

Improved thermal stability of LiCoO_2 by nanoparticle AlPO_4 coating with respect to spinel $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$

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Abstract

The thermal instability of the LiCoO_2 cathode material was greatly improved by the nanoparticle AlPO_4 coating. The AlPO_4 coating appears to minimize the violent exothermic reaction of the cathode with the flammable electrolytes, resulting in excellent thermal stability even at the overcharged state. Moreover, the results of the overcharge and elevated temperature cycling tests show that, when compared with the spinel $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$, the AlPO_4 nanoparticle coating results not only in enhanced thermal stability of the cathodes but also in reduced Co dissolution in the electrolytes.

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The production of Li secondary batteries has rapidly expanded due to their applicability to mobile electronics, such as cellular phones, camcorders, personal digital access (PDAs), and notebook-PCs. Currently, most Li secondary batteries use LiCoO_2 as a cathode material due to the higher volumetric energy density and excellent cyclability [1]. In spite of this, many safety accidents related to LiCoO_2 cathodes have been reported [2]. The main cause of the disastrous failure is that LiCoO_2 cathode undergoes a violent exothermic reaction with the electrolyte during overcharging, which short-circuits the cell [3–6]. In this regard, CoO_2 is a stronger oxidizing agent than $\lambda\text{-MnO}_2$, and therefore is more exothermically reactive with the electrolytes, resulting in oxygen generation [7]. In addition, the deposited lithium on the graphite anode increases the reaction rate, resulting in a large increase in temperature [3,4]. A combination of the temperature increase and the internal short-circuit of the cell can cause an explosion.

This communication reports an improvement in the thermal stability of LiCoO_2 by using an AlPO_4 nanoparticle coating. An AlPO_4 coating led to a more uniform coating layer than that when using either Al_2O_3

or ZrO_2 coatings derived from the sol–gel method. The thermal stability of the coated material was compared with $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ spinel, which is known as the most thermally stable compound during overcharging. Along with DSC measurements, the 12 V overcharge tests of the cathodes were conducted in the Li-ion cells to understand the thermal stability above 5 V following the guidelines for a safety evaluation of secondary lithium cells [8,9]. The guidelines require that the cells should not explode and catch fire. However, cell-case swelling is permitted [8,9].

Appropriate amounts of aluminum nitrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ were dissolved in distilled water until a light white suspension solution (the AlPO_4 nanoparticle solution) was observed. LiCoO_2 powders (with an average particle size of $\sim 10 \mu\text{m}$) were then added to the coating solution slowly and mixed until the final viscosity of the slurry reached $\sim 10,000 \text{ P}$. The slurry was then poured into a tray, dried in an oven for 6 h at $130 \text{ }^\circ\text{C}$, and annealed at $700 \text{ }^\circ\text{C}$ for 5 h in a furnace. $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ was prepared from a stoichiometric mixture of MnO_2 and $\text{LiOH} \cdot \text{H}_2\text{O}$ at $750 \text{ }^\circ\text{C}$ for 20 h. The AlPO_4 nanoparticle-coated LiCoO_2 , bare LiCoO_2 , or $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ was used as a cathode, and the anode material was synthetic graphite with a dimensional ratio of 1.2:1 for the anode to cathode. At this ratio, lithium

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deposition on the anode did not occur below 4.3 V vs. graphite. The cell standard capacity was set at 820 mA h [cell size: $5.5 \times 48 \times 30 \text{ mm}^3$ (thickness \times length \times width)], and a laminated film was used for the cell case. On the other hand, the cell capacity containing $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ cathode was set at 700 mA h due to the low electrode density of the spinel $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$. The electrolyte used was 1.03 M LiPF_6 with ethylene carbonate/diethylene carbonate/ethyl-methyl carbonate (EC/DEC/EMC) (3/3/4 vol%). For the differential scanning calorimetry (DSC) experiments, a coin-type half-cell containing lithium metal as the anode was used. The fresh cells were charged to 4.6 V at a rate of 0.1 C (= 14 mA/g). These cells were then disassembled in a glove box to remove the charged cathode that typically contained ~ 30 wt% electrolyte, ~ 30 wt% Al foil, 5 wt% of the combined binder and carbon black, and ~ 35 wt% of the cathode material. Approximately 10 mg of the cathode was cut and hermetically sealed into an aluminum sample pan. Only the cathode material was used to calculate the specific heat flow. Cycling tests of the bare, AlPO_4 -coated LiCoO_2 , and $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ cathodes were carried out in Li-ion cell between 3 and 4.2 V at the rate of 1 C at 60 °C.

