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In-situ spectroscopic characterization of a working solid-oxide electrochemical cell

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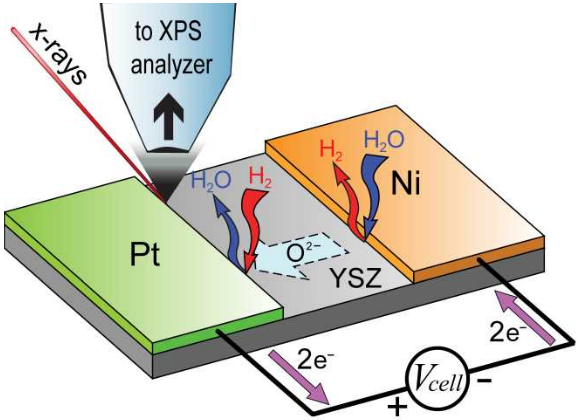

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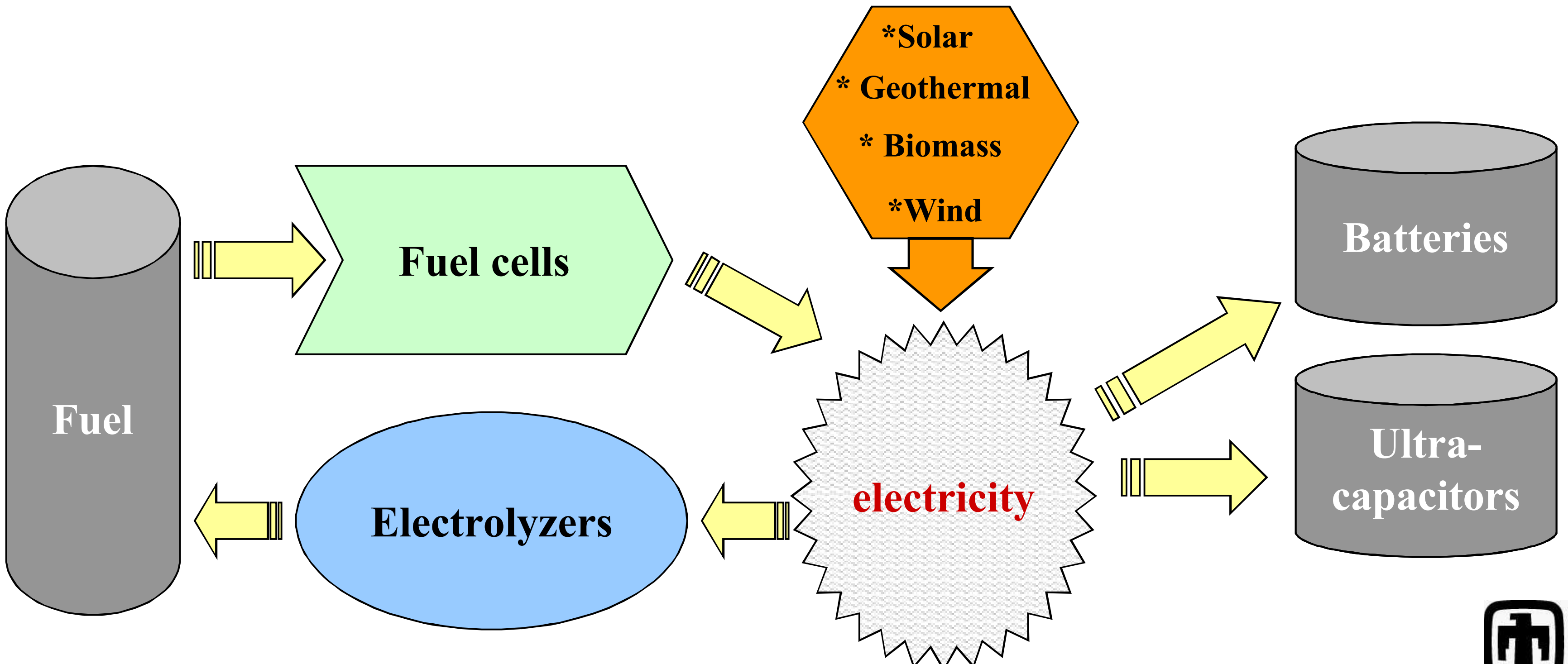
Electrochemistry technology will be increasingly used to store & convert energy

- **Electrochemical technology will be a critical part of energy security in the near future:**
  - High efficiency: 40%-95%
  - Little contribution to climate-change (carbon neutral)



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These are the fundamental questions in electrochemical energy conversion

1. **What is the nature of charge-transfer reactions?**
   - Where do reactions occur and through what species?

