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PNNL-32741

Developing in-situ capabilities for synchrotron light source relevant to PNNL mission research areas

March 2022

S. Thevuthasan
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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Abstract

The main objective of the proposed research is to engage synchrotron light source capabilities to address the critical mission areas at PNNL. We have carried out Multi-modal chemical analysis and imaging to unravel the role of surface chemistry during realistic heterogeneous interfacial processes - through a close collaboration that will help BES and BER research projects. In particular, we performed the following activities to understand role of surface chemistry on metal and oxide reactivity and metal ion transfer across oxide surface and aqueous solutions:

- Perform light source experiments utilizing samples generated at PNNL
- Develop early career PNNL scientists utilizing light sources
- Build collaborations with ALS scientists in developing new in-situ capabilities
- Complete AMBER capabilities in collaborations with ALS scientists and make those available to the scientific community including PNNL scientists

Summary

This three year project developed capabilities that can be utilized to observe material and chemical transformations under realistic conditions.

Acknowledgments

The research described in this report was conducted under the Laboratory Directed Research and Development (LDRD) sponsored by the PCSD Mission Seed Program at the Pacific Northwest National Laboratory (PNNL), a multiprogram national laboratory operated by Battelle for the U.S. Department of Energy. PNNL is a multi-program national laboratory operated for the U.S. Department of Energy (DOE) by Battelle Memorial Institute under Contract No. DE-AC05-76RL01830.

1.0 Introduction

This project involves with developing in-situ capabilities for synchrotron measurements can help address the science behind interfacial processes, which is a critical mission area of Pacific Northwest National Laboratory (PNNL). This project also facilitates inter-laboratory collaborations by developing a consortium of critical expertise to solve DOE-identified grand challenges associated with energy materials. In particular, this undertaking brings together PNNL's core scientific expertise in nuclear magnetic resonance (NMR), transmission electron microscopy (TEM), and atom probe tomography (APT) with synchrotron light source capabilities available at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL) to address the scientific questions.

The main objective of the proposed research is to engage synchrotron light source capabilities to address critical mission areas at PNNL. In particular, we will focus in the following scientific areas to develop collaborative science by engaging light source scientists utilizing our AP Program, approved individual proposals, and beam line enhancements:

(i) Understanding redox pathways and coordination geometries in iron oxide and aluminum (oxy) hydroxide materials using in-situ x-ray absorption capabilities,

(ii) Studying well-ordered oxide surface interactions with water vapor and understanding photochemistry on these surfaces through in-situ ambient pressure (AP) XPS experiments,

(iii) Understanding the chemical environment and coordination geometries of elements in materials relevant to chemical conversions and energy storage under operating conditions using STXM, XANES and EXAFS; and

(iv) Determining the chemical and structural properties of new materials synthesized at PNNL using STXM, XANES and EXAFS.

Our major focus has been in -situ capabilities, which can be further continued by PNNL scientists.

2.0 Results and Accomplishments:

Our major focus has been in three different research area; (i) in-situ AP-XPS, XANES and EXAFS activities, (ii) XANES and STXM analyses of mineral-organic matter associations and (iii) XANES/STXM analyses of aerosols. In-situ AP-XPS, XANES and EXAFS activities: in this ambient pressure XPS work, we synthesized (001)-oriented epitaxial films of LFO distinctly terminated on (LaO)+ or (FeO2)− planes to probe the influence of perovskite surface termination on chemical reactivity using AP-XPS (see Figure 1). We have demonstrated that that LaO terminated LFO (LaO-LFO) is more reactive toward water, forming hydroxyl species at lower relative humidities than its FeO2-terminated (FeO2-LFO) counterpart, consistent with DFT calculations that indicate a greater stability of hydroxylated LaO-LFO. The results are summarized below:

