Short communication

# Investigation of positive electrodes after cycle testing of high-power Li-ion battery cells
# III: An approach to the power fade mechanism using FT-IR-ATR

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## Abstract

Surface materials on positive electrodes of lithium-ion batteries which have been degraded are characterized by ATR technique of FT-IR. Lithium carbonate, P=O bond based material, lithium alkyl carbonate ($ROCO_2Li$), and polycarbonate-type compound are detected which have been formed by decomposition reactions of electrolyte solvent and $LiPF_6$ as lithium salt. Stability of lithium carbonate for charging to SOC = 100% is depended on the condition during degradation. Especially, it changes to unstable by long time cycling at low temperatures. Formation of polycarbonate-type compound during cycling is remarkable at elevated temperatures. Degradation of batteries is larger in higher temperatures, and it is suggested that the variation of surface structure has relation to degradation of batteries.
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*Keywords:* Lithium-ion battery; Positive electrode; Surface material; Degradation; FT-IR; ATR

## 1. Introduction

Nowadays, rechargeable lithium-ion batteries have been recognized as the most fascinating secondary power sources for the portable electronic devices mainly due to their high energy densities [1]. It is also expected that the lithium-ion batteries would be used as auxiliary power sources for fuel cell electric vehicles (FCEV) and hybrid electric vehicles (HEV) in the near future. With view to realizing these imminent applications, intensive research is needed to improve calendar life of the lithium-ion battery over 15 years which is average service life of vehicles.

Heretofore, research works based on improvement of shelf life have been conducted by many groups. For instance, three battery manufacturers are developing the batteries for such usage under national R&D project in Japan [2]. In order to support their research, a precise prediction method of the life of the batteries from slight variation of battery characteristics in short time is necessary. Hence, our present research is aiming to establish such estimation method. In this regard, the important things are to know the degradation mechanism and the rate of the reactions controlling the degradation. In our previous study, it was suggested that exothermic side-reactions of the lithium-ion battery during cycling caused increase of impedance especially as enlargement in reaction resistance of the positive electrode [3]. This result is informative to study about surface structure of the positive electrodes. Therefore, recently we are mainly focusing to analyze the surface of the positive electrodes of the degraded batteries. However, some researchers' fruitful efforts on analysis of positive electrode surface [4,5], identification in detail of the surface materials and correlation between degradation of the batteries performance and the formation of various surface materials are still obscure. Our collaborative researchers have recently used XPS and XANES to study about surface materials of positive electrodes which are same samples we are analyzing in this study [6,7]. These methods give some suggestive information about valence of transition metals in the active electrode materials, binding energy of the chemical bonds in surface materials, and so on. In order to identify the surface materials and to discuss their formation mechanism, more specific nature of the materials is important such as the types of functional groups and their arrangement in the surface. Fourier transform infrared spectroscopy (FT-IR) is one of effective characterization methods to obtain information on functional groups of especially organic materials. In addition, attenuated total reflectance (ATR) tech-

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nique enables to analyze thin filmy materials on solid plate for FT-IR [8]. In this study, we will discuss about surface materials on the positive electrode and the formation reactions using ATR. Finally, this research is aiming to find out primary reactions causing degradation of lithium-ion batteries during cycling.

## 2. Experimental

Trial manufactured small model lithium-ion batteries which were cylindrical shape of 17 mm in diameter and 50 mm in length were used as sample. The nominal capacity $C$ was 420 mA h. The standard condition of charging and discharging was constant current of $C/3$ A (140 mA), and the cut-off voltage was 4.2 V in charging while 2.5 V in discharging. $Li_xNi_{0.73}Co_{0.17}Al_{0.10}O_2$ and hard carbon were used for positive and negative electrode, respectively. As electrolyte, 1 mol dm$^{-3}$ of $LiPF_6$ in mixed solvent of propylene carbonate (PC) and dimethyl carbonate (DMC) (3:2 in volume ratio) was used.

