SAND2011-7324C

Shining Light on Energy Conversion at Gas/Solid Interfaces

Anthony McDaniel

Sandia National Labs

Sandia National Laboratories

Acknowledgments

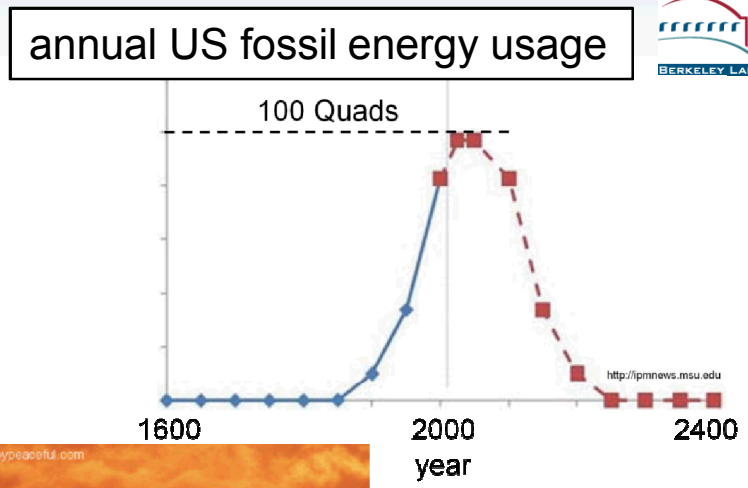
- **Sandia Labs**
  - Farid El Gabaly
  - William Chueh
  - Kevin McCarty
- **California Inst. Technology**
  - Sossina Haile
- **ALS**
  - Michael Grass
  - Andrey Shavorskiy
  - Naila Jabeen
  - Zhi Liu
  - Zahid Hussain
  - Hendrik Bluhm
- **Former Sandians**
  - Roger Farrow
  - Mark Linne
    Chalmers University, Gothenburg Sweden
- **University of Maryland**
  - Chunjuan Zhang
  - Steven DeCaluwe
  - Greg Jackson
  - Bryan Eichhorn

Funding and support

This research was supported by the U. S. Department of Energy under Contract No.DE-AC04-94AL85000 (Sandia) and DE-AC02-05CH11231 (LBNL)

Harness the power of the sun (8×10^6 Quads per year)

- **Use of fossil fuels will end.**
  - Burn out
  - Fade away
- **Energy storage needed to balance supply intermittency.**
  - Chemicals or electricity
- **Electrochemical technologies will play a vital role.**
  - Batteries, electrolyzers, fuel cells



Sandia National Laboratories

Gas/solid interactions drive many electrochemical technologies

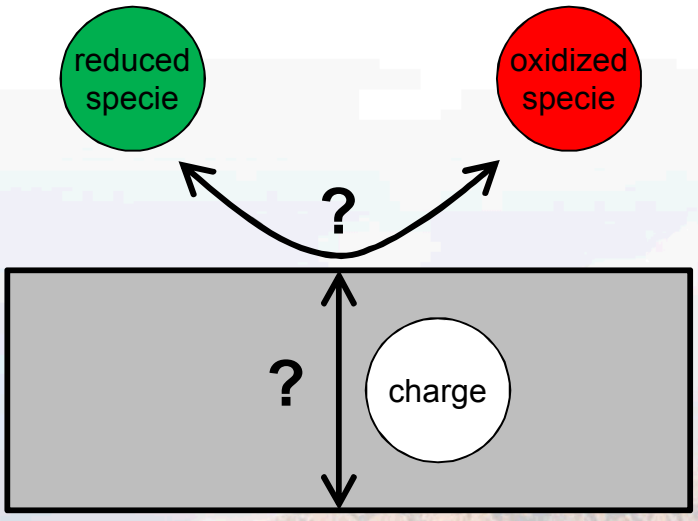
thermochemical cells

metal-air batteries

electrolyzers

photochemical cells

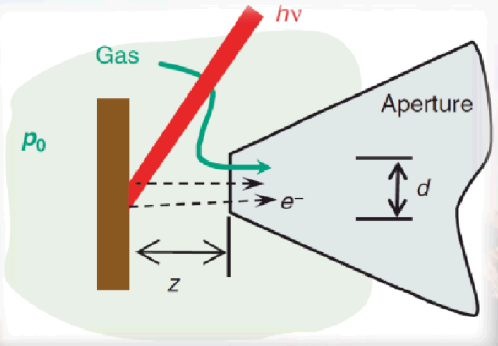
fuel cells



- **What is largely unknown:**
  - What molecular species transfer charge?
  - Where on the surface is the charge transferred?
  - What are the slow steps?
  - What is the chemical state of the reactive surface?
  - Are the surface and bulk the same?
- **Experiment under operating conditions.**

