Brookhaven National Laboratory

U.S. DEPARTMENT OF ENERGY

Advancing Research with Combined Synchrotron Techniques

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NSLS II, Brookhaven National Laboratory

10/11/2023

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Outline

Introduction

- Overview of synchrotron X-ray characterization techniques
- Importance of combined techniques

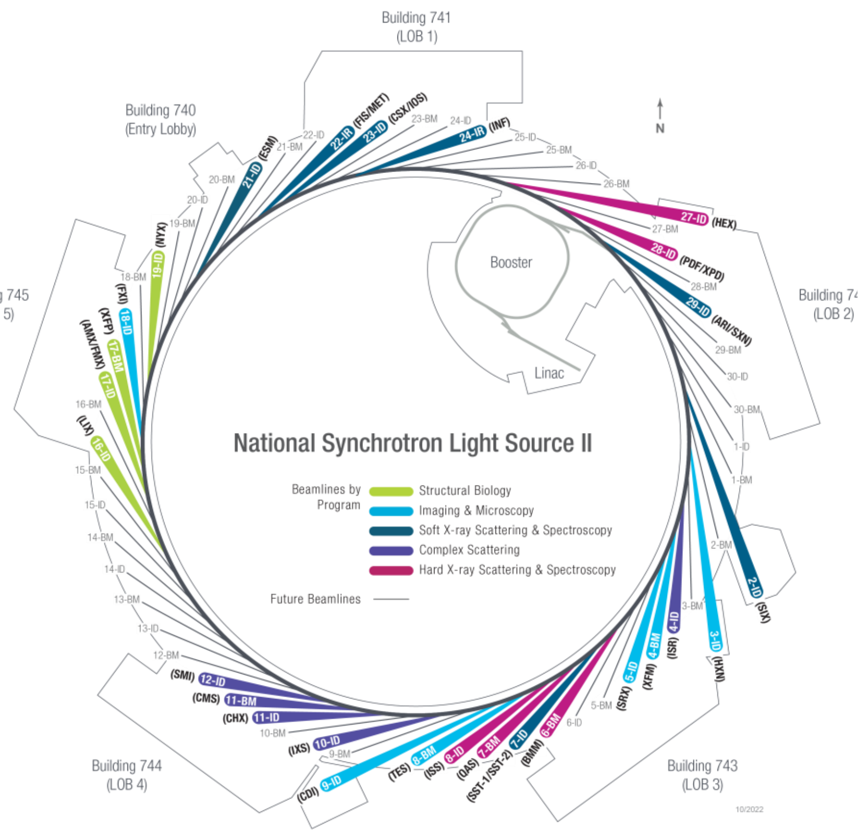
Combining Techniques

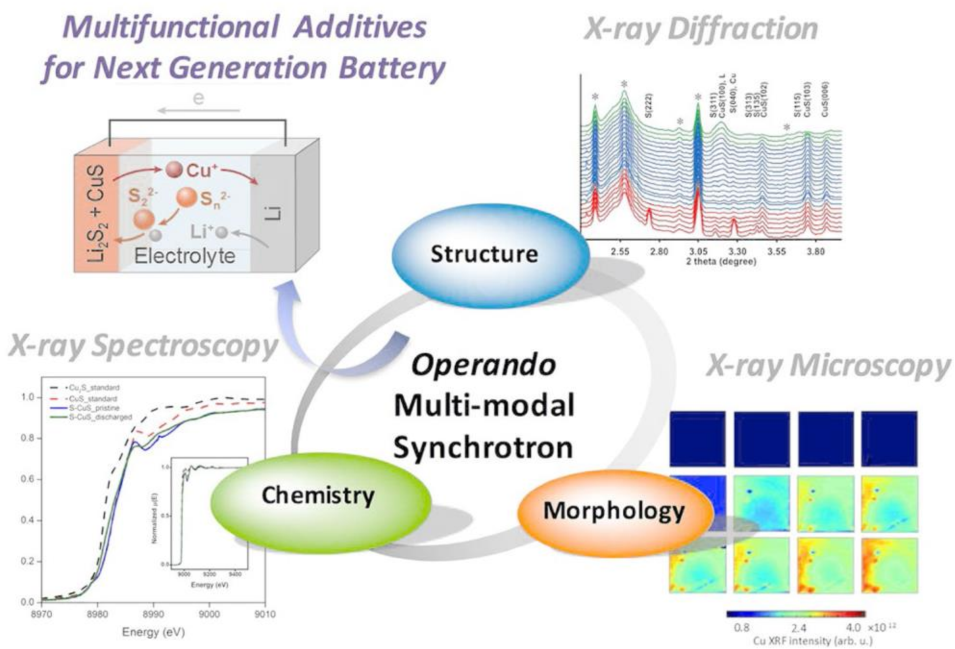
- XAS + XRD: Comprehensive structural analysis
- XAS + DRIFTS: Catalyst insights

Challenges & Future

- Technical limitations & upcoming advancements

Introduction





- Comprehensive Analysis
- Real-Time Monitoring
- Maximize data yield from valuable beamtime
- Reveal unexpected properties or phenomena
- Bridge gaps between research fields.

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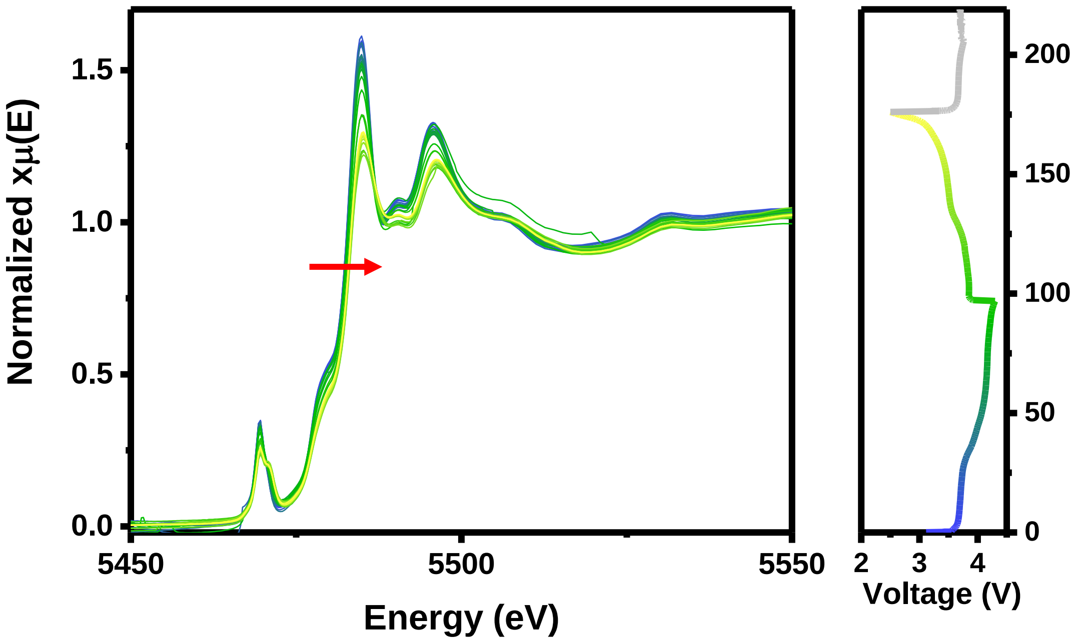
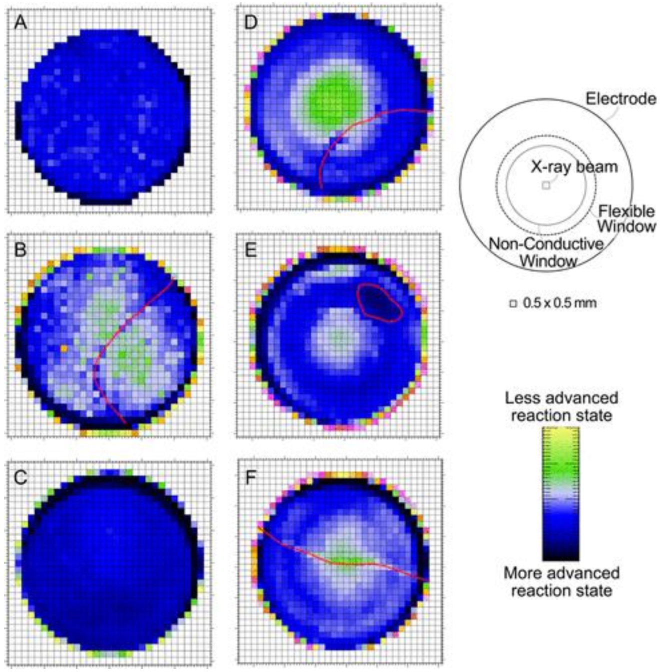
Sci. Rep. 7, 12976 (2017)

Introduction

Na-ion battery, slow reaction??





