

Understanding a battery with high-energy X-ray Compton scattering

Lithium-ion batteries have a high degree of hierarchical complexity, ranging from the quantum scale to the product scale. The respective hierarchies have their own scientific disciplines, such as physics, chemistry, materials science and engineering. As the hierarchies are interdependent on properties and functionality, a single multifunctional probe that can simultaneously provide multiple pieces of information used in different disciplines at different hierarchies is essential to develop economical and safe batteries. In this article, we present the capability of X-ray Compton scattering as a multifunctional probe of commercial batteries by demonstrating a quantum-scale characterization of redox orbitals in an electrode material and a product-scale mapping of the lithium distribution in a commercial battery.

An advantage of X-ray Compton scattering over other techniques is its high bulk-sensitivity, which enables us to measure disordered materials under various sample conditions. The electron momentum density observed by this technique is a ground-state property of an electron system, which allows us to interpret the experimental results straightforwardly with band structure calculations. Moreover, it can also probe materials inside a metal container, such as a commercial battery, which can be penetrated by high-energy X-rays. Therefore, high-energy X-ray Compton scattering is a unique tool for investigating a battery at the quantum and product levels under *in situ* and operando conditions.

The redox orbital is one of the essential concepts in electrochemistry and is defined as an electron orbital involved in the lithium insertion and extraction process.

The redox process is mostly described by the change in the formal valency of cations, but its real nature is still controversial. Recently, the redox orbital in spinel $\text{Li}_x\text{Mn}_2\text{O}_4$, a positive electrode material, has been studied by high-energy X-ray Compton scattering with highly accurate data measured at beamline BL08W [1]. In order to extract the redox orbital, the difference in Compton profiles between two samples with different lithium concentrations is considered (see Fig. 1). This difference enables us to zoom in on changes in electron occupancy near the Fermi level associated with the redox process by eliminating contributions of other irrelevant electrons. The Compton profile is a double integral of electron momentum density, which can be computed directly by modern band structure calculations. In general, each electron orbital has its own radial dependence on electron momentum density, depending on the orbital quantum number. Therefore, an oxygen $2p$ orbital contributes to the electron momentum density at low momenta, whereas the contribution of a manganese $3d$ orbital extends to high momenta. This means that the Compton profile of oxygen $2p$ states is narrow while that of manganese $3d$ states is broad. This tendency applies to the solid state, whose electron momentum density is correctly predicted by first-principles band structure calculations.

As shown in Fig. 1, the band structure calculation is in excellent agreement with the experimental result. The calculation also predicts that the number of electrons in the interstitial region, whose electron charges mostly originate from oxygen $2p$, increases as the lithium concentration increases, whereas the number of manganese $3d$ electrons is almost constant. This shows

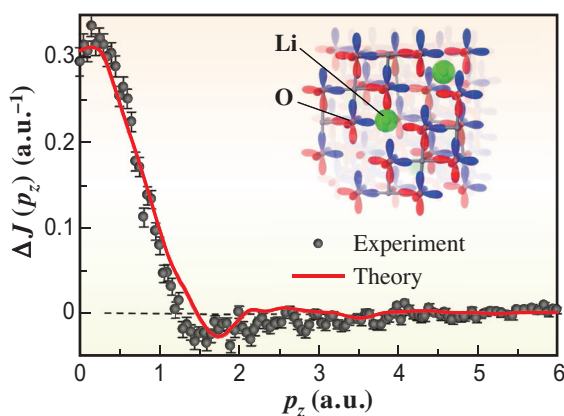


Fig. 1. Electron momentum density distributions (i.e., Compton profiles) of the redox orbitals in $\text{Li}_x\text{Mn}_2\text{O}_4$. The experimental results are well reproduced by the theory, implying that electron charge is transferred to oxygen $2p$ states from inserted lithium.

that the active redox orbital possesses a strong oxygen $2p$ character, implying a strong anionic redox process in $\text{Li}_x\text{Mn}_2\text{O}_4$. Interestingly, the manganese $3d$ states are inactive in terms of the number of electrons, but the negative excursion observed between 1 a.u. and 2 a.u. in the difference Compton profile reveals the behavior of manganese $3d$ states. The manganese $3d$ states become delocalized in real space by lithium insertion.

One of the current focuses in battery engineering is to understand and control the course of electrochemical reactions throughout the battery. *In situ* and operando observations of inhomogeneous lithium distributions are needed since electrochemical states in batteries are unstable. A new attempt has been made at BL08W using high-energy X-ray Compton scattering. Taking advantage of the intense, highly parallel X-ray beams, the behaviors of materials inside a commercial battery (CR2032) has been imaged (see Fig. 2) [2]. Scanning an incident X-ray beam with an energy of 115 keV, the intensity of Compton scattered X-rays from a local probing volume inside the battery has been measured under discharge as a function of position and discharging time. Here, the X-ray intensity is defined as the area under Compton-scattered X-ray lines, centered around 94 keV, between 84 keV and 104 keV. The scattered X-ray intensity is proportional to

the average electron density over the probing volume, which depends on the lithium concentration in the electrode materials. The battery was discharged under a constant current of 5.5 mA for 15.75 h, which was much larger than the standard value of 0.2 mA. The blue area is the negative electrode of lithium metal, and the red and yellow areas are MnO_2 and Li_xMnO_2 in the positive electrode. The obtained intensity-time image captures the migration of lithium ions in the positive electrode and reveals the internal structural change due to the volume expansion of the positive electrode and the shrinkage of the negative electrode. The interplay between the electrochemical process and the internal structure under a working condition is critical to battery design.

Integration of the two methods mentioned above is straightforward and provides a link between quantum-level characteristics and product-level behaviors in batteries. For example, orbital occupation and electron configuration are closely related to phase transitions and volume changes, which lead to the fracture of the electrode and the degradation of battery performance with repeated cycle operations. This new methodology paves the way for an advanced characterization of commercial batteries and other electrochemical devices, such as fuel cells.

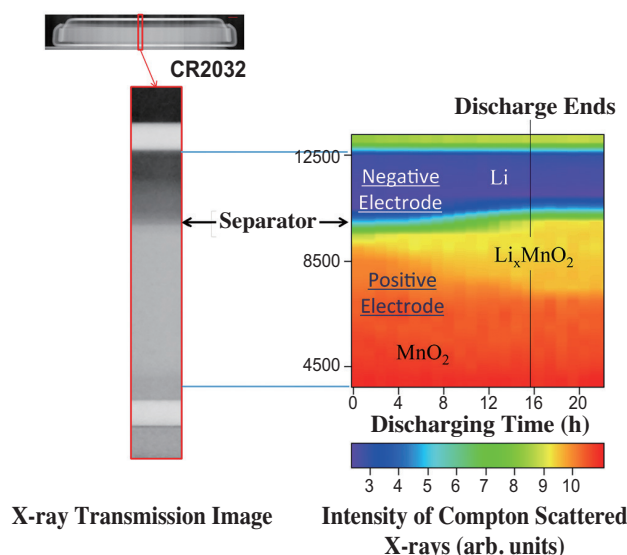


Fig. 2. Intensity map of Compton-scattered X-rays as a function of vertical position and discharge time of the battery (CR2032). Lithium migration and internal structure changes are clearly observed.

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