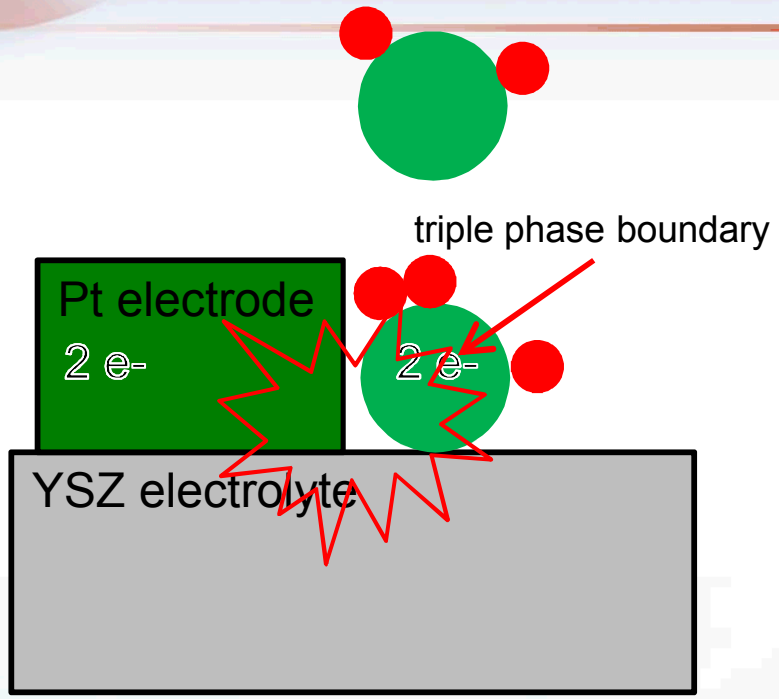
Revealing insights near ambient pressure

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



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

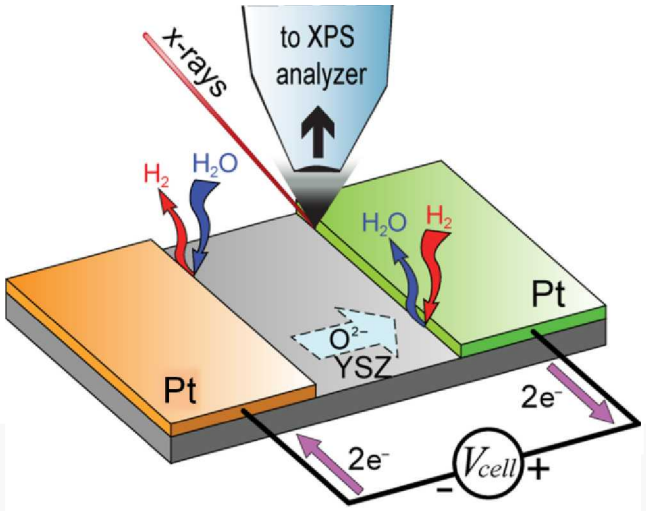
Water electrolysis converts electrons into fuel

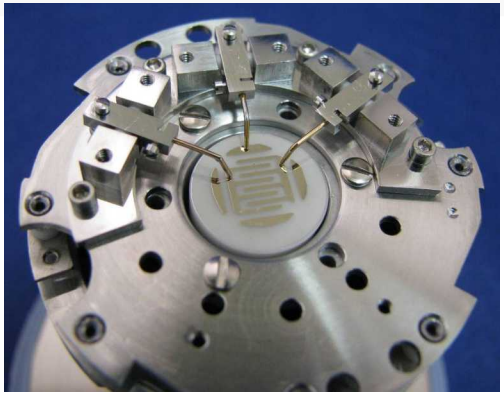


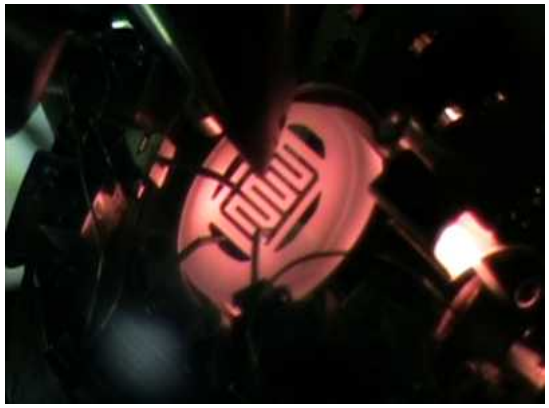
$$H_2O + 2e^- \rightarrow O^{2-} + H_2$$

- **Benchmark reaction for electrochemistry.**
  - Mechanism still debated
  - Only 1 e^- transferred at a time
- **Interrogate region near the triple phase boundary.**
  - Identify reactive intermediates

