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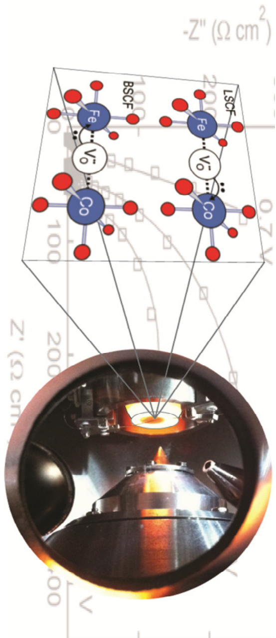

Probing Surface and Bulk States of Electrode Materials With Synchrotron-based Soft X-rays in a Functioning Solid Oxide Fuel Cell

Anthony H. McDaniel

Sandia National Labs

Sandia National Laboratories

Exceptional service in the national interest

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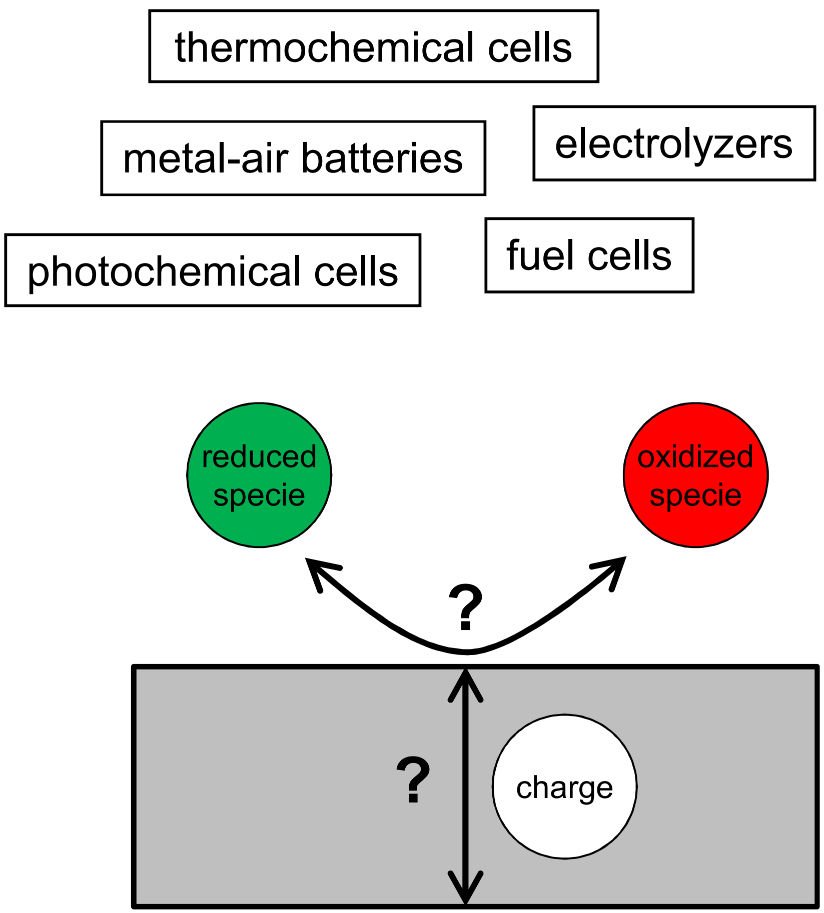
Outline.

- Motivation.

- Summarize efforts to build *soft x-ray* user platforms for operando studies.
  - Ambient pressure photoemission (APXPS)
  - X-ray absorption (XANES)

- SOFC systems we have investigated.
  - H_2 oxidation and H_2O reduction on a platinum electrode
  - O_2 reduction on a perovskite electrode

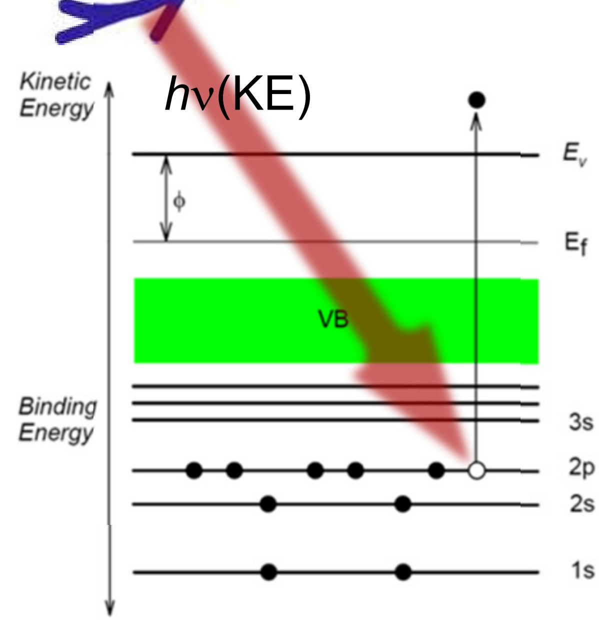
Chemistry and charge transfer at interfaces drive many electrochemical technologies.

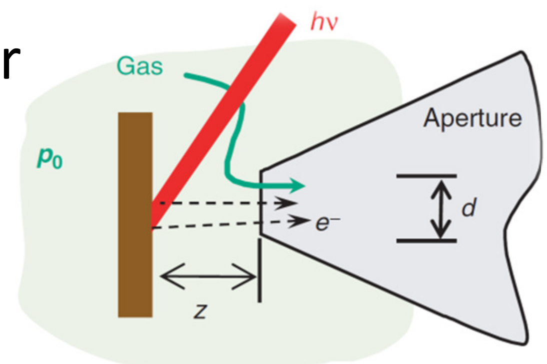


- What is largely unknown:
  - The chemical state of the reactive surface
  - The rate limiting processes
  - Differences between surface and bulk
- Clear need to experiment under operating conditions.
  - SOFC environment is hostile
    - high temperature
    - “high” pressure

Ambient pressure XPS.

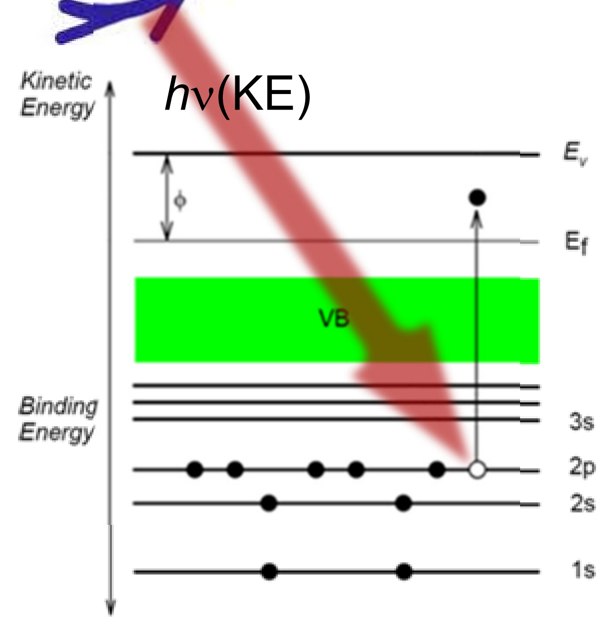
- Photon in — electron out (XPS).
  - Measure kinetic energy of electrons at fixed photon energy
- Probe electronic states of atoms near surface.
  - Identify surface species
  - Resolve oxidation state
  - Measure surface potential
- Differentially pumped analyzer
  - BL 11.0.2 and BL 9.3.2
  - operate at 10 Torr and 700 °C

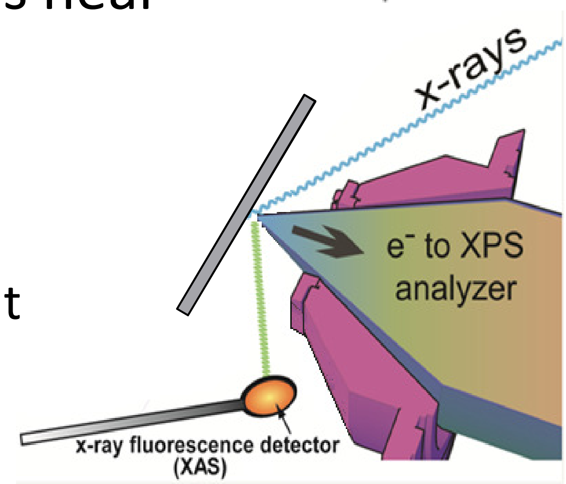




X-ray absorption (XANES).

