High-Energy X-ray Compton Scattering for Non-destructive and Quantum Characterization in Batteries

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3-1. Non-destructive characterization for battery

Compton scattering experiment is applied to the commercial lithium coin battery and done non-destructive measurement.

3-2. Quantum characterization for materials

Compton scattering experiment is applied to positive electrode material.

4. Conclusion
Introduction

Although lithium-ion batteries are already widely used in our daily life, further development of high-performance batteries are expected.

- Problems in real battery
  - Inhomogeneous lithium reaction
  - Capacity degradation

- Problems in material
  - High-capacity electrode materials
  - High-stability electrode materials

Non-destructive measurement

Understanding of electrode reaction

We focus on Compton scattering technique to resolve these problems.
Compton scattering is well known as an inelastic scattering technique between photons and electrons.

- **Energy conservation law**: \( \hbar \omega_1 + E_1 = \hbar \omega_2 + E_2 \)
- **Momentum conservation law**: \( \hbar k_1 + p_1 = \hbar k_2 + p_2 \)

\( \hbar \omega_1, \hbar \omega_2 \): Photon energy  
\( \hbar k_1, \hbar k_2 \): Photon momentum  
\( E_1, E_2 \): Electron energy  
\( p_1, p_2 \): Electron momentum

Compton scattering is well known as an inelastic scattering technique between photons and electrons. The scattering process conserves both energy and momentum. The energy of the scattered photon is given by:

\[
\hbar \omega_2 = \hbar \omega_1 - \frac{\hbar^2 |k|}{2m} - \frac{\hbar k \cdot p_1}{m}
\]
Compton profile

- Scattered X-ray energy
  \[ \hbar \omega_2 = \hbar \omega_1 - \frac{\hbar^2 |\mathbf{k}|}{2m} - \frac{\hbar \mathbf{k} \cdot \mathbf{p}_1}{m} \]

- Energy spectrum: \( I(\hbar \omega_2) \)
  \[ I(\hbar \omega_2) \propto J(p_z) \]

- Compton profile: \( J(p_z) \)
  \[ J(p_z) = \int \int \rho(p) dp_x dp_y \]

- Electron momentum density: \( \rho(p) \)
  \[ \rho(p) = \sum_j n_j \left| \int \psi_j(r) \exp(-i\mathbf{p} \cdot \mathbf{r}) d\mathbf{r} \right|^2 \]

Compton profile can directly compare with theoretical Compton profile. It is enables to discuss electronic structure underlying reduction-oxidation reaction on the electrodes.
Advantage of Compton scattering

Compton scattering technique have mainly two advantages.

(1) High-energy (>100keV) X-rays

Incoherent scattering is enhanced by using over 100keV X-rays.

NIST (http://www.nist.gov)

(2) Line-shape of Compton profile

Quantitative analysis will be possible by digitalizing the line-shape of Compton profile

Biggs et al., Atomic Data and Nuclear Data Tables 16, 201 (1975).

These features are suitable for analyzing lithium-ion batteries.
Shape-parameter (S-parameter)

We have developed analysis method using a shape-parameter (S-parameter) to analyze line-shape of Compton profile.

\[ S = \frac{H}{W} \]

\[ H = \int_{d_2}^{d_3} J(p_z) p_z \]

\[ W = \int_{d_1}^{d_4} J(p_z) p_z + \int_{d_3}^{d_4} J(p_z) p_z \]

In this study, \( d_1=d_4=5 \text{a.u.}, \ d_2=d_3=1 \text{a.u.} \) were decided.

Lithium quantitation is possible by using S-parameter analysis.

Non-destructive characterization for real batteries

Compton scattering technique is applied to commercial VL2020 coin battery to observe lithiation state
Non-destructive measurement

Many experimental techniques are demonstrated to monitor lithium reactions.

- **X-ray absorption near-edge structure (XANES)**

- **Nuclear magnetic resonance (NMR)**
  S. Chandrashekar et al., Nature Mat., 11, 311 (2012).

- **Micro X-ray diffraction**

- **Particle induced γ–ray/X-ray emission (RIGE/PIXE)**

- **Raman micro-spectroscopy**

- **Hard X-ray photoemission spectroscopy (HX-PES)**

- **Neutron diffraction**
  Xun-Li Wang et al., Scientific Reports, 2, 1 (2012).

These experiments are mainly adopted to the test cells and it is difficult to measure Li directly.

We focus on Compton scattering technique.
Sample and Experimental setup

- **Sample (Panasonic VL2020)**
  - Stainless steal (SUS)
  - Positive electrode ($V_2O_5$) 0.8mm
  - Separator 0.1~0.3mm
  - Negative electrode (LiAl) 0.3mm
  - Spacer 0.1mm

- **Experiment setup (BL08W SPring-8)**
  - Incident X-rays 115keV
  - Ge solid-state detector
  - Collimator slit Φ 500 μm
  - Scattered X-rays
  - Incident slit 25 μm (H), 500 μm (W)
  - Sample
  - X-ray camera
  - Charge-discharge device
  - z-stage, x, y-stage
Energy spectrum was measured in order to distinguish battery components.

Energy spectra change with the components of the battery.

S-parameters can reveal internal structure of the battery.

S-parameter distribution during charge-discharge cycle was obtained.

