

Analysis of Capacity Fading for High-power Lithium Ion Rechargeable Batteries

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ABSTRACT

An analysis for elucidating the mechanism of capacity loss due to calendar aging in high-power lithium ion rechargeable batteries have been performed. The degradation of the batteries used in this research did not follow any particular trend with storage time, so that it could not be explained by the general, simple square root law. Electrochemical measurements revealed two factors that lead to degradation by a capacity balancing shift among the electrodes. The two factors are: the loss of active lithium which flows between anode and cathode, and cathode capacity fading. In order to identify the above two factors, we performed some material analyses of the battery. The results clearly showed that the loss of active lithium is caused by the formation of a solid electrolyte interphase due to reduction of solvent in electrolyte on the anode surface, and cathode capacity loss due to partial crystalline structure transition of the active material. A further detailed chemical composition analysis of the solid electrolyte interphase showed clearly that as the electrolyte components undergo electrochemical reductive degradation on the anode surface, an initial film largely dominated by organic components is first formed, then change in chemical composition and structure occurs whereby those organic components transform into inorganic components. However, the total amount of lithium in the film that was measured by material analysis did not match with the amount of cyclable lithium lost between the cathode and anode as obtained by electrochemical measurement techniques. We newly showed that there is the crucial need to determine the amount of the active lithium loss using electrochemical measurement techniques.

1. Introduction

Lithium ion rechargeable batteries came into practical use in 1991⁽¹⁾. Given their high capacity, high power⁽²⁾, and other such features, these batteries have entered notably widespread use in portable equipment since then. In recent years they have also been used as batteries to drive electric vehicles, and their use is expected to expand greatly in the future^{(3), (4)}. Although lithium ion rechargeable batteries can realize high capacity and high power, however, they face the issue of aging⁽⁵⁾ just as other chemical batteries do. Battery aging is known to occur from cycle aging, which depends on the number of charge-discharge cycles, and from storage aging, which depends on storage time (and is hereafter referred to as calendar aging in order to correspond to cycle aging). When batteries with features like these are used, a long-term performance prediction is generally made on the basis of test data gathered over a limited period of time. Therefore many evaluations are implemented under diverse test conditions, and maps of the relationships between each

condition and aging are created. Calendar aging in a battery is dependent on temperature and state of charge (SOC), but since they are not in a simple linear relationship, creating a map requires an enormous number of tests and times in accordance with the matrix of conditions. In order to reduce the development period this requires, the usual approach used to be to employ the prediction technique using the square root law⁽⁶⁾⁻⁽¹⁰⁾ on the hypothesis that the capacity fading by the battery was proportional to the square root of the storage time or the number of cycles. The foundation for use of the square root law is the rate of formation of the solid electrolyte interphase (SEI) film on the surface of the anode. In other words, the basic hypothesis is that the cyclable lithium ions that transfer back and forth between cathode and anode (hereafter referred to in short as active lithium) are lost to form the SEI so they can no longer transfer back and forth between the cathode and anode, and battery capacity declined as a result. However, battery aging is the result of a complex interaction of multiple factors^{(5), (11)-(18)}. As shown in Chapter 3 of this paper,

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behavior that does not agree with the simple square root law is also known to occur^{(11), (14)}. In light of reports that battery capacity can be evaluated from the single-electrode capacities of the cathode and anode severally and from the shift in the electrode balancing between them⁽¹¹⁾⁻⁽¹⁴⁾, it is anticipated that a new, highly accurate predictive equation will be derived to account for this kind of capacity fading behavior by incorporating the substance of these findings.

In order to derive a new predictive equation, the cause of the above balancing shift will need to be clarified, and the amount of the shift will need to be determined. There are reports that the amount of lithium incorporated into the SEI correlates with the active lithium loss^{(8), (10), (13)}. However, there have been no reports as yet that explain the cause and effect relationship between single-electrode capacity fading and active lithium loss and that cite the creation of predictive equations for capacity fading based on those mechanisms.

The aim of the present research, therefore, has been to explain the mechanism of battery aging, which is important for predicting battery aging behavior accurately, and for that purpose, to carry out an analysis that combines electrochemical measurements with an analysis of the substances that make up the battery. This report will discuss this process up to the results from an analysis of capacity fading in batteries. The derivation of a new predictive equation is scheduled to be covered in detail in the next report. Here, the below phenomenon of capacity fading due to battery aging will be referred to simply as aging.

2. Experimental Method

2.1. Specifications of Batteries Studied

Prismatic lithium ion batteries for high-power applications were used for this research. The external dimensions of the batteries were approximately 100 mm × 80 mm × 16 mm. The battery cathode was of NMC, a layered oxide composition of nickel, manganese, and cobalt. The anode was a carbon material. A microporous polyethylene film was used for the separator. The electrolyte was a carbonates solvent with LiPF₆ added as the supporting salt. The batteries used for testing had already been through a conditioning process when they were shipped, so they were in an immediately usable state.

