Approaching the Complex Composite Electrode Interface with *Operando* AP-XPS

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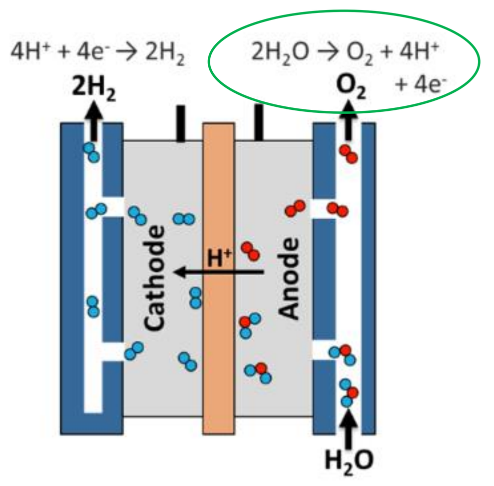
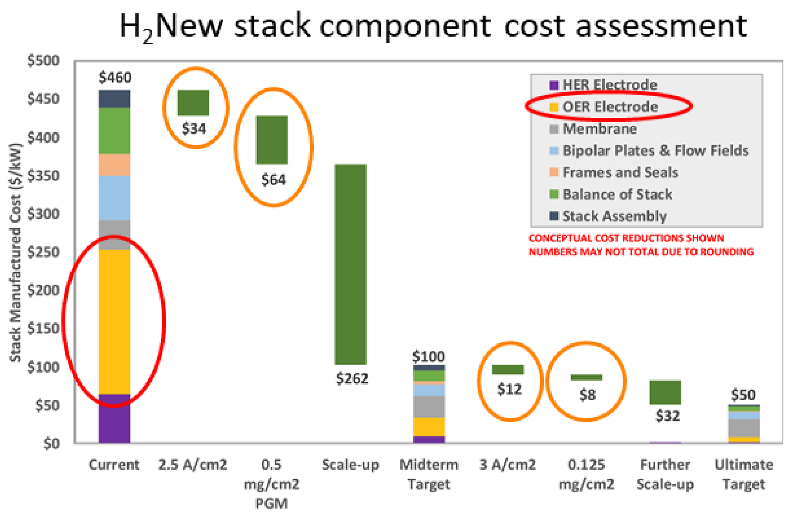
MOTIVATION: Green Hydrogen at scale – OER Anode studies

- Bringing green hydrogen to scale requires improvements in efficiency and long term performance
- A primary hurdle is the rate limiting step of oxygen evolution at the anode, which accounts for the largest cost in the electrolyzer stack