No Cross-Validation!

J. Phys. Chem. Lett. 2015, 6, 11, 2081–2085

Sci. Rep. 7, 12976 (2017)

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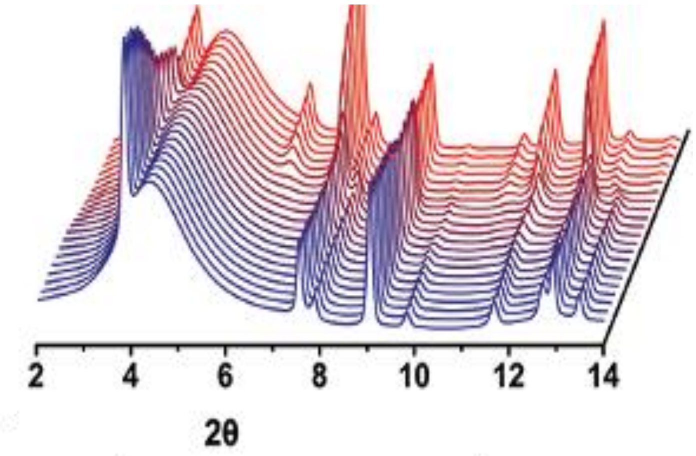
Combined XAS & XRD

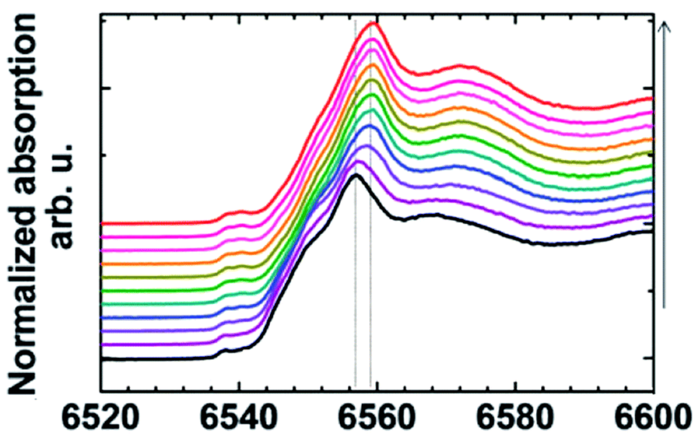
X-ray diffraction (long-range order):

- Phase identification of crystalline materials
- Crystal structure.
- Particle size, strain, and other microstructural properties.



X-ray absorption spectroscopy (short-range order):

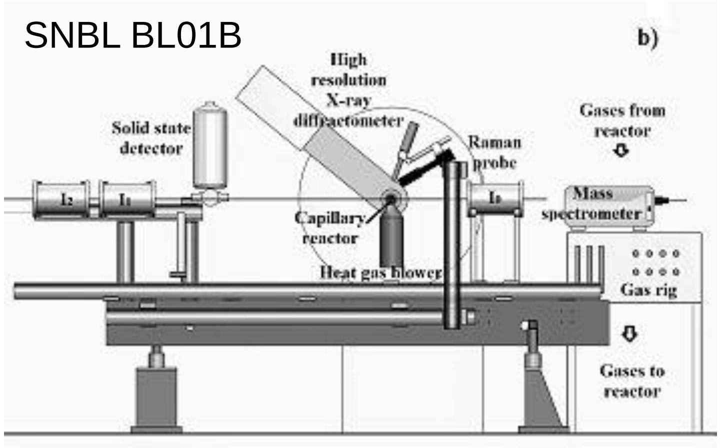
- Electronic structure and oxidation state of specific elements
- Local coordination geometry and bond lengths.