Cycle test was conducted by Kihira and co-workers [9,10] with periodical check of battery characteristics such as capacity, dc resistance, power capability, and ac impedance. Detail of procedure and condition of those tests and the results were described elsewhere [7,9]. Here, we only mention that the cycle test has been carried out at 0, 20, 40, 60 or 80 °C in order to examine temperature dependency for degradation of batteries during cycling.

After the test, state of charge (SOC) of the batteries was set to 0 or 100%. The positive electrodes were collected by the disassembly of the batteries in an argon-filled glove box, washed in DMC, and then dried under vacuum condition. For ATR measurement, the electrodes were cut into specimen whose size was ca. 12 mm × 12 mm. The Nicolet Magna 560 spectrometer with MCT detector installed in the room with low humidity was used for the spectroscopic study. A multiple angles reflection accessory Seagull from Harrick with a hemispherical Ge crystal (refractive index is 4.0) was mounted on the spectrometer for ATR analysis. The electrode surface to analyze was adhered to the crystal. Angle of incidence was controlled to 60°.

## 3. Results and discussions

In order to discuss about variation caused by the cycle test, surface chemistry of the positive electrodes in initial battery before applying cycle test was examined by ATR at first. The typical ATR result is shown in Fig. 1 as spectrum a. Since the electrode contains polyvinylidene fluoride (PVdF) binder, influence of the bands of PVdF is not negligible. Actually, the profile of the spectrum is similar with infrared spectrum of PVdF which is plotted in Fig. 2A. However, by the principle of ATR, wavenumbers of each band between these two spectra are not coincident. Hence, we prepared a pristine electrode containing PVdF as the binder in laboratory, though the active electrode material is $Li_xNi_{0.80}Co_{0.15}Al_{0.05}O_2$, and measured ATR spectrum of the pristine electrode. The result is plotted as spectrum b in Fig. 1 where all bands could be attributed to PVdF. Compared with two ATR spectra, bands at 1016, 1425, and 1486 cm$^{-1}$ are not attributed to PVdF, and it is suggested that the electrode sur-
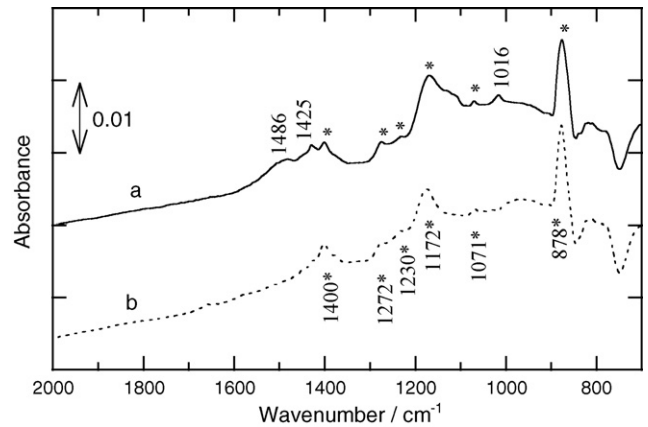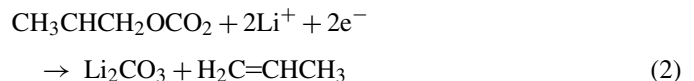


Fig. 1. ATR spectra of positive electrodes: (a) electrode from initial cell at SOC = 0% without cycle test, and (b) pristine electrode prepared in laboratory.

face has already been covered by some surface materials even before the test, which would thought to be formed by contact of the electrode with the electrolyte after construction of battery or produced during initial several cycles to characterize the initial performance of the battery. Andersson et al. [4] showed that the $Li_2CO_3$ could be formed by the reaction between atmospheric $CO_2$ and ion-mixed regions in the $Li(Ni, Co)O_2$ as follows

$$Li(Ni, Co)O_2 + \tfrac{1}{2}xCO_2 + \tfrac{1}{4}xO_2$$
$$\rightarrow Li_{1-x}(Ni, Co)O_2 + \tfrac{1}{2}xLi_2CO_3 \qquad (1)$$
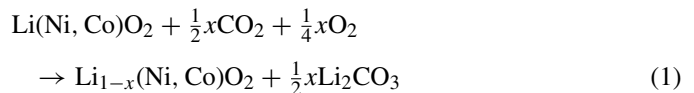
The infrared spectrum of $Li_2CO_3$ is shown in Fig. 2B, and thus the peaks at 1425 and 1486 cm$^{-1}$ of the positive electrode are assigned to $Li_2CO_3$. Though the above reaction is thermodynamic, the formation of $Li_2CO_3$ by electrochemical reaction is also to be considered. It was proposed that $Li_2CO_3$ could be formed on lithium metal negative electrode during charging due to the decomposition of PC through two-electron transfer as follows [11].

