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In-situ Investigation of SOFC Patterned Electrodes Using Ambient Pressure X-ray Photoelectron Spectroscopy

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Spatially Resolve Measurements Of Surface Species And Surface Potentials Across Charged Double Layers

- **Validate detailed mechanisms of charge transfer reactions**
  - Detailed physical models posed by several groups for Ni/YSZ/Pt system

- **Few if any direct observations of surface state and composition during operation**

Zhu, H., Kee, R.J., Janardhanan, V.M., Deutschmann, O. and Goodwin, D.G. “Modeling Elementary Heterogeneous Chemistry and Electrochemistry in Solid-Oxide Fuel Cells” *J. Electrochem. Soc.* **152**, A2427 (2005).

Bessler, W., Gewies, S. and Vogler, M. “A New Framework for Physically Based Modeling of Solid Oxide Fuel Cells” *Electrochimica Acta* **53**, 1782-1800 (2007)

Kee, R., Zhu, H., Sukeshini, A.M. and Jackson, G. “Solid Oxide Fuel Cells: Operating Principles, Current Challenges, and the Role of Syngas.” *Combustion Sci. and Tech.* **180**, 1207-1244 (2008)

Goodwin, D.G., Zhu, H., Colclasure, A.M. and Kee, R.J. “Modeling Electrochemical Oxidation of Hydrogen on Ni–YSZ Pattern Anodes” *J. Electrochem. Soc.* **156**, B1004 (2009)

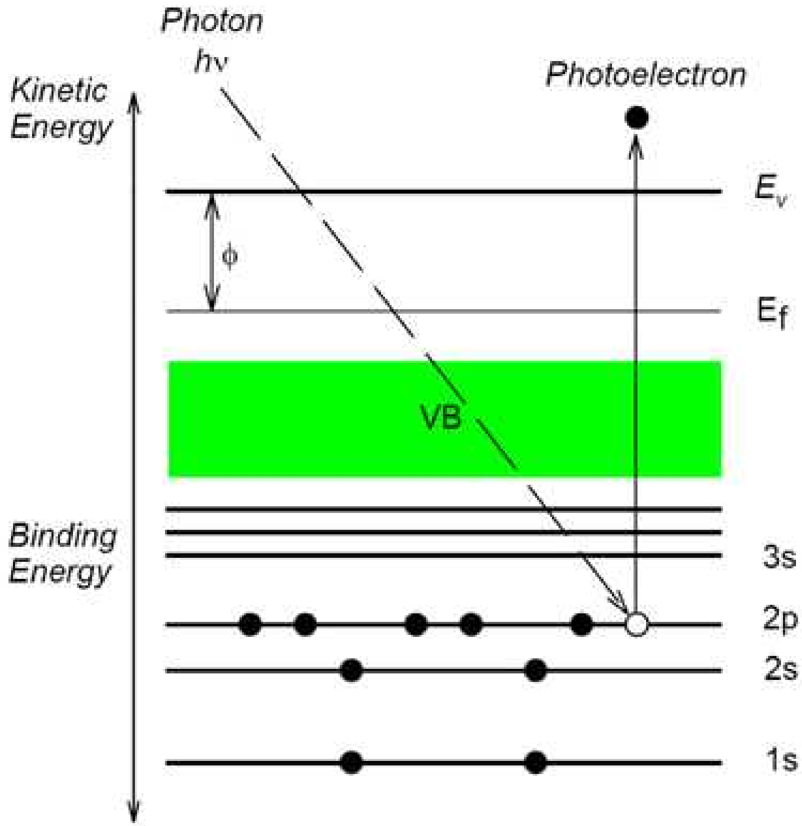
XPS Used To Probe Chemical Composition, Oxidation State And Electrical Potential Of Surface

- **Photon in — Electron out process**
  - Measure kinetic energy of photoelectrons

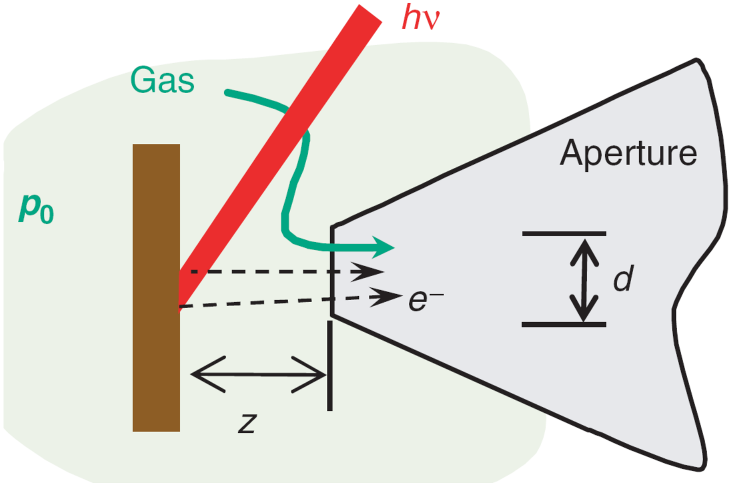
$$KE = h\nu - BE_f - \phi$$

- **Identify elements**
  - Energy of core level electrons discrete and well defined for all atoms
- **Chemical shifts**
  - Higher positive oxidation state yields higher binding energy
- **Rigid shifts**
  - Higher positive surface charge yields higher binding energy