Hydrogen Shot — 1 Dollar, 1 Kilogram, 1 Decade



Energy.gov/eere/fuelcells/hydrogen-production-electrolysis

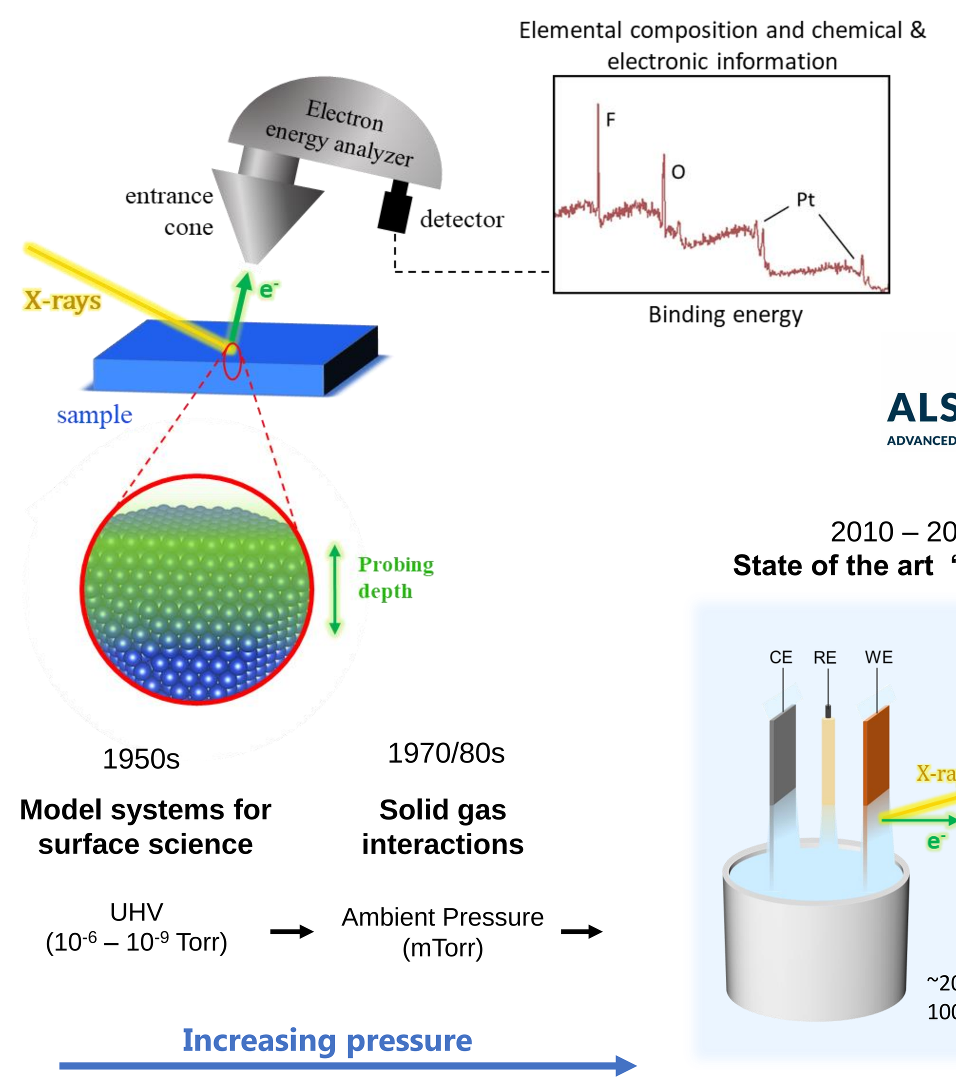


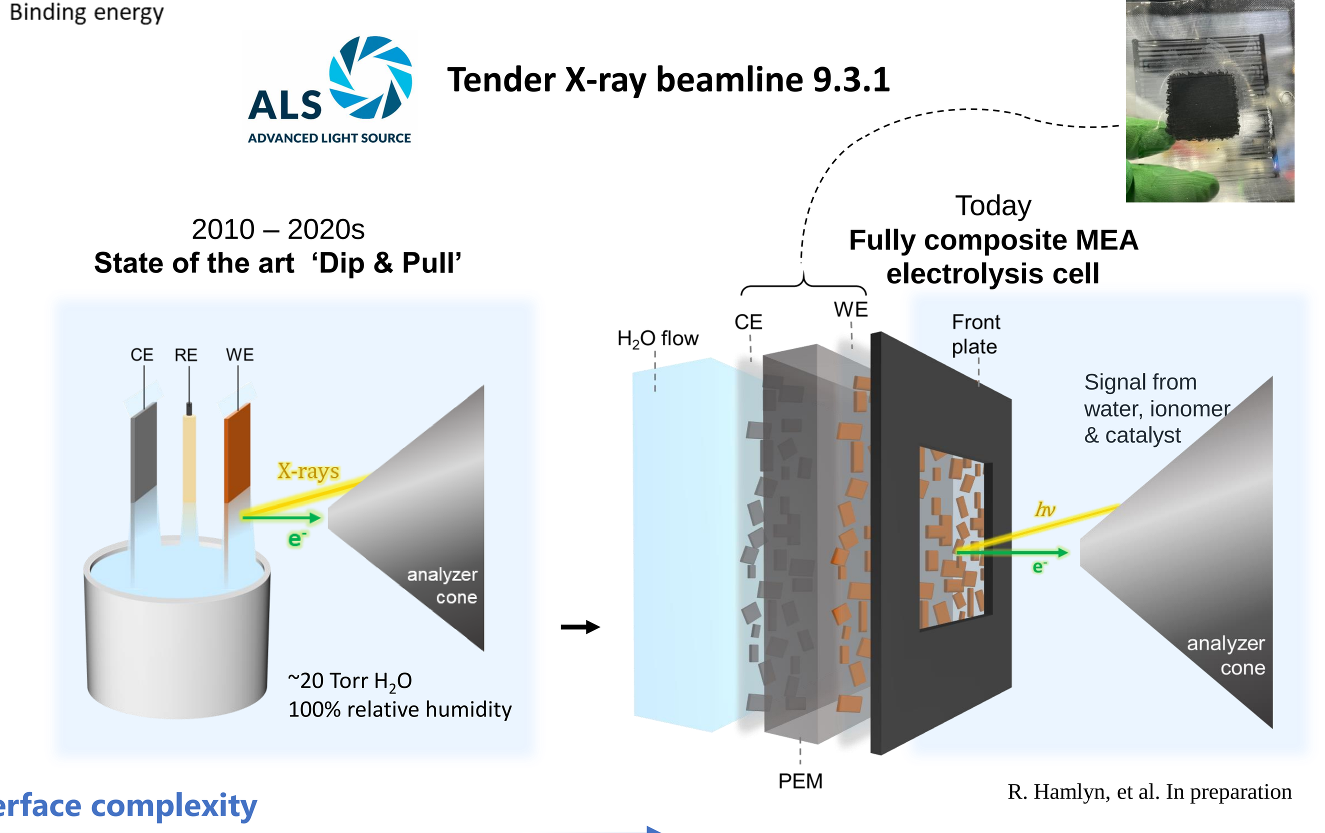
- How does the anode work? And what are the mechanisms that cause anode degradation?
  - → Turn to spectroscopy to understand the complex interface of membrane electrode assemblies

