

Synthesis and electrochemical performance of spinel $\text{LiMn}_{2-x-y}\text{Ni}_x\text{Cr}_y\text{O}_4$ as 5-V cathode materials for lithium ion batteries

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Abstract

A series of spinel-structured $\text{LiMn}_{2-x-y}\text{Ni}_x\text{Cr}_y\text{O}_4$ have been prepared and their electrochemical performances as 5-V cathode materials for lithium ion batteries are evaluated. The synthesis reactions for these materials are characterized by TG/DSC, XRD and SEM. TG/DSC measurements show that the chemical reactions for the final product are completed below 400 °C. XRD analysis indicates that spinel structure is formed at around 650 °C. However, SEM images show well-defined polyhedron crystalline particles do not appear until 800 °C. Electrochemical evaluation shows that $\text{LiMn}_{1.4}\text{Ni}_{0.4}\text{Cr}_{0.2}\text{O}_4$ prepared at 850 °C boasts the best electrochemical performance with an initial discharge capacity of 128 mA h/g and a capacity retention of more than 90% after 230 cycles between 3.5 and 4.98 V.

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1. Introduction

Lithium ion batteries are well regarded as a new promising power source for both portable electronic devices and zero emission vehicles (ZEV) due to their longer cycle life and higher energy density than other rechargeable battery systems. Currently there are mainly two types of cathode materials for lithium ion batteries. One is the layered LiMO_2 ($M = \text{Ni}, \text{Co}, \text{or Mn}$) and the other is the spinel LiMn_2O_4 series. Recently, Goodenough and co-workers [1] proposed another promising cathode material for lithium ion batteries, LiFePO_4 of the phospho-olivine family. Nevertheless, the poor electronic conductivity hinders its application [2–4].

Reversible lithium extraction from spinel LiMn_2O_4 and the existence of two reversible plateaus at 4.0 V and 3.0 V (versus Li/Li^+ couple) were first reported by Goodenough and co-workers [5,6]. Spinel LiMn_2O_4 is studied extensively because it owns a number of advantages over other cathode materials for secondary lithium batteries, such as low cost, high safety and high abundance in the earth. However, this material suffers from Mn dissolution and structural degradation during cycling. Partial substitution of a transition metal for Mn, yielding $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ ($M = \text{Co}, \text{Mg}, \text{Cr}, \text{Ni}, \text{Fe},$

Ti and Zn [7–15]), has been proved effective in improving the cathodic stability of the spinel lattice. The doped metal ions in such a spinel-framework structure are exposed to an environment quite different from the self-assembled lithiated metal oxide of their own kind. Extending the concept of Mn replacement in the spinel, Davidson et al. [16] and Amine et al. [11] used Cr and Ni, respectively, to prepare $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ electrodes ($x \approx 0.5$) with improved electrochemical stability at 3 V.

Some authors found that the lost capacity at the 4-V plateau in $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ ($M = \text{Cr}$ and Ni) reappears on a higher voltage plateau (e.g. 4.9 V for $M = \text{Cr}$ and 4.7 V for $M = \text{Ni}$) [10,12] due to the valence variation of Cr and Ni. $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ shows higher energy density and operating voltage than LiMn_2O_4 . Guyomard and co-workers [10] showed that lithium extraction from the Cr-substituted spinel occurs at 4- and 4.9-V plateaus. These reactions were attributed to the oxidation of manganese and chromium, respectively. Gao et al. [17] discovered that lithium extraction from $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ takes place at 4.7 V as Ni^{2+} is oxidized to Ni^{4+} . The nickel in the spinel $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ can be reversibly transformed between Ni^{2+} and Ni^{4+} during cycling, making it possible to replace Mn^{3+} with a small quantity of other transitional metals and elevate the operation potential of the material. As energy density is the product of the average voltage and the specific capacity of a battery, such substitution is beneficial in raising the specific energy density of the material.

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In this article, spinel phase 5-V cathode materials with excellent electrochemical performance are prepared by simultaneously substituting Ni and Cr for Mn^{3+} through a solution reaction. The reaction processes and electrochemical performances will be reported.