2. **Where are the electrical overpotentials that limit rates and efficiencies?**
   - Find electrochemical “bottlenecks”

3. **What are the phase changes that store energy?**

Relevant to **fuel cells, batteries**, and **ultra-capacitors**

We aim to solve these in a model fuel cell system

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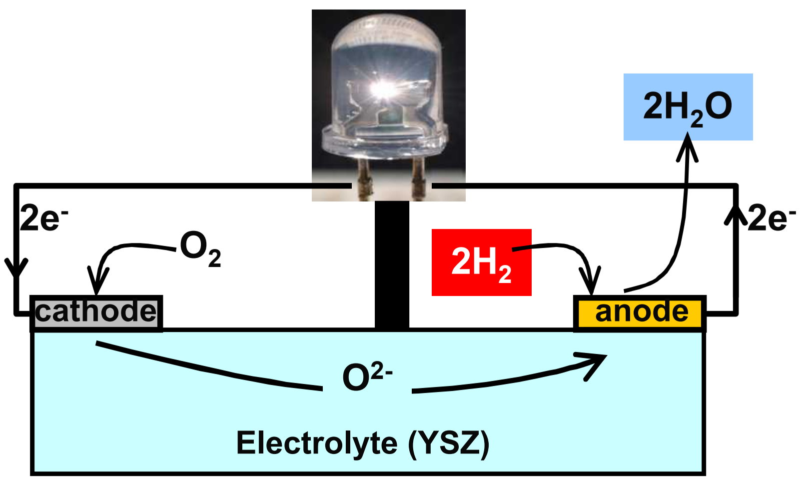
A fuel cell provides a model platform for fundamental studies

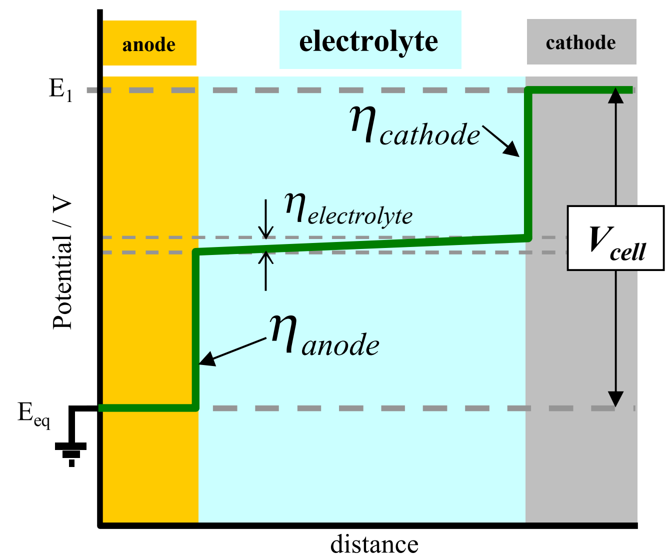
- **Why does the fuel-cell voltage drop when current is being produced?**

$$V_{cell} = \eta_{anode} + \eta_{electrolyte} + \eta_{cathode}$$

Current: $i \propto i_0 e^{\eta}$

Which overpotential is limiting the current?





Fuel cell optimization requires understanding where the overpotentials occur

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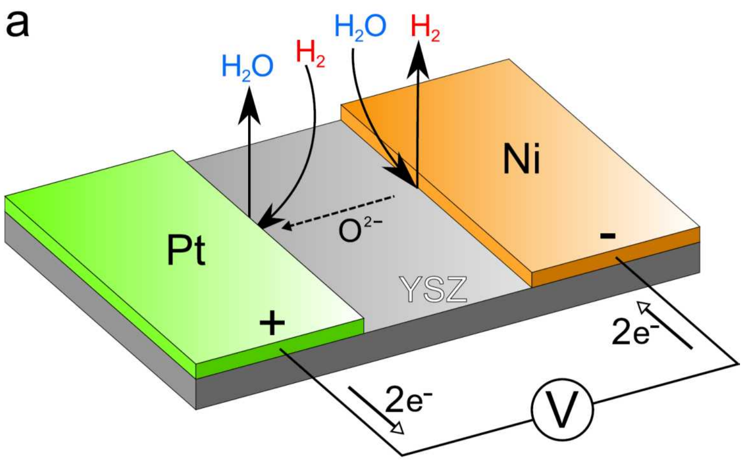
The Ni-YSZ-Pt cell serve as a model system for addressing basic questions

