

High-rate capability of spinel $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ cathode for Li-ion batteries prepared via coprecipitated precursor

SUN Bin(孙 斌)^{1,2}, SHEN Guo-pei(申国培)², HU Yan-long(胡燕龙)²

1. College of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, China;

2. Guangzhou Hongsen Material Co. Ltd., Guangzhou 510760, China

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Abstract: Spinel $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ cathode material for lithium ion batteries was synthesized by solid-state reaction from coprecipitated Ni-Mn hydroxide precursors and characterized by X-ray diffraction(XRD), scanning electron microscopy(SEM) and galvanostatic charge-discharge tests. It is found that $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ powder has an ordered cubic spinel phase (space group $\text{Fd}\bar{3}\text{m}$) and exhibits superior rate capability. After 450 cycles, the $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ /carbonaceous mesophase spheres(CMS) Li-ion batteries can retain 96.0% and 93.3% capacity at 5C and 10C charge/discharge rate, respectively, compared with 85.3% (5C) and 80.5% (10C) retention for LiMn_2O_4 batteries. However, the initial discharge capacity of $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ /CMS batteries at 1C charge/discharge rate (96.20 mA·h/g) is slightly lower than that of the LiMn_2O_4 batteries (100.98 mA·h/g) due to the increased average oxidation state of Mn in $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$.

Key words: Li-ion battery; rate capability; Ni-doped Mn spinel; coprecipitation

1 Introduction

Lithium-ion batteries have been successfully applied to portable electronic devices such as cellular phones and laptop computers. Besides, they have become possible high power sources for electric tools and HEVs. However, the high cost and toxicity associated with the currently used LiCoO_2 cathodes suppress their application to electric tools and HEVs. It is necessary to develop inexpensive and environmentally benign cathode materials to satisfy the requirement for the high power lithium-ion batteries. In this regard, spinel LiMn_2O_4 has become an attractive cathode due to its low cost, non-toxicity and its high voltage[1–2], but LiMn_2O_4 also has some disadvantages to high-rate batteries. For example, LiMn_2O_4 shows severe capacity fade particularly at elevated temperatures that is ascribed to Jahn-Teller distortion[3–4], manganese dissolution into electrolyte[5], and loss of crystallinity during cycling[6]. Additionally, the rate capability of LiMn_2O_4 is expected to be low because the solid-phase diffusivity of Li^+ in LiMn_2O_4 is poorer than that of LiCoO_2 [7]. Substitution of other cations for manganese has been found to

improve the cyclability at elevated temperatures[8–9] and rate capability of LiMn_2O_4 spinels[10–11].

As a precursor synthesis method, coprecipitation can mix metal ions homogeneously, resulting in an easier control of the stoichiometric synthesis of the materials at an atomic level[12–14]. In this paper, the Ni-Mn hydroxide with a given ratio was synthesized by coprecipitation, and then the as-obtained precursor was calcined with Li_2CO_3 at high temperature to form a $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ spinel. The crystal structure, morphology and electrochemical performance of this cathode were investigated. It is found that the $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ spinel shows excellent rate capability even at a charge/ discharge rate as high as 10C.

2 Experimental

$\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ spinel was prepared as follows. Firstly, stoichiometric ratios of $\text{MnSO}_4\cdot\text{H}_2\text{O}$ and $\text{NiSO}_4\cdot6\text{H}_2\text{O}$ were completely dissolved into distilled water and then slowly dropped into the NaOH solution with a pH value of 12 that was being stirred rapidly at ambient temperature. The precipitate was filtered and washed with distilled water and then dried at 110 °C in

air overnight. A 5% excessive Li_2CO_3 (compensation for possible Li loss during high temperature calcination) was mixed with the as-prepared precursor and preheated at $450\text{ }^\circ\text{C}$ for 5 h, then calcined at $800\text{ }^\circ\text{C}$ for 24 h and next annealed at $600\text{ }^\circ\text{C}$ for 5 h in air. For comparison, spinel LiMn_2O_4 was prepared following the same procedures as $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$. The crystal structure of as-prepared powders was analyzed by XRD using a D/Max-2400 (Rigaku, Japan) diffractometer equipped with Cu K_α radiation. The particle morphology was examined by SEM (LEO 1530VP, Germany).