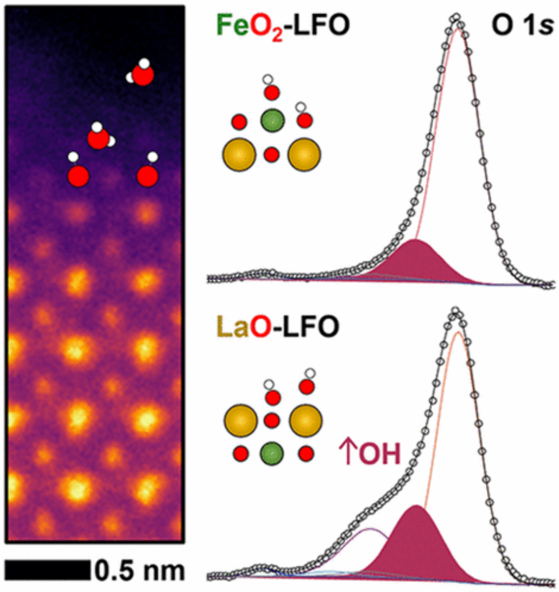


Figure 1. TEM micrograph of the film is presented along with ambient pressure XPS O 1s scans from water adsorbed FeO2 and LaO terminated surfaces of LFO thin film.

- The polarity of the oxide surfaces impacts their surface reactivity
- LaO terminated surface appears to be more reactive to water than FeO2 terminated surface

In the in-situ XANES and EXAFS work we have utilized the gaseous in-situ cell S to carry out various experiments associated with correlating chemical and topographical arrangements of copper sites in oxide-based catalysts to the reaction efficiency by (i) Identifying the chemical and bonding nature of substituents with host material by in situ XANES and validating with TD-DFT derived spectroscopic signatures, and (ii) studying local structural evolution of active metal sites through XANES and EXAFS under in situ reaction conditions and at varying copper concentrations. In addition, we have carried out Al and O K-edge x-ray absorption spectroscopy along with Fe and Cr L-edge studies using the solution in-situ cell capabilities. Characteristic features in x-ray absorption spectra are expected to provide unique geometrical information on

Al in tetrahedral (undistorted and distorted), square planar, and octahedral coordination environments.
XANES and STXM analyses of mineral-organic matter associations: In the first project, we used combined C-Ca STXM spectra to investigate interaction of soil organic matter (OM) with Ca-minerals. In particular, we were focusing on understanding the correlations in images/spectra collected on the same region of the sample.

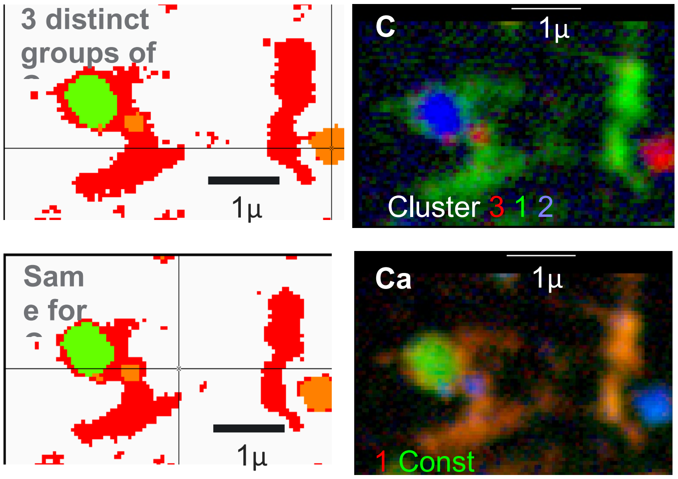
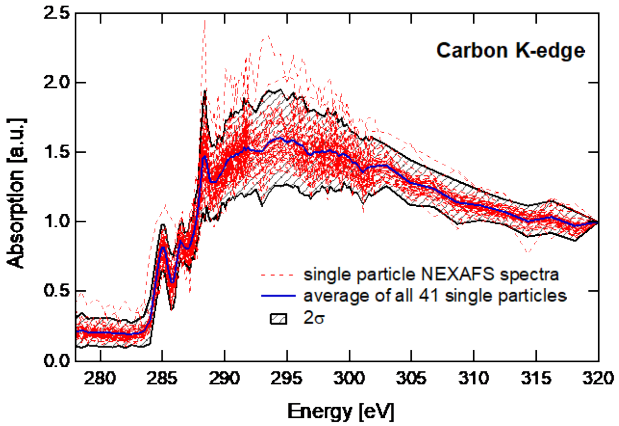


Figure 2. PCA (left) and tricolor (right) of both C and Ca data shows strong correlation between the C from OM and Ca, indicating Ca-OM bridging that stabilize OM.

XANES/STXM analyses of aerosols:
In this project, we investigated the spectroscopic signatures of particles from wildfire. Aerosol samples collected on filters were analyzed using STXM.



