SAND2011-3185C

In operando Investigation of SOFC Electrodes Using Synchrotron-based Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) in a Novel Two-Environment Chamber

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Motivation and approach

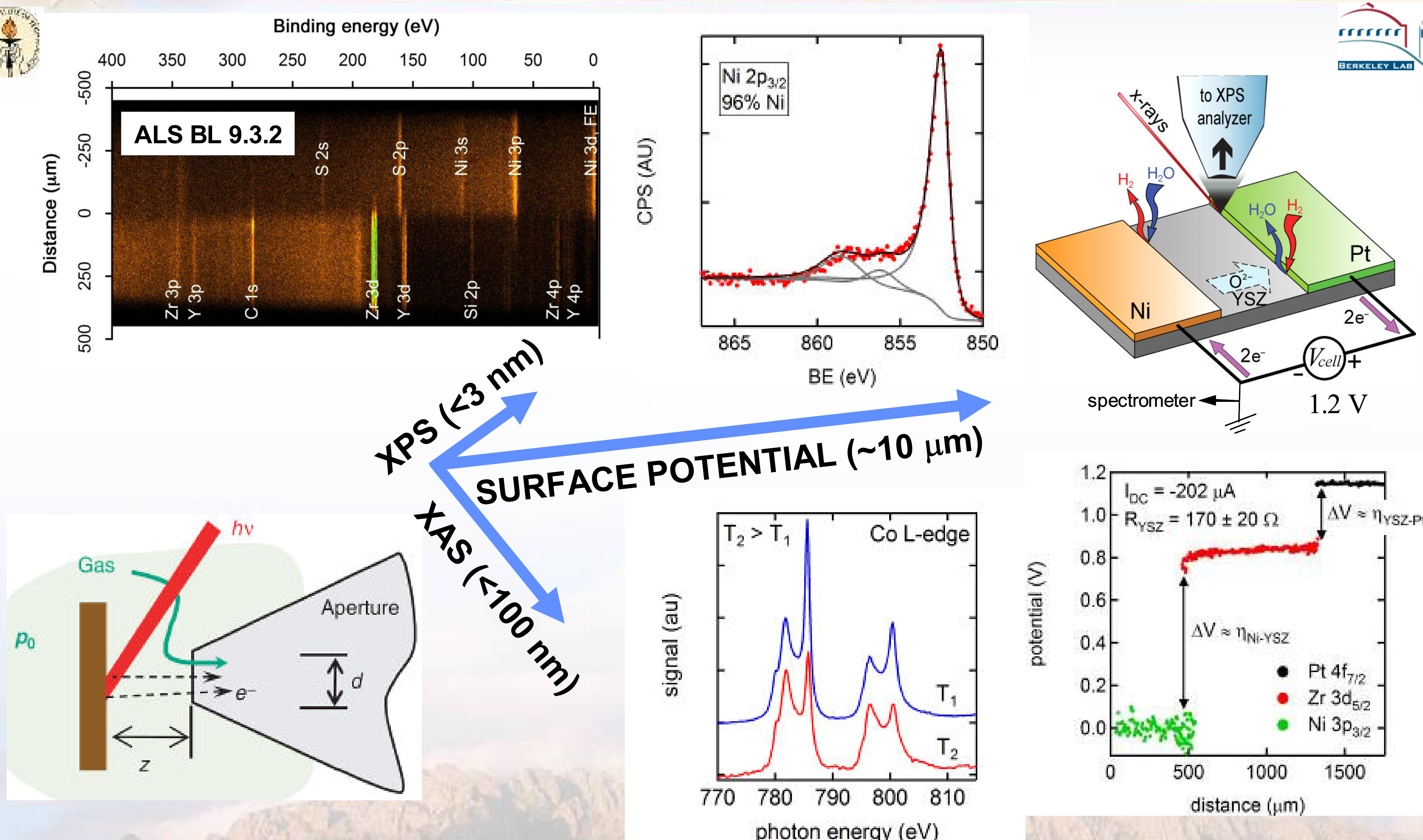
- **Perovskite-structured oxides**
  - SOFC cathodes and proton conducting membranes