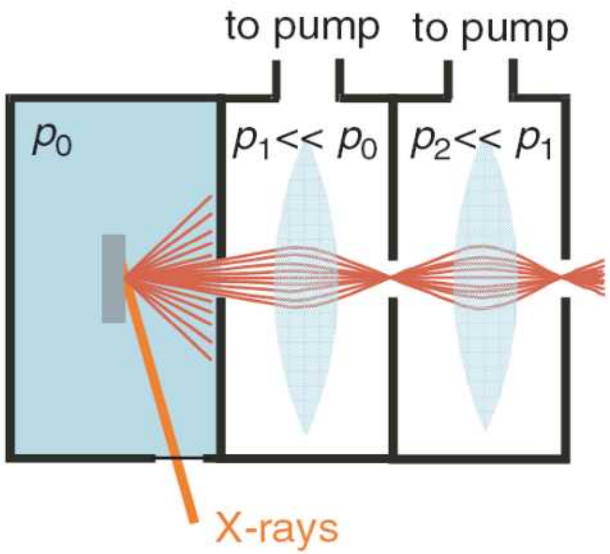
$$KE_\eta - KE_{OCV} = \eta \text{ “overpotential”}$$



Key Developments Needed To Extend Operating Pressure Of XPS To Ambient P_0



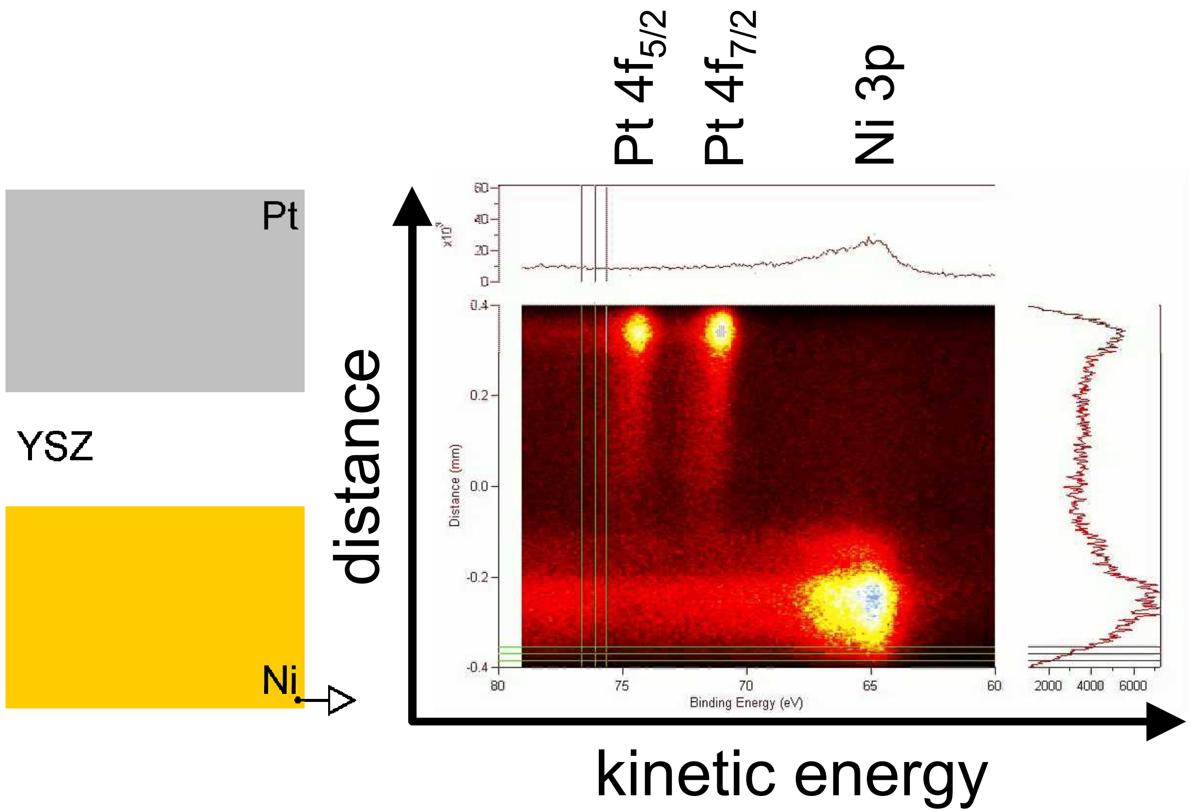
- **Differentially pumped energy analyzer and electron optics**
  - Increase transmission efficiency of electrons to analyzer
- **Operate at Torr pressures**
  - Appreciable Faradic current



- **Photoelectrons collected in close proximity to surface**
  - Short electron mean free path
- **Synchrotron radiation**
  - Monochromatic photons
  - High flux