$$CH_3CHCH_2OCO_2 + 2Li^+ + 2e^-$$
$$\rightarrow Li_2CO_3 + H_2C{=}CHCH_3 \qquad (2)$$

Hence, it is possible to think that similar electrochemical reaction has occurred on the positive electrode in the initial cell.
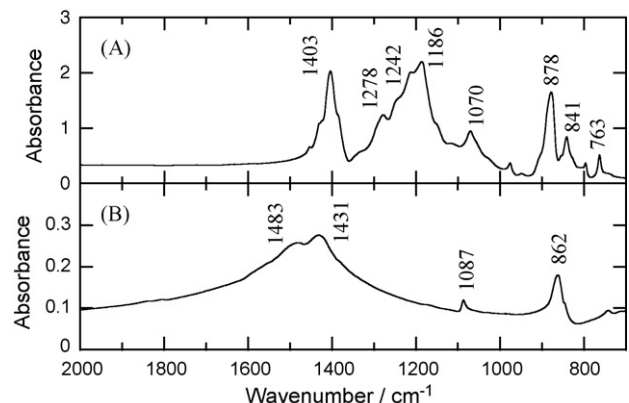


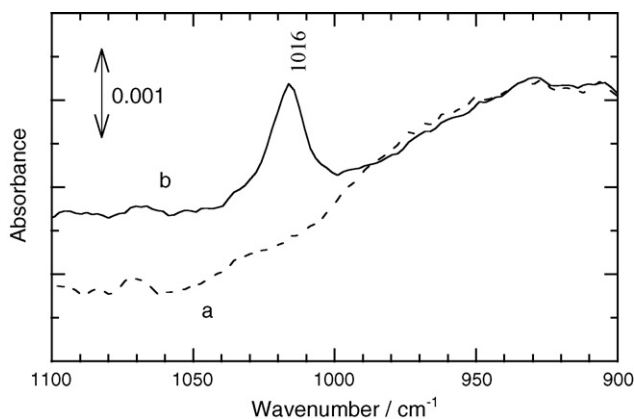Fig. 2. Infrared spectra of (A) PVdF and (B) lithium carbonate.

Fig. 3. ATR spectra of prepared electrode in laboratory: (a) pristine, and (b) 90 days after immersion into mixed solvent of EC and DMC containing $1 \, mol \, dm^{-3}$ of $LiPF_6$.

The peak at $1016 \, cm^{-1}$ in the spectrum a in Fig. 1 is not attributed to $Li_2CO_3$. Fig. 3 shows the ATR spectra of the pristine electrode before and after immersion into solvent electrolyte consisted of $1 \, mol \, dm^{-3}$ $LiPF_6$ and mixed solvent of EC and DMC. Note that the angle of incidence in ATR was 80° only in this measurement because the peak at $1016 \, cm^{-1}$ was not observed when 60° was selected, suggesting that extremely thin material was formed on the surface. From this result, the material with IR band at $1016 \, cm^{-1}$ is concluded as a reaction product by contact of the electrode with the electrolyte, and thought to be P=O bond based materials. In the batteries, $LiPF_6$ is used as supporting electrolyte and it may occasionally decompose as LiF and $PF_5$ which can further hydrolyze with trace water to form HF and $POF_3$ as follows [12,13]