- **Open questions that impact electrochemical activity, conductivity, and chemical stability**
  - Material stoichiometry
    - A- and B-site substitutions and dopants
    - Phase segregation and substitution-site enrichment
    - Oxygen defects
  - Reactive environment
    - Gas composition, impurities, applied electrical potential

- **In operando observations using soft X-rays**
  - Determine elemental composition of surface and bulk
  - Determine oxidation state of elements on surface and in bulk
  - Spatially resolve surface potential landscape

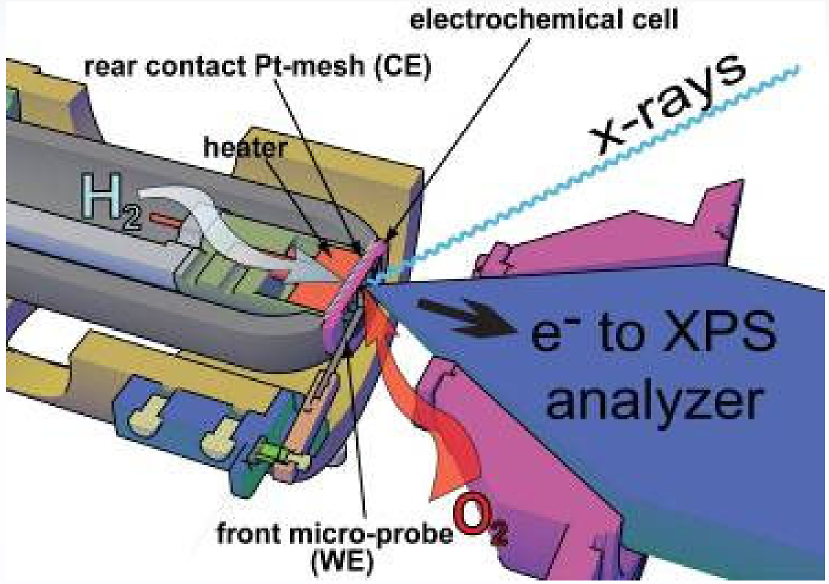
- **Experimental platform operating at near ambient pressure with XPS, XAS, and ACIS**

AP-XPS and XAS on SOFC-type materials at realistic operating conditions

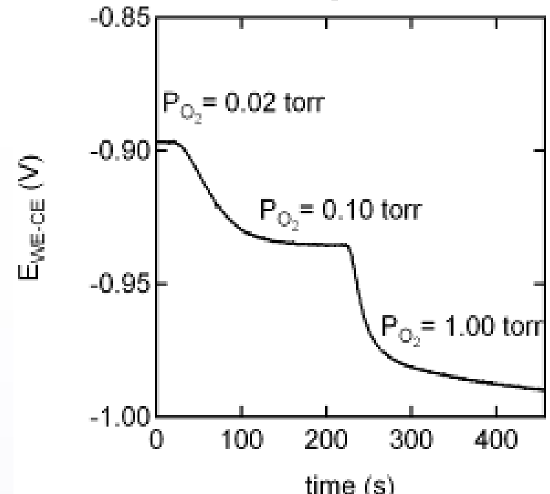


Bluhm, H. et al. *MRS Bulletin-Materials Research Society* **32**, 1022 (2007)
El Gabaly, F. et al. *Phys. Chem. Chem. Phys.* **12**, 12138 (2010)

ABO_3/YSZ/SDC/Pt membrane electrode assembly (MEA)



Nernst potential



- **Electrolyte supported MEA**
  - High temperature glass seal between YSZ support tube and MEA
  - Electrodes patterned by PLD and metal evaporation through shadow masks

