In Situ and Operando Electron Spectroscopy Analysis of Photoelectrochemical Interfaces for Solar Fuel Production

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Surface Science Group

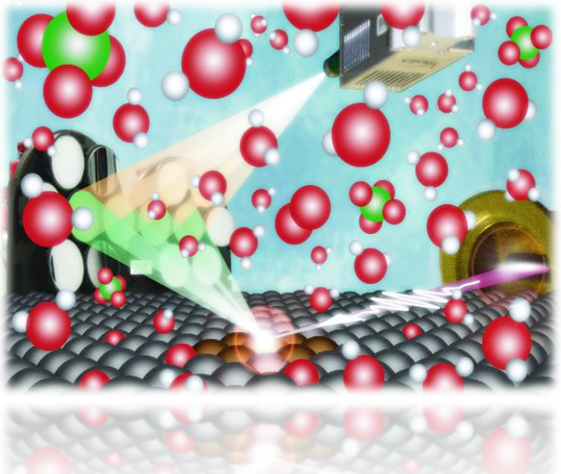
Photonics Laboratory

Tampere University

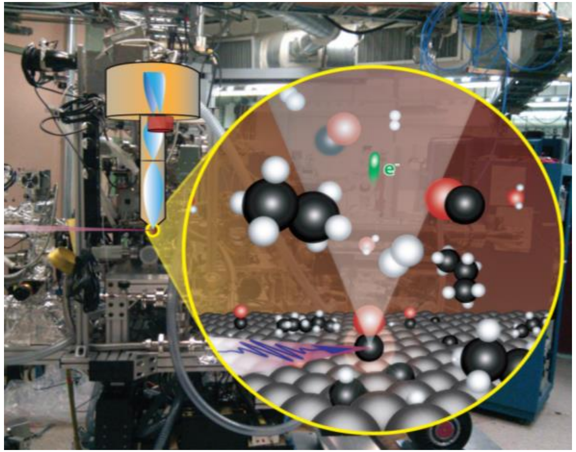
Joint Center for Artificial Photosynthesis
https://www.youtube.com/watch?v=NCN_xFRL28Y
ELO – your cicerone to MAX IV Laboratory
https://www.youtube.com/watch?v=XE6eiNk6-7I
MAX IV HIPPIE beamline
https://www.youtube.com/watch?v=pkv0Zp2q0U8

Content

- Surface Science Group
- Solar Fuel Production
- Probing (photo)electrochemical interfaces using synchrotron radiation mediated electron spectroscopy
- Electrochemical Ambient Pressure X-ray Photoelectron Spectroscopy (EC-APXPS)
  - *Case 1: Ni-Fe for OER*
  - *Case 2: Dissolution of Pt (HER catalyst)*
  - *Case 3: OD-Cu for CO2RR*
- Outlook



photon-in/photon-out



photon-in/electron-out

Surface Science Group

https://research.tuni.fi/surfsci/

Group Leader Prof. Mika Valden

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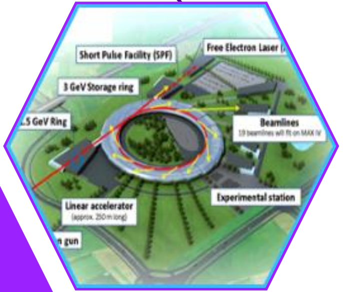
Tampere University

MAX IV Laboratory
Synchrotron Light
(FinEstBeAMS)



