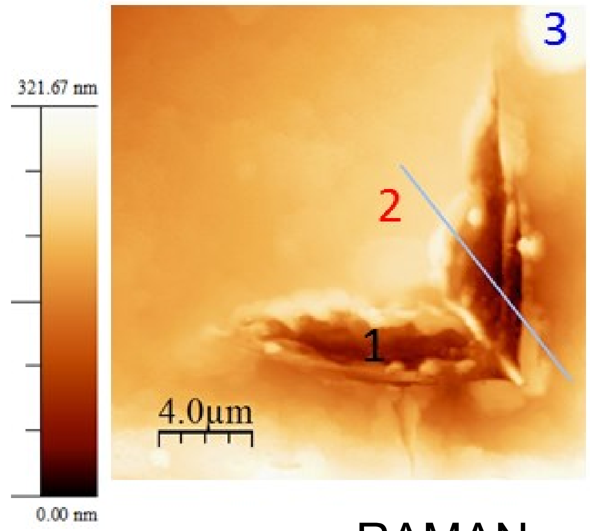
- Fe(II/III) redox is an important reaction.
  - Chemical looping
  - Fischer-Tropsch
  - Water splitting
  - Thermal storage
- Formation of surface Fe_3O_4 during oxidation at 650 °C observed by LEEM.
- New Fe must come from bulk.

S. Nie *et al.*, Insight into Magnetite's Redox Catalysis from Observing Surface Morphology during Oxidation, *Journal of the American Chemical Society* **135**, 10091–10098 (2013).

α-Fe_2O_3 inclusions form during oxidation.

- Heterogeneous surface composition discovered by Raman.
- α-Fe_2O_3 region recessed from surface.
  - 2-D array of hematite stripes
  - Surface Fe_3O_4 grows faster near inclusions
  - γ-Fe_2O_3 phase not found