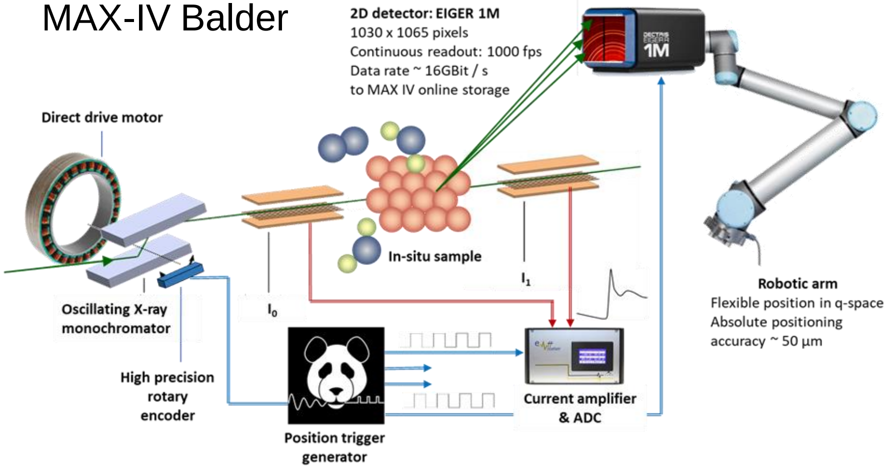
Combined XAS & XRD

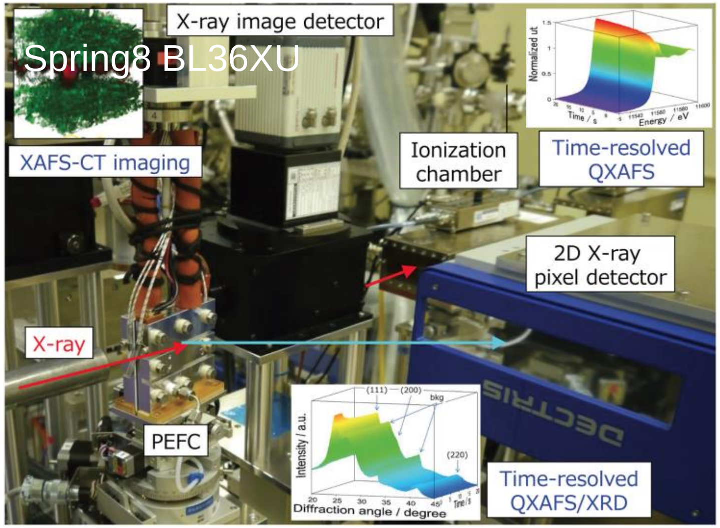
NSLS II 7-BM

SNBL BL01B



MAX-IV Balder

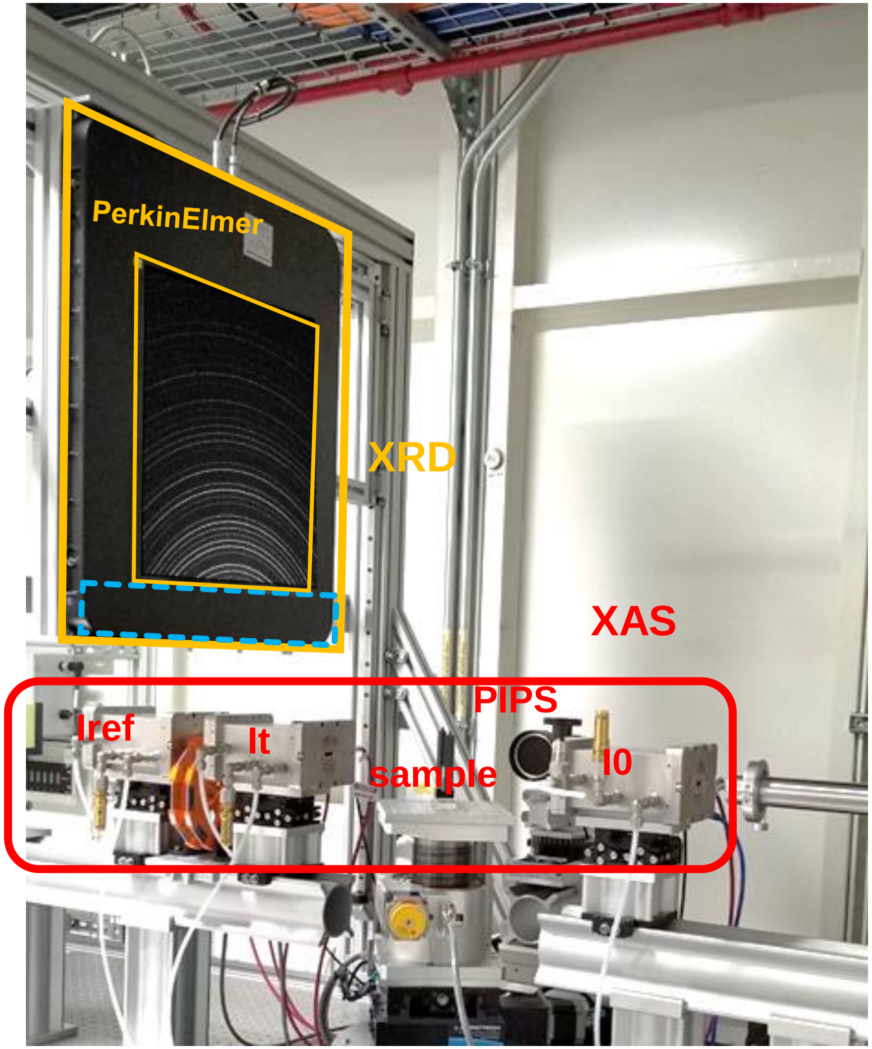




J. Appl. Cryst. (2014). 47, 449–457.
J. Phys. Chem. C 2017, 121, 18202−18213.

Chem. Rec. 2019, 19, 1444–1456.
ACS Sustainable Chem. Eng. 2017, 5, 3631−3636.

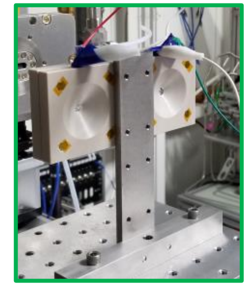
Combined XAS & XRD



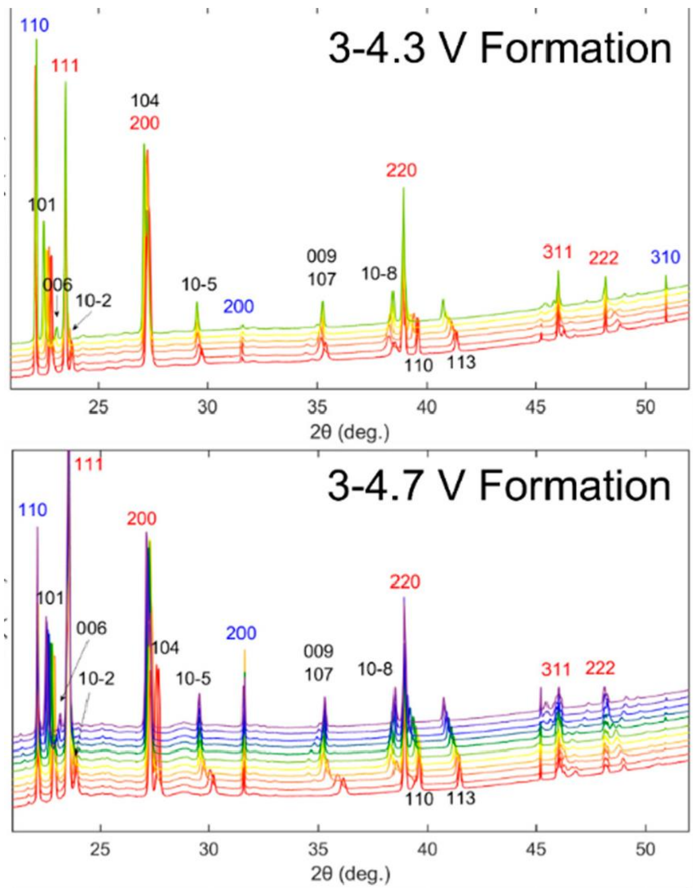
Combined XAS & XRD

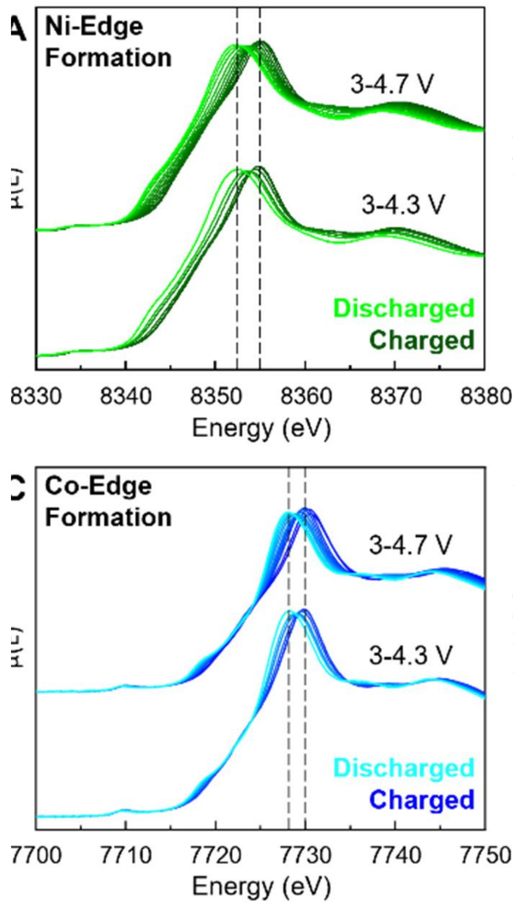
- Case study 1: Battery

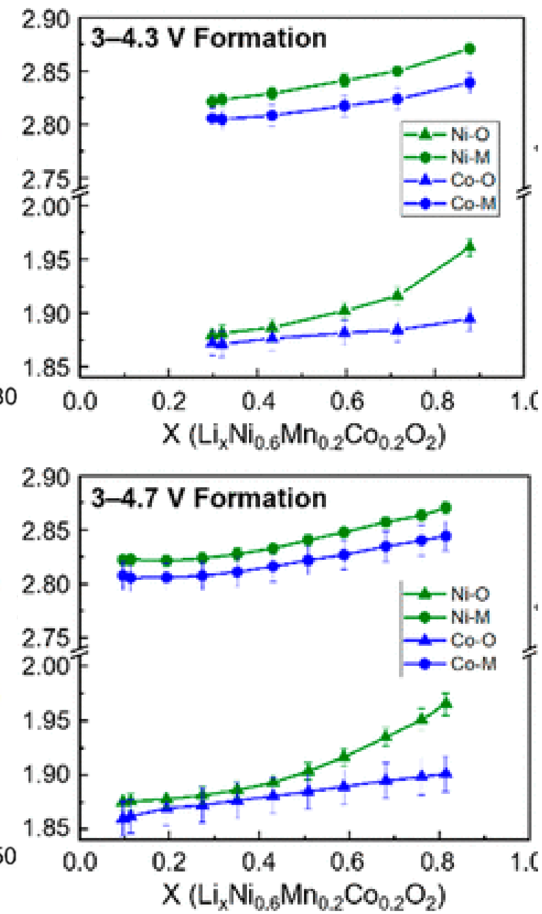
C/5 rate
XAS: Mn, Co, Ni K-egde
XRD: λ = 0.9547 Å