2. Experimental

$\text{LiNi}_x\text{Cr}_y\text{Mn}_{2-x}\text{O}_4$ were prepared by mixing stoichiometric amounts of reactants $\text{Mn}(\text{NO}_3)_2$ (Beijing Xinhua Reagents, 50% solution), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Beijing Xinhua Reagents, 99%), $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Beijing Xinhua Reagents, 99%) and LiNO_3 (Beijing Xinhua Reagents, 95%) in distilled water. While the solution was stirred, ammonium hydroxide was slowly added until the pH value of the solution reached 7.5. Then the solution was heated at 80–90 °C to remove water and got a powder. After dried in a vacuum oven at 120 °C the powder was sintered between 600 and 900 °C for 18 h in air.

Powder X-ray diffraction (XRD) was performed on Rigaku D/MAX-RC X-ray diffractometer with $\text{Cu K}\alpha_1$ monochromated radiation in order to identify the crystalline phase of the materials. The XRD data were collected from 10 to 80° of 2θ values. TG/DSC measurements were conducted on NETZSCH STA 409C differential scanning calorimeter at a scanning rate of 10 °C/min from 30 to 1200 °C. The particle morphologies of the samples were examined with a scanning electron microscope (SEM, Hitachi, S-4000).

For the preparation of cathode sheets, a slurry was formed by mixing the active material (85 wt.%), carbon black (10 wt.%) and binder (5 wt.%, polyvinylidene fluoride dissolved in *N*-methyl-2-pyrrolidone (NMP)). The slurry was cast and spread on a piece of aluminum foil. Later it was dried at 120 °C for 24 h in a vacuum oven. LiPF_6 (1 M) dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v) was used as the electrolyte. Coin cells were assembled with Li foil as the anode and Celgard 2300 (polypropylene) as the separator in an Ar-filled glove box (MBraun). The electrochemical performance of the cell was characterized by galvanostatically cycling it between 3.8 and 4.98 V (versus Li/Li^+) at different current densities on Land 2000T (Wuhan, China) tester. In order to insure the accuracy of the measured specific capacity, the same active material was made into 10 cells at least to determine their specific capacity and these cells show excellent consistency.

3. Results and discussion

3.1. Material synthesis and structural characterization

The discharge capacity of an ideal 5-V cathode material should be no less than that of LiMn_2O_4 and its voltage plateaus should be converged above 4.5 V. Our previous

studies indicate that it is difficult to prepare single spinel phase 5-V cathode materials by replacing Mn^{3+} with a single transition metal through conventional solid state reaction. Some impurity phases are detected in the product when $x \geq 0.5$ in $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$. In addition, the discharge capacity of the sample drops with increasing Ni content in $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$, from 100 mA h/g at $x = 0.5$ to 50 mA h/g at $x = 0.75$, although the ratio of the discharge capacities of the higher (above 4.5 V) to the lower plateaus (4.0 V) increased from 50 to 70%. Guyomard and co-workers [10,18,19] studied the electrochemical performance of $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$ ($0 \leq x \leq 1$). The following experimental results will show that it is possible to prepare 5-V cathode materials with standard spinel structure and excellent electrochemical performance by simultaneously substituting some Mn^{3+} with Ni and Cr and by a novel solution preparation method.

TG/DSC, XRD and SEM are employed to study the preparation process of the sample and determine the dynamically dominating factors and the appropriate sintering temperature. TG/DSC curves (Fig. 1) of a 5-V cathode material $\text{LiMn}_{1.4}\text{Ni}_{0.4}\text{Cr}_{0.2}\text{O}_4$ between 30 and 1200 °C shows that the main chemical reactions for the final product are completed below 400 °C. Fig. 2 shows the XRD patterns of the samples prepared at different temperatures. The prepared samples between 650 and 900 °C have the standard spinel structure although there are some very weak impurity peaks of NiO. In the structure, Ni and Cr replaced part of Mn and occupied the 16d site.