The SOC of the batteries was determined from the state of charge-open circuit voltage (SOC-OCV) curve for the new batteries. Capacity retention was defined as battery capacity after aging as a percentage of the battery capacity before aging. For aging testing, the tested battery was charged to a specified SOC after which it was stored for a specified period of time in a thermostatic chamber at a specified temperature. Table 1 shows an example of changes in capacity fading over time obtained from charge-discharge test results for the batteries studied at each of various specified storage periods.

Table 1 Capacity retention during calendar degradation test

Temperature (°C)	SOC (%)	Aging time		Capacity retention (%)
		days	day ^{1/2}	
65	80	610	24.7	62.7
65	50	450	21.2	85.7
65	20	450	21.2	91.5
55	80	450	21.2	84.3
55	50	250	15.8	89.9
55	20	450	21.2	95.8
45	80	190	13.8	83.7
45	50	200	14.1	93.6

2.2. Electrochemical Measurements

The batteries used in testing were disassembled afterward and the electrodes, separator, and electrolyte were extracted separately. These components were used for the electrochemical measurements to be described later and for the analysis in section 2.3.

The disassembled electrodes were used to fabricate 2032 coin type cells configured as shown in Table 2^{(12), (13)}. These coin cells were then used to carry out remaining discharge capacity measurements and capacity measurements. Measurements were carried out by discharging the assembled cathode half-cells from OCV down to 2.5 V, and the anode half-cells from OCV up to 1.5 V, respectively. After that the cathode half-cells were cycled between 2.5 V and 4.2 V, and the anode half-cells between 1.5 V and 0.1 V, and these were taken as the capacity of the single electrodes, respectively. Three cells were prepared for each measurement and the average value was adopted.

The work of extracting electrodes from new batteries and aged batteries, and of incorporating the extracted electrodes in coin cells, was carried out entirely in a glove box filled with argon gas.

2.3. Analysis of Disassembled Batteries

2.3.1. Observation with scanning electron microscope and scanning transmission electron microscope

A cross section polisher (CP) was used to make cross sections of the cathodes and anodes extracted from disassembled batteries. An Ultra 55 model scanning electron microscope (SEM) made by Carl Zeiss AG was used to make observations of the cross sections. A specialized transfer vessel was then used to load the test specimens into the SEM apparatus without exposing it to the atmosphere. Separate samples were sliced off the extracted cathodes and the cross sections were observed using a JEM-ARM 200

Table 2 Coin cell configurations for electrochemical measurements

	Cathode half cell	Anode half cell	Full cell
Cathodes	Extracted cathode	Extracted anode	Extracted cathode
Anodes	Li metal	Li metal	Extracted anode
Separators	New	New	New
Electrolyte	New	New	New

model scanning transmission electron microscope (STEM) from JEOL Ltd. Samples for observation were made using a focused ion beam (FIB) apparatus.

2.3.2. Nuclear magnetic resonance spectroscopic analysis

A nuclear magnetic resonance (NMR) spectroscopic analysis of solid ^7Li was carried out for the purpose of confirming the state of lithium metal deposition on the anode. Working in a glove box, the composite layer was peeled off from a portion of the extracted anode, loaded into an NMR sample tube with an outside diameter of 4 mm, sealed, then subjected to measurement. Solid NMR measurement was performed using an AVANCE III 400 from the Bruker Corporation.

An electrolyte component analysis and anode SEI extract analysis was carried out with solution ^1H NMR. The electrolyte components extracted from the batteries were dissolved in deuterated acetonitrile (CD_3CN) and subjected to NMR measurement. For SEI component extraction, deuterium oxide (D_2O) was used to extract it from the anode composite peeled off inside a glove box. After separation of the extracted solid residue, the extract solution was subjected to NMR measurement. An ECA 400 from JEOL Ltd. was used for the solvent NMR measurement.

2.3.3. Measurement of separator air permeability

The separator extracted from disassembled batteries was washed using dimethyl carbonate inside a glove box. It was then removed from the glove box and its air permeability measured in the atmosphere. A G-B3C Gurley-type densometer from Toyo Seiki Seisaku-sho, Ltd., was used for measurement.

2.3.4. Analysis by inductively coupled plasma atomic emission spectroscopy

A quantitative analysis of lithium ion concentration in the electrolyte was carried out using inductively coupled plasma atomic emission spectroscopy (ICP-AES). A specified amount of electrolyte was measured, a mixed acid added to it, then it was heated and the electrolyte was decomposed to form a solution containing lithium

ions. The solution was diluted to a specified concentration using ultra pure water, and ICP-AES measurement was then performed. For an ICP-AES analysis of the anode composite, the composite layer peeled off inside the glove box was weighed to a specified amount, a mixed acid was added and the mixture was heated to decompose the carbon component and form a solution containing ions. The solution was diluted to a specified concentration using ultra pure water, and ICP-AES measurement was then performed. An SPS3000 from Seiko Instruments Inc., was used as the ICP-AES analysis apparatus.