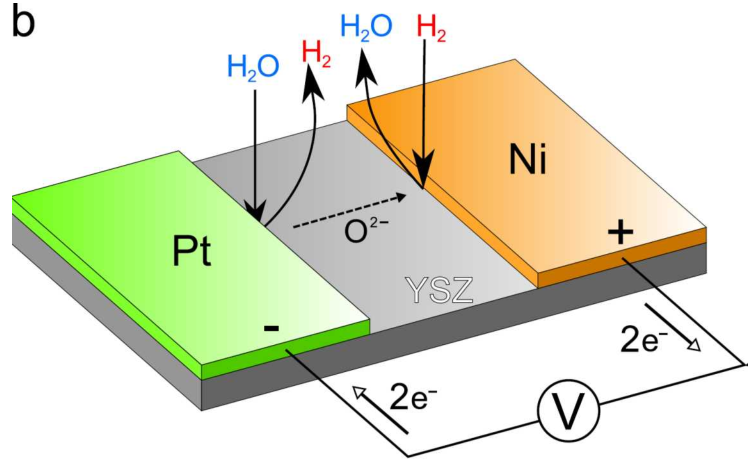
1. We will focus on standard electrodes: Ni and Pt
2. Our solid-state electrolyte: Y_2O_3-stabilized ZrO_2 (YSZ)
3. We will *drive* (apply bias) the cell on H_2O+H_2 atmosphere

a



Ni as SOFC anode
(Ni oxidizing H_2)

b



Ni as electrolyzer cathode
(Ni splitting H_2O)

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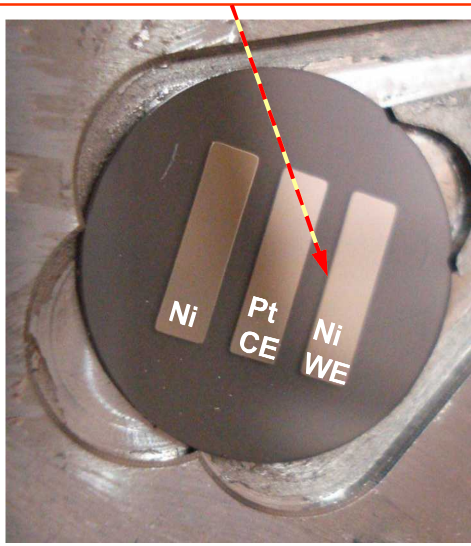
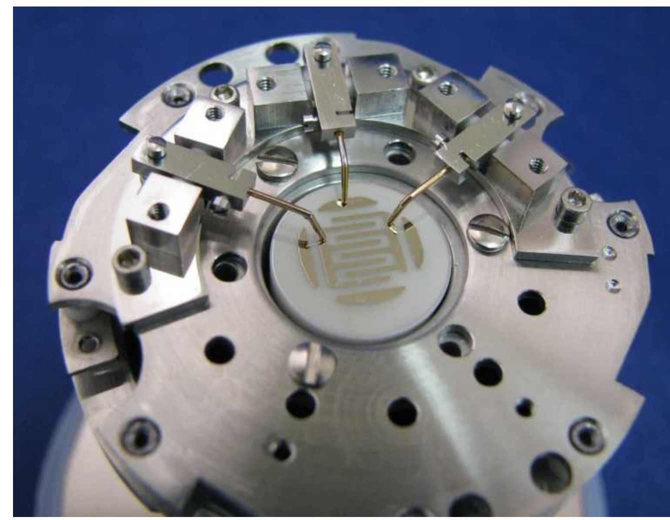
First step: solid-oxide fuel cell fabrication

Three-phase boundary (TPB)



Our electrochemical platform:



Our designed/fabricated ALS-compatible electrochemical holder

Josh Whaley, Sandia

- Goal: study simple cells under working conditions:
    - Temperature >700°C
    - Pressure ~1 Torr
    - Under electrochemical bias (three independent connections)

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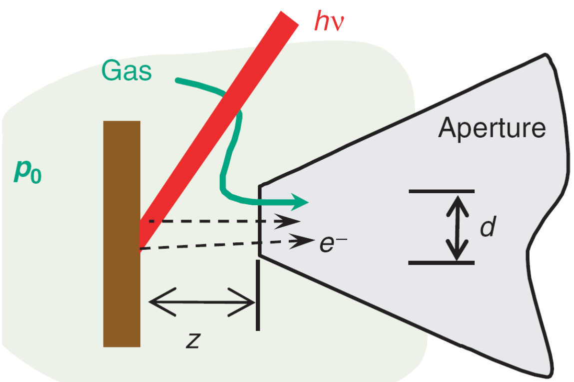
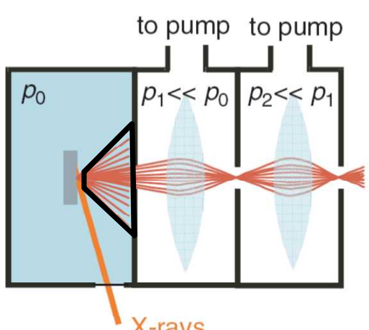
Ambient-pressure photoemission (APXPS)

