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# Influences of graphite electrode on degradation induced by accelerated charging–discharging cycling in lithium-ion battery

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## ABSTRACT



To investigate the effects of degradation on the Li-ion battery (LIB) during fast charging–discharging under various ambient temperatures, the structural changes and elemental distributions were investigated on the graphite electrode between pristine and degradation (Cell capacity < 50%) samples in LIB under room temperature (RT, 25°C) and low temperature (LT, 0°C) ambient using scanning electron microscope (SEM), transmission electron microscope (TEM), and time of flight-secondary ion mass spectrometry (ToF-SIMS). We focused our studies on the structural changes and element distributions via cross-section image for graphite electrode, which were cycled during fast charging–discharging under RT and LT (0°C), respectively. The TEM results show that the surface of graphite in case of LT (0°C) was only changed to amorphous state with cracks on the surface (~10 μm thickness) partially, whereas the graphite of RT was not changed. Also, ToF-SIMS results confirm that the inhomogeneously concentrated elements of Li, F, and P originated from LiPF<sub>6</sub> electrolyte were observed on the graphite surface only in the case of LT (0°C). Our measurement results are expected to contribute to revealing the degradation mechanism during fast charging–discharging cycling under LT (0°C) ambient.

## KEYWORDS

Fast charging–discharging; graphite; Li ion battery; time of flight-secondary ion mass spectrometry (ToF-SIMS); transmission electron microscope (TEM)

## 1. Introduction

In recent years, lithium ion battery (LIB) has attracted an attention for applications such as portable electronic devices, electric vehicles (EVs), and hybrid electric vehicles (HEVs) [1–3]. In order to satisfy the various applications, the LIB cells are needed to meet the requirements of battery performance such as long lifetimes, high energy density, high stability, fast charging–discharging and low/high temperature operations. Recently, there has been an increasing interest of the fast charging–discharging operations in LIB cell, as the result of demands on convenience toward portable mobile devices, EVs, HEVs, and electrical energy storage (EES) applications. In order to guarantee their performances, the clarification of degradation mechanism in LIB is much more important than before [4]. In general, the degradation

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of LIB especially depends on the growth of solid electrolyte interphase (SEI) on negative graphite electrode and decomposition of electrolyte. During the intercalation of lithium ion into the graphite electrode under charging–discharging process, the intercalated lithium reacts immediately with the electrolyte, forming a passive layer called SEI. Thus, the SEI layer on graphite electrode has a significant effect on the degradation of LIB compared to that of positive electrode. Therefore, most researches have been mainly investigated in terms of SEI layer on the graphite electrode for revealing the degradation mechanism of LIB. In the case of EVs, the reduction of charging time is crucial in promoting consumer interest to increase its marketability. Similarly, fast charging–discharging capability is required in portable mobile electronics to enhance mobility and required in battery powered renewable EES systems. In general, the fast charging–discharging process may affect the battery's performance due to accelerated aging. This process is typically related to the high discharge rate (C-rate or C) and ambient temperature known as the main factors in battery aging and degradation [5]. The discharge rate means the maximum output current of the battery during discharge and C-rate plays a strong role in determining the rate of degradation of LIB cell [6, 7]. Therefore, the more detailed mechanism of battery degradation induced by the fast charging–discharging phenomenon needs to be identified and simultaneously the effects of the fast charging–discharging process on the commercial LIB need to be quantified. The performance of LIB depends on various factors for fast charging–discharging technique, such as acceptability of the active materials, cell design, and charging algorithm. In particular, the demands for fast charging–discharging performance under low temperature (LT, 0°C) ambient conditions increase in proportion to the expectation of the improved battery suitable for electric vehicles and potable electronics consuming high capacity. However, the detailed examination on the degradation mechanism of battery electrodes is often neglected especially under accelerated charging–discharging cycling at LT (0°C) ambient, comparing with pristine condition [8, 9].