2.3.5. Ion chromatography analysis

The anode composite that was peeled off in an inert atmosphere was extracted using ultra pure water, and the extract solution that remained after removal of solid residue was analyzed using ion chromatography (IC). The ions in the extract solution were qualitatively and quantitatively determined. A DX-320 ion chromatography system from Dionex Corporation was used. The column was a Dionex IonPac AS4A-SC, 4 mm in diameter and 250 mm in length. An aqueous solution of sodium bicarbonate was used as the eluent.

2.3.6. X-ray photoelectron spectroscopy analysis

The electrodes that were extracted inside a glove box were loaded using a specialized transfer vessel into an X-ray photoelectron spectroscopy (XPS) instrument and measurements were carried out. The apparatus used was a PHI Quantera SXM from ULVAC-PHI, Inc. Monochromatic $\text{Al K}_{\alpha 1,2}$ (1486.6 eV) was used as the X-ray excitation source. The X-ray beam diameter was 200 μm . The surface analysis carried out by XPS here reflects mainly information on components to a depth of approximately 2 nm from the surface.

2.3.7. Soft X-ray absorption fine structure technique

The electrodes that were extracted inside a glove box were loaded using a specialized transfer vessel into an apparatus for soft X-ray absorption fine structure measurement and measurements were made. The size of the incident light was 1 mm $\times$ 1 mm. The soft X-ray absorption fine structure technique obtains composition information on chemical compounds at different depths from the surface depending on the detection mode. The partial electron yield (PEY) mode obtains composition information on chemical compounds in a region to a depth of approximately 2 nm, the total electron yield (TEY) mode to a depth of approximately 20 nm, and the partial fluorescence yield (PFY) mode to a depth of approximately 200 nm.

2.3.8. In-depth analysis by Auger electron spectroscopy

The electrodes that were extracted inside a glove box were loaded using a specialized transfer vessel into a scanning Auger electron spectrometer (AES) and measurements were made. The apparatus used was a

SAM670 from ULVAC-PHI, Inc. The electron excitation beam had a diameter of 100 nm. Repeated measurements were made while etching the sample, yielding an in-depth analysis of changes in chemical composition.

3. Analysis Results and Discussion

3.1. Results of Capacity Fading Testing

Figure 1 shows an example of aging testing results from the batteries studied in the present research (Table 1). The graph plots the change of capacity retention against aging, with the horizontal axis showing the square root of the number of days in storage and the vertical axis showing capacity retention. The results (Table 3, Reference 1) indicate that capacity fading in storage testing does not accord with the simple square root law, or, in other words, does not fit on a single straight line. The aging rate was instead found to be divided into three different regions, shown in the figure as A, B, and C. Within each region, the capacity retention is proportional to the square root of the number of days in storage. Each region follows a square root law, but the regions are discontinuous and they could not be accounted for by a single simple square root law.

As this indicates, the aging behavior of a lithium ion battery does not follow a simple square root law. It became clear that the cause of capacity fading cannot readily be accounted for by SEI growth alone.

3.2. Results of Electrochemical Measurements

Figure 2 shows the results of electrochemical measurements^{(12), (13)}. The values shown in this figure were obtained by the methods shown in Fig. 3(a). That is, the remaining cathode discharge capacity $Q_{R,cathode}$ was determined by discharging down to 2.5 V from the terminal voltage of the assembled half-cell and the remaining anode

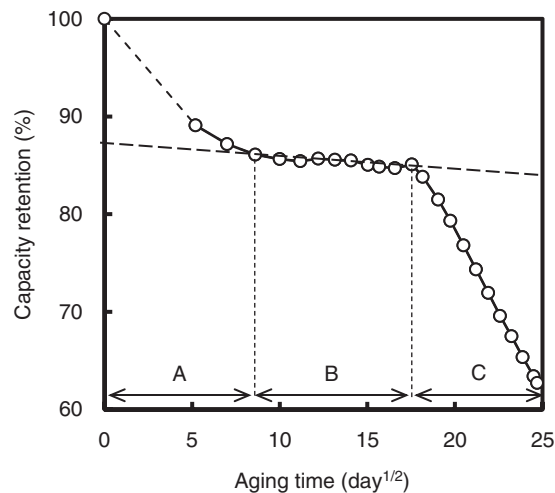


Fig. 1 Capacity retention of Li ion battery during aging (aging condition: SOC=80% at 65°C)

Table 3 Degradation analysis results

Aging phenomena	Analysis method	Results	Reference
Capacity loss	Electrochemical measurement	Observed	1
Active Li loss	ICP of electrodes and electrochemical measurement	Observed	2
Cracking	Cross section SEM observation	Not observed	3
Delamination	Cross section SEM observation	Not observed	4
Li plating	Solid state ⁷ LiNMR	Not observed	5
Loss of electrolyte	NMR, ICP of electrolyte	Not observed	6
Clogging of separator	Gurley densometer	Not observed	7

discharge capacity $Q_{R,anode}$ by discharging up to 1.5 V from the half-cell terminal voltage. These quantities were used to calculate the amount Q_{shift} of the capacity balancing shift among the electrodes by the following equation.