SEM imaging was employed to show the morphology of the particles at different temperatures (Fig. 3). It is found that the particle morphology of the 5-V cathode material prepared at 600 °C is almost the same as that of the precursor and no spinel crystals can be observed. With increasing synthesis temperature, spinel crystals begin to be formed. At 800 °C integrated spinel crystals with an average particle diameter of 1–3 μm were grown. This indicates that the formation temperature of spinel phase is rather low, but growth of the crystalline particles takes place at rather high temperatures. Therefore, the formation and growth of the crystalline particles are the dominating factors during the sample synthesis.

3.2. Electrochemical performance

Profiles for the first 10 charge–discharge cycles of a lithium cell using $\text{LiMn}_{1.4}\text{Ni}_{0.4}\text{Cr}_{0.2}\text{O}_4$ as cathode materials are shown in Fig. 4. The discharge capacity of the material reaches 128 mA h/g, when cycled between 3.5 and 4.98 V. Although we tried to substitute Ni and Cr for Mn^{3+} completely, small amount of Mn^{3+} still exists in $\text{LiMn}_{1.4}\text{Ni}_{0.4}\text{Cr}_{0.2}\text{O}_4$. The remaining 4-V plateau could be caused by electrochemically active Mn^{3+} . Therefore, three voltage plateaus are observed in the profile, corresponding to three electrochemical reactions from low to high voltages: $\text{Mn}^{3+} - e \rightarrow \text{Mn}^{4+}$; $\text{Ni}^{2+} - 2e \rightarrow \text{Ni}^{4+}$ (see [14]); $\text{Cr}^{3+} - e \rightarrow \text{Cr}^{4+}$ (see [10,18,19]). The faradaic efficiency

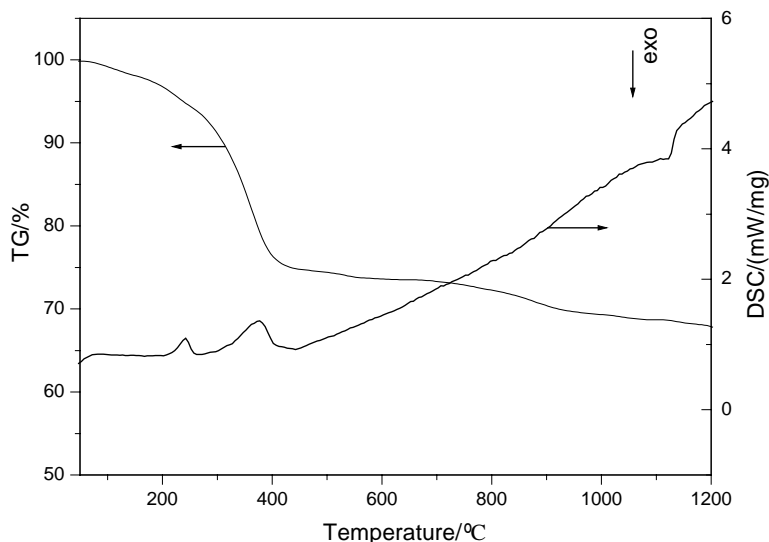


Fig. 1. TG/DSC traces of $\text{LiNi}_{0.4}\text{Cr}_{0.2}\text{Mn}_{1.4}\text{O}_4$ preparation process.

of the first charge–discharge cycle is only 75% due to electrolyte decomposition at high voltage. The cycling efficiency is more than 90% in the subsequent cycles. The improved cycling efficiency of the sample after the first charge–discharge process is attributed to formation of protection layer on the electrode surface that prevents further oxidation of the electrolyte.

The synthesis temperature has significant effects on the electrochemical performance of the 5-V cathode material. With rising synthesis temperature, the reversible capacity increases gradually from 105 mA h/g for the sample sintered at 700 °C to 125 mA h/g for the sample sintered at 850 °C. However, the reversible capacity of the sample drops to 110 mA h/g when the sintering temperature rises to 900 °C.

