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Short communication

Phosphorus derivatives as electrolyte additives for lithium-ion battery: The removal of O_2 generated from lithium-rich layered oxide cathode

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HIGHLIGHTS

- Phosphorus derivatives can absorb O_2 generated from Li-rich layered oxide cathode.
- The cell internal pressure at the end of charging can be significantly reduced.
- Phosphorus derivatives also improve the cycle life when used as additives.

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ABSTRACT

Direct internal pressure measurements of the cylindrical Li-ion cells with a mixture of $LiCoO_2$ and $Li_{1.167}Ni_{0.233}Co_{0.1}Mn_{0.467}Mo_{0.033}O_2$ (a solid solution between 0.4 $Li_2Mn_{0.8}Ni_{0.1}Mo_{0.1}O_3$ and 0.6 $LiNi_{0.4}Co_{0.2}Mn_{0.4}O_2$) as cathode and graphite as anode have been performed during cell charging. Cell internal pressure at the end of charging is greatly reduced from 2.85 to 0.84–1.84 bar by adding a small amount of phosphorus derivatives such as triphenyl phosphine (TPP), ethyl diphenylphosphinite (EDP), and triethyl phosphite (TEP) into a carbonate-based electrolyte. The phosphorus derivatives are supposed to react with O_2 generated from the decomposition of the Li_2MnO_3 component. The chemical states of additive molecules before and after the charging process have been characterized with a nuclear magnetic resonance (NMR) spectroscopy and gas chromatography–mass spectrometry (GC–MS). It has also been shown that those additives improve the cycle life when applied in coin full cells.

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1. Introduction

Li-ion batteries rapidly become essential for powering today's mobile electronic devices as they exhibit high energy density and long cycle life compared with other rechargeable systems [1]. While the research of electrode materials for Li-ion battery is usually covering how to store more energy repeatedly, the electrolyte research is typically restricted to overcoming its own issues such as enlarging electrochemical window, forming a better SEI layer, increasing ionic conductivity, and improving safety [2]. However, the importance of electrolyte is growing and more functions of electrolyte are demanded for the practical use of advanced Li-ion batteries especially to employ new electrode materials. We show in this study an example of electrolyte design circumventing a safety issue of the cell by scavenging the oxygen gas evolved from cathode material.

A major challenge of Li-ion battery research is to develop systems with even higher energy and power densities, especially satisfying the requirements of electric vehicles or new multifunctional portable electronics. In this regard, Li-rich Mn-based layered oxide cathode materials – denoted below as overlithiated layered oxide (OLO) for simplicity – with a formula of $Li[Li_xMn_yM_z]O_2$, where M represents one or more transition metal elements, are considered to be promising for advanced Li-ion batteries due to their high rechargeable capacity (>200 mAh g^{-1}), good thermal stability, and low cost compared with widely used $LiCoO_2$ [3–8].

Despite those advantages, the charging of OLO cathode over 4.5 V vs. Li/Li^+ causes irreversible decomposition of its surface positioned Li_2MnO_3 component, generating O_2 gas. The reaction can be represented as in Equation (1).

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$$Li_2MnO_3 \rightarrow MnO_2 + 2Li^+ + 1/2O_2 + 2e^- \quad (1)$$

Several research groups showed direct evidence of O_2 generation using *in situ* differential electrochemical mass spectrometry (DEMS) [9–11] and *ex situ* gas chromatography (GC) [12]. Those reports focused on proving the generation of O_2 gas, and efforts to solve the issue in practical battery systems are not yet made. Since the increase in internal pressure might activate the ventilation system of the cell or cause safety problems, the pressure of oxygen inside the cell should be kept as low as possible. Our previous results showed the surface coating of OLO powder or electrode with VO_x, Al_2O_3, or $AlPO_4$ mitigated the evolution of oxygen to a significant extent [13,14]. However, considering the cell might experience elevated temperatures while being used by customers, the possibility of potential oxygen evolution still remains since part of Li_2MnO_3 phase is not activated in the first charging process.

In this study, we demonstrated the reduction of internal pressure to the level of one third by using phosphorus derivatives as electrolyte additives, which can react with O_2 forming stable compounds. It is noted that phosphorus derivatives have occasionally been used as flame retardant for Li-ion batteries [15–18]. For the direct measurement of cell internal pressure, we used cylindrical Li-ion cells of 18650 size linked to a pressure sensor with a blend of $LiCoO_2$ and OLO as cathode and a graphite as anode. Also, we investigated the influence of such additives on the cycle life of coin full cells.

2. Experimental

The overlithiated layered oxide (OLO) powder was synthesized as described in a previous report [19]. The composition of OLO employed in this study was $Li_{1.167}Ni_{0.233}Co_{0.1}Mn_{0.467}Mo_{0.033}O_2$. Cathodes were made of 94 wt.% electrochemically active material (a mixture of 30 wt.% OLO and 70 wt.% $LiCoO_2$), 3 wt.% conductive carbon black (Super P), and 3 wt.% polyvinylidene fluoride (PVDF) binder. A separate cathode made of only $LiCoO_2$ without OLO was prepared as a control sample. The density of active mass layer was controlled at 3.7 g cm^{-3} for all the cathodes regardless of the composition. Jelly rolls comprising the cathodes above, graphite anodes, and polyethylene separators as well as the internal pressure measurement units [20] were provided by Samsung SDI.