ΔS-parameter distribution

In order to clarify the change of S-parameter at the positive and negative electrodes, ΔS-parameter is taken.

\[ \Delta S = S_t - S_{ave} \]

\( S_t \): S-parameter at \( t \) sec
\( S_{ave} \): averaged S-parameter on total measurement time

When the battery charged, high S-parameter region exist in the separator.

Uniform reactions are occurred.

The reactions occur at the surface.

The reproducibility was confirmed between 1\textsuperscript{st} and 2\textsuperscript{nd} full discharged state.

- The S-parameters increase at the separator position when full charged state.

Some lithium-ions remain into the separator.
This fact might be induce capacity loss of the battery.
Lithium compositions during charge-discharge cycle are determined.

<table>
<thead>
<tr>
<th>Li composition</th>
<th>ICP analysis</th>
<th>S-parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive electrode SOC0</td>
<td>0.426</td>
<td>0.470±0.012</td>
</tr>
<tr>
<td>Negative electrode SOC100</td>
<td>0.178</td>
<td>0.170±0.006</td>
</tr>
</tbody>
</table>

Li composition is agree with that of obtained from ICP analysis.

Non-destructive and in-operando analysis are possible by our technique.
Quantum characterization for battery materials

High-resolution Compton scattering and magnetic Compton scattering experiments are applied to LiMn$_2$O$_4$ to reveal electrode reaction
LiMn$_2$O$_4$ is a representative positive electrode material for lithium-ion batteries.

**Advantage**
- Thermodynamic stability
- Low cost

**Disadvantage**

- Cell voltage of LiMn$_2$O$_4$ decreases 60% at 100 cycles

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**Charge/discharge curve**


The capacity decreases 60% at 100 cycles
Electrode reaction of LiMn$_2$O$_4$

$$\text{LiMn}_2\text{O}_4 \xrightarrow{\text{Charge}} x\text{Li}^+ + \text{Li}_{(1-x)}\text{Mn}_2\text{O}_4 + xe^-$$

The volume expansion by Jahn-Teller ion induces capacity loss

- LMTO-ASA (H. Berg et al., J. Mater. Chem. 9, 2813 (1999))
- LDDFT (M. K. Aydinol et al., J. Electrochem., 144, 3832 (1997))

On the other hand

- O 2$p$ orbital plays important role

The electrode reaction is not fully understood yet.

The nature of the electrode reaction is investigated.
Previous study

Compton profiles of $\text{Li}_x\text{Mn}_2\text{O}_4$ ($x = 0.496$ and $1.079$) were measured. The difference Compton profile are shown with KKR-CPA first-principle calculation result.

**The O 2$p$ orbitals play a dominant role on the electrode reaction of LiMn$_2$O$_4$ positive electrode.**

Magnetic Compton scattering is applied to study electronic structure of Mn atom.

Magnetic Compton profiles of Li$_x$Mn$_2$O$_4$ ($x = 0.41, 0.50$ and $0.92$) were measured.

The line-shape of MCPs does not show significantly change. Spin magnetic moment increase with increasing Li concentration. We do comparison with theoretical calculation results to reveal increase of spin magnetic moments in operation region of the battery.
Theoretical magnetic Compton profile was calculated by first-principle DFT calculation using exchange-correlation function of SCAN meta-GGA.

Theoretical MCP and magnetic moment

Calculated spin magnetic moment in lithium concentration 0 < x < 1 have same trend with experimental spin magnetic moment.

Exp.: Li$_{0.92}$Mn$_2$O$_4$
Theo.: Li$_{0.75}$Mn$_2$O$_4$

H. Hafiz et al., PRB, submitted.
Spin-dependent partial density of state

Spin-dependent partial density of state associated with the $e_g$ and $t_{2g}$ orbitals of Mn$^{3+}$ and Mn$^{4+}$ ions are calculated.

The Mn $e_g$ orbital split and Mn 3$d_z^2$ bands move to lower energies

**LiMn$_2$O$_4$ has band gap**

Mn 3$d_z^2$ bands are partially occupied

**Li$_{0.75}$Mn$_2$O$_4$ becomes metallic and have ferrimagnetic state**

H. Hafiz et al., PRB, submitted.
Magnetic configuration models are considered.

Magnetic structure

(a) x=1.0

(b) x=0.75

Charge-ordering is prominent.

Charge-ordering become unstable, and spin-flipping of Mn$^{4+}$ is occur.

H. Hafiz et al., PRB, submitted.
Magnetic orbital of $\text{Li}_{0.75}\text{Mn}_2\text{O}_4$ is visualized.

Mn 3d magnetic electrons in $\text{Li}_x\text{Mn}_2\text{O}_4$ ($x < 1$) have mainly $t_{2g}$ symmetry, and they prevent structural distortion promoted by $e_g$ character.

The O 2$p$ orbitals play a dominant role on the electrode reaction and Mn 3d orbitals contribute to the stability of the structure in $\text{LiMn}_2\text{O}_4$. 
Summary

Non-destructive characterization study for the commercial battery and quantum characterization study for the electrode material were shown.

- Non-destructive characterization for VL2020 battery
  - Lithium reactions of the electrodes are revealed nondestructively.
  - Remnant lithium ions are observed in the separator when the battery was charged.

- Quantum characterization for LiMn$_2$O$_4$
  - The O 2$p$ orbitals play a dominant role on the electrode reaction.
  - The Mn 3$d$ orbitals contribute to the stability of the structure.

Compton scattering technique is powerful tool for non-destructive and quantum characterizations in the batteries.