

Department of Chemical Engineering Seminar Series

Measuring and Understanding Local (Dis)order: Crystallization of Zeolite Nanosheets & Defects in Li-ion Battery Electrodes



Robert J. Messinger

Postdoctoral Researcher, CNRS & Grenoble
Institute of Technology

Thursday, February 5, 2015

Seminar: 4:00-5:00 p.m.

[Hitchcock \(HCK\)](#) 132

Reception: 3:30 p.m. – Benson Lobby

Abstract

Measuring and understanding how order develops in crystallizing materials is a challenging problem, especially during the syntheses of self-assembled materials that exhibit both crystalline and mesoscopic order. Surfactant-directed zeolite MFI nanosheets exhibit improved transport and catalytic properties compared to their bulk zeolite counterparts, particularly with respect to large molecules. During their hydrothermal syntheses, coupled framework crystallization and surfactant self-assembly processes occur that are poorly understood and difficult to control. Local compositions, atomic and mesoscale structures, and surfactant-framework interactions were monitored throughout their syntheses by multi-dimensional solid-state nuclear magnetic resonance (NMR) spectroscopy, X-ray diffraction (XRD), and electron microscopy measurements. The analyses establish how the atomic and mesoscale framework structures evolve during hydrothermal synthesis, revealing that the zeolite MFI nanosheets form via intermediate nano-layered frameworks with 2D crystal-like structures. The materials are shown to result from competing organic self-assembly and inorganic crystallization processes, where the interplay between them governs the development of framework order over different length and time scales.

Similarly, identifying and characterizing atomic-level disorder in crystalline materials can also be difficult experimentally, particularly for lithium-ion intercalation compounds that can exhibit multiple oxidation and spin states as well as local ordering of lithium and charges. LiVPO_4F is an intercalation electrode material for lithium-ion batteries with one of the highest known energy densities among polyanionic compounds. Highly crystalline LiVPO_4F samples were synthesized, as established by XRD and scanning transmission electron microscopy (STEM) measurements. However, solid-state ^7Li NMR spectra reveal unexpected lithium environments that can account for up to 20% of the total lithium content. Multi-dimensional solid-state NMR experiments that recouple through-space magnetic dipolar interactions between ^7Li nuclei establish unambiguously that the unexpected lithium environments are defects within the LiVPO_4F crystal structure, further revealing their relative sub-nanometer-scale proximities. The lithium defects are shown to exhibit local electronic environments distinct from lithium ions in the crystallographic LiVPO_4F site, which result from altered oxidation and/or spin states of nearby paramagnetic vanadium atoms. The results provide a general strategy for characterizing sub-nanometer-scale disorder in lithium-containing crystalline solids, including paramagnetic lithium-ion battery materials.

Speaker Biography

Robert J. Messinger is a postdoctoral fellow at the CNRS and Grenoble Institute of Technology. He earned a B.S. from The Ohio State University (2006) and a Ph.D. from the University of California, Santa Barbara (2012), both in chemical engineering. He then joined the CNRS, France, where he was a Marie Curie Postdoctoral Fellow at the CEMHTI laboratory, Orléans, and associated with the RS2E French Network for Electrochemical Energy Storage. He recently joined the LEPMI laboratory (2014), affiliated with both the CNRS and Grenoble Institute of Technology, to further his research in energy materials.