



## Synthesis and Electrochemical Properties of ZnO-Coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Spinel as 5 V Cathode Material for Lithium Secondary Batteries

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ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders with excellent electrochemical cyclability and structural stability at elevated temperature have been synthesized by a sol-gel method. The structural degradation of the as-prepared  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  and ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrodes before and after cycling in the 5 V region has been studied. The ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrode showed almost no capacity loss and retained its original cubic spinel structure after 50 cycles. We found that ZnO played an important role in reducing the HF content in the electrolyte solution.

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Spinel  $\text{LiMn}_2\text{O}_4$  is one of the most promising cathode materials due to low cost, abundance, and nontoxicity.<sup>1-3</sup> It is well known that the spinel  $\text{LiMn}_2\text{O}_4$  electrode shows good stability during cycling at room temperature, but poor cycling behavior at elevated temperature, *e.g.*, 50–80°C, which prevents its wider use as cathode materials for lithium secondary batteries.<sup>4,5</sup>

In larger scale batteries for zero emission vehicles, the cathode materials with the high energy density are critical for development. Some research groups have recently reported that transition metal-substituted spinel materials ( $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ ,  $M = \text{Cr}, \text{Co}, \text{Fe}, \text{Ni}$ ) showed a higher voltage plateau at ~5 V.<sup>6-10</sup> They also reported that the 5 V plateau originates from oxidation of substituted transition metals (M), while a 4 V plateau is associated with  $\text{Mn}^{3+}$  oxidation to  $\text{Mn}^{4+}$ . Furthermore, it is well known that the discharge capacity and 5 V plateau in  $\text{Li/LiM}_x\text{Mn}_{2-x}\text{O}_4$  cells strongly depend on the kind of transition metals (M) and their concentration. Recently improved electrolytes have made it possible to explore the cathode materials using potential range extended to *ca.* 5 V. To improve both the cycleability and the rate capability of electrode at elevated temperature, many researchers have studied the surface treatment of electrode active materials by sol-gel coating with the  $\text{LiCoO}_2$  and  $\text{Al}_2\text{O}_3$ .<sup>11-14</sup> However, there are no reports of the cycling performance of 5 V cathode materials at elevated temperatures so far.

In this paper, we report the improved cycling performance of ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrodes at elevated temperatures and the role of ZnO on the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  particle surface during electrochemical cycling. Structural changes of host materials before and after cycling at elevated temperature were also studied by charge/discharge experiments and X-ray diffraction (XRD).

### Experimental

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders were prepared by a sol-gel method using glycolic acid as a chelating agent.  $\text{Li}(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$ ,  $\text{Ni}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ , and  $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$  (cationic ratio of  $\text{Li}:\text{Ni}:\text{Mn} = 1:0.5:1.5$ ) were dissolved in the distilled water, and added drop wise to a continuously stirred aqueous solution of glycolic acid. The pH of the solution was adjusted to 8.5–9.0 using ammonium hydroxide. The resultant solution was evaporated at 70–80°C until a transparent sol and gel was obtained. The resulting gel precursors were decomposed at 500°C for 10 h in air, and calcined at 850°C in air for 10 h. To coat ZnO on the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders,  $\text{Zn}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$  was first dissolved in the distilled

water. The synthesized  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders were poured into the solution and then mixed for 4 h at room temperature. The amount of Zn in the coating solution corresponded to 1.5 wt % of the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders. After drying the ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders at 120°C, they were further calcined at 400°C for 1 h in air.

Powder XRD (Rigaku, Rint-2000) using  $\text{Cu K}\alpha$  radiation was used to identify the crystalline phase of the materials and cycled electrodes. The particle morphology of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders was observed using a field-emission-scanning electron microscope (Hitachi Co., S-4100). The HF content in the electrolyte was measured by neutralization titration method and the average manganese oxidation state of the as-prepared  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders by a potentiometric titration method described in the literature.<sup>15</sup> The acid-base indicator was BTB (Bromothymol blue).