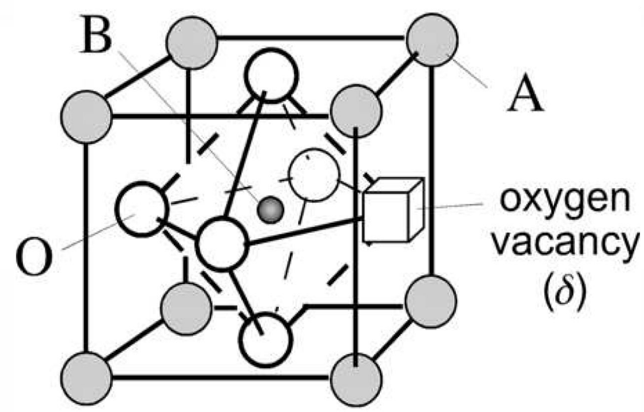
- **P ≤ 10 torr, T < 800 ºC**

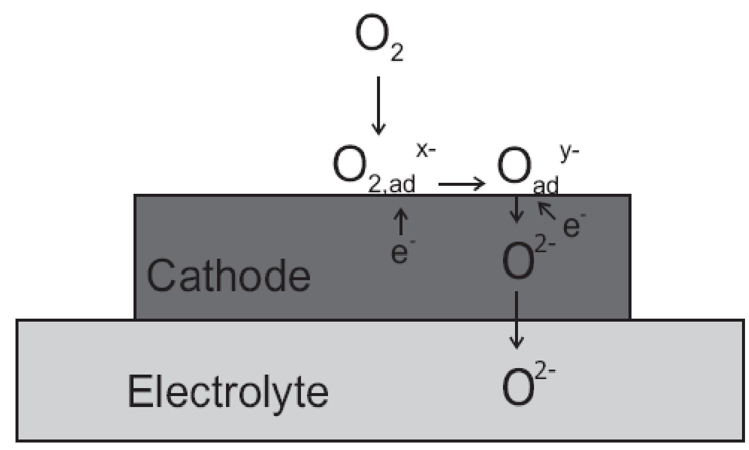
- **Precision X-Y-Z manipulation using stepping motors for spatially-resolved measurement (~ 5μm)**

- **FRA/potentiostat used to conduct electrochemical experiments**
  - AC-impedance spectroscopy

Oxygen reduction reaction on $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ perovskite cathode

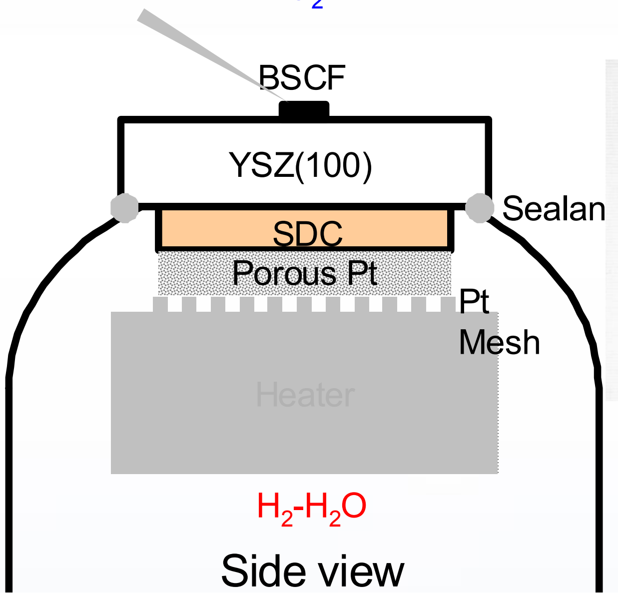
- **Understand why stoichiometry impacts performance**
  - Conductivity, electrocatalytic activity, chemical stability
- **Understand how system responds to oxygen activity**
  - Cation oxidation state
    - Thermochemically driven
    - Electrochemically driven
- **Resolve differences between bulk and surface composition**
  - Phase segregation
  - Cation valency