David Bock, BNL



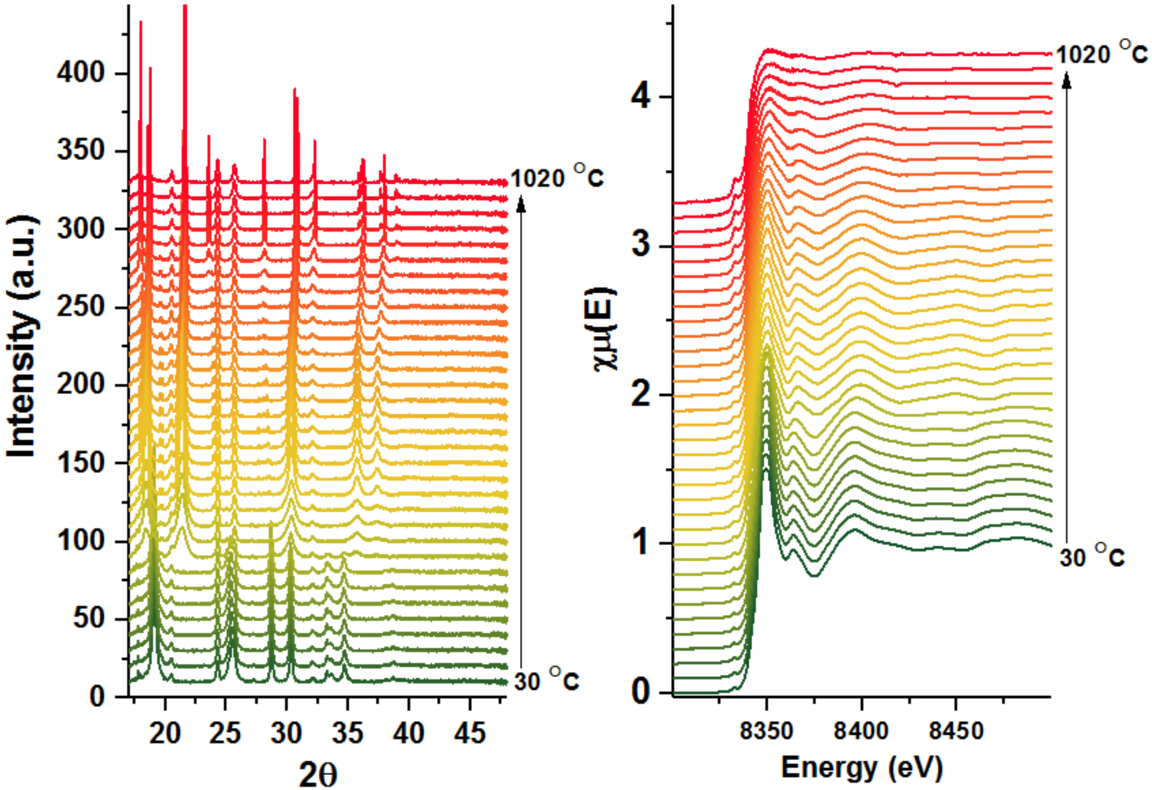


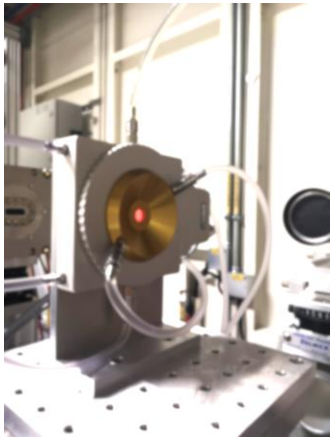


ACS Appl. Mater. Interfaces 2021, 13, 43, 50920−50935.