Single chamber experimental configuration





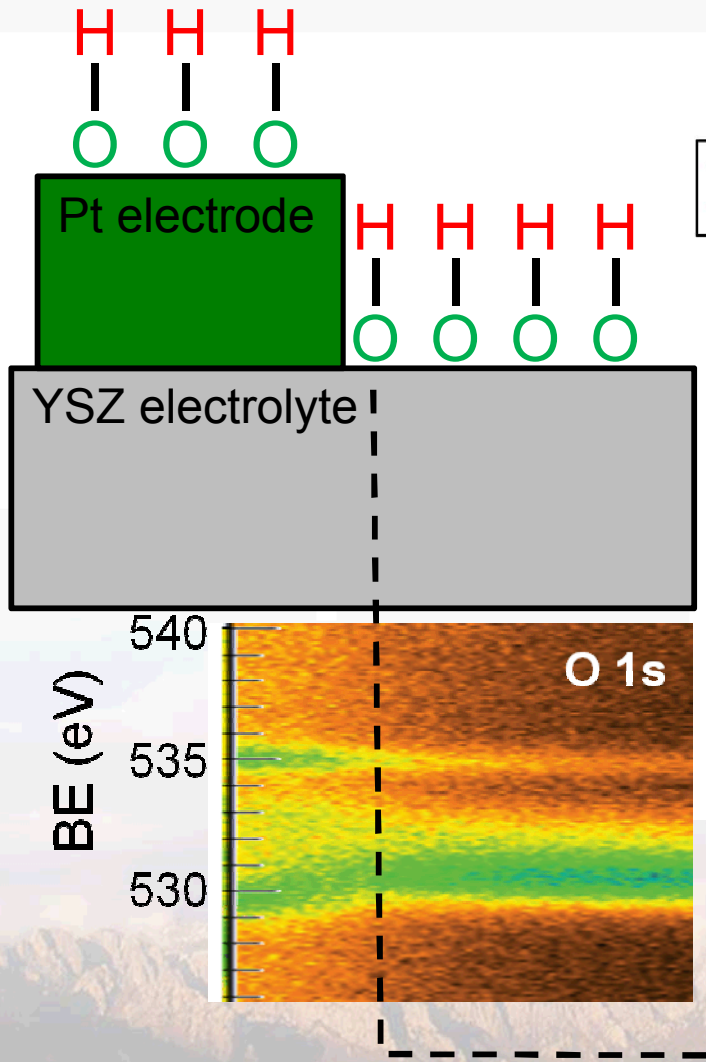


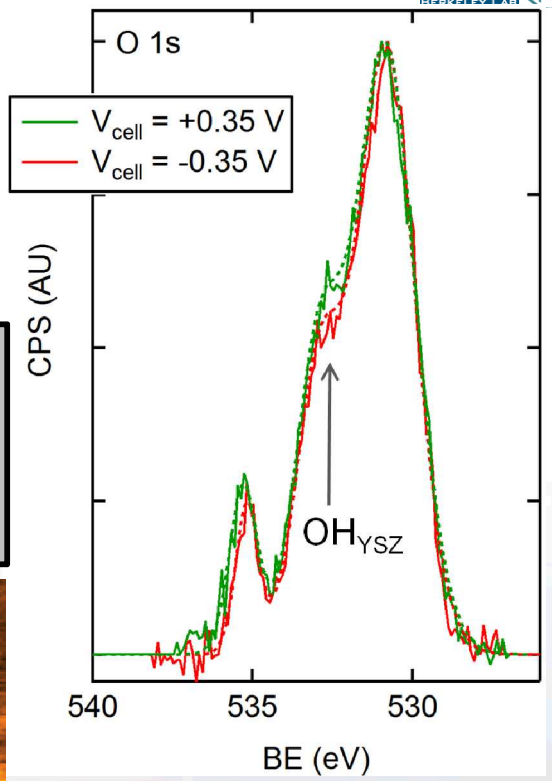
- Patterned metal film electrodes on YSZ (Pt/YSZ/Pt).
- Mixtures of H_2/H_2O.
- P ≈ 500 mTorr.
- 550 °C < T < 750 °C.

Sandia National Laboratories

XPS reveals the identity of electrochemical reaction intermediate specie

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

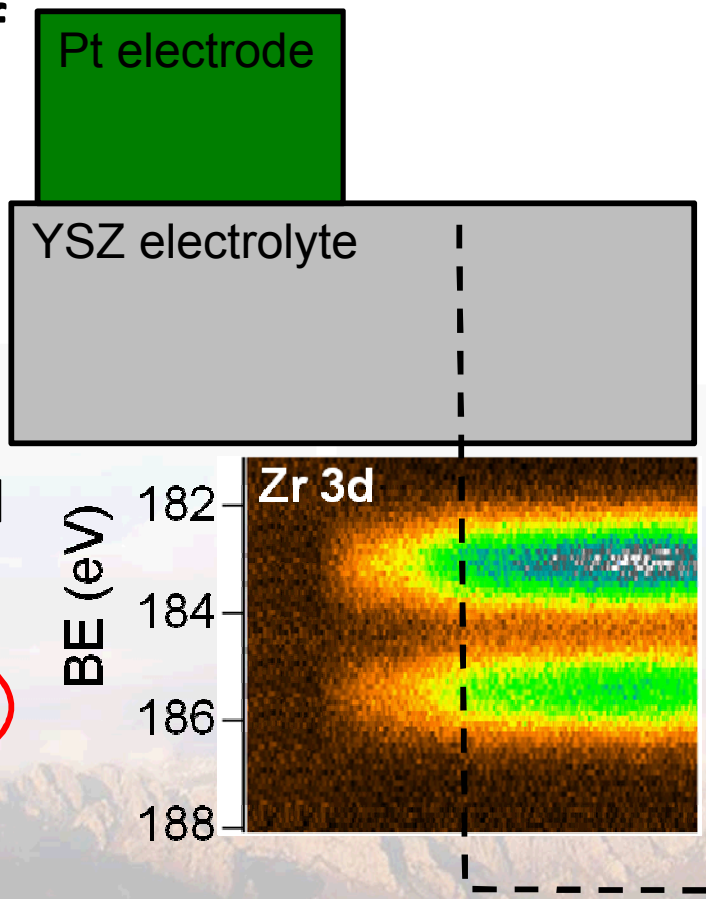


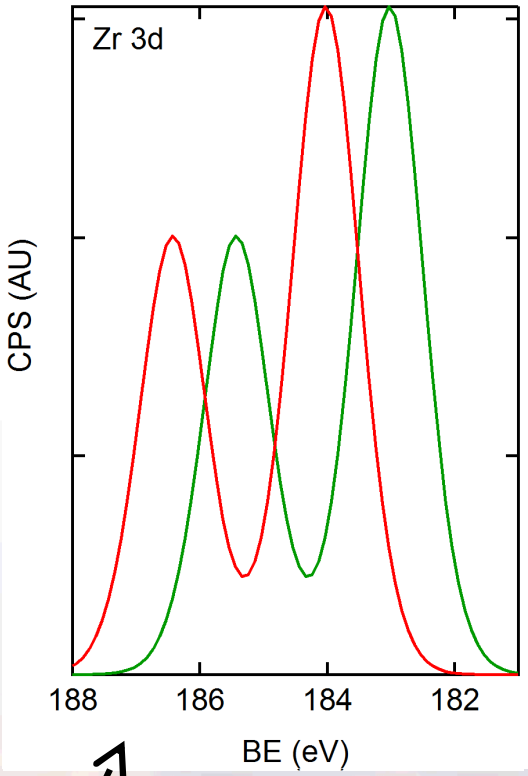


Sandia National Laboratories

Energy shifts in photoelectrons also reveal local surface potential

- **Spatially resolve surface potential of an electrified cell.**
  - Non-contact
  - Non-perturbing