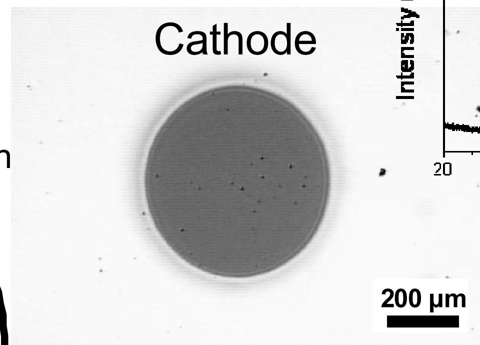
Oriented thin films deposited by pulsed laser deposition

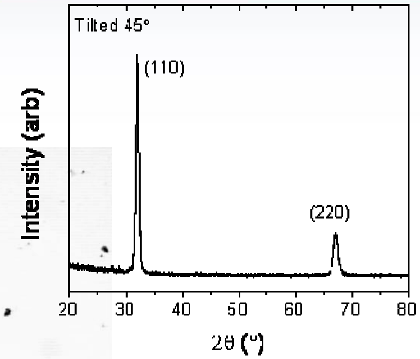
Cell Geometry



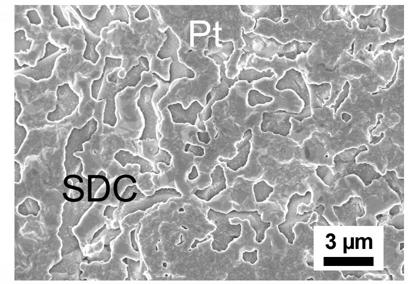
Side view

Top view





Anode



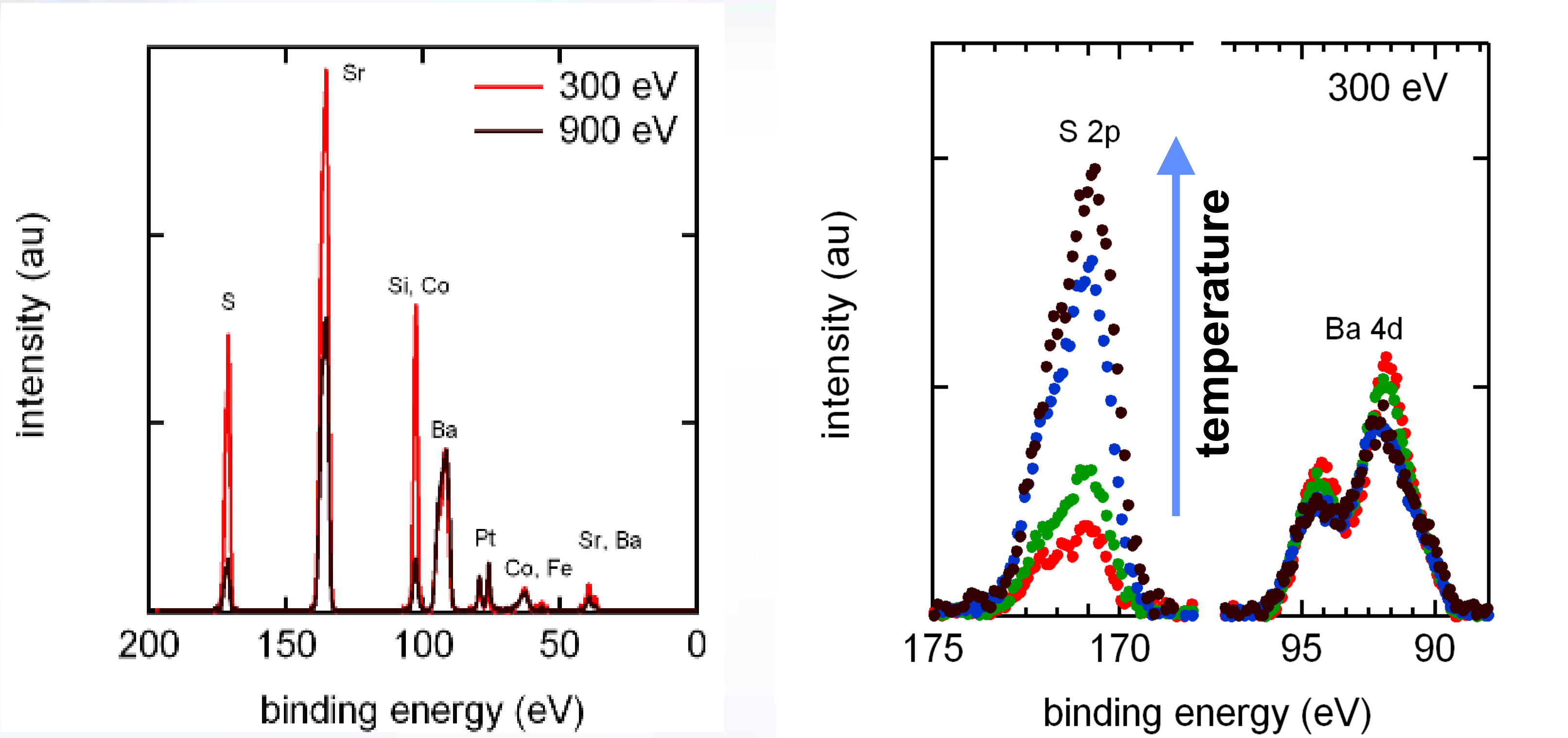
Highly reversible thin film SDC/porous Pt anode

