Effect of Mg Doping On Electrochemical Properties Lini1/3Co1/3Mn1/3O2 for High Performance Cathode Material in Lithium Batteries

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Abstract. The Mg-doped LiNi1/3Mn1/3Co1/3O2 cathode materials have been successfully synthesized via a rheological phase reaction method. The structure and properties of the as-obtained samples were measured by XRD, SEM and electrochemical test methods. Though the Mg-doped samples delivered lower initial capacities, the rate performance and the cycling stability were dramatically enhanced. The Mg2+ doped LiNi1/3Mn1/3Co1/3O2 sample (1%) has the most excellent electrochemical performances, it delivers an initial discharge capacity of 177 mAh g\textsuperscript{–1} at 0.2 C in the voltage of 2.5–4.5 V, and has a capacity retention of 97.7% after 50 cycles.

1. Introduction
Further improvements in LIB technology will require the exploration of high-performance cathode materials [1]. In recent years, the ternary layered oxide material LiNi1/3Co1/3Mn1/3O2, characterized by high discharge capacities, moderate voltage platforms, low cost, and low environmental toxicity, has garnered interest in research and applied studies [2]. In these compounds, electrochemical active nickel and cobalt produce high capacity by changing their valence states involving Ni2+/Ni4+ and Co3+/Co4+ redox couples, while inactive manganese ions stabilize the crystal structure and lower the costs [3]. Nevertheless, the performance of pristine LiNi1/3Mn1/3Co1/3O2 is rather limited, because of the Li+/Ni2+ disorder in lattice, which leads to irreversible capacity loss. The increased disorder also has negative impact on the rate capability and cycling life. To solve these problems, various strategies have been proposed, such as coating with carbon and metal oxides, fabricating porous micro/nano-structures, and doping. Among these methods, doping is one of the most effective strategies to reduce the Li+/Ni2+ disorder and improve the performance. Various elements (such as Mg, Al, Zr, Fe, Cr, V, F, etc.) have been introduced into lithium transition metal oxides [4, 5].

In this work, we synthesized a magnesium-doped LiNi1/3Co1/3Mn1/3O2 by a rheological phase reaction followed by annealing. The structural characterization and electrochemical measurements are carried out to study the properties of the magnesium-doped LiNi1/3Co1/3Mn1/3O2.
2. Experimental

The molar ratio of reactants was LiOH·H₂O: NiAc₂·2H₂O: CoAc₂·2H₂O: MnAc₂·2H₂O: Citric acid =1.05: 1/3: 1/3: 1/3: 3.15. Stoichiometric amounts of MgAc₂·2H₂O and suitable distilled water were added in an agate mortar and an appropriate amount of water was added to the mixture to obtain a rheological phase. The rheological phase mixture was reacted to form precursor in an oven at 120 °C for 24 h. Then, a mixture of precursor was ground into fine powder in a mortar of agate. The powder of precursor were heated at 600 °C for 6 h and 850 °C for 12 h in air. Respectively. The LiNi₁/₃Mn₁/₃Co₁/₃O₂ and Mg-doped LiNi₁/₃Mn₁/₃Co₁/₃O₂ were obtained (marked as LNCM, LNCM-0.5%Mg, LNCM-1%Mg, LNCM-2%Mg, and LNCM-5%Mg).

XRD measurements were carried out on a Bruker D8 Advance X-ray diffractometer. The morphologies were characterized by field-emission scanning electron microscopy (SEM, JEOL JSM-7400F, and Japan).

Electrochemical performances of these samples were tested in a model test cell system. Positive electrodes were prepared by pressing the mixtures of the active material (70%), acetylene black (20%), and polytetrafluoroethylene (PTFE) (10%) onto a nickel grid. Prior to being used, the positive electrodes were dried at 120 °C in a vacuum furnace for 24 h. The electrolyte was a solution of 1 M LiPF₆/ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume). The separator was Celgard 2400 porous polypropylene. The counter and reference electrodes were lithium foil. The model test cells were assembled in an argon-filled dry box. Charge-discharge tests were carried out at different current densities in the range of 2.5 V to 4.5 V. Electrochemical impedance spectroscopy (EIS) measurements were collected on an electrochemistry workstation (Shanghai Chenhua Instrument Co. Ltd.).

3. Results and discussion

Fig. 1 shows XRD patterns of the pristine and Mg-doped LiNi₁/₃Co₁/₃Mn₁/₃O₂ samples. All LiNi₁/₃Co₁/₃Mn₁/₃O₂ samples were indexed to the layered structure of α-NaFeO₂ with R-3m space group. There are some clear splits of (006)/ (102) and (108)/ (110) peaks of the samples, which indicates the formation of layered structure. Moreover, no other mixed phase appears, indicating that Mg ion has been successfully into the crystal lattice. It is obvious that all of the Mg-doped LiNi₁/₃Co₁/₃Mn₁/₃O₂ samples show similar lines as that of the pristine one.

![Figure 1. XRD patterns of all the LiNi₁/₃Co₁/₃Mn₁/₃O₂ samples.](Image)

It is well known that the particle size, particle size distribution and morphology of the sample will directly influence the electrochemical performance of the electrode materials. Fig. 2 show the morphologies of the pristine and Mg-doped LiNi₁/₃Co₁/₃Mn₁/₃O₂ samples. The size of the primary particles ranges from 100 nm to 400 nm with a relatively homogeneous distribution, which can be perceived distinctly from Fig.2. The similarity between LiNi₁/₃Co₁/₃Mn₁/₃O₂ and Mg-doped
LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ samples in morphology illustrates that Mg-doping has no impact on the morphology of LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$.

