**ABSTRACT**

A LiCoO$_2$/LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ composite was prepared by the combination of mechanical ball milling and heat treatment. The as-prepared LiCoO$_2$/LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ composite was characterized by X-ray diffraction, scanning electron microscopy, and energy-dispersive X-ray spectroscopy. The LiCoO$_2$/LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ composite was utilized as cathode material for lithium-ion batteries. Compared with the milled LiCoO$_2$/LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ composite, the LiCoO$_2$/LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ composite after heat treatment exhibited superior performance, including in an increased coulombic efficiency, better capacity retention and enhanced rate capability. The present work demonstrated that Ni and Mn from LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ were co-doped for the LiCoO$_2$ during high temperature, resulting in improving the electrochemical properties of the LiCoO$_2$/LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ composite.

**Keywords**: Heat Treatment, LiCoO$_2$, LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$, Lithium-ion Battery

1. Introduction

Rechargeable lithium-ion batteries (LIBs) are the most promising candidates for applications in hybrid electric vehicles (HEVs) and electric vehicles (EVs), due to their high energy density and power density.\(^1\)\(^-\)\(^4\) To adopt a large-scale battery in EV and HEV, a strong demand has been driven by customer expectation to increase the energy density of LIBs.\(^5\)-\(^9\) Despite of some inherent limitations such as poor safety and high cost, LiCoO$_2$ still is the most applied cathode material for rechargeable LIBs due to its high electronic conductivity, excellent cycling performance, and great rate capability.\(^9\)\(^,\)\(^11\) Increasing the operation voltage to higher than 4.2 V easily enhances the capacity of LiCoO$_2$.\(^12\)\(^-\)\(^15\) However, capacity retention and thermal stability of the LiCoO$_2$ at voltage above 4.2 V is not satisfactory because of its instable structure at a highly delithiated state.\(^3\)\(^,\)\(^6\)\(^-\)\(^8\)\(^,\)\(^16\)\(^-\)\(^20\) LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ is an especially attractive cathode material due to its lower cost and higher capacity than commercial cathode materials such as LiCoO$_2$.\(^9\)\(^,\)\(^21\)\(^-\)\(^26\) However, it suffers from a lower volumetric power cycling stability and conductivity.\(^27\)-\(^32\) Many efforts have been made to settle those problems of cathode materials and improve their performance. Some battery companies have demonstrated a new concept of mixing two different types of compounds to make a cathode to enhance overall performance of battery.\(^33\)-\(^34\) Therefore, LiCoO$_2$ by Ni and Mn co-doping from LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ could be an interesting alternative and could help in compensating for their disadvantages each other. In present work, a LiCoO$_2$/LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ composite was prepared though a heat treatment after a mechanical ball-milling process. The electrochemical properties of as-prepared mixture as cathode material were studied in LIBs.

2. Experimental

Commercially available LiCoO$_2$ (Easpring, China) and LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ (Jinhe Share, China) were used in this research. The LiCoO$_2$ powder was mixed with LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ powder in the mole ratio of 3:2 by planetary ball milling at 400 rpm for 12 h to obtain the LiCoO$_2$/LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ composite material, and then the composite was heat-treated under 900°C for 2 h. For comparison, LiCoO$_2$, LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$, and the milled LiCoO$_2$/LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ composite without heat treatment were utilized as cathode active materials. The raw materials of LiCoO$_2$ and LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ were also mixed by hand milling, and then the obtained mixture was treated under the same temperature of 900°C for 2 h. All samples were characterized using a Bruker D8 Advance diffractometer (XRD) with CuK$_\alpha$ radiation, at 2θ range of 10–80° with 0.02° per step. The morphology of particles was determined by a NanoSEM 630 scanning electron microscope (SEM, Hitachi, Japan) with energy dispersive X-ray spectroscopy (EDS). Slurries were prepared containing 85 wt.% active materials, 10 wt.% super P and 5 wt.% PVdF in N-methyl-2-pyrrolidone. The slurries were coated onto aluminum foil, and then dried at 110°C for 12 h in a vacuum oven, and then punched to 12 mm diameter disk for testing. The electrochemical properties were carried out using CR2032 coin-type half-cells. Cells were assembled in a glove-box filled with argon. A lithium-foil and a polypropylene film (Celgard 3501) were used as the counter electrode and separator, respectively. The electrolyte used was 1 mol dm$^{-3}$ LiPF$_6$ dissolved in a mixture of ethylene (EC) and dimethyl carbonate (DMC) (1:1 by volume). The galvanostatic charge-discharge tests were carried out at a constant current density in a voltage range of 3.0–4.3 V using a LAND battery test system (Wuhan, China). Cyclic voltammetry (CV) was performed at a CHI-660E workstation with voltage range of 3.0–4.3 V at a scan rate of 0.1 mV s$^{-1}$.\(^-\)

3. Result and Discussions

Figure 1 shows the X-ray diffraction patterns of LiCoO$_2$ (LCO),
LiNi0.8Co0.1Mn0.1O2 (NCM) and treated-LCO/NCM composites were also studied as shown in Fig. 5. As expected, the LCO electrodes showed better rate capability than either, while the rate capability of NCM electrodes was superior to that of NCM and LCO/NCM composites was also studied. However, the discharge capacities of all samples decreased with the increase of cycle number, especially for the NCM and LCO/NCM. It was well known that the active material can be reacted and dissolved in the electrolyte during the cycling. It is herein, similar phenomenon should happen in all the cases during the charge and discharge processes.