STM/STS

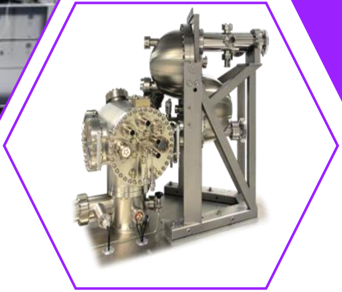
Surface and Interface Physics

Nano-phase Materials

Surface Reactions

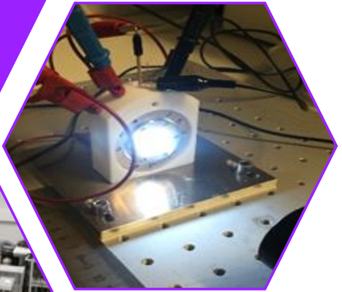
Electronic structure

ALD



NanoESCA/XPEEM

Multilab/XPS



PEC
ICP-MS
GC

Al_2O_3
TiO_2
CuO
Fe_2O_3

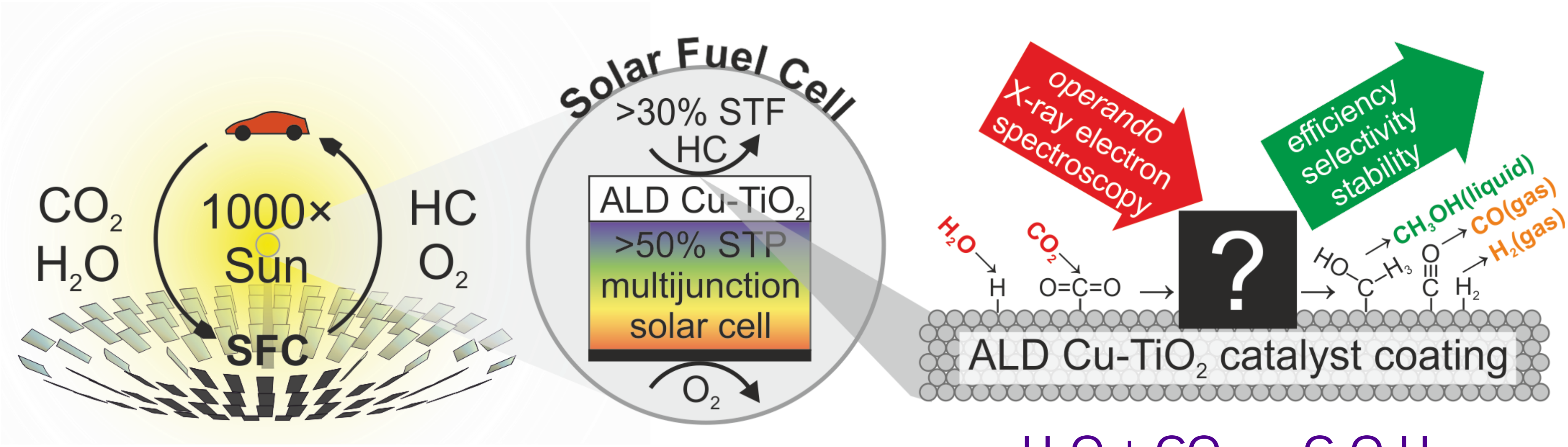
PREIN

Joint Center for Artificial Photosynthesis

https://solarfuelshub.org/

Solar Fuel Production

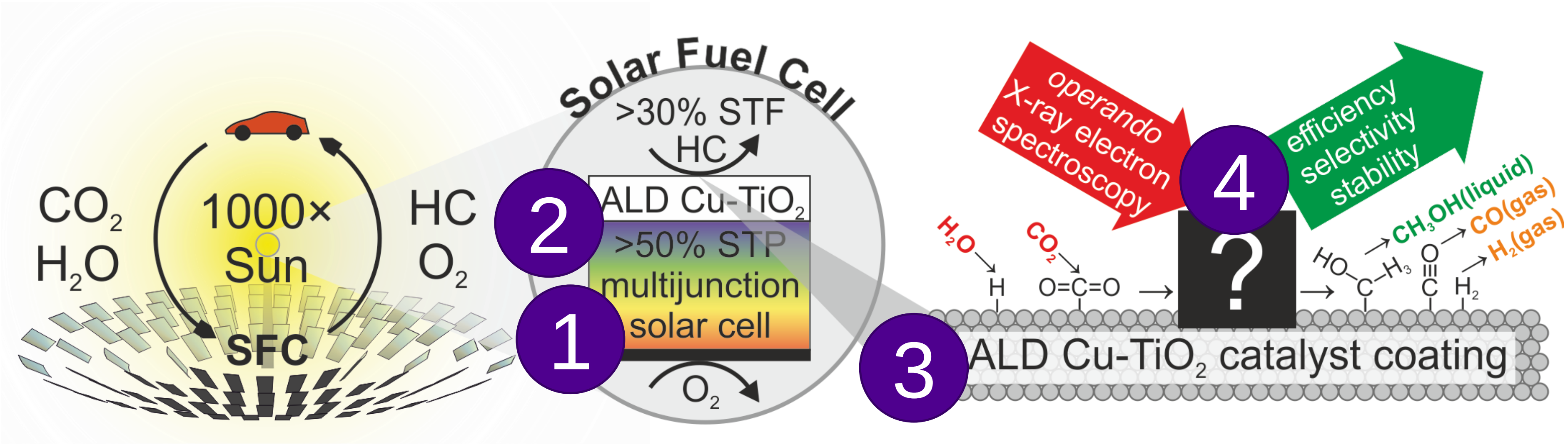
Research and development of photoactive materials and surface reactions for artificial photosynthesis.



