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Effect of diphenylethane as an electrolyte additive to enhance high-temperature durability of $LiCoO_2$/graphite cells

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ABSTRACT

We have studied a new electrolyte additive, 1,1-diphenylethane (DPE), to $LiCoO_2$/graphite cells to reduce capacity loss during high temperature storage. It is demonstrated to be effective to reduce polarization after storage at 60 °C for one month in charged state. In half-cell tests, a $LiCoO_2$/Li cell with DPE additive in electrolyte shows less capacity loss than that without DPE, while no significant difference is observed between DPE-added and DPE-free graphite/Li half cells. Scanning electron microscopy, X-ray diffraction, electrochemical impedance spectroscopy, time of flight-secondary ion mass spectroscopy, and hard X-ray photoelectron spectroscopy measurements are applied to elucidate the mechanism how DPE suppresses the increase in electrode resistance and polarization during the high temperature storage. All the results consistently show that less amount of surface layer is formed by electrolyte decomposition on $LiCoO_2$ electrode surface in DPE-added electrolyte than the DPE-free one, leading to reduction of the electrode resistance and polarization.

1. Introduction

Lithium-ion batteries are one of major batteries all around the world, which are widely used from pocketable mobile electronics to electrified vehicles such as pure electric vehicles and plug-in hybrid electric vehicles. However, they still have some technical issues such as flammability of electrolyte solution, capacity and power degradation at low temperatures, and insufficient durability in high-temperature storage. The former two issues are due to the intrinsic properties of battery materials and require the development of new electrolyte or active material, while the latter seems to be approached by other strategy. Operation of lithium-ion batteries at high temperatures from 40 to 60 °C does not cause crucial damage to electrode active materials, *e.g.*, oxygen loss from charged positive electrodes. Therefore, we assume that high-temperature durability can be improved by surface modification of electrode materials through changing and/or tuning the electrolyte compositions of solvent, lithium salt and additive.

It is well-known that many kinds of electrolyte additives are already in use for commercial lithium-ion batteries [1,2]. Their functions are related to the formation of negative electrode passivation film, so-called SEI [3–5], positive electrode protection [6], overcharge protection [7], gas evolution suppression, etc. Among them, electrolyte additives for negative electrodes were reported actively in the many publications so far, because the formation of stable SEI is necessary to stabilize the interface at negative electrodes/electrolyte of lithium-ion batteries. On the other hand, we find less number of papers on additives for positive electrode protection compared to those for negative electrodes because of the lower reactivity of positive electrodes to electrolyte than negative ones under their normal operation conditions. However, additives for positive electrodes play a very important role when the cells are used under extraordinary conditions such as overcharge and high temperatures. Charged state of positive electrodes is merely metastable state in general, therefore, high temperatures must be severe and critical conditions for the electrodes, which require some countermeasure to cope with them by forming stable interface between the active material and electrolyte. To use electrolyte additives is a quite simple and inexpensive way to solve an issue of high temperature degradation of lithium-ion batteries among many ideas for the issue.

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The number of previous works on electrolyte additives affecting to positive electrodes is limited; one category is for overcharge protection using such as benzenoid compounds [7,8], and another is for high temperature durability. Although most of the papers on the additives for high temperature durability describe regarding to negative electrodes [9–11], a previous literature reported on the effect of 1,1-diphenylethylene as a new additive which suppresses the degradation of $LiCoO_2$ electrodes at a high temperature [12]. In the literature, 1,1-diphenylethane is also listed as a reference material without any test results on the additive effect and detailed mechanisms. Therefore, in this paper, we report the effect of 1,1-diphenylethane (DPE) on the high temperature durability and elucidate the working mechanisms. Although there are many choices of positive electrode material, we chose $LiCoO_2$ as the first sample of our study on DPE additive, because $LiCoO_2$ is conventional and one of the most well-characterized positive electrode materials for lithium ion batteries. Therefore, we chose $LiCoO_2$/graphite as a model cell chemistry and applied DPE as an additive to improve high temperature durability of the cell chemistry. The effect and the mechanism were examined in detail by employing scanning electron microscopy, X-ray diffraction, electrochemical impedance spectroscopy, time of flight-secondary ion mass spectroscopy and hard X-ray photoelectron spectroscopy. From these results, we will discuss the factors affecting the degradation of electrode materials at elevated temperatures.

2. Experimental

2.1. Materials and electrode preparation

Positive electrodes consisted of commercially available $LiCoO_2$ as an active material, acetylene black (AB) as conductive agent, and poly (vinylidene fluoride) (PVdF) binder with the ratio of 85: 5: 10 (w/w). Negative electrodes consisted of artificial graphite, conductive agent AB, and PVdF binder with the ratio of 94: 1: 5 (w/w). After preparation of each homogenous NMP (*N*-methylpyrrolidone) slurry containing the ingredients, each slurry was carefully spread on aluminum and copper foils for $LiCoO_2$ and graphite electrodes, respectively, by a blade coater and dried, followed by punching into discs 10 mm in diameter.