- **Measure interfacial overpotential.**

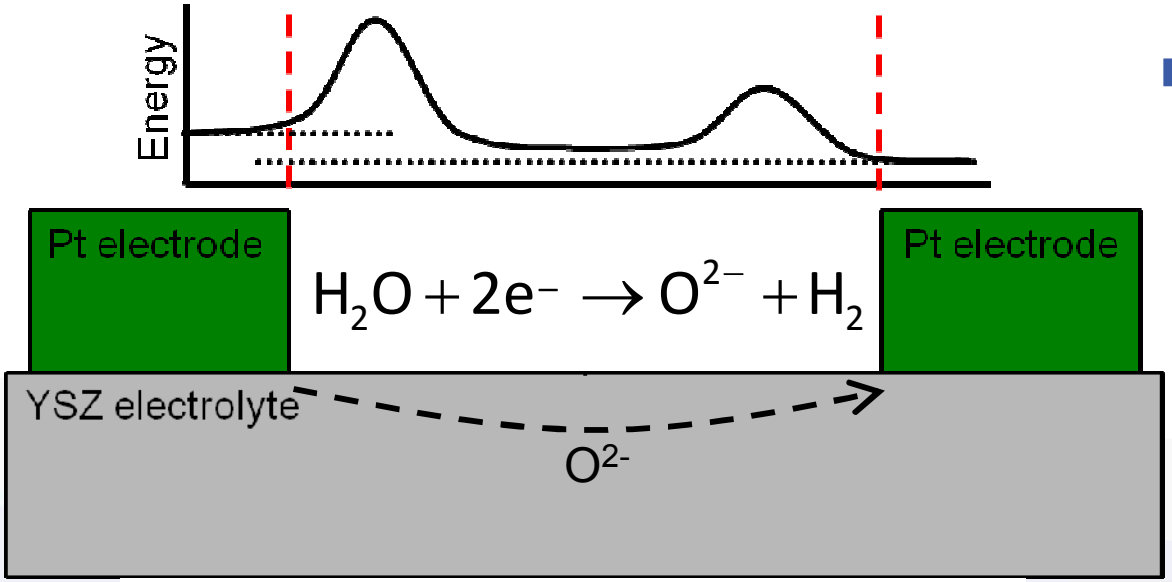
$$KE^{bias} - KE^{equil} \propto \eta_{interface}$$