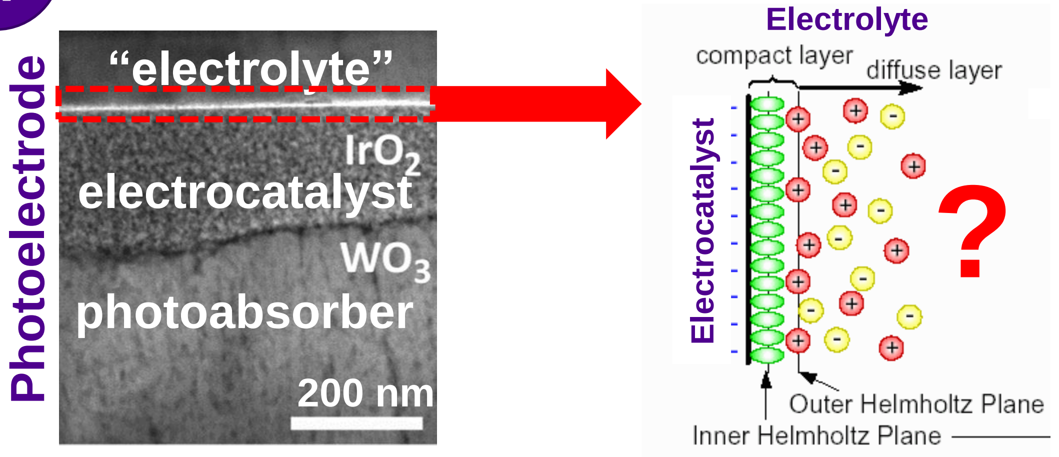
$$H_2O + CO_2 \rightarrow C_xO_yH_z$$

Solar Fuel Production

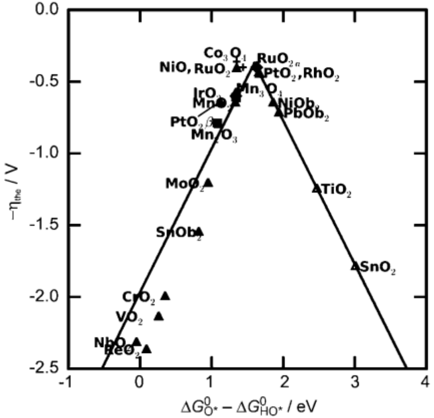
Figures to beat: Solar-to-Hydrogen efficiency of **19.3%**, Stability of **20 h**
25.6.2018, ACS Energy Lett. 2018, 3 (8), 1795–1800



4 Analysis of photoelectrochemical interfaces by electron spectroscopy



O*, HO*, CO*…



Activity vs. bonding
Man, I. C. *et al. ChemCatChem* **3,** 1159–1165 (2011).

Target: to understand the structure-performance relationships during operation

Challenging length scales: How to probe chemical species at the electrocatalyst/electrolyte interface under electrochemical potential control?

Choice of probe:

- thickness of a monolayer of atoms ~0.1 nm, electrical double layer ~1 nm, electrolyte solution
- attenuation length of 1 keV electrons ~1 nm vs. X-rays ~1000 nm: How to collect signal through electrolyte?

TEM-image: Spurgeon et al. Phys. Chem. Chem. Phys., 16, 3623 (2014)

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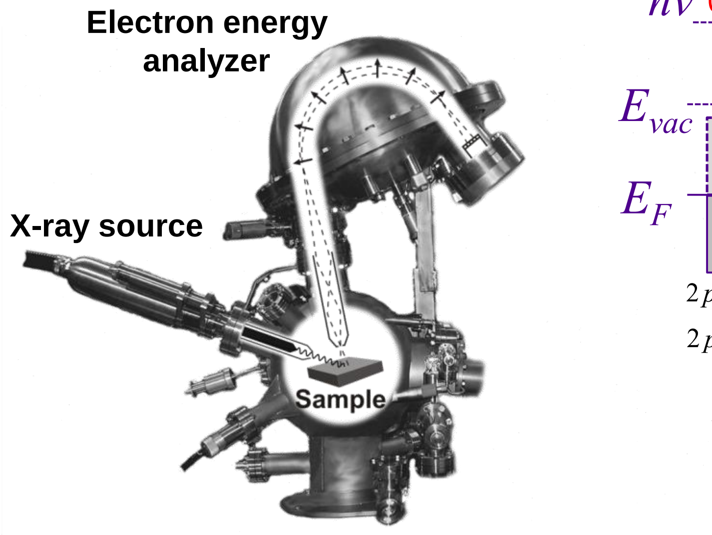
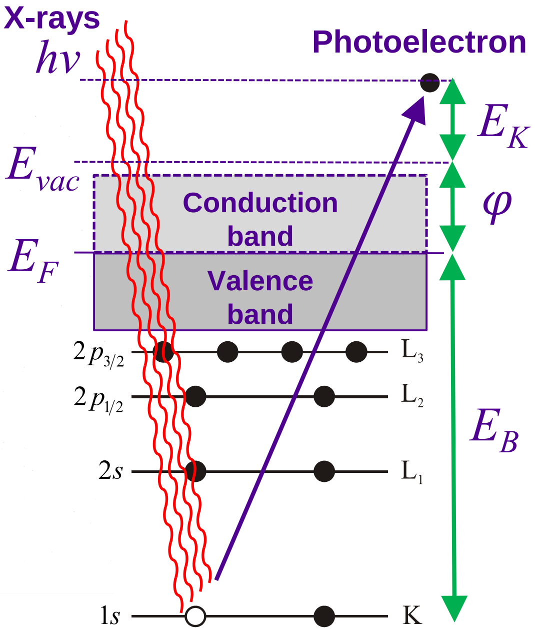
X-ray Photoelectron Spectroscopy (XPS)



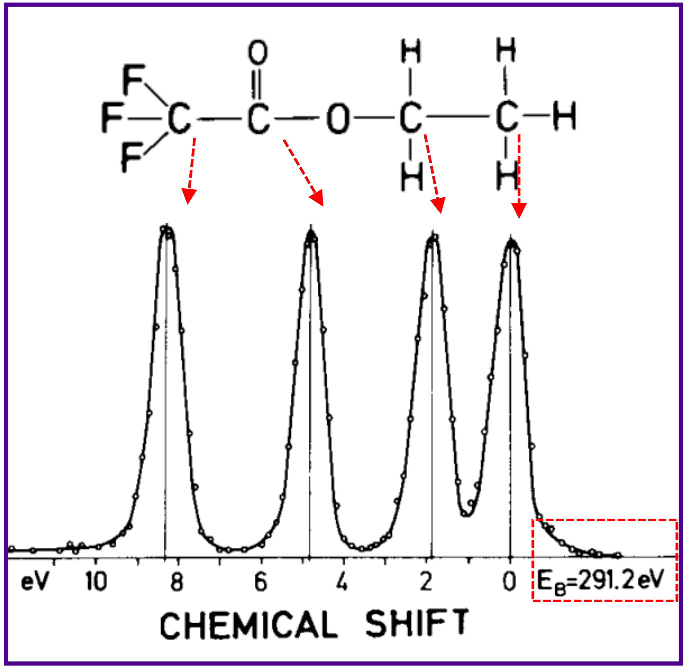
$$E_K = h\nu - E_B - \varphi$$

Photoelectric effect
Albert Einstein, Nobel Prize 1921



Information depth using…
soft X-rays: 1–3 nm
tender X-rays: 3–30 nm
hard X-rays: 30–100 nm