Combined XAS & XRD

- Case study 2: Linkam stage heating

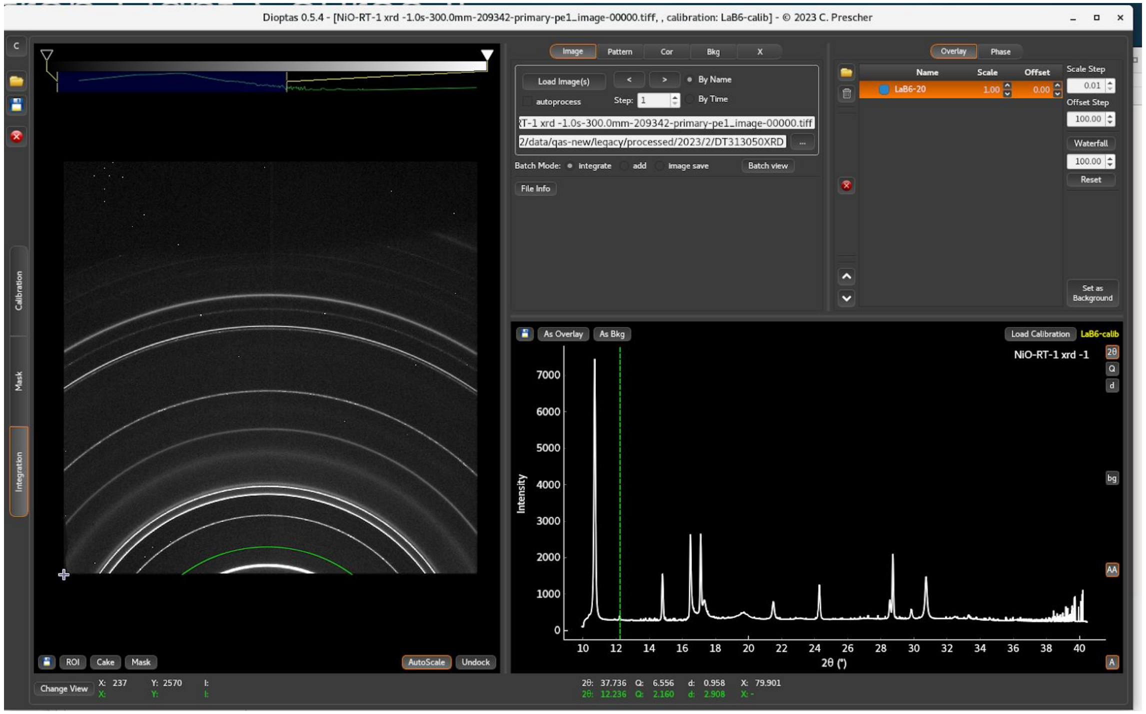


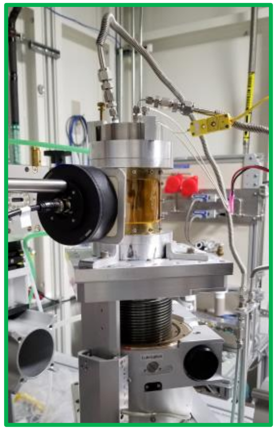


Unpublished data by S. Liu

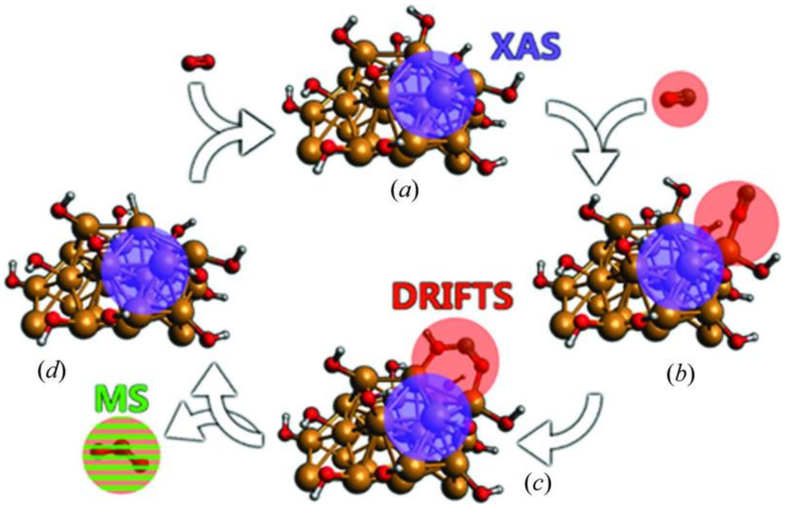
Combined XAS & XRD

- Also works with Nashner-Adler cell





Combined XAS & DRIFTS



XAS provides information on the oxidation state, electronic structure, and local coordination environment around specific elements.

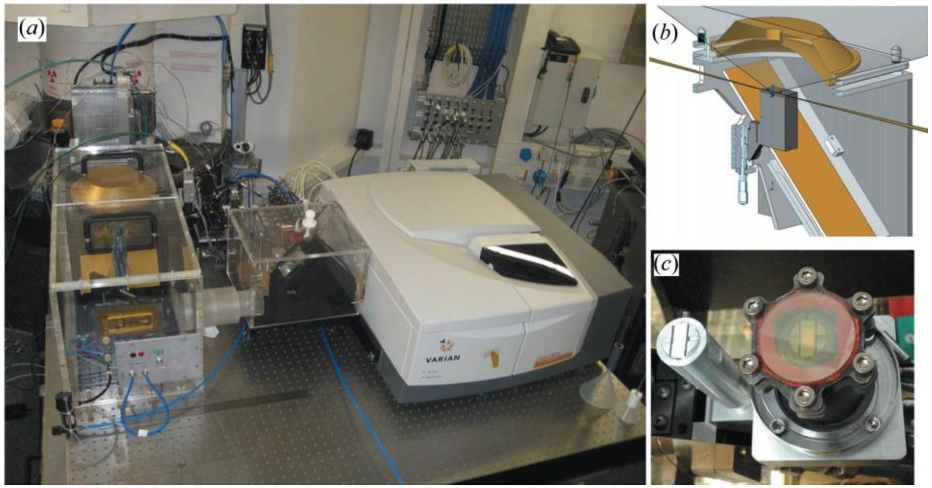
DRIFTS is sensitive to molecular vibrations and offers insight into surface species, functional groups, and adsorbed molecules on catalyst surfaces.

Combined XAS/DRIFTS: simultaneously monitor changes in the metal center (via XAS) and the organic species or reactants/products (via DRIFTS) during a reaction.

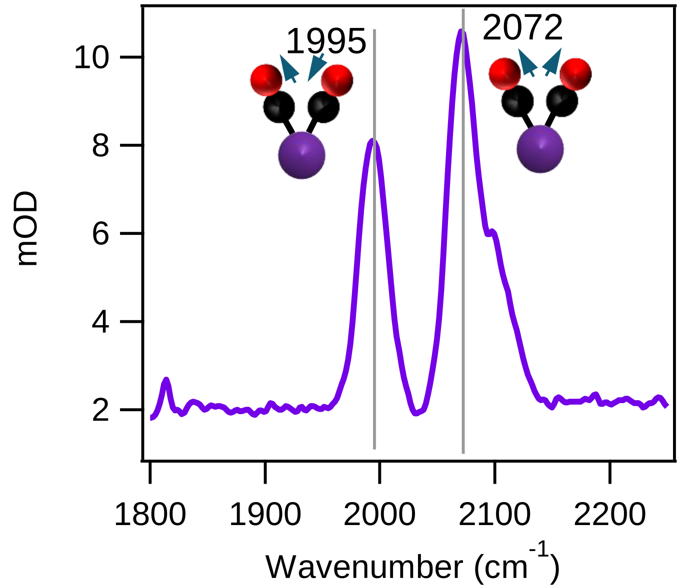
J.SynchrotronRad.(2019).26,801–810.