We use both AP-XPS endstations:
- ALS BL 9.3.2
- ALS BL 11.0.2





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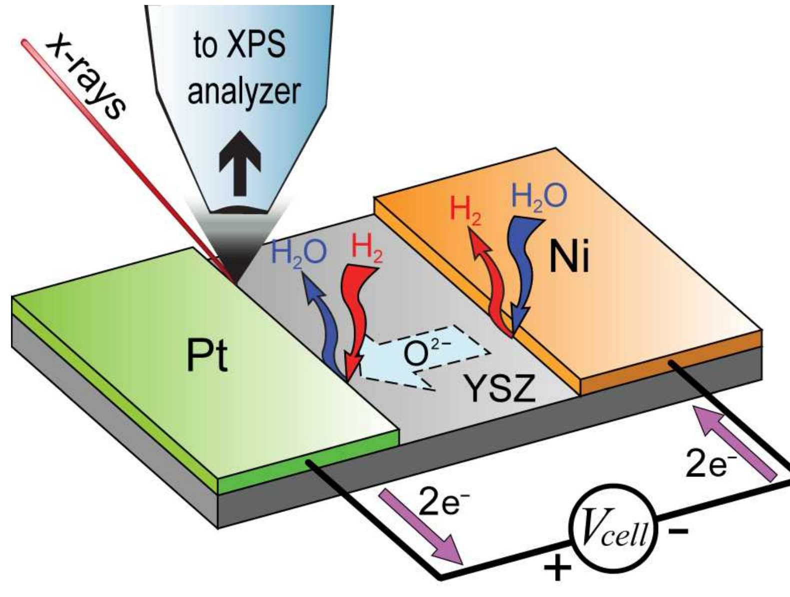

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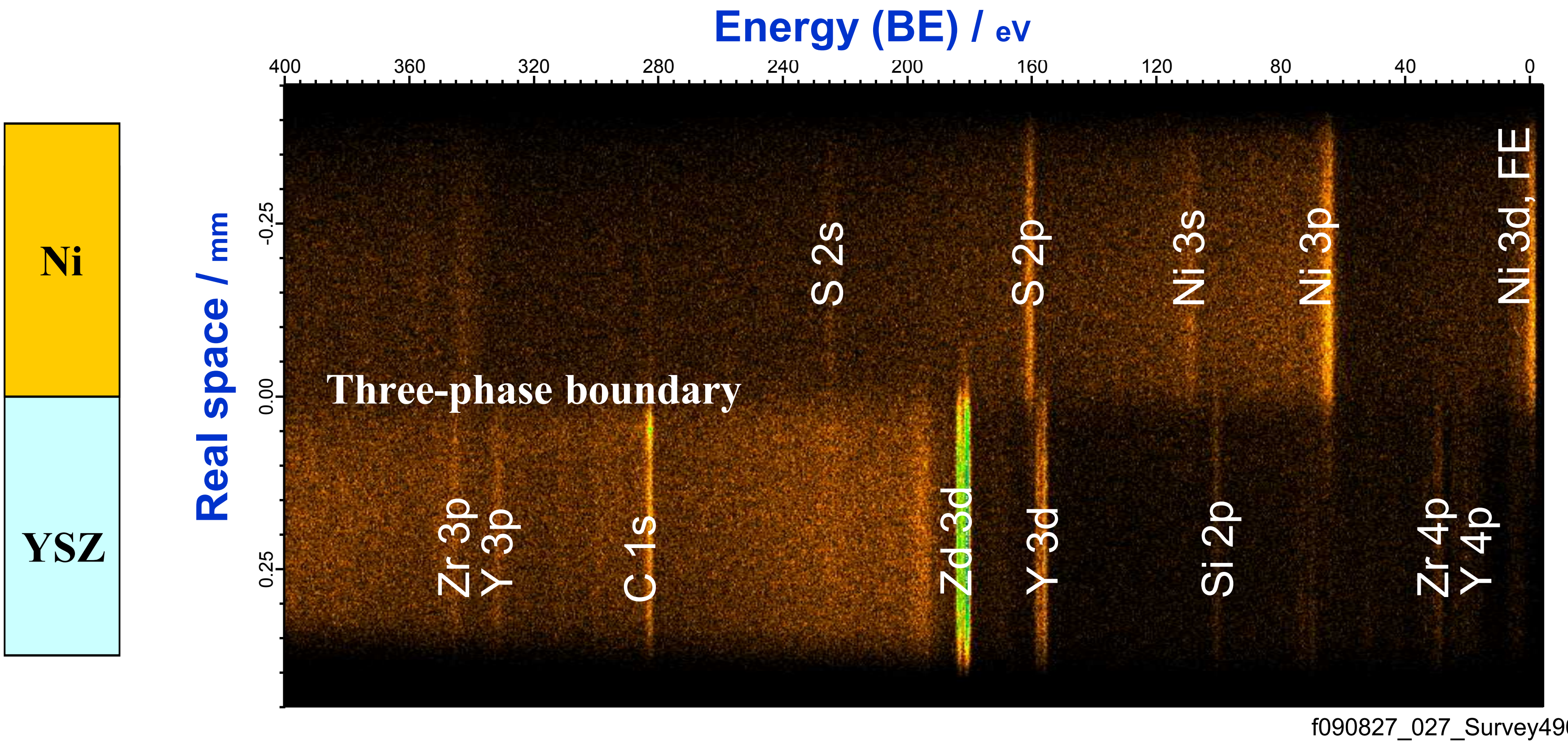
Spatially-resolved APXPS allows us to access the TPB