TEM studies confirmed that the AlPO_4 nanoparticles were completely coated over the LiCoO_2 surface on the nanoscale (~ 15 nm) [10]. The nanoscale-coating layer consisted of randomly oriented AlPO_4 nanoparticles with an average diameter of ~ 3 nm, and the Al and P components were distributed evenly throughout the nanoscale-coating layer, as confirmed by EDS [10]. Fig. 1 shows the DSC scans of bare, AlPO_4 -coated LiCoO_2 , and $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ after 4.6 V charging in the temperature range 100–300 °C. Bare LiCoO_2 exhibited substantial exothermic peaks between 100 and 300 °C, which is due to the oxygen generation from cathode decomposition. On the other hand, $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ showed significantly smaller heat

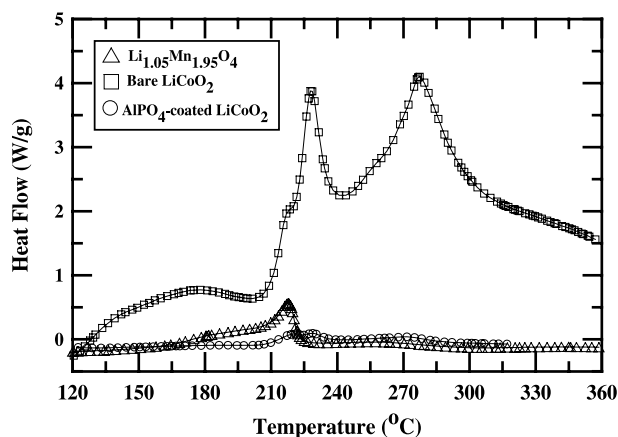


Fig. 1. DSC scans of the bare, AlPO_4 -coated LiCoO_2 , and $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ cathodes at a 4.6 V charge cut-off as a function of temperature. The scan rate was 3 °C/min.

generation than the bare LiCoO_2 , as expected, but the peak release was larger than the AlPO_4 nanoparticle-coated LiCoO_2 . This suggests that AlPO_4 nanoparticle-coating layer minimizes the exothermic reaction with the electrolyte.

In order to further understand the behavior of the cathodes at the higher charged state, 12 V overcharge experiments were carried out using the Li-ion cells. Fig. 2 shows the voltage and cell-surface temperature profiles of the cell with the bare and AlPO_4 nanoparticle-coated LiCoO_2 , and $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$. The cells used for the 12 V overcharge safety test were charged to 4.2 V, and subsequently charged to 12 V at a rate of 2 C and held at 12 V until the current decreased to 20 mA (equivalent to 280 mA/g = 1.68 A and 220 mA/g = 1.4 A, respectively, for LiCoO_2 and $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$). Fig. 2(b) shows the voltage and cell-surface temperature profiles during the 2 C rate overcharge test to 12 V. Overcharging over 5 V increased the electrolyte decomposition rate, and the internal cell resistance (joule heat) increased due to electrolyte decomposition. During overcharging, the separator melted down and shrank when the temperature inside the cell reached

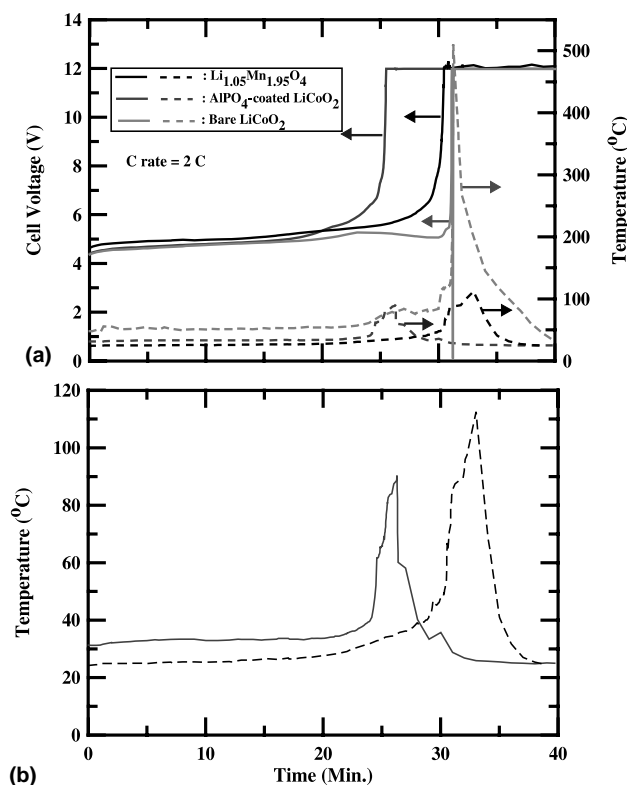


Fig. 2. (a) Voltage and temperature profiles of a cell with a bare, AlPO_4 -coated LiCoO_2 , and $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ cathodes as a function of time. The cell with the bare cathode electrode exhibits an abrupt voltage drop to 0 V due to a short-circuit and a rapid temperature increase to ~ 500 °C. (b) Expanded plot of the temperature profiles of a cell with AlPO_4 -coated LiCoO_2 , and $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ cathodes as a function of time.