C 1s XPS spectrum of ethyl trifluoroacetate



XPS (ESCA)
Kai Siegbahn, Nobel Prize 1981

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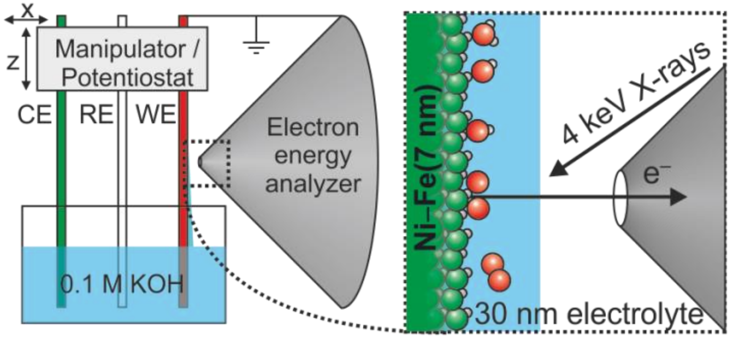
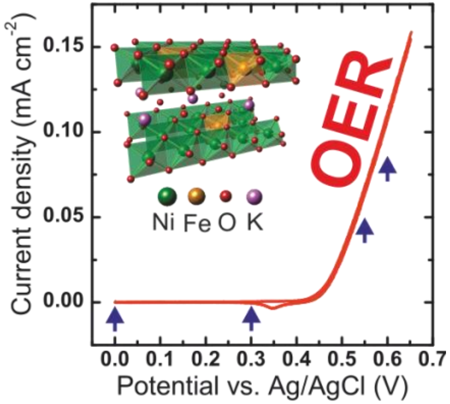
Ambient pressure XPS of electrochemical interfaces at ALS bl9.3.1, hv = 4000 eV

Case: Operando XPS of **planar** Ni-Fe Electrocatalyst for the Oxygen Evolution Reaction





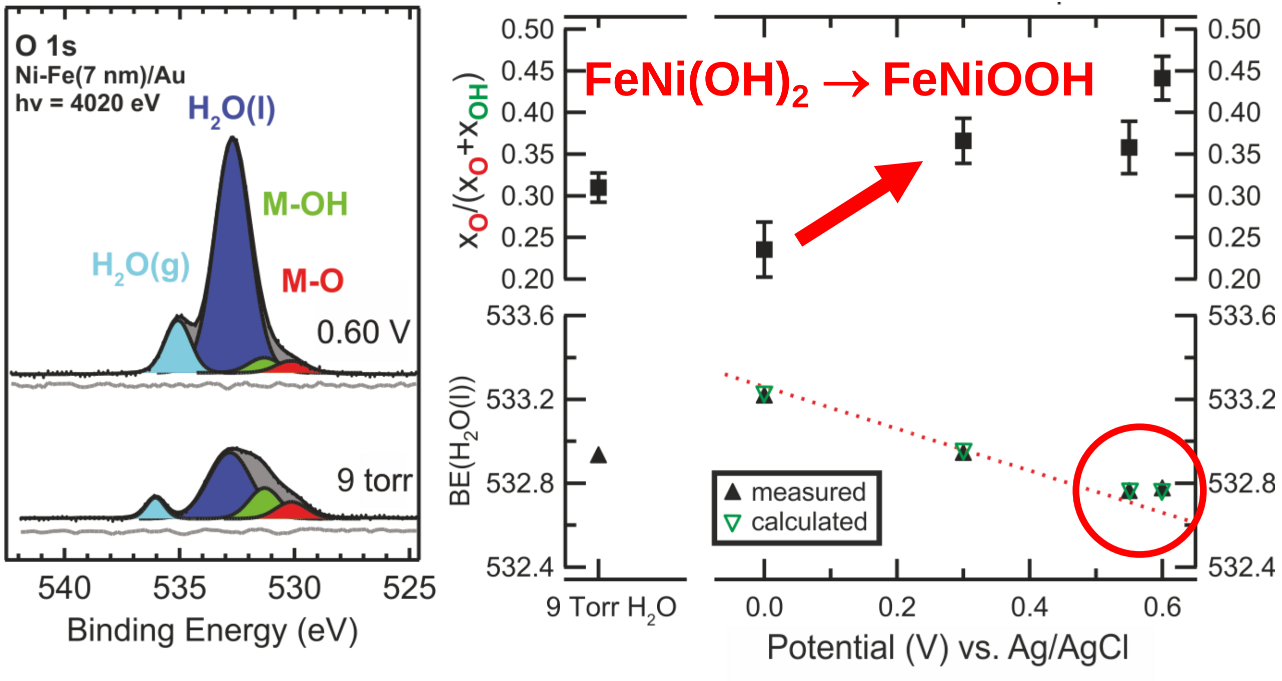
Similar setup at HIPPIE beamline (270–2200 eV) MAX IV Laboratory