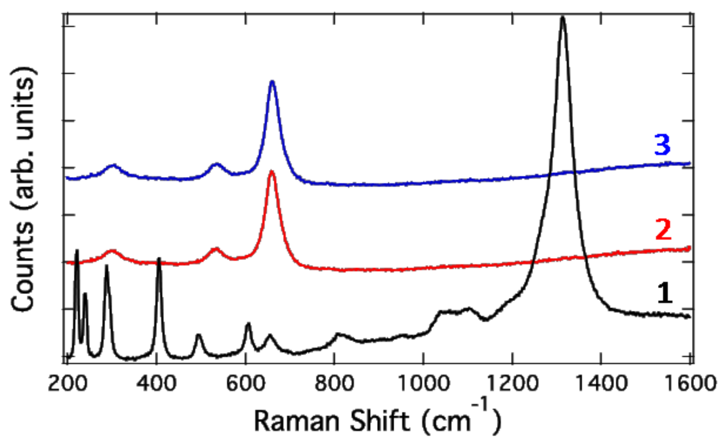
AFM



2, 3 = Fe_3O_4

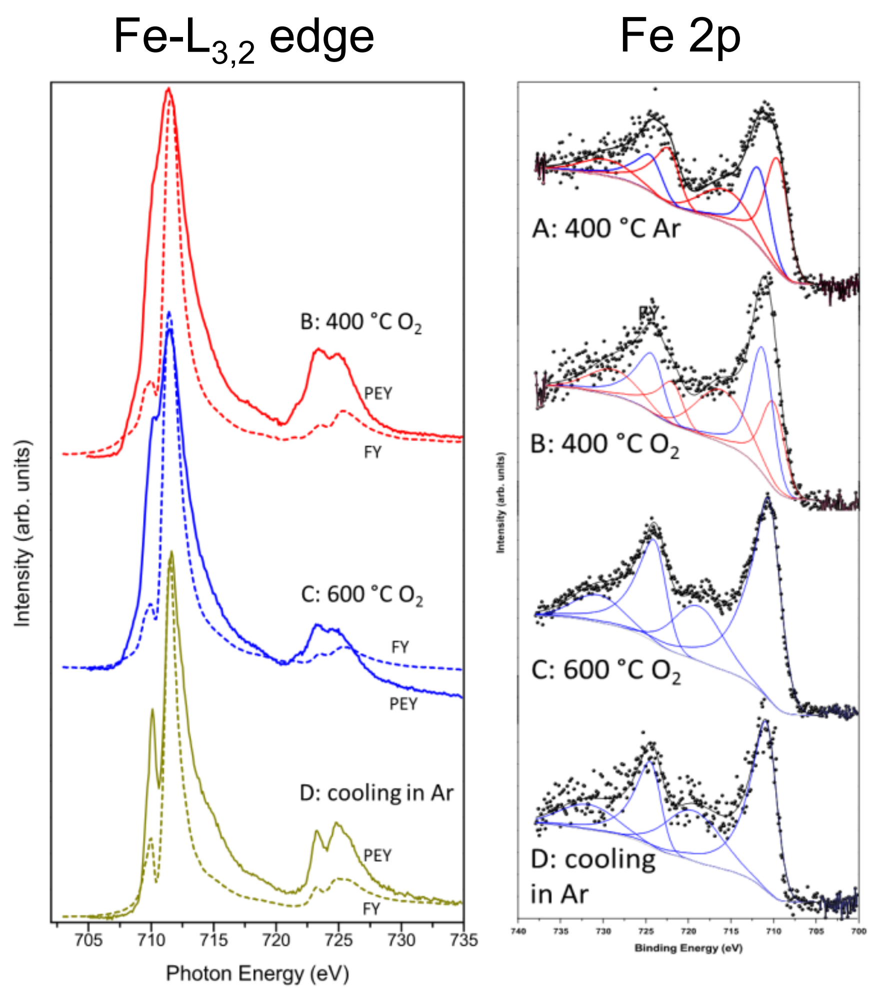
1 = α-Fe_2O_3

RAMAN

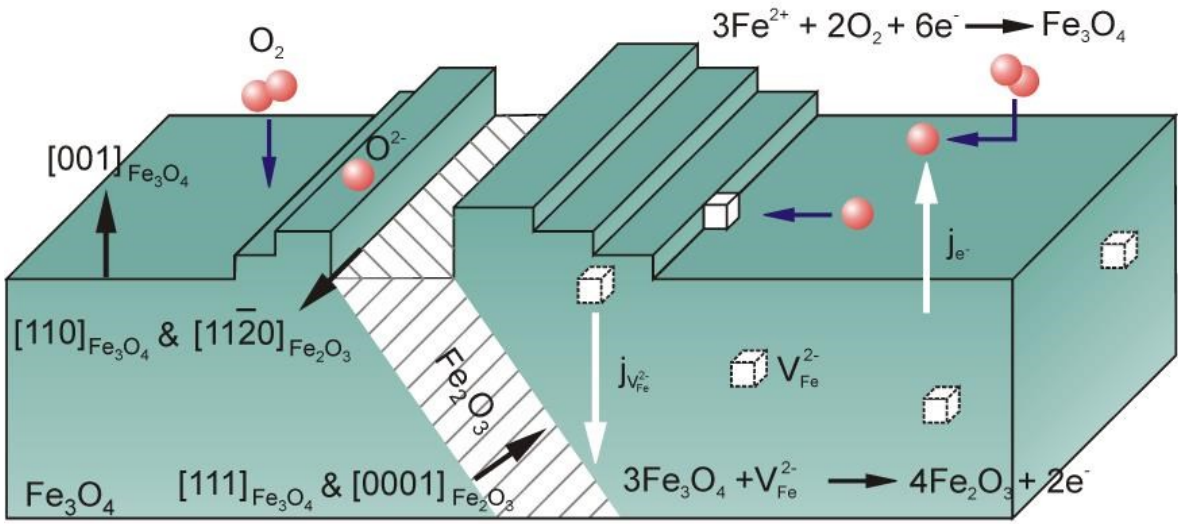


XPS and XAS show bulk more oxidized than surface.

- PEY and FY spectra differ at low Temperature.
  - Evidence for Fe^{2+} on surface
- XPS best described by mixture of Fe^{2+} and Fe^{3+} peaks.
- After oxidation at 600 °C:
  - PEY and FY spectra similar



Picture of Fe_3O_4 oxidation.



