Abstract #2256, 224th ECS Meeting, © 2013 The Electrochemical Society

IR Synchrotron Radiation Analysis of Battery Materials

Jarosław Syzdek*, Yuri Janssen[1], Peter Khalifah[1], Taras Stanislavchuk[2], Andrei Sirenko[2], Alexander McLeod[3], Dmitri Basov[3], Derek Middlemiss[4], Hans Bechtel and Robert Kostecki

Lawrence Berkeley National Laboratory, 94720 CA
[1] Stony Brook University, Stony Brook 11790 NY
[2] New Jersey Institute of Technology, Newark 07103 NJ
[3] University of California, San Diego, La Jolla 92093 CA
[4] Cambridge University, Cambridge CB2 1TN, UK

*jsyzdek@lbl.gov

Lithium iron phosphate has been in the center of attention of electrochemical energy storage community for the past 15 years. Although significant engineering efforts were able to make this insulating material provide near-theoretical capacities and extremely fast charge/discharge rates, its mechanism or operation is still poorly understood and controversial.

Multiple methods were applied for studying its properties but often compromised by powerful X-ray or electron beams that tend to damage the sample, poor contrast between LFP and FP and/or inability to discern a mixture of phases from a solid solution. We have used this material as a platform for developing near-field imaging for battery materials taking full advantage of the definition of the IR spectra of the end-members and clear ability to distinguish solid solution phases from mixture of the pure $LiFePO_4$ and $FePO_4$. We were able to image micron and sub-micron size particles using IR lasers, with 20 nm resolution.

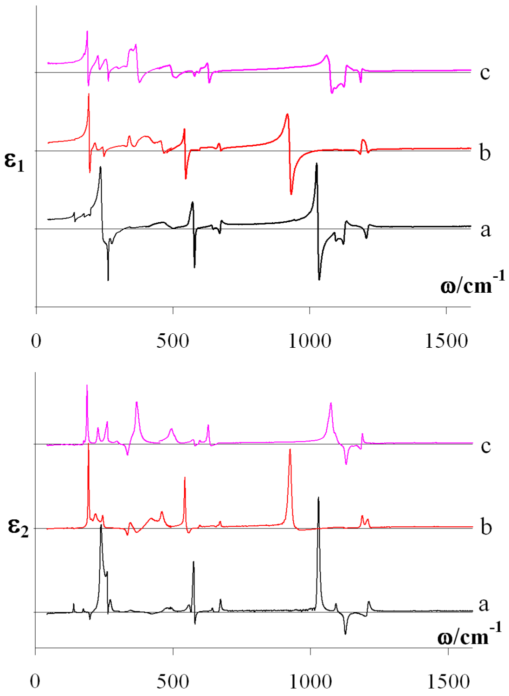

Figure 1. Real (ε_1) and Imaginary (ε_2) part of the pseudo-dielectric function of $LiFePO_4$ along three crystallographic directions of the orthorhombic unit cell (Pnma, 62).

However the analysis of near-field IR signal cannot be confidently based on classical FTIR spectra principles. For that purpose the complex dielectric function of the sample is needed. It was obtained for the "standard" near-field materials: Si, SiO_2 and Au, which dielectric functions have been measured in the past through single crystal ellipsometry. In order to obtain dielectric function of $LiFePO_4$, crystals ~1 cm in size were grown and polished along all three crystallographic axes (orthorhombic = anisotropic material).

Preparing $FePO_4$ samples was another challenge because it cannot be grown in orthorhombic form (not a stable crystal form of this compound). However, careful optimization of crystal growth vs. chemical treatments allowed us to obtain large and smooth samples, well-suited for ellipsometric studies.

To obtain spectral information of the baseline materials we have used broadband IR lasers that cover ~300 cm^{-1} of the IR spectrum and can be effectively focused onto an AFM tip for near-field FTIR spectroscopy. These results combined with DFT calculations and dielectric functions allowed us to draw conclusions about phase distribution in micron-sized particles.

Given limited spectral coverage, price and availability of broadband IR sources that can be successfully applied for near-field spectroscopy we decided to take took full advantage of excellent stability and brightness of synchrotron IR beams to obtain localized spectral information on the studied material in a broad spectral range. One of the very first synchrotron-light near-field spectra ever recorded is presented in Figure 2.

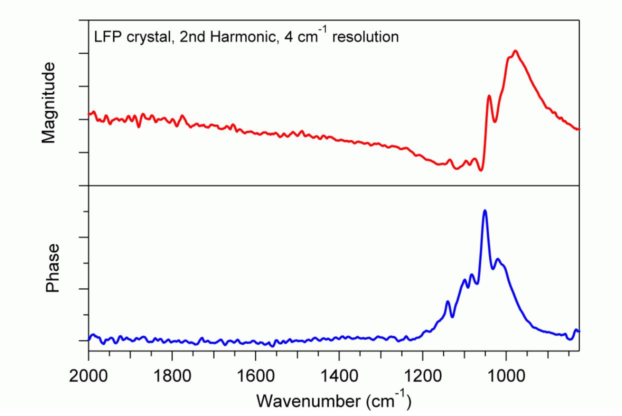

Figure 2. Magnitude and phase near-field spectra of $LiFePO_4$ using IR synchrotron radiation (Advanced Light Source, LBNL).

These results open a new route for materials analysis at unprecedented resolution and in ambient conditions.

Acknowledgement

JS and RK have been supported by the Northeastern Center for Chemical Energy Storage, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under award number DESC0001294.