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-,$$

$$E^0 = 1.229\,V - 0.059\,V \times pH$$

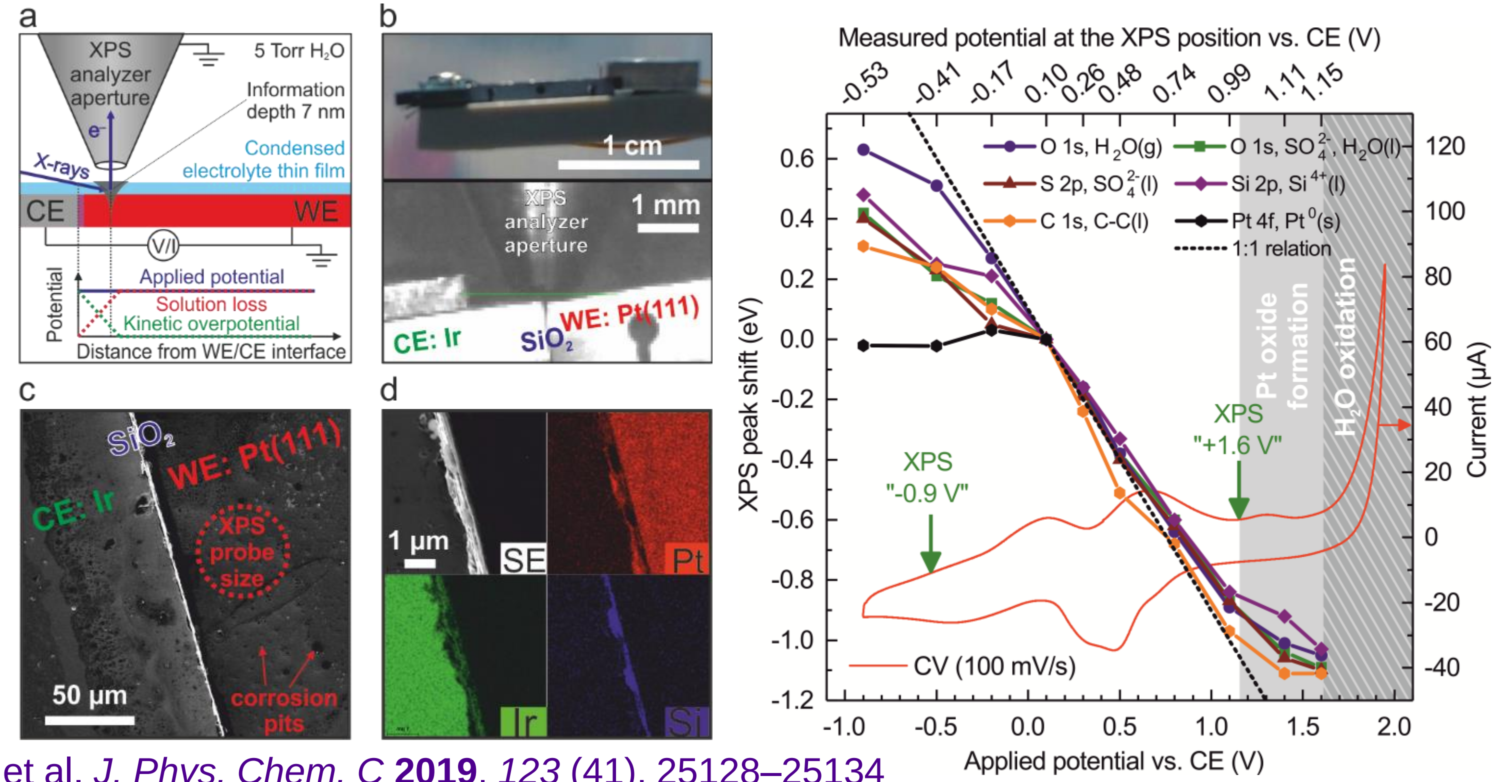
Ali-Löytty et al. *J. Phys. Chem. C* **120,** 2247–2253 (2016).

Initial oxidation of Ni-Fe hydroxide to catalytically active oxyhydroxide below the OER onset potential



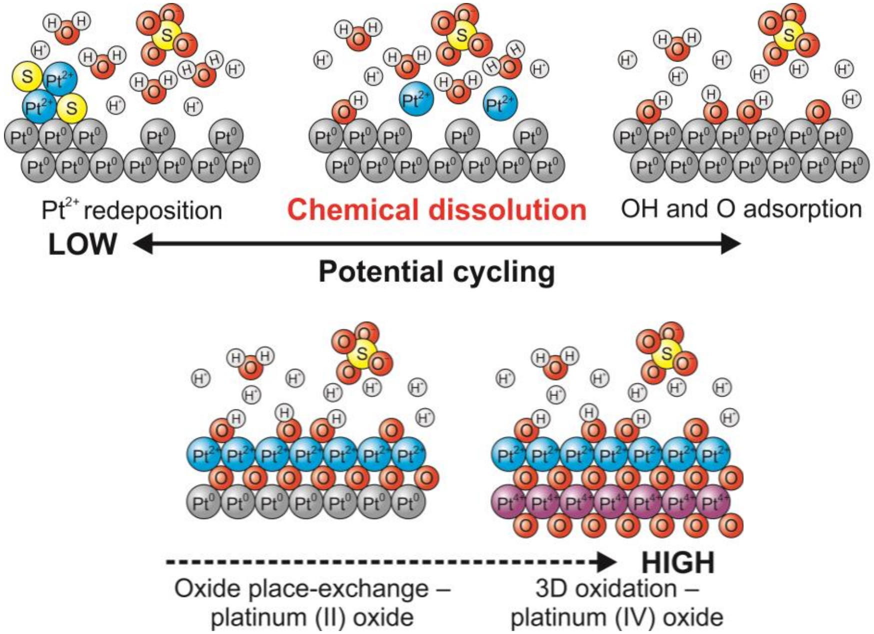
Ali-Löytty et al. *J. Phys. Chem. C* **120,** 2247–2253 (2016).

