

STRUCTURAL CHANGE OF LITHIUM ION BATTERY CAUSED BY REPETITIVE CHARGE AND DISCHARGE

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ABSTRACT

Lithium ion battery is one of the most promising technologies for electric power storage and soft energy path. However, inadequate handling of Lithium ion battery may cause spontaneous ignition. To reduce the risk of such accidents, changes of Lithium ion battery during repetitive charge and discharge cycles were investigated. By 400 cycles of charge and discharge, battery capability was reduced to about 80% of new one. After charge/discharge experiment, composition of organic materials in the electrolyte was analyzed by GC-FID. Gradual rise of diethyl fluorophosphate concentration in the electrolyte was observed. Surface structures of the electrodes were also investigated by SEM and XRD. XRD data of anode electrode also showed gradual decrease of diffraction angle. This suggests the increase of lattice constant during the deterioration process. Reflecting such structural change of molecular scale, morphological change of electrode surface was also observed. Surface grain of cathode electrode had more numbers of cracking with increasing cycle numbers. Image of cell volume change was captured by X-ray CT. Volume expansion of battery occurred in rectangular 006P type battery. These results may be caused by asymmetric dissociation and association of Lithium ion on the cathode surface.

Keywords: Lithium ion battery; deterioration; discharge curve; volume expansion.

1. INTRODUCTION

Conservation of fossil resource consumption is a crucial issue in environmental problems. It will help reduction of carbon dioxide emission and reservation of natural resources (IEA, 2012, IPCC, 2013). Utilization methods of natural energy as electricity source are explored for replacement of fossil energy resources. Solar and wind energy are the most expected natural energy source, except for the hydroelectric power, because of their vast amount of potential energy resource. Conversion efficiency of photovoltaic (PV) cell reached over 40%. PV electric power generation is useful enough in some cases, such as distant place from large power plant or desert area where agricultural production is low because of little rain fall. Over all energy cost of windmill electric power became almost the same order to that of fossil energy resources, such as oil or liquid natural gas. The largest obstacle of introducing such natural energy is the instability of power generation. Power production of solar PV cell and windmill are largely dependent upon the weather of the place. If storage of electric power in large scale is possible,

natural energy become practical solution. In this context, high energy density battery is the key technology for next generation power management.

Li-ion battery is one of the most expected technology for its high energy density per weight. It is used for mobile use for cellular phone, camera, computer and so on. Now it's application for vehicles is already spreading all over the world, for automobiles and airplanes. Especially in case of transportation equipment, safety related issues are considered of highest importance. Self-ignition of Li-ion battery is a threat for use in large scale. To avoid such an accident, a Li-ion battery cell is equipped with multiple safety devices, namely, over current fuse, temperature fuse, voltage limiter and so on. These devices are efficient as foolproof system for inappropriate use of battery or human error. However, accident arose from chronic deterioration of battery characteristics is not well understood. In this study, the chemical and physical characteristics of Li-ion battery were investigated to clarify the chronic change of the cell during repetitive charge and discharge process. Discharge characteristics after repetitive charge/discharge were measured in 0-400 cycles. Degradation in the cycles is also analyzed by chemical analysis of electrolyte and XRD of electrode. Macro and micro scale morphological change was investigated by X-ray CT images and SEM observation of electrodes.

2. METHODOLOGY

2.1 *Li-ion batteries specimens*

In the experiments, commercially available Li-ion batteries, with LiCoO₂ cathodes electrode and graphitized carbon anode electrode, were used as test specimen. 006P type rectangular battery (DLG 022-LEP, 9.6 V, 220mAh, DLG Power Battery (Shanghai) Co., Ltd, China) and 18650 type cylindrical shape battery (Panasonic CGR-18650CH, 2250mAh, 3.6V, Panasonic Co., Osaka, Japan) were purchased.

2.2 *Repetitive charge and discharge experiments*

Deteriorated Li-ion battery specimens were prepared by repetitive charge/discharge cycles and storage periods in this study. Charge and discharge experiments were conducted by connecting the batteries to Programmable Charge/ Discharge Controller, HJ1005SD8 (Hokuto Denko. Co., Tokyo, Japan). Charge and discharge of 006P type battery was performed at 1C rate, but not in fully charged condition to operate under chemically stressed condition, from minimum rated voltage, 8.1 V, to maximum rated voltage, 10 V, at room temperature. CC(constant current) charge current and CC discharge current was 220 mA. Charge time was set to one hour but, if battery voltage reached 10 V maximum in shorter time, charging mode will be changed to constant voltage(CV). Discharge time was also set to one hour but it would end before programed time as it reached the minimum voltage. Charge and discharge of 18650 type battery was performed at 1C rate, commonly used condition, from minimum rated voltage, 2.7 V, to maximum rated voltage, 4.2 V, at room temperature. CC(constant current) charge current and CC discharge current was 2250 mA. CC charging phase ends at 4.2 V and charge to CV mode before the end of charging period. Full charge and full discharge take one hour for each. One charge/discharge cycle was 2.5 hours including resting intervals.

2.3 *Chemical analysis of electrolyte*

Li-ion batteries were disassembled and separated into anode electrode, cathode electrode and separator, for chemical analysis, in glove box AS-800S (Asone Co., Tokyo, Japan), filled with Ar atmosphere. Each part was washed by chloroform solvent in a beaker just after disassembly by keeping dipped for 4 hours. Chloroform soluble chemical fraction was analyzed by GC-FID (Gas chromatograph equipped with a flame ionization detector, GC-14B, Shimadzu, Kyoto, Japan) and GC-MS (Gas chromatograph equipped with a mass spectrometer, GC-2010/GC-MSQP2010, Shimadzu, Kyoto, Japan).

2.4 XRD, SEM and X-ray CT analysis of electrode surface and overall morphology

X-ray diffraction (XRD) analysis was conducted by XRD Ultima IV diffract meter (Rigaku, Tokyo, Japan), using Cu K α radiation over two-theta values of 5 to 70 $^{\circ}$. Surface diffraction of anode electrode of Li-ion batteries (type 18650), before and after cyclic charge/discharge experiment, was measured to examine the effect of aging and electrode degradation. Surface morphology of anode electrode of Li-ion batteries (type 18650), before, during and after cyclic charge/discharge experiment, was observed by scanning electron microscope (JSM-5200, JEOL, Japan). Overall morphological change of Li-ion batteries (type 006P) by cyclic charge/discharge experiment was observed by X-ray computed tomography (inspeXio SMX-225CT).

3. RESULTS AND DISCUSSIONS

Discharge curve of 18650 type Li-ion battery, in 1C constant current condition, is shown in Figure 1. Battery capacity decreased as it suffered repetitive charge and discharge cycles. After 400 cycles, capacity was decreased to about 80% of new one.

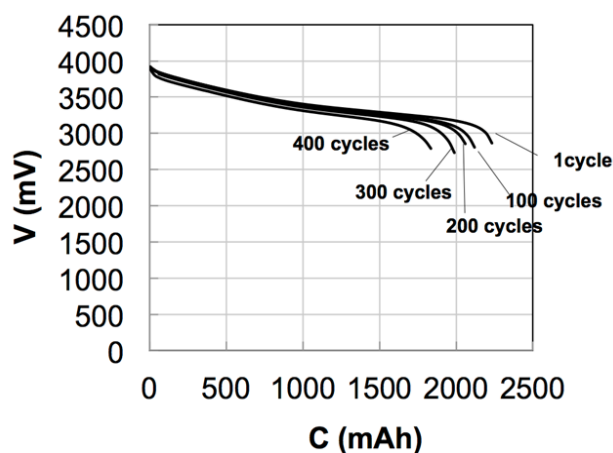


Figure 1: Discharge curves of a 18650 Li-ion battery after different numbers of repetitive charge and discharge cycles. Reproduced from Kato et. al (2014).

3.1 Chemical and physical change of degraded battery

In GC-FID analysis of electrolyte, specific peak of diethyl fluorophosphate was observed. As shown in Figure 2, the peak area ratio to that of inner standard increased with the number of charge and discharge cycle. Original electrolyte of Li-ion battery does not contain diethyl fluorophosphate, so it may be a reaction product of lithium hexafluorophosphate and ethylene

carbonate in the electrolyte. Along with the change of chemical components, increase of lattice constant was observed by XRD in anode electrode, as shown in Figure 3. Shift of diffraction angle is in good accordance with the decrease of battery capacity.

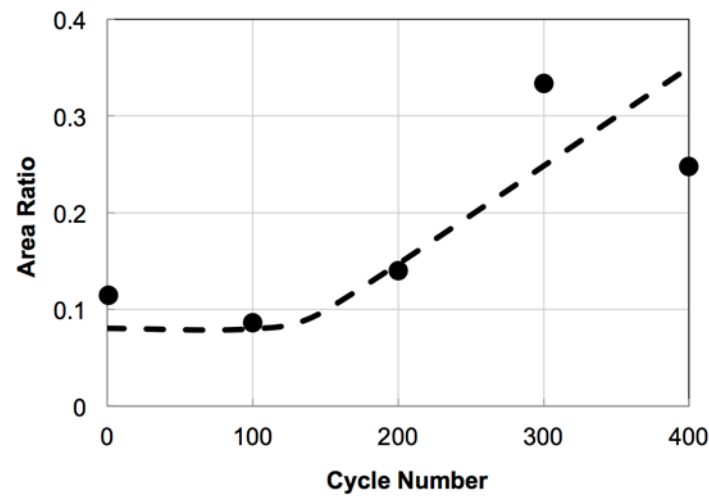


Figure 2: Concentration change of diethyl fluorophosphate in the electrolyte of 18650 Li-ion batteries by repetitive charge and discharge cycles. Reproduced from Kato et. al (2014).

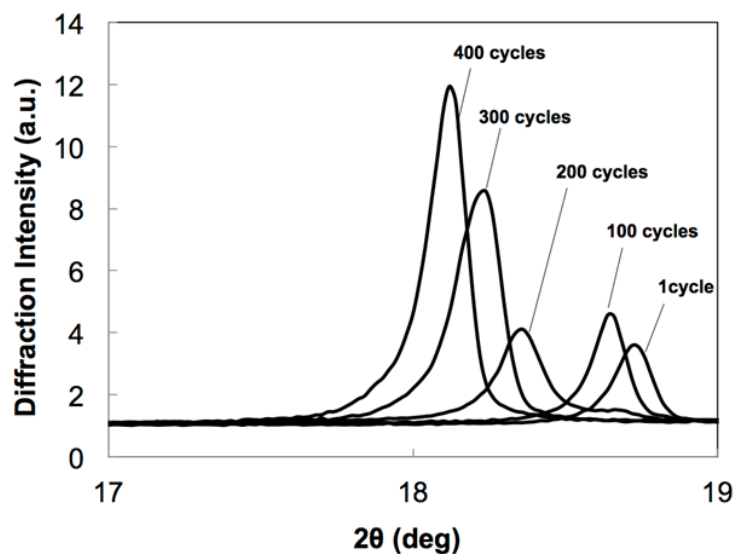
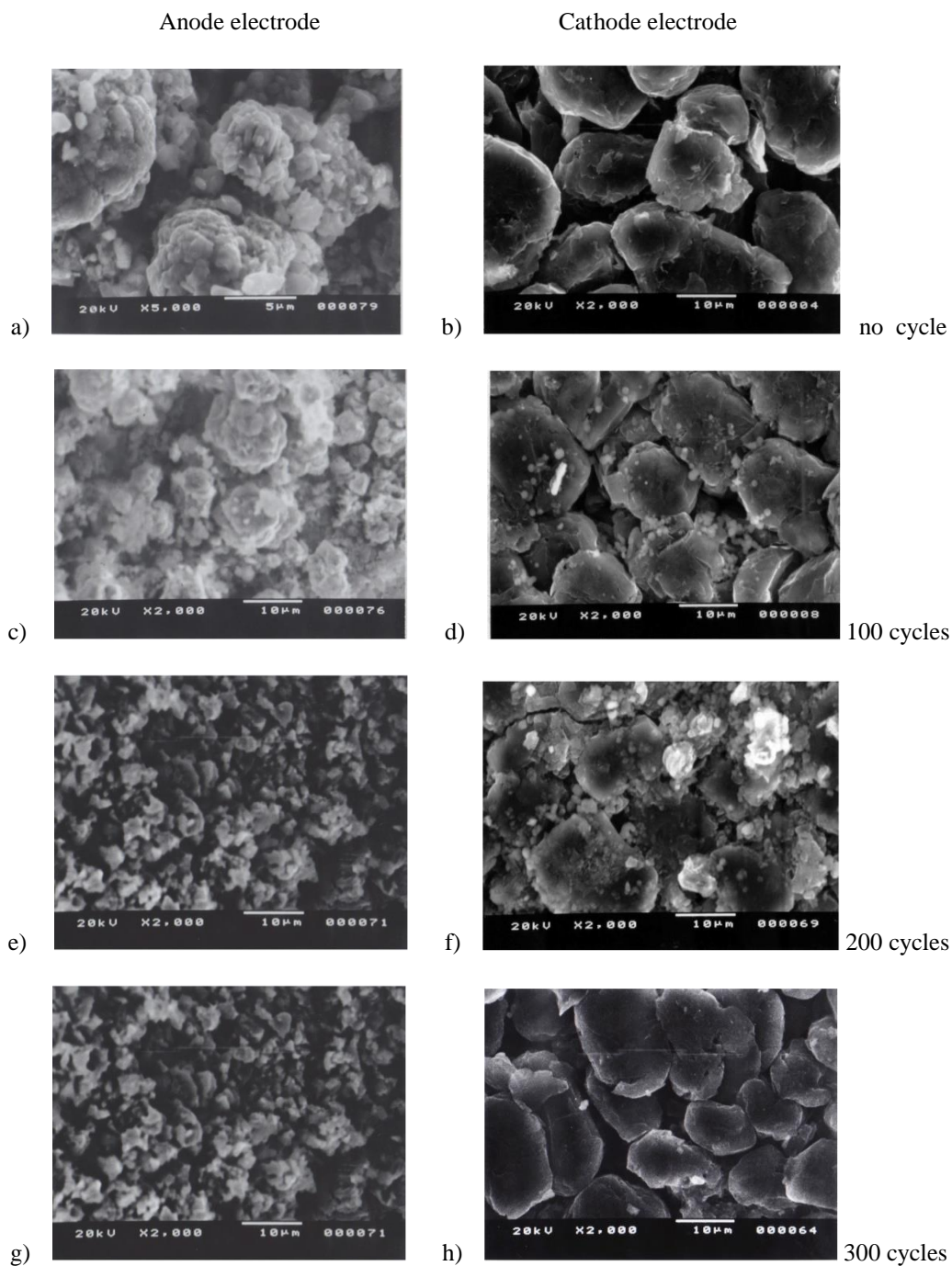


Figure 3: X-ray diffraction of 18650 Li-ion batterie's anode electrodes surface, suffered 1-400 cycles of charge and discharge. Reproduced from Kato et. al (2014).

3.2 SEM observation of electrode surface

Morphological change of anode and cathode electrodes surface structure, captured by SEM were shown in Figure 4. LiCoO_2 layer is polycrystalline and has porous structure of submicron sized granule. The texture of anode electrode showed no significant change by degradation of battery in spite of the shift of lattice constant with the battery degradation. On the other hand, deposition of submicron size granule can be observed on the cathode electrode. Deposition area

is inhomogeneous and so the amount found in each image is not proportional to the decrease of capacity.



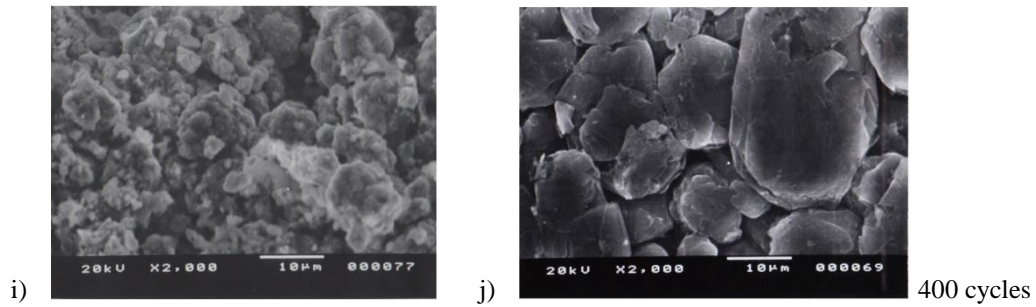


Figure 4: SEM images of Li-ion battery 006P anode and cathode electrodes surface, after respective charge/discharge of 0 – 400 cycles.

3.3 X-ray CT images and reconstructed structure

X-ray CT image and re-constructed stereo model of 006P Li-ion battery were shown in Figure 5 and 6. Volume expansion of the battery after 1500 cycle charge and discharge is found in Figure 5 b), compared with original volume. In Figure 6, increasing widening of electrode gap can be seen along with the cycle number. This extension of layer spacing causes the volume expansion in Figure 5.

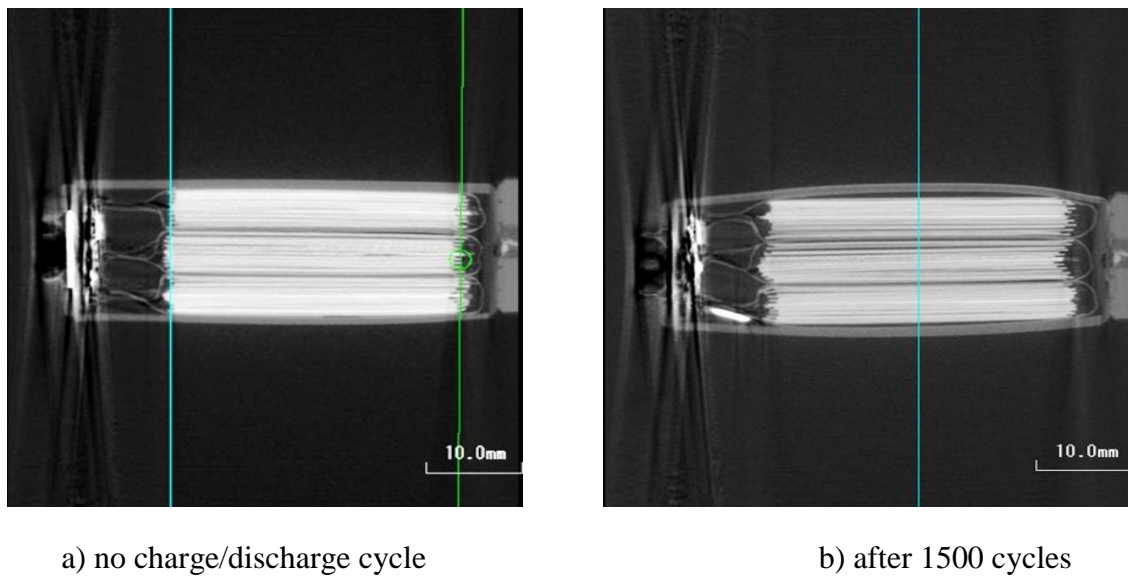


Figure 5: X-ray CT images of 006P Li-ion battery, before and after 1500 cycle charge and discharge cycles. Volume expansion of deteriorated battery can be seen in plate b).

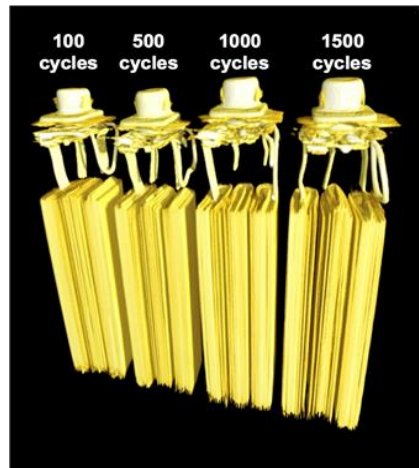


Figure 6: Reconstructed 3D image of 006P type Li-ion battery. Electrode gap is spreading with the number of charge and discharge cycle, which provides inner force to expand battery shell volume.

4. DISCUSSIONS AND CONCLUSIONS

4.1 Morphological change of electrode surface and chemical deposition

Chemical change of electrolyte and physical change of anode electrode materials were measured for 18650 Li-ion batteries with increase number of charge and discharge cycles. Concentration of diethyl fluorophosphate in the electrolyte increased with degradation of the battery. This chemical specie doesn't exist in the original electrolyte, but may be produced by chemical reaction of hexafluorophosphate ion and solvent such as ethylene carbonate or propylene carbonate. This result clearly shows the change of chemical composition of the electrolyte, which also suggests coincidence of some associated chemical reactions, on the surface or in the bulk of the electrodes. Actually deposition of granular material was observed on the SEM images in Figure 4, especially on the cathode electrode. Deposition was limited to local area and does not cover the total surface of the electrode, so the increase of inner resistance may be small and this phenomenon cannot give complete explanation of energy capacity loss. There should be some invisible change by morphological observation.

4.2 Volume expansion of the cell and shift of crystal structure

Actually lattice constant of anode electrode was continuously expanded during the degradation of the battery. The expansion of lattice constant suggests that crystal structure change occurs in some region of LiCoO_2 crystal domain and it spread gradually with decrease of battery capacity. It gives an assumption that, the altered crystal structure has less or no Li-ion intercalation domain, and as a result, less amount of Li-ion in the electrolyte can exchange electron on the anode surface. This hypothetical mechanism is supported by the expansion of cell volume. If it were caused by the increased volume of electrolyte or gaseous chemical product, expansion of electrode gap won't occur as can be seen in the Figure 6. Possible mechanism of electrode gap expansion is volume or aspect ratio change of the anode material as crystal structure shift from active layered rhombohedral structure to inactive spinel structure (Santiago, Andradeb, Paiva-Santos & Bulho 2003).

5. OVERALL CONCLUSION

Chemical and physical change of Li-ion battery cell was observed through repetitive charge and discharge experiments. The deposition of chemical product in the electrolyte was observed but reduction of battery capacity cannot be fully explained only by the coverage of electrode surface by the deposition. Qualitative change of anode electrode material was found as increase of lattice constant, which is reflected as volume expansion of battery. Total deterioration of battery performance, by repetitive charge and discharge, is estimated to be caused by both deposition of chemical by-product and alteration of electrode material.

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