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

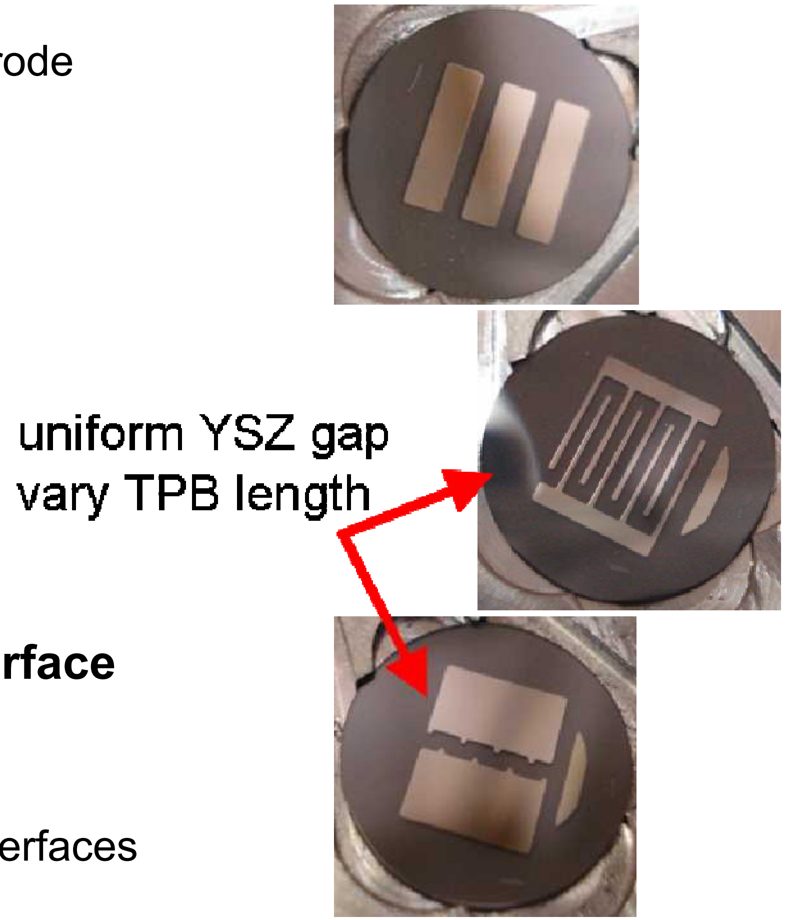
Imaging Detector Simultaneously Resolves 1-D Space and Electron Energy Dispersion



- **Electrostatic lens yields real space image of sample**
  - Pixel rows provide spectral information
  - Pixel columns provide spatial information

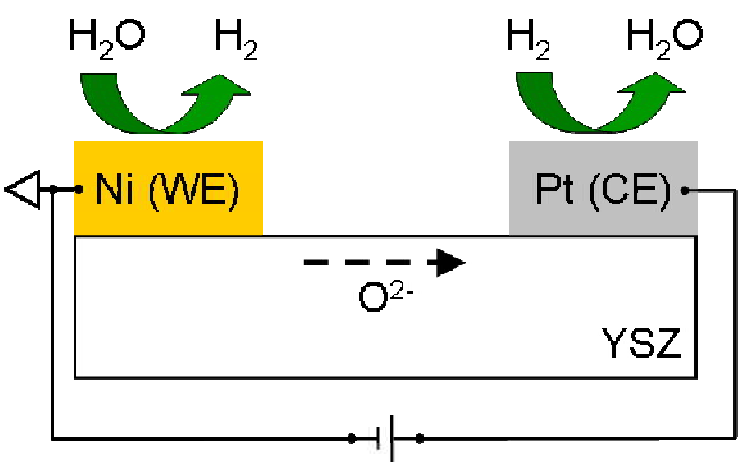
Planar Electrochemical Cells Made From Patterned Metal Film Electrodes On Single Crystal YSZ

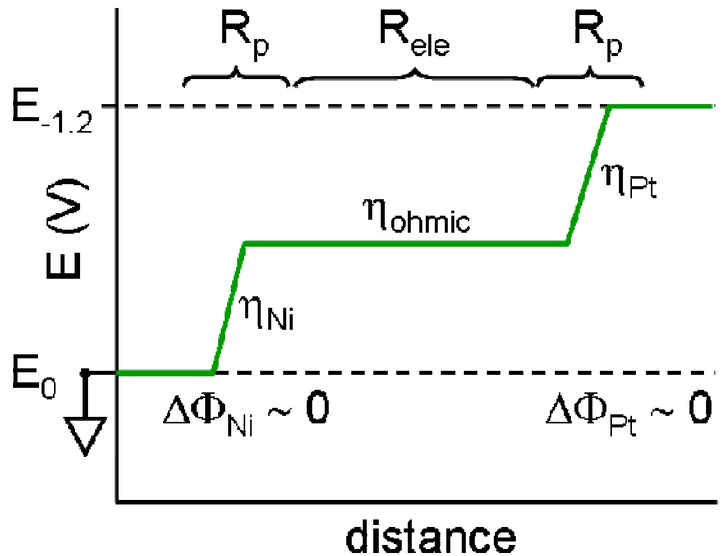
- **Simple Ni/YSZ/Pt material system**
  - Well developed thermochemistry and electrode kinetics
    - compare results to theoretical predictions
- **Films patterned by shadow masks**
  - Electron beam evaporation
  - 200 to 500 nm thick films
  - Surface cleanliness absolutely critical
    - AVIOD CONTACT LITHOGRAPHY
- **O^{2-} ion conduction orthogonal to the surface normal**
  - Surface and subsurface ion conduction
  - Expose TPB at both Ni/YSZ and YSZ/Pt interfaces