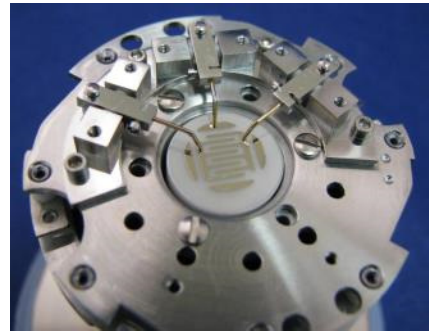
- Photon in — electron out (EY, surface).
  - Measure electron flux while scanning photon energy across absorption edge
- Photon in — photon out (FY, bulk).
  - Measure fluorescent photon flux while scanning photon energy across absorption edge
- Probe electronic states of atoms near surface and in bulk.
  - Identify species
  - Resolve oxidation state
  - Resolve coordination environment
  - Assess ligand field effects

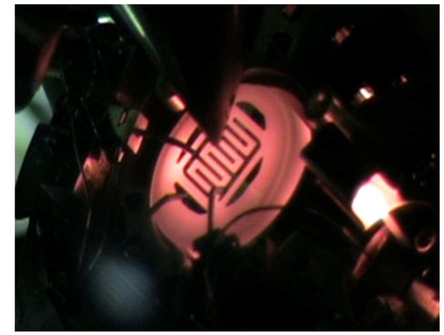


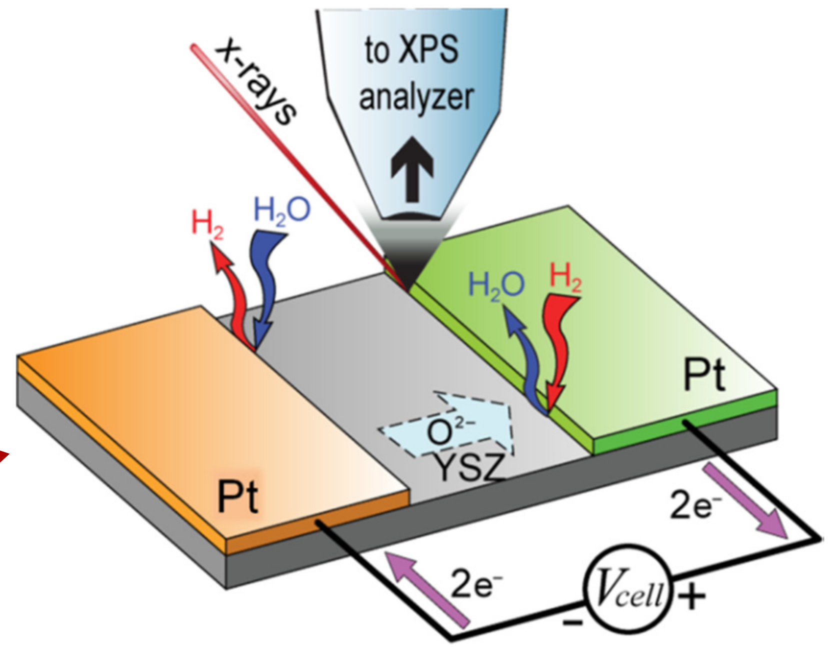


One environment configuration.

- 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.



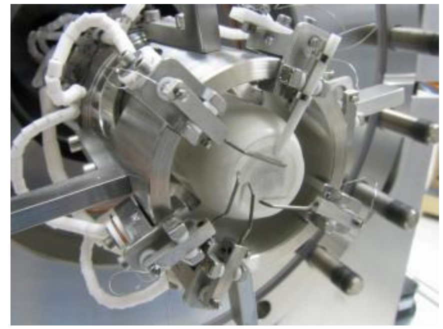


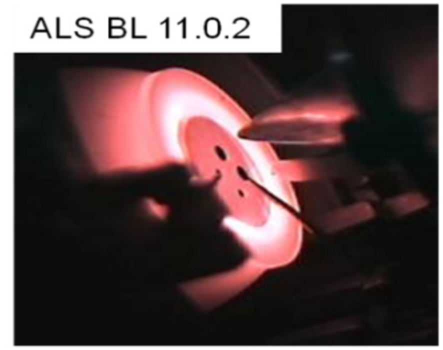


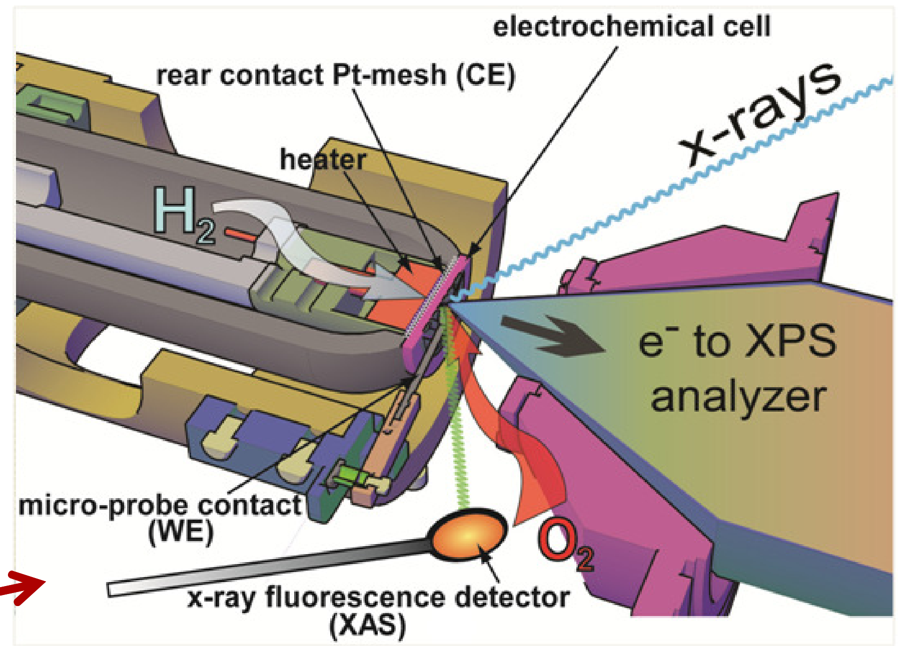
J. A. Whaley *et al.*, *Rev. Sci. Instrum.* **81**, 086104 (2010).

