

Research Article

In Situ Carbon Coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathode Material Prepared by Prepolymer of Melamine Formaldehyde Resin Assisted Method

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Carbon coated spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ were prepared by spray-drying using prepolymer of melamine formaldehyde resin (PMF) as carbon source of carbon coating layer. The PMF carbon coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was characterized by XRD, SEM, and other electrochemical measurements. The as-prepared lithium nickel manganese oxide has the cubic face-centered spinel structure with a space group of $\text{Fd}\bar{3}\text{m}$. It showed good electrochemical performance as a cathode material for lithium ion battery. After 100 discharge and charge cycles at 0.5 C rate, the specific discharge capacity of carbon coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was $130 \text{ mAh}\cdot\text{g}^{-1}$, and the corresponding capacity retention was 98.8%. The 100th cycle specific discharge capacity at 10 C rate of carbon coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was $105.4 \text{ mAh}\cdot\text{g}^{-1}$, and even the corresponding capacity retention was 95.2%.

1. Introduction

Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is a promising and attractive cathode material because of its good electrochemical properties and high working potential ($\sim 5.0 \text{ V}$) [1–3]. But the high rate discharge capacity is far less than the theoretical capacity due to low electronic conductivity and Li^+ ion diffusion coefficient of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [4]. Therefore, many efforts have been devoted to enhance the electronic conductivity and Li^+ ion diffusion coefficient by different synthesis routes [5–7], doping [8–12], and coating [13–16].

Carbon coating is easy and popular method at present [17]. In our prophase research, we found that the prepolymer of melamine formaldehyde resin would evenly coat on the surface of metal oxide and obtained the carbon coated metal catalysts with abundant pore structure after high temperature sintering [18]. In this study, in order to prepare the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as well as to improve the high rate discharge performance, polymer-complex-assisted method

was applied. Prepolymer of melamine formaldehyde resin (PMF) is used as carbon source to accomplish the carbon coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

2. Experimental Sections

2.1. Material Synthesis. The synthesis route was as follows: LiOH , $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and $\text{MnSO}_4\cdot \text{H}_2\text{O}$ were used as starting precursors with molar ratio of $\text{Li} : \text{Ni} : \text{Mn} = 1.0 : 0.5 : 1.5$. $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and $\text{MnSO}_4\cdot \text{H}_2\text{O}$ were dispersed in deionized water under continuous stirring and then slowly dripped the $(\text{NH}_4)_2\text{C}_2\text{O}_4$ aqueous solution. After reaction at 50°C for 12 h, then centrifugal washing to obtain the $\text{Ni}_{0.5}\text{Mn}_{1.5}(\text{C}_2\text{O}_4)_2$ precipitates. $\text{Ni}_{0.5}\text{Mn}_{1.5}(\text{C}_2\text{O}_4)_2$, LiOH , and PMF (10 wt.%) were dispersed in deionized water by ultrasonic dispersion 30 min into suspension. The suspension was dried by spray-drying method (inlet temperature 220°C and feed rate $6 \text{ mL}\cdot\text{min}$). The dried products were presintered

at 500°C in N₂ atmosphere for 5 h and then sintered at 800°C in N₂ atmosphere for 20 h to obtain the carbon coated LiNi_{0.5}Mn_{1.5}O₄. For comparison, LiNi_{0.5}Mn_{1.5}O₄ was also synthesized without PMF.

2.2. Characterization. The structure of the LiNi_{0.5}Mn_{1.5}O₄ materials was characterized using powder X-ray diffraction (XRD, XD-3, Beijing Purkinje General, China) with Cu K α radiation at 36 kV and 20 mA. The morphology of LiNi_{0.5}Mn_{1.5}O₄ was identified by field emission scanning electron microscopy (FE-SEM, JSM-5600, JEOL, Japan).

For electrochemical characterizations, 2032 type coin cells were used. The coin-type cells (2032) were assembled with Li plate as anode and LiNi_{0.5}Mn_{1.5}O₄ electrode as cathode. The LiNi_{0.5}Mn_{1.5}O₄ electrodes were prepared by coating the slurry of a mixture composed of LiNi_{0.5}Mn_{1.5}O₄ (80 wt.%), conducting agent (Super-p, 10 wt.%), and binder (polyvinylidene difluoride, 10 wt.%) onto an aluminum foil, and then dried at 120°C for 24 h in a vacuum drier. The weight of active material in the LiNi_{0.5}Mn_{1.5}O₄ electrode was 3.0 mg·cm⁻². The electrolyte was 1 mol·L⁻¹ LiPF₆ in the mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of 1:1. A polypropylene (PP) film (Celgard 2300) was used as the separator. Afterwards, the coin-type cells were assembled in argon-filled glove box. NEWARE multichannel battery-testing unit (CT-3008W, China) was employed to test the cycling and rate performances of LiNi_{0.5}Mn_{1.5}O₄ over a voltage range between 3.5 and 5.0 V versus Li/Li⁺ electrode at room temperature. Firstly, the cell should discharge and charge two cycles at 0.5 C and then discharge and charge 100 cycles at different rates. The cyclic voltammetric (CV) tests were carried out on an electrochemical workstation (CHI660A) at a scan rate of 0.1 mV·s⁻¹ in the range of 3.5–5.0 V versus Li/Li⁺. The electrochemical impedance spectroscopy (EIS) data of the electrodes were acquired at room temperature by an electrochemical workstation (CHI660A) before cycling in the frequency range 10 mHz–100 kHz by imposing an alternate current with an amplitude of 10 mV on the electrode.

3. Results and Discussion

Figure 1 shows the XRD pattern of the as-prepared LiNi_{0.5}Mn_{1.5}O₄. Compared with the PDF powder diffraction data file (JCPDS Card No. 80-2162), the diffraction peaks of as-prepared LiNi_{0.5}Mn_{1.5}O₄ are in agreement with the standard diffraction peaks. This illustrates that the as-prepared LiNi_{0.5}Mn_{1.5}O₄ has the cubic face-centered spinel structure with a space group of Fd3m [19]. There is no change of the position of diffraction peak after carbon coating and no coating. The diffraction peak intensity would be enhanced after PMF carbon coating. The carbon coating would be helpful to improve LiNi_{0.5}Mn_{1.5}O₄ crystallinity. Figure 2 shows FE-SEM images of LiNi_{0.5}Mn_{1.5}O₄ with no coating and after 10 wt.% PMF carbon coating. The LiNi_{0.5}Mn_{1.5}O₄ maintains the micronanostructure after carbon coating, but the surface of samples becomes roughed, and the roughness