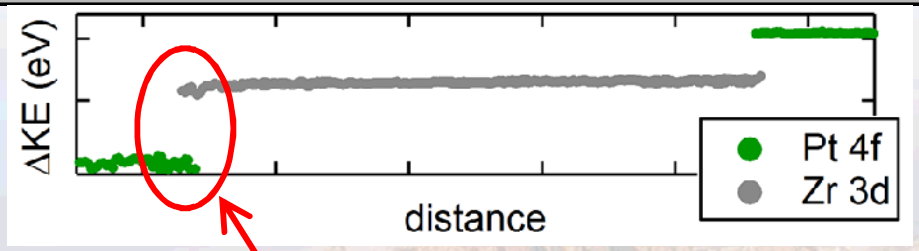
fundamental property

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

Sandia National Laboratories

Water reduction is slow step on Pt



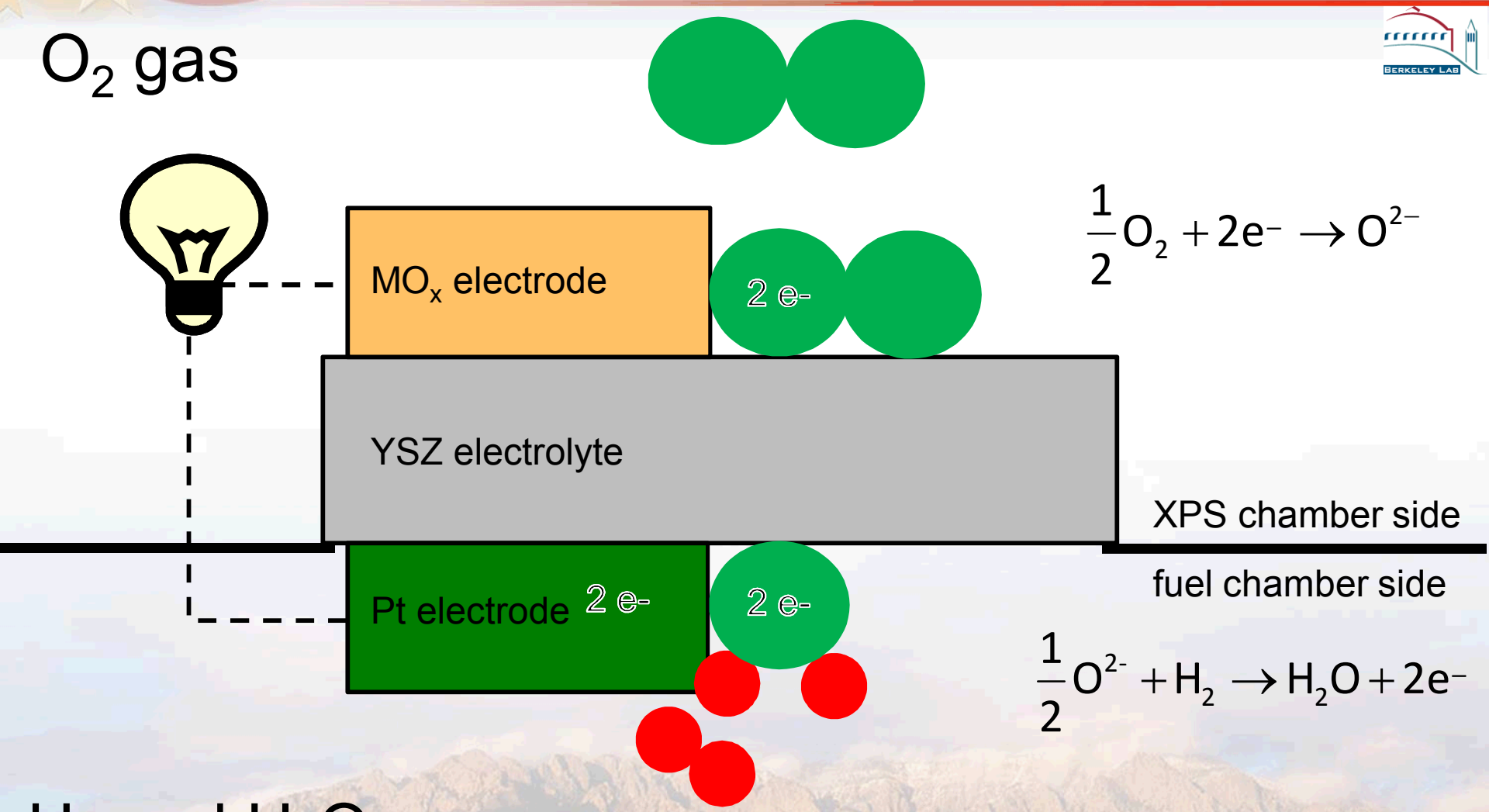


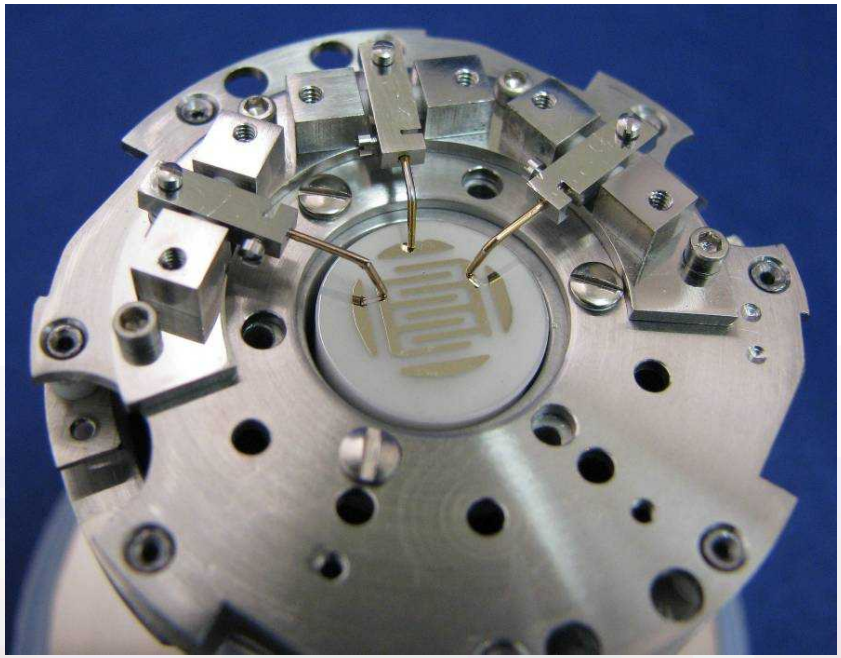
- **Magnitude of potential step is a measure of electrode reactivity.**

$\eta_{Pt\text{-}YSZ}$

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

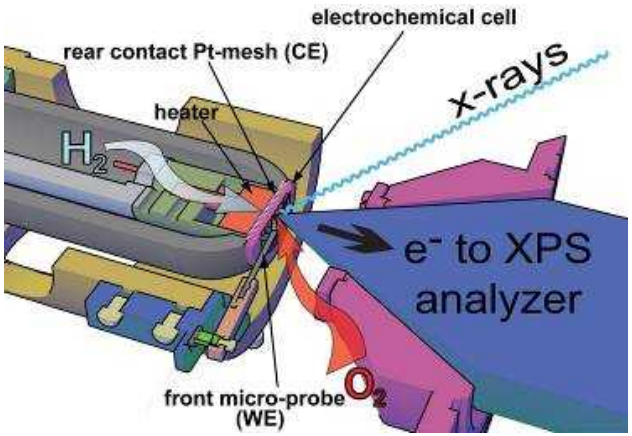
Converting chemical bonds to electrons

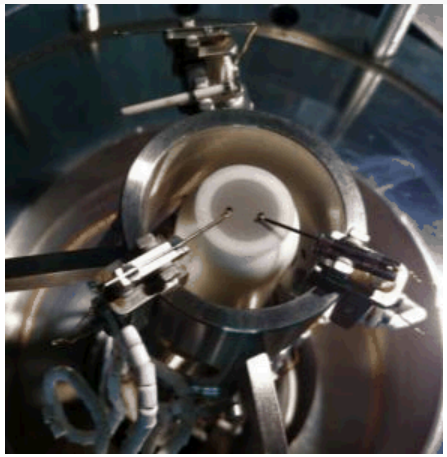


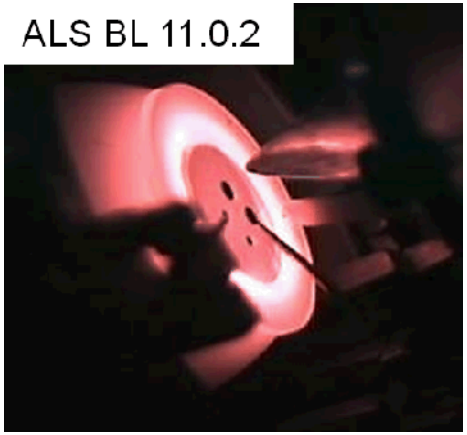


Whaley et al., Rev. Sci. Inst., **81**, 086104 (2010)