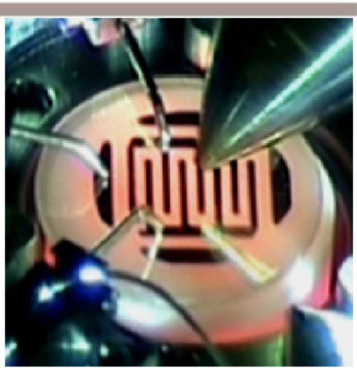


Single Chamber Configuration Used To Establish Electrochemical Environment

H_2O reduction on Ni @ -ΔV



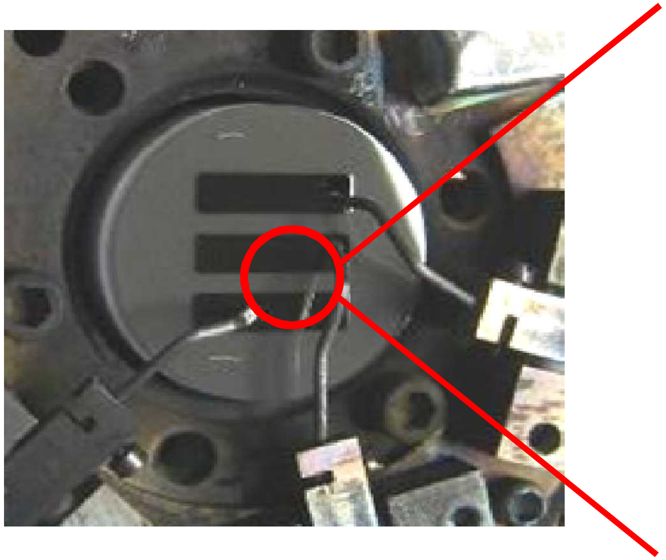


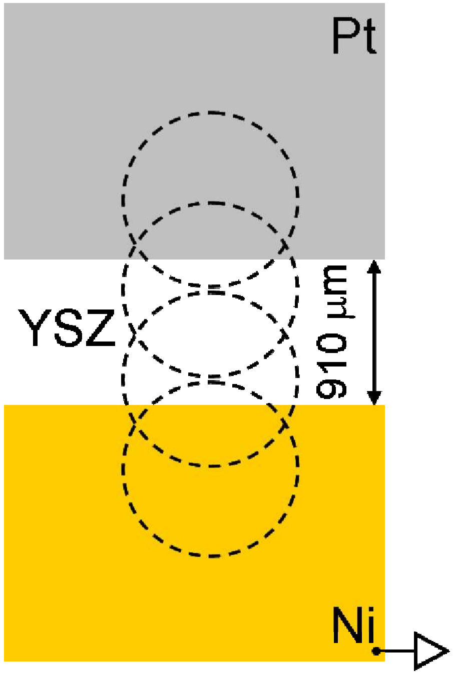


- **Experimental conditions**
  - H_2:H_2O of 1:1 and 1:20, P_0 = 500 mTorr, T = 873 to 1073 K
    characterize competition between thermochemistry and electrochemistry
- **2-electrode configuration**
  - Ni = WE = analyzer ground, Pt = CE = tied to RE

XPS Spectra Collected for Seven Elements At Four Positions And Five Electrode Potentials

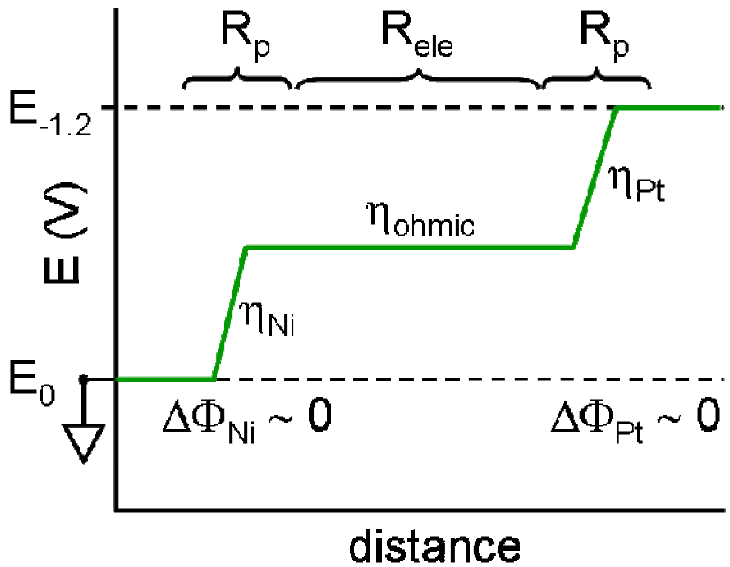
	hν	KE
O 1s	730 eV	200 eV
C 1s	490 eV	210 eV
Zr 3d		310 eV
S 2p		330 eV
Y 3d		330 eV
Ni 3p		420 eV
Pt 4f		420 eV