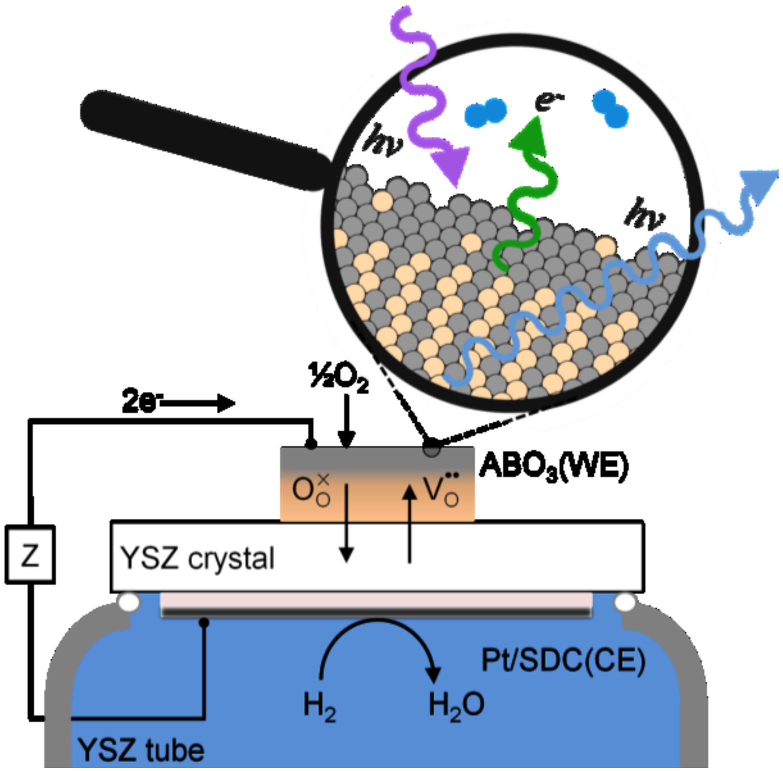
- O_2 dissociates everywhere on the surface.
- Magnetite forms on surface creating Fe vacancies.

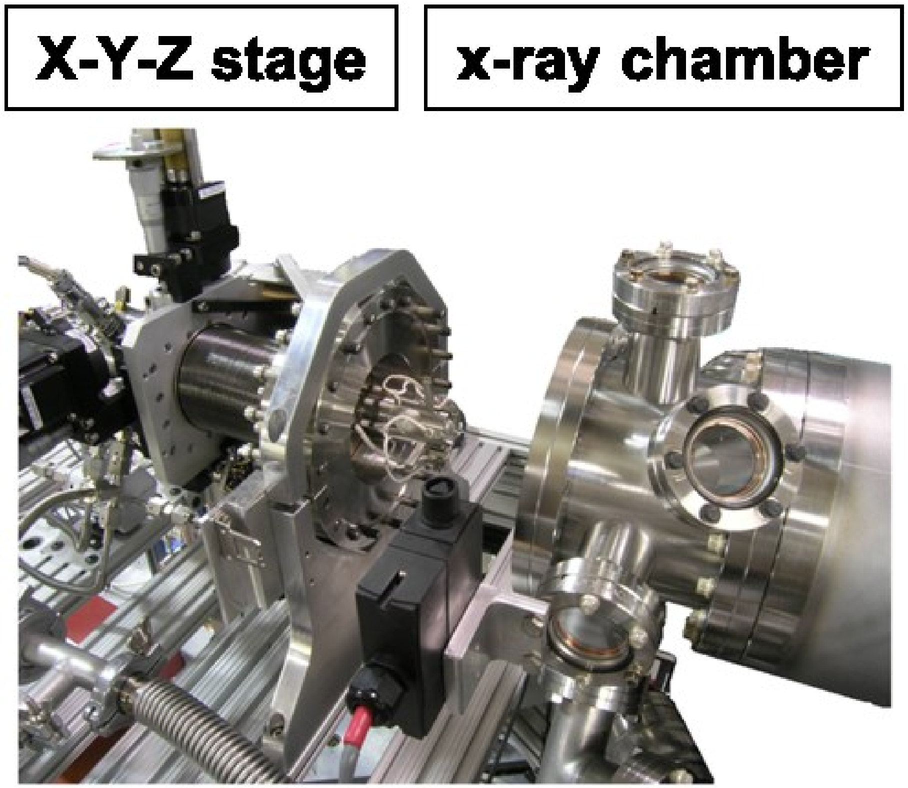
$$3Fe^{2+} + 2O_2 + 6e^- \rightarrow Fe_3O_4$$

- Subsurface nucleation and growth of hematite inclusions.

$$3Fe_3O_4 + V_{Fe}^{2-} \rightarrow 4Fe_2O_3 + 2e^-$$

Custom chamber for SOFC studies.