Charge-discharge cycles were performed in CR2032 button type cells. The cell consisted of a cathode and a lithium metal anode separated by a porous polypropylene film. For the fabrication of the electrode, the mixture, which contained 25 mg  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders and 15 mg conducting binder (10 mg Teflonized acetylene black and 5 mg graphite), was pressed on 2.0  $\text{cm}^2$  stainless screen at 800  $\text{kg cm}^{-2}$ . The electrolyte was a 1:2 mixture of ethylene carbonate and dimethyl carbonate containing 1 M  $\text{LiPF}_6$  by volume. Charge-discharge cycles were performed galvanostatically at a current rate of C/3 (0.4  $\text{mA cm}^{-2}$ ) between 5.2 and 3.5 V.

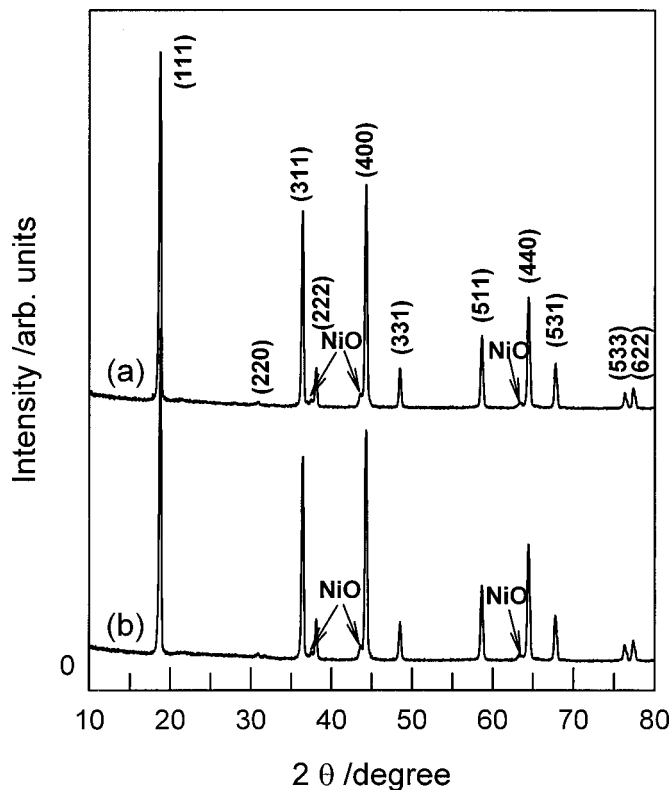
### Results and Discussion

XRD patterns of the as-prepared  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  and ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders are shown in Fig. 1. It was confirmed that two materials were well-defined spinel phases with the space group  $Fd\bar{3}m$ , although there were small amount of NiO peaks as impurity near the (311), (400), and (440) peaks. Even if ZnO related phases do not appear on the XRD pattern of the ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders, it is speculated that a small amount of ZnO might exist on the surface. The lattice constants (*a*) of the as-prepared  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders were calculated by Rietveld refinement from the XRD data to be 8.160 Å, which is much lower than that of stoichiometric spinel.<sup>4</sup> Recently, Amatucci and co-workers reported that  $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$  spinels with smaller lattice constants showed better cycling performance in the 4 V region.<sup>16</sup> The average manganese oxidation state of the as-prepared  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powder was 3.98, which was identical to the theoretical value.

