

Neutron single crystal diffraction study of hydrogen bonding in energy materials

Xiaoping Wang

*Chemical and Engineering Materials Division, Neutron Sciences Directorate,
Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA. wangx@ornl.gov*

Abstract: Recent advances in neutron time-of-flight Laue diffraction at the ORNL Spallation Neutron Source (SNS) have made it possible to collect high resolution data set in 3D volumetric space from sub-millimeter size single crystal samples. In this presentation, I will showcase the applications of neutron wavelength-resolved Laue technique implemented by the SNS TOPAZ instrument. The benefits of 3D reciprocal space mapping with a large array of area detectors at sub-atomic resolution will be demonstrated in the study of hydrogen bonding in energy materials. Synthetic biologically inspired complexes exhibiting reactivity similar to hydrogenase enzymes have provided evidence of hydride transfer to the metal and proton transfer to an amine. However, key structural information about the intermediate is not readily discernible since positions of hydrogen atoms can't be measured accurately using X-rays. Using neutron diffraction data collected on TOPAZ, we have succeeded in characterizing the structural details of a supershort dihydrogen bond resulted from heterolytic cleavage of dihydrogen in an iron-based molecular electrocatalyst. The dihydrogen Fe complex undergoes single-crystal to single-crystal chemical reaction to produce hydrogen, demonstrating that the Fe complex as a functional model for the [FeFe]-hydrogenase enzyme. The neutron structure confirms previous hypotheses and provides insight into how to make the electrocatalyst work better for alternate energy applications. The hybrid inorganic-organic perovskite, methylammonium lead iodide (MAPbI₃), is a promising material for photovoltaics. The positioning and orientation of MA cations have a strong influence on photovoltaic performance. High resolution single crystal neutron structure measured on TOPAZ revealed the details of the orientation of the methylammonium cation in the tetragonal and cubic phases of MAPbI₃, showing that the C–N bond is located off-center from the high symmetry sites in the crystal structure. The off-center placement of MA cation is induced by the formation of hydrogen bond-like interactions between the ammonium substituent of the organic cation and the iodine atoms of [PbI₆] octahedral, an important structural information for understanding the origin of its high photovoltaic performance.

Key Words: Neutron Time-of-Flight Laue, Neutron wavelength-resolved Laue, Neutron single crystal diffraction, Hydrogen bond, Molecular electrocatalyst, Dihydrogen Fe complex, Methylammonium lead iodide, TOPAZ Single Crystal Neutron Diffractometer, Spallation Neutron Source.