$$LiPF_6 \leftrightarrow LiF + PF_5 \qquad (3)$$

$$PF_5 + H_2O \rightarrow POF_3 + 2HF \qquad (4)$$

Fig. 4 shows the FT-IR spectra of the electrolyte used in the above experiment, which have been normalized to the peak intensity of C–O–C stretching in EC at $1076 \, cm^{-1}$. After addition of water until concentration of water reach to $0.01 \, mol \, dm^{-3}$, slow growth of a peak at $1022 \, cm^{-1}$ which derives from the P=O
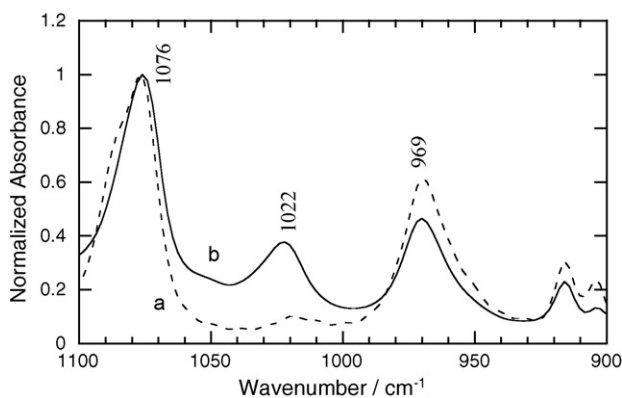
bond in $POF_3$ was confirmed as shown in Fig. 4. Note that $POF_3$ decomposes to $H_3PO_4$ in condition with excess water, and the peak intensity changed to the decrease after long time in this experiment. However, P=O bond shows the band at $1000 \, cm^{-1}$ and around, it is difficult to think that the peak of $POF_3$ could exist in the ATR spectrum of the positive electrode because the $POF_3$ is a gaseous compound in room temperature. Aurbach et al. reported that $Li_xPF_y$ or $Li_xPF_yO_z$ type compound was produced from the electrochemical reaction concerning $POF_3$ as follows [13]

$$POF_3 + 2xLi^+ + 2xe^- \rightarrow Li_xPF_{3-x}O + xLiF \qquad (5)$$

and these materials show a band at $1030 \, cm^{-1}$. Although, electrochemistry is not required for the formation of the material with the band at $1022 \, cm^{-1}$ as shown in Fig. 3. Recently, reaction mechanism of $LiPF_6$ with electrolyte solvent such as diethylene carbonate, EC, and DMC, initiated by ROH (alcohol or water) was proposed [14]. In this scheme, $OPF_2OR$ and its derivatives are produced via $POF_3$. It is considered such kinds of P=O bond based materials are formed on the positive electrode in our initial batteries. According to reaction of Eq. (3), LiF is also thought to be produced on the electrode. Since LiF does not have the IR bands in the wavenumber range of ATR, any information on LiF cannot be obtained only from this experiment. However, we could confirm the formation of LiF as the surface material in Shikano's report [6].

Summarizing the results of the ATR analysis of positive electrode of the initial battery before the cycle test indicates that the $Li_2CO_3$ and P=O bond based materials (and LiF) has already formed as the surface materials.

Fig. 5 shows the dc resistance of the cells after the cycle test as an example of degradation. At lower temperatures from 0 to 40 °C, dependency on tested temperature for increase in dc resistances is not significant while degradation is remarkable in the test at 60 °C and above. This result suggests that additional and decisive side-reaction occurred at elevated temperatures beyond 60 °C and accelerates degradation of battery performance strongly. ATR spectra of the positive electrode in these degraded batteries are plotted in Fig. 6 where SOC has been controlled to 0% after the test. As a first glance, remarkable



Fig. 4. Infrared spectra of mixed solvent of EC and DMC containing $1 \, mol \, dm^{-3}$ of $LiPF_6$, normalized by a peak at $1076 \, cm^{-1}$ of EC. (a) Control and (b) 300 h after addition of water.
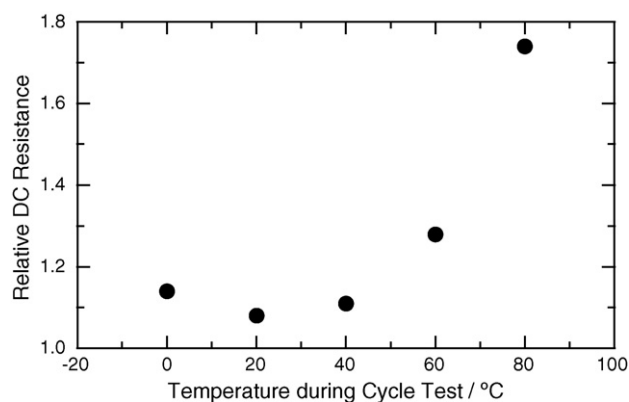


