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Operando observation of lithiation state in commercial 18650-type lithium-ion cell using Compton scattering imaging

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In this study, Compton scattering imaging was applied to commercial 18650-type lithium ion battery cell to observe the change of lithiation state in *operando* condition. By analysing line-shape of Compton scattered X-ray energy spectrum (*S*-parameter analysis), *S*-parameter distributions of charged and discharged state were visualized. From these results, the cathode and anode positions shift regarding volume expansion or contraction of the electrodes were observed. Moreover, the change of *S*-parameter corresponding to charge and discharge was observed in both the cathode and anode in operando condition.

Keywords: 18650-type cell, Lithiation state, Compton scattering, Non-destructive measurement

Background and Objective:

Although lithium-ion batteries are already used widely in our daily life, demand for them is rapidly increasing, because the development of electric vehicles is attracting much attention all over the world. To farther expand the use of electric vehicles, battery cells are required not only high capacities but also high safety and long life time. Moreover, it is needed fast charging batteries. However, previous neutron diffraction study using cylindrical-type cell has revealed inhomogeneous reactions of the carbon anode on a high-rate[1]. These inhomogeneous reactions are related to the degradation of cell performance. Although the neutron diffraction technique is a powerful tool for non-destructive measurement, it reveals the reaction mechanism through the change of the lattice parameter in the electrode materials. In order to deeply understand the mechanism of the lithium reaction, it is important to monitor lithiation state and lithium reactions directly in the cells under in *operando* condition.

Gunma University group has been developed direct monitoring method of the lithiation state from Compton scattered X-ray energy spectrum which obtained Compton scattering experiment[2]. This method has been mainly applied to commercial coin-type cells[3, 4]. Most recently, we have adapted to commercial cylindrical-type cell and successfully observed lithiation state on the full charged and discharged state [5]. Moreover, the difference of lithiation states between the fresh and aged cells has been revealed. Purpose of this study measure the change of lithiation state in *operando* condition and show dependency of charge-discharge speed in lithiation state.

Experiments:

The schematic image of the sample and the experimental setup of Compton scattering imaging is shown in figure 1. The sample is commercial 18650 formats cylindrical lithium-ion battery cell (MH1) made by LG Chem, Ltd. as shown in Fig. 1(a). This cell mainly composed of $LiNi_{1-x-y}Mn_xCo_yO_2$ cathode (0.15 mm in thickness), graphite anode (0.187 mm in thickness), and separator (0.015 mm in thickness). The experimental setup of Compton scattering imaging is shown in Fig. 1(b). The incident X-ray energy is 115.56 keV and the scattering angle was fixed at 90 degrees. The Compton scattered X-ray energy spectrum was measured by nine-segments of a pure Ge solid-state detector. The proving volume in the cell is determined by an incident slit and a collimator slit which arranged between the sample and the detector. The

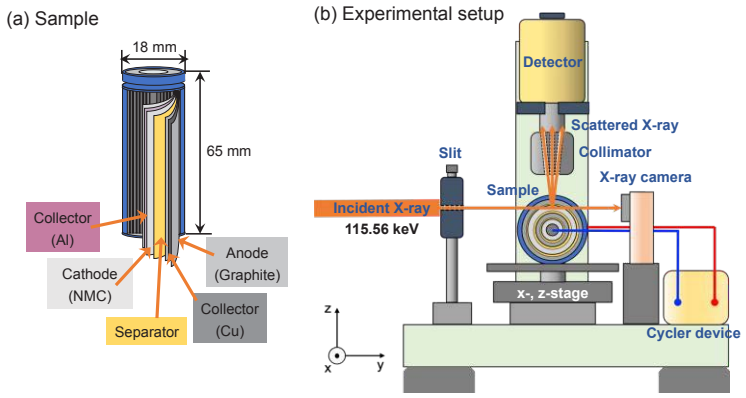

Fig. 1. Schematic image of the sample and experimental setup.

size of the incident and collimator slits in this study was 0.015 mm in height, 0.75 mm in width and 0.5 mm in diameter. The cell was set on a movable stage along x, y and z-directions and scanned incident X-rays along z direction which correspond to the stacking direction of the electrodes to measure Compton scattering X-ray energy spectra. The Compton scattered X-ray energy spectra were measured with changing the state of charge of the cell.

Results and Discussion:

Figure 2(a) and (b) are Compton scattered X-ray intensity and *S*-parameter obtained by scanning X-rays along z direction of the cell, respectively. Here, Compton scattered X-ray intensity mainly proportional to electron density of the matter[6] and *S*-parameter digitalizes line-shape of Compton scattered X-ray energy spectrum[2]. The blue, grey, yellow and green background colours in these figures show the region of outer case, collector, anode and cathode, respectively. There is separator between the cathode and anode and this is shown by weak Compton scattered X-ray intensity in Fig. 2(a). Fig. 2 clearly show inner structure of the 18650-type cell non-destructively.

