



Electrochemical performance of layer–spinel composite cathode materials at elevated temperature and high rate

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ABSTRACT

$x\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2\text{-LiMn}_{1.95}\text{Ni}_{0.05}\text{O}_{3.98}\text{F}_{0.02}$ composite cathode materials with various mass ratios ($x = 5.0\%$, 7.5% , and 10.0%) are prepared by the Pechini method. The relationship between the structural and electrochemical properties of the layer–spinel composite cathode materials is investigated. XRD shows the composite materials still possess cubic spinel structure of the pristine matrix (space group of $Fd\bar{3}m$). SEM and TEM show that a uniform coating layer of polycrystalline $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was formed on the surface of the octahedral spinel grains. $10.0\% \text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2\text{-}90.0\% \text{LiMn}_{1.95}\text{Ni}_{0.05}\text{O}_{3.98}\text{F}_{0.02}$ cathode exhibits better cycle performance and rate capability at elevated temperature (i.e., 55°C) arising from the protective role of layer of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. The coating material, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, is one of most widely applied cathodes for lithium-ion batteries as well, which possesses high capacity retention, rate ability and discharge capacity at elevated temperatures, not only protect spinel $\text{LiMn}_{1.95}\text{Ni}_{0.05}\text{O}_{3.98}\text{F}_{0.02}$ from electrolyte corroding but also enhance Li-ion transport compared with inert coatings.

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1. Introduction

Spinel LiMn_2O_4 has been extensively and profoundly investigated and is viewed as one of the most promising cathode materials for lithium-ion batteries (LIBs) due to its proper redox potential of $\text{Mn}^{4+}/\text{Mn}^{3+}$ ($4\text{V vs. Li}^+/\text{Li}$), fast kinetics, nontoxicity, low cost and high thermal stability [1–3]. Nevertheless, LiMn_2O_4 exhibits grievous capacity fading during cycling at elevated temperatures [4]. The corrosive reaction between LiMn_2O_4 and electrolyte solution should take responsibility for the deteriorated performance. To restraint the manganese dissolution of LiMn_2O_4 caused by the side reaction, many researchers have attempted to improve the high temperature cyclic performance by controlling surface feature of electrode materials. Up to now, the majority of the coating materials have been carbon [5], inert oxides (such as Al_2O_3 [6], TiO_2 [7], SiO_2 [8] and CeO_2 [9]), lithium-ion solid electrolytes (such as LLTO [10,11], LATP [12], LLZO [13], LBSO [14] and LASO [15]) and electrode materials (such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [16], LiFePO_4 [17], ZnMn_2O_4 [18], LiCoO_2 [19] and $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ [20]). In the meantime, spinel LiMn_2O_4 mixed with different types of insertion compounds [e.g., layered LiMO_2 ($M = \text{Ni, Co, and Mn}$)] exhibits better cycling

performance and safety characteristics at high temperatures. Several works have been reported about the mixed spinel LiMn_2O_4 and layered LiMO_2 composite cathode materials [21–23].

It is widely known that layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (Abbr. NCM) with a theoretical capacity of 277mAh g^{-1} shows high practical discharge capacity [24], which is positively related to temperature. In addition, it can inhibit manganese dissolution without blocking Li-ion transport on account of its good rate capability [25]. NCM possesses a similar electrochemical window ($2.5\text{--}4.6\text{V}$) with spinel LiMn_2O_4 [26] and good thermostability, implying that it would not decompose during charging and discharging [27] of layer–spinel composite cathode materials. In consequence, it seems to be a suitable candidate for LiMn_2O_4 surface modifying. Several researches have concentrated on the structural behavior of mechanically mixed $\text{LiMn}_2\text{O}_4\text{-NCM}$ composite cathode materials, but NCM has not been applied as surface modified material for spinel LiMn_2O_4 to our best knowledge. In this study, we report the preparation of NCM- $\text{LiMn}_{1.95}\text{Ni}_{0.05}\text{O}_{3.98}\text{F}_{0.02}$ composite cathode materials using the Pechini method rather than mixing them simply. Our previous study has shown that co-doping can improve the electrochemical performance of LiMn_2O_4 at room temperature [15].

Fig. 1 shows the two different composite forms of layered structure and spinel structure cathode materials. In the case of mechanical mixing, there are pairwise contacts among

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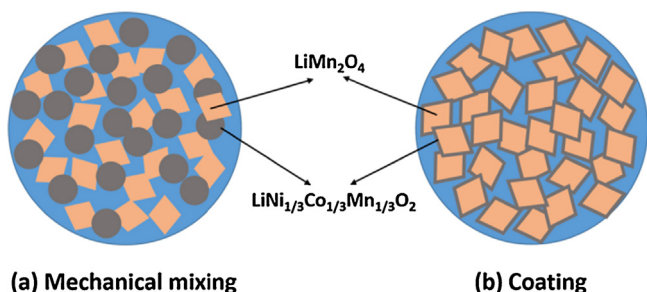


Fig. 1. Schematic illustration for the structure of NCM-LiMn₂O₄ composites prepared by (a) mechanical mixing and (b) coating.

LiMn_{1.95}Ni_{0.05}O_{3.98}F_{0.02} (Abbr. LMNOF), NCM and electrolyte solution. For composites prepared by surface coating, the direct exposure of LMNOF to electrolyte solution could be blocked by NCM, and contact between LMNOF and NCM is closer. We expect good cycle-ability and rate capacity [28] of NCM would protect LMNOF from electrolyte without influencing the diffusion of Li-ion. The structure and electrochemical performance of the composite cathode materials are discussed.