EXPERIMENTAL APPROACH – *Operando* Tender X-ray XPS

Ambient Pressure X-ray Photoelectron Spectroscopy

- *Operando* characterization with ambient pressure X-ray Photoelectron Spectroscopy (AP-XPS) gives catalyst and ionomer elemental and chemical state information at the surface.
- Tender X-rays (2-7 keV) allow electrons to escape the liquid water layer necessary for operando studies



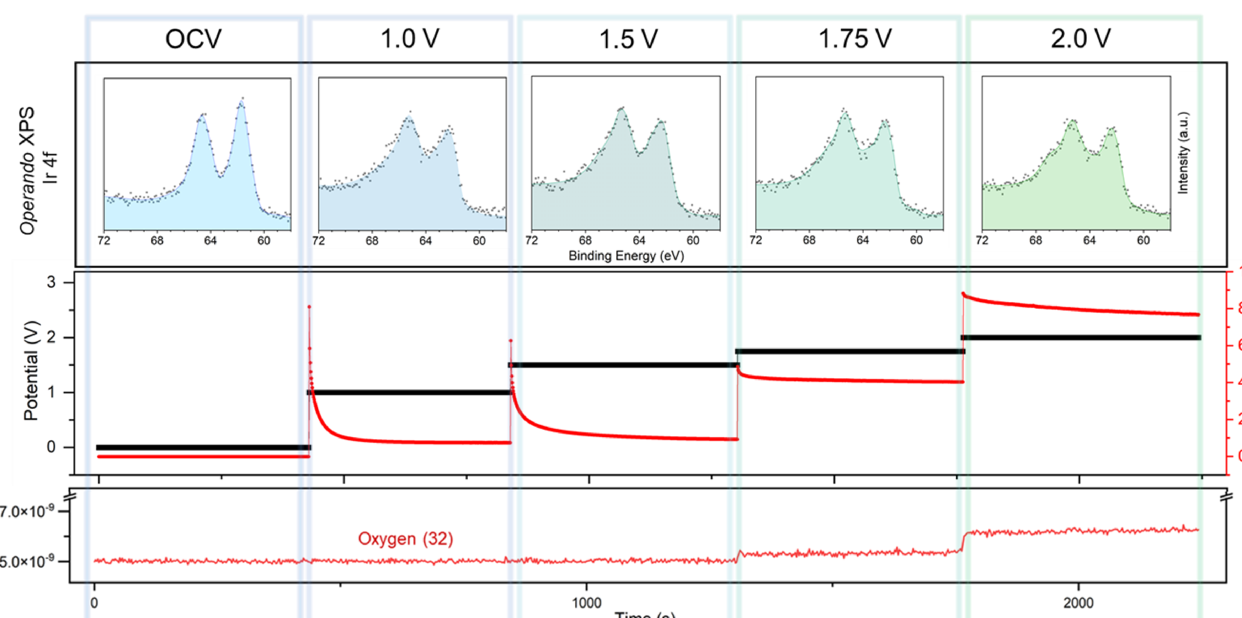


Bridging the "valley of death": fundamental to applied

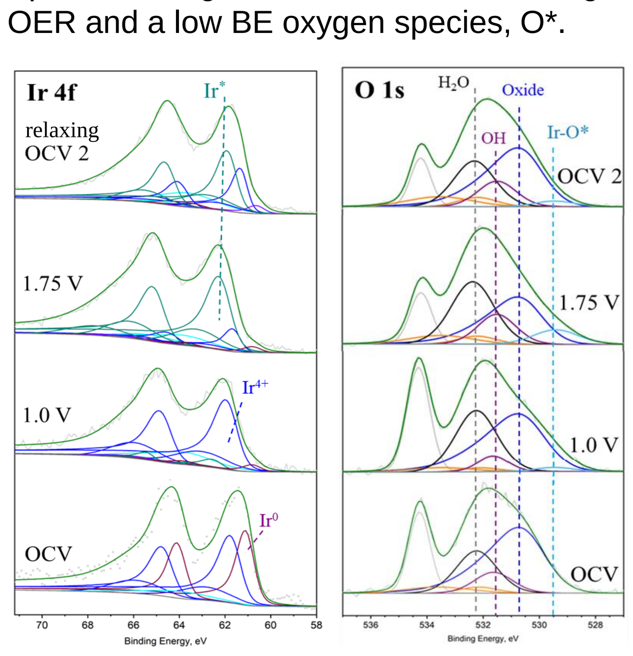
'CONVENTIONAL' RESULTS: The good & the bad

Successes

Full working system with catalyst oxidation and oxygen evolution



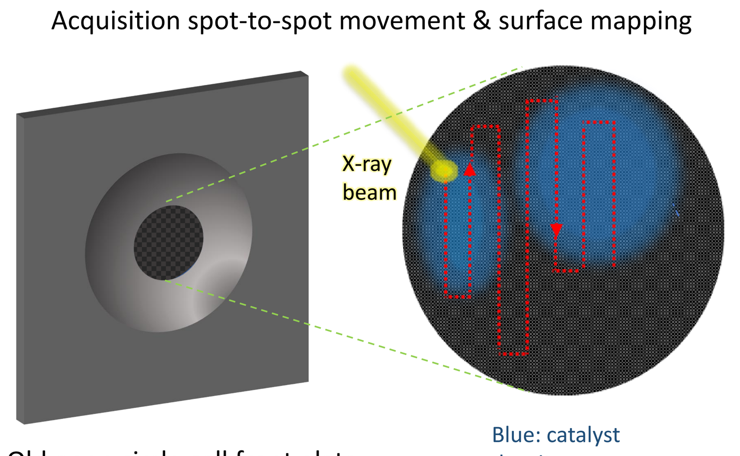
Speciation: high oxidation state Ir^{5+} during OER and a low BE oxygen species, O*.



