Visualizing redox orbitals and their potentials in advanced lithium-ion battery materials using high-resolution x-ray Compton scattering

Hasnain Hafiz1, K. Suzuki2, B. Barbiellini3, Y. Orikasa4, V. Callewaert5, S. Kasprzyk2,5, M. Itou6, K. Yamamoto7, R. Yamada7, Y. Uchimoto7, Y. Sakurai8, H. Sakurai8, A. Bansil1

1Department of Physics, Northeastern University, Boston, Massachusetts 02115, USA
2Faculty of Science and Technology, Gunma University, Kiryu, Gunma 376-8515, Japan
3Department of Applied Chemistry, Waseda University, Kita-ku, Tokyo 169-8555, Japan
4Japan Synchrotron Radiation Research Institute (JASRI), Shonan-ku, Hayama 240-0193, Japan
5Graduate School of Human and Environmental Studies, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

Introduction: Redox orbitals in Li batteries

- Reduction-Oxidation (redox) reactions are the key processes that underlie the batteries powering smartphones, laptops and electric cars.
- In a lithium-ion battery, current is generated when conduction electrons from the lithium anode are transferred to the redox orbitals of the cathode material.
- The ability to visualise or image the redox orbitals and how these orbitals evolve under lithiation and delithiation processes is a great fundamental and practical interest for understanding the workings of battery materials.

Compton effect and Compton profile

- Conservation of energy and momentum $E_{in} = E_{photon} = E_{out}$, $p_{in} = p_{photon} = p_{out}$.
- Final energy of the scattered photon $E_{out} = E_{in} - E_{photon}$.
- Energy spectrum of the scattered photons, $J(p_{photon})$, is proportional to a quantity called Compton profile $D(p)$.

$J(p_{photon}) = \int D(p)\frac{dp}{2\pi}$

Advantages of Compton scattering

- Compton scattering can access the momentum dependence of the electronic states.
- Directly probe wave function: The shape of Compton scattered waves (Compton profile) is sensitive to the chemical composition of target materials.
- Bulk sensitive measurement: Compton scattering uses high energy ($E_{in} > 100$ keV) x-rays as an incident beam which can achieve a high penetration depth.

$\sqrt{1 + \frac{x}{\gamma^2}} - \frac{x}{\gamma^2}$

$\gamma = \frac{E_{photon}}{m_e c^2}$

$\Delta p = \frac{\hbar}{\gamma}$

LiFePO4 structure

- It has a one-dimensional Li channel.
- The strong bonding between phosphorus and oxygen atoms makes very stable PO4 tetrahedra.
- The planar structure in FeO6 is furthered and produces an inhomogeneous crystal field.
- This reduction in symmetry splits the Fe d-states into multiple non-degenerate d-states.
- However, these d-states keep a gap at Fermi level, make the system insulating.

Methods

- Vienna ab-initio simulation package (VASP) is used for electronic ground state calculation.
- High-k point-atom orbitals are used to calculate the 3D X-ray $D(p)$.
- Compton scattering measurement was performed with BL8R2 beamline at the Spring-8, Japan.

Density of states

- The EMU possesses the same point group symmetry as the charge density in real space.
- High-rigid band and rigid octahedron models show Fe d states to be delocalized in momentum space.
- FeO6 octahedral relaxation brings new contribution at low momentum $p_{out} < 1$ a.u.

Conclusions

- Compton scattering can yield momentum space images of the redox orbitals.
- Compton spectra harbor a unique signature of the octahedral distortion and the related distortion profile $D(p)$ is connected with the degradation of the battery voltage.
- Our study establishes a spectroscopic basis for monitoring changes in redox orbitals during charging-discharging processes in ex-situ, in-situ and in-operando setups.

Compton contouring techniques can facilitate the design and development of high performance cathodes for Li batteries.