The cycling performance of the sample is improved, but the percentage of its discharge capacity in the 4-V region increases when the preparation temperatures are increased from 650 to 900 °C. This means that the Mn^{3+} content in spinel $\text{LiMn}_{1.4}\text{Ni}_{0.4}\text{Cr}_{0.2}\text{O}_4$ increases with rising preparation temperature. By adjusting the Ni and Cr contents in the spinel structure, the electrochemical conversion $\text{Mn}^{3+} - e \rightarrow \text{Mn}^{4+}$ can be restrained resulting in negligible discharge capacity in the 4-V region. Fig. 5 shows the third charge–discharge profile of $\text{LiMn}_{1.3}\text{Ni}_{0.35}\text{Cr}_{0.35}\text{O}_4$ prepared at 850 °C. The discharge capacity of the sample in the 4-V region becomes negligible.

Fig. 6 shows the cyclability of 5-V cathode material $\text{LiMn}_{1.4}\text{Ni}_{0.4}\text{Cr}_{0.2}\text{O}_4$ at C/4 charge–discharge rate

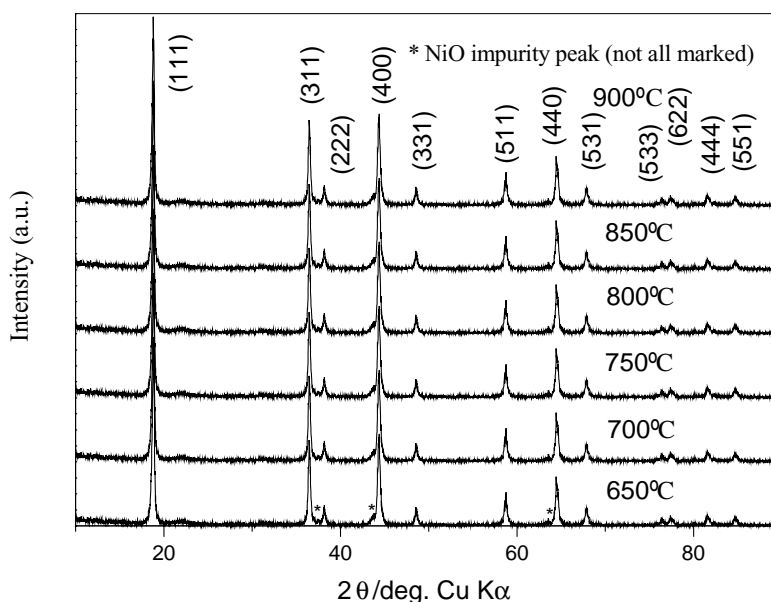


Fig. 2. Powder XRD patterns of $\text{LiNi}_{0.4}\text{Cr}_{0.2}\text{Mn}_{1.4}\text{O}_4$ prepared at different temperatures.