First time spatially resolved APXPS!

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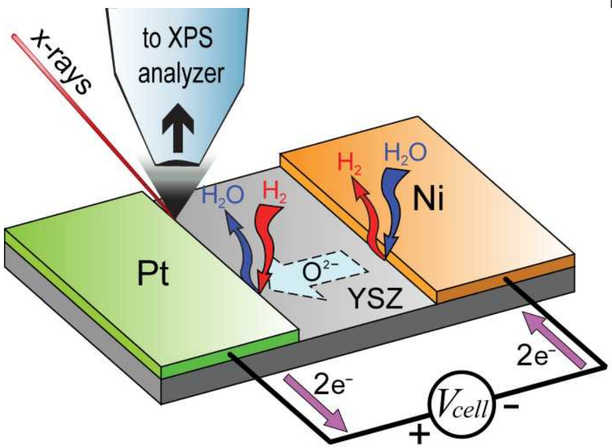
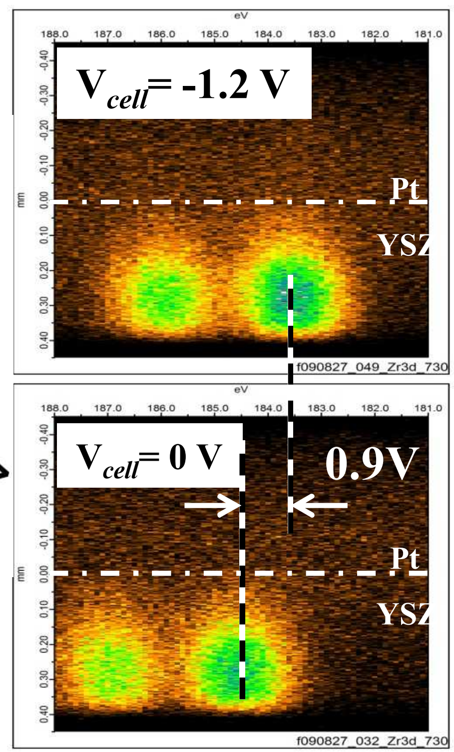
We have made the first measurement of individual overpotentials

$$V_{cell} = \eta_{anode} + \eta_{electrolyte} + \eta_{cathode}$$

$$i \propto i_0 e^{\eta}$$

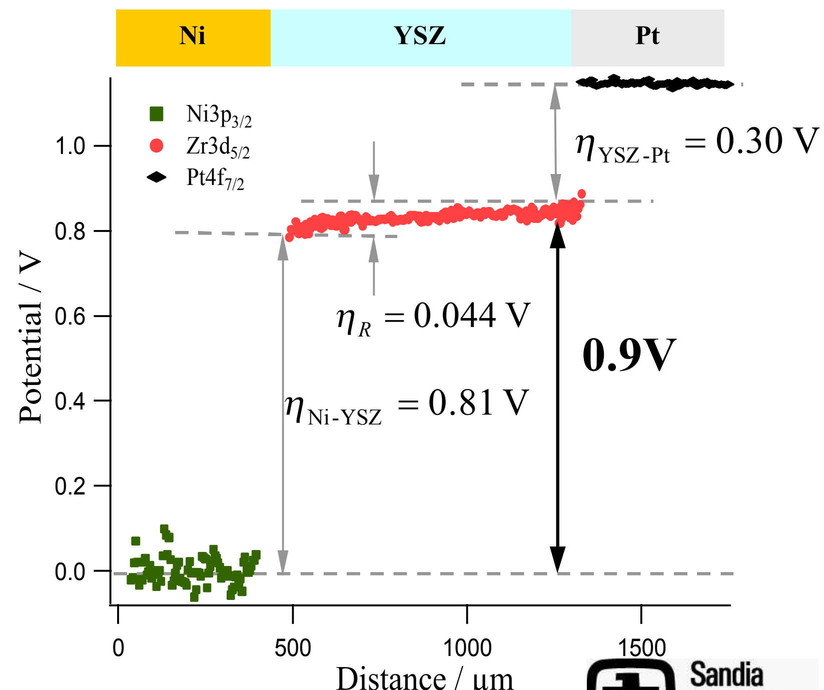


$Zr3d_{5/2}$



Potential landscape of the cell

(H_2O reduction on Ni)