$$Q_{shift} = Q_{R,cathode} - Q_{R,anode} \quad (1)$$

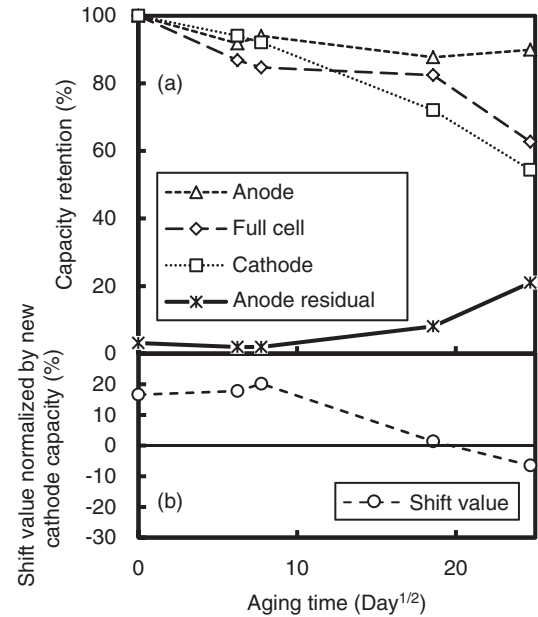
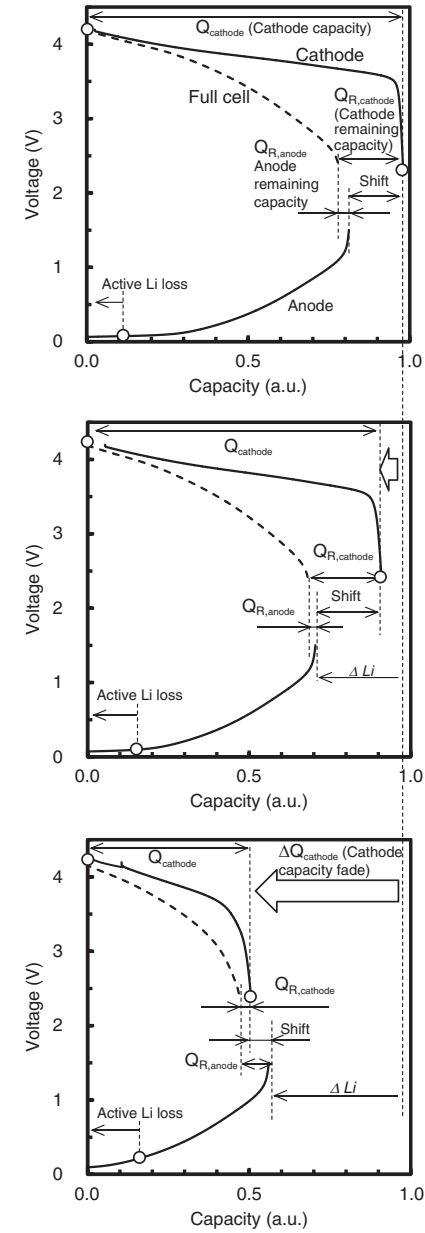
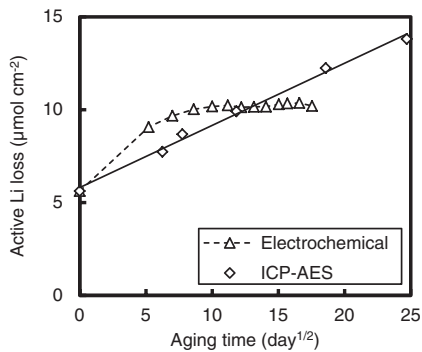


Fig. 2 Capacity retention of full cells and electrodes (a) Capacity retention (b) Shift value normalized by new cathode capacity. (aging condition: SOC=80% at 65°C) (Triangle: anode capacity retention; diamond: full cell capacity retention; square: cathode capacity retention; asterisk: residual anode capacity normalized by new anode capacity; circle: shift value normalized by new cathode capacity)



(a) Schematic drawings about active Li loss, cathode capacity fade, and capacity shift between anode and cathode.



(b) Li amount on the anode surface measured by ICP-AES (diamond) and active Li loss measured electrochemically (triangle)

Fig. 3 Active Li loss by SEI growing

The amount of the shift in the balance and the remaining anode discharge capacity were normalized by the cathode and anode capacities before aging, respectively.

As shown by the three schematic views in Fig. 3(a), the amount of active lithium loss ΔLi can be determined from the amount of the shift in the balance and the amount of cathode capacity fading using the below equation (Table 3, Reference 2).

$$\Delta Li = Q_{shift} + \Delta Q_{cathode} \quad (2)$$

Here,

$\Delta Q_{cathode}$: Amount of cathode capacity fading

Figure 3(b) shows the amount of active lithium loss derived by this method together with the ICP-AES measurement results.

3.3. Battery Materials Analysis Results

3.3.1. Observation with SEM and STEM

SEM observation of cross sections of electrodes from aged items found that neither cracking of electrode layers in both cathode and anode nor delamination from collectors had occurred (Table 3, Reference 3, Reference 4). On the anode, however, SEI formation was observed on the surface of the anode active material (white areas indicated by arrow symbols in Fig. 4).