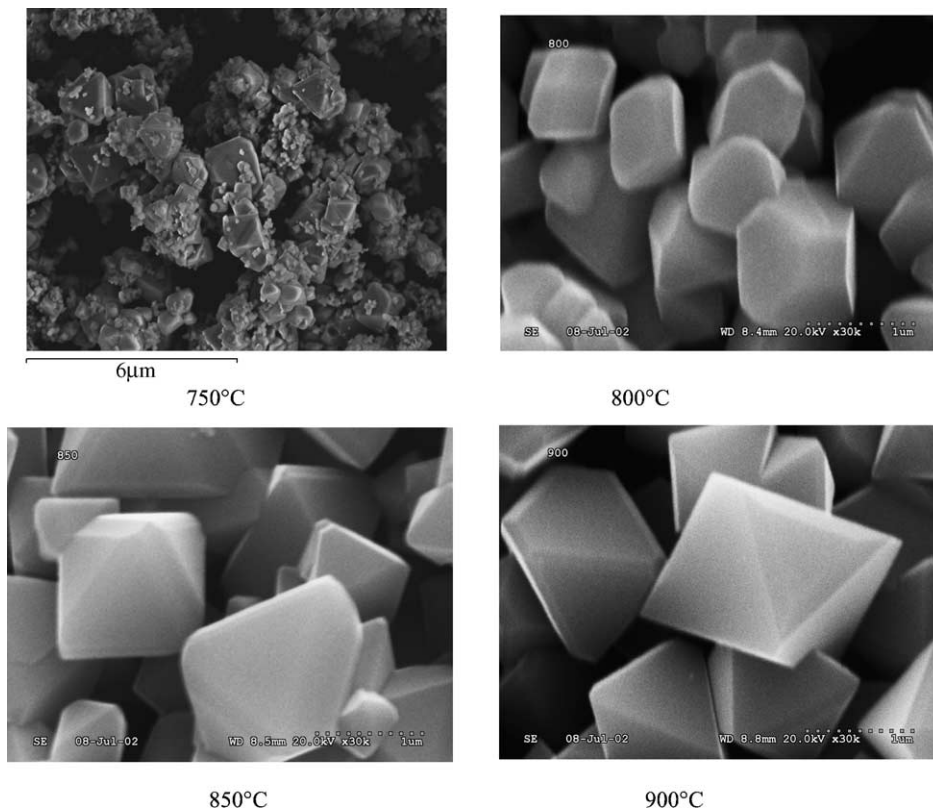


Fig. 3. The crystallite growth of $\text{LiNi}_{0.4}\text{Cr}_{0.2}\text{Mn}_{1.4}\text{O}_4$ particles at various synthesis temperatures.

at room temperature. The initial discharge capacity of $\text{LiMn}_{1.4}\text{Ni}_{0.4}\text{Cr}_{0.2}\text{O}_4$ prepared at 850°C is 128 mA h/g . More than 90% of the initial capacity is retained after 230 cycles between 3.5 and 4.98 V. The Jahn–Teller effect at higher Mn^{3+} content (over-discharged) in the spinel and its dissolution in the electrolyte are believed to be the

main reason for the capacity fading. The excellent electrochemical performance of the 5-V cathode materials can be ascribed to the improved structural stability due to substitution of Ni and Cr for the unstable Mn^{3+} in the spinel and the elimination of the Mn^{3+} Jahn–Teller effect. Meanwhile the above electrochemical results indicate that the spinel

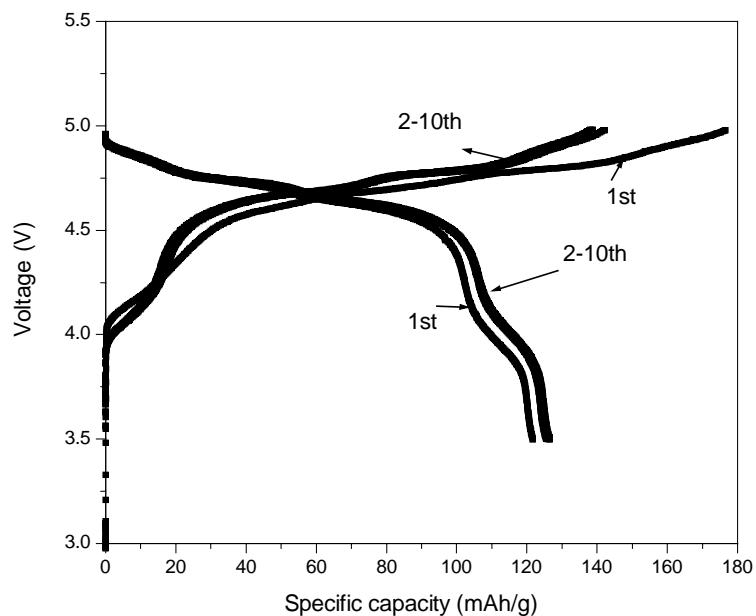


Fig. 4. The charge–discharge profiles in the first 10 cycles of a lithium cell with $\text{LiNi}_{0.4}\text{Cr}_{0.2}\text{Mn}_{1.4}\text{O}_4$ prepared at 850°C as cathode material.