Figure 3 shows the first three CV curves of LCO, NCM, LCO/NCM and treated-LCO/NCM at scan rate of 0.1 mV s⁻¹, respectively. Obviously, the LCO showed a reversible oxidation and reduction of lithium extraction and insertion. For the NCM cathode, three oxidation peaks were observed at around 3.9, 4.0 and 4.2 V, respectively, which were attributed to the oxidation of Ni and Co transition metals in the NCM composite. Compared with the LCO and NCM, the CV curves of the LCO/NCM should be the combination of LCO and NCM, while the treated-LCO/NCM exhibited extremely similar oxidation/reduction behaviors to that of NCM, implying that part of LCO was doped by Ni and Mn elements from NCM after heat treatment.

The cycling stability and Coulombic efficiency of the LCO, NCM, LCO/NCM, and treated-LCO/NCM electrodes were also compared at the same current density of 90 mA g⁻¹, as shown in Fig. 4. For NCM cathode, although it had high capacity, the cell showed fast capacity fading (154.2 mAh g⁻¹ after 100 cycles) with an initial Coulombic efficiency of 87%. The LCO showed a small capacity of ~150 mAh g⁻¹ and a better cycling stability compared to NCM cathode. Noticeably, the LCO/NCM without heat treatment gave the worst performance among them. However, the treated LCO/NCM exhibited an excellent battery performance. A specific capacity of ~162 mAh g⁻¹ was achieved in the initial cycle, which was much higher than LCO. Furthermore, this cell also presented an excellent cycling stability, with a capacity of ~148 mAh g⁻¹ remaining after 100 cycles. On the other hand, the treated LCO/NCM also showed a relatively high initial Coulombic efficiency of ~89%, which increased to ~100% at the second cycle, and finally stabilized at ~99.8% in subsequent cycles. However, this phenomenon was quite different from LCO/NCM, and the Coulombic efficiency of LCO/NCM dropped quickly during the cycling, caused by a side reaction between cathode and electrolyte. Obviously, the heat treatment can remarkably enhance the performance of LCO/NCM cathode material. Furthermore, compared with the treated-LCO/NCM, the heat-treated mixture prepared by the raw materials showed lower capacity, lower coulombic efficiency and worse cycling stability. Hence, the improved electrochemical performance should be closely related to the co-doping of Ni and Mn for LiCoO₂ powder.

The rate capability of the treated LCO/NCM composites was investigated with increasing current densities from 0.5 C to 5 C (1 C = 180 mA g⁻¹). For comparison, the LCO, NCM, and LCO/NCM were also studied as shown in Fig. 5. As expected, the LCO showed better rate capability than either, while the rate capability of the treated LCO/NCM composite was superior to that of NCM and
LCO/NCM. The treated LCO/NCM composite can still deliver a reversible capacity of \( \sim 125 \text{ mAh g}^{-1} \) at a high current density of 5 C rate. The much improved rate capability of the treated LCO/NCM could be ascribed to the small particle size after ball milling, which lithium ions had shorter diffusion length compared to the large particles during charge/discharge processes.

To better understand the much-improved electrochemical performance achieved by heat treatment process, scanning electron microscopy (SEM) was performed on all the samples. Figure 6 shows SEM images of LCO, NCM, LCO/NCM, and treated LCO/NCM powders, respectively, together with EDS elemental mappings of the treated LCO/NCM composite. It was found that the LCO
particles were irregularly-shaped particles with the particle size between 20 and 40 µm, while the NCM composites were spherical particles in the size of \( \sim 10 \) µm, composed of small primary crystals. After mechanical ball milling, the NCM were damaged to small particles, which were dispersed on the surface of LCO particles (Fig. 6c). However, after heating at elevated temperature, some of the NCM primary particles were integrated into the surface of LCO, as shown in Fig. 6d and f. The corresponding selected area EDS elemental mapping of the composite showed that Ni, Co, and Mn were distributed homogeneously (Fig. 6f). This result confirmed that Ni and Mn elements of NCM were doped into the LCO particle after heating, resulting in improving the electrochemical properties of the LCO/NCM cathode.

4. Conclusions

In summary, a LiCoO\(_2\)/LiNi\(_{0.8}\)Co\(_{0.1}\)Mn\(_{0.1}\)O\(_2\) composite was prepared using the combination of mechanical ball milling and heat treatment. The as-prepared LiCoO\(_2\)/LiNi\(_{0.8}\)Co\(_{0.1}\)Mn\(_{0.1}\)O\(_2\) composite showed enhanced electrochemical performance, including higher reversible capacity, improved capacity retention, and superior rate capability. The improved performance of the LiCoO\(_2\)/LiNi\(_{0.8}\)-Co\(_{0.1}\)Mn\(_{0.1}\)O\(_2\) composite can be attributed to the fact that some of LCO was co-doped by Ni and Mn from LiNi\(_{0.8}\)Co\(_{0.1}\)Mn\(_{0.1}\)O\(_2\) during high temperature.

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