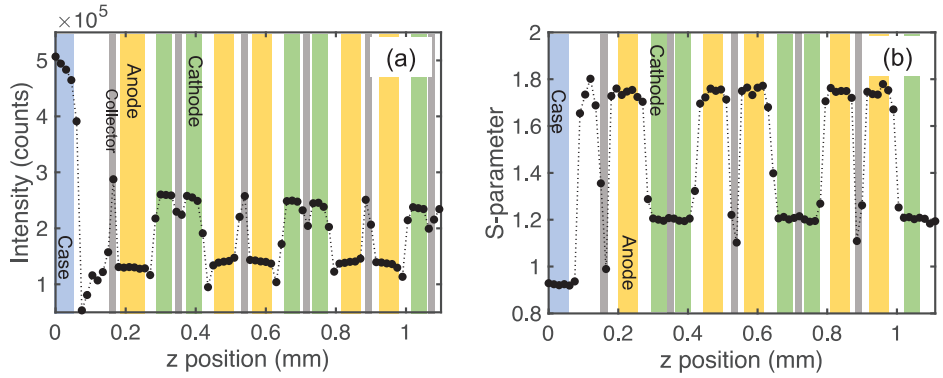

Fig. 2. (a) Compton scattered X-ray intensity and *S*-parameter

Then, Compton scattered X-ray energy spectra were measured during charge and discharge. The state of charge of the cell was changed by constant current (7 hours) and constant voltage (3 hours) mode. The constant current mode corresponds to 0.14C rate. *S*-parameter distribution are shown in Fig. 3. Fig.3 (a) and

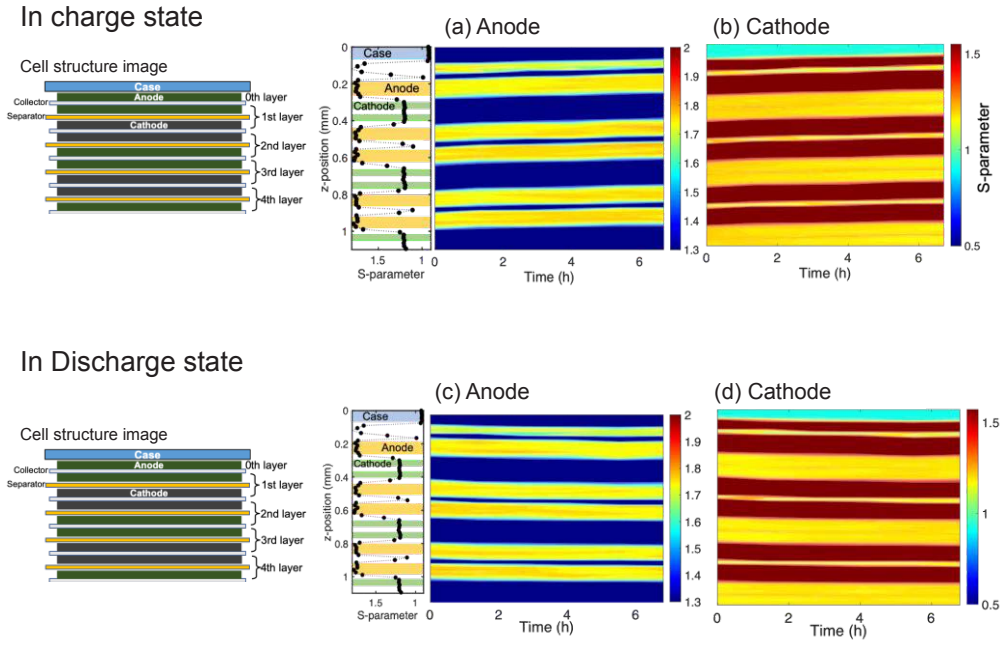

Fig. 3. (a) and (b) are *S*-parameter distribution of anode and cathode in charge state. (c) and (d) are *S*-parameter distribution of anode and cathode in discharge state.

(b) are *S*-parameter distribution of the anode and cathode during charge and Fig. 3 (c) and (d) are *S*-parameter distribution of the anode and cathode during discharge, respectively. The colour in these figures is *S*-parameter intensity. In order to see the change of the *S*-parameters, the colour scale was optimized. By changing the state of charge of the cell, the cathode and anode positions shifts since volume expansion or contraction of the electrodes. Moreover, as shown in Fig. 3 (a) and (b), *S*-parameter increased in anode with charging the cell and *S*-parameter decreased in the cathode with discharging. On the other hand, S-parameter distributions in discharged state show opposite trend to charge state. Actually, amount of change of *S*-parameters at each electrode layers is summarised in Table 1. In Table 1, 0th layer is anode which do not have counter cathode. Hence the amount of change of *S*-parameter is almost constant. This change of *S*-parameters corresponds to the lithiation state from our previous study [3, 5] therefore we could observe the change of lithiation state in operando condition in each electrode layer of the 18650-type cell.

Table 1. Amount of change of S-parameter

	Anode		Cathode	
	Charge	Discharge	Charge	Discharge
0th layer	0.0004	−0.0001		
1st layer	0.0026	−0.0027	−0.0035	0.0036
2nd layer	0.0041	−0.0021	−0.0043	0.0036
3rd layer	0.0018	−0.0028	−0.0035	0.0034
4th layer	0.0017	−0.0035	−0.0027	0.0036

Next Steps:

We reveal lithiation state along thickness direction in one electrode layer by analysing experimental data obtained from high spatial resolution. Moreover, cycle rate dependency of lithiation state will be shown by analysing experimental data obtained from another charge-discharge rate.

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