Figure 2 shows scanning electron microscope (SEM) images for the as-prepared and ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders. The par-

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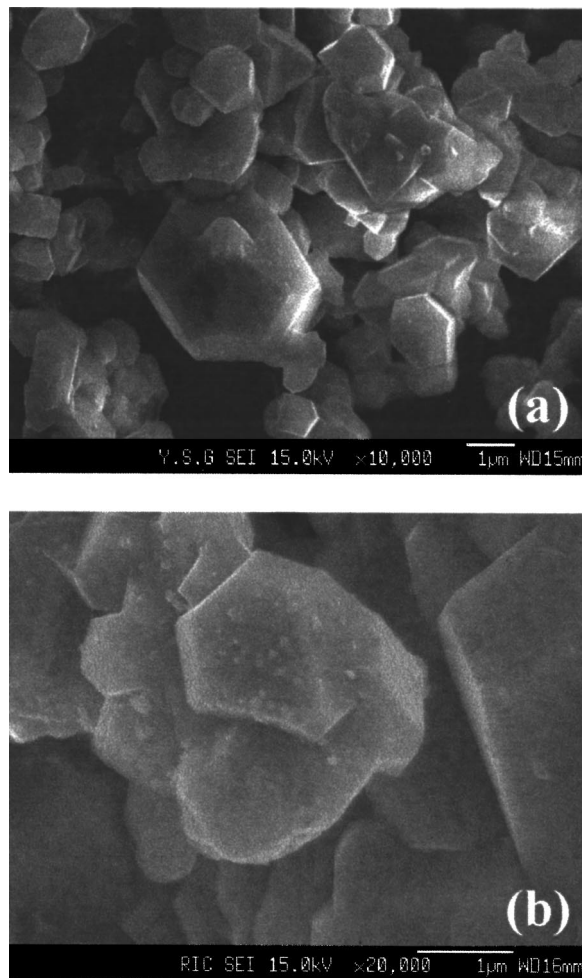
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**Figure 1.** XRD patterns of (a) the as-prepared  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  and (b) ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders.

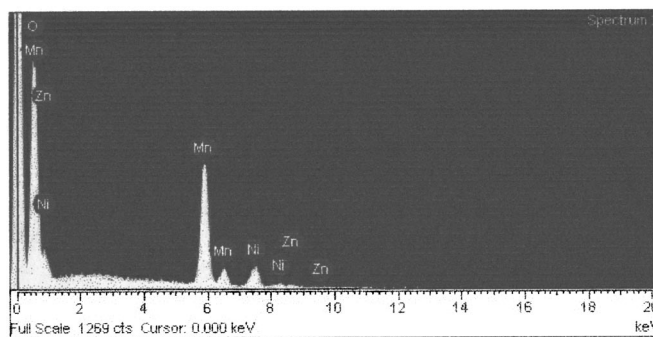
ticles of the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders have a well-developed (100) planes and a size distribution ranging from 0.5 to 2  $\mu\text{m}$ . For the ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders, ZnO with the order of 10 nm or less is uniformly distributed over the surface of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders as shown in Fig. 2b. To confirm the component of the coated material on the surface of the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders, energy-dispersive analysis by X-ray (EDAX) analysis was performed in Fig. 3. It clearly revealed that Zn existed on the surface of the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  particles.

Figure 4 shows charge/discharge curves for the as-prepared and ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrodes as a function of the cycle number at 25°C. The  $\text{Li}/\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cell shows a very flat discharge plateau at 4.75 V vs.  $\text{Li}/\text{Li}^+$ . When comparing voltage profiles of as-prepared  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrode with that of the ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrode, we could not find any difference between the two. The as-prepared and the ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrodes cycled at 25°C delivered an initial capacity of 140 and 137 mAh/g, respectively. The capacity retention was 92% for as-prepared  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  and 94% for ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrodes after 50 cycles. However, the cycling characteristics for the as-prepared and ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrodes at 55°C are quite different. Figure 5 shows discharge capacities as a function of cycle number for the two electrodes. Although the two materials at elevated temperature delivered almost the same initial discharge capacity of about 135 mAh/g, the discharge capacity of as-prepared  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  decreased dramatically on cycling, and then displayed 36 mAh/g after 50 cycles. On the other hand, the discharge capacity of the ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrode slowly increased with cycling and remained 136 mAh/g after 50 cycles. The cycling behavior of the ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  material could be a unique feature, contradictory to that of the as-prepared  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders.