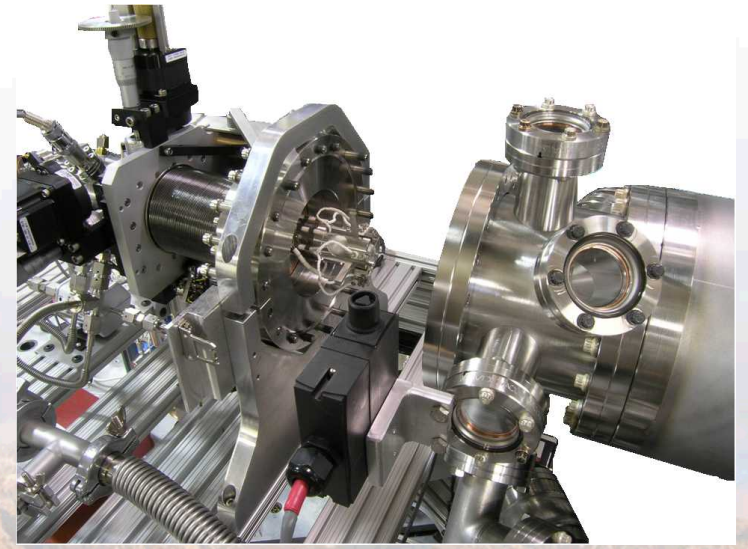
Membrane isolates electrode environments







- **Fully functioning fuel cell.**
  - Establish a Nernst potential
- **XPS, XAS, EC.**
- **Precision X-Y-Z manipulation.**
  - ~ 5 μm resolution via stepping motors
  - ~ 50 μm diameter X-ray beam



Electrode composition effects O_2 reduction reaction rate

- **State-of-the art complex oxide cathodes.**
  - ABO_3 perovskite structure
- **Stoichiometry impacts performance.**
  - Electrocatalytic activity
- **How does the A-site substitution change the material?**
  - Ionic radii Ba < Sr < La
  - Formal oxidation state