Fig. 5. Relative dc resistance for the initial value of the lithium-ion batteries after the cycle tests at various temperatures. The cycle numbers at finish of the tests are 50,000 except 80 °C in which 45,000 [9,10].
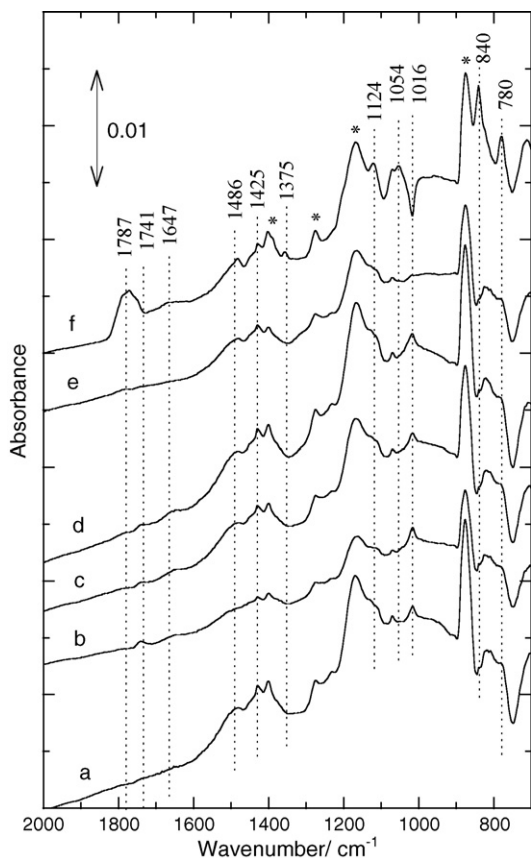
Fig. 6. ATR spectra for the positive electrodes from (a) an initial cell without cycle test, and from the tested cells at (b) 0 °C, (c) 20 °C, (d) 40 °C, (e) 60 °C and (f) 80 °C. SOC of the cells are 0%.

changes in the spectra of samples tested at 60 °C and below are not observed compared with the initial state. However, appearance of small peaks may be seen at 1647 and 1741 cm$^{-1}$ in the spectra b, c, and d which have been tested at 0, 20, 40 °C, respectively. These are in region of stretching vibration region of carbonyl group (C=O). Since PC and DMC have a strong characteristic band of alkyl carbonate (–O–CO–O–) at 1750 cm$^{-1}$ and around, the peak at 1741 cm$^{-1}$ suggest that alkyl carbonate with ethyl functional group [11] has been formed by cycling at low temperatures under 60 °C. Another carbonyl band at 1647 cm$^{-1}$ indicates that the existence of alkyl carbonates (ROCO$_2$Li) with methyl or propyl or butyl functional group of which electro-chemical formation reaction has been proposed [11] as

$$CH_3CHCH_2OCO_2 + Li^+ + e^- \rightarrow ROCO_2Li \qquad (6)$$
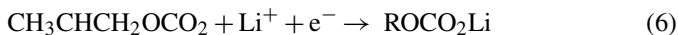
This material is well known as one of main components of surface film on negative electrode. Same decomposition reaction is also thought to be occurred on the positive electrode.