This study investigates the influences of graphite electrode on degradation induced by the accelerated charging–discharging cycling in lithium-ion battery. In particular, in order to clarify the degradation mechanism due to the fast charging–discharging process under LT ambient, the structural changes and elemental distributions of cross-section of graphite electrode between pristine and 50% degraded LIB cells are mainly examined with respect to different temperature conditions, that is, room temperature (RT, 25°C) and low temperature (LT, 0°C) based on the analysis techniques such as the scanning electron microscope (SEM), transmission electron microscope (TEM), and time of flight-secondary ion mass spectrometry (ToF-SIMS).

## 2. Experiment

This study employs commercial LIB cells of cylindrical type of 18650-model with high capacity. The LIB cells consist of  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  (NCM) and graphite electrode materials, as shown in Table 1. The positive electrode was coated on an aluminum foil with mixtures of NCM material, carbon black, and PVDF binder in N-methylpyrrolidone (NMP) solvent.

**Table 1.** Specifications of each layers in Li ion battery (LIB) device.

	Positive electrode Negative electrode		NCM ( $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ) Graphite
Electrolyte		Salt	$\text{LiPF}_6$
Solvent			DMC: EC: EMC
Additives			FEC

**Table 2.** Operation conditions for accelerated charging–discharging cycling in LIB cells.

Cell capacity for degradation	< 50%
constant current (CC)	30 A
discharge time	10 sec
rest time	5 sec
charge process	4.7 A, 4.25 V, 100 mA
discharge process	7.5 A, 1.8 V
Temperature	25°C, 0°C

The thickness of positive electrode was about 60  $\mu\text{m}$ . Whereas, the negative electrode was deposited on a copper foil with mixtures of natural graphite, carbon black, and styrene butadiene rubber (SBR) binder in N-methylpyrrolidone (NMP) solvent. The thickness of negative electrode was about 80  $\mu\text{m}$ . The full-cells of positive and negative, with microporous membranes as the separator, were assembled. The electrolyte was used to 1 M  $\text{LiPF}_6$  dissolved in the mixtures of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC). The vinylene carbonate (VC), and fluoroethylene carbonate (FEC) were used as additives to the electrolyte solution.

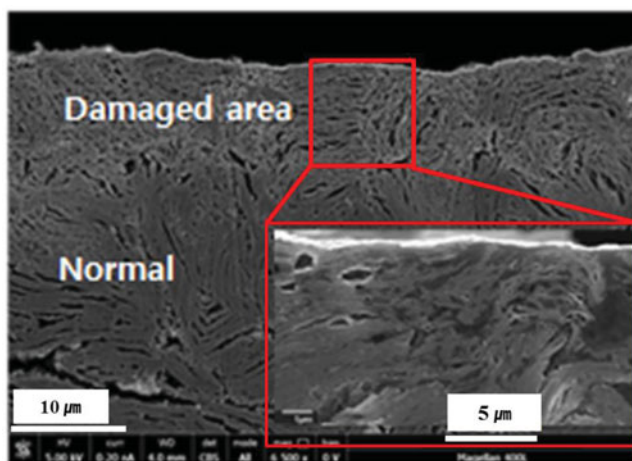
The degraded graphite electrodes after 1000 cycles were prepared by the accelerated charging–discharging cycling under LT (0°C) conditions, as listed in Table 2. After the cycling tests, the graphite electrode was removed from the LIB cell in an Ar filled glove box, washed with dimethyl carbonate (DMC) and then transferred for analysis using a sealed transfer vessel to avoid air exposure. The cross-section image and structural changes of graphite electrode were examined in side plane by scanning electron microscope (SEM; FEI, Nova) and transmission electron microscope (TEM; Titan 80–200ST, FEI). The elemental distribution of cross-section in graphite electrode was obtained by a time of flight-secondary ion mass spectrometry (ToF-SIMS; TRIFT V, ULVAC-PHI) with 30 keV – 1 pA pulsed  $\text{Bi}_1^+$  primary ion beam. The  $\text{Bi}_1^+$  ion current and a scan area were 1 pA and 150  $\mu\text{m} \times 150 \mu\text{m}$ , respectively. The ToF-SIMS measurement was performed in the positive and negative ion modes, and a full spectrum from 1 to 1000 amu was measured.

### 3. Results and discussion

To investigate the morphology and micro structure of the surface, SEM and TEM analyses were performed with several samples under LT (0°C) and high discharge rate (C-rate or C) conditions.

Figure 1 shows the SEM cross-section images of the graphite electrode that is accelerated charging–discharging environment (50% degradation) under LT (0°C). Based on the SEM cross-section images, the comparison of the damaged and normal areas on the graphite electrode clearly indicated that the damaged area was more porous than the normal area, as shown in Fig. 1. The thickness of damaged area was about 10  $\mu\text{m}$ .

Figure 2(a) shows the cross-sectional SEM photograph for clarifying the differently damaged states depending on the cross-sectional position of the graphite electrode. Figures 2(b) and (c) show the TEM images measured in the cross-section of degraded graphite electrode under LT (0°C), named (b) ‘Edge’ and (c) ‘Center’. Some cracks were observed at the ‘Edge’ and the micro structure was changed from crystalline to amorphous state in partial graphite, as shown in Fig. 2. The damage in surface area of graphite electrode was observed to be more severe than that in the inner area because the lithium ions was moved mainly to the graphite surface during charging–discharging cycling under LT (0°C) conditions. On the other hand, unlike LT (0°C) conditions, there was no difference of the damages between the surface and inner areas of degraded graphite under the RT condition [not shown here] [9].



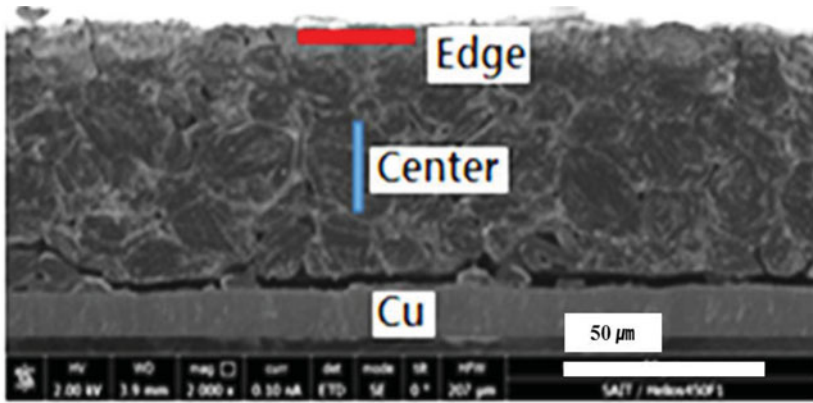
**Figure 1.** Cross-section images of scanning electron microscopy (SEM) measured on degraded graphite electrode at LT (0°C).

Figure 3 represents the electron energy loss spectroscopy (EELS) spectra of TEM for the degraded graphite electrode, named 'Edge' and 'Center'. According to the EELS spectra by the TEM, the  $\pi^*$  and  $\sigma^*$  bonds in the 'Edge' regions were decreased, as shown in Fig. 3, which meant that the degree of crystallinity changed to amorphous at edge area. According to the report of K. Takahashi et al. [9], obvious cracking was observed after cycling under 10 discharge rates (C-rate or C) at LT (0°C). In contrast, there is no change after severe cycling under 30 C at RT [9]. Although the charging–discharging conditions are different between the previous report and our experiment under 30 C and LT (0°C), it is well agreement with our TEM results at 'Edge' of degraded graphite electrode, as shown in Fig. 2. It is well-known that when the temperature of material is decreased, the diffusion coefficient becomes lower. In graphite system, the diffusion coefficients of RT and LT (0°C) were reported to be  $9.5 \times 10^{-13}$  m<sup>2</sup>/s,  $6.5 \times 10^{-14}$  m<sup>2</sup>/s, respectively [9]. Thereby, it is possible to consider that the cracking of graphite electrode can occur at LT (0°C) due to the small diffusion coefficient. Accordingly, it is meaningful to understand the reason of cracking at the graphite surface after fast charging–discharging cycling under high C-rate and LT (0°C) condition.

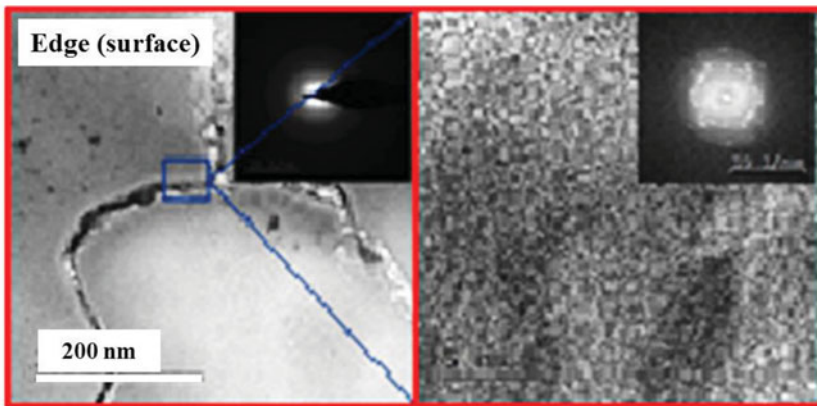
To investigate the element information of surface on the degraded graphite electrode, ToF-SIMS was measured with several samples under high 30 C-rate and LT (0°C).

Figure 4 shows the positive ion mass spectra of ToF-SIMS, which is obtained on the 'Edge' of degraded graphite electrode surface after fast charging–discharging cycling (1000 cycles) with respect to temperature conditions such as RT and LT (0°C).

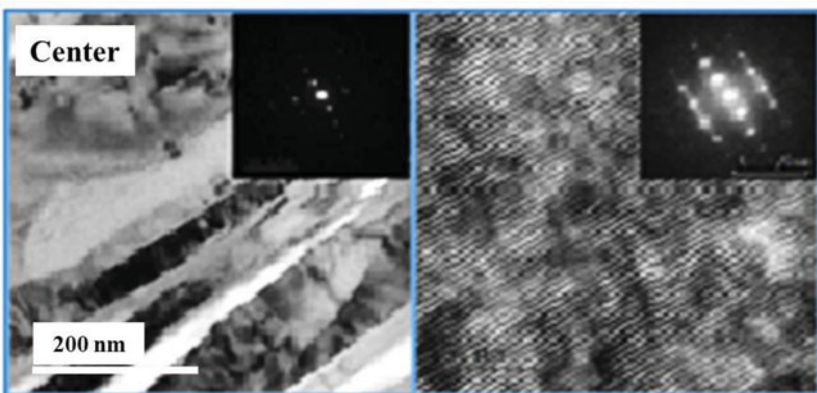
Figure 5 represents the ToF-SIMS intensity ratio, which is calculated from the ToF-SIMS positive ion spectra results of Figs. 4(a) and (b). The normalized intensity ratio of  ${}^7\text{Li}^+$ ,  ${}^{30}\text{Li}_2\text{O}^+$ , and  ${}^{31}\text{Li}_2\text{OH}^+$  for LT (0°C) were increased after degradation compared to those of RT. It meant that the reaction compounds accumulating on the graphite surface were increased after degradation at LT (0°C). In particular, if the lithium ion and Li elements are significantly accumulated on the graphite surface, the electrical connection of positive and negative electrodes can be broken by Li [15]. Therefore, it is possible to grow up the Li dendrite, thereby resulting in the reduction of capacity in LIB cell caused by the Li metal plating. This fact may be considered as one of the important clues for understanding the degradation mechanism during fast charging–discharging cycling under LT (0°C) environment.



(a)

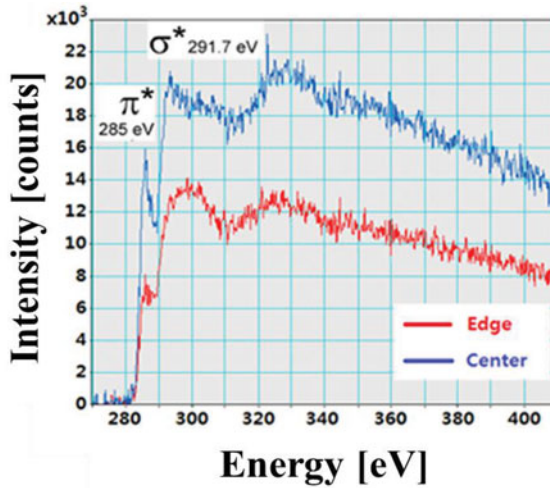


(b)



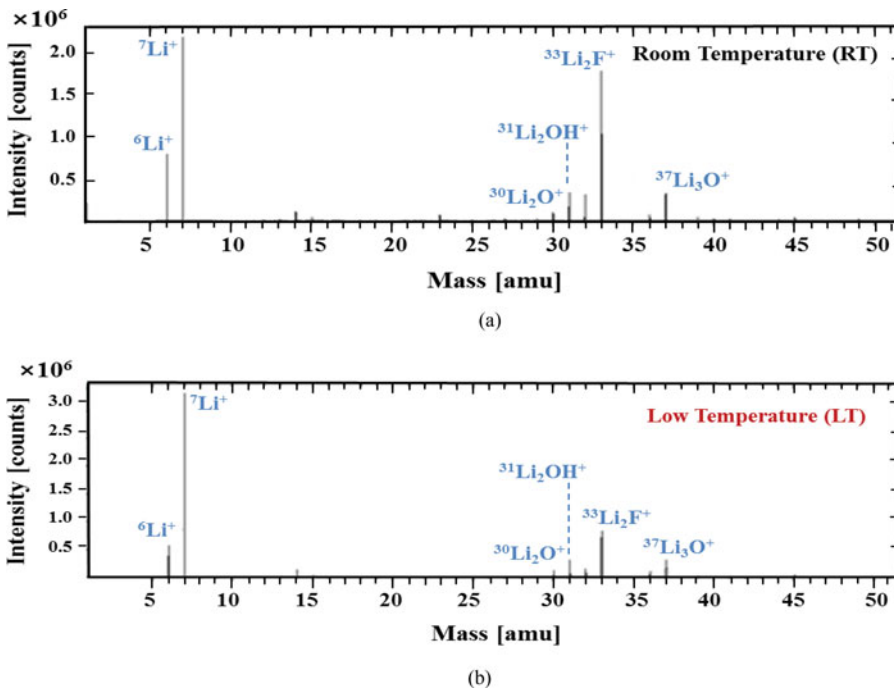
(c)

**Figure 2.** (a) SEM cross-section images for indicating analysis positions, and transmission electron microscopy (TEM) image measured in cross-section of degraded graphite electrode, named (b) ‘Edge’ and (c) ‘Center’ under LT (0°C).

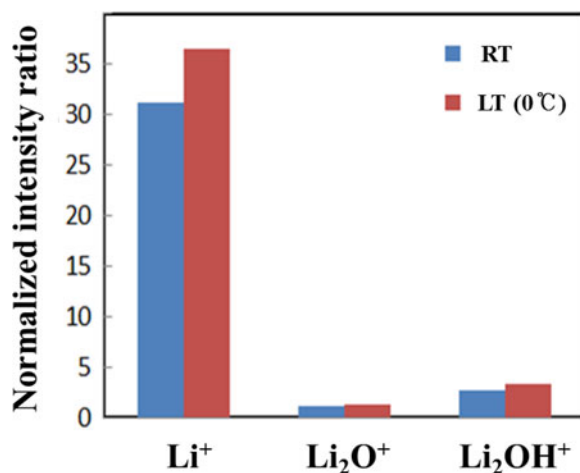


**Figure 3.** Electron energy loss spectroscopy (EELS) spectra of TEM detected on degraded graphite electrode, named 'Edge' and 'Center' in Fig. 2.

From these results, we suggest that the degradation mechanism of LIB strongly depends on the high C-rate and LT ( $0^{\circ}\text{C}$ ) ambient. After fast charging–discharging cycling, the volume of graphite electrode was changed, thus resulting in the structural fragmentation of graphite particles, which might be one cause of capacity fading of LIB cell [10–15]. It is important to understand the reason of crack generation in graphite electrode.



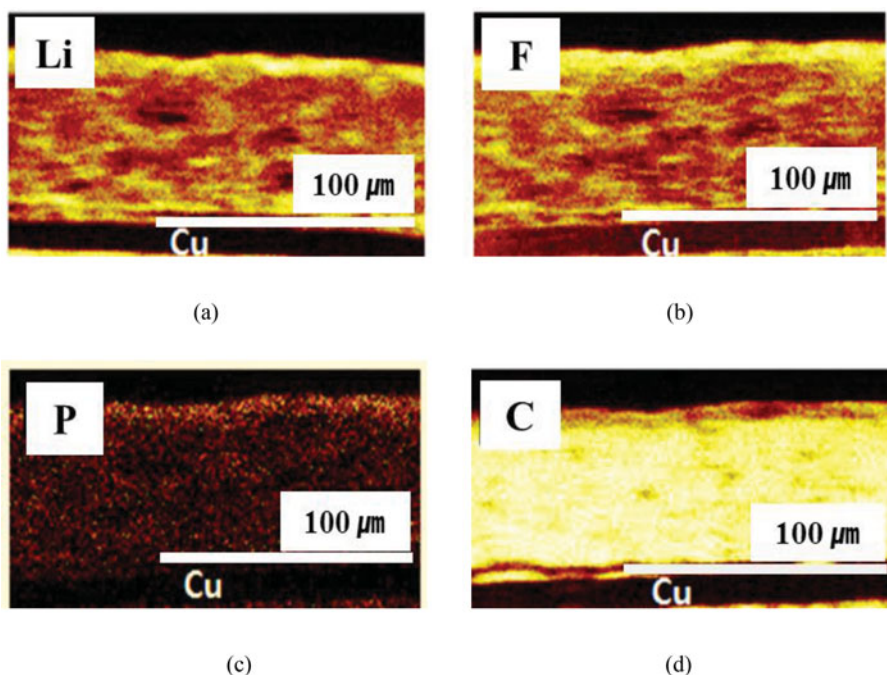
**Figure 4.** Positive ion mass spectra using time of flight-secondary ion mass spectrometry (ToF-SIMS) detected on surface of degraded graphite electrode after degradation with respect to temperature conditions such as (a) RT ( $25^{\circ}\text{C}$ ) and (b) LT ( $0^{\circ}\text{C}$ ).



**Figure 5.** Normalized intensity ratio of ToF-SIMS spectra obtained positive ion mode on surface of graphite electrode with respect to temperature conditions such as RT and LT (0°C).

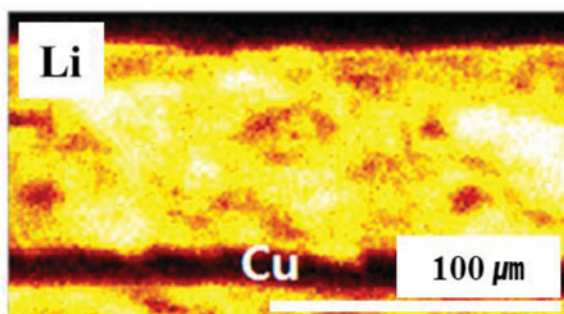
Figure 6 shows the cross-section images of (a) Li (b) F, (c) P, and (d) C elements for the degraded graphite electrode measured by ToF-SIMS in case of LIB cell (50% degradation) after severe charging–discharging cycling (0°C and high 30 C-rate). Figure 7 shows the cross-section images of (a) Li and (b) C elements for the degraded graphite electrode measured by ToF-SIMS after severe charging–discharging cycling (25°C and high 30 C-rate).

As shown in the ToF-SIMS mapping images of Fig. 6, the bright and dark colors mean the high and low density of element at the ToF-SIMS images, respectively. Some elements such as Li, F and P only with the bright colors appeared at the surface area of degraded graphite,

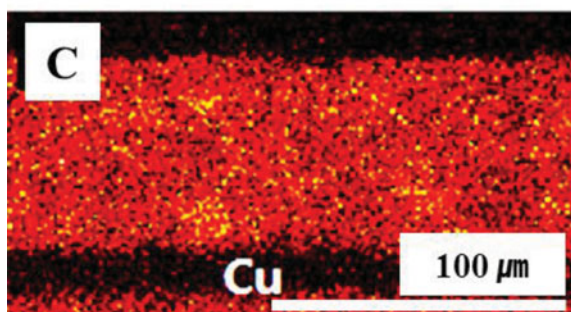


**Figure 6.** Cross-section images of (a) Li, (b) F, (c) P and (d) C element for degraded graphite electrode obtained by ToF-SIMS after severe charging–discharging cycling (0°C and high 30 C-rate).





(a)



(b)

**Figure 7.** Cross-section images of (a) Li and (b) C element for degraded graphite electrode measured by ToF-SIMS after severe charging–discharging cycling (25°C and high 30 C-rate).

whereas the dark color of carbon (C) was observed at the surface area. Accordingly, the mapping images of Fig. 6 clearly illustrated that Li, F and P elements were densely accumulated at surface instead of carbon (C). These elements were originated from the accumulated products of EC, DEC, EMC and LiPF<sub>6</sub> electrolyte in LIB cell. Also, it is clear that the elemental accumulation was observed at graphite surface after severe charging–discharging cycling (0°C and high 30 C-rate). In contrast, no elemental accumulation was observed at the graphite surface after severe charging–discharging cycling under RT, as shown in Fig. 7.

#### 4. Conclusions

To clarify the degradation mechanism of the graphite electrode for the fast charging–discharge process under LT condition, this article employs a new analytical method that can investigate the structure changes and elemental distributions in the cross-section of battery electrode without air exposure under low and room temperatures. The SEM, TEM, and ToF-SIMS analyses illustrate that the Li, F, and P elements were accumulated only at the surface of graphite electrode, which was prepared under severe charging–discharging process with low temperature and high C-rate. In particular, the SEM and TEM results revealed that the surface of graphite electrode was changed from crystalline to amorphous state with cracks on the damaged area (~10 μm thickness) in partial. These measurement results will provide one of the important clues for understanding the degradation mechanism during fast charging–discharging cycling under low temperature ambient.

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## References

- [1] Scrosati, B., & Garche, J. (2010). *J. Power Sources*, 195, 2419.
- [2] Armand, M., & Tarascon, J. M. (2008). *Nature*, 451, 652.
- [3] Zhang, Z., Zeng, T., Lai, Y., Jia, M., & Li, J. (2014). *J. Power Sources*, 247, 1.
- [4] Honkura, K., & Horiba, T. (2014). *J. Power Sources*, 264, 140.
- [5] Ansean, D. et al. (2016). *J. Power Sources*, 321, 201.
- [6] Ning, G., Haran, B., & Popov, B. N. (2003). *J. Power Sources*, 117, 160.
- [7] Chuangfeng, H., Pingan, L., & Xueyan, J. (2011). *Procedia Eng.*, 15, 2619.
- [8] Harks, P. P. R. M.L., Mulder, F. M., & Notten, P. H. L. (2015). *J. Power Sources*, 288, 92.
- [9] Takahashi, K., & Srinivasan, V. (2015). *J. Electrochem. Soc.*, 162(4), A635.
- [10] Langenhorsta, F., & Solozhenko, V. L. (2002). *Phys. Chem.*, 4, 5183.
- [11] Bhattacharya, S., Riahi, A. R., & Alpas, A. T. (2011). *J. Power Sources*, 196, 8719.
- [12] Ebner, M., Marone, F., Stampanoni, M., & Wood, V. (2013). *Science*, 342, 716.
- [13] KC, S., Longo, R. C., Xiong, K., & Cho, K. J. (2014). *J. Electrochem. Soc.*, 161(11), F3104.
- [14] Sethuraman, V. A., Hardwick, L. J., Srinivasan, V., & Kostecki, R. (2010). *J. Power Sources*, 195, 3655.
- [15] Birkel, C. R., Roberts, M. R., Mcturk, E., & Bruce, P. G. (2017). *J. power Sources*, 341, 373.