Characteristic electron migration length @ OCV $L_C = \sqrt{\sigma_{eon} \tilde{R}^* l} \approx 2{,}000 \mu m$

Film Composition: $Ba_{0.53}Sr_{0.53}Co_{0.80}Fe_{0.20}O_x$ (determined via EDS calibrated with ICP-OES)

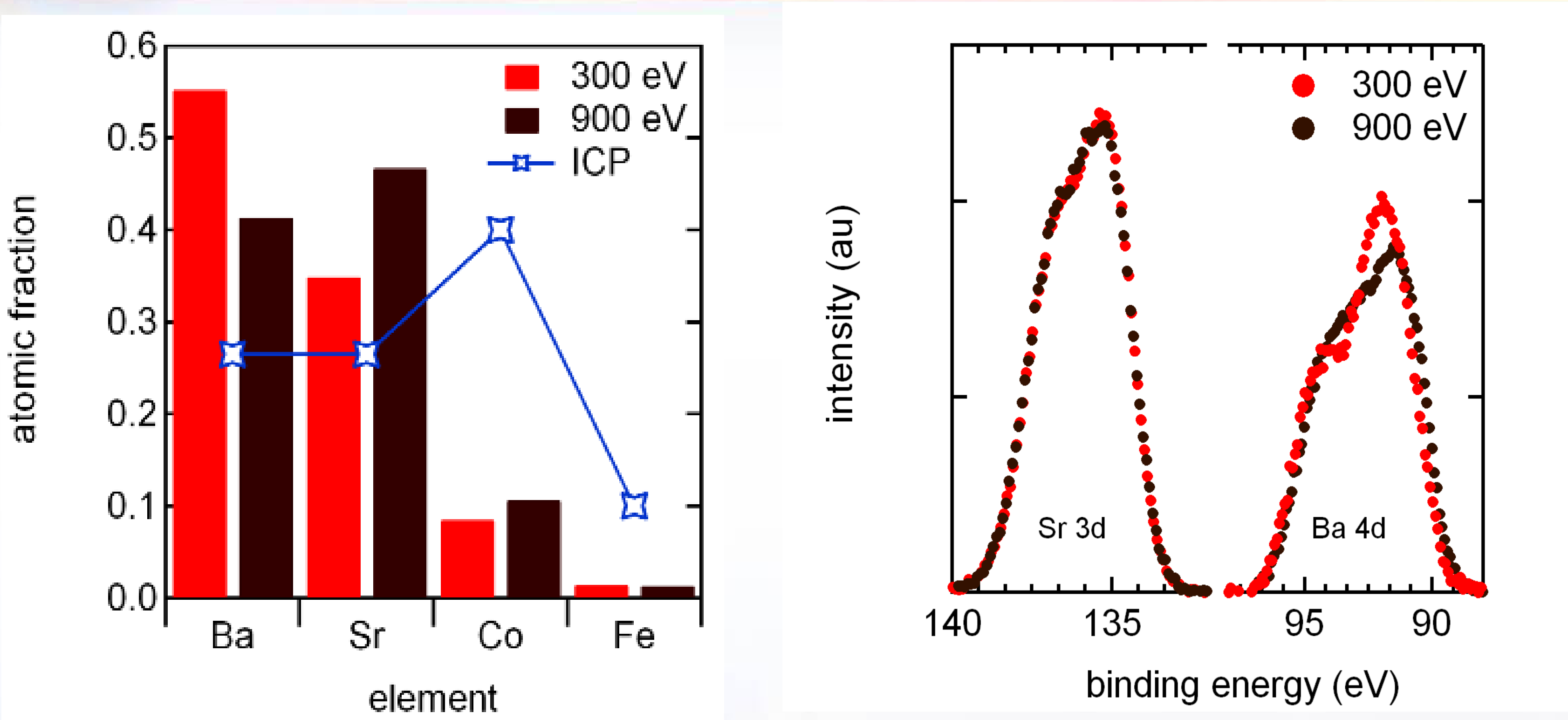
- **Dense geometrically well-defined microelectrodes**