2. Experimental

Spinel LMNOF was prepared by solid-state reaction process and recrystallization through a follow-up molten-salt growth method, see details in our previous paper [13]. The high crystallinity LMNOF grains were coated with NCM by the Pechini method. The sol was prepared using the following steps: lithium nitrate, nickel nitrate, cobalt nitrate and manganese nitrate were dissolved in deionized water. Soon afterwards, ethylene glycol and citric acid with a molar ratio of 1:3 were put in to form a transparent solution. Intensive agitation was applied to achieve a uniform distribution of metal ions. Subsequently, the as-synthesized spinel powder was immersed in the solution, and the ratio between the solution and LMNOF was adjusted to study the effect of the amount of coating on the electrochemical properties. The solution containing cathode powder was constantly stirred at 60 °C to evaporate the solvent, accompanied with polycondensation of citric acid and ethylene glycol. The obtained polymer citrate gel precursor was dried in air at 120 °C for 1 h and then heated at 750 °C for 4 h to produce the NCM-coated LMNOF composite. The LMNOF sample composited with 5.0 wt.%, 7.5 wt.% and 10.0 wt.% of NCM are abbreviated as LMNOF-1, LMNOF-2 and LMNOF-3 respectively.

The crystal structure of the samples was analyzed by XRD using Cu K α radiation source. The morphology was observed with a field emission scanning electron microscope (SEM). High resolution transmission electron microscope (HRTEM) measurements were employed by Tecnai G2 F30 S-TWIN instrument.

To assemble the electrodes, a mixture of 10 wt.% of acetylene black and 85 wt.% of active material were added to an N-methyl-2-pyrrolidone solution containing 5 wt.% of polyvinylidene fluoride. The obtained slurry was pasted onto an Al foil substrate and then dried at 120 °C for 6 h. The coated foil was cut into circular discs of 15 mm in diameter, the electrode thickness is about 120 μ m, and the area of the working electrode is 1.767 cm². The electrolyte solution was 1.0 M LiPF₆ in ethylene carbonate (EC)–dimethyl carbonate (DMC) mixture (1:1 ratio by volume). R2032 coin-type cells were assembled in an Ar-filled dry glove box. The galvanostatic cycle tests were carried out between 3.0 V and 4.3 V at 55 \pm 0.5 °C using a battery tester (LAND CT2001A, China). The electrochemical impedance spectroscopy (EIS) was examined over the frequency range of 0.01 Hz to 100 kHz and the cyclic voltammogram (CV)

experiments were carried out at a scan rate of 100 μ V s⁻¹ using Shanghai Chenhua CHI660D electrochemical analyzer.

3. Results and discussion

3.1. XRD analysis

Fig. 2(a) shows the XRD patterns of the pristine LMNOF and NCM-LMNOF composite materials. Peaks of all the four samples match well with the spinel LiMn₂O₄, revealing that the NCM coating did not alter the structure. The spinel LMNOF grains were recrystallized through a follow-up molten-salt growth after solid-state method, so it might be difficult for atoms of coatings to diffuse into spinel crystal structure. The NCM precursor gel without LMNOF was calcined through the same heating process as well, and its XRD pattern is illustrated in Fig. 2(b), along with LMNOF mechanically mixed with 10.0 wt. % NCM. We can find all the peaks of NCM match well with the layered structure. Though the diffraction patterns of LMNOF and NCM overlap with each other, there is an obvious right shift of NCM peaks compared with that of LMNOF. Li Lu et al. [29] synthesized LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ at 700 °C by the Pechini method with extremely fine crystallite size. XRD pattern of LMNOF mechanically mixed with 10.0 wt.% NCM powders shows peaks of the layered structure, while the LMNOF-3 sample does not. Absence of diffraction peaks of NCM for NCM-LMNOF is possible because NCM exists as a uniform continuous film on the surface of the spinel grain.

3.2. Morphology analysis

The morphology of the uncoated LMNOF and NCM-LMNOF composites is shown in Fig. 3. The bare LMNOF appears octahedral

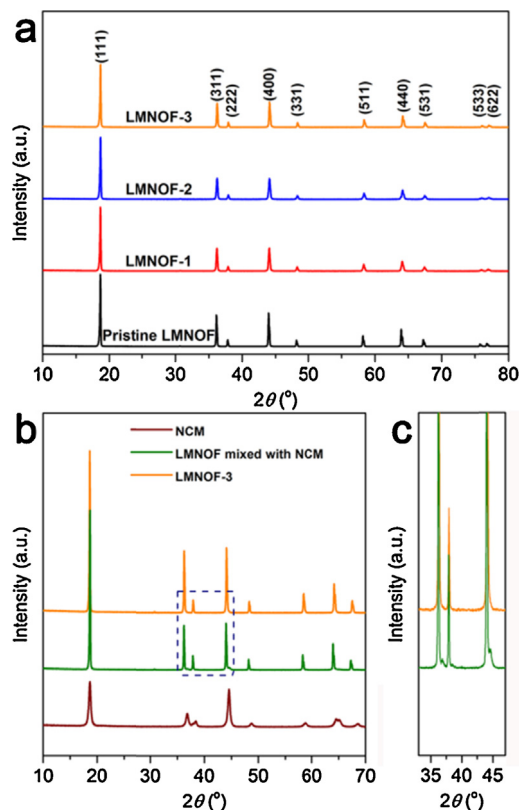


Fig. 2. XRD patterns of (a) the pristine LMNOF and LMNOF-1, LMNOF-2, LMNOF-3 composites, (b) NCM, LMNOF mechanically mixed with 10.0 wt.% NCM and LMNOF-3 powders and (c) enlarged view of (b).

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