The charge-discharge experiments were conducted on a lithium-ion cell consisting of a spinel cathode, a CMS (Shanshan Tech Group, China) anode and an electrolyte of 1 mol/L LiPF_6 in a 1:1 (in volume) mixture of ethylene carbonate(EC)/dimethyl carbonate(DMC). The cathode was prepared by mixing 90% (mass fraction) spinel, 6% carbon black, and 4% polyvinylidene fluoride(PVDF) binder in a solvent of N-methyl-2-pyrrolidone(NMP) to form slurry. The slurry was coated onto aluminum foil and dried at $120\text{ }^\circ\text{C}$. After dried, electrodes were cut into appropriate sizes. Then the electrode was pressed to a thickness of $160\text{ }\mu\text{m}$. The CMS electrode, composed of 92% CMS with 8% PVDF binder and NMP solvent, was made following the same processing steps as the cathode electrode, except that it was coated onto copper foil. Resultant thickness of the CMS electrode was $120\text{ }\mu\text{m}$. After dried, electrodes were cut into appropriate sizes. Next the cathode and anode were wound with separator (Celgard 2300, USA). The roll of electrodes and separator was inserted into a stainless steel case and then dried at $80\text{ }^\circ\text{C}$ for 12 h in a vacuum chamber before the case was sealed except the injecting hole using laser welder. The sealed cases were moved into a glove box (temperature $25\text{ }^\circ\text{C}$, relative humidity 0.3%). Electrolyte was injected and then the injecting hole was sealed. The fresh battery had external dimensions of $5.8\text{ mm}\times 30\text{ mm}\times 40\text{ mm}$.

3 Results and discussion

3.1 Phase structure of cathode

Fig.1 shows the XRD patterns of the LiMn_2O_4 and $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ powder. Both samples were confirmed to have an ordered cubic spinel structure with space group $\text{Fd}\bar{3}\text{m}$ and no secondary phase or impurity phases can be observed, implying that in the $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ sample, the Mn site is substituted fully by Ni doping. The diffraction lines shifted slightly towards higher angles with Ni substitution, indicating a smaller lattice parameter for the Ni-doped sample. The lattice parameters are 0.825 nm and 0.824 nm for LiMn_2O_4 and $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$, respectively. The decreased lattice

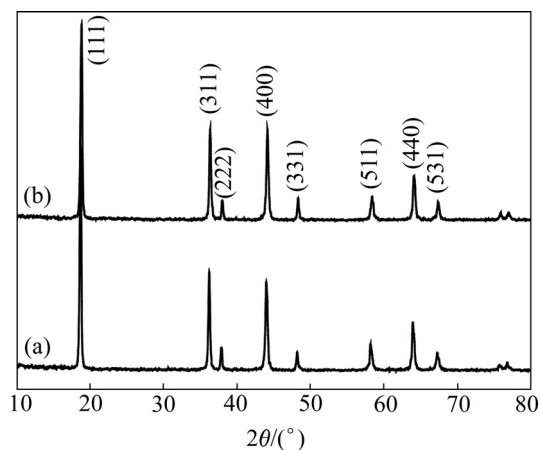


Fig.1 XRD patterns of LiMn_2O_4 (a) and $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ (b)

parameter of $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ is consistent with the increased concentration of Mn^{4+} in the spinel structure, which has a much smaller ionic radius ($r=0.053\text{ nm}$) than Mn^{3+} ($r=0.064\text{ nm}$)[15]. It is well known that the Jahn-Teller distortion of the $[\text{MnO}_6]$ octahedron in LiMn_2O_4 is caused by the Mn^{3+} cations at the 16d sites and the decreased amount of Mn^{3+} in LiMn_2O_4 can suppress the Jahn-Teller distortion[16–17]. Another reason for the decreased lattice parameter of $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ was proposed to be that $\text{Mn}(\text{Ni})\text{—O}$ bond ($1\text{ }029\text{ kJ/mol}$) in $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ is stronger than the Mn—O bond (946 kJ/mol) in LiMn_2O_4 , which could enhance the structural stability of the $[\text{Mn}(\text{Ni})\text{O}_6]$ octahedron[18]. Therefore, it was expected that $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ would exhibit better structural stability and cyclic performance than the non-substituted LiMn_2O_4 .

3.2 Surface morphology analysis

Fig.2 shows the surface morphology LiMn_2O_4 and $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$. Figs.2(a) and (b) indicate that both samples are composed of small primary faceted crystallites in octahedral shape with clean surfaces. The primary particles sizes are about $1\text{ }\mu\text{m}$. No change in morphology is observed between the Ni-doped and non-doped Mn-spinels.

3.3 Electrochemical performance

In order to investigate the rate capability of the cathode, we charged both the $\text{LiMn}_2\text{O}_4/\text{CMS}$ and $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4/\text{CMS}$ lithium-ion batteries using constant-current at 1C rate followed by constant-voltage at 4.2 V , then discharged the batteries at 1C , 5C and 10C rate, respectively. The discharge plots at various rates are shown in Fig.3. While LiMn_2O_4 exhibits huge polarization losses with increasing rate, the $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ exhibits remarkable rate capability, especially