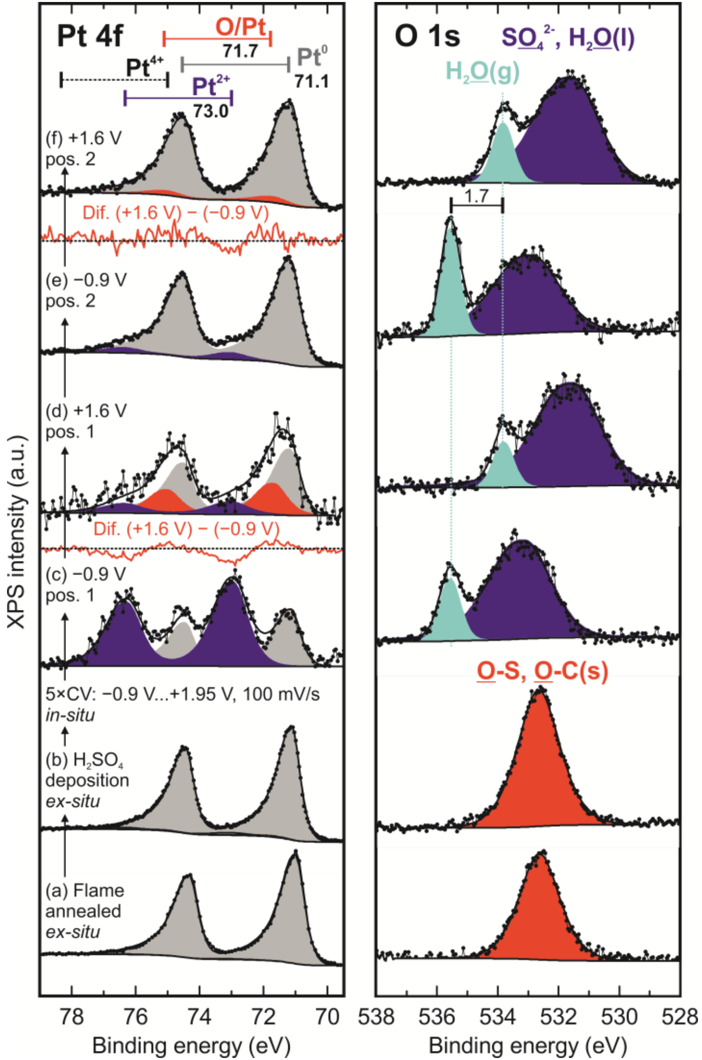
Soft X-ray APXPS of condensed electrolyte film electrochemical cell at SSRL bl13-2, single crystalline Pt(111) electrode, hv = 688 eV



Ali-Löytty, H et al. *J. Phys. Chem. C* **2019**, *123* (41), 25128–25134

Chemical dissolution of Pt(111) during potential cycling without oxide place exchange





Ali-Löytty, H et al. *J. Phys. Chem. C* **2019**, *123* (41), 25128–25134

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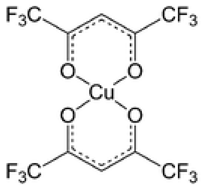
Copper(II) hexafluoroacetylacetonate ($Cu(hfac)_2$)



Oxide-derived ALD Cu catalyst for CO2RR

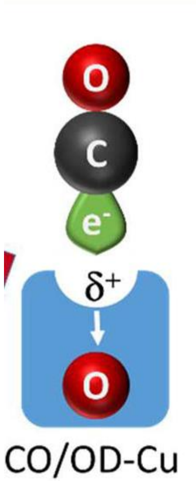
CO2RR mechanism

- CO binding energy determines the selectivity towards methanol and multicarbon products:

  $CO_2 + H_2 \rightarrow$ CO $+ H_2O$

  CO $+ 2H_2 \rightarrow CH_3OH$

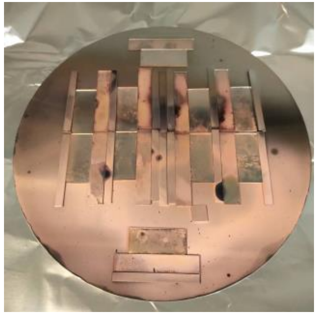
- Reduced Cu oxides (OD-Cu) are the best catalyst for CO2RR
- Why? Cu_2O or subsurface oxygen?