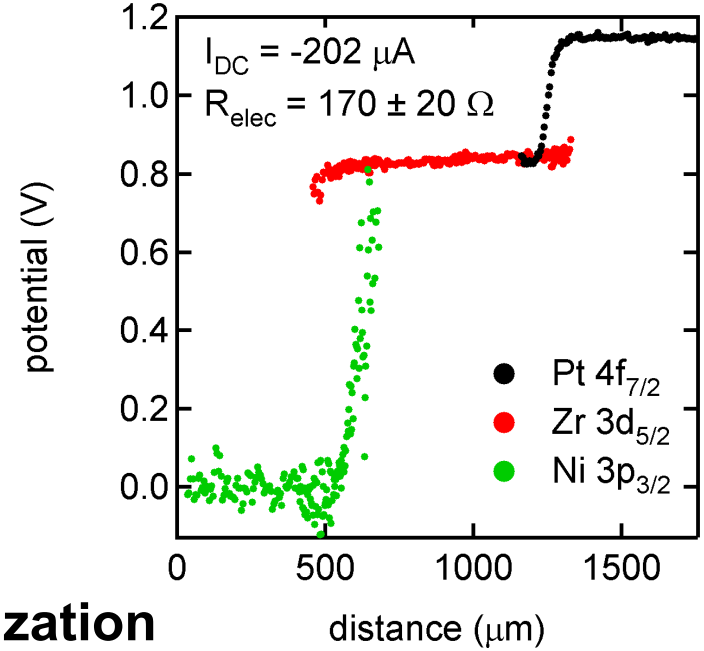


- **Sample position manipulated with stepping motors**
- **Thousands of images analyzed**
  - Fitted peak position used to determine rigid and chemical shifts
  - Peak area to determine atomic composition (< 3 nm probe depth)

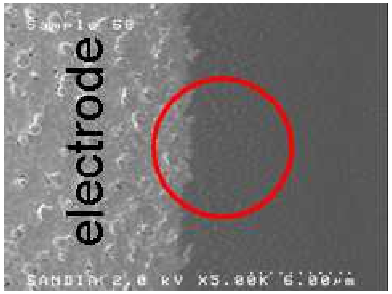
Direct Measurement Of Anode And Cathode Overpotentials By XPS



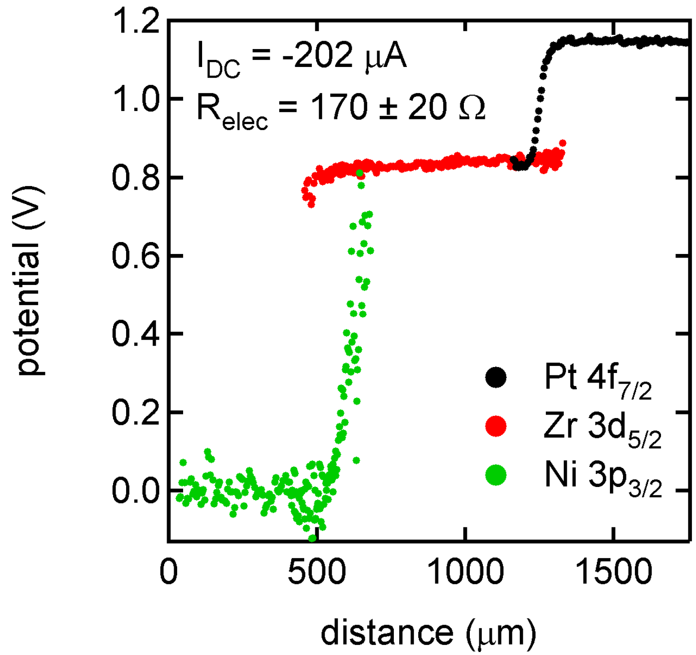
H$_2$O reduction on Ni @ -1.2V

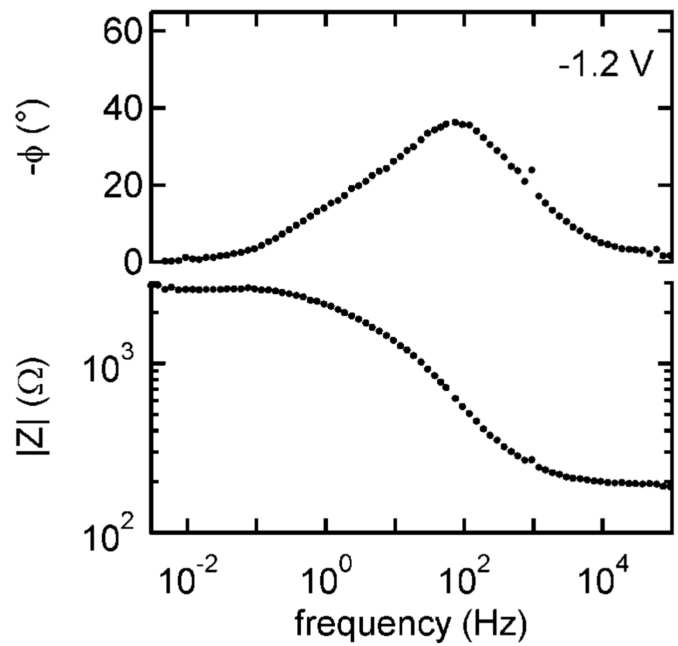


- **Ni electrode exhibits higher polarization resistance than Pt**
  - Limiting kinetics
- **Disconnected metal islands cause XPS peaks to rigidly shift and broaden**