120 °C. When the cell-surface temperature reaches 90 °C, the cell internal temperature can be over 180 °C. Therefore, any direct contact of the anode and cathode electrodes induces a short-circuit. This has been the problem in the cells with a bare LiCoO_2 cathode, as shown in Fig. 2(a). Immediately after the cell voltage reached 12 V, an internal short-circuit occurred (note the abrupt voltage drop to 0 V), and the surface temperature increased to over 500 °C, resulting in a fire and explosion of the cell. When the AlPO_4 nanoparticles were coated uniformly on the cathode, the cells did not exhibit any short-circuit problems after being held at 12 V until the temperature decreased to below 30 °C (Fig. 2(b)). The temperature decreased because of the separator shutdown, followed by the current drop at 12 V. Similar to the AlPO_4 -coated LiCoO_2 , the spinel cathode exhibited good thermal stability without showing any thermal runaway at 12 V. However, it should be noted that the cell-surface temperature of the spinel (110 °C) was higher than that of the coated LiCoO_2 . This indicates that the AlPO_4 coating led to less exothermic reactions with the electrolyte, and in turn less heat generation (note that the AlPO_4 -coated LiCoO_2 showed a faster voltage increase to 12 V ahead of 6 min than bare LiCoO_2 and $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$). This result is well correlated with the DSC results, as shown in Fig. 1. This result can be attributed to the strong covalence of the PO_4 polyanions with the Al in AlPO_4 [11–13]. For instance, completely delithiated Li compounds with $(\text{PO}_4)^{3-}$ showed an endothermic peak above 300 °C, in contrast to other compounds showing exothermic peaks below 250 °C [14,15].

Fig. 3 compares the 60 °C cycling life of the bare, and AlPO_4 -coated LiCoO_2 , and $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ at the rate of 1 C (= 105 mA h/g). A slight excess of Li in

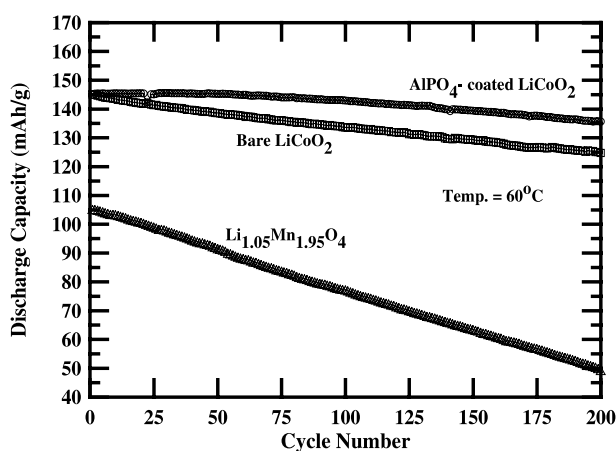


Fig. 3. Plot of the discharge capacity of the bare, AlPO_4 -coated LiCoO_2 , and $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ cathodes in the Li-ion cells as a function of the cycle number at 60 °C.

spinel has been reported to reduce capacity fading at an elevated temperature because Mn ions in the octahedral (16d) sites are replaced by lithium ions with a concomitant increase in the Mn oxidation state to maintain charge neutrality [15,16]. However, the capacity of the spinel decreases rapidly from 105 to 50 mA h/g after 200 cycles, while AlPO_4 -coated LiCoO_2 retained the best capacity (135 mA h/g), after 200 cycles, followed by bare LiCoO_2 with 125 mA h/g. Codissolution from the bare and coated LiCoO_2 was 300 and 80 ppm, respectively, while Mn dissolution from the spinel cathode was over 4000 ppm after cycling. These results clearly show the superior chemical stability of the AlPO_4 -coating layer in the thermal stability during overcharging. It can be therefore concluded that AlPO_4 coating enhanced the structural stability of the LiCoO_2 more than the well-known spinel material and bare LiCoO_2 both at the overcharged state and at elevated temperature cycling.

Acknowledgement

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