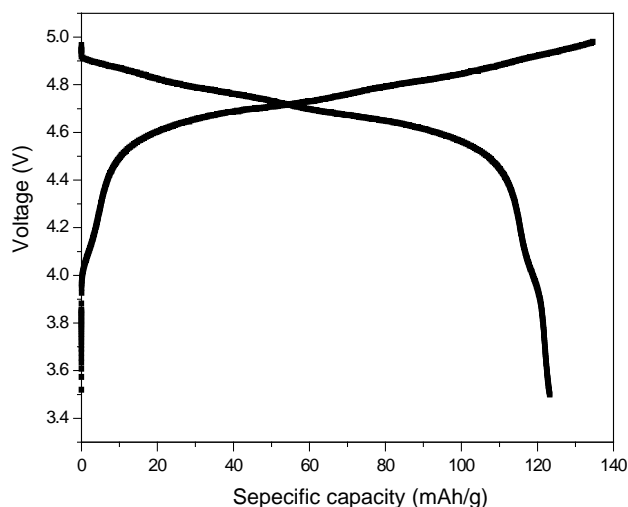


Fig. 5. The charge–discharge profiles of a lithium cell with $\text{LiNi}_{0.35}\text{Cr}_{0.35}\text{Mn}_{1.3}\text{O}_4$ sintered at 850°C as cathode material.

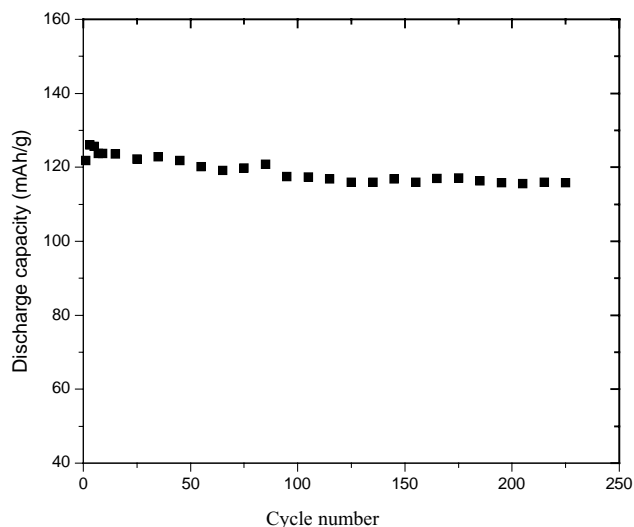


Fig. 6. The cycling performance of the 5-V cathode material $\text{LiNi}_{0.4}\text{Cr}_{0.2}\text{Mn}_{1.4}\text{O}_4$ sintered at 850°C .

structure based on MnO_6 is very stable and suitable for Li^+ extraction–insertion. 5-V lithium ion batteries with high specific energy density can be developed provided that new electrolyte with higher stability is available.

4. Conclusions

Five-volt cathode materials with spinel structure and excellent electrochemical performance have been successfully prepared by simultaneously substituting Mn^{3+} with Ni and Cr and by solution reaction technique. The crystalline structural features and electrochemical properties of these materials are characterized by TG/DSC, SEM, XRD and electrochemical measurements. Although the synthe-

sis reactions occur at as low as 400°C , the formation of well-defined polyhedron crystalline grains of the material is completed at around 800°C . The average diameter of the crystal grain is $1\text{--}3\ \mu\text{m}$. Electrochemical investigation shows that $\text{LiMn}_{1.4}\text{Ni}_{0.4}\text{Cr}_{0.2}\text{O}_4$ synthesized at 850°C has the best electrochemical performance with an initial discharge capacity of $128\ \text{mAh/g}$ and 90% of which can be retained after 230 cycles between 3.5 and 4.98 V. The high structural stability of the material is attributed to the substitution of unstable Mn^{3+} with more stable Ni and Cr ions. These materials can be used to build lithium ion batteries with higher energy density and longer cycle life by matching with a suitable new electrolyte.

Acknowledgements

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