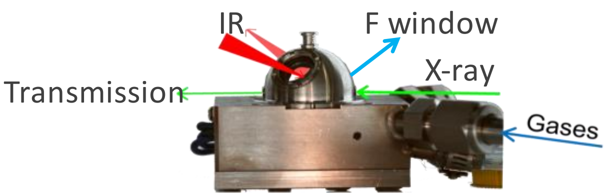
Combined XAS & DRIFTS

ESRF ID24

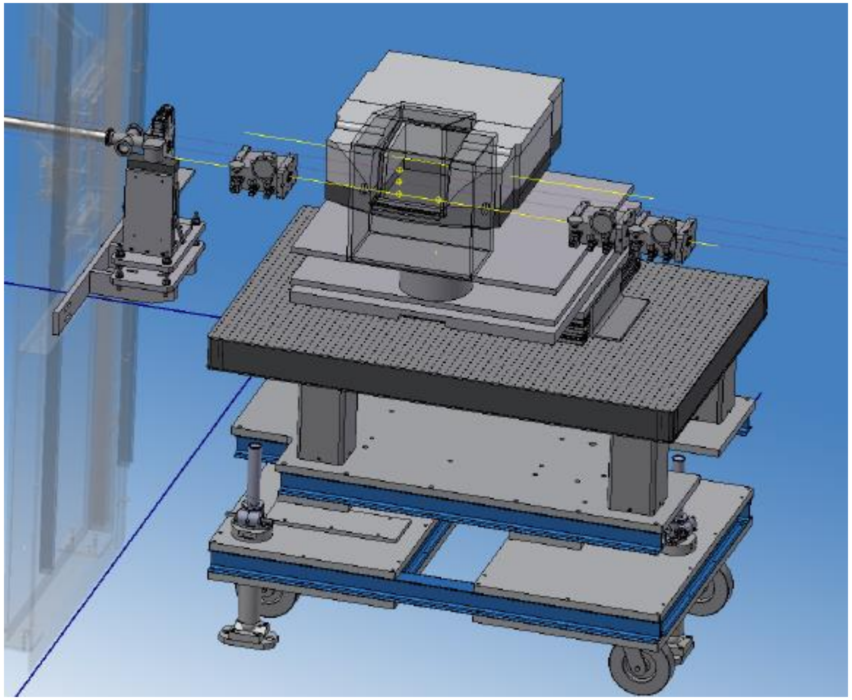


APS 9-BM



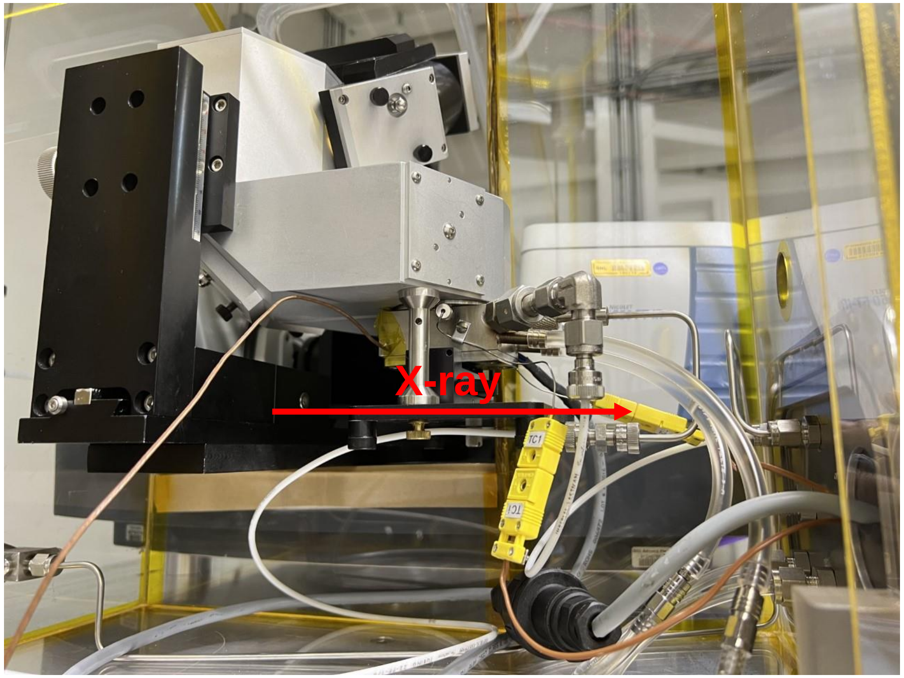


QAS hutch C endstation -- DRIFTS



- Combined XAS and DRIFTS measurements with gas flow
- Thermo-Nicolet iS-50 IR spectrometer and Harrick cell

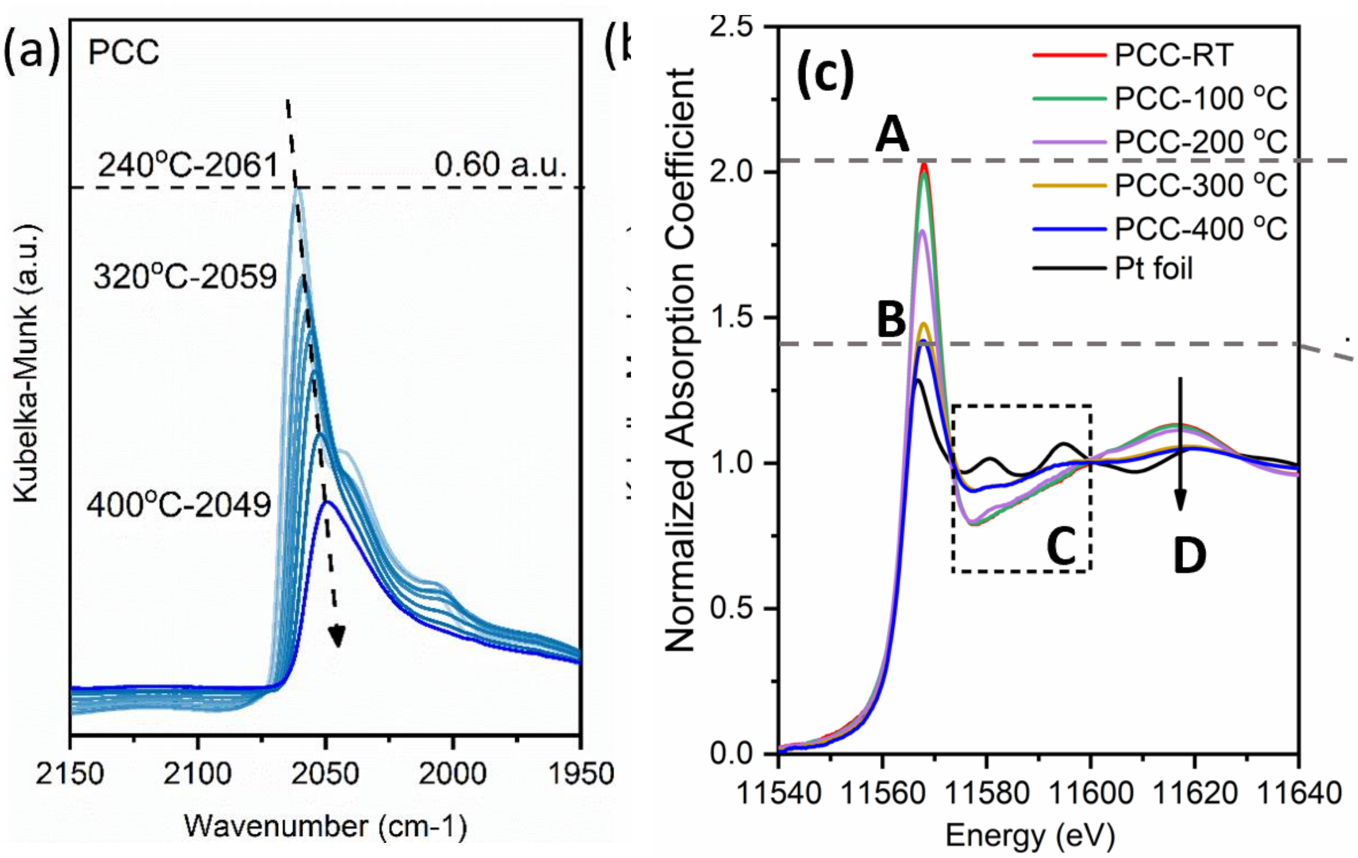
QAS hutch C endstation -- DRIFTS



- Plexiglass box to avoid influence from the air for DRIFTS measurement.
- The water line and gas line are hooked up to Harrick cell.

Combined XAS & DRIFTS

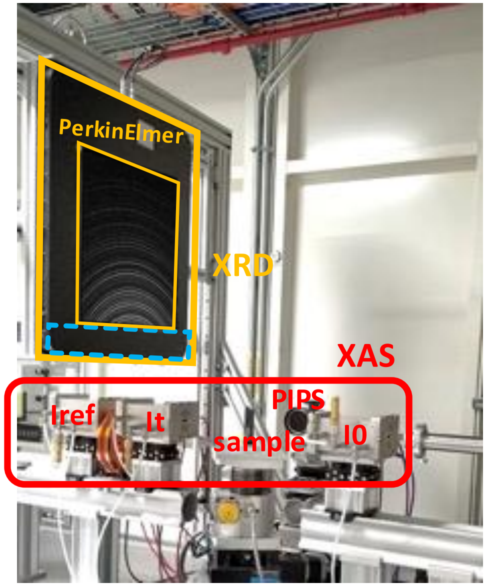
- Science commissioning result



Unpublished data by H. Wang

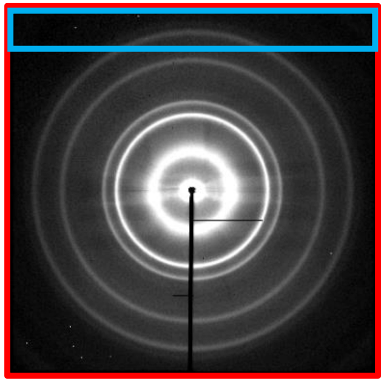
Current Limitations of combined XAS & XRD

