Technical Paper

Chemical and Physical Deterioration of Lithium-ion Battery

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The life cycle assessment of lithium-ion (Li-ion) rechargeable battery was evaluated by charge and discharge processing. The influence of the temperature was studied during several hundred cycles of charge/discharge process of Li-ion battery. The charging capacity was observed to be decreased with increased number of cycle, especially at higher temperature of the environment of 60°C. The cathode of Li-ion battery was found to be affected by heat stress and charge/discharge cycles by XRD analysis. The GC-FID and GC-MS studies revealed that the diethylfluorophosphate (DEFP) is a degraded product of electrolyte. Though the decomposition of ethylene carbonate (EC), a major component of the electrolyte in the Li-ion battery was not clearly found, the relative area of DEFP to that of EC was found to be increased with increased charge /discharge cycle number at 60°C.

リチウムイオン二次電池の経年使用に伴う性能劣化の評価を、充電 / 放電サイクルを数百回繰り返すことにより行った。室温と60°Cで実験を行うことにより、環境温度の影響も検討した。充電容量は、使用開始時には60°Cの方が高かったが、使用とともに速く減少した。60°Cでは電池正極であるLiCoO₂結晶格子の面間隔は、サイクル数の増大とともに拡大する様子がXRDより観察された。電解液のGC-FIDおよびGC-MSにより炭酸エチレンが主要な成分であり、またジエチルフルオロリン酸エステルが分解生成物として検出された。後者の前者に対する相対比は、60°Cにおけるサイクル数の増大とともに増大した。

Key Words

Lithium-ion, Electrolyte, Charge and discharge, Lattice spacing

1. Introduction

One of the most promising battery types under development for use in both pure electric and hybrid electric vehicles is the lithium-ion (Li-ion) battery. The development of Li-ion batteries has been rapid since their introduction in the mid-nineties. These batteries are well on their way to meet the challenging technical goals that have been set for vehicle batteries.

Currently Li-ion batteries are one of the most attractive targets of many chemists in terms of strict requirements in instantaneous power and energy density. There exist a large number of different types of Li-ion batteries, ranging from low-cost mass-produced batteries used in portable electronic devices such as laptop computers and mobilephones. Several new manufacturers are targeting application of Li-ion batteries to electric vehicle market, though market scale is still small compared

to the production of batteries for portable electronic devices. Moreover, there are a large number of different electrochemical designs of Li-ion batteries, each with advantages and disadvantages related to cost, performance, cycle life and safety.

Considering safety and production cost, one of the most promising battery type is the LiFePO₄-based Li-ion rechargeable battery, introduced to the market in recent years^{1) 2)}. Lifetime of Li-ion batteries for electric vehicles is still uncertain. All rechargeable batteries show a decreasing performance with usage and/or time. That is, the capacity, measured as the ability to repeatedly store and release electricity, decreases. Likewise, the battery's ability to be charged or recharged at high electric power is reduced with the used time and the number of charge/discharge cycles. This storage ability reduction in battery performance is usually referred to as battery ageing (deterioration). For Li-ion batteries, it has been shown that the performance is affected by both storage time and usage, often categorized as calendar ageing years and cycle numbers.

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The deterioration of the battery is usually quantified as instantaneous power and capacity as a function of number of charge/discharge cycles. Deterioration mechanism of Li-ion batteries is complex and affected by the operating conditions^{3)~6)}. In some cases it is possible to assign the observed deterioration to a certain ageing process⁷⁾⁸⁾. It is typically the case that the battery is used under extreme conditions such as elevated temperatures³⁾ and high rate charging⁹⁾¹⁰⁾, or it is charged up to high state of charge (SOC) levels. Though conditions are optimized to lengthen the total battery life in the standard usage of the batteries, the observed deterioration is the result of several processes. Furthermore they are sometimes coupled together and cannot be regarded as independent⁶⁾¹¹⁾.

