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Comparison of Al_2O_3- and $AlPO_4$-coated $LiCoO_2$ cathode materials for a Li-ion cell

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Abstract

The electrochemical and thermal properties of $AlPO_4$-coated $LiCoO_2$ were compared with those of the Al_2O_3-coated cathode. Even though cycling stability of the Al_2O_3-coated cathode was apparently similar to that of the $AlPO_4$-coated sample at 4.6 V cycling, increasing the charge-cutoff voltage to 4.8 V led to the rapid capacity decay, exhibiting ∼20% larger capacity-fading than the $AlPO_4$-coated cathode. The irreversible capacity of the Al_2O_3-coated cathode ($\sim 34\,mAh\,g^{-1}$) was also larger than that of $AlPO_4$-coated cathode ($\sim 24\,mAh\,g^{-1}$) at a charge-cutoff voltage of 4.8 V. This was attributed to the increase in the amount of Co dissolution into the electrolyte at higher voltage. Differential scanning calorimetry results showed that the overall exothermic-heat release of the Al_2O_3-coated cathode was similar to that of the bare cell, but the onset temperature of oxygen evolution from the cathode was increased to ∼190 °C (up from ∼170 °C in the bare cell). On the other hand, $AlPO_4$-coated $LiCoO_2$ showed a much improved onset temperature of the oxygen evolution at ∼230 °C, and a much lower amount of exothermic-heat release, compared to the Al_2O_3-coated sample. These results were correlated with the 12 V overcharge experiments: the Li-ion cell containing $AlPO_4$-coated $LiCoO_2$ did not show a thermal runaway behavior in contrast to that containing bare, or Al_2O_3-coated cathode.

Keywords: $AlPO_4$ coating; Al_2O_3 coating; $LiCoO_2$; Cycling stability; Co dissolution; Overcharge

1. Introduction

The most critical factors for evaluating the performance of Li-ion cells are the rate capability, the cycle life, and the thermal stability, which are mostly affected by the cathode materials. Among them, the thermal stability of the cell becomes more important factor as the cell capacity increases. The cells without protective devices shows the thermal runaway inducing the over-current, over-charge, and abrupt temperature increase during the 12 V overcharging test recommended by the safety guidelines [1,2]. Many safety accidents of Li-ion cells due to the malfunction of the devices in mobile electronics have been reported [3]. The increase in the weight portion of the cathode accelerated the heat-accumulation rate, and an internal short circuit resulted in a cell explosion with the external temperature exceeding ∼500 °C [4].

The most detrimental factor causing such problems is the violent exothermic reaction of the delithiated cathode materials with the flammable electrolytes at elevated temperatures. Its effect has been widely evaluated using differential scanning calorimetry (DSC) and accelerating rate calorimetry as a function of temperature [5–9]. Several authors have reported that additives in the electrolytes can prevent thermal runaway [10–14]. However, they reported that the additives, such as phosphorus compounds or aromatic compounds with two methyl groups, could reduce the flammable nature of the electrolytes. γ-Butyrolactone was used to reduce the direct reaction of the cathode with the electrolyte at the charged state, and this solvent has been reported to decompose into the organic products, which encapsulate the cathode and block any

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direct reaction with the electrolytes [10]. As a consequence, Li-ion cells containing this solvent did not explode during a nail penetration test at 4.35 V. However, these additives damaged the electrochemical properties of the cathode and anode materials.

Recently, Cho et al. used a fundamental approach to minimize the thermal instability of the cathode materials by an $AlPO_4$ nanoparticle coating [5]. Li-ion cells containing the coated cathodes showed no thermal runaway with a maximum cell external temperature of ∼60 °C up to 12 V charging in contrast to that containing the bare cathode showing the external temperature of over ∼500 °C. This study further reported that the thermal runaway occurred immediately after the internal short at 12 V. This method is quite useful, because it provides information on the thermal behavior of the cathode material up to 12 V. Similar approaches were reported to improve the electrochemical properties of the cathode materials by a sol–gel coating of Al_2O_3 and ZrO_2 [15–17]. However, its overcharge behavior was not yet reported despite its superior rate capability and cycle-life performance, compared to the bare cathodes.

In this paper, differences in the Al_2O_3- and $AlPO_4$-coated $LiCoO_2$ are investigated for the electrochemical and thermal behavior.