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

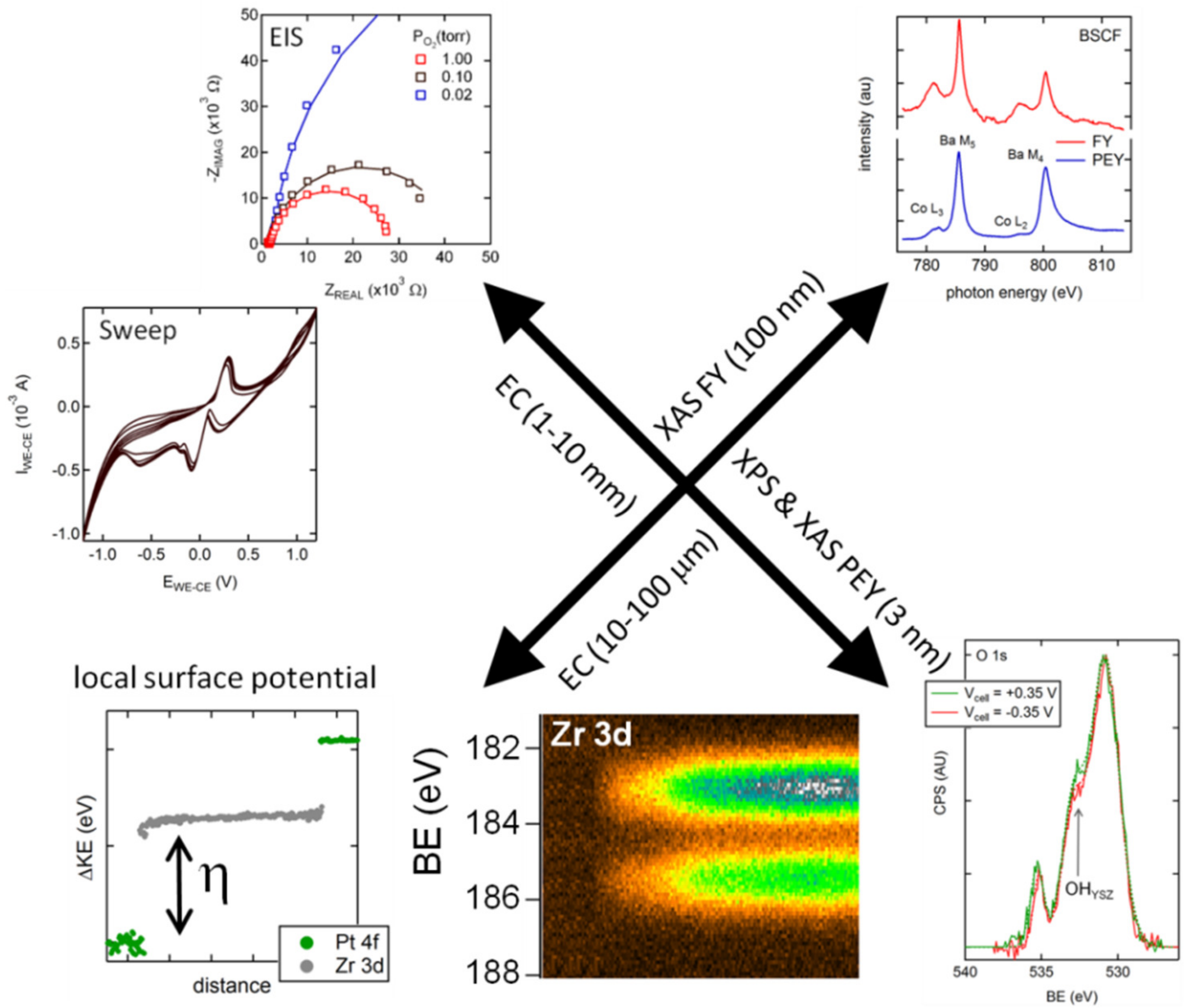






- Galvanic full-cell.

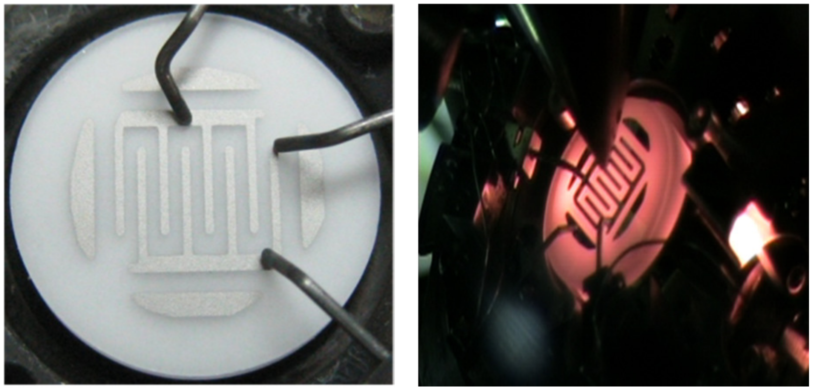
Suite of characterization tools available.



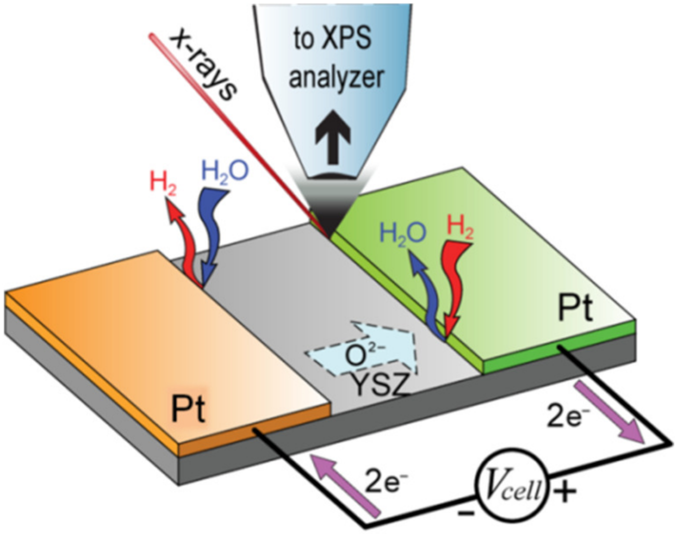
H_2 oxidation and H_2O reduction at a platinum electrode.

Patterned Pt films on YSZ crystal.

- Symmetric electrolytic cell.
  - Evaporated Pt
  - Shadow mask lithography
- Experimental conditions.
  - 150 mTorr H_2
  - 150 mTorr H_2O
  - 550 – 750 °C
  - $\pm$ 1.2 V (V_{WE}-V_{CE})
- XPS peaks of interest.
  - Pt 4f, Zr 3d taken at 490 eV
  - O 1s taken at 750 eV