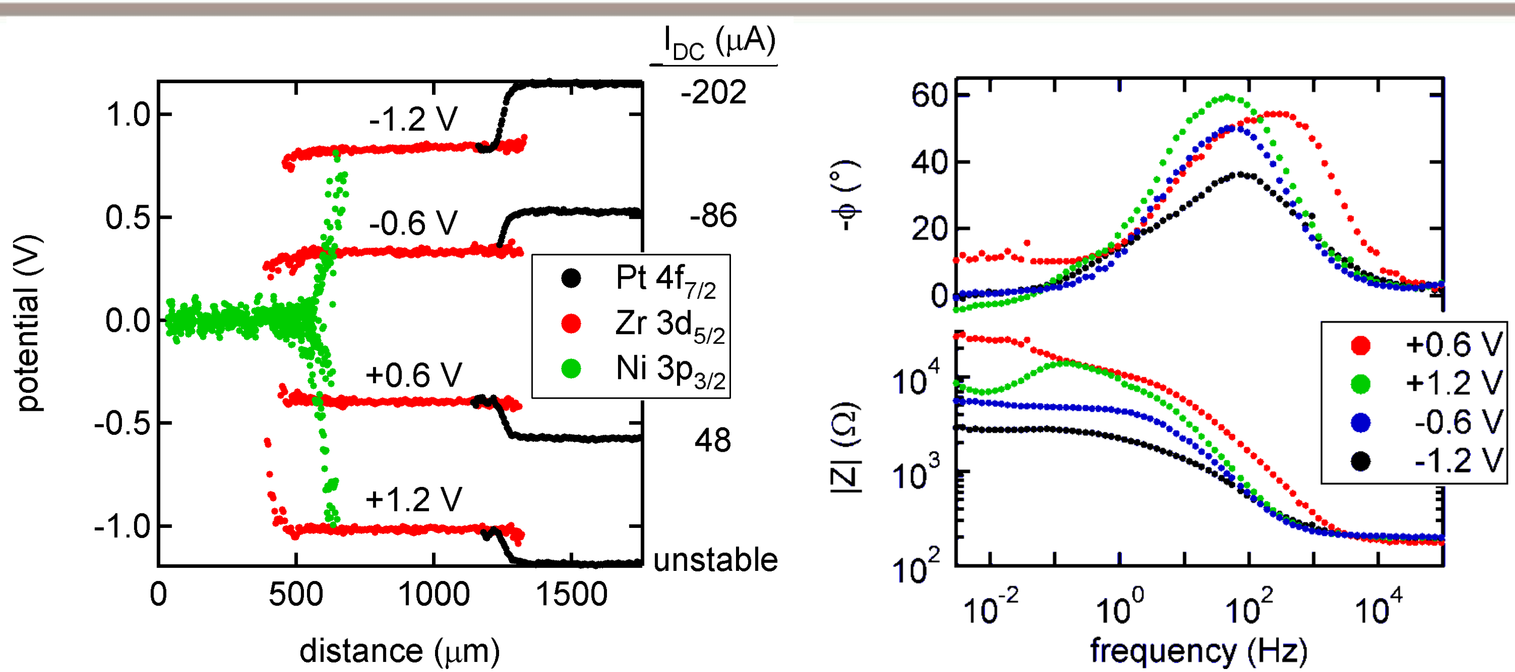
Observe Characteristic Impedance Behavior For Electrochemical Cell





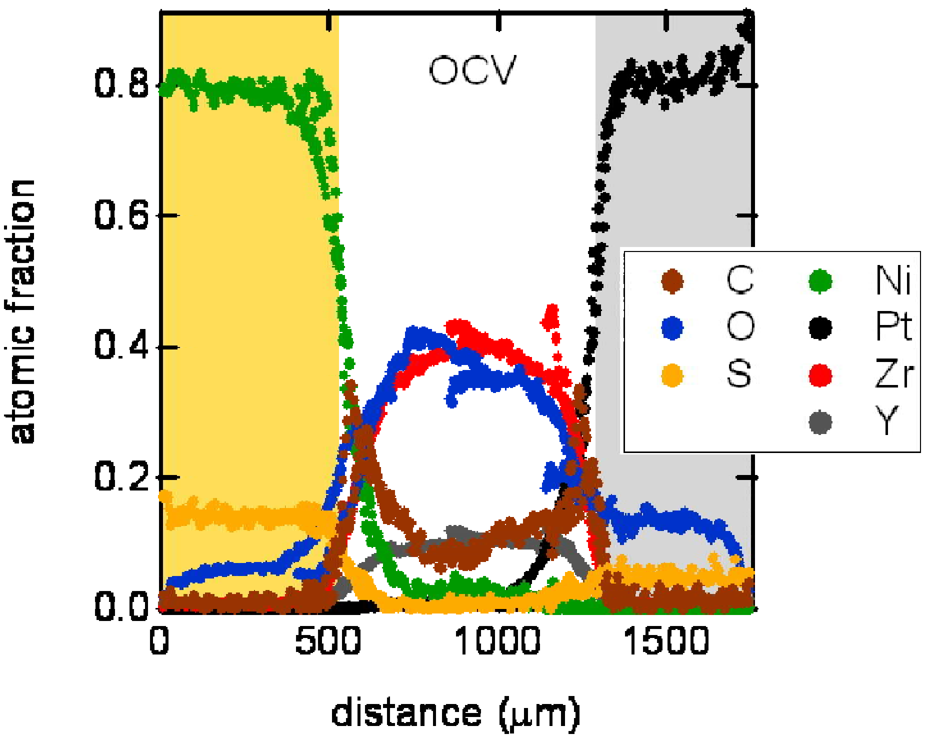
- **Ohmic drop across electrolyte consistent with high frequency |Z|**
  - Values for I_{DC} and R_{elec} are not weighted by area or TPB length
- **Low frequency |Z| (~ 3 kΩ) < $\Delta V / I_{DC}$**
  - Difference between local surface potential and “area averaged” EIS
  - Characteristic of inhomogeneous potential fields