Si and S impurities surface segregate



- **Higher photon energies probe deeper into bulk**
  - Greater escape depth for photoelectrons with higher kinetic energy
- **S impurity comes to surface on heating, returns to bulk on cooling**
- **All impurities (S, Si, Pt) amount to < 35% of surface atomic fraction excluding oxygen**

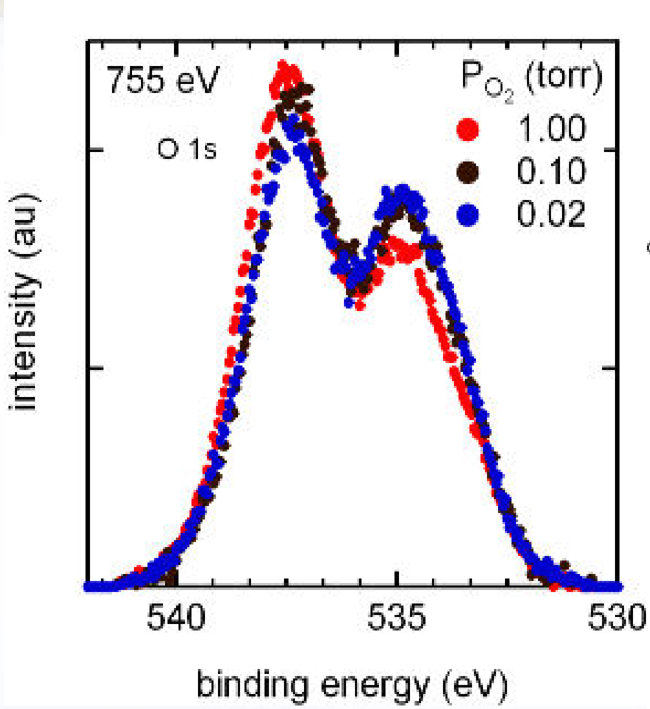
A-site cations (Ba, Sr) behave differently at OCV