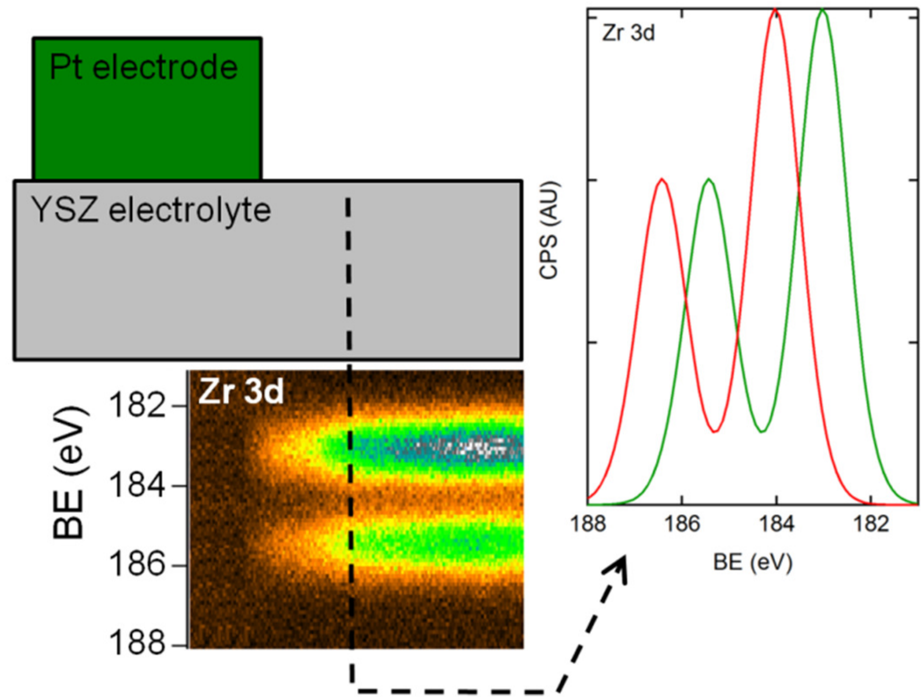
Pt/YSZ/Pt cell



Rigid energy shifts in photoelectrons reveal local surface potential.

- Spatially resolve surface potential in electrified cell.
  - Non-contact
  - Non-perturbing

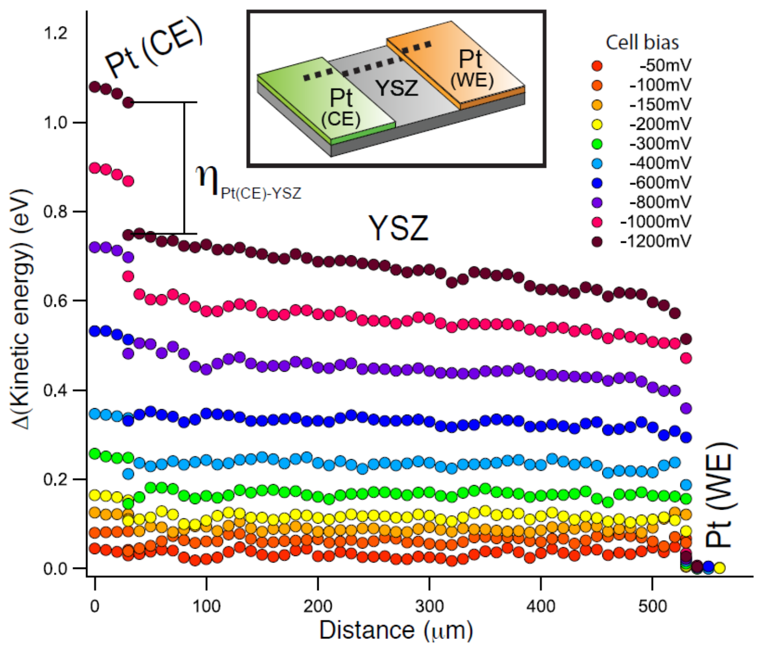
- Measure interfacial overpotential for a metal electrode.

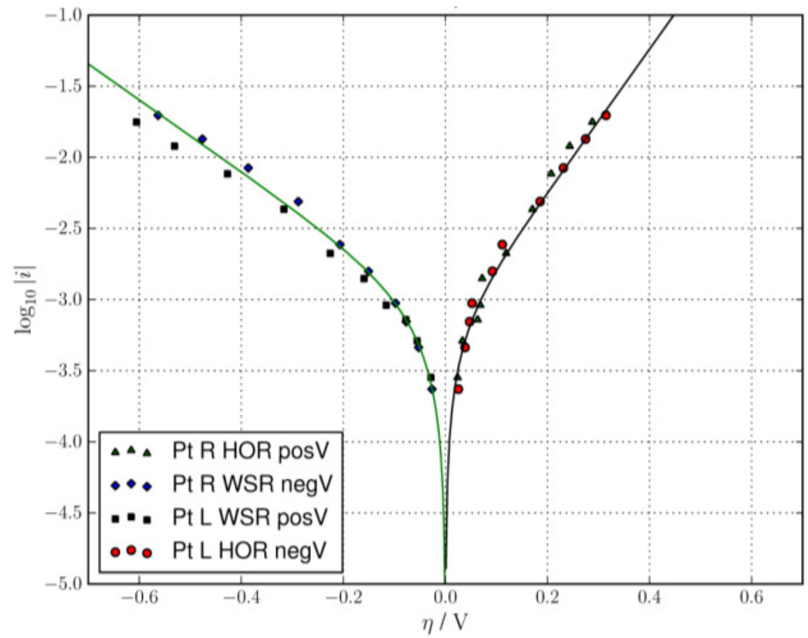


$$\eta = \left(\phi_{bias}(\mathrm{Pt}) - \phi_{eq}(\mathrm{Pt})\right) - \left(\phi_{bias}(\mathrm{YSZ}) - \phi_{eq}(\mathrm{YSZ})\right)$$

El Gabaly et al., *Phys. Chem. Chem. Phys.*, **12**, 12138 (2010)

Resolve local surface potential landscape.

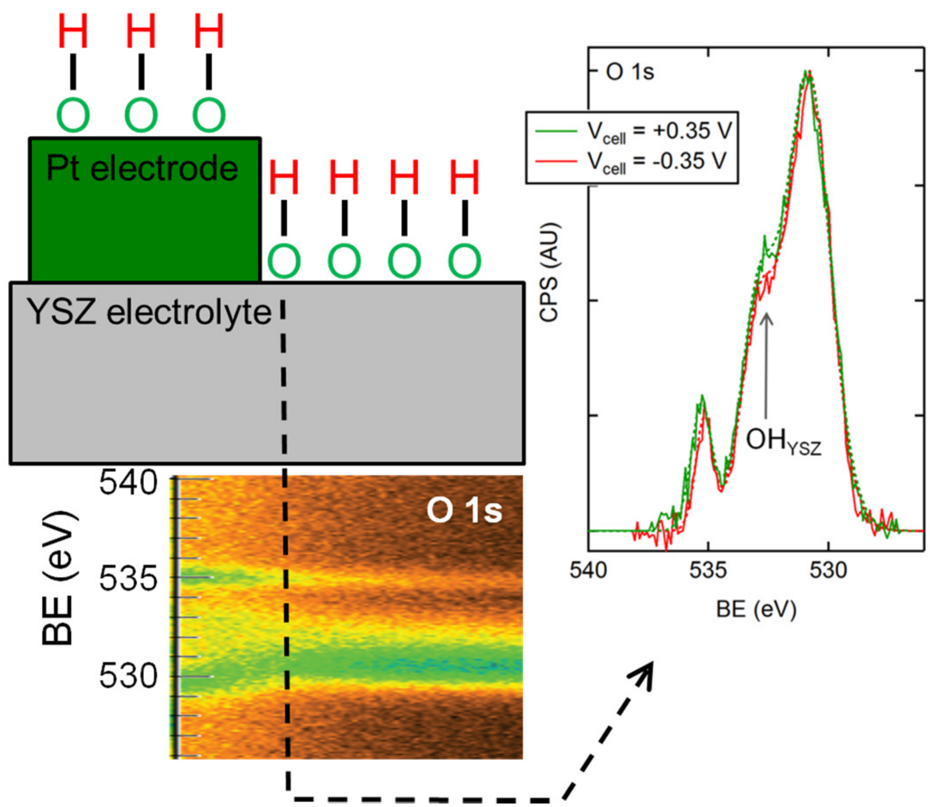




- Each data point based on fitted XPS spectrum.
  - Energy resolution = ± 10 meV
  - Spatial resolution = ± 20 μm
- Tafel plot generated using XPS measured overpotentials (η).