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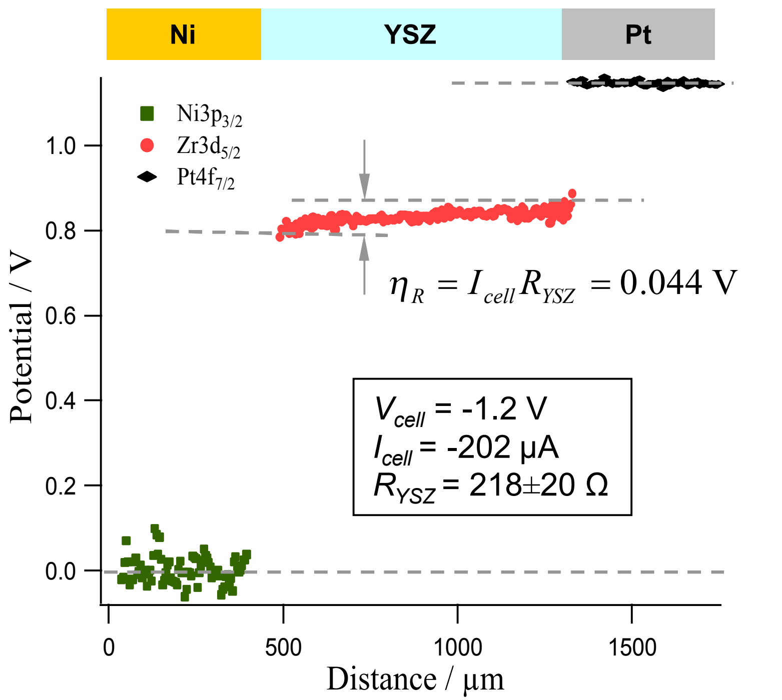
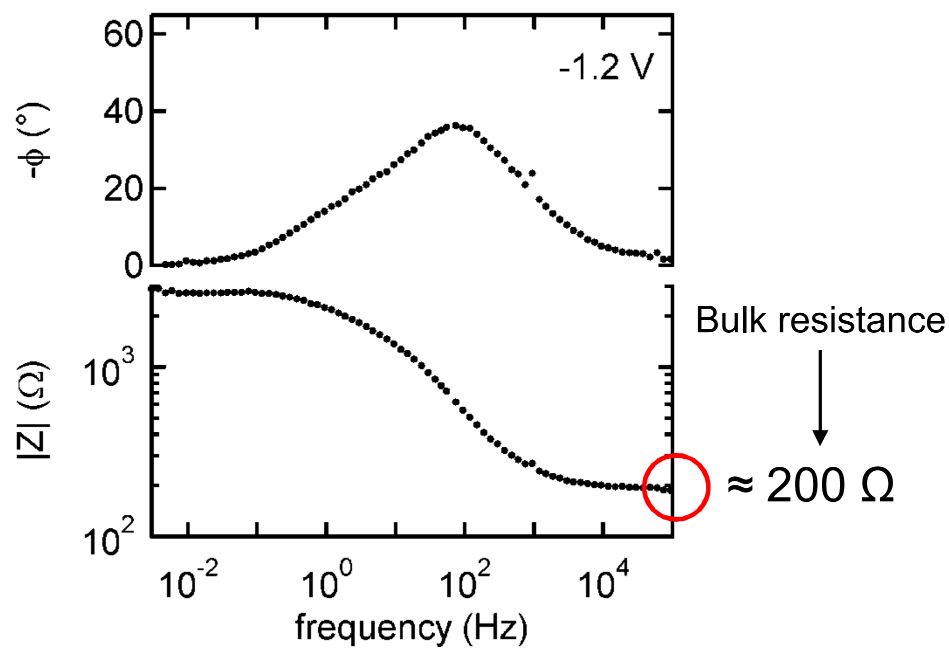
We successfully validated our method against traditional electrochemical tests