Figure 5 shows the result from observation of cathode active material cross sections by STEM. The active material in the batteries used for the present research was a rhombohedral layered rock-salt type lithium transition metal oxide. The STEM images showed a marked contrast indicating the existence of two regions within a single crystal grain of this material. From fast Fourier transform (FFT) patterns in STEM images of both portions, spinel-like crystal structures can be observed in the transformed portions⁽¹⁷⁾⁻⁽¹⁹⁾, confirming that partial crystalline structural transformation had occurred in the active material.

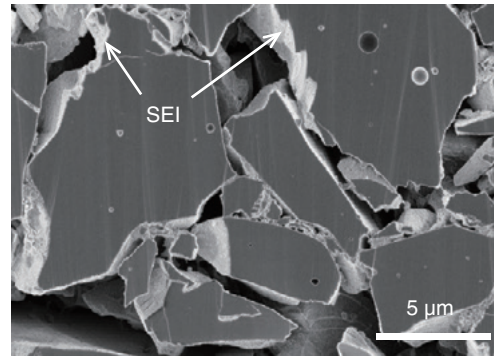


Fig. 4 Cross section SEM image of anode (arrows indicate SEI)

3.3.2. Nuclear magnetic resonance spectroscopic analysis

In the spectrum of the solid ^7Li NMR from the anode composite, only a peak in the vicinity of 0 ppm (LiCl standard) was observed. The peak in the vicinity of 0 ppm can be attributed to lithium salts. When deposition of lithium metal occurs, a peak should appear in the vicinity of 268 ppm. However, this peak portion was not detected in the batteries studied for the present research, and deposition was therefore not taken into consideration in this research (Table 3, Reference 5).

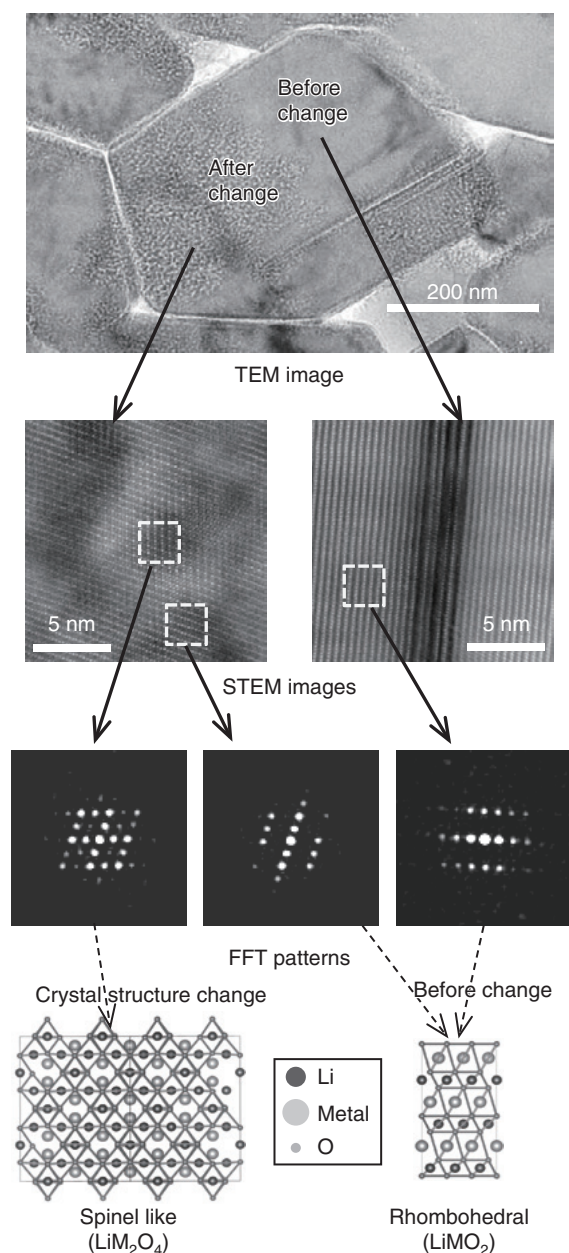


Fig. 5 Cross section TEM, STEM images and FFT patterns of cathode active material

The results from a solution ^1H NMR analysis of the extracted electrolyte solution showed that no transformation of the principal components of electrolyte occurred within the scope of the present research (Table 3, Reference 6).

The ^1H NMR results for anode deuterium oxide extracts show the detection of a small amount of trace organic components methoxy, ethoxy, glycoxy, formate ions, and acetate ions. Phosphorus compounds detected were phosphite and methyl phosphate derivatives. Alkoxy compounds are thought to be products of degradation of electrolyte solvent components, and phosphorus compounds the products of degradation of electrolyte or additives^{(15), (16)} (Table 3, Reference 2).

3.3.3. Measurement of separator air permeability

No noticeable difference was found in the air permeability of separator extracted from new batteries and from aged batteries. Therefore clogging of separator pores can be considered not to have occurred (Table 3, Reference 7).