XPS reveals the identity of an electrochemical reaction intermediate specie.

- Locate OH on YSZ near triple phase boundary.
- Surface coverage changes with bias.
  - [OH_{YSZ}] decreases when water is reduced



Allen-Hickling analysis of H_2 oxidation based on XPS measured overpotentials.

$$\log_{10}\left(\frac{|i|}{e^{\left(\frac{n}{\nu}\frac{F}{RT}\eta\right)}-1}\right)=\log_{10}(i_0)-\alpha_f\frac{F}{2.303RT}\eta$$

We find:

$$\vec{\alpha}\equiv\left(\frac{\vec{\gamma}}{\nu}+r\beta\right)=1$$

$$\nu=1$$

$$i_0^{HOR}=5.6\times10^{-4}\ \mathrm{A\cdot cm^{-2}}$$

- Overall hydrogen oxidation reaction:

$$\mathrm{H_2+O^{2-}\leftrightarrow H_2O+2e^-}$$

- The linear fit gives a unique combination of parameters:

$$n=2,\nu=1,\vec{\gamma}=1,r=0$$

- Hydrogen oxidation in Pt/YSZ reaction mechanism:

1.- Charge-transfer reaction ($1e^-$)
2.- Chemical reaction (no e^-). This is the RDS. **Occurs 1 time.**
3.- Charge-transfer reaction ($1e^-$)

El Gabaly, F. *et al., Chem. Comm.* **48**, 8338 (2012)

Charge-transfer mechanism of hydrogen electrochemical oxidation.

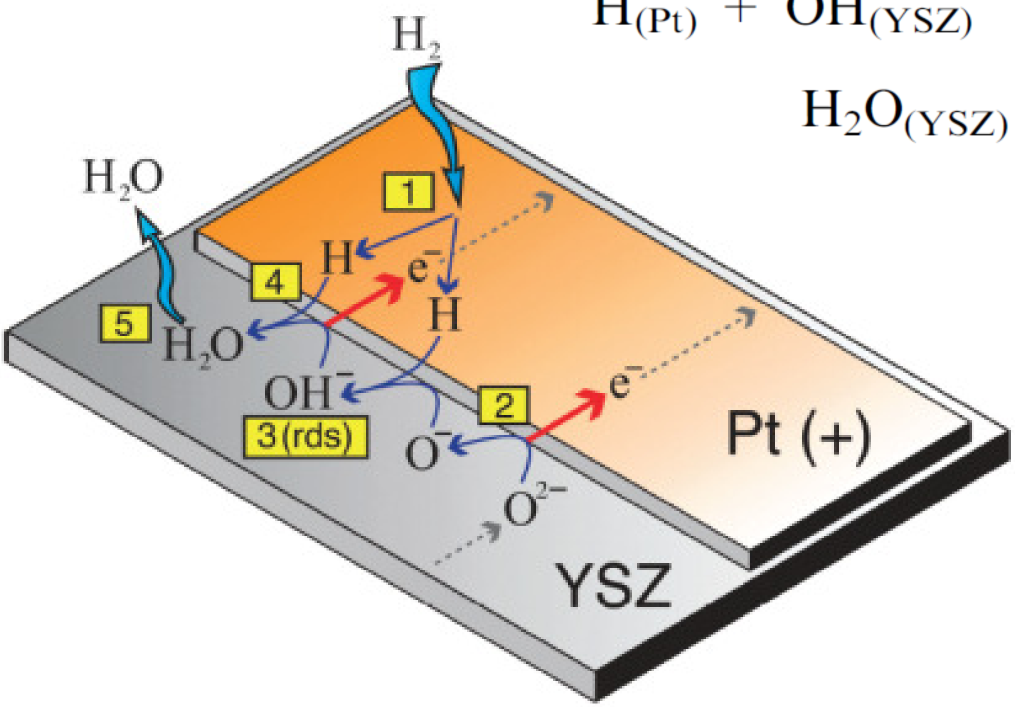
$$H_{2(gas)} \rightleftharpoons 2H_{(Pt)} \qquad (1)$$

$$O_{(YSZ)}^{2-} \rightleftharpoons O_{(YSZ)}^{-} + e_{(Pt)}^{-} \qquad (2)$$

$$H_{(Pt)} + O_{(YSZ)}^{-} \rightarrow OH_{(YSZ)}^{-} \qquad (3)$$

$$H_{(Pt)} + OH_{(YSZ)}^{-} \rightleftharpoons H_2O_{(YSZ)} + e_{(Pt)}^{-} \qquad (4)$$

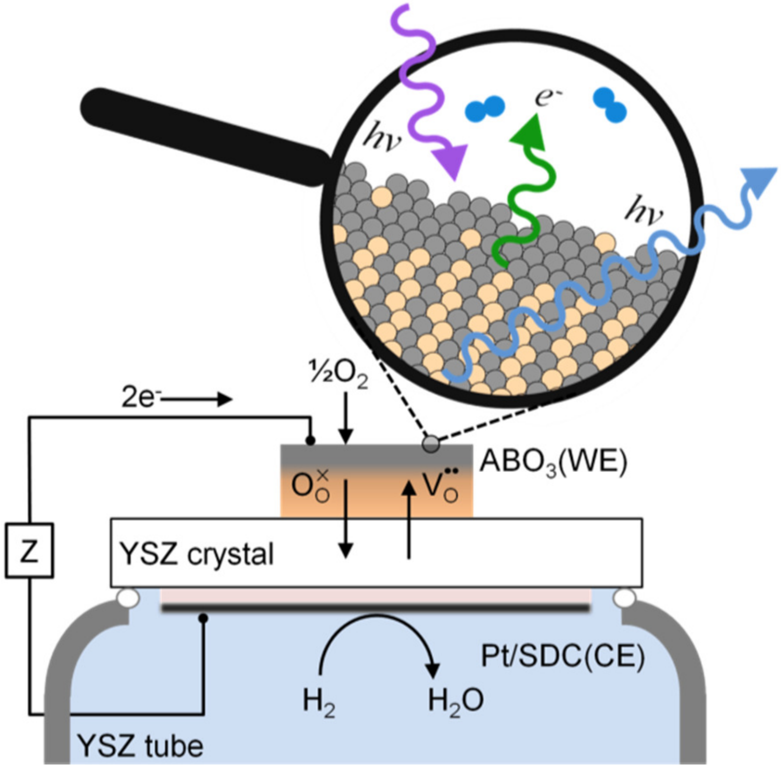
$$H_2O_{(YSZ)} \rightleftharpoons H_2O_{(gas)} \qquad (5)$$