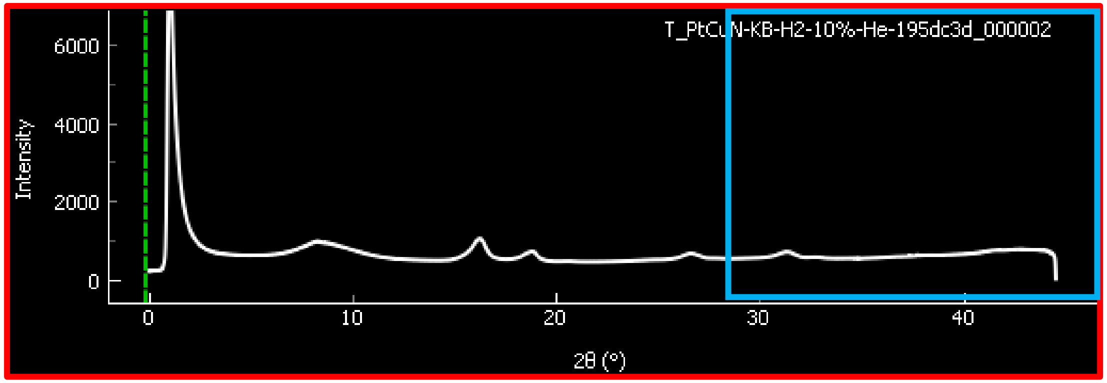
- Large 100mm wide bottom gap blocking low angle diffraction
- Limited detector active energy range
  - **≥20 keV** for PE
- Limited field of view
- Long changeover time between XAS and XRD
- Background noise and low dynamic range



ex situ
300mm from detector

in situ electrochemical
300mm from detector

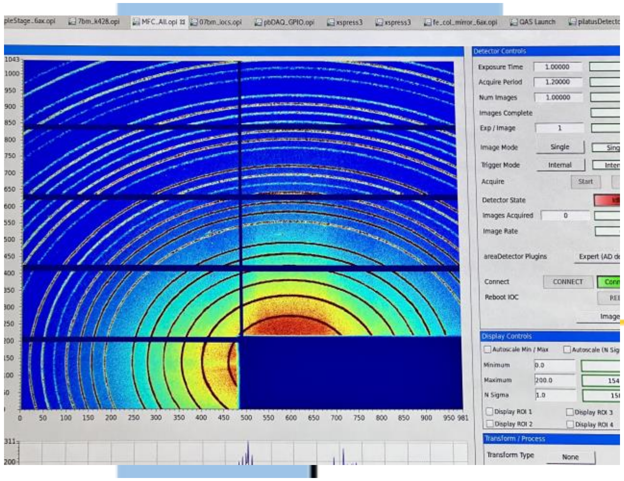


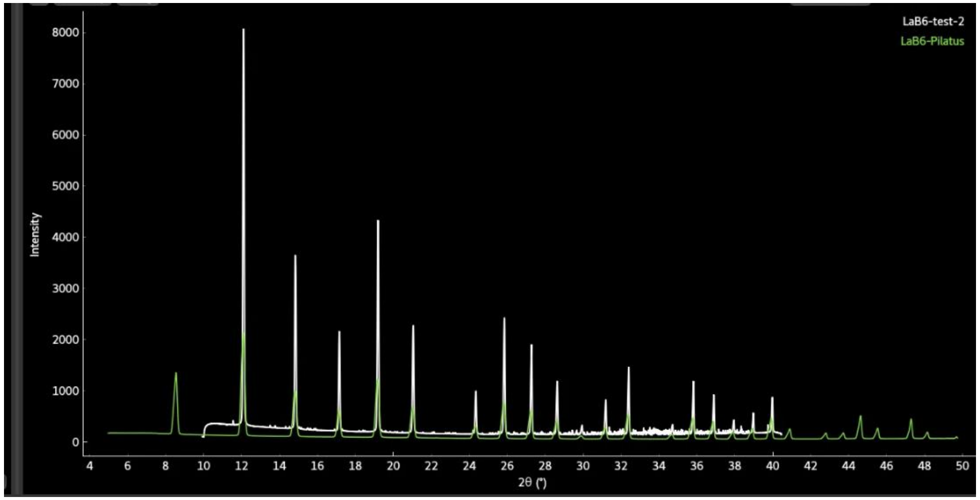


Improved Combined XAS & XRD

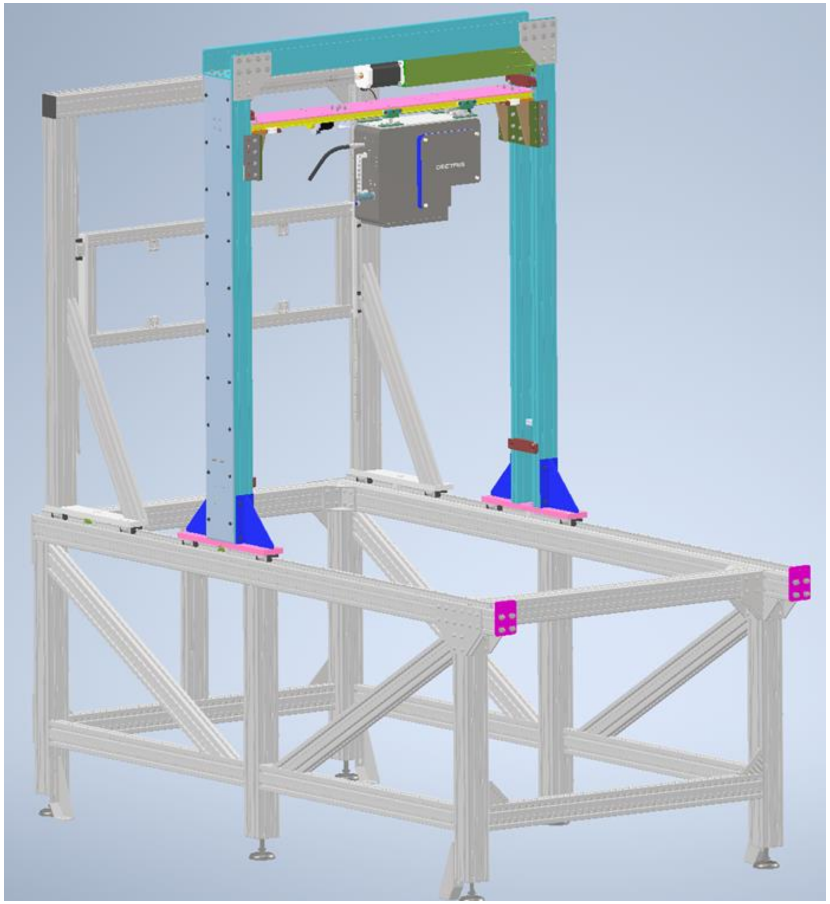
Pilatus3 S 900K

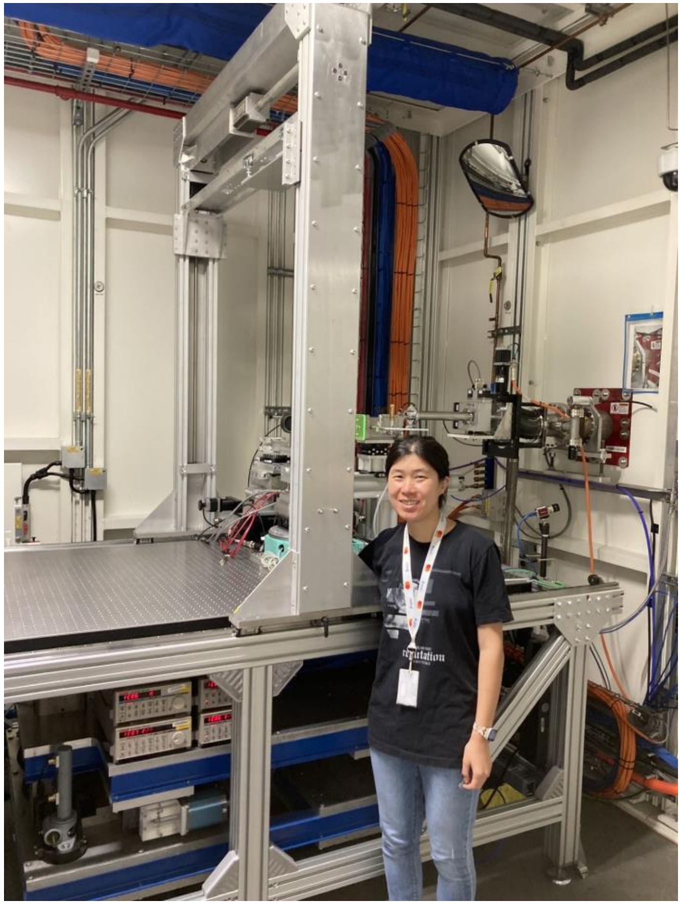
- Extended 2θ angle range, 3.0º - 45.2º
- Extended energy range (5.0 - 32 keV)
- Larger field of view
- Fast switching
- Single-photon counting, 10^7 photon/sec/pixel