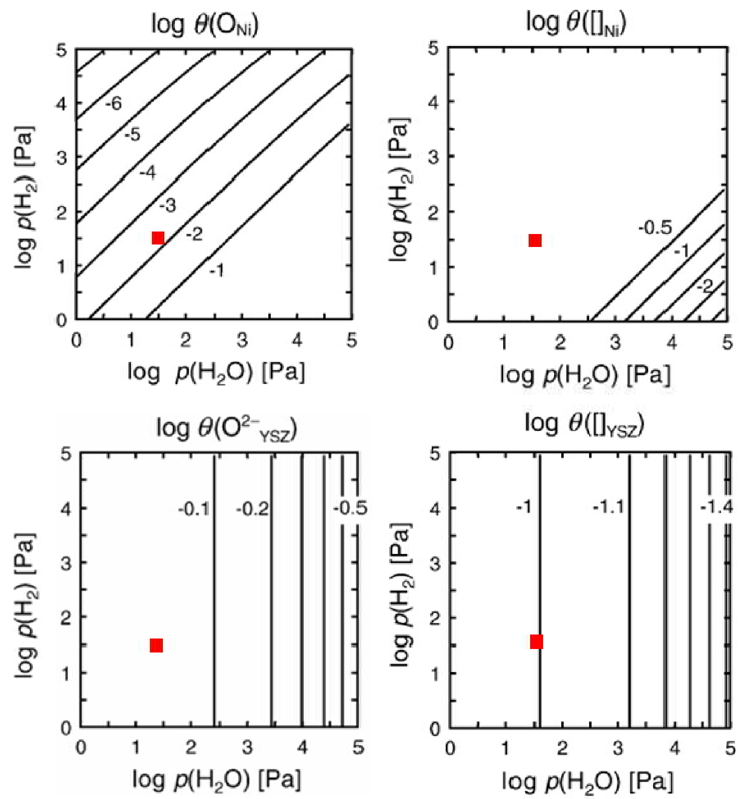
Electrode Overpotentials Measured By XPS Between -1.2 and + 1.2 V



- **H_2O reduction on Ni (WE) @ -ΔV**
- **Ni oxidation above +0.3 V clearly evident in I-V sweeps**
  - Polarization resistance increases due to oxidation of Ni at the TPB
  - More extreme conditions required to oxidize the bulk electrode