Only in the spectrum f, remarkable peaks are observed at 780, 840, and 1787 cm$^{-1}$ accompanied by small peaks at 1054, 1124, and 1375 cm$^{-1}$. A broad band at 1787 cm$^{-1}$ is corresponding to stretching vibration of carbonyl group intensified the strength of the band by the neighboring groups with strong electron-withdrawing. A relative intensity of peak at 1275 cm$^{-1}$ which overlaps with the band of PVdF may be seen to increase, sug-
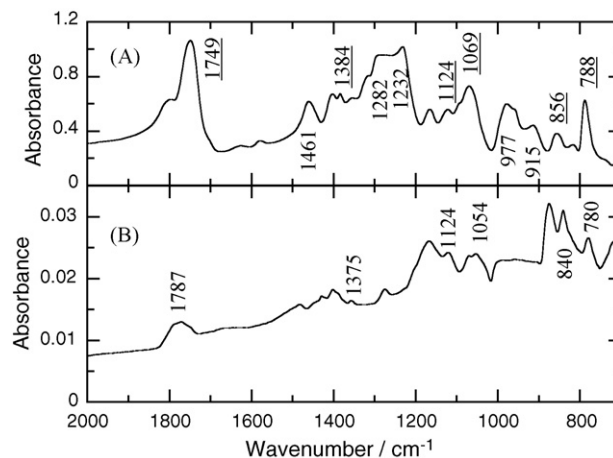


Fig. 7. (A) Infrared spectra of poly (propylene carbonate), and (B) ATR spectrum of the positive electrode from the cell at SOC = 0% tested at 80 °C.

gesting formation of dialkyl carbonate (ROCOOR′) as C–O–C stretching vibrations. A weak band at 1054 cm$^{-1}$ and a medium intensity band at 1124 cm$^{-1}$ bring supporting information on dialkyl carbonate. In addition, the peak at 840 cm$^{-1}$ can be attribute to the O–CO–O bending vibration. Aurbach et al. mentioned about polymerization reaction of ethylene carbonate (EC) to poly (ethylene carbonate) initiated by RO$^-$ formed by electro-chemical reduction of EC [15]. Same polymerization reaction might be possible for PC. In Fig. 7A, an FT-IR spectrum of poly (propylene carbonate) is plotted. Compared with Fig. 7B which is same as the spectrum f in Fig. 6, it is hard to say that just poly (propylene carbonate) is formed on the electrode. However, poly (propylene carbonate) has peaks at similar regions where all new peaks have appeared in the spectrum of the electrode. Hence, we consider that polycarbonate-type material could be formed at elevated temperature, and this is one of sources of high resistance of the electrode.

The ATR measurement was also applied to the positive electrode of which SOC had been controlled to 100% after the cycle test, and the result gave interesting information on stability of Li$_2$CO$_3$. Fig. 8 shows dependency on SOC of peak intensity at 1486 cm$^{-1}$ which is normalized to the band at 1400 cm$^{-1}$ of PVdF. Even in the initial samples, relative intensity becomes lower in charged state, and the difference depending on SOC is expanded by the cycle test. Since the only difference between two samples for each tested temperature is SOC which has been controlled after the final capacity measurement between SOC = 100 and 0% following the cycle test, this result suggests that the amount of Li$_2$CO$_3$ decreases by charging and increases by discharging. It has already been discussed that two kinds of formation reactions are proposed for Li$_2$CO$_3$, and from this result, it is certain that the formation of Li$_2$CO$_3$ is happened by direct electrochemical reaction (Eq. (2)) rather than Eq. (1). For the electrodes from the batteries tested at 60 °C, it is suggested that total amount of Li$_2$CO$_3$ has been increased during the test, from the growth of relative intensity of the bands of Li$_2$CO$_3$ compared with the initial samples. Similar result is obtained by XPS study [6], and the reversibility of Li$_2$CO$_3$ was confirmed. Since the bands of ROCO$_2$Li is not clearly seen in the spectrum
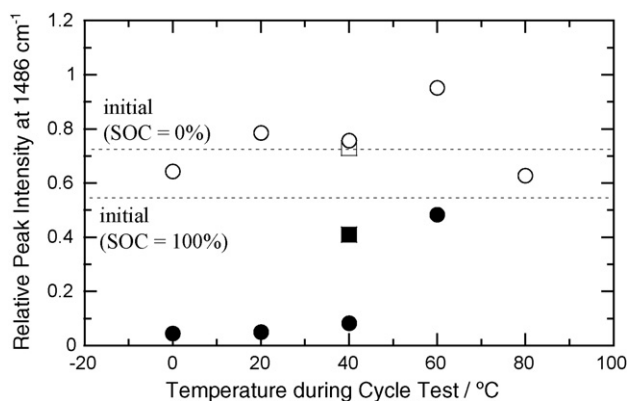
Fig. 8. Relative intensities of absorbance at $1486 \, cm^{-1}$ in the ATR spectra normalized to the peak at $1400 \, cm^{-1}$ as a function of temperature during the cycle test. The SOC of the cells are (○) 0% and (●) 100% for the cycle test and (□) 0% and (■) 100% for preserved samples for 631 days. Dotted lines are levels in the initial cells.

