

Olivine LiCoPO_4 phase grown LiCoO_2 cathode material for high density Li batteries

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Abstract

Olivine LiCoPO_4 phase grown LiCoO_2 cathode material was prepared by mixing precipitated $\text{Co}_3(\text{PO}_4)_2$ nanoparticles and LiCoO_2 powders in distilled water, followed by drying and annealing at 120 °C and 700 °C, respectively, for 5 h. As opposed to ZrO_2 or AlPO_4 coatings that showed a clearly distinguishable coating layer from the bulk materials, $\text{Co}_3(\text{PO}_4)_2$ nanoparticles were completely diffused into the surface of the LiCoO_2 and reacted with lithium of LiCoO_2 . An olivine LiCoPO_4 phase was grown on the surface of the bulk LiCoO_2 , with a thickness of ~ 7 nm. The electrochemical properties of the LiCoPO_4 phase, grown in LiCoO_2 , had excellent cycle life performance and higher working voltages at a 1C rate than the bare sample. More importantly, Li-ion cells, containing olivine LiCoPO_4 , grown in LiCoO_2 , showed only 10% swelling at 4.4 V, whereas those containing bare sample showed a 200% increase during storage at 90 °C for 5 h. In addition, nail penetration test results of the cell containing olivine LiCoPO_4 , grown in LiCoO_2 at 4.4 V, did not exhibit thermal runaway with a cell surface temperature of ~ 80 °C. However, the cell containing bare LiCoO_2 showed a burnt-off cell pouch with a temperature above 500 °C.

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1. Introduction

Since the cylindrical 18650R-type Li-ion cell, with a capacity of 1200 mAh, was first developed in 1991, its capacity has increased by about 7–10% every year, and a 2600 mAh (500 mAh/cc) cell was developed in 2005 [1]. However, such a capacity achievement was possible only by maximum utilizing the cell dead space, modifying the thickness of the current collectors, and decreasing the amounts of binder and conducting agent in the electrodes. As of yet, the cathode material, LiCoO_2 , has remained unchanged due to its high electrode density (3.7 g/cc) and good electrochemical properties at 4.3 V. However, achieving capacities beyond 2600 mAh (e.g. 2800 mAh

(550 mAh/cc)) requires an increase in the cut-off voltage of the cell from 4.2 V to 4.4 V (vs. graphite). As an alternative, we can consider new cathode materials for replacing LiCoO_2 and Ni-rich cathode materials with a specific capacity as high as 185 mAh/g [2–6]. However, the hardware of portable electronics, such as cellular phones and note-PCs, still require average working voltages above 3.7 V even in the pulse mode. In this regard, Ni-based cathode materials (electrode density, 3.4 g/cc) cannot be used.

A problem with LiCoO_2 is that, when the cut-off voltage increases to 4.5 V from 4.3 V (vs. lithium metal), the x in Li_xCoO_2 decreased from 0.45 to 0.3, resulting in a large anisotropic volume change of over 3% due to the phase transition between hexagonal, monoclinic, and H1-3 phases [7,8]. Furthermore, highly oxidized Co^{4+} ions are apt to decompose electrolytes in the particle surface, resulting in substantial amounts of gas generation. In addition, Co dissolution at 4.5 V at elevated temperatures induces

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the simultaneous Li dissolution from the cathode surface. Accordingly, this results in Li ion intercalation sites which, in turn, increase structural degradation. In order to address these problems, metal oxide and AlPO_4 coatings have been suggested [9–14], but ZrO_2 and Al_2O_3 coatings caused explosions during thermal abuse tests, such as the nail penetration test [15–17]. On the other hand, nanoparticle coatings, such as AlPO_4 coatings, have raised concerns about possible Li dissolution from LiCoO_2 during the coating procedure due to the use of water as a solvent [18]. Hence, during heat-treatment at 700°C , Li sources co-precipitated as forms of LiOH and Li_2CO_3 on the coating layers. Since these impurity phases do not react with AlPO_4 at 700°C and can reside on the coating layers, they eventually lead to swelling during storage at 90°C .

In this study, we report a new coating material that reacts with lithium, resulting in the formation of a LiCoPO_4 phase, grown in the bulk LiCoO_2 . The olivine LiCoPO_4 phase is very electrochemically and thermally stable even after full delithiation [19]. Accordingly, an olivine LiCoPO_4 phase, grown in the surface of the LiCoO_2 cathode material, can significantly reduce cell swelling at 90°C at 4.4 V and also enhance the electrochemical performance.

2. Experimental section

Cobalt nitrate ($\text{Co}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 1 g) and diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$, 0.38 g) were dissolved in distilled water and mechanically mixed until a white-colored, $\text{Co}_3(\text{PO}_4)_2$ nanoparticle-dispersed solution was observed. The solution was mixed with LiCoO_2 (with an average particle size of $\sim 10\ \mu\text{m}$ and BET surface area of $0.4\ \text{m}^2/\text{g}$), followed by drying at 120°C for 5 h and annealing at 700°C for 5 h. The estimated $\text{Co}_3(\text{PO}_4)_2$ content in the powder was 0.9 wt%.