Atomic Composition Of Cell Surface Measured by XPS Can Be Compared To Theory

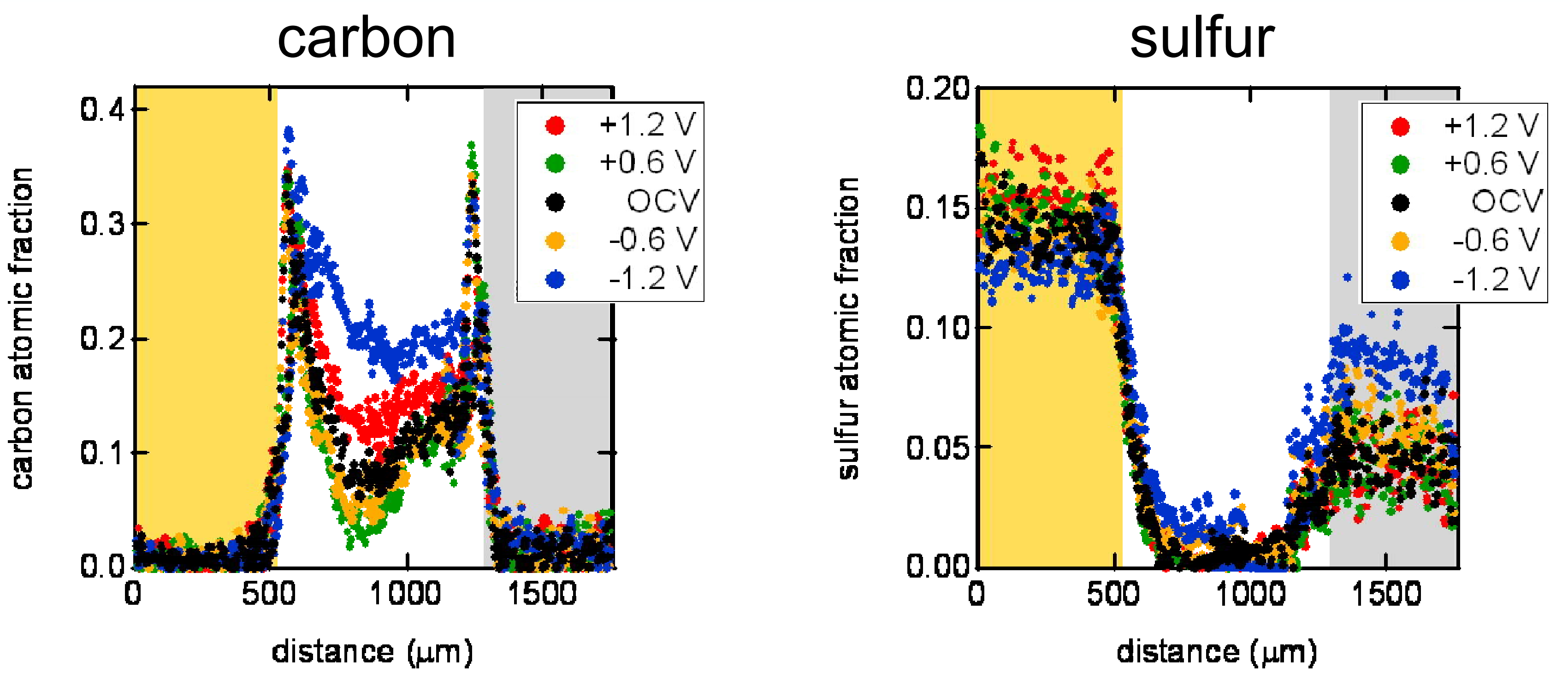




- **Significant amount of sulfur on Ni electrode**
  - Stable in extreme environment, may go subsurface when oxidized
- **Significant amount of carbon at the electrode/YSZ interfaces**

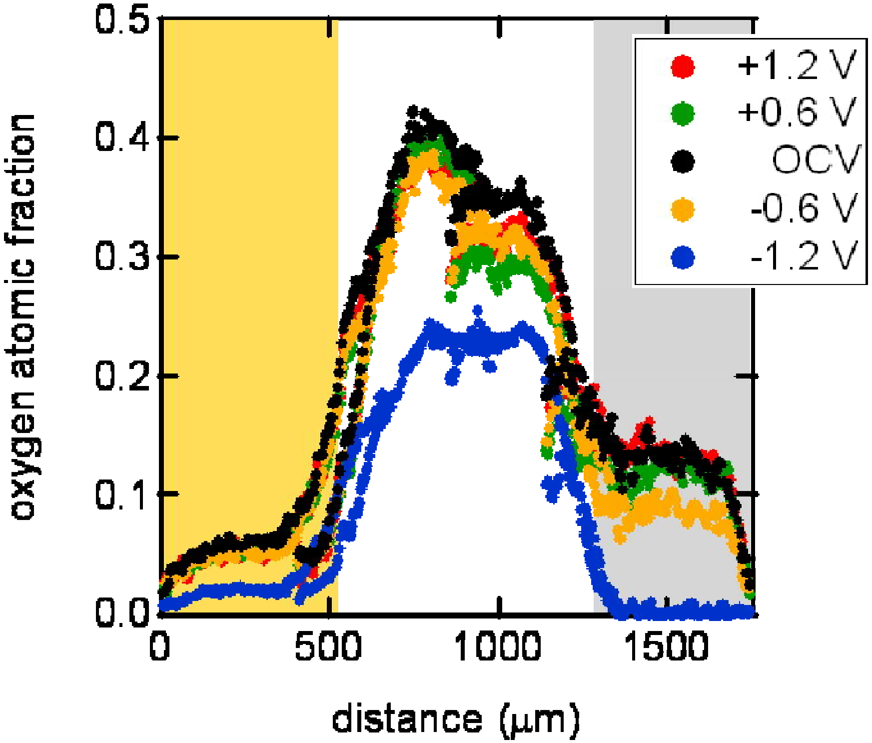
Bessler, W.G. et al. *Solid State Ionics* **177**, 3371 (2007)

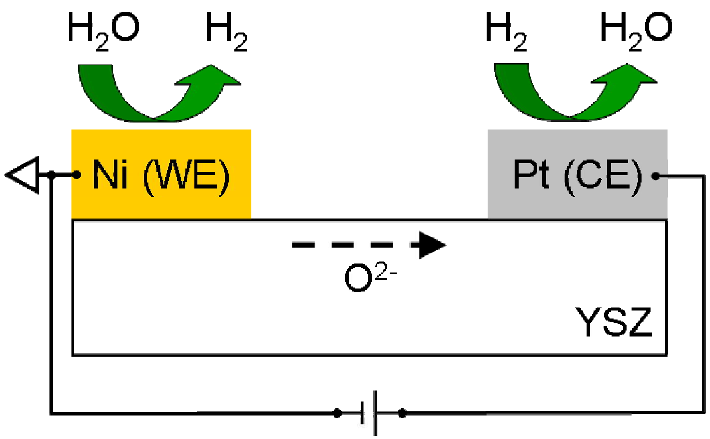
Distribution Of Surface Contaminants And The Effect Of Applied Potential



- **Carbon not present on the metal electrodes**
  - Electrochemical oxidation removes C from Ni and Pt
  - Carbon on "floating" metal islands oblivious to applied potential
- **Trends in surface sulfur *likely* explained by oxygen loss from Pt but not Ni**

Oxygen Spillover Species





- **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**

Concluding Remarks And Future Direction

- **Mapped the local surface potential of an active Ni/YSZ/Pt electrochemical cell**
- **Established the efficacy of ambient pressure XPS as an in-situ diagnostic**
  - Spillover species
- **Moving towards a two-chamber experimental apparatus**
- **Moving towards non-metallic electrodes**

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