2. Experimental

$LiCoO_2$ was prepared using Co_3O_4 (with the average particle size of 2–3 μm) and finely ground $LiOH{\cdot}H_2O$ powders as starting materials. They were mixed at a molar ratio of 1:1.05 and homogenized in an automatic mixer for 2 h. The mixture was heat-treated at 600 and 900 °C in an oxygen atmosphere for 6 and 24 h, respectively. The as-prepared $LiCoO_2$ powders had an $x = 1.00$ in Li_xCoO_2. The $LiCoO_2$ electrode powder with an average particle of size ∼10 μm, which was sampled from the batches sieving through a 500-mesh screen (26 μm), was used for the electrochemical tests. To obtain the sol–gel coating of Al_2O_3 on $LiCoO_2$, Al(IV)ethylhexanoisopropoxide ($Al(OOC_8H_{15})_2(OC_3H_7)_2$, 5 g) was dissolved in isopropanol, followed by continuous stirring for 20 h at 21 °C. After drying the $LiCoO_2$ powders coated with Al alkoxide gel at 130 °C, the batch was fired at 700 °C for 5 h. Aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$, 3 g) and diammonium phosphate ($(NH_4)_2HPO_4$, 1 g) were dissolved in distilled water until a light white suspension solution (with $AlPO_4$ nanoparticles) was observed. The $LiCoO_2$ powders (100 g with the average particle size of ∼10 μm) were then slowly added to the coating solution, and mixed until the final viscosity of the slurry reached ∼100 P. Subsequently, the slurry was poured into a tray, dried in an oven for 6 h at 130 °C, and annealed at 700 °C for 5 h in a furnace.

The cell standard capacity was set at 1600 mAh [cell size: 3.2 mm × 85 mm × 53 mm (thickness × length × width)]. The electrolyte for the coin-type half cells and the Li-ion cells was 1 M $LiPF_6$ with ethylene carbonate/diethylene carbonate/ethyl-methyl carbonate (EC/DEC/EMC) (30: 30:40 vol.%). The coin-type half cells were initially cycled at a 0.1 C rate for two cycles, and continued to increase to 0.2 and 0.5 C rates for each cycle, followed by a 1 C rate afterwards, with 4.6 and 4.8 V charge-cutoffs. The discharge voltage was set to 3 V. Coin-type half cells containing Li metal anode were used for cycling tests with 4.6 and 4.8 V cutoffs. Cycling tests of the Li-ion cells between 3 and 4.5 V was performed with synthetic graphite. Rate capability tests of the coated cathodes was carried out using 1600 mAh Li-ion cell between 3 and 4.2 V with synthetic graphite anode at different C rates at room temperature. The same dimensional weight ratio of cathode to anode (1:1.06) was used for all the test cells. To determine the apparent Li diffusivities as a function of the cell potential, a galvanostatic intermittent titration technique (GITT) was used for the uncoated and Al_2O_3- and $AlPO_4$-coated $LiCoO_2$ powders. The experimental methods for the DSC and 12 V overcharge tests were described elsewhere [18].

3. Results and discussion

A comparison of the transmission electron microscopy (TEM) images between the Al_2O_3- and $AlPO_4$-coated $LiCoO_2$ particles is shown in Fig. 1. In both cases, the Al or P elements are distributed over the $LiCoO_2$ surfaces. The possible formation of a solid solution from a reaction between the coating materials and Li (or even Co) during the heat treatment is not ruled out. X-ray photoelectron spectroscopy (XPS) was used to compare the bonding nature of the Al_2O_3- and $AlPO_4$-coated cathodes, as shown in Fig. 2. The binding energies of the Al 2p in the bulk Al_2O_3 and $AlPO_4$ were reported to be observed at ∼74.7 and 74.5 eV, respectively [19,20]. A peak in the Al_2O_3-coated $LiCoO_2$ at ∼71 eV agrees with the metallic nature of Al. The variation in the binding energies of Al in the coated cathodes may be related to a Li (or even Co) reaction with the coating layer, and future study aimed at understanding the detailed microstructures of the nanoscale coating layer is currently underway.

Fig. 3 compares the voltage profile and cycle-life performance of bare, and Al_2O_3- and $AlPO_4$-coated cathodes between 4.6 and 3 V. The initial capacity and cycle-life performance of the Al_2O_3-coated cathode are similar to those in the $AlPO_4$-coated samples. However, increasing the charge voltage from 4.6 to 4.8 V leads to a drastic difference between these two cathodes, as shown in Fig. 4. Even though the charge capacities of both cathodes are similar to each other (244 and 247 $mAh\,g^{-1}$ for Al_2O_3- and $AlPO_4$-coated $LiCoO_2$, respectively), the discharge capacity is obviously different: Al_2O_3- and $AlPO_4$-coated $LiCoO_2$ show 220 and 233 $mAh\,g^{-1}$, respectively. Cobalt dissolution into the solution is coupled with the release of lithium and oxygen, resulting in structural degradation [21]. The Co dissolution rate in the Al_2O_3-coated cathodes was four times higher than that in