For the 4.4 V nail penetration and swelling tests at 90°C , the Li-ion cells with an 840 mAh standard capacity [cell size: $4.6 \times 34 \times 50\ \text{mm}^3$ (thickness \times length \times width)] were used. Bare and LiCoPO_4 phases, formed in the LiCoO_2 , were used as the cathode, and the anode material was synthetic graphite. For assembling the Li-ion cells, we used 2 kg each of samples A and B for cell manufacturing. For swelling and nail penetration tests, 4 to 5 cells of each were used. The cell surface temperature was monitored, using a K-type thermocouple, placed on the center of the largest face in the cell pouch, and the thermocouple was tightly glued with an insulating tape. For the nail penetration test, a nail with a diameter of 2 mm was used, and the cell voltage was fixed at 4.4 V. Coin-type half-cell tests were conducted, using samples A and B at different C rates of 0.1, 0.2, 0.5, and 1C (= 180 mA/g) between 3 and 4.5 V, using the same C rate for charging and discharging. Cathodes for battery test cells were made of the active material ($\sim 25\ \text{mg}$), super P carbon black (MMM, Belgium), and polyvinylidene fluoride (PVdF) binder (Kureha Company) in a weight ratio of 96:2:2. A cathode-slurry was prepared by thoroughly mixing a *N*-methyl-2-pyrrolidone (NMP)

solution with the PVdF, the carbon black, and the powdery cathode-active material. Electrodes were prepared by coating the cathode-slurry onto an Al foil, followed by drying at 130°C for 20 min. Coin-type battery test cells (size 2016), containing a cathode, a Li metal anode, and a microporous polyethylene separator, were prepared in a helium-filled glove box. The electrolyte used was LiPF_6 with ethylene carbonate/diethylene carbonate/ethyl-methyl carbonate (EC/DEC/EMC) (3/3/4 vol %) (Cheil Ind. Korea). After addition of the electrolyte, test cells were aged at room temperature for 24 h before electrochemical testing was performed. Field-emission transition electron microscopy (FE-TEM) (JEOL 2100F), operating at 200 kV was used for investigating the microstructure of the samples. The soft oxygen K-edge XAS measurements of bare, coated LiCoO_2 , and LiCoPO_4 powder were performed on U7 beamline in the storage ring of 2.5 GeV with the ring current of 130–180 mA at Pohang Light Source (PLS).

3. Results and discussion

Fig. 1 shows a TEM image of precipitated $\text{Co}_3(\text{PO}_4)_2$ nanoparticles at pH 5 in distilled water. Nanoparticles were relatively well-dispersed without aggregation, with a particle size of 5 nm. XRD patterns of the bare (sample A) and LiCoPO_4 phase, grown in the surface of the LiCoO_2 , (sample B) were nearly identical to each other without any secondary phases (see supporting information). Fig. 2a and b exhibit TEM images of the sample A, and the lattice fringe of layered LiCoO_2 (003), with a space R-3m, has very smooth particle surface morphology. However, the TEM images of the sample B (Fig. 2c and d) do not show the coating layer, and, instead, the lattice fringe of (3 1 1), corresponding to an olivine LiCoPO_4 phase, is clearly observed. This result indicates that $\text{Co}_3(\text{PO}_4)_2$ nanoparticles completely reacted with Li in LiCoO_2 , forming LiCoPO_4 and partial lithium-deficient Li_xCoO_2 , according to the following reaction:

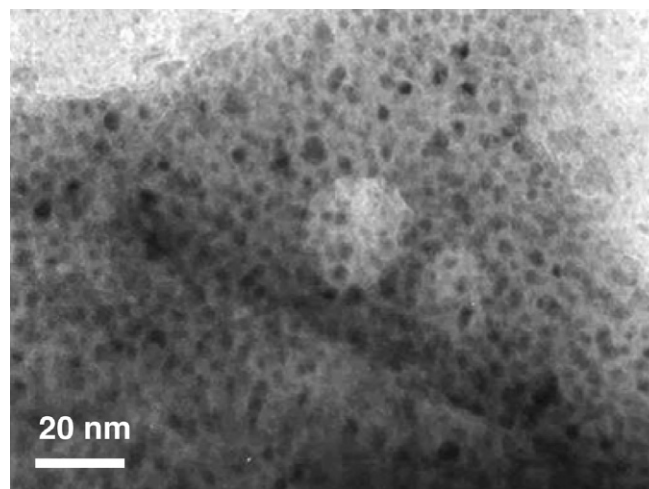


Fig. 1. TEM image of $\text{Co}_3(\text{PO}_4)_2$ nanoparticles precipitated at pH 5.

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