Synthesis and Characterization of Mg$_3$(PO$_4$)$_2$-coated Li$_{1.05}$Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ Cathode Material for Li-ion Battery

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Abstract: Mg$_3$(PO$_4$)$_2$-coated Li$_{1.05}$Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ cathode materials were synthesized via co-precipitation method. The morphology, structure, electrochemical performance and thermal stability were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), charge/discharge cycling and differential scanning calorimeter (DSC). SEM analysis shows that Mg$_3$(PO$_4$)$_2$-coating changes the morphologies of their particles and increases the grains size. XRD and CV results show that Mg$_3$(PO$_4$)$_2$-coating powder is homogeneous and has better layered structure than the bare one. Mg$_3$(PO$_4$)$_2$-coating improved high rate discharge capacity and cycle-life performance. The reason why the cycling performance of Mg$_3$(PO$_4$)$_2$-coated sample at 55℃ was better than that of room temperature was the increasing of lithium-ion diffusion rate and charge transfer rate with temperature rising. Mg$_3$(PO$_4$)$_2$-coating improved the cathode thermal stability, and the result was consistent with thermal abuse tests using Li-ion cells: the Mg$_3$(PO$_4$)$_2$-coated Li$_{1.05}$Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ cathode did not exhibit thermal runaway with smoke and explosion, in contrast to the cells containing the bare Li$_{1.05}$Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$.

Key words: lithium-ion batteries; cathode materials; Li$_{1.05}$Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$; co-precipitation

1 Introduction

Lithium ion cells with LiCoO$_2$ cathode and graphite anode have been widely used for portable election facili-
ties in recently years, because of their high energy den-
sity and long cycle-life. However due to their high cost and low safety of LiCoO$_2$ at overcharge, the high capacity and dynamical lithium ion batteries development is hindered$^1$. Because of the difficulties of synthesis, structural instability during cycling and lower thermal safety of LiNiO$_2$, it is difficult for LiNiO$_2$ to substitute LiCoO$_2$ as an alter-
tnative to LiNiO$_2$ as it combines some of the benefits of LiNiO$_2$ (capacity) with those of LiCoO$_2$ (stability), but it has been only used for small cells to obtain high capacity$^3$. Recently many researchers are interested in layer LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ for its higher capacity and better safety compared with LiCoO$_2$$. However the capacity fad-
ing of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ cathode material with high rate discharge can not satisfy the dynamical lithium ion cells demand which was related to the particle density and particle surface state. It was reported that a nano-particle AlPO$_4$ coating on the surface of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ can improved the material high rate discharge ability and safety. In this paper, we synthesized Mg$_3$(PO$_4$)$_2$-coated Li$_{1.05}$Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ cathode materials and assembled 18 650 type cells testing their rate discharge performance and safety.

2 Experimental

2.1 Synthesis of Mg$_3$(PO$_4$)$_2$-coated Li$_{1.05}$Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$

Mn$_{1/3}$Co$_{1/3}$Ni$_{1/3}$(OH)$_2$ starting powders were prepared by co-precipitation from a solution containing molar ratio of nickel/cobalt/manganese sulfate by the addition NaOH and NH$_3$OH solution in a specially designed reactor. The Mn$_{1/3}$Co$_{1/3}$Ni$_{1/3}$(OH)$_2$ particle size was controlled by reaction time in order to enhance the BET surface area. A longer reaction time in the solution resulted in a larger

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particle size. The co-precipitated particles continued to be rotated at 1 000 rpm in the reactor at 45-50 °C. The pH value was maintained at 11 by controlling the amount of NH4OH. After filtration, rinsing, and drying, the Li1.05Ni1/3Mn1/3Co1/3O2 (called A) was prepared by mixing LiOH and Mn1/3Co1/3Ni1/3(OH)2 in the molar ratio of 1.05 : 1, and then followed by a heat-treatment procedure at 900 °C for 20 h in a stream of dry air. In order to coat Mg3(PO4)2 particles on the Li1.05Ni1/3Mn1/3Co1/3O2 cathode, Mg(NO3)2 and Na3PO4 in the molar ratio of 3 : 2 was slowly dissolved in water until the white Mg3(PO4)2 nano-particle suspension was observed. Li1.05Ni1/3Mn1/3Co1/3O2 was added to the suspension and then thoroughly mixed the solution for 30 min. The slurry was then dried at 120 °C for 12 h, and heat-treated in furnace at 800 °C for 6 h. After cooling and grinding, Mg3(PO4)2-coated Li1.05Ni1/3Mn1/3Co1/3O2 was added to the suspension and then thoroughly mixed the solution for 30 min. The slurry was then dried at 120 °C for 12 h, and heat-treated in furnace at 800 °C for 6 h. After cooling and grinding, Mg3(PO4)2-coated Li1.05Ni1/3Mn1/3Co1/3O2 was obtained (called B).

