Effect of Mn Content on the Microstructure and Electrochemical Performance of $LiNi_{0.75-x}Co_{0.25}Mn_xO_2$ Cathode Materials

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Due to the lower cost and higher discharge capacity, $LiNiO_2$ is the most attractive cathode material to replace $LiCoO_2$ in lithium-ion batteries. Nevertheless, stoichiometric $LiNiO_2$ is difficult to synthesize, and it is necessary to substitute Ni partially with other elements to stabilize the structure. In this work, the newly developed $LiNi_{0.75-x}Co_{0.25}Mn_xO_2$ ($0.1 \leqq x \leqq 0.25$) cathode materials were successfully synthesized by mixing $Ni_{0.75-x}Co_{0.25}Mn_x(OH)_2$ and Li_2CO_3 via the solid-state reaction followed by heating to elevated temperatures. The $Ni_xCo_yMn_{1-x-y}(OH)_2$ precursors were derived by the chemical co-precipitation method with pH value controlled by the concentration ratio of NaOH, NH_4OH and transition metal sulfate solution.

X-ray diffraction patterns showed that the samples calcined at 900℃ exhibited a typical hexagonal □-$NaFeO_2$ structure without any other impurities. The scanning electron microscopy (SEM) micrograph revealed uniform particle size, and the particles then agglomerated to form the secondary ones with size distribution in the range of 6-9 □m, as shown in Fig. 1. For $LiNi_{0.75-x}Co_{0.25}Mn_xO_2$ calcined at 900℃, the grain sizes reduced with the increasing of Mn content.

The cathode materials showed good electrochemical performance with initial discharge capacity about 160-175 mAh/g at 0.1C rate in the voltage range of 3-4.3 V. After 20 cycling test, Fig. 2 showed that the discharge capacity retentions of $LiNi_{0.75}Co_{0.25-x}Mn_xO_2$ calcined at 900 ^oC were 97.8%, 96.7%, 95.1% and 94.6%, respectively, for x = 0.1, 0.15, 0.2 and 0.25. The rate capabilities of $LiNi_{0.75-x}Co_{0.25}Mn_xO_2$ decreased with increasing Mn content.

To further investigate the effect of Mn content on the electrochemical performance of $LiNi_{0.75-x}Co_{0.25}Mn_xO_2$, the electrochemical states of Ni, Co and Mn were evaluated. X-ray photoelectron spectroscopy (XPS) measurements revealed that the amount of Mn content had no influence on the oxidation states of Co and Mn. The oxidation states of Co and Mn were +3 and +4, respectively. However, the addition of Mn impacted the oxidation state of Ni ions in $LiNi_{0.75-x}Co_{0.25}Mn_xO_2$ cathode materials. With increasing Mn content, the Ni $2p_{3/2}$ peak at 855.3 eV shifted to the lower energy, indicating that the oxidation state of Ni was decreased, as revealed in Fig. 3.

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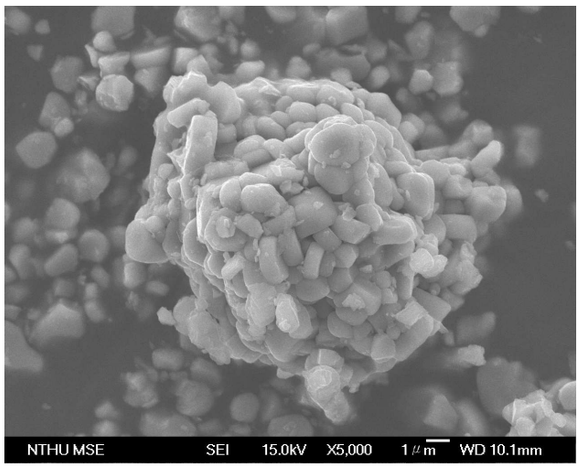

Fig. 1. FESEM photograph of $LiNi_{0.65}Co_{0.25}Mn_{0.1}O_2$ calcined at 900℃

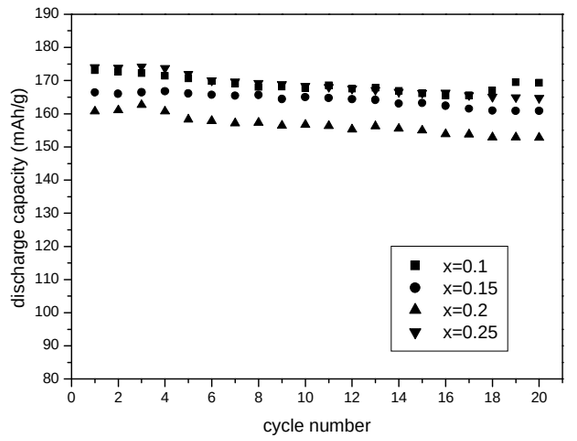

Fig. 2. Specific discharge capacities of $LiNi_{0.75-x}Co_{0.25}Mn_xO_2$ (x= 0.1, 0.15, 0.2, 0.25) calcined at 900℃ for several hours cycled at the 0.1C rate with 3-4.3 V at room temperature.

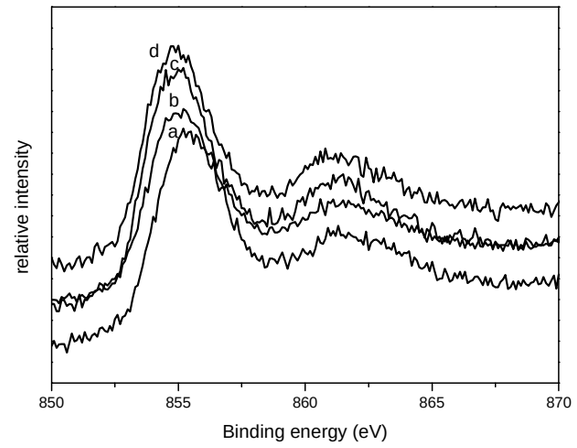

Fig. 3. Ni 2p spectra of $LiNi_{0.75-x}Co_{0.25}Mn_xO_2$ at various Mn contents (a) x= 0.1, (b) x=0.15, (c) x=0.2 and (d) x=0.25.