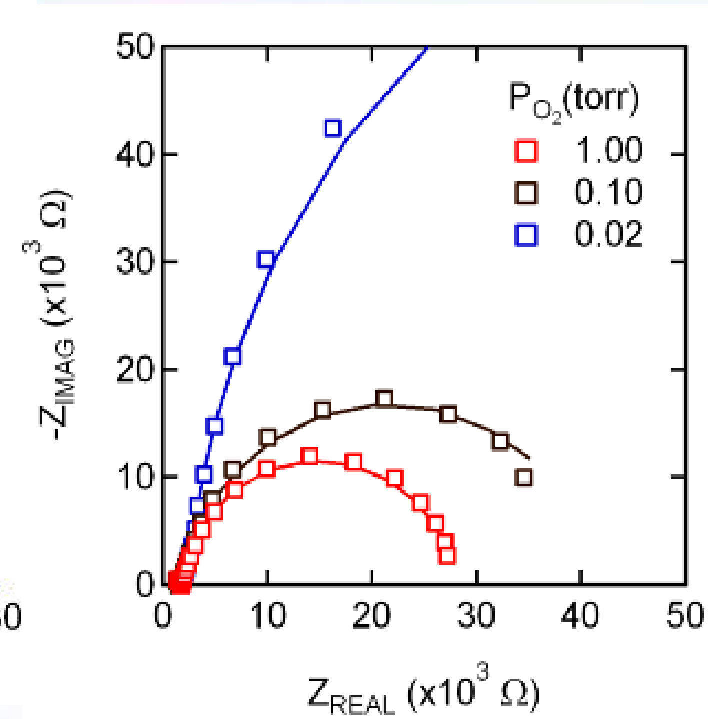


- **Ba atomic fraction enriched on surface and exists in a chemical state different than bulk**
  - Sr does not bond differently in the bulk

- **Co and Fe are also depleted in the near surface region**

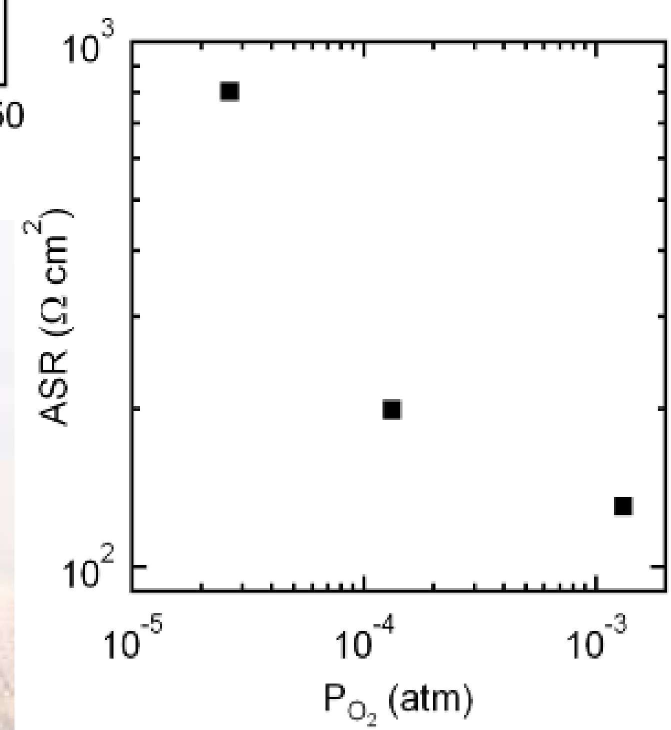
Oxygen activity consistent with literature reports