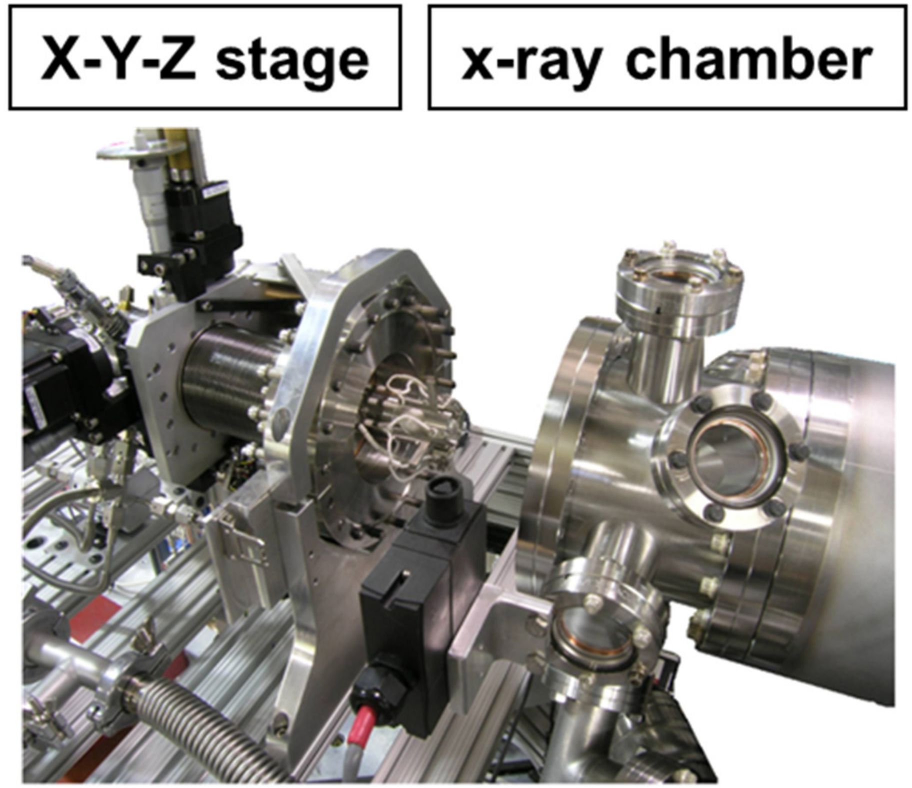


El Gabaly, F. *et al., Chem. Comm.* **48**, 8338 (2012)

O_2 reduction on a perovskite electrode.

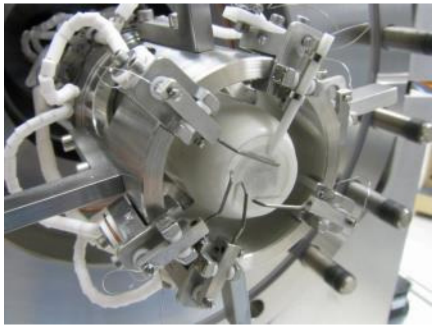
Custom chamber for SOFC studies.





- Fully functioning SOFC.
  - T < 750 °C, P < 10 Torr
  - Supports a Nernst potential

Patterned ABO_3 perovskite films on YSZ crystal.



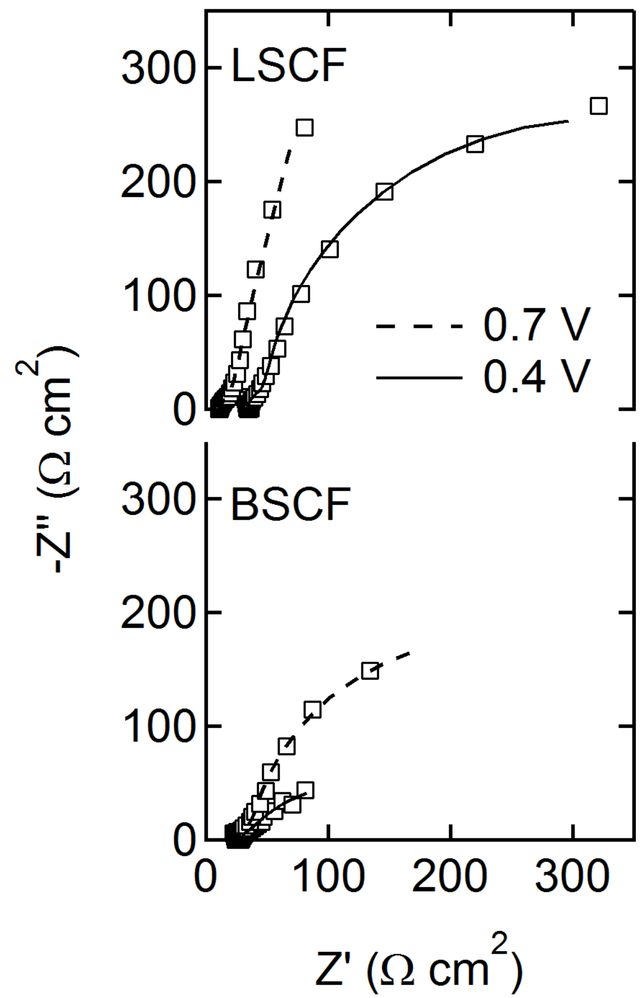
- Galvanic cell.
  - $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF)
  - $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)
  - PLD microelectrodes
  - Shadow mask lithography
- Experimental conditions.
  - 1.0 Torr O_2 (cathode)
  - 1.0 Torr H_2/H_2O (anode)
  - 650 °C
  - 1.0 V Nernst potential
- XPS peaks of interest.
  - Sr 3d, Ba 4d taken at 1005 and 300 eV
- XANES edges of interest.
  - O-K
  - Fe-L_3
  - Co-L_3

Ba substitution dramatically increases ORR rate.

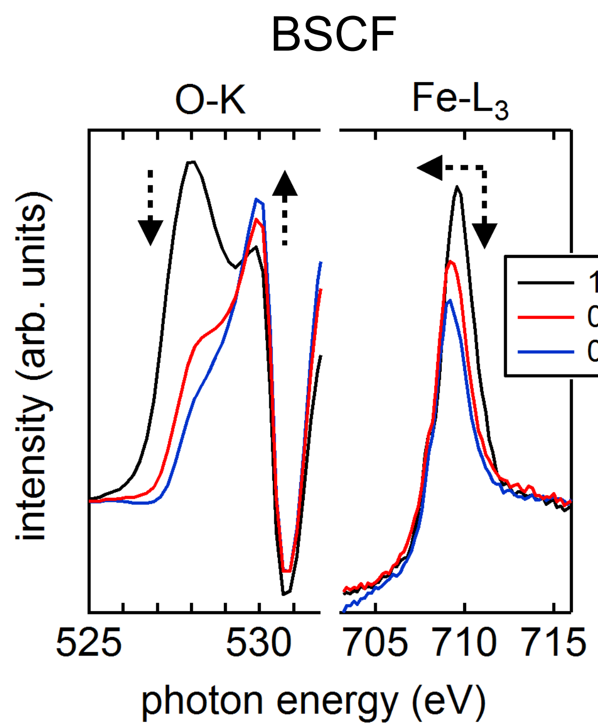
- Ionic radii differ by 30%.
  - $R_{Ba}(2+) > R_{La}(3+)$ expands the lattice
  - Affects vacancy formation energy
- Charge difference affects B-site.
  - $(BaSr)^{2+}(B'B)^{4+}$ vs. $(LaSr)^{2.5+}(B'B)^{3.5+}$
  - Alters Co and Fe charge compensation mechanism