2.2 Preparation of test cells

Positive electrodes slurry for 2 032 type simulated cells was prepared by thoroughly mixing active material (85 wt%) with carbon black (10 wt%) and polytetrafluoroethylene (5 wt%) in ethanol. Electrodes with 0.5 cm-2 area and 0.02 mm depth extruded onto aluminum foil were dried for 12 h at 120 °C under vacuum. 2032 type coin cells were then assembled in a argon filled dry box using foils of Li metal as counter electrodes and Celgard 2400 saturated with 1 M LiPF6 in EC/EMC/DMC (1 : 1 : 1 by weight) as separators.

Positive electrodes slurry for 18 650 type cells was prepared by thoroughly mixing active material (91 wt%) with carbon black (5 wt%) and polyvinylidene fluoride (4 wt%) in N-methyl-pyrrolidinone and slurry was pasted on the aluminum foil. Negative electrodes slurry was prepared by thoroughly mixing graphite (92 wt%) with carboxymethyl cellulose sodium (1.5 wt%) and styrene butadiene rubber (6.5 wt%) in water and slurry was pasted on the copper foil. Batteries of 18 650 type with 1 800 mAh capacity were assembled by winding positive electrodes, separators and negative electrodes, adding the electrolyte and sealing.

2.3 Morphology and structure tests

The surface morphology was observed by means of an environment scanning electron microscopy (ESEM, Philips XL-30). The particle diameter and surface area were tested by the laser granularity instrument (winner2000) and the surface analytical instrument (SSA-3500) respectively. Powder X-ray diffraction (XRD) (Philips X’ Pert Pro Pro MPD Co-Ka) was done to determine the material structure.

2.4 Electrochemical tests

The cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were performed by electrochemistry working station (Gamry Instruments). The rate performance and cycling performance were tested by BS9300 battery testing instrument. The rate capability of the cells were tested by charging to 4.3 V using a constant current of 900 mA and discharging to 2.75 V under the constant currents of 900 mA, 1 800 mA, 3 600 mA, 5 400 mA, respectively.

2.5 DSC tests

For DSC experiments, the cells were finally fully charged to 4.3 V and opened in the Ar-filled dry box. After opening carefully, the extra electrolyte was removed from the surface of the electrode using DMC rinsing while the electrode materials were removed from the current collector. An aluminum sealed pan with a gold plated copper seal was used to collect 3-5 mg samples. The measurements were carried out in differential scanning calorimeter (NETZSCH-204) with a temperature scan rate of 10 °C/min.

3 Results and Discussion

3.1 SEM analysis

Fig.1 shows the ESEM images of the bare and Mg3(PO4)2-coated Li1.05Ni1/3Mn1/3Co1/3O2 samples. Li1.05Ni1/3Mn1/3Co1/3O2 exhibited an sphericity morphology with the size of the primary particles about 8 μm and their surface was very even. After Mg3(PO4)2 coating, the surface morphology of the particle increased slightly and showed densely packed, rock-shaped grains. This indicated that Mg3(PO4)2 had partially reacted with Li1.05Ni1/3Mn1/3Co1/3O2 during firing at 800 °C. Bare and Mg3(PO4)2-coated Li1.05Ni1/3Mn1/3Co1/3O2 particle diameter of D50 was 10.69 μm and 11.28 μm tested by the laser granularity instrument and the surface area was 0.83 m2/g and 0.85 m2/g, which were fit for ESEM testing results. For cathode materials of lithium ion cells, the bigger the particle size is, the more incompact performance and the better fluidity will get, which is propitious to slurry pasting of cathode preparation[5]. Mg3(PO4)2-coating led to a formation of the bigger and denser sinters and were fit for lithium ion battery preparation.