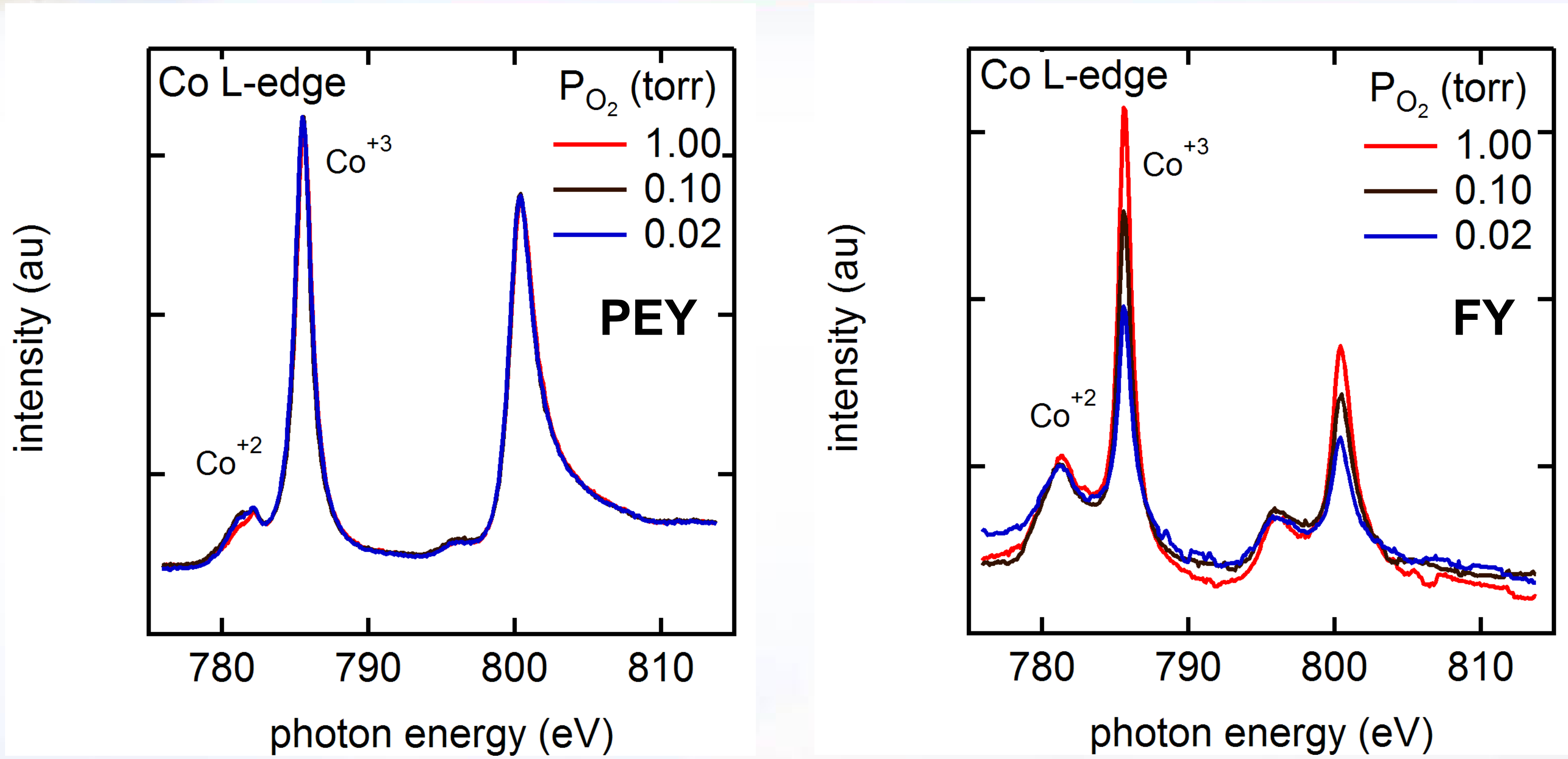


- **O 1s spectra very complex and involves contributions from surface-oxide impurities**
  - Clear trends are evident with O_2 pressure

- **Measured ASR is consistent with other PLD microelectrode studies**



XAS reveals interesting B-site cation (Co) behavior



- **Partial electron yield (PEY) probes surface states (< 3 nm)**
  - Co oxidation state invariant to O_2 partial pressure at OCV
- **Fluorescence yield (FY) probes bulk states (< 100 nm)**
  - Bulk Co^{+3} concentration decreases with oxygen activity

Conclusions

- **No significant variations in cation chemical behavior** *at surface* **observed when MEA is biased**
  - Photoelectron spectra at 300 eV unchanged at 0.6 V bias
  - Still working through complete data set

- **Successfully developed an experimental platform for applying synchrotron-based AP-XPS and XAS to investigating MEA in operando**

- **BSCF cathode**
  - Ba appears to have a different bulk state than surface state at OCV
  - Co has a mixed valency at OCV
    - Surface state remains oxidized as bulk reduces when P_{O2} decreases
  - Impurities (S, Si) surface segregate
    - Unclear how surface electrochemistry is impacted

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)

LDRD

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