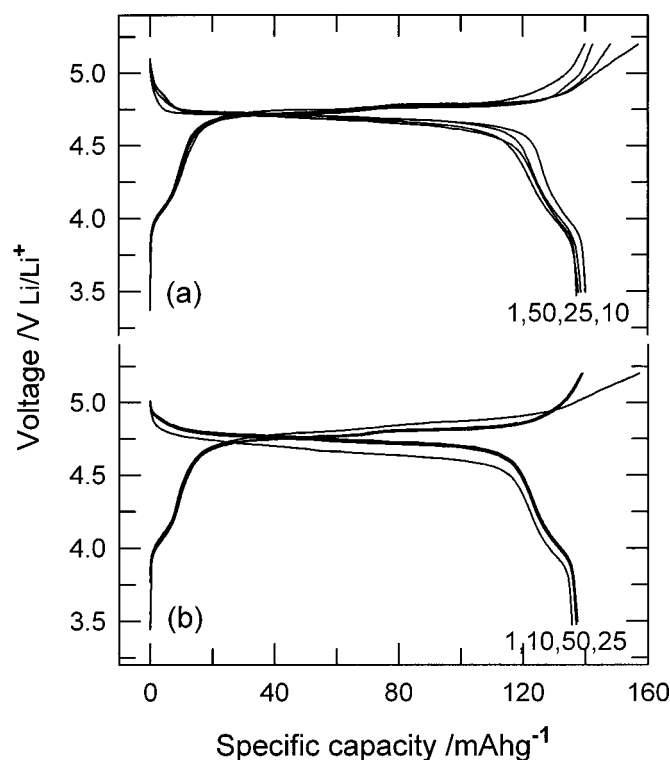


**Figure 2.** SEMs of (a) the as-prepared  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  and (b) ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders.

To explore this different cycling characteristics between the as-prepared  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  and ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  materials, *ex situ* XRD measurements were taken of both electrodes in the discharged state at 55°C after 50 cycles as shown in Fig. 6. The two electrodes had quite different XRD patterns after cycling. The as-prepared  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrode, which showed a serious capacity loss, exhibited a mixture of tetragonal phase ( $\text{Li}_2\text{Mn}_2\text{O}_4$ ), rock salt phase ( $\text{Li}_2\text{MnO}_3$ ), and cubic phase, while the ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrode maintained an almost perfect cubic spinel structure even after 50 cycles. It is commonly accepted that the

