

Improvement of Electrode Performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ for 5 V Cathode Material by Optimizing Preparation Conditions

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Among spinel-type cathode materials such as $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ (M=Cr, Fe, Co, Ni, Cu) for 5 V class lithium rechargeable batteries, Ni-doped spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has been received great attention because of its high theoretical capacity (147 mAh/g) at 4.7 V region and good phase stability [1-3]. High capacity of this material is believed to be due to the oxidation of Ni^{2+} to Ni^{4+} , and theoretically the Mn valence is fixed to 4+ during electrochemical cycling. In practice, however, 4.1 V plateau which is originated from $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox reaction is not completely disappeared in the samples prepared by the conventional solid-state reaction. Therefore, some research groups have reported various synthetic routes such as sol-gel [4], composite carbonate process [5] and post-annealing method [6].

In this study, in order to improve the practical electrode performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ such as high temperature (55°C) cycleability, rate capability, coulombic efficiency, we have optimized the variables of solid-state reaction method combined with high-energy ball milling process. In addition, effects of the conductor (acetylene black) portion in cathode mixture, composition of electrolyte solvent, and surface coating of the particles with ZrO_2 were also investigated.

To prepare well-ordered and homogeneous $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders, Li_2CO_3 , $\text{Ni}(\text{OH})_2$ and MnO_2 were thoroughly mixed and mechanically activated using a high-energy ball mill (Pulverisette 6). The ball milling conditions were optimized to obtain fine particles smaller than 5 μm with exact composition and no contamination. Then one-step or two-step heat treatments were carried out at various temperatures of 600~900°C. The heating time, atmosphere and cooling rate were varied for better cathode performance. Surface coatings with ZrO_2 were conducted by a wet process or a mechanical method [7].

XRD, FE-SEM, PSA and ICP analyses were performed to characterize the crystalline structure, powder morphology and size distribution, and elemental composition of prepared samples. The electrochemical cycling performances were evaluated using CR2032 coin cell with a lithium foil anode. The electrolytes were 1M LiPF_6 in various combinations of inorganic solvents (EC/DMC, EC/DEC, EC/EMC/DMC etc.). The cells were galvanostatically cycled between 3.5 V and various charge cut-off voltages up to 5.2 V at various C rates (0.2C ~ 3C, 1C = 140 mA/g). Galvanostatic intermittent titration technique (GITT) and cyclic voltammetry (CV) experiments were performed to investigate the chemical diffusivity and kinetics of Li transportation.

Fig.1 shows initial discharge curves of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ samples synthesized by different heating schedule. The final heating temperatures were same as 800°C. As can be seen, the 4.1 V capacity measured in the range of 3.5~4.2V was decreased from 20 to 10 mAh/g by changing the heating schedule from one-step to two-step heating. This means that Mn^{3+} ions can be effectively replaced by Ni^{2+} ions by changing the heat treatment

conditions. Fig.2 shows the improvement of cycle life by changing the combination of organic solvents. The lithium salt was fixed to 1M LiPF_6 . With the best electrolyte system, prepared $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode exhibited high initial discharge capacity of 130 mAh/g and good capacity retention of 97% after 50 cycles.

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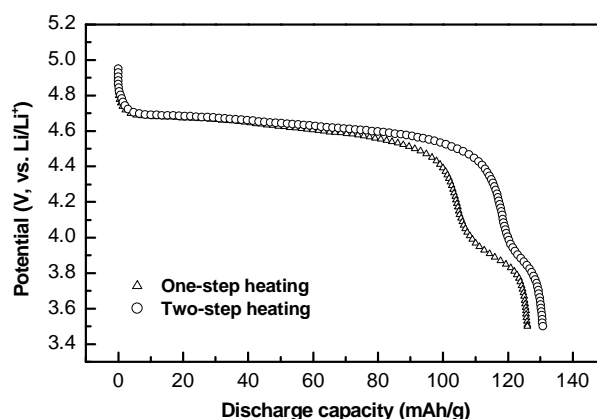


Fig.1. Comparison of initial discharge curve for the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ samples prepared by different heat treatment schedule (cycled between 3.5~5.0 V at C/2 rate).

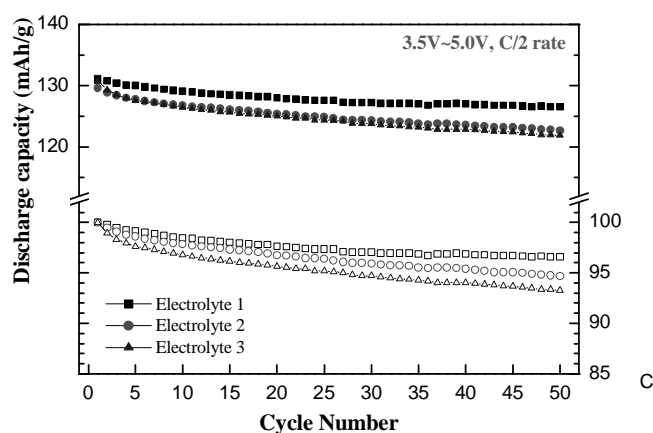


Fig.2. Discharge capacity and the capacity retention as a function of cycle number for a prepared $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ sample in different electrolyte systems (combination of various organic solvents).