3.3.4. ICP-AES analysis

In order to distinguish the lithium ions in the SEI from the lithium ions that exist in active material, the remaining discharge capacity of the anode was measured before carrying out ICP-AES measurement, and the amount of lithium ions remaining in the anode active material was quantified. The amount of lithium ions in the SEI was determined by subtracting the amount of lithium ions corresponding to the remaining discharge capacity [Fig. 2(a)] from the total amount of lithium ions in the anode (Table 4) obtained by ICP-AES measurement. Figure 3(b) and Table 4 show the relationship between the amount of lithium ions in the SEI and the square root of aging time. Although the amount of lithium ions agreed with the widely-known square root law^{(6), (7)} [Fig. 3(b)], it did not agree with the ΔLi value obtained by the method shown in Fig. 3(a) [Fig. 3(b)].

For ICP-AES measurement of the anode, quantifications of nickel, cobalt, and manganese were also made as shown in Table 4. The amount of the transition metals included in the SEI was less than 0.01 wt% in every case, and no increase due to storage time was observed. This therefore confirmed that deposition on the anode of transition metals originating in the cathode did not occur.

3.3.5. IC analysis

The results from an IC analysis of anode ultra pure water extracts showed that fluorine ions, oxalate ions, and phosphate ions were detected. These ions can be considered the products of degradation of electrolyte or of additives. Among them, the amount of fluorine ions increased as aging progressed. The existence of the fluorine ions can be considered to suggest the existence of LiF components in the SEI⁽²⁰⁾.

Table 4 ICP-AES results for anodes

Aging time (Day ^{1/2})	Results (wt%)			
	Li	Ni	Co	Mn
0.0	1.42	<0.01	<0.01	<0.01
6.2	1.73	<0.01	<0.01	<0.01
7.7	1.94	<0.01	<0.01	<0.01
18.6	3.01	<0.01	<0.01	<0.01
24.7	4.27	<0.01	<0.01	<0.01

Aging condition: SOC=80% at 65°C

3.3.6. X-ray photoelectron spectroscopy analysis

It was found from the XPS analysis results that, of the carbon components, carbonate and carboxylate made up from 3% to 7% of total components. Since XPS cannot readily distinguish between carbonate components and hydrocarbon components, carbonate components could not be quantified. However, it can be inferred that no major change accompanying the progressive aging of carbon components occurred down to approximately 2 nm from the surface.

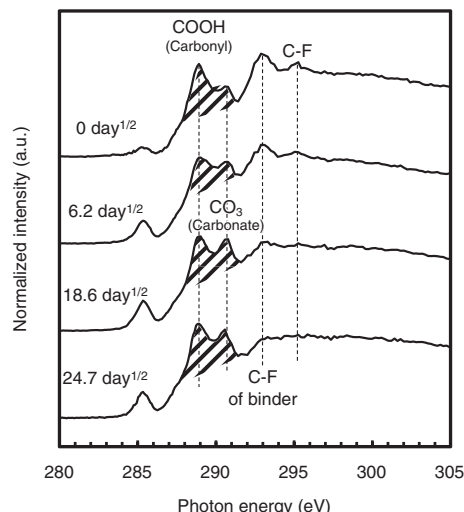
3.3.7. Soft X-ray absorption fine structure analysis

Figure 6 shows the spectra of K-edge X-ray absorption near-edge structure (XANES) of carbon on the anode surface. Peaks at photon energy of 289.0 eV and 290.6 eV is attributed to the carbonyl group and carbonate, respectively⁽²²⁾. Compared to the peak of the carbonyl group at a depth down to approximately 2 nm, the carbonate peak was weaker [Fig. 6(a)]. When observing to a depth of 20 nm from the surface, however, the carbonate peak became stronger [Fig. 6(b)]. In the anode at 18.6 day^{1/2} and 24.7 day^{1/2} of storage, in particular, the peak of carbonate became greater than the peak of the carbonyl group. Information down to a depth of 200 nm from the surface mainly indicates carbon components originating primarily in anode active material [Fig. 6(c)].

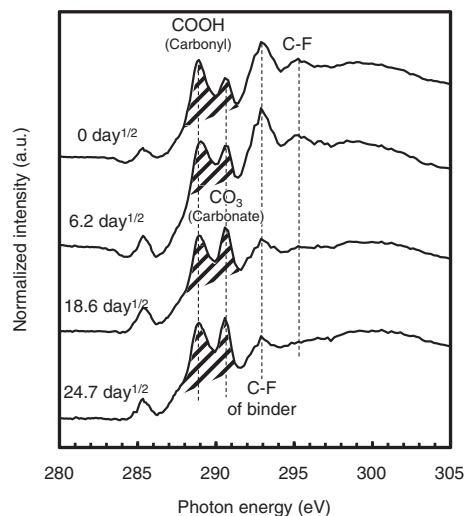
Given these results, it is conceivable that more carbonate is included in regions that are close to active material than on the outermost SEI surface. Peaks at 293.0 eV and 295.5 eV can in both cases be attributed to binder C-F⁽²²⁾. Compared to new batteries, C-F peaks strength grew weaker as aging progressed. This happens because the SEI grows thicker as aging progresses, and the result here can be taken as indirect indication of that growth.