- Fully functioning SOFC.
  - T ~ 650 °C, 0.67 mbar O_2 on cathode, 0.67 mbar H_2/H_2O on anode
  - 1.0 V Nernst potential

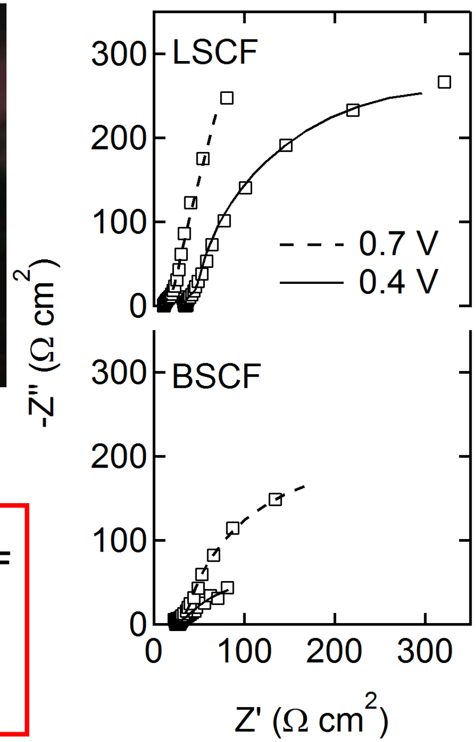
electrical energy ⟷ chemical energy

- Oxygen reduction reaction (ORR).
  - Important rate limiting step
- State-of-the-art cathodes.
  - $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF)
  - $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)
- Ba substitution dramatically increases ORR rate.
  - $R_{Ba(2+)} > R_{La(3+)}$ expands lattice
  - Charge difference affects B-site

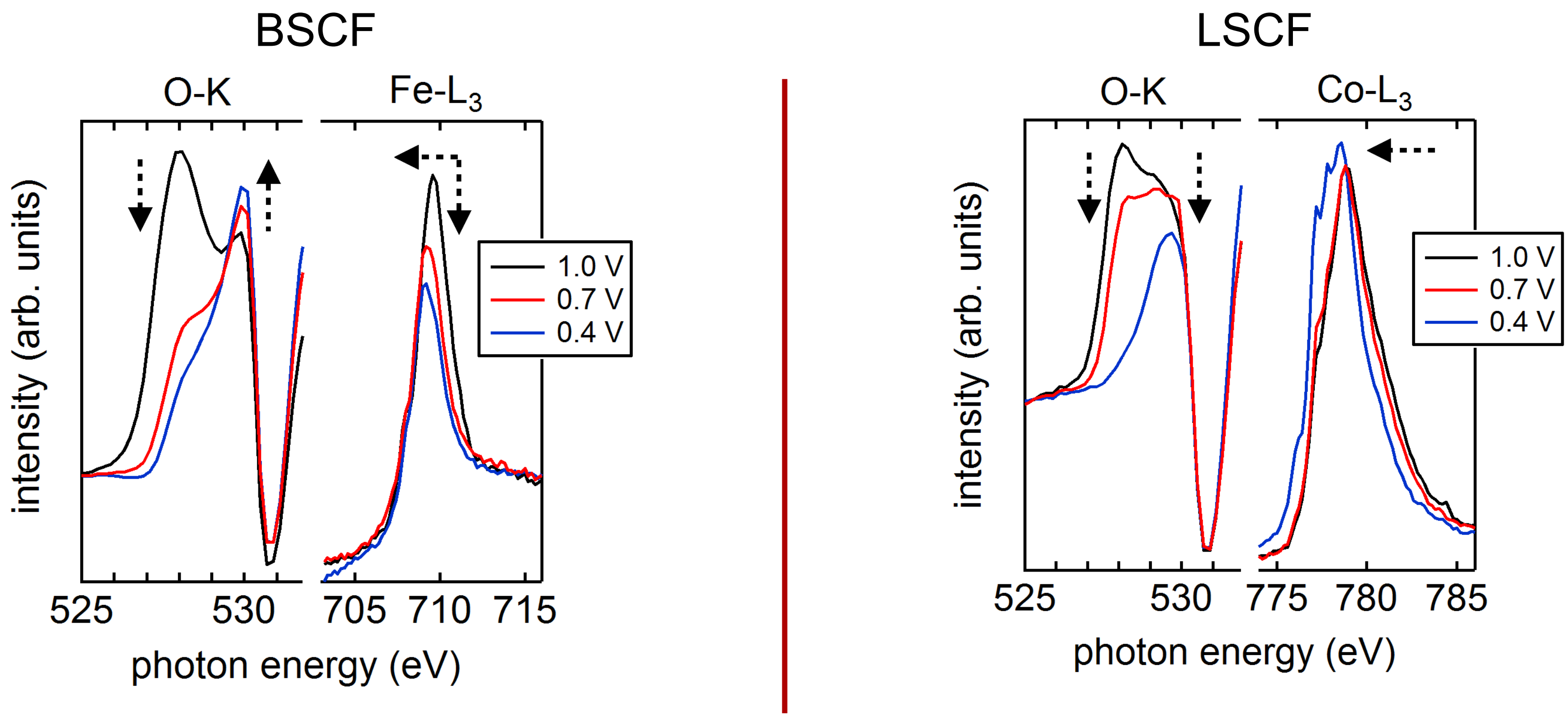
    $(BaSr)^{2+}(B'B)^{4+}$ vs. $(LaSr)^{2.5+}(B'B)^{3.5+}$

$\text{Rate}_{BSCF} >> \text{Rate}_{LSCF}$

$$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$$



XAS reveals differences in bulk behavior.