e in Fig. 6, the formation of $Li_2CO_3$ may be more primary than $ROCO_2Li$ as the side-reaction during discharge at $60 \, °C$. Larger amount of $Li_2CO_3$ would also cause increasing in resistance. In the elevated temperature of $80 \, °C$, priority would be given to the generation of polycarbonate-type material than $Li_2CO_3$ resulting in further large resistance.

For the decrease of the peak intensity of $Li_2CO_3$ during the final charging, two possible mechanisms are considered; decomposition by direct electrochemical reaction, and chemical reaction attacked by products of electrochemical oxidation. In the former case, the reaction is described as

$$2Li_2CO_3 + 4e^- \rightarrow 2CO_2 + O_2 + 4Li^+ \tag{7}$$
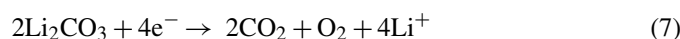
On the latter case, Broussely et al. anticipated a mechanism where partly soluble organic species formed by reduction on the negative electrode diffusing to the positive electrode surface and then oxidized to produce protons [16]. Lithium carbonate may be decomposed by this proton as follows

$$Li_2CO_3 + 2H^+ \rightarrow CO_2 + H_2O + 2Li^+ \tag{8}$$

The reason why decomposition reaction becomes active after cycling is indefinite only from the present data. We suppose that stability of $Li_2CO_3$ against charging to high voltage decreases with the cycle test due to structure change of the surface materials. The stability is higher in the initial state, and even after 631 days preservation of the batteries at $40 \, °C$ without the cycle test, lowering of the stability is not so large as shown in Fig. 8. On the contrary, the cycle test brings unstable $Li_2CO_3$ within 100 days. Hence, it is difficult to think that simply progress in the time is the cause of unstable $Li_2CO_3$. Any electrochemical reactions should be concerning to this peculiar phenomenon as the reason. In the initial state, $Li_2CO_3$ is probably protected by the other surface materials such as LiF from the decomposition reactions. During long time cycling, the initial surface structure might be disturbed by any affects, for instance, repeating of expansion and contraction of the active material particles caused by lithium de-intercalation and intercalation, and then the protective materials are lost from $Li_2CO_3$.

In Fig. 6, some samples show the IR band at $1016 \, cm^{-1}$ of P=O bond based material as like the initial sample. However, this material might be not the primary source of degradation of the batteries because sometimes the band is not observed by the measurement position even in the identical sample. We are considering that the P=O bond based material is localized on the surface.

The results obtained from ATR analysis after the cycle tests are not seemed to be linked univocally with the degradation pattern of the batteries. A number of surface materials are formed on the positive electrode, and the surface structure of the positive electrode is complicated. The primary source of degradation may be different by the temperature during cycling. In the lower temperatures, $ROCO_2Li$ might cause slight increase of reaction resistance. In the temperature range around $60 \, °C$, large amount of stable $Li_2CO_3$ may relate to larger resistance. In more elevated temperature, polycarbonate-type compounds would become obstacle of the smooth electrode reaction.

## 4. Conclusions

Several kinds of surface materials of the positive electrodes of degraded lithium-ion batteries were detected using ATR technique of FT-IR. They were mainly decomposition materials of the electrolyte components such as P=O bond based material, $Li_2CO_3$, $ROCO_2Li$, and poly(propylene carbonate)-like compound, and the main reaction product is dependent on the temperature. Stability of $Li_2CO_3$ against charging of the batteries decreased after the cycle test suggesting the surface structure changed by cycling.

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