$$(La,Sr)(Co,Fe)O_{3-\delta}$$

A-site ↕

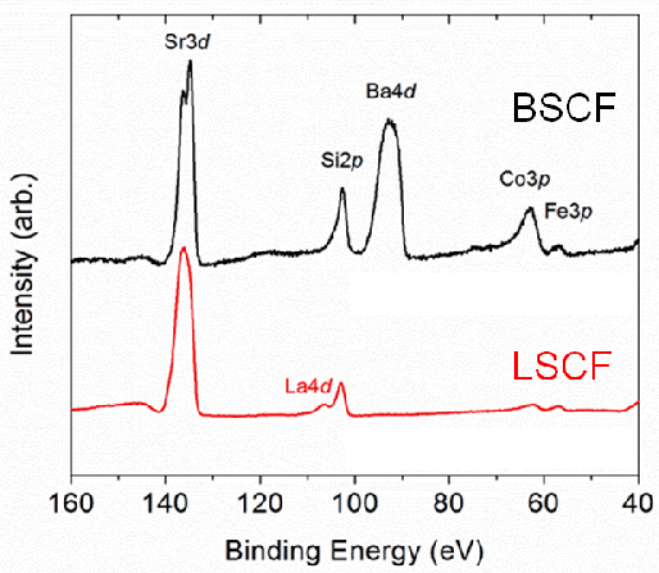
$$(Ba,Sr)(Co,Fe)O_{3-\delta}$$

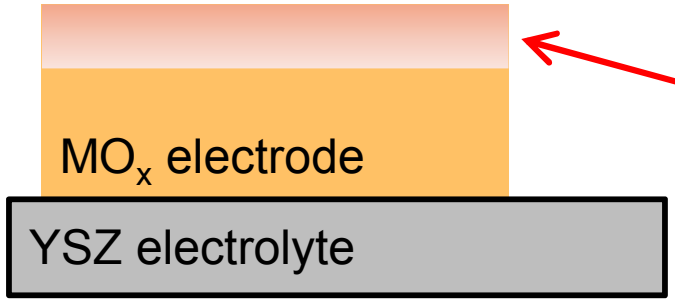
$$Rate_{BSCF} >> Rate_{LSCF}$$

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

+2	+3
56 Ba Barium 137.327	57 La Lanthanum 138.90547

XPS reveals surface composition vastly different than bulk

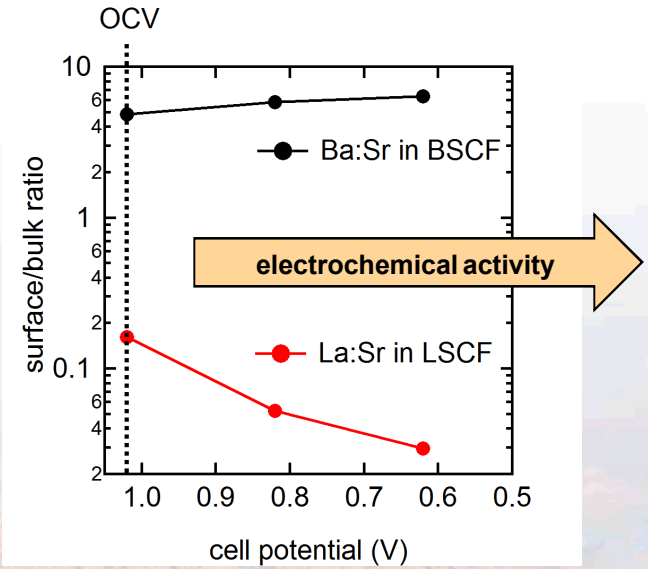




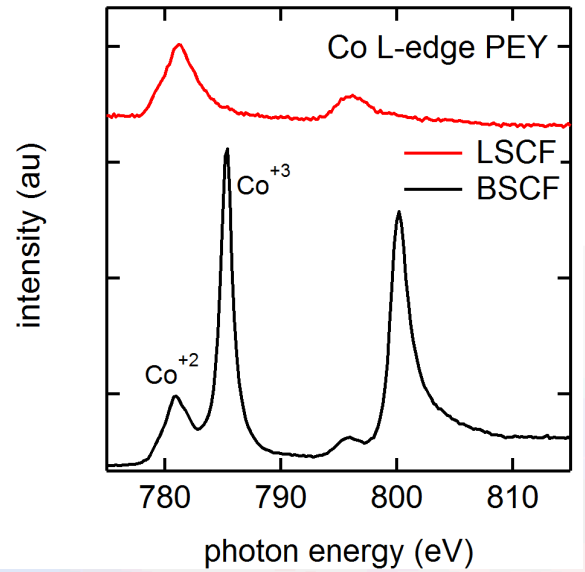
Sr rich in LSCF

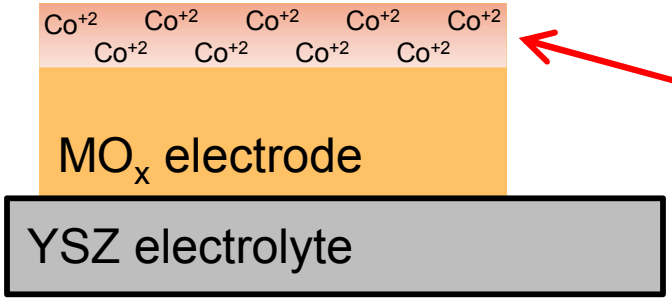
Ba rich in BSCF

- **Electrochemical activity increases the extent of Sr surface segregation in LSCF.**

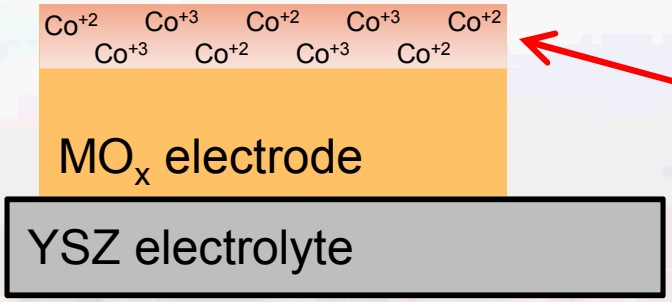


X-ray absorption (XAS) reveals difference in Co oxidation states





Co^{+2} in LSCF



$Co^{+2,+3}$ in BSCF

Sandia National Laboratories

Consequences of changing A-site cation from La to Ba

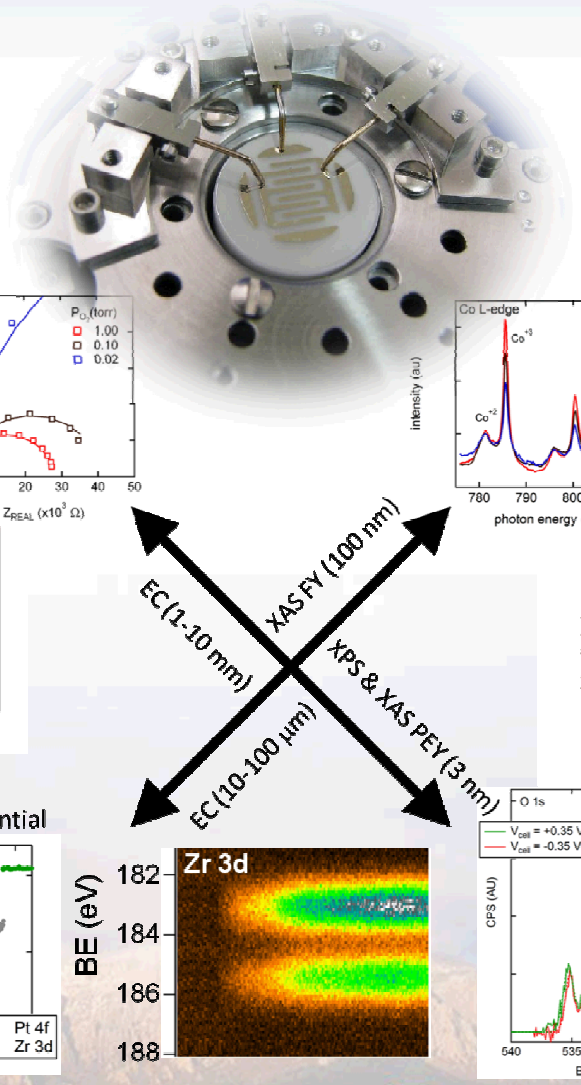
- Surface composition changes from Sr—enriched to Ba—enriched.
- Surface Co in LSCF exists as a mono-valent specie.
- These are the reasons why:

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

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

Soft X-rays are shining light on electrochemistry

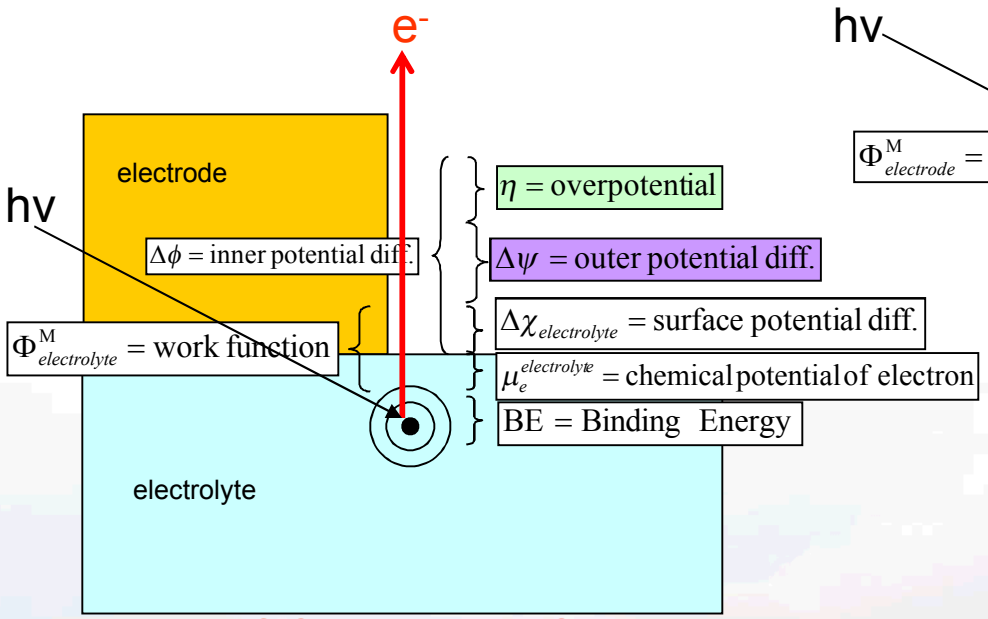
- **These techniques provide information that is essential to advancing the understanding of electrochemical devices.**
  - Advance the technology
  - Increase market acceptance
- **Surface chemistry**
  - Core level XPS
  - Valence band XPS
  - XAS partial electron yield
- **Bulk states.**
  - XAS fluorescence yield
- **Macroscopic behavior.**
  - Impedance spectroscopy
  - Potential steps/sweeps
  - Reaction rates



Sandia National Laboratories

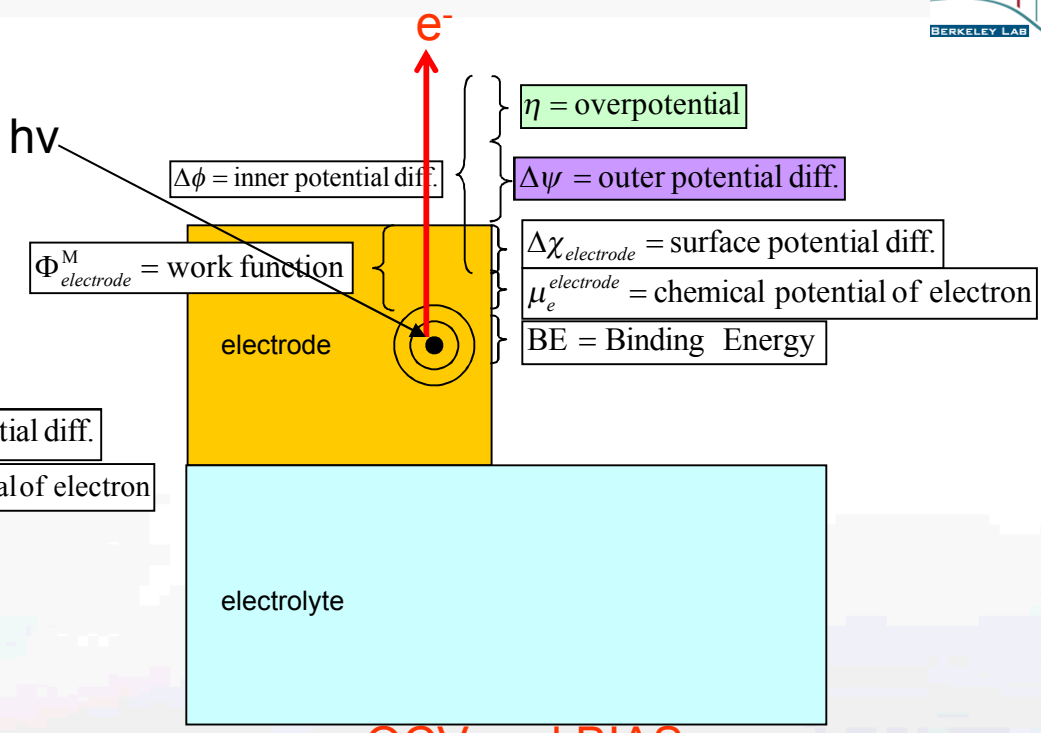
Lights on or lights *out*?

Measurement of local overpotentials



OCV and BIAS

Measurement of $\left(\phi_{bias}(\mathrm{YSZ}) - \phi_{eq}(\mathrm{YSZ})\right)$



OCV and BIAS

Measurement of $\left(\phi_{bias}(\mathrm{Pt}) - \phi_{eq}(\mathrm{Pt})\right)$

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