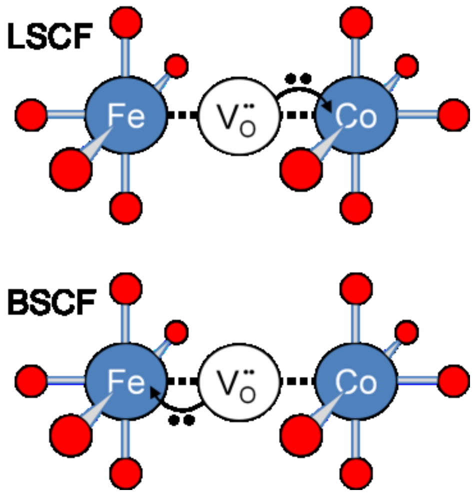
- Fe reduced in BSCF when Vö form electrochemically.
- Co reduced in LSCF when Vö form electrochemically.
- BSCF more strongly reduced at lower overpotentials.

Theory needed for detailed understanding.

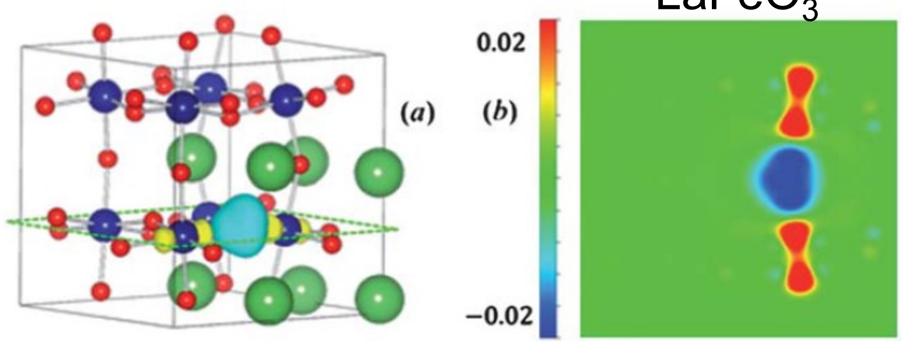
- TM likely in mixed ground states.

  $3d^n + 3d^{n+1}L_0$
- Correlate TM-O covalency to:
  - Vacancy formation energy
  - Vacancy concentration
  - ORR activity
- Where do the electrons go?
  - Localized to TM-Vö defect
  - De-localized
  - Disproportionate

too simple?