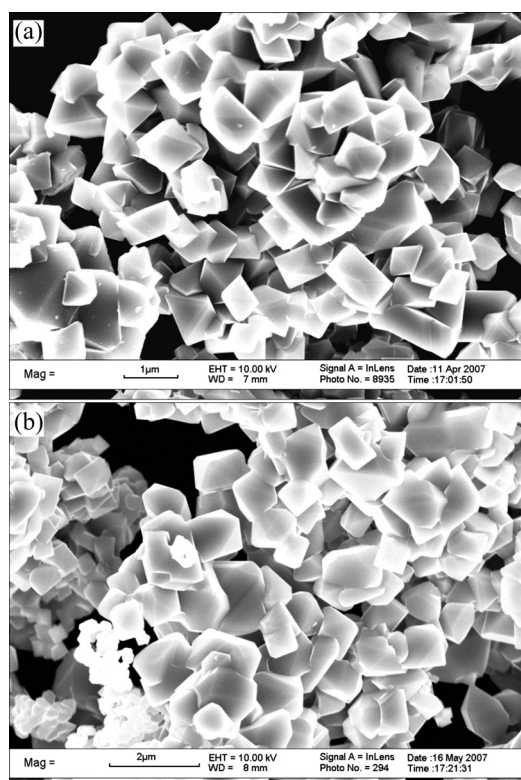


Fig.2 SEM images of LiMn_2O_4 (a) and $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ (b)

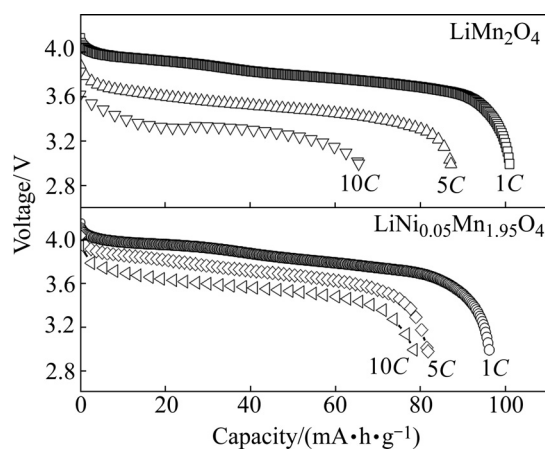


Fig.3 Discharge profiles of $\text{LiMn}_2\text{O}_4/\text{CMS}$ and $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4/\text{CMS}$ lithium-ion batteries at various discharging rates (1C, 5C and 10C) between 3.0 and 4.3 V (charge rate is fixed at 1C)

at higher rate as 10C. But the initial discharge capacity at 1C rate of $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ (96.20 $\text{mA}\cdot\text{h}/\text{g}$) is slightly lower than that of LiMn_2O_4 (100.98 $\text{mA}\cdot\text{h}/\text{g}$) because of the less content of Mn^{3+} in $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ as a result of Ni substitution for Mn[19].

The cycling performance of two spinels at high charge/discharge rates was also measured as shown in Fig.4. The batteries were charged using constant-current at 5C or 10C rate followed by constant-voltage at 4.2 V, then discharged at the same rate as its charging rate.

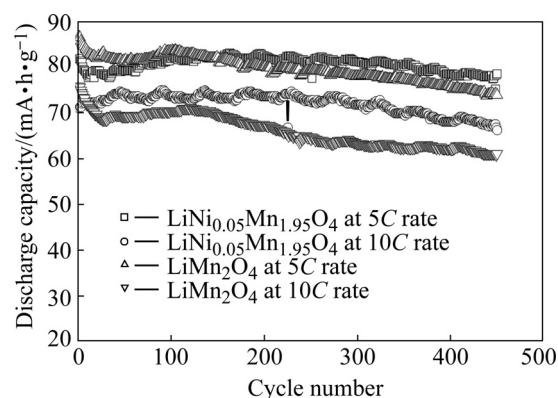


Fig.4 Discharge capacity vs cycle number plots of $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4/\text{CMS}$ lithium-ion batteries between 3.0 and 4.3 V at 5C and 10C charge/discharge rate, respectively

After 450 cycles, $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4/\text{CMS}$ lithium-ion batteries can still retain 96.0% and 93.3% capacity at 5C and 10C, respectively. In contrast, $\text{LiMn}_2\text{O}_4/\text{CMS}$ batteries just remain 85.3% (5C) and 80.5% (10C). Since both spinel samples show quite similar morphology in term of particle shape and particle size, the difference in the rate capability between LiMn_2O_4 and $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ does not result from particle size. According to the structural analysis results (section 3.1), we attributed the excellent cycling stability of $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ at high rate to the increase in stability of spinel structure resulting from the suppression of the Jahn-Teller distortion and stronger Mn(Ni)—O bond as Mn^{3+} are substituted by Ni^{2+} .

In addition to the superior rate capability, the spinel $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ offers the advantages of low cost, low toxicity, and easy synthesis. Therefore, we expect that $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ cathode would be attractive for high power applications such as electric tools and HEVs despite slightly lower initial capacity.

4 Conclusions

1) The spinel $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ synthesized from coprecipitated Ni-Mn hydroxide precursors exhibits superior rate capability at 5C and 10C charge/discharge rate with a small sacrifice in the initial discharge capacity.

2) The excellent rate capability of $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ cathode at high rate is attributed to the increase in structural stability resulting from the depression of the Jahn-Teller distortion caused by decreased content of Mn^{3+} and stronger Mn(Ni)—O bond as Mn^{3+} are substituted by Ni^{2+} .

3) The $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ cathode would be attractive for high power applications such as electric tools and

HEVs because of its advantages of low cost, low toxicity, easy synthesis and superior rate capability.

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