Potential landscape of the cell

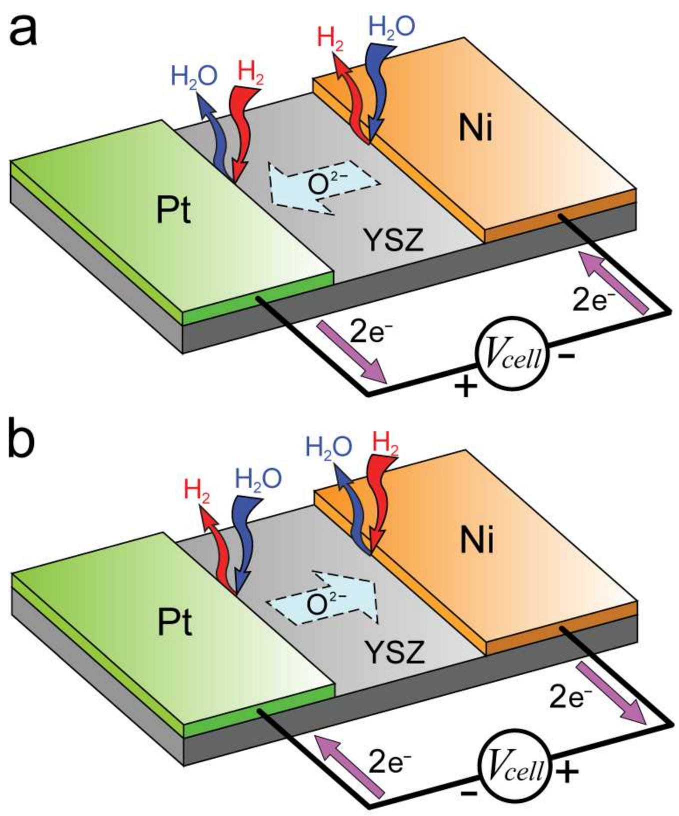


Electrochemical impedance spectroscopy EIS

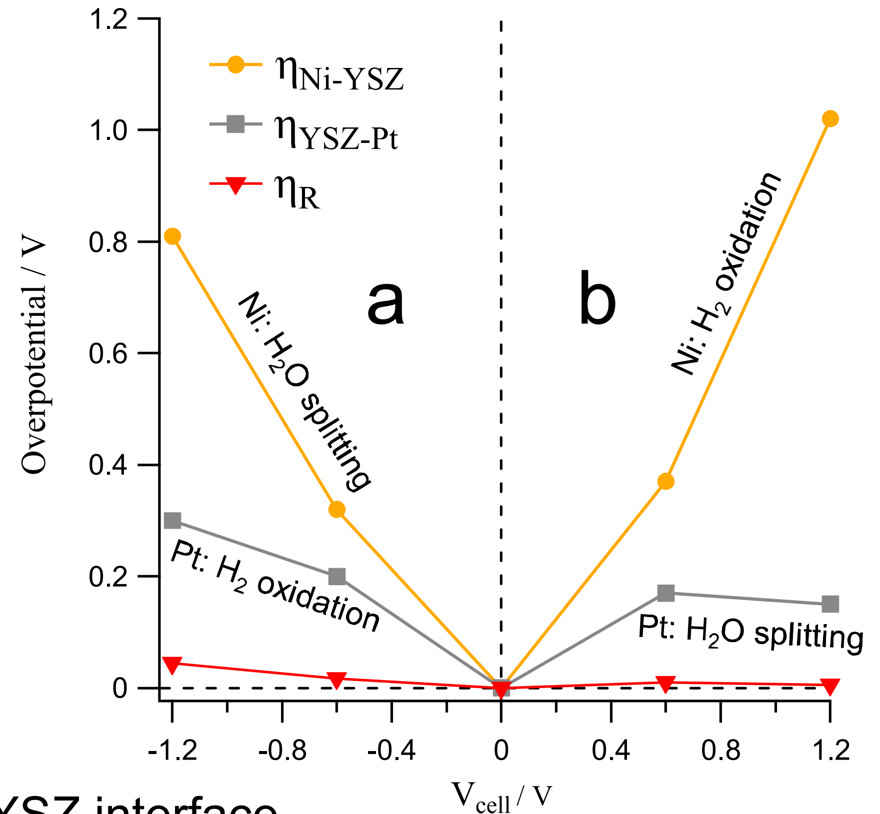


1. **Ohmic loss (R_{YSZ}) across electrolyte consistent with high frequency |Z|**
   - **XPS**: R_{YSZ}=218 ± 20 Ω (local measurement)
   - **EIS**: R_{YSZ}= 200 Ω (global measurement)