Cylindrical cell was fabricated with a jelly roll surrounded by an also cylindrical Teflon spacer filling the void between jelly roll (dia. 10 mm) and cell wall (dia. 18 mm). The bottom of each cell had a hole connected to a pressure sensor (Valcom, VPRF2-2MP). The base composition of electrolytes was 1.3 M $LiPF_6$ in a mixture of ethylene carbonate (EC), fluoroethylene carbonate (FEC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) (1:2:2:5 v/v). In the experiments for evaluating additives, the amount of phosphorus derivatives was set at 5 wt.%. Triphenyl phosphine (TPP), ethyl diphenylphosphinite (EDP), and triethyl phosphite (TEP) were purchased from Aldrich and used without further purification.

The cell internal pressure was monitored and recorded during charging at a current density of 0.22 mA cm^{-2} up to 4.53 V with a battery testing system (TOSCAT-3000). The charging capacities of cylindrical cells were around 1050 mAh. After the completion of electrochemical experiment, the electrolyte samples were extracted by centrifugation and analyzed with nuclear magnetic resonance spectroscopy (Bruker, AVANCE Digital 300, 300 MHz and AVANCE III 600, 600 MHz) and a gas chromatography–mass spectrometry (Hewlett Packard, HP 6890/5973).

Linear sweep voltammetry was carried out using a Solartron 1480 potentiostat with a scan rate of 1 mV s^{-1} to assess the electrochemical stability of each phosphorus derivative. A Pt working electrode, an Ag/$AgNO_3$ reference electrode, and a Pt grid counter electrode were employed. The potential of the Ag/$AgNO_3$ reference electrode was calibrated using the reaction between ferrocene and ferrocenium ion before use. For each electrolyte sample, anodic and cathodic linear sweeps were carried out separately with freshly polished Pt working electrode.

The influence of phosphorus derivatives as electrolyte additives on the long-term cycle life of cells were examined using 2032-type coin full cells made of the electrodes prepared above. The cells were cycled for 300 times between 4.53 V and 2.75 V at 1.6 mA cm^{-2} (0.5C). All the electrochemical tests were conducted at room temperature.

3. Results and discussion

While the density of OLO cathode is usually around 2.9 g cm^{-3} or less, it can be comparable to that of $LiCoO_2$, 3.7 g cm^{-3}, if mixed with $LiCoO_2$ as described in the Experimental section. With this approach, the high capacity benefit of OLO can be effectively utilized without sacrificing the volumetric energy density that is particularly important in portable electronics applications.

Fig. 1 compares the voltage profiles and the variation in internal pressure of cylindrical cells during the first charging process. With only $LiCoO_2$ used as cathode material, the change of internal pressure is not significant and the small pressure growth might be caused by gas evolution accompanying the electrolyte decomposition. On the other hand, with the mixture of OLO and $LiCoO_2$ applied, the internal pressure increases dramatically up to 2.85 bar at the late stage of charging process, associated with the O_2 gas evolution from the activation of Li_2MnO_3 phase [9–12]. Considering only about 30% of available volume of cell is occupied with the jelly roll while the remaining part filled with Teflon spacer, this value corresponds to nearly 10 bar in a full 18650 cell, which is enough to activate the ventilation system of commercial cylindrical cells.

The molecular structures of phosphorus derivatives used in this study are drawn in Fig. 2. When included in the electrolyte as additives, all of them are found to be effective in reducing the internal pressure of cell comprising the OLO-based mixture cathode (Fig. 1). The maximum levels of pressure are 1.84, 0.96, and 0.84 bar in the case of TPP, EDP, and TEP, respectively. In other words, the magnitudes of pressure reduction are 1.01 bar (TPP), 1.89 bar (EDP), and 2.01 bar (TEP) compared with the additive free electrolyte. The reason TEP shows the highest effect might be in its low molecular weight. If the weight fraction of each additive is the same, the molar ratio of TPP:EDP:TEP equals 1:1.14:1.58. Accordingly, the molarity of

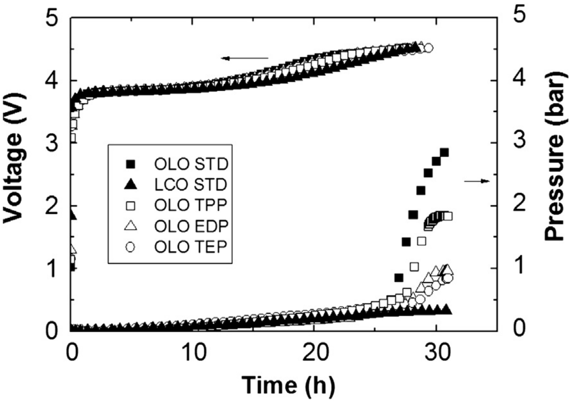

Fig. 1. The voltage profiles and the variations of internal pressure during the first charging of cells containing (■) OLO/$LiCoO_2$ cathode and no additives in the electrolyte (▲) $LiCoO_2$ cathode and no additives in the electrolyte (□) OLO/$LiCoO_2$ cathode and 5 wt.% TPP in the electrolyte (△) OLO/$LiCoO_2$ cathode and 5 wt.% EDP in the electrolyte, and (○) OLO/$LiCoO_2$ cathode and 5 wt.% TEP in the electrolyte.

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