IN SITU AND OPERANDO EXPERIMENTS

UTA RUETT
LEADER OF STRUCTURAL SCIENCE GROUP AT APS
SECTOR 11 & 17-BM
MODERN CHALLENGES
MODERN CHALLENGES

Synthesis of new Materials
- Understanding intermediates and tuning factors → Efficient growth

Properties of materials
- Understanding of phenomena

Functionality of materials and devices
- Observing mechanisms
- Understanding limitations
  → Optimized functionality
Synthesis of new Materials
Reactor
High pressure cell
Deposition system
Furnace for annealing
Multi-modal

Properties of materials
Temperature (heating, cooling)
Magnetic Field
Electrical field
Pressure
Load frame
Viscosity
...

Functionality of materials and devices
Battery cycler
Gas loading
Reactor for catalysis
Load frame
Rheology
SYNTHESIS
SYNTHESIS REACTORS: WATCHING CHEMISTRY IN ACTION

In situ synthesis / annealing / deposition

Synchrotron

Nanoparticles

Global Optimizer

Theory

EXAFS

PDF

Raman, NMR

Solved Structure

TEM

Courtesy by Kirsten Jensen
SYNTHESSES REACTORS

Diffraction – Total scattering – Small angle scattering – Spectroscopy

Flow cell / Furnace

Synthesis reactor, 600° C

Raman probe

Protective Gas

Heater

Heater

Argonne National Laboratory
SYNTHESES REACTORS

Diffraction – Total scattering – Small angle scattering – Spectroscopy

Mixed flow reactor

Syringes

Reactor

Stir plate

To pump

Observation of structural changes
• Morphology
• Intermediates
• Metastable intermediates
→ Tuning reaction pathway

Courtesy by Olaf Borkiewicz
SYNTHESES REACTORS:

Flash Sintering

DC flash experiments

Anode, +

CeO$_2$

100V/cm

Cathode, -

O$_2$ $\rightarrow$ 1/2O$_2$ + 2e$^-$

1/2O$_2$ + 2e$^-$ $\rightarrow$ O$_2^-$

Thermal expansion during flash sintering

Thermal expansion at furnace temperature

Lattice parameters (Å)

CeO$_2$ $\rightarrow$ CeO$_{2-\delta_2}$

δ2 > δ1

CeO$_{2-\delta_1}$

Anode

Cathode

Chemical composition

Ionic conductivity

Jha, Charalambous, Wang, Phuah, Mead, Okasinski, Wang, & Tsakalakos, Ceram. Int. 2018
ATOMIC LAYER DEPOSITION
Deposition of precursors on substrates, but also on porous material or nanoparticles through gas flow

commercial

Emergency solution

Coating of nanoparticles
IN SITU FILM GROWTH WITH MULTIMODAL APPROACH
Molecular Beam Epitaxy (MBE) @PETRA III (Germany)

Courtesy by Anita Ehnes and Ann-Christin Dippel

- gazing incident geometry for surface sensitivity
- no detector motion using large 2D detector
- only sample rotation required

→ follow the growth of an epitaxial thin film with time resolution below 5 sec

Collaboration with J. Wollschläger (BMBF project)

F. Bertram | scientist, DESY
J.T. Röh | engineer, DESY
IN-SITU SPUTTER CHAMBER FOR PDF ANALYSIS

Time resolution: 15Hz

Photonenergy > 80 keV


A.C. Dippel | scientist, DESY
M. Roelsgaard | scientist, Aarhus Uni, Denmark
J.T. Röh | engineer, sample environment, DESY
ADDITIVE MANUFACTURING RESEARCH AT APS

Address the critical issues in metal additive manufacturing

- Structure defects
- Failure mechanisms
- High-fidelity models
- Reliability and repeatability

In situ/operando synchrotron x-ray experiments

Courtesy by Tao Sun
IN SITU/OPERANDO X-RAY STUDIES ON AM PROCESSES

- Melt pool morphology
- Melt flow velocity
- Keyhole dynamics
- Spatter velocity
- Solidification rate
- Cooling rate
- Phase transformation rate
- Internal temperature distribution

Courtesy by Tao Sun
PROPERTIES OF MATERIALS
FURNACES

Commercial / modified/ home made

Linkham (~1500° C)

Anton Paar

Hot air blower (up to 900° C)

Resistive capillary heater (up to 1000° C)
FURNACES

Home made

Batch reactor for capillaries: simultaneous heating of several samples
Extreme Conditions: Aerodynamic Levitation

Laser heating & aerodynamic levitation.
Access structures at extreme temperatures from 1500 to >3300°C.
Oxides processed in Ar, O, N, air, CO/CO₂ atmospheres.
Containerless: no container contamination, supercool liquids several hundred degrees.
Observation of meta-stable states.

Levitating liquids

Detection of First-Order Liquid/Liquid Phase Transitions in Yttrium Oxide–Aluminum Oxide Melts

Network topology for the formation of solvated electrons in binary CaO–Al₂O₃ composition glasses

Courtesy by Chris Benmore
CRYOSTATS – CRYOCOOLER

Displex: sample shielded (<10 K)
Bath cryostat: sample shielded (<10 K)
LN2/He- Cryostream: sample in air (80K/4K)

Courtesy by Joerg Strempfer
MAGNETIC FIELDS

Earth: 0.00004 T
Refrigerator magnet: 0.005 T
Permanent magnet neodymium: 1.25 T

Continuous field Superconductor: <20 T
Pulsed field: 100 T
DIFFRACTION STUDIES IN PULSED MAGNETIC FIELD (GEOMETRY)

Split-pair magnet:
TRANSVERSE (no optical access limitation)
LONGITUDINAL (out-of-plane; very limited)

Solenoid:
TRANSVERSE (forward scattering; limited)
LONGITUDINAL (back-reflection; sensitive)
MAGNETIC FIELD

Electromagnet ~ 0.1 T

For XMCD

Courtesy by Joerg Strempfer
MAGNETIC FIELD:
Superconducting

6.5 T spectroscopy

7 T HEX diffraction

14 T diffraction

APS

PETRA III
Large safety margin (use lower voltages than maximum rated voltage of 10 kV reduces chances of capacitor failures

- **30 Tesla, 10 ms pulse every 12 minutes**

- Longer pulse matching fast (~1 kHz) 2D detectors (e.g. MMPAD) to improve efficiency
FRUSTRATED MAGNETISM: MAGNETO-ELASTICS OF A SPIN LIQUID

Conceptually important model system
- Strong correlations/fluctuations
- Coupled degrees of freedom
- Novel (quantum) phases

Material has no magnetic order down to ~70mK. Magnetostriction observed below 25T and structural transition above 25T.

1ms pulse every >20 minutes
Single Crystal Uniaxial Strain: Razorbill CS100, $5 \times 10^6$ N/m, 6 μm displacement

Temperature + Strain + Electrical field

Courtesy by Philip Ryan
FUNCTIONALITY
COMPRISES & MODEL SYSTEMS
Actual devices ↔ Reduction to the relevant

Industry standard coin cell

“X-ray enabled coin cell

Coin cell substitute
LOAD FRAME
In-grip Rotation During Mechanical Loading

• Rotation and Axial Motion System (RAMS)
• Enables HEDM and tomographic imaging during mechanical loading

RAMS developed by AFRL/PulseRay and partner users at ANL/CMU/LLNL/Petra-III

P. Shade, B. Blank et al, RSI 86 (2015), 093902
Grain-resolved Strains Along Loading Direction (FF-HEDM)

Full 3D strain/stress tensors of all grains in ~1mm$^3$ volume
Axial strains in elastic regime shown – heterogeneous!
During creep, stress heterogeneity increases (not shown)
Rich set of data to test material models

J. Schuren, P. Shade et al, COMMS 19 (2015), 235-244
ELECTROCHEMISTRY
Comprises & Model Systems
Actual devices ↔ Reduction to the relevant

Industry standard coin cell

“X-ray enabled coin cell

Coin cell substitute

Courtesy by Kamila Wiaderek
ELECTROCHEMISTRY
BRIDGE To The Gap Between Performance And Data Quality; AMPIX cell

Courtesy by Kamila Wiaderek

Electrode homogeneity is a true commercial challenge.

Sample environments that allow full cell studies and deconvolution of the signal coming from anode and cathode are in demand.

Existing cells are still in the development stages and have poor reliability.
ELECTROCHEMISTRY

Electrochemical Lithiation Cycles Of Gold Anodes In Model System


High Energy X-rays, 80 keV
GAS LOADING AND CATALYSIS

Mass flow controller

Switching valve

Vapor generator (for water, methanol, etc)

Syringe pump (up to 600 bar, for high-P gas loading)

Resistive heating: RT to 1273 K

Other temp. control options:
Cryostream: 90 to 475 K
Hot air blower: RT to 873 K

Temperature controller

Residual gas analyzer

Backpressure regulator (up to 100 bar, for high-P flow/catalysis)

RGA of reactants and products

XRD

H2, CO2, CH3O+
Evolution of Active Sites in Pt-Based Nanoalloy Catalysts for the Oxidation of Carbonaceous Species by Combined in Situ Infrared Spectroscopy and Total X-ray Scattering

Valeri Petkov,*† Yazan Maswadeh,* Aolin Lu,*‡ Shiyan Shan,*‡ Haval Kareem,*‡ Yinguang Zhao,*‡ Jin Luo,*‡ Chuan-Jian Zhong,*‡ Kevin Beyer,*§ and Karena Chapman*§
CATALYSIS

Pd surface, CO $\rightarrow$ CO2

Courtesy by Johan Gustafson, PETRA III

TAKE HOME MESSAGE:
DON’T LIMIT YOURSELF TO THE EXISTING TOOLS, BUT GET INSPIRED BY THE VARIETY
THE EXISTING SAMPLE ENVIRONMENTS SHOW WHAT WE CAN DO TODAY, THEY DON’T DETERMINE WHAT YOU WILL DO IN THE FUTURE.

ALBERT EINSTEIN: “YOU HAVE TO LEARN THE RULES OF THE GAME, AND THEN YOU HAVE TO PLAY BETTER THAN ANYONE ELSE.”