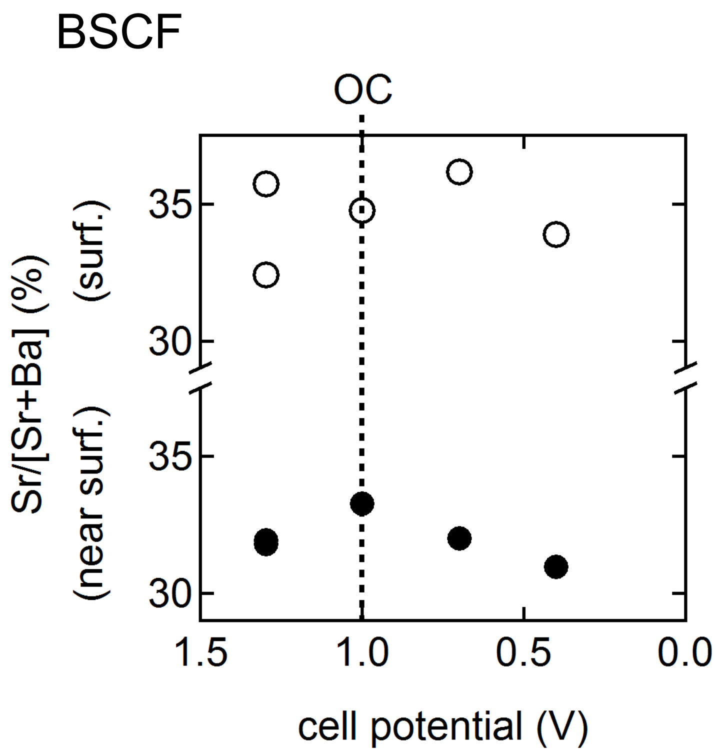


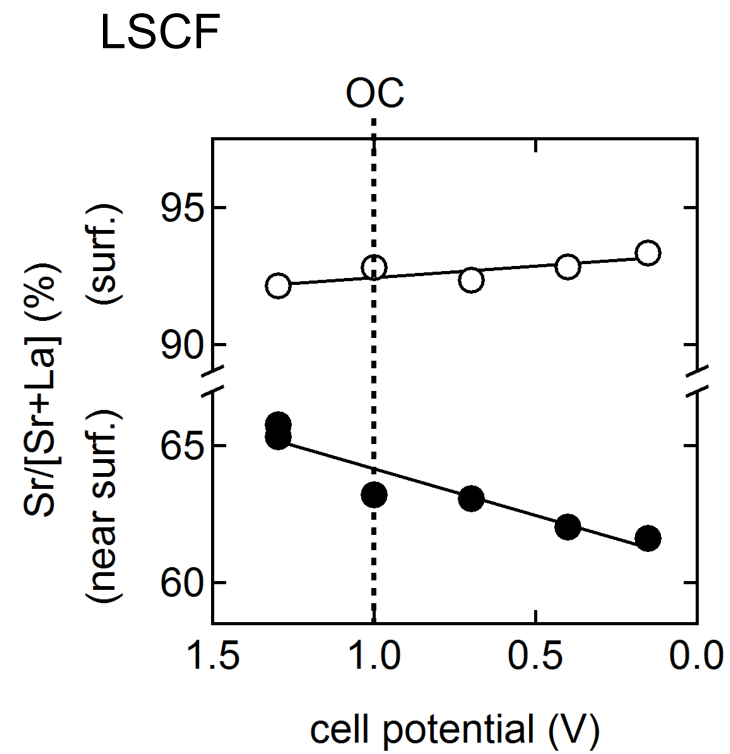
LaFeO$_3$



M. Pavone, A. M. Ritzmann, E. A. Carter, Quantum-mechanics-based design principles for solid oxide fuel cell cathode materials, *Energy Environ. Sci.* **4**, 4933 (2011)

XPS reveals differences in surface composition.

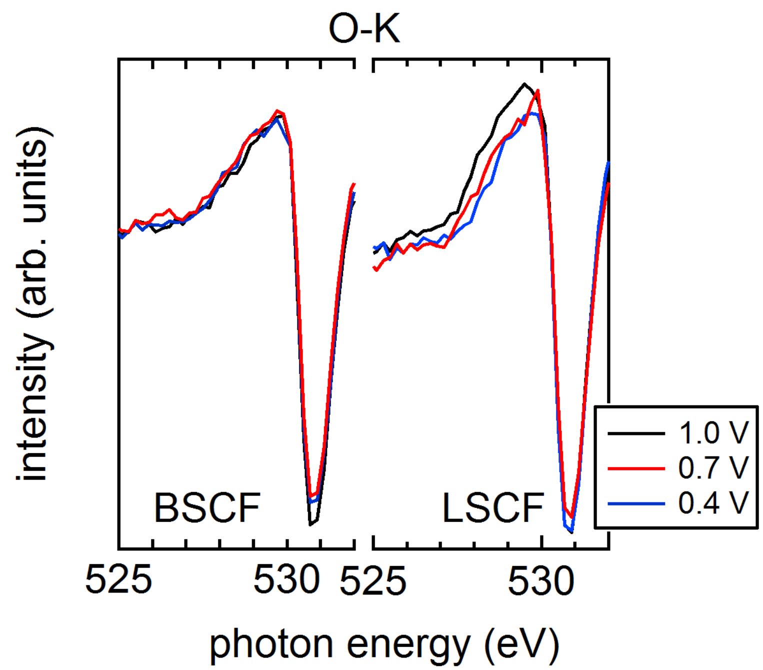




- Surface Ba-rich in BSCF (stoichiometric = 50%).
- Surface Sr-rich in LSCF (stoichiometric = 40%).
  - Perovskite phase no longer predominant at surface

2p-(Fe,Co)3d hole states diminished at surface.

- Surface composition dominated by oxides of Ba and Sr.
  - O stoichiometry very different
- BO_6 symmetry broken?
- High surface vacancy concentration?
- Can theory improve our understanding?
  - Very complex systems...



Will there be a day when we have unlimited access to x-rays?