Improved Combined XAS & XRD

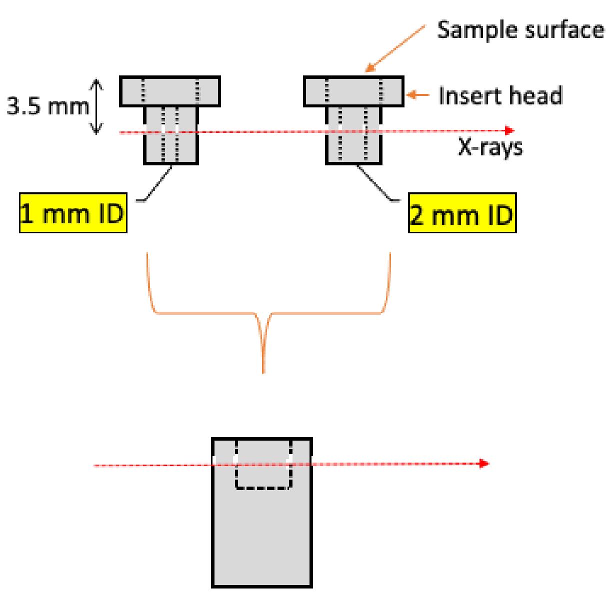




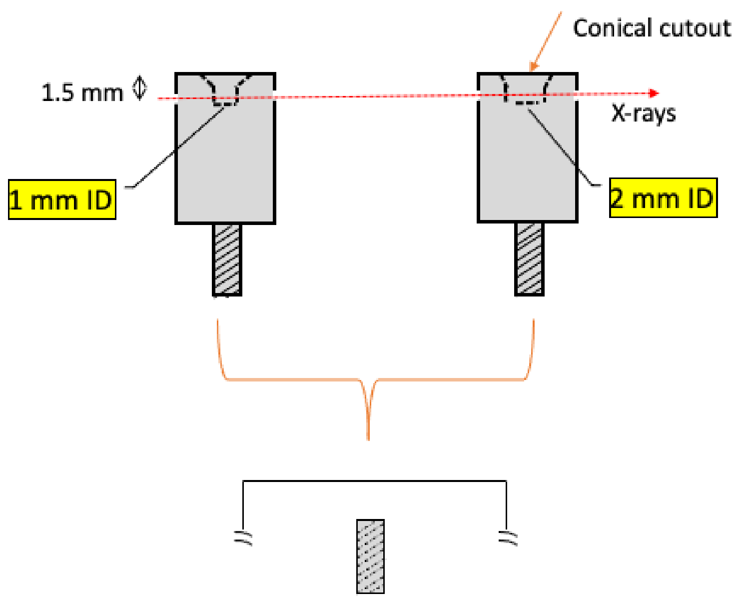
Current Limitations and ongoing improvement of combined XAS & DRIFTS

- 3mm thick sample would be too absorbing at relatively low energy.
- The gas lines are too thick to achieve a fast response on RGA.

Interchangeable inserts

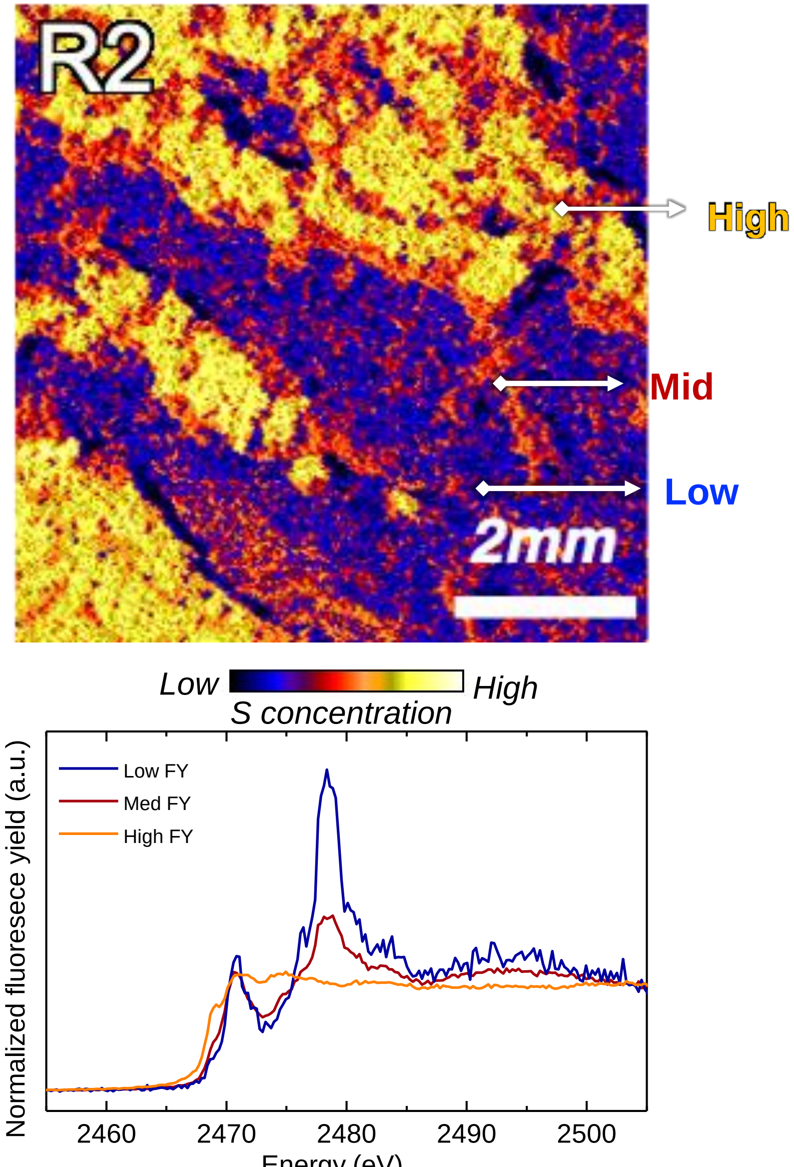


Interchangeable cups

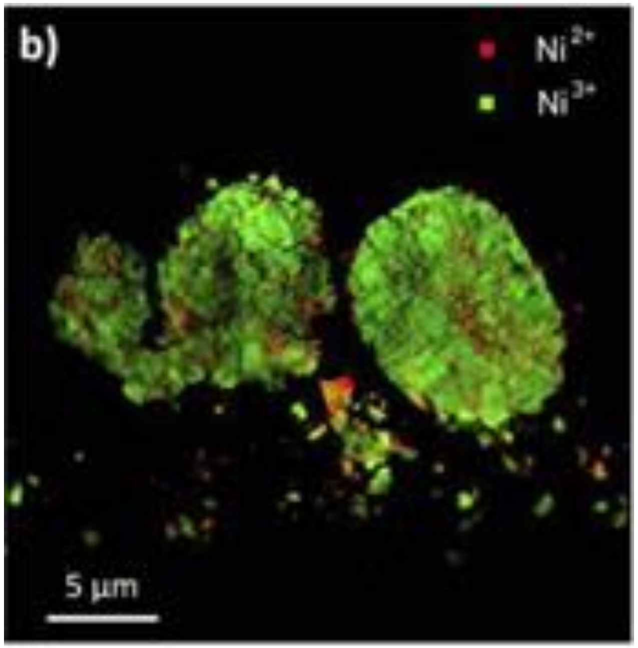


Other combined techniques with XAS

XRF mapping



XANES tomography



Energy Environ. Sci. 13, 3620-3632 (2020)

Thank you!