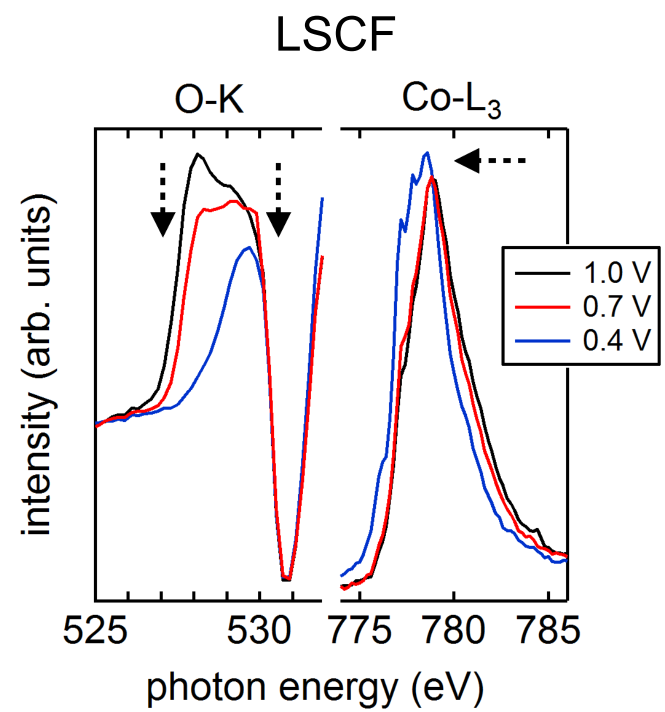
$Rate_{BSCF} >> Rate_{LSCF}$

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



XANES reveals differences in bulk behavior.



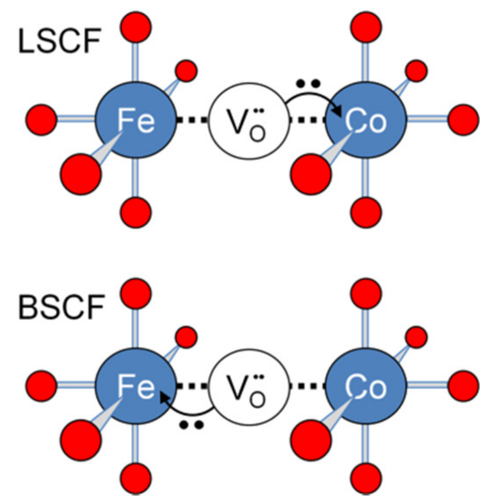


- Fe reduced in BSCF when Vö form electrochemically.
- Co reduced in LSCF when Vö form electrochemically.
- BSCF more strongly reduced at lower overpotentials.

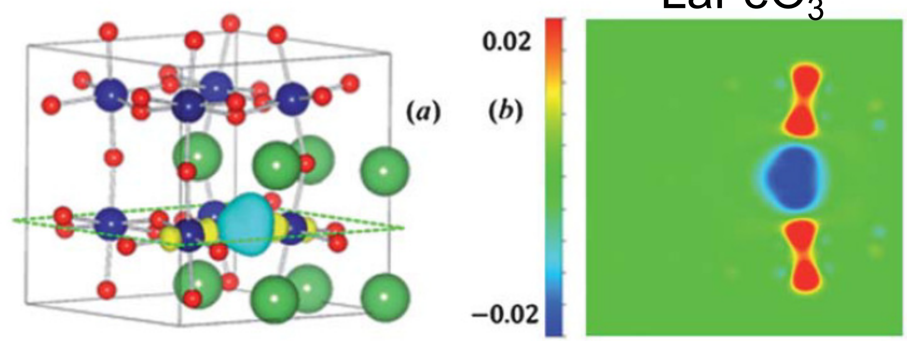
Theory needed for detailed understanding.

- 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?

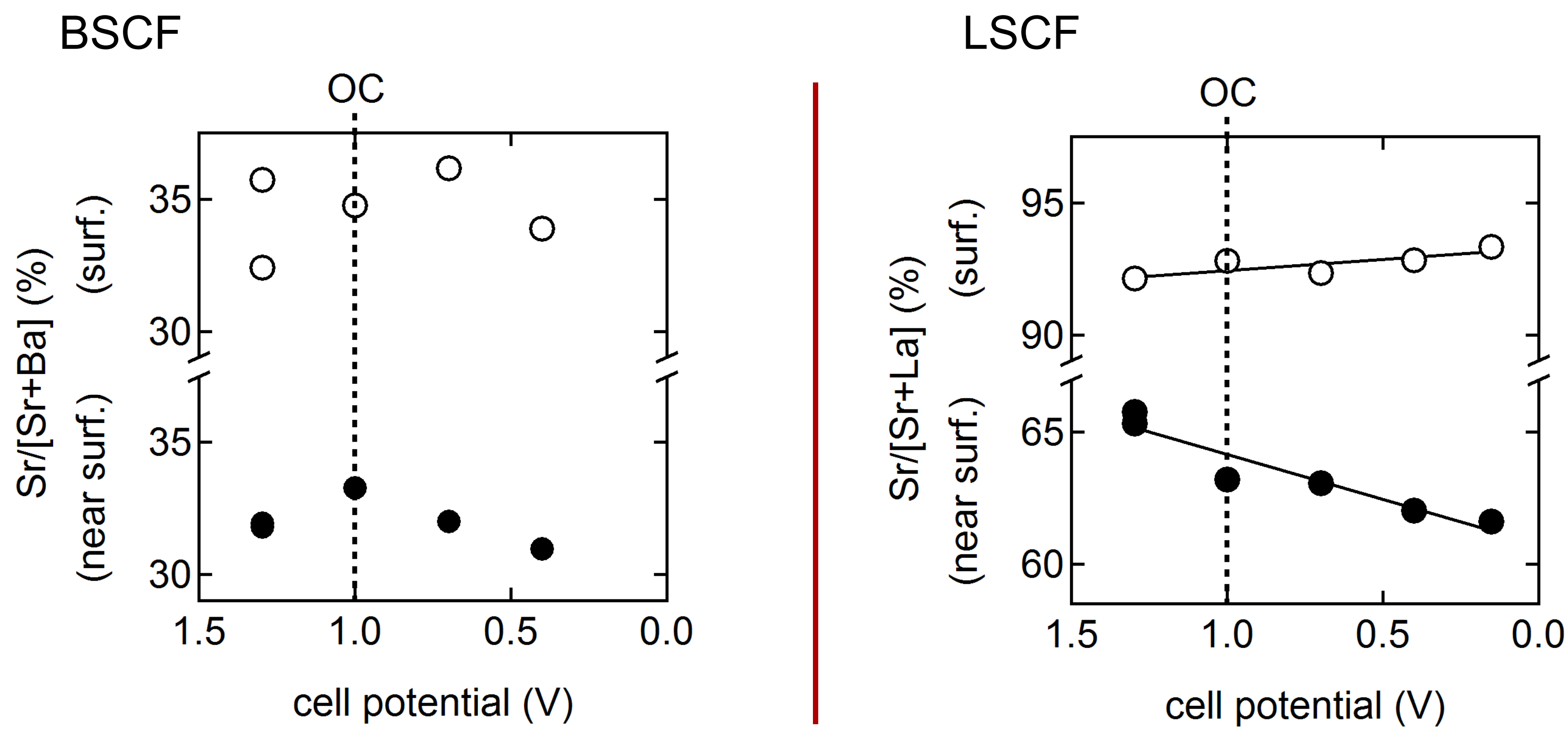


LaFeO$_3$



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)