Spatially-resolved SOFC overpotentials



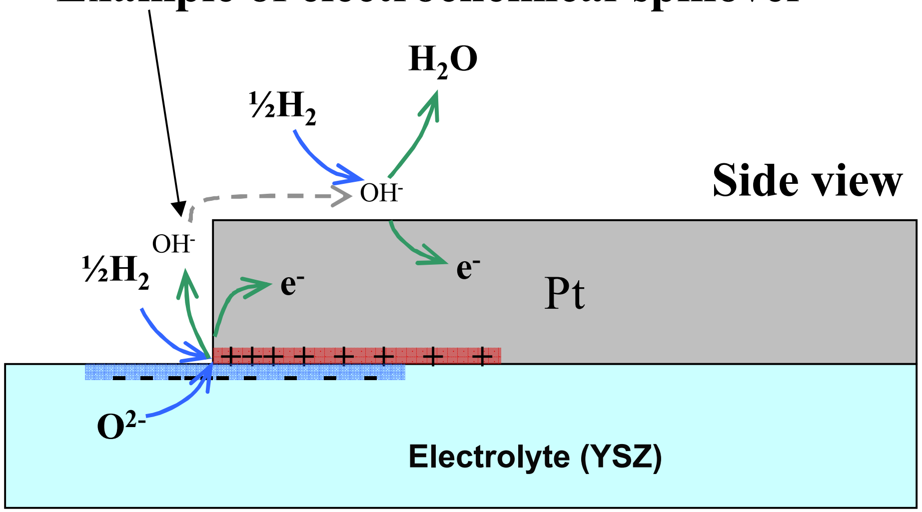
Overpotentials plot



1. Most of the overpotential is at the Ni-YSZ interface
2. η_{Pt} is small and almost constant, i.e., Pt is a good Counter Electrode
3. We are working on how to model the cell from the data

XPS allows us complete chemical speciation

Example of electrochemical spillover

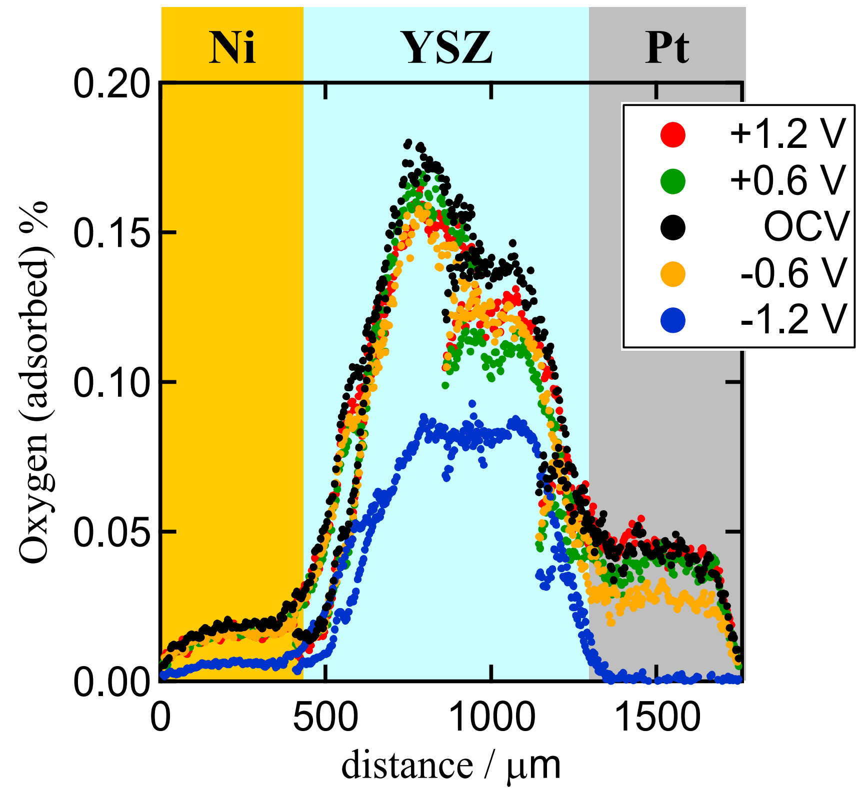


example

$$1/2\, H_2^{gas} + O_{YSZ}^{2-} \rightarrow OH_{Pt}^{-} + e_{Pt}^{-}$$

$$1/2\, H_2^{gas} + OH_{Pt}^{-} \rightarrow H_2O^{gas} + e_{Pt}^{-}$$

Adsorbed oxygen



- H_2 oxidation on Pt fast enough to shift equilibrium surface coverage over a large area away from TPB
  - Need to compare this observation to theory (need to do the calculation)
- Trends in surface oxygen on YSZ *maybe* explained by carbon loss?

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Summary

- *In-situ* surface electrochemistry experiments give us new information about fundamental processes in energy conversion/storage devices.
- We have mapped the local surface potential of an active Ni/YSZ/Pt electrochemical cell
- We established the efficacy of ambient pressure XPS as an in-situ diagnostic
- Moving towards additional in-situ x-ray characterization techniques:
  - X-ray micro-diffraction, x-ray absorption

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