R2032 coin cells were assembled with the two electrodes in an argon-filled glove box, a multilayered polyolefin separator (Ube, Upore UP3025) and 1 M $LiPF_6$/ethylene carbonate (EC): dimethyl carbonate (DMC) (3: 7, v/v) supplied by Kishida Chemical Co., Ltd. We prepared full cells with $LiCoO_2$/graphite, and half cells with graphite/Li or $LiCoO_2$/Li, which were applied to meet the purpose for the individual experiment. As the negative electrode capacities are larger than those of positive electrodes in commercial lithium-ion cells to avoid possible risk of lithium dendrite deposition and to make the cells cycle life long enough, we assembled our full cells to have the capacity ratio of graphite to $LiCoO_2$ to be 1.5. Therefore, this excessive capacity of the graphite electrode results in decrease in the utilization of graphite leading to reduce the effect of capacity fading of the graphite electrode on the full cell capacity and also the fading rate of the graphite electrode in the full cell operation. The electrolyte additive used in this study was 1,1- diphenylmethane (DPE, supplied by JXTG Nippon Oil & Energy Corp.) and the content in the electrolyte was 5 wt% for the full cells and 2 wt% for the Li half cells. The reason why larger amount of DPE was used for the full cells is that the full cells comprise a $LiCoO_2$ electrode, separator, and a graphite electrode of which the two electrodes are porous and absorb much of electrolyte solution and assumed to consume some of the additive by surface reaction at both electrodes.

2.2. Electrochemical measurements

A galvanostatic charge-discharge test was conducted at C/8 rate, 20 mA (g of $LiCoO_2$)$^{-1}$, in the first cycle and C/4 rate after that with voltage ranges of 3.0–4.15 V for full cells, 3.0–4.2 V for $LiCoO_2$/Li cells, and 0.0–0.8 V for graphite/Li cells. The cell temperature during the cycles was usually kept at 25 °C, and was elevated up to 60 °C and kept for one month for full cells or ten days for half cells in the high temperature storage test.

Electrochemical impedance spectra were measured with a potentiogalvanostat (Hokuto Denko Co., Ltd., HZ-3000) and a frequency response analyzer (NF Electronic Instruments, Ltd., FRA 5080S). The test cells were $Li_{0.75}CoO_2$/$Li_{0.75}CoO_2$ symmetric cells [13], which were assembled by disassembling two $LiCoO_2$/Li cells as described below. The applied AC modulation was 10 mV and frequency range was 100 kHz to 10 mHz.

2.3. Characterization

The tested full cells were disassembled after four cycles, inserting 60 °C storage for one month under charged state, to examine the $LiCoO_2$ or graphite electrodes, and the electrodes were rinsed with DMC solvent, and dried in the glove box for electrode characterization. The electrode surfaces were observed with field emission scanning electron microscope (FE-SEM SUPRA40, Carl Zeiss, Ltd.). The crystal structure was examined by an X-ray diffractometer with an X-ray tube of Cu target and a Ni filter (MultiFlex, Rigaku Corp.).

The outermost surface of electrodes tested in full cells after 4 cycles was analyzed by time of flight-secondary ion mass spectroscopy (TOF-SIMS, PHI TRIFT V nanoTof, ULVAC-PHI, Inc.). Hard X-ray photoelectron spectroscopy (HAXPES) spectra were collected by using a SCIENTA R4000 hemispherical electron energy analyzer at synchrotron facility, BL46XU in SPring-8, Japan. The excitation energy used for HAXPES was 7939 eV, take-off angle of photoelectrons was 80°, and the total energy resolution was 235 meV [14].

3. Results and discussion

3.1. DPE effects in full cells and half cells

Fig. 1 shows the first charge and discharge voltage profiles of the full cells consisting of $LiCoO_2$ and graphite with and without DPE used as an electrolyte additive. Both of them are similar except the last part of the discharge curves below 3.75 V, showing a slight difference in discharge capacities and charge reversibility: 128 and 117 mAhh g^{-1} of $LiCoO_2$, and 83 and 76% for the cell with and

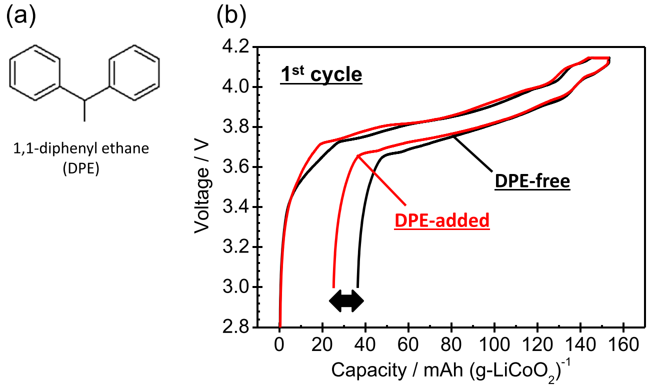

Fig. 1. (a) DPE, and (b) the 1st cycle charge-discharge curves of $LiCoO_2$/graphite cells.