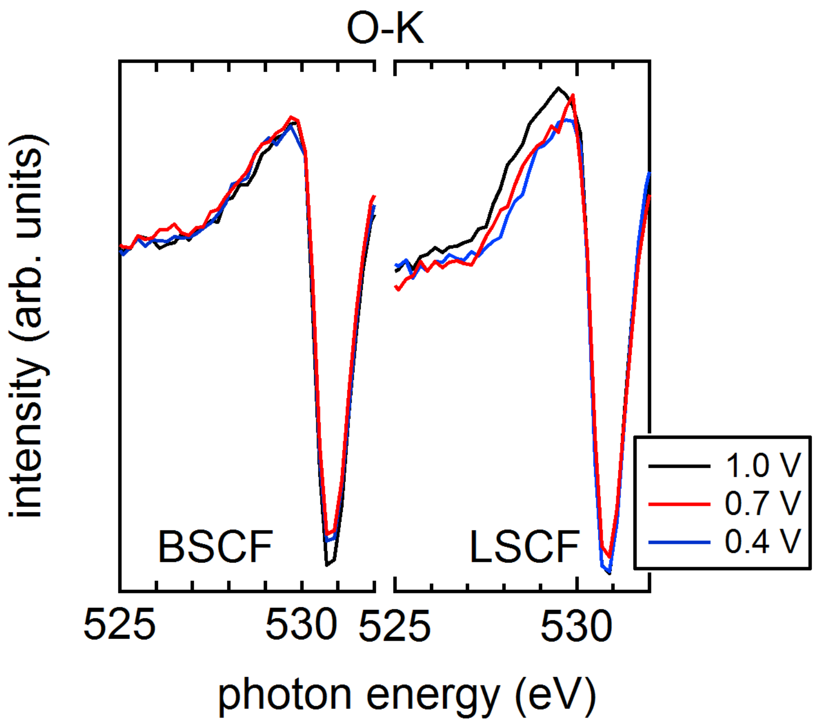
XPS reveals differences in surface composition.



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

O 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 likely broken.
- May have high surface vacancy concentration.
- Is the ORR rate more dependent on bulk properties?



Outlook and challenges.

- Operando soft x-ray spectroscopy can provide composition and electronic structure information on electrochemical systems pulled out of equilibrium by the applied potential.
  - Reveal surface and bulk states
  - Reveal reactive intermediates
  - Map surface potential landscape

- APXPS is first and foremost a surface science experiment.
  - Challenge to develop well-controlled model systems
- XANES requires quantum theory to interpret.
  - Parameter-free multiple scattering based on electronic structure models
  - Develop an atomistic understanding of electrochemical processes
- Access to soft x-rays is a huge bottleneck.

There may come a day when we have unlimited access to tunable x-rays.

SLAC NATIONAL ACCELERATOR LABORATORY

Researchers Demonstrate 'Accelerator on a Chip'

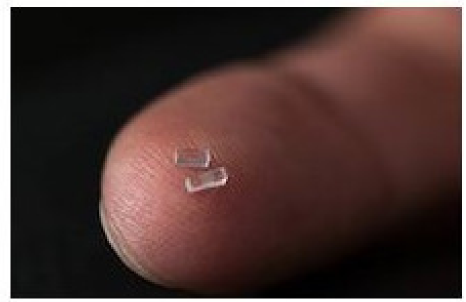
Technology could spawn new generations of smaller, less expensive devices for science, medicine

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 particle
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)

Acknowledgments.

- Sandia Labs
  - Farid El Gabaly
  - Kevin McCarty
  - William Chueh (Stanford)
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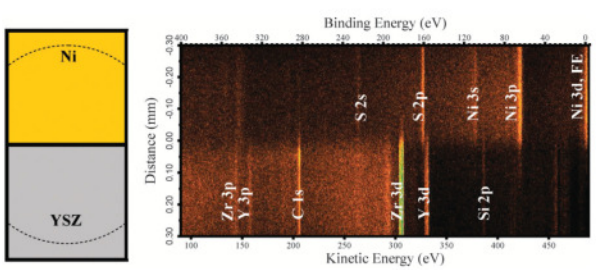
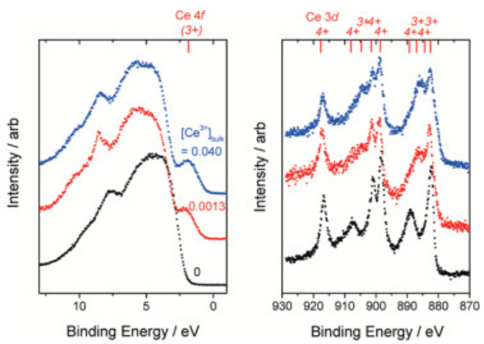
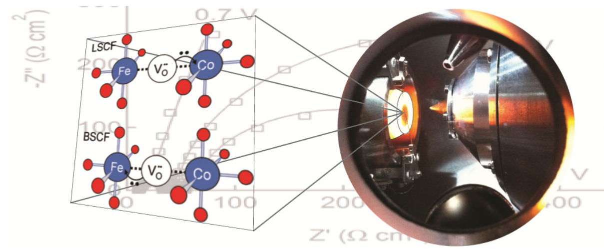
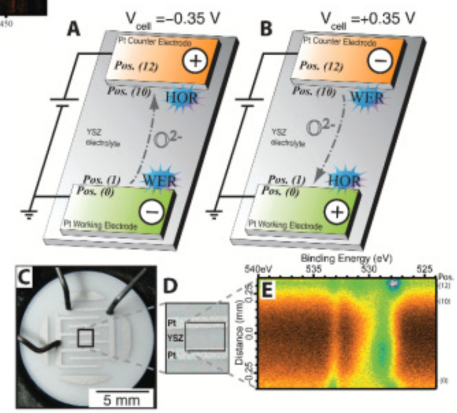
  - Andrey Shavorskiy
  - Tolek Tyliszczak
  - Hendrik Bluhm
- ALS BL 9.3.2
  - Zhi Liu
  - Michael Grass

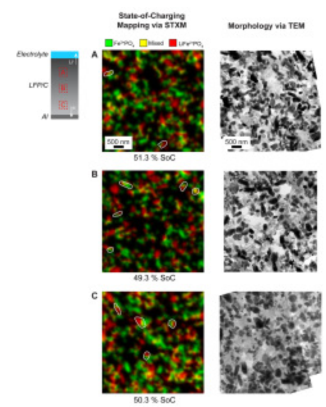
Thank you.

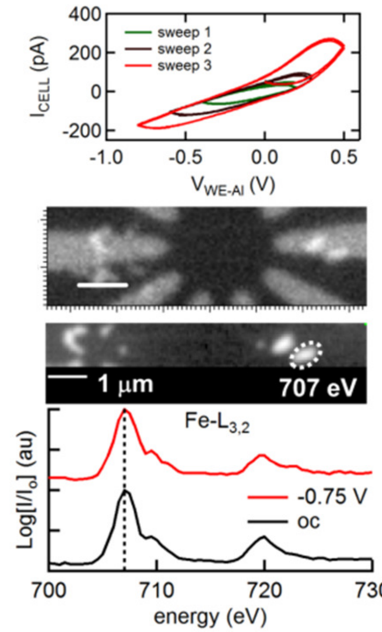












El Gabaly, F. et al. Oxidation Stages of Ni Electrodes in Solid Oxide Fuel Cell Environments, *Phys. Chem. Chem. Phys.* **15**, 8334 (2013).

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).