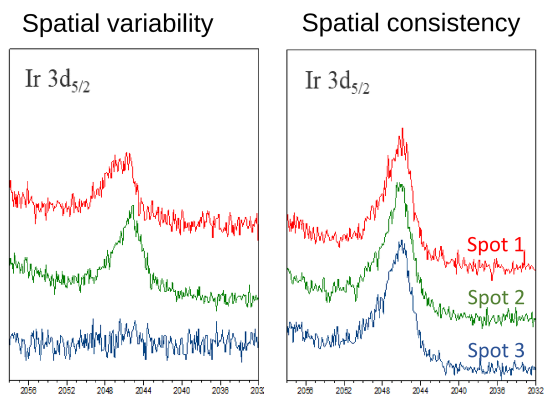
Issues

Spatial variability on sample → data analysis & interpretation difficulties

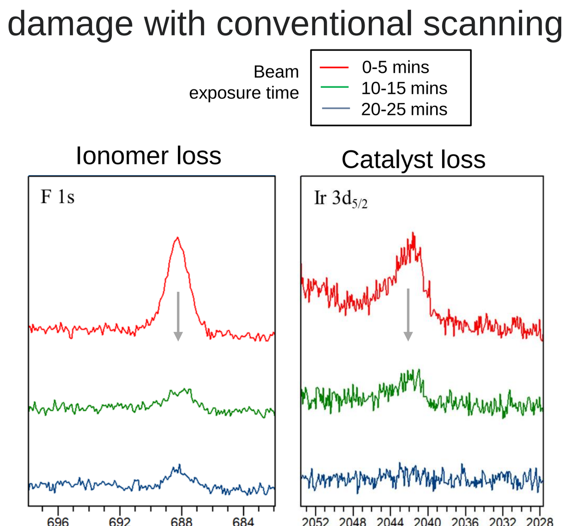
Acquisition spot-to-spot movement & surface mapping



Old open circle cell front plate



Beam damage with conventional scanning

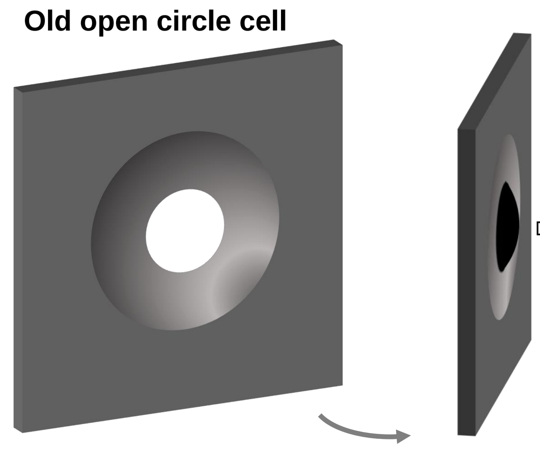


(in all samples) (some samples, e.g.: AA, JM)

REASSESS EXPERIMENTAL APPROACH

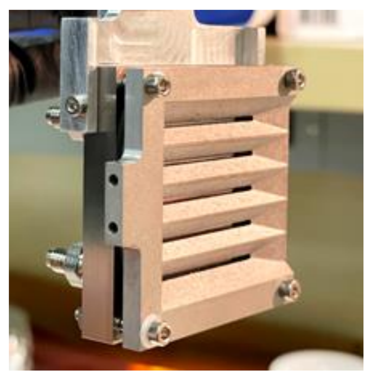
Upgraded *Operando* cell design

Old open circle cell

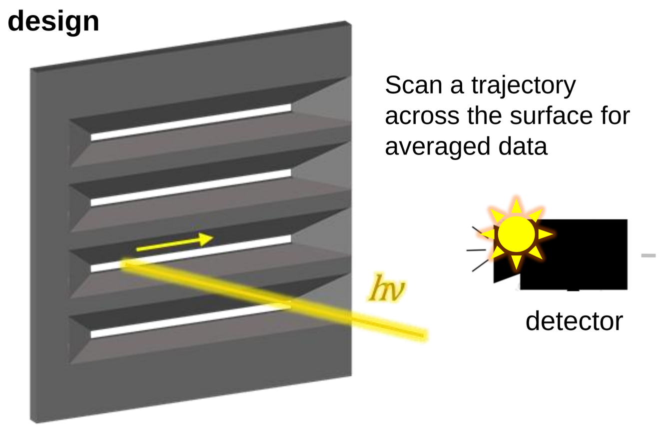


Membrane swelling means calibrating XPS position at every spot

New slit cell design



Keeps sample flat for easy movement across surface

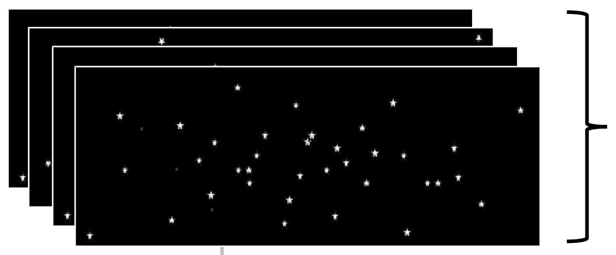


Scan a trajectory across the surface for averaged data

Keeps distance from current collector uniform

New "snapshot" acquisition mode

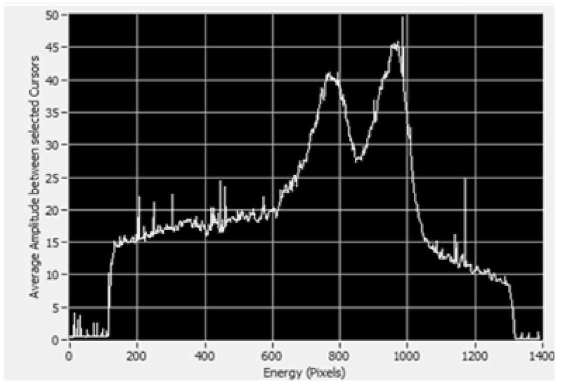
Sub-second"scans" instead of allows for collecting data from electrodes previously unobtainable due to fast beam damage