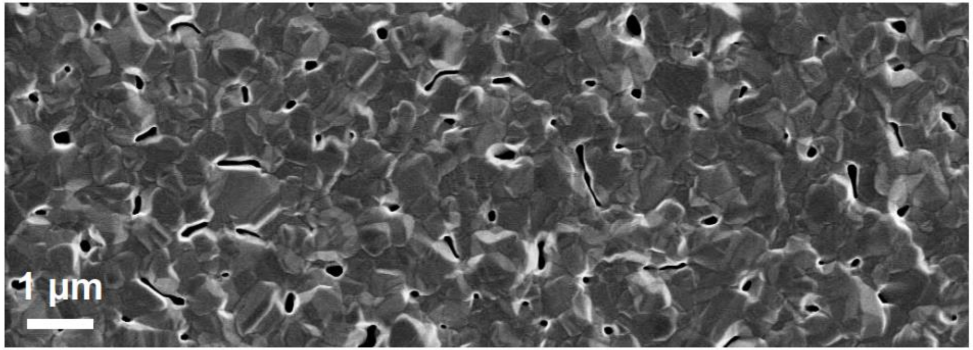


A. Eilert *et al.* J. Phys. Chem. Lett. 8 (2017) 285–290.

ALD of Cu oxide

- $Cu(hfac)_2 \cdot xH_2O$, IPA, and H_2O
- 4500 cycles, ~50 nm at 260 °C



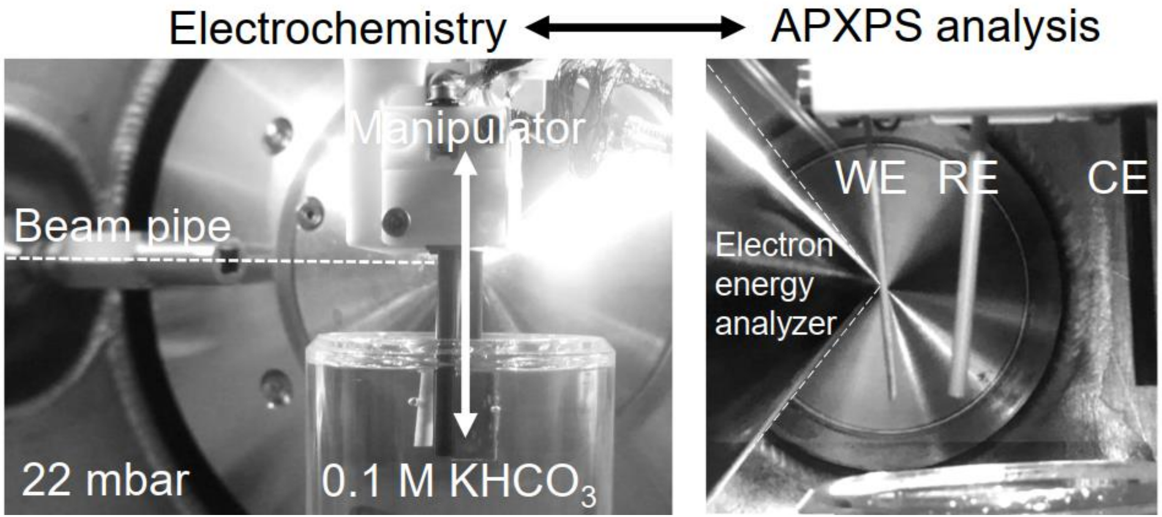


Ambient pressure X-ray photoelectron spectroscopy at HIPPIE beamline (270–2200 eV), MAX IV Laboratory

- Electrochemistry Cell
- Electrochemical reduction at –0.8 V vs. Ag/AgCl in 0.1 M $KHCO_3$

→ **CO2RR conditions**

- APXPS measurements were performed *in situ* without potential control with electrodes fully removed from the electrolyte



Electrochemical APXPS:
Ali-Löytty *et al.* J. Phys. Chem. C **2019**, 123 (41), 25128–25134.
Ali-Löytty et al. J. Phys. Chem. C **2016**, 120 (4), 2247–2253.