![Figure 2. SEM images](image)

Figure 2. SEM images (a) LNCM, (b) LNCM-0.5%Mg, (c) LNCM-1%Mg, (d) LNCM-2%Mg, and (e) LNCM-5%Mg

The electrochemical performance of the pristine and Mg$^{2+}$ doped LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ samples are shown in Fig. 3. These charge–discharge was conducted at a current of 0.2C (1C = 220 mA g$^{-1}$) in the voltage range of 2.5–4.5 V. The pristine LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ electrode delivers an initial discharge capacity of 176 mAh g$^{-1}$. The discharge capacity reduces to 158 mAh g$^{-1}$ after 50 cycles. The capacity retention was 89.7% after 50 cycles. With Mg$^{2+}$ doped LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ samples (0.5%, 1%, 2%, and 5%), the initial discharge capacities were 182, 177, 170, and 162 mAh g$^{-1}$, respectively. After 50 cycles, the discharge capacities could retain 164, 173, 153, and 150 mAh g$^{-1}$, respectively. The capacity retention was 90.1%, 97.7%, 90.0%, and 97.4% after 50 cycles, respectively. It is indicated that cycle performance has been improved by Mg$^{2+}$ doping with a small doping amount of 0.5% and 1%. However, the discharge capacity decreased obviously when the coating amount increase to 2% and 5%. Therefore, this result indicates that only an appropriate amount of Mg$^{2+}$ doping can facilitate the diffusion of Li ions. The reasons may be: (1) An appropriate amount of Mg doping can suppress Li$^+$/Ni$^{2+}$ cation mixing; (2) Mg-O with stronger bond energy can improve the structure stability during cycling.
Figure 3. The first cycle (a) and 50th curves (b), cycling performance, and electrochemical impedance spectroscopy (EIS) of LNCM, LNCM-0.5%Mg, (c) LNCM-1%Mg, (d) LNCM-2%Mg, and (e) LNCM-5%Mg.

Fig.3d illustrates the electrochemical impedance spectra of the samples which were recorded in the fresh cell. Two depressed semicircles are observed for both electrodes, the one located in high frequency ranges assigned to surface film resistance and the one located in medium frequency ranges assigned to charge transfer impedance. The kinetics difference of the electrodes was further investigated by modeling AC impedance spectra based on the Randles equivalent circuit. In this equivalent circuit, Rs represents the ohmic resistance of the electrolyte solution, Rct is the resistance of the charge transfer reaction, Cdl is the capacitance of the electrode–electrolyte double layer, and Zw is the Warburg impedance. Analysis of the experimental data was performed by fitting equivalent circuits. The charge transfer resistance Rct was significantly lower for the LNCM-1%Mg electrode (117 Ω) compared to that for other LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 electrodes (137, 126, 182, and 249 Ω for the 0, 0.5%, 2%, and 5%, respectively). These facts support that the LNCM-1%Mg sample has good electrochemical properties suitable for electrode material in lithium ion battery.

4. Conclusion
Herein, the magnesium-doped LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 cathode materials by a rheological phase reaction followed by annealing. The structural characterization and electrochemical measurements are carried out to study the properties of the magnesium-doped LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2. The LNCM-1%Mg electrode material showed outstanding electrochemical performance. After 50 cycles at 0.2C, the discharge capacity remains 173 mAh g^{-1}, corresponding to 97.7% of its initial capacity. The splendid property derives from the increase of lithium ions diffusion coefficient and electronic conductivity by the substitution of vanadium.
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References
[1] H. Li, Z. Wang, L. Chen, X. Huang, Research on Advanced Materials for Li-Ion Batteries, Adv. Mater., 21(2009) 4593-4607.
[2] H. Zheng, X. Chen, Y. Yang, L. Li, G.H. Li, Z.P. Guo, C.Q. Feng, Self-Assembled LiNi1/3Co1/3Mn1/3O2 Nanosheet Cathode with High Electrochemical Performance, ACS Appl. Mater. Interfaces, 9 (2017) 39560-39568
[3] Q. Sa, J.A. Heelan, Y. Lu, D. Apelian, Y. Wang, Copper Impurity Effects on LiNi1/3Mn1/3Co1/3O2 Cathode Material, ACS Appl. Mater. Interfaces, 7 (2015) 20585-20590.
[4] Z. Chen, J. Wang, D. Chao, T. Baikie, L. Bai, S. Chen, Y. Zhao, T.C. Sum, J. Lin, Z. Shen, Hierarchical Porous LiNi1/3Co1/3Mn1/3O2 Nano-/Micro Spherical Cathode Material: Minimized Cation Mixing and Improved Li+ Mobility for Enhanced Electrochemical Performance, Sci. Rep., 6 (2016) 25771-2776.
[5] L. Peng, Y. Zhu, U. Khakoo, D. Chen, G. Yu, Self-Assembled LiNi1/3Co1/3Mn1/3O2 Nanosheet Cathodes with Tunable Rate Capability, Nano Energy, 17 (2015) 36-42