3.3.8. In-depth component analysis by Auger electron spectroscopy

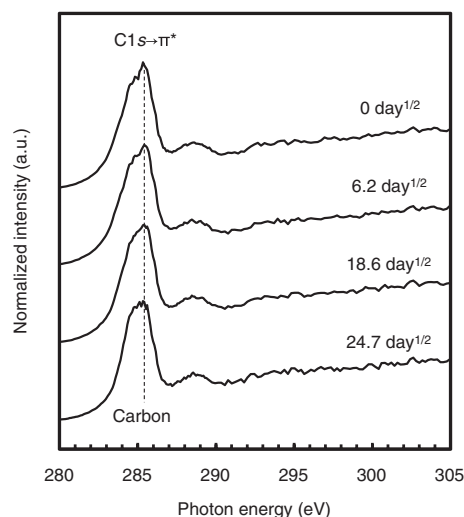
Figure 7 shows the in-depth distribution of fluorine, carbon, lithium, phosphorus, and oxygen on the anode



(a) Partial electron yield mode



(b) Total electron yield mode



(c) Partial fluorescence yield mode

Fig. 6 Soft X-ray near edge absorption fine structure of carbon K-edge for anodes (aging condition: SOC=80% at 65°C)

surface. Since the measurement method used here involved measuring while etching the SEI surface, the accurate depth cannot readily be normalized, but a relative comparison could be made. Here, the half value of the oxygen component is defined as the SEI thickness, and the components in that portion were taken as SEI components. It is apparent from the component distribution in the interior of the active material shown in Fig. 7 that the main component of the active material was carbon, but a small amount of lithium was also included. As shown with the electrochemical measurements in Section 3.2, there was a minimal residual capacity in the extracted anode (Fig. 2), so the lithium in the active material can be considered residual lithium that was remaining in the anode when the battery was disassembled. In the SEI, however, the main

components in the layers close to the surface, as shown in Fig. 7(a), were lithium, carbon, and oxygen. Then as aging progresses, the growth of the SEI causes a reduction in the proportion of carbon in deep regions, while the amount of lithium instead increased. Considering the influence of additives, the proportion of fluorine was relatively small [Fig. 7(b)].

3.4. Discussion

3.4.1. Electrochemical measurements

As shown in Fig. 2, the capacity retention of the full cell diminishes with the passage of time in storage. The capacity retention of the anode, by contrast, diminished to about 90% and then stopped. The capacity retention of the cathode, however, diminished to 94.1% at 6.2 day^{1/2} in storage, to 92.1% at 7.7 day^{1/2}, to 72.0% at 18.6 day^{1/2}, and to 54.4% at 24.7 day^{1/2}. Meanwhile, although the amount of the shift as calculated according to Eq. (1) was 17% at 0 day^{1/2} in storage, then at 7.7 day^{1/2} it rose to 20%, at 24.7 day^{1/2} it turned back down and diminished to -6.5%. Here, when the amount of the shift in the balance is a positive value, it signifies that even in a fully discharged state, the cathode still retains some capacity to receive lithium. In other words, it indicates a state in which the amount of active lithium has diminished. When the value is negative, however, it signifies that even in a fully discharged state, there is still some lithium remaining in the anode. In other words, it indicates a state in which the cathode capacity has diminished. These results clearly showed that battery aging has two causes, the reduction in the amount of active lithium and the loss of cathode capacity.

3.4.2. Active lithium loss

As described in the previous clause, the amount of lithium ions incorporated into the SEI as determined by ICP-AES did not agree with the amount of active lithium loss determined by electrochemical measurements [Fig. 3(b)]. A portion of the SEI that is a product of reductive degradation of the electrolyte at the anode is known to be dissolved into the electrolyte and not incorporated into the SEI^{(15), (16), (20), (21)}. There have also been reports of instances in which a portion of the electrolyte components that are oxidized at the cathode is dispersed and travels to the anode, is reduced on the anode, and is incorporated into the SEI^{(20), (21)}. It is conceivable that this could be the reason why the amount of lithium included in the SEI did not agree with the amount of active lithium loss. In this case, it would appear that in order to achieve a highly accurate prediction, a value determined using Eq. (2) would need to be adopted for the amount of active lithium loss ΔLi .

