

Bulk and Surface Modification of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ Materials as 5-V Cathodes for Li-ion Batteries

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Developing cathode materials with high energy densities is one of the key challenges for adopting the lithium-ion battery technology for HEV and EV green transportation. One of the candidates is the 5-volt spinel phase $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (denoted LMN) that, depending on the ordering of Ni/Mn in the octahedral sites, crystallizes as disordered LMN ($Fd\bar{3}m$ S.G) or ordered LMN ($P4_332$ S.G) [1-2]. It was demonstrated that ordering of the Ni(II) and Mn(IV) retards the lithium diffusivity and therefore lowers the rate capability compared to the disordered phase. To eliminate the impurity phases and to reduce the oxygen deficiency in disordered LNM spinel phase, doping with chromium and post-annealing treatment have been realized, which results in enhancement of electrochemical performance [2].

In this work, we prepared two types of 5-V LNM cathode materials modified by (i) Cr doping (10 mol.%) and (ii) surface modification by LiFePO_4 coating. The structural analyses and electrochemical properties are reported and data are compared with those of a commercial sample.

The structural analyses of $\text{LiMn}_{1.45}\text{Cr}_{0.1}\text{Ni}_{0.45}\text{O}_4$ spinel prepared by a co-precipitation method assisted by a post-annealing at 600 °C suggest that a post annealing process at lower temperature is an effective way to tune the oxygen deficiency while keeping the spinel in the disordered structure. The electrochemical properties have been investigated with Li as the counter electrode, and the electrolyte was 1 mol. L^{-1} LiPF_6 dissolved in ethylene carbonate-dimethyl carbonate (1:1 v/v). Compared with the commercial LMN, the $\text{LiMn}_{1.45}\text{Cr}_{0.1}\text{Ni}_{0.45}\text{O}_4$ sample gave a better rate capability along with capacity retention. $\text{LiMn}_{1.45}\text{Cr}_{0.1}\text{Ni}_{0.45}\text{O}_4$ cathode materials delivered a reversible capacity of ~115, 104, 95 and 40 mAh g^{-1} at 0.2C, 1C, 2C and 5C, respectively (Fig. 1). After 125 cycles, about 99% of reversible capacity was retained for the $\text{LiMn}_{1.45}\text{Cr}_{0.1}\text{Ni}_{0.45}\text{O}_4$, while about 6% of capacity loss was obtained after 125 cycles for the bare $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$.

The surface reactions between cathode-electrolyte have been confirmed to be one of the

major reasons leading to the degradation in the electrochemical performance of the 5-V spinel [3]. In this regard, LiFePO_4 phosphate (LFP) was used as surface coating to improve the electrochemical performance of the spinel LMN. Two different routes have been explored: the traditional sol-gel method and the mechano-fusion dry process. The studies demonstrate that the LFP coating should offer important benefits to increase the rate property as well as cycling performance for lithium-ion batteries (Fig. 2).

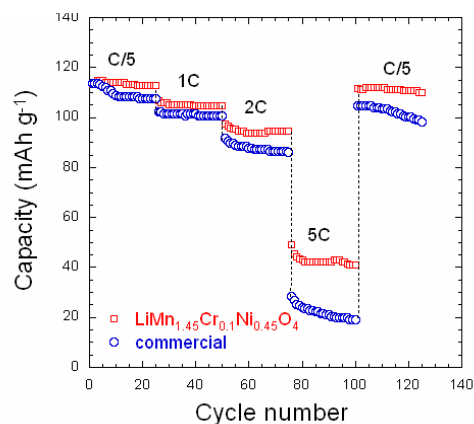


FIG. 1. Cycling performance of the (a) Cr:LMN and (b) bare LMN at various C rates.

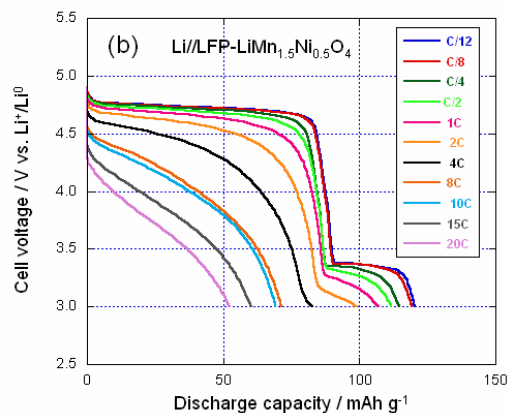


FIG. 2. Voltage profiles of the Li/LFP-coated LMN cells in the range 3.0-4.9 V vs. Li at various C-rate.

References

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