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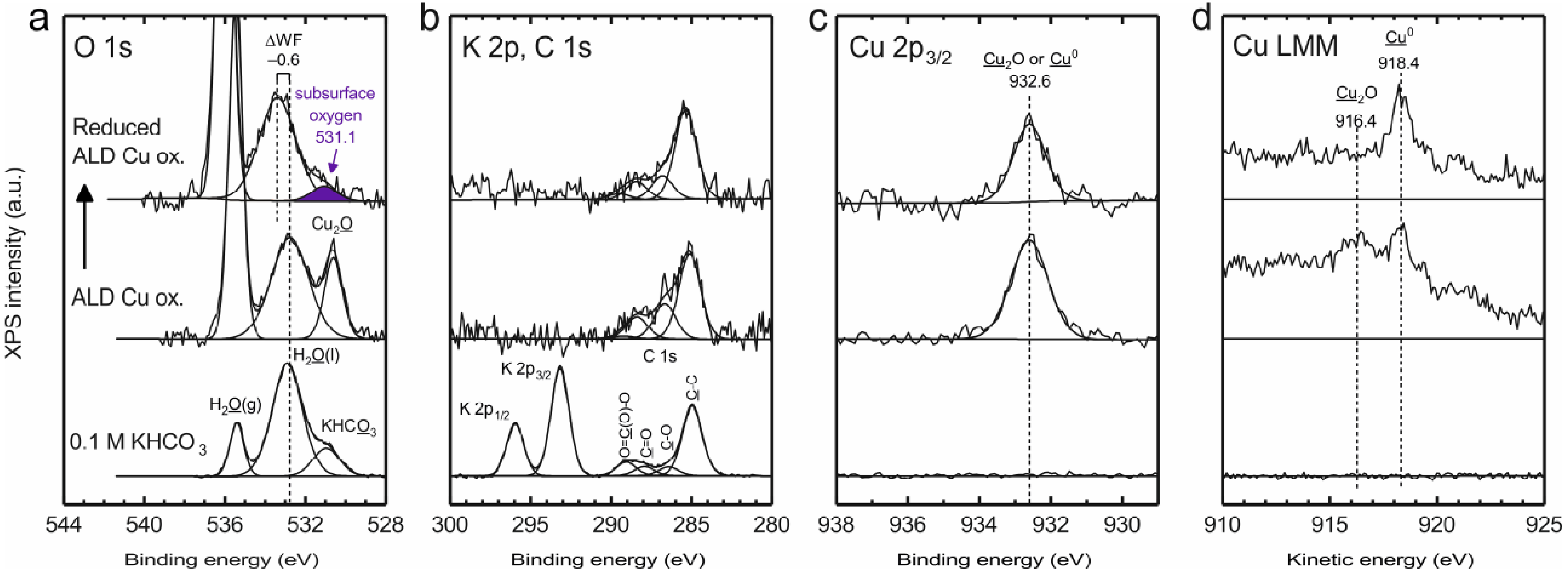
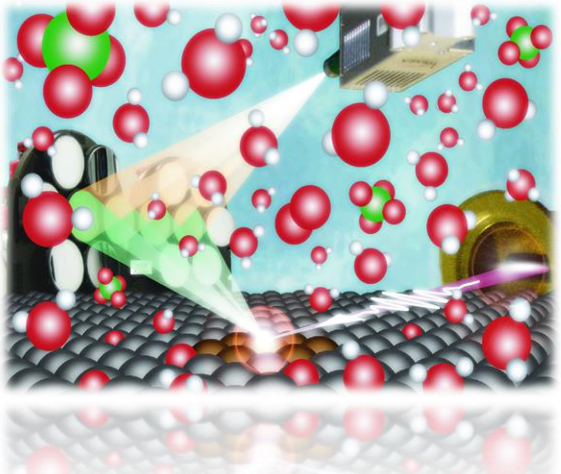
In situ APXPS analysis evidence *subsurface oxygen* and *no Cu_2O* under CO2RR conditions on oxide-derived ALD Cu electrocatalyst



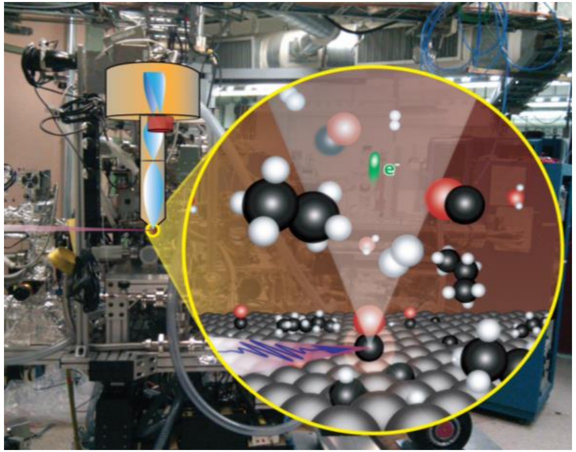
Conclusions & outlook

- We develop photocatalyst materials for solar fuel production
- *Operando* electron spectroscopies can provide understanding on structure/composition–performance relationships
- There is strong interest towards syncrotron light mediated *in situ* and *operando* analysis of electrochemical systems

Challenge: How to probe chemical species at the electrochemical interface under realistic operation conditions (10 mA/cm^2)? Surface sensitive XPS vs. bulk sensitive XAS?



photon-in/photon-out



photon-in/electron-out

Acknowledgements

PREIN

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BUSINESS FINLAND

ACADEMY OF FINLAND

References

[1] H. Ali-Löytty, M. Hannula, M. Valden, A. Eilert, H. Ogasawara, A. Nilsson, Chemical Dissolution of Pt(111) during Potential Cycling under Negative pH Conditions Studied by Operando X-ray Photoelectron Spectroscopy, J. Phys. Chem. C. 123 (2019) 25128–25134.

[2] Li, L.; Yang, J.; Ali-Löytty, H.; Weng, T.-C.; Toma, F. M.; Sokaras, D.; Sharp, I. D.; Nilsson, A. Operando Observation of Chemical Transformations of Iridium Oxide During Photoelectrochemical Water Oxidation. ACS Appl. Energy Mater. 2019, 2 (2), 1371–1379.

[3] Ali-Löytty, H.; Louie, M. W.; Singh, M. R.; Li, L.; Sanchez Casalongue, H. G.; Ogasawara, H.; Crumlin, E. J.; Liu, Z.; Bell, A. T.; Nilsson, A.; et al. Ambient-Pressure XPS Study of a Ni–Fe Electrocatalyst for the Oxygen Evolution Reaction. J. Phys. Chem. C 2016, 120 (4), 2247–2253.

https://research.tuni.fi/surfsci/