Probing the energy storage in Li ion batteries with hard X-ray Compton scattering

A comprehensive quantum mechanical understanding of the principles underlying rechargeable batteries is still evolving after several decades of research. In this connection, our recent work shows how X-ray Compton scattering experiments can help unravel relationships between useful battery characteristics and the nature of the electronic orbitals involved in ion intercalation reactions [1,2]. The discharge process in which positive lithium ions intercalate or lithiate the cathode and drive current in an external circuit lies at the heart of the Li-ion battery (LIB). The reverse reaction produces the charging of the battery and involves delithiation of the cathode material.

Compton scattering experiments using brilliant, high-energy X-rays at SPring-8 **BL08W**, provide a unique window for probing the electron momentum distributions (EMDs) of the redox orbitals involved in lithiation and delithiation processes. The measured spectra can be compared with model Compton profiles obtained from accurate electronic structure calculations based on Density Functional Theory (DFT) to extract redox wave functions associated with the Li electron transfer process. Along similar lines, we have previously investigated effects of doping in high temperature superconductors [3].

In this study, we focused on lithium iron phosphate (LFP) as an exemplar LIB cathode material. LFP was proposed for use in rechargeable batteries by Padhi, Nanjundaswamy and Goodenough about 20 years ago [4] and commercial LFP batteries are available today. The olivine crystal structure of LFP is composed of perfect PO_4 tetrahedra and distorted FeO_6 octahedra as shown in Fig. 1. The electronic and magnetic structure of LFP is interesting as it displays antiferromagnetic and insulating behavior. Moreover, delithiation of LFP is a two-phase process that leads to microscopic phase separation in equilibrium.

We have previously investigated LFP using X-ray absorption spectroscopy (XAS) and parallel DFT computations to monitor the evolution of the redox orbitals under different lithiation levels [5]. In this way, we identified spectroscopic signatures of the lithiation process in LFP, and obtained information on phase transformations, valence and spin states, and local structural distortions. XAS, however, can only access the energy dependencies of electronic states and the associated spectral functions. Compton scattering, in contrast, is capable of accessing the momentum characteristics of the correlated ground state, which are beyond the reach of XAS. In particular, the experimental Compton profile is directly related to a two-dimensional integral of the EMD. Since the EMD is given by an energy integral of the spectral function over occupied states, the spectral function and its momentum dependence near the Fermi level can be obtained via an energy derivative of the EMD. Compton scattering technique thus enables unique insight into the evolution of redox orbitals with lithiation and delithiation processes in battery materials.

The EMD (integrated along the [100] direction) of the orbital involved in lithium insertion in LFP is shown in Fig. 2. This visualization can be used to gain insight into voltage shifts in the LIB and how these shifts are connected with the modification of the bond between transition metal and oxygen atoms. For this purpose, we introduce a 'deformation profile,' *D(p)*, which isolates the contribution to the Compton profile from the effects of octahedral deformation, and reveals losses in redox potential generated by the shrinking of the FeO_6 octahedron produced by the delithiation, see Fig. 3 and discussion in Ref. [1]. Interestingly, strains and octahedral distortions present in olivine phosphate compounds in which some iron atoms are substituted with other transition metals (Mn, Co and

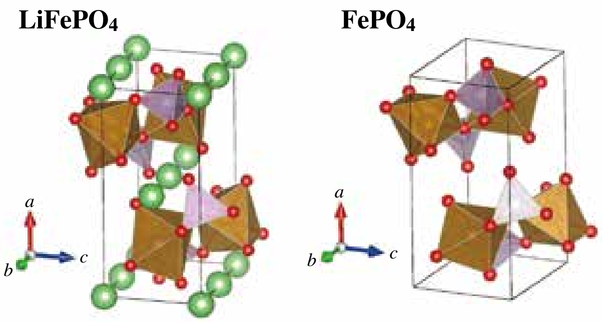

Fig. 1. Crystal structure of LFP. Li (green) and O atoms (red) are shown. Phosphorus and oxygen atoms form tetrahedral units, which link planes of corner-sharing FeO_6 octahedra.

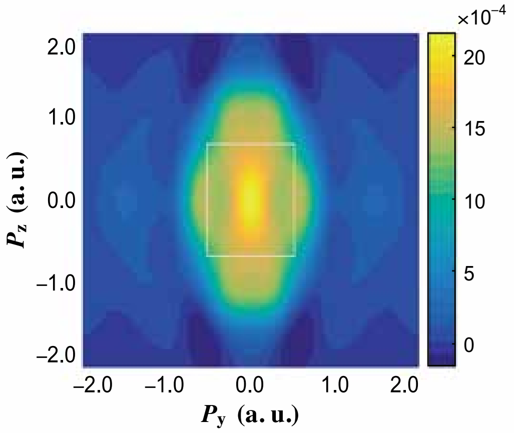

Fig. 2. Difference of 2D electron momentum densities of LFP and $FePO_4$. P_y and P_z axes are parallel to [010] and [001] direction, respectively. White rectangular box marks the boundary of the first Brillouin zone.

Ni) could improve the limited energy density of the pristine LFP and this trend can be monitored by using the deformation profile *D(p)*.

It is important to keep in mind that the energy density in a lithium battery pack in an electric car is about 0.4 MJ/liter, which is 100 times smaller than that in gasoline. This large difference indicates that there is much room for improving energy densities of rechargeable battery materials and that further work in this direction is needed. Since high-energy X-rays can easily penetrate closed electrochemical cells, Compton scattering experiments provide a unique spectroscopic tool for monitoring changes in redox orbitals during charging and discharging processes, and thus facilitate the design and development of high-performance rechargeable batteries.

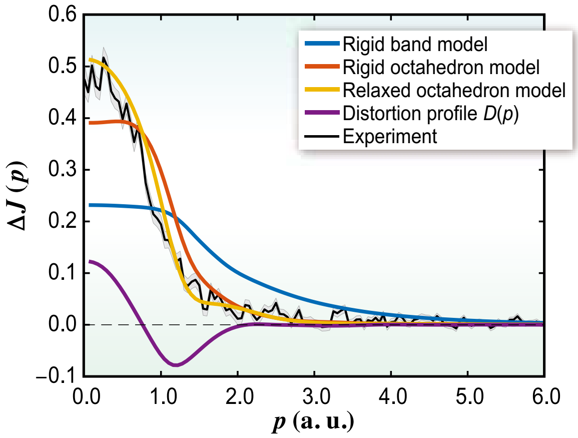

Fig. 3. Compton profile difference $\Delta J(p) = J_{LiFePO_4}(p) - J_{FePO_4}(p)$ for various models of LFP introduced in Ref. 1, along with the corresponding experimental results. Deformation profile, *D(p)*, gives the contribution to the theoretical profile from effects of octahedral distortion.

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