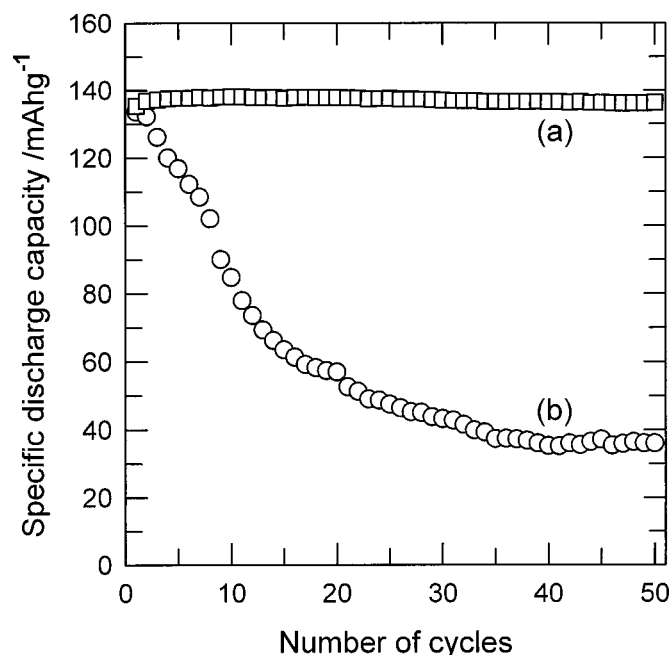


**Figure 3.** EDAX spectrum of the ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders.

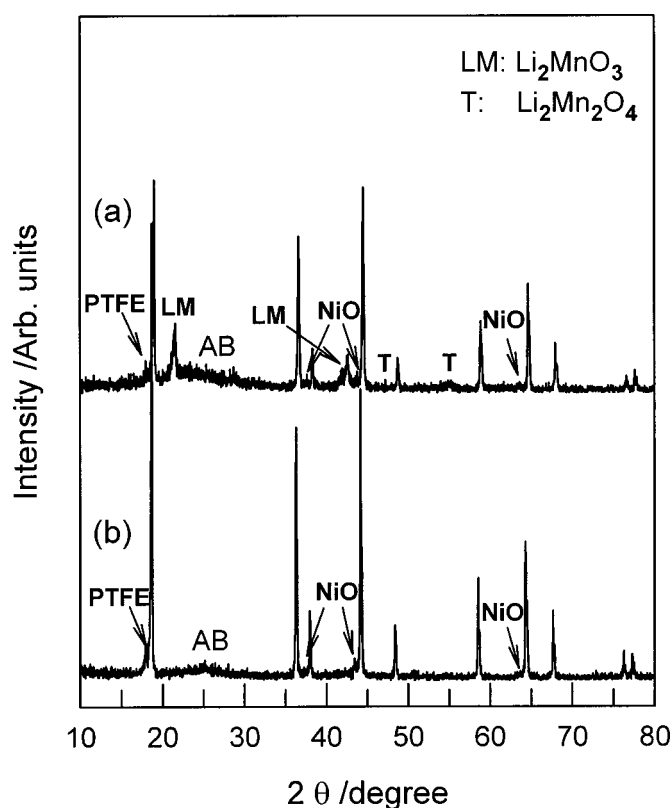


**Figure 4.** Charge-discharge curves for (a) the as-prepared  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  and (b) ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrodes at  $25^\circ\text{C}$  at a constant current densities of  $0.4 \text{ mA/cm}^2$ .

capacity loss for the spinel  $\text{LiMn}_2\text{O}_4$  electrode is attributable largely to a slow dissolution of MnO from the spinel particle into the electrolyte due to HF.<sup>4,17,18</sup> Therefore, we assume that the decrease of HF content at the surface of cathode electrode (or in the electrolyte)



**Figure 5.** Specific discharge capacity for (a) the as-prepared  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  and (b) ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrodes at  $55^\circ\text{C}$  at constant current densities of  $0.4 \text{ mA/cm}^2$ .



**Figure 6.** XRD patterns for (a) the as-prepared  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  and (b) ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrodes after 50 cycles at  $55^\circ\text{C}$ .

results in the decrease of Mn dissolution and improves the cycling performance of  $\text{Li/LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cell. To verify the ZnO effect, we checked the HF content in the electrolyte. The as-prepared and ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders were first statically exposed to the electrolyte solution (HF content 274 ppm) for a week and the HF contents in the two electrolyte solutions were analyzed. The HF contents in the electrolyte of the as-prepared and ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders were 274 and 7.3 ppm, respectively. Note that the HF content in the electrolyte added to the ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders is 37 times less than that of the electrolyte solution added to the as-prepared  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders. Although we still cannot explain clearly the whole reaction mechanism and the key parameters governing the excellent cycling characteristics of the ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrode, we speculate that a small amount of ZnO plays an important role in improving the cycle characterization of the Mn cathode materials in the 5 V region. Further work is now in progress to reveal the reaction mechanism and structural stability for the ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders.

### Conclusions

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  material with cubic spinel structure has been synthesized and coated with nanosized ZnO. It shows excellent electrochemical and structural stability when cycled at 5 V. The capacity retention of the as-prepared and ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrode after 50 cycles at  $55^\circ\text{C}$  are 27 and 99% of the initial discharge capacity, respectively. The main reason for the excellent cycling and structural stability of ZnO-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrode at elevated temperature is attributed to significantly reduced HF content in the electrolyte.

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