Putting together the results of analyses from the previous section, the chemical composition of SEI includes a large proportion of organic lithium compounds on the surface, while the amount of inorganic components becomes greater in regions extending to a depth of more than 2 nm from the surface. As inorganic components, lithium

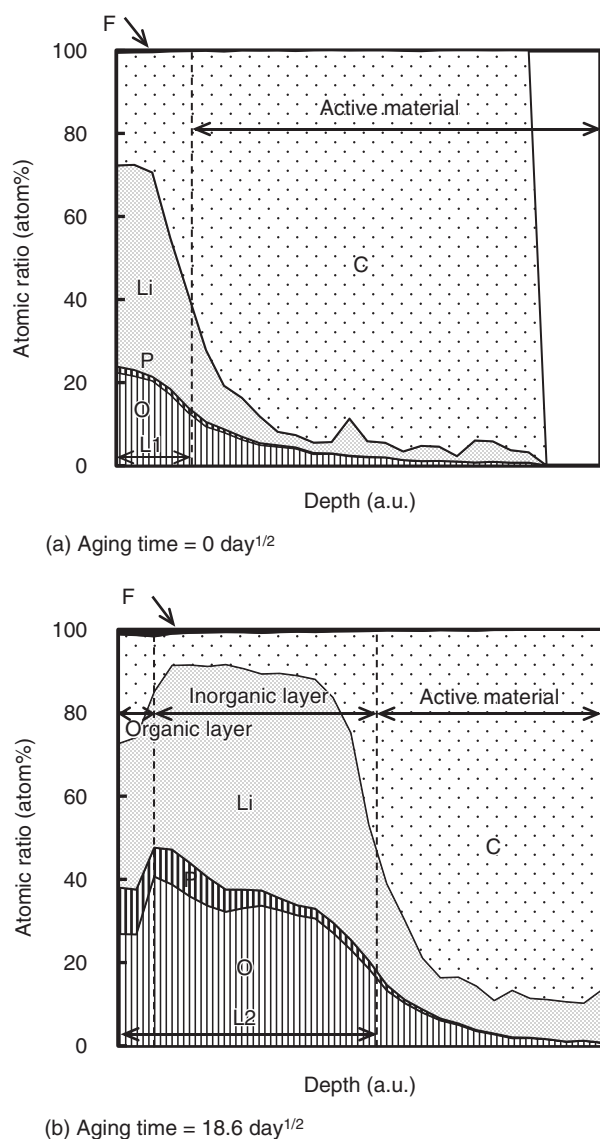


Fig. 7 AES depth profiles of anodes surfaces

carbonate, phosphate compounds, and lithium fluoride are thought to exist. The fact that the SEI takes on this kind of structure can be explained by the idea⁽²⁴⁾ that when additive components and electrolyte undergo reductive degradation at the anode, a layer containing large amounts of organic components is formed initially, and over time, the organic components transform to inorganic components.

It has also been reported⁽²²⁾ that the cause of active lithium loss is the dielectric breakdown of the SEI that occurs due to the deposition of transition metals on the anode surface. The experiment here, as related in Clause 3.3.4., confirmed that deposition did not occur. Consequently, it was decided not to take this into account in calculating the diminishment in lithium ions when creating the aging predictive equation to be covered in the next report.

3.4.3. Cathode capacity fading

It has been reported⁽¹⁷⁾⁻⁽¹⁹⁾ that in a charged state, the rhombohedral layered rock-salt type lithium transition metal oxide undergoes partial crystal structure transformation in its layered structure because of the inhomogeneous lithium distribution inside the crystal. In such cases, the parts that have transformed are thought to be a mixture of spinel-like structure expressed by the structural formula of LiM_2O_4 and rock-salt structure expressed by MO. Here, “M” represents transition metals nickel, cobalt, and manganese. As shown in Fig. 5, similar crystal structure transformation were also observed to take place in the present research in conjunction with calendar aging. Taking the case when M is manganese, for example, the amount of lithium that can be included per unit volume in a thermal equilibrium state is 42.8 mol/L in a layered rock-salt structure (LiMO_2) before aging, and after aging it is 22.2 mol/L in a spinel-like structure (LiM_2O_4)⁽²⁵⁾. The spinel-like structure contains less lithium. It is thought to be for this reason that cathode capacity diminished.

4. Conclusion

The calendar aging of lithium ion rechargeable batteries used to be predicted by a simple square root law that made aging proportional to the square root of the number of days in storage⁽⁶⁾⁻⁽⁹⁾. The foundation for this is explained to be that active lithium is lost due to the electrochemical degradation reaction of the electrolyte (SEI formation reaction) during the period of storage.

However, that aging did not follow the square root law in the prismatic high-power lithium ion rechargeable battery that was the object of the present research, and it could not be explained by a simple square root law alone. The present research, therefore, attempted to explain the mechanism of aging by a combination of electrochemical and materials analysis techniques. As a result, it was found that there are two main causes of aging in the battery, the partial crystal structure transformation in the cathode active material and the loss of active lithium due to the SEI

formation and growth reaction that occurs on the anode. Here it was also found that the quantitative results for the amount of lithium ions incorporated into the SEI as determined using an ICP-AES analysis, which is in general use, do not agree with the amount of active lithium loss as determined electrochemically. This made clear that the capacity balancing shift among the electrodes cannot be quantitatively determined from the amount of lithium ions in the SEI. Taking the findings obtained from the present research as a basis, it is expected that an equation can be created for the accurate and rapid prediction of aging in battery performance over the long term.

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