Snapshots of electrons at detector (12 Hz)

Energy (~16 eV)

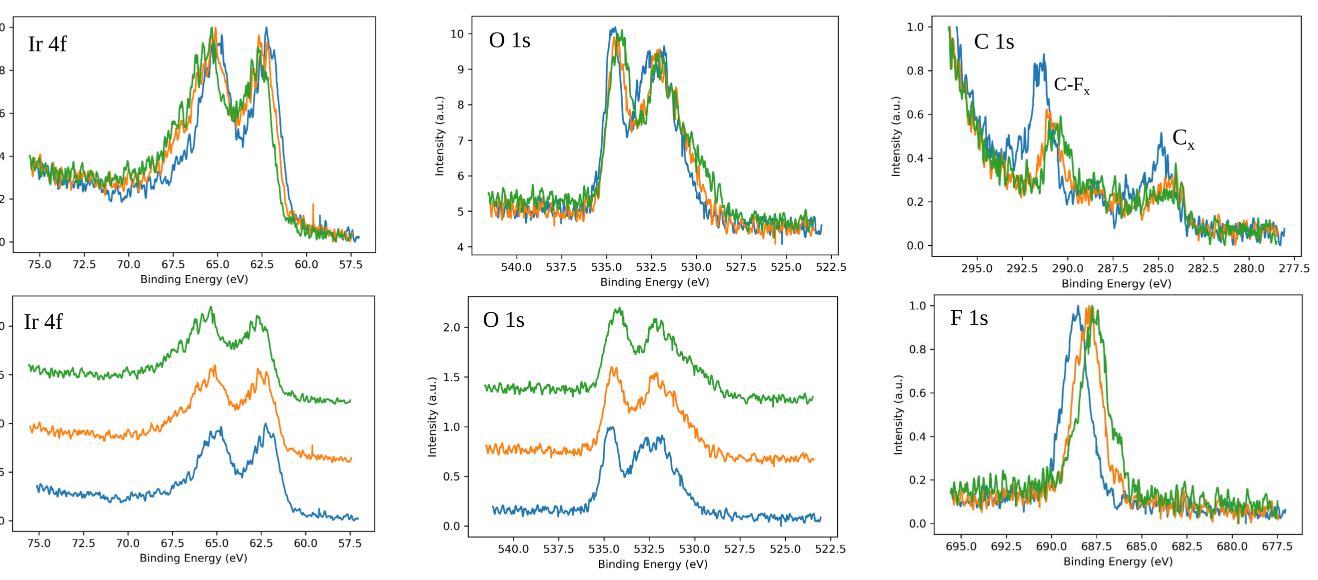
Sum together for full spectrum



PRELIMINARY RESULTS: Snapshot data

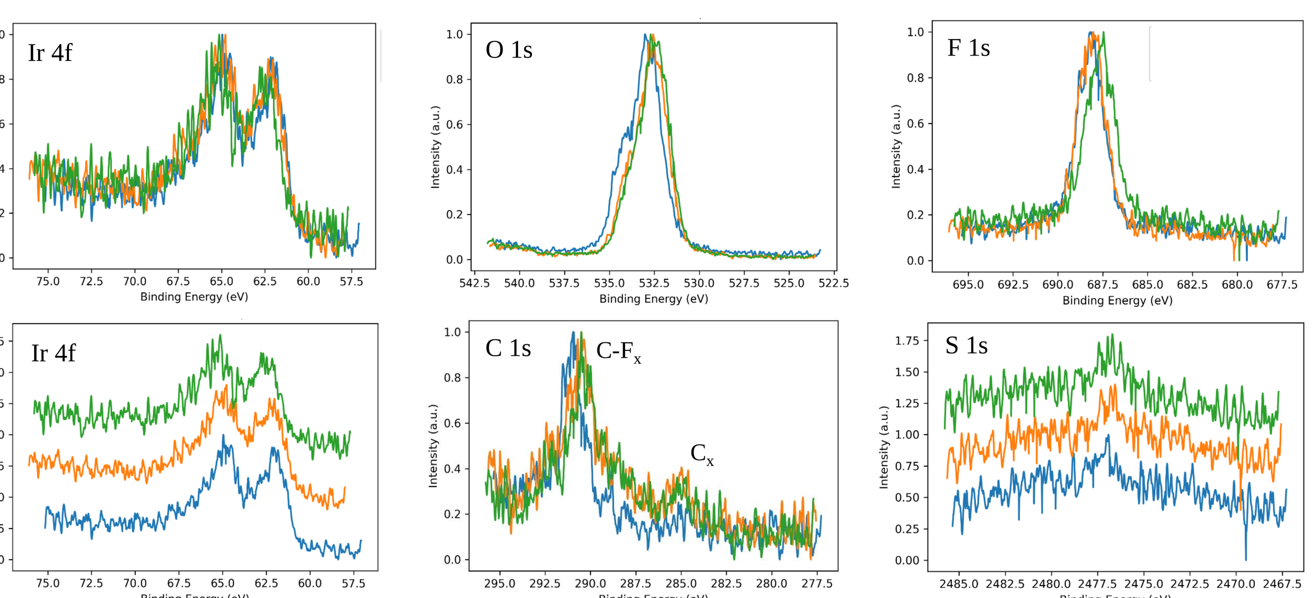
TKK IrO_x

- Begin with more metallic Ir and see oxidation with applied potential
- Typical water content (O 1s)
- See oxide growth in O 1s (~ 529 eV)
- Shift in F 1s with potential



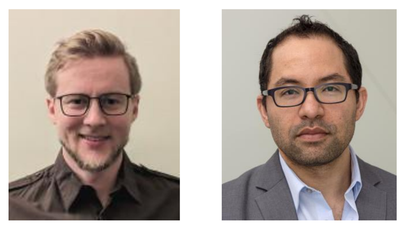
Alfa Aesar

- Begin with more oxidized Ir than TKK (Amorphous starting state)
- Smaller change in catalyst state with increasing potential
  - Don't see growth of oxide in O 1s
- Much higher water content
- Smaller shift in F 1s than TKK
  - Less 'felt' potential or different chemical environment?



COLLABORATIONS

- Colleagues:
  - Johannes Mahl built coding infrastructure to view and process snapshot data.
  - Ethan Crumlin helped to design the cell and guide experimental direction.

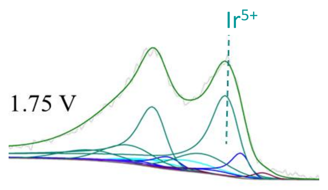


Dr. Mahl Dr. Crumlin

- Collaborators:
  - Jason Keonhag Lee and Rangachary Mukundan provided the samples shown here.
  - H2New Consortium provides fruitful network for assessment of data across spectroscopy and microscopy types for a full view, multi-pronged approach to understanding how these devices work best.

CONCLUSIONS & FUTURE WORK

- Accomplishments:
  - Established an effective procedure for the collection of representative XPS data, avoiding most effects of beam damage and sample spatial variability.
  - Higher oxidation state of Ir 5+ and O* moiety during OER, likely Ir-O
  - Expands the data set to include samples previously inaccessible due to excessive beam damage. (Alfa Aesar, Johnson Matthey, Hereaus)



- Key findings:
  - Data is new and needs workup, but already have varying signatures in response to annealing temperature, thickness and preparation.
  - Can see the differences in catalyst state & response to potential between ink types & formulations.
- Future:
  - Expand sample studies of various types. Increase resolution of current data sets (esp. sulfur).
  - Use 3-electrode cell for better voltage reference
  - Time-resolved studies. New detector/camera system at 9.3.1 beamline.

H2NEW U.S. DEPARTMENT OF ENERGY — UAW UNION LABOR Local 4811 — BERKELEY LAB — ALS ADVANCED LIGHT SOURCE