SLAC NATIONAL ACCELERATOR LABORATORY

Researchers Demonstrate 'Accelerator on a Chip'

Technology could spawn new generations of smaller, less expensive devices for science, medicine

September 27, 2013

Menlo Park, Calif. — In an advance that could dramatically shrink p
researchers used a laser to accelerate electrons at a rate 10 times
glass chip smaller than a grain of rice.

The achievement was reported today in *Nature* by a team including
SLAC National Accelerator Laboratory and Stanford University.

"We still have a number of challenges before this technology becon
substantially reduce the size and cost of future high-energy particl
particles and forces," said Joel England, the SLAC physicist who le
accelerators and X-ray devices for security scanning, medical ther
science."

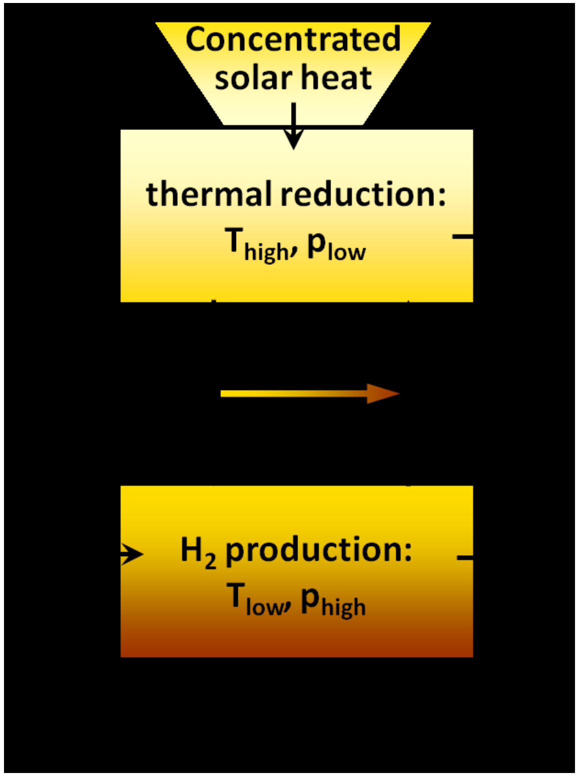
Nanofabricated chips of fused silica just 3 millimeters long were used to accelerate electrons at a rate 10 times higher than conventional particle accelerator technology. (Brad Plummer/SLAC)

THANK YOU

Backup Slides

Thermochemical fuel production.

MW scale concentrating solar power facilities exist today.



Two-step non-volatile metal oxide cycle :

$$CeO_2 \rightarrow CeO_{2-\delta} + \frac{\delta}{2} O_2$$ STEP 1 @ T_{high}, REDUCTION

$$CeO_{2-\delta} + \delta \cdot H_2O \rightarrow CeO_2 + \delta \cdot H_2$$ STEP 2 @ T_{low}, OXIDATION

$$\delta \cdot H_2O \rightarrow \frac{\delta}{2} O_2 + \delta \cdot H_2$$ NET RESULT

- The challenge is to develop efficient and scalable solar-powered reactors.

Thermochemical energy storage.

U.S. DEPARTMENT OF ENERGY
SunShot Initiative

Concentrating Solar Power: Efficiently Leveraging Equilibrium Mechanisms for Engineering New Thermochemical Storage (CSP: ELEMENTS)

Funding: Up to $20M Over 4 Years Total

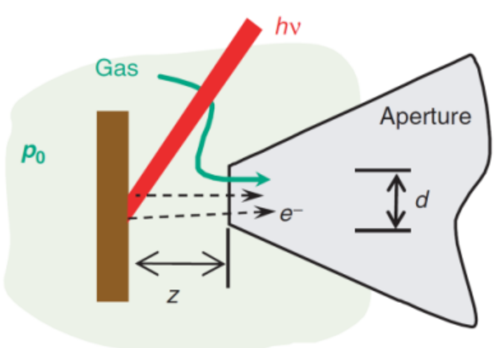
- Simple, non-volatile metal oxide thermal storage cycle.
  - Store reduced oxide at night
  - Recover oxidation enthalpy to run power block

