

Study of the Crystal Growth Process and the Electrochemical Properties of High Voltage Cathode Active Materials: $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$

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Introduction

Spinel structured $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ is expected as a next generation cathode active material for high-voltage lithium-ion batteries. The biggest problem of the cathode is the poor cycleability due to the decomposition of the electrolyte. However a recent study revealed that the highly crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ cathode showed significant improvement in the cycling performance[1]. We also successfully demonstrated >95% of capacity retention after 100 cycles at 60°C using the highly crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ cathode as shown in Fig. 1. However the formation process of the highly crystalline cathode is not well understood yet.

In this study, the crystal growth process of the $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ spinel was investigated using high temperature X-ray diffraction (HT-XRD) and discussed the influences of the crystallinity of the cathodes to the electrochemical properties.

Experimental

Highly crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ was synthesized by a conventional solid-state method. A nickel manganese double hydroxide (Ni:Mn=0.99:3.01) was annealed at 500°C for 8 hours. The obtained complex oxide was mixed with stoichiometric amount of $\text{LiOH}\cdot\text{H}_2\text{O}$ and calcined at 1000°C for 10 hours in air and subsequently Re-oxidized at 700°C for 12 hours, 650°C for 12 hours and 600°C for 24 hours.

The HT-XRD measurements were periodically taken during the calcination process. Furthermore, the morphology of the samples during the heating process was observed using scanning electron microscope (SEM).

Result & discussion

The HT-XRD results during the heating process are shown in Fig.2. Formation of spinel phase started at 400°C and then all the peaks corresponding to the raw materials disappeared at 700°C.

Above 900°C, diffraction peaks corresponding to the spinel phase got weaker, and several new peaks appeared. The new peaks observed at the high temperature could be assigned to a NiO-like rock salt phase. The formation of the rock salt phase indicates that the diffusion of the transition metal ion was occurring at the high temperature. Once the temperature reached to 1000°C, the peak intensity for the spinel phase significantly dropped, while the peaks for the rock salt phase increased more. However the spinel phase was reformed once the temperature dropped down to 700°C. It could be a reversible phase transformation between the spinel phase and the rock salt phase.

In addition, SEM observation results were in good agreement with the HT-XRD. The morphology of the particles below 700°C did not show any change while the primary particle growth was observed at 900°C. Moreover the morphology of the particle significantly changed during the calcination at 1000°C. After 10 hours,

most of the particle transformed to the beautiful octahedral shape as reported.

These results suggests that the diffusion of the transition metal ion in the spinel phase was accelerated at 1000°C resulting in the phase transformation to the rock salt phase. We suspect the particle growth was initiated in this process to minimize the surface energy of the particle.

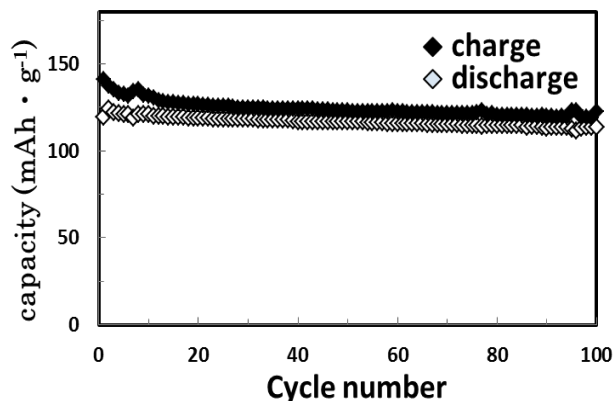


Fig.1 Cycling performance of the highly crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$. The cycling test was performed at 60 °C

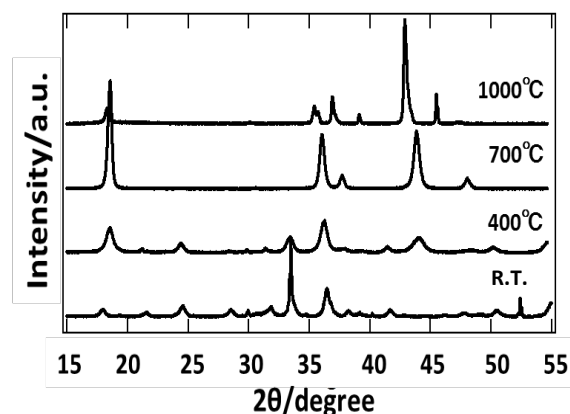


Fig.2 HT-XRD patterns during the heating process of the $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$

References

- [1] K. Ariyoshi, Y. Maeda, T. Kawai, T. Ohzuku, Journal of the Electrochemical Society, 158 (2011) A281.