Surface modification of LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ with Cr$_2$O$_3$ for lithium ion batteries

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Abstract
Cr$_2$O$_3$-coated LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ cathode materials were synthesized by a novel method. The structure and electrochemical properties of prepared cathode materials were measured using X-ray diffraction (XRD), scanning electron microscopy (SEM), charge-discharge tests, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). The measured results indicate that surface coating with 1.0 wt.% Cr$_2$O$_3$ does not affect the LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ crystal structure ($\alpha$-NaFeO$_2$) of the cathode material compared to the pristine material, the surfaces of LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ samples are covered with Cr$_2$O$_3$ well, and the LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ material coated with Cr$_2$O$_3$ has better electrochemical performance under a high cutoff voltage of 4.5 V. Moreover, at room temperature, the initial discharging capacity of LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ material coated with 1.0 wt.% Cr$_2$O$_3$ at 0.5C reaches 169 mAh·g$^{-1}$ and the capacity retention is 83.1% after 30 cycles, while that of the bare LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ is only 160.8 mAh·g$^{-1}$ and 72.5%. Finally, the coated samples are found to display the improved electrochemical performance, which is mainly attributed to the suppression of the charge-transfer resistance at the interface between the cathode and the electrolyte.

Keywords: lithium ion batteries; LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$; Cr$_2$O$_3$ coating

1 Introduction
Recently, much attention has been paid to the layered LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ as a promising alternative to LiCoO$_2$ cathodes material due to its low cost, enhanced safety, and increased energy density [1–4]. Compared to LiCoO$_2$ cathodes material, there is no structural degradation, although LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ is charged to 4.6 V, and the capacity is approximately 200 mAh·g$^{-1}$ [2]. However, it shows low rate capability and considerable capacity loss at a high voltage compared to LiCoO$_2$, which limits its further application [5–7]. Kageyama et al. [8] regarded that the mechanism of the capacity loss at a high rate and in a high cutoff voltages of layered LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ should be due to the instability of the electrode surface. Recent experimental results indicated that the coating with metal oxides, such as Al$_2$O$_3$ [9–10], ZnO [11], MgO [12], TiO$_2$ [13], ZrO$_2$ [14–15], Y$_2$O$_3$ [16], and CeO$_2$ [17], was an effective way to significantly improve their electrochemical performance. For example, Hu et al. [15] reported that the rate capability and cycling stability under a high cutoff voltage of 4.5 V of LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ were modified by coating their surface with a uniform and nanosized layer of ZrO$_2$. Nevertheless, to our knowledge, there are few reports on surface modification LiNi$_{1/3}$Co$_{1/3}$-Mn$_{1/3}$O$_2$ materials with Cr$_2$O$_3$. In this paper, we attempted to modify the surface of LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ by Cr$_2$O$_3$. The effects of Cr$_2$O$_3$ coating on the electrochemical properties were studied in detail.

2 Experimental
Layered materials of LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ were prepared as follows: an aqueous solution of stoichiometric amounts of LiOH·H$_2$O(AR), Ni(CH$_3$COO)$_2$·4H$_2$O(AR), Co(CH$_3$COO)$_2$·4H$_2$O(AR), and Mn(CH$_3$COO)$_2$·4H$_2$O(AR), and Mn(CH$_3$COO)$_2$·4H$_2$O(AR) were dissolved in distilled water. Then, 0.5 mol·L$^{-1}$ citric acid aqueous solution was added slowly to mixture (obtain a clarifying solution) with constant stirring at 80 °C for 10 h. After that, the obtained gel was dried in an oven at 120 °C to get a solid precursor and then pre-heated at 500 °C. Finally, it was calcined at 850 °C for 15 h in air.

To prepare LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ coated with 1.0 wt.% Cr$_2$O$_3$, 3.0 g LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ was dissolved in distilled water, and then the calculated quantities of Cr(NO$_3$)$_3$·9H$_2$O and polyvinyl alcohol (PVA, degree of polymerization is 1500) were added. The mixture was stirred at 60 °C until the solvent was vaporized. After calcining the dried mixture at 600 °C for 6 h, the LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ coated with 1.0
wt.% Cr$_2$O$_3$ materials was obtained. The detailed process was reported elsewhere [17].

The phases of the prepared samples were analyzed with an X-ray diffractometer, with a Cu K$_\alpha$ radiation source ($\lambda = 0.15405$ nm). The 2θ Bragg angles were scanned over a range of 10° to 70°. Scanning electron microscopy (SEM) studies of the samples were performed using a JSM-7500F electron microscope. The charge-discharge tests were performed with CR2025 coin-type cell on the Land CT-2001A apparatus at 20 mA·g$^{-1}$ and 0.5C (80 mA·g$^{-1}$) between 2.8 and 4.5 V (vs. Li/Li$^+$). Cyclic voltammetry (CV) curves were measured on the electrochemical workstation. Electrochemical impedance spectroscopies (EIS) were also conducted using electrochemical workstation (CHI660C) in the frequency range from 0.01 to 100 kHz with voltage perturbation amplitude of 5 mV.

The cathode electrode was prepared by blending a mixture of cathode materials, carbon black (Super P), and polyvinylidene fluoride (PVDF) binder in a weight ratio of 80:10:10 with enough N-methyl pyrrolidinone (NMP) to form the slurry. The obtained slurry was pasted onto aluminum foil followed by drying at 110 °C for 12 h in a vacuum oven and then punched and weighed. The test cell comprised a positive electrode and lithium foil anode, and they were separated by a porous polypropylene membrane (Celgard 2300). The electrolyte was 1 mol·L$^{-1}$ LiPF$_6$ in the mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and dimethyl carbonate (DMC) with volume ratio being 1:1:1. Coin cells (R2025) were assembled in a glove box filled with dry argon gas.

3 Results and discussion

The X-ray diffraction (XRD) patterns of bare and LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ coated with 1.0 wt.% Cr$_2$O$_3$ powders are shown in Fig. 1. All the observed diffraction peaks can be well indexed on the basis of α-NaFeO$_2$-type structure and no obvious evidence for the presence of impurity phases are found within the sensitivity of measurement [18]. That is, the Cr$_2$O$_3$ coating does not change the crystalline structure of LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$. Typical SEM images of bare and LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ coated with 1.0 wt.% Cr$_2$O$_3$ samples are shown in Figs. 2(a) and (b), respectively. No significant difference of the grain sizes between samples is observed. Compared to LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$, the surface of the Cr$_2$O$_3$-coated LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ seems to be coarser, which indicates the presence of the Cr$_2$O$_3$ on the surface.

The first cycle charge-discharge curves of bare and Cr$_2$O$_3$-coated LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ with the rate of 20 mA·g$^{-1}$ between 2.8 and 4.5 V (vs. Li$^+$/Li) are shown in Fig. 3. From the figure, it is observed that the initial discharge capacity of the Cr$_2$O$_3$-coated LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ is 196.3 mAh·g$^{-1}$, while that of bare sample is 196.8 mAh·g$^{-1}$. This result indicates that the initial discharge capacity of surface modification with 1.0 wt.% Cr$_2$O$_3$ does not obviously change compared to the bare material under a small current density.

Figure 4 shows the cycling performance of bare and LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ coated with 1.0 wt.% Cr$_2$O$_3$ at a constant current density of 20 mA·g$^{-1}$.