$$MO_x \leftrightarrow MO_{x-\delta} + \frac{\delta}{2} O_2$$

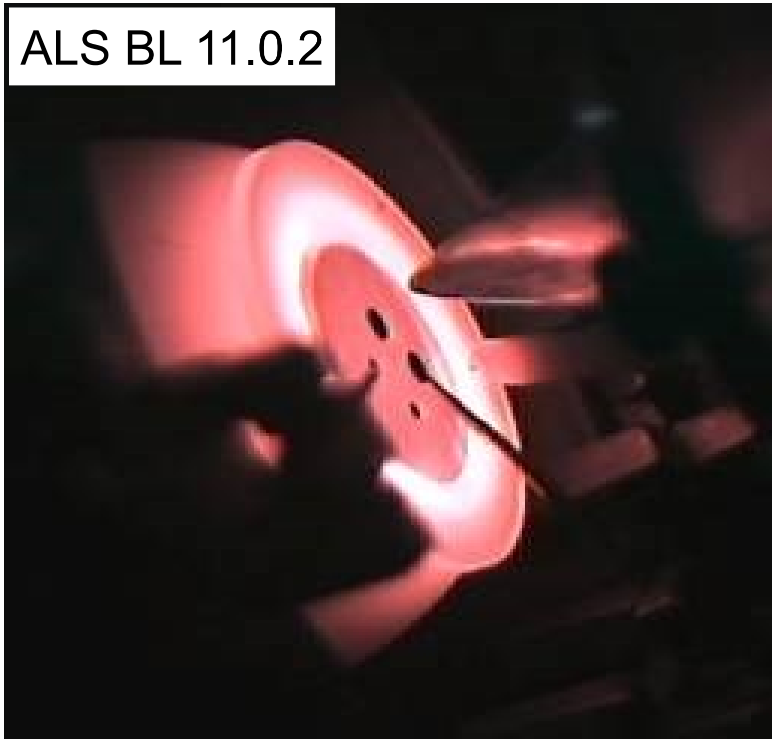
MW scale concentrating solar power facilities exist today.

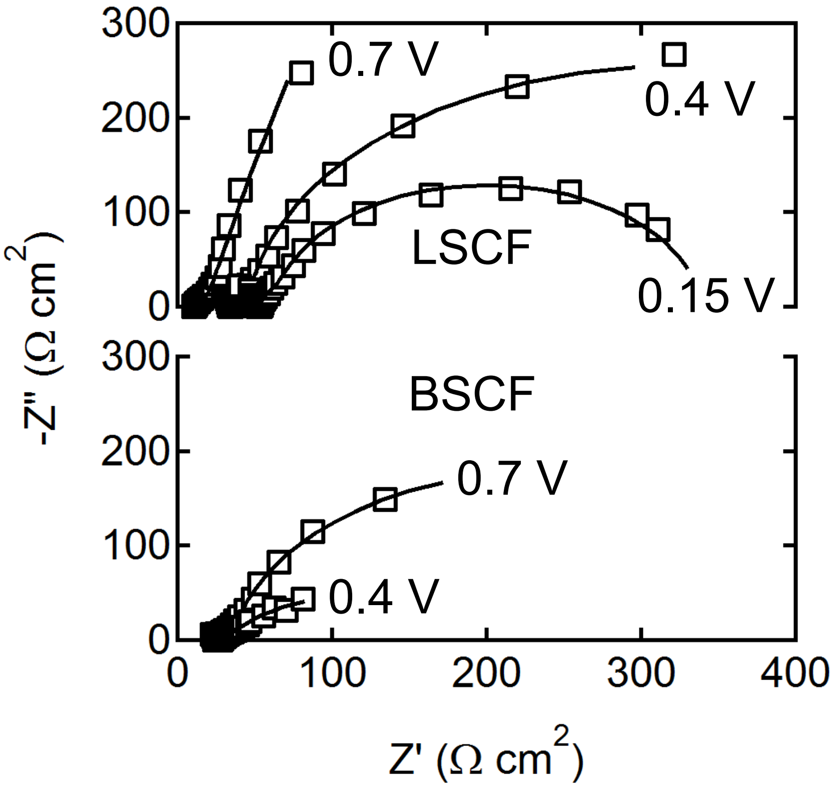
Revealing insights near ambient pressure

- Challenge:
  - Spectroscopy of electrified interfaces exposed to gases
- Solution:
  - Ambient pressure X-ray photoelectron spectroscopy
- Soft X-rays and electrochemist on BL 11.0.2 and BL 9.3.2



Bluhm, H. et al., MRS Bulletin-Materials Research Society, **32**, 1022 (2007)


ALS BL 11.0.2


0.7 V
0.4 V
LSCF
0.15 V
BSCF
0.7 V
0.4 V
-Z'' (Ω cm²)
Z' (Ω cm²)
300
200
100
0
0
100
200
300
400

STXM images of a biased liquid cell containing $LiFePO_4$ particles