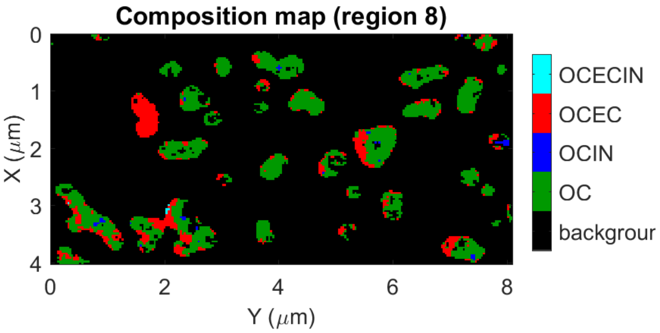


Figure 3. The first component of the figure demonstrates the C K-edge XANES spectrum from a single particle and averaged spectrum over the spectra from 41 single particles. The second component shows the spatial distribution of various functional groups in particles with different sizes.

The extensive investigations from all these topics resulted in several presentations and publications. Engaging synchrotron light source capabilities to address critical mission areas at PNNL was successful and several research activities are continuing.

3.0 Publications/Presentations associated to the project:

Some of the publications and presentations are listed below:

Stoerzinger, K.A., L. Wang, Y. Ye, M.E. Bowden, E. Crumlin, Y. Du, and S.A. Chambers, "Linking surface chemistry to photovoltage in Sr-substituted LaFeO3 for water oxidation," J. Mater. Chem. A 6(44), 22170-22178 (2018). (doi:10.1039/C8TA05741A) 9.3.2

Summary: Mechanistic investigation of solar-driven water oxidation on Sr-substituted LaFeO3 linking the ability of oxidized Fe sites to be hydroxylated to the presence of surface electronic states that require filling prior to oxygen evolution

Albuquerque, G.H., K.-J. Kim, J.Isac. Lopez, A. Devaraj, S. Manandhar, Y.-S. Liu, J. Guo, C.-H. Chang, and G.S. Herman, "Multimodal characterization of solution-processed Cu3SbS4 absorbers for thin film solar cells," Journal of Materials Chemistry A 6(18), 8682-8692 (2018). (doi:10.1039/C8TA00001H) 6.3.1.2

Summary: Understanding of new synthesis methods to synthesize chalcogenide based solar cell material thin films to improve the solar cell performance

Roy S., M. Bandi, V. Shutthanandan, S. Thevuthasan, and C. Ramana. 2018. "Structural, Chemical and Dielectric Properties of Iron Doped Gallium Oxide (Ga2-xFexO3) Ceramics" J. Phys. Chem. C 2018, 122, 27597−27607 (doi: 10.1021/acs.jpcc.8b07921)

Summary: Mechanistic understanding of Fe dopant chemistry in gallium oxide materials for sensor applications

Wildman A, Martinez-Baez E, Fulton, J, Schenter G, Pearce C, Clark A.E, and Li X, Li, "Anticorrelated Contributions to Pre-edge Features of Aluminate Near-Edge X-ray Absorption Spectroscopy in Concentrated Electrolytes", J. Phys. Chem. Lett. 2018, 9, 2444−2449

Summary: XAS is a promising tool for investigating ion pairing in complex solutions and we have used this capability in concentrated sodium aluminate solutions. A shift in the pre-edge shoulder in Al XAS correlated to sodium concentration is observed, and the physical origins of that shift are investigated using energy specific TD-DFT of sub-ensembles obtained from ab initio molecular dynamics.

Elsaidi, S.K., M.A. Sinnwell, D. Banerjee, A. Devaraj, R.K. Kukkadapu, T.C. Droubay, Z. Nie, L. Kovarik, M. Vijayakumar, S. Manandhar, M. Nandasiri, B.P. McGrail, and P. Thallapally, "Reduced Magnetism in Core–Shell Magnetite@MOF Composites," Nano Letters 17(11), 6968-6973 (2017). (doi:10.1021/acs.nanolett.7b03451) 6.3.1.2.

Summary: Multimodal chemical imaging of MOF materials grown on iron oxide microspheres for extraction of rare earth elements enabled by correlating XAS from ALS 6.3.1.2 with SEM and magnetic susceptibility measurements and extraction performance

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