In this study, cylindrical types of commercial grade Li-ion batteries were used for elucidation of deterioration mechanism. The performance change, including capacity fading was measured and electrolyte components were analyzed for cycled and stored batteries. By the comparison of batteries stored at 25 °C and those charge/discharge cycled at 60 °C, charge/discharge effect under elevated temperature on deterioration was examined. The structure of the electrode surfaces before and after storage/cycles was measured by X-ray diffraction (XRD). Chemical components of electrolyte were analyzed by gas-chromatograph (GC) and gas-chromatograph mass-spectrometer (GC-MS).

2. Material and methods

2.1 Li-ion batteries used in experiments

In this experiment, we used commercial-grade Li-ion batteries with LiCoO₂ as cathodes and graphitized carbon as anodes. Cylindrical type (type 18650, 18 mm in diameter and 65 mm in length) batteries of Panasonic CGR-18650CH (2150 mAh, 3.6 V, Panasonic Co., Osaka, Japan) were used.

2.2 Charge and discharge experiment

Simple and standardized cycles were used. The most commonly used cycle life test, is the one hour full charge and one hour full discharge profile (named 1C rate) using the full battery capacity (0-100%, SOC) at room temperature.

Deteriorated Li-ion batteries were prepared by using the charge/discharge cycles and storage periods in this study. Device for full charge and full discharge used was HJ1005SD8 (Hokuto Denko. Co., Tokyo, Japan). Charging condition was the constant current charging (2250 mA, corresponding to 1C-rate, defined as one hour full charge current) up to the maximum charging voltage of 4.2 V and discharging condition was also the constant current

charging (2250 mA) up to 2.7 V. One charge/discharge cycle was 2.5 hours including intervals for Panasonic CGR-18650CH.

2.3 Li-ion battery deterioration by heat stress experiment

Accelerated test methods are important for development of new Li-ion batteries. The combination of a narrow temperature range and non-linear temperature ageing processes often cause the difficulty of the results analyses. Hence in order to find an efficient and reliable method for significantly reducing the time to evaluate battery lifetime, we firstly stored the batteries at 25°C with and without cycles. For the comparison, we also conducted charge/discharge cycles at 60°C in an incubator OFW-300B (Asone Co, Tokyo, Japan) and charge/discharge effect under elevated temperature was examined.

2.4 Disassembly of battery and chemical analyses

Li-ion battery samples were disassembled under Ar-filled glove box AS-800S (Asone Co., Tokyo, Japan). Batteries were disassembled and separated into anode, cathode and separator, respectively. Each part promptly was steeped in chloroform solvent in a beaker and kept for 4 hours. Chloroform soluble 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).

2.5 Analysis of anode active material by X-ray diffraction (XRD)

X-ray diffraction (XRD) studies were conducted on anode samples obtained from commercial Li-ion batteries (type 18650) to examine the effect of battery aging on electrode degradation. The data were obtained from XRD Ultima IV (Rigaku, Tokyo, Japan) diffract meter using CuK α radiation for two-theta values from 5 to 70°.

3. Results and discussions

3.1 Battery capacity and cycle deterioration

Deterioration of Li-ion battery capacity may also be caused by changes in surface properties such as porosity and tortuosity⁹⁾. In this reasoning it is important to state that the available capacity might be further reduced by an increased voltage drop due to a rise of battery impedance that prevents the battery from being fully discharged (or charged) at a specific current. In many cases, the capacity loss and battery impedance rise are clearly correlated¹²⁾¹³⁾.

The mechanisms of Li-ion battery power fade and

impedance rise are summarized as follows; (1) surface film formation of both electrodes (anode and cathode) with low conductivity^{14) ~ 16)}, (2) reduction of electrode area and loss of electrode material leading to a higher local current density¹⁷⁾, (3) lower diffusivity of Li-ions into active electrode particles and slower kinetics (increased charge transfer resistance) due to surface film formation¹⁷⁾.

The lifetime of a conventional Li-ion battery is said to be about some hundred cycles between the fully charged and fully discharged conditions. Fig. 1 shows change of discharge characteristic V-A curve of Li-ion batteries with increased charge/discharge cycle numbers at 25°C. Fig. 2 also shows change of discharge characteristic V-A curve by charge/discharge at 60°C. While the initial power voltage was around 3.9 V just after the full charge at 4.2 V, the voltage was gradually

Fig. 1 Change of characteristic V-A curve at discharge with cycle number(at 25°C)

Fig. 2 Change of characteristic V-A curve at discharge with cycle number (at 60°C)

Fig. 3 Deterioration with cycle number

decreased and then started to drastically decrease at around 3.0 V. Hence the Li-ion battery capacities usually defined as that from full charge to 2.7 V. The battery capacity was reduced by around 20% after 400 cycles at 60 °C heat treatment. The Li-ion battery deterioration was found to be a little faster by charge/discharge at 60°C than at 25°C.

Fig. 3 shows the change in the battery capacity in mAh defined as above with increased cycle number when commercial Li-ion batteries are fully charged and fully discharged up to 400 times at 25°C and 60°C. Though the difference in the results between two temperatures is not so large, it looks the capacity of fresh battery at 60°C is a little larger than that at 25°C, while the deterioration phenomena observed as the reduction in battery capacity proceeds more rapidly at 60°C than at 25°C.

These results indicate that (1) surface film formation of both electrodes (anode and cathode) with low conductivity, (2) loss of electrode area and electrode material leading to a higher local current density, (3) lower diffusivity of Li-ions into active electrode particles and slower kinetics due to surface films, (4) reduced conductivity between particles due to both surface films and degradation of binders. Eventually, deterioration of rechargeable Li-ion battery advance to power fade with complex deterioration mechanisms.

3.2 Crystal structural determination by X-Ray Diffraction

Graphite is widely used as anode material for Li-ion batteries; graphite is not electrochemically stable when used together with commonly used electrolytes¹⁾. A Li-ion battery is rechargeable battery in which Li-ions move from the anode to the cathode during discharge and back when charging. As the battery is charged for the first

time, Li-ion reacts directly with the graphite to form a thin solid surface film (SEI, Solid electrolyte interface) mainly consisting of Li_2CO_3 , alkyl-carbonates, and polymers¹⁸⁾. SEI is very thin and its conductivity for Li-ion remains sufficient to enable an efficient intercalation of Li-ions into the graphite particles. On the other hand, a too thin SEI allows electrons to tunnel through the film, in turn enabling other side reactions and further SEI formation. Consequently, SEI continues to grow until a steady-state thickness is established, usually reaching after the few first cycles. Further SEI formation has a significant effect on the impedance of the battery. Thin SEI is needed to limit the direct reaction of the graphite with the electrolyte. It has been shown that the SEI formed at low to medium temperature partly dissolves at high temperatures, exposing the graphite surface to further reaction with electrolyte and Li-ion is subsequently consumed. The volume change occurring in the graphite particles upon intercalation/ de-intercalation of Li-atom might lead to micro cracks in the surface film, which also exposes the graphite to further SEI formation. SEI formation is according to directly linked to the Li- corrosion^{19) 20)}.

X-ray diffraction (XRD) studies were conducted on anode samples obtained from charge/discharge cycled commercial Li-ion batteries to examine the effect of battery aging on electrode degradation. While active material of anode is thought to repeatedly expand and constrict in volume and transformation of crystal structure during charge/discharge processes is expected, the clear graphite peak was not observed in the XRD chart of anode of the batteries.

The XRD charts of the cathode of Li-ion batteries of before and after charge/discharge cycles are shown in Fig. 4. The typical LiCoO_2 peaks are clearly observed. Among the many peaks, in the present study, we noted the peak of LiCoO_2 at around $2\theta = 19$ deg, the maximum one.

The magnified chart between $2\theta = 17$ deg and 19 deg is shown in Fig. 5. The peaks of XRD of cathode discharged

Fig. 4 XRD analysis result of anode (at 60°C)

Fig. 5 XRD analysis result of anode active material, LiCoO_2 (at 60°C)

Fig. 6 Change of lattice constant with cycle number (at 60°C)

Li-ion battery clearly shift from at around $2\theta = 19$ deg to lower angle site with increased number of cycles. Lattice spacing of LiCoO_2 was thought to be gradually shifted to lower angle site with increased charge and discharge cycle numbers. This results means Li-ion goes and returns preserved layered structure during discharge and charge.

The lattice spacing, d , is calculated from the peak position by using the Bragg equation. Fig. 6 shows the change of lattice spacing calculated from peak value of θ in Fig. 5 with increased number of charge/discharge cycle. Lattice spacing of LiCoO_2 was gradually stretched with increased charge/discharge cycle numbers. This can be speculated these data mean that Li-atom of active material is gradually accumulated in graphite phase during charge/discharge process of Li-ion battery.

3.3 Battery deterioration and degradation of electrolytes

Graphite is one of the common anode materials for Li-ion batteries operating in organic electrolytes, such as LiPF_6 , with co-solvents like ethylene carbonate (EC),

dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC) and so on, denoted as $(RO)_2CO$. The reaction of the anode with the electrolyte solution in the formation stage results in the formation of species such as $ROCO_2Li$ and CO_2OLi_2 , on the anode surface. The layer formed by these species is referred to as the solid electrolyte interphase (SEI). The $ROCO_2Li$ can undergo reduction reaction with CO_2 and traces of H_2O in the electrolyte to form Li-carbonate which further react with EC²¹⁾. At higher battery potentials, during the intercalation of Li-ions into the anode lattice structure, the graphite anode oxidizes. At this potential, electrolyte co-solvents, such as EC, which is highly reactive, react with the Li-ions and the reaction products quickly precipitate and grow on the anode surface^{22) 23)}. The presence of these reaction products on the surface retards the intercalation kinetics of the carbon anode²⁴⁾. The surface layer grows in thickness as the decomposition reaction continues^{25) ~ 29)}.

Main component of electrolyte was identified as EC in used Li-ion battery by GC-FID and GC-MS. Also, ethylmethyl carbonate and diisopropyl carbonate were identified as electrolytes in chloroform soluble fraction by GC-MS analysis. In the present study, the change in EC amount or those of other solvents was not clearly observed in the batteries with cycle number, because our extraction process of the co-solvents was deficient. Degradation of nonaqueous liquid electrolytes for Li-ion batteries was studied³⁰⁾. However we considered that the amount ratio of some product to the raw material of EC may be an index of deterioration.

Diethylfluorophosphate was identified as main degraded compound in Chloroform soluble fraction by GC-MS analysis. The peak area of diethylfluorophosphate was divided by that of EC and the change with cycle number is

Fig. 7 Change of diethylfluorophosphate concentration (relative area ratio to ethylene carbonate) with cycle number

shown in Fig. 7 in heat accelerated test of Li-ion battery by repetition of charge and discharge at $60^\circ C$. Relative amount of diethylfluorophosphate gradually increased with repetition of charge/discharge cycles. The source of phosphate is suggested as follows. $LiPF_6$ was proposed as an electrolyte solute for Li-based batteries in the 1960s. $LiPF_6$ chemical and thermal instabilities were known³¹⁾. The generation of the gaseous product, PF_5 , derives the equilibrium to the right and this process is favored by elevated temperatures. In the presence of non-aqueous solvents, the strong Lewis acid PF_5 tends to initiate a series of reactions with electrolytes in Li-ion battery, such as ring-opening of EC or cleavage of ether linkages of EC. The P-F bond is rather labile toward hydrolysis by even trace amounts of moisture in non-aqueous solvents, producing a series of corrosive product. Hence this diethylfluorophosphate was suggested to be derived from $LiPF_6$ and ethylene carbonate as main degradation product in Li-ion battery by deterioration processes.

4. Conclusion

The charging capacity was observed to be decreased with increased number of cycle, especially at higher temperature of the environment of $60^\circ C$. The $LiCoO_2$ crystal used as the cathode of Li-ion battery was found to stretch with increased cycle number at $60^\circ C$. The ethylene carbonate (EC) and the diethylfluorophosphate (DEFP) were found to be the main component and a degraded product of electrolyte. The relative amount of DEFP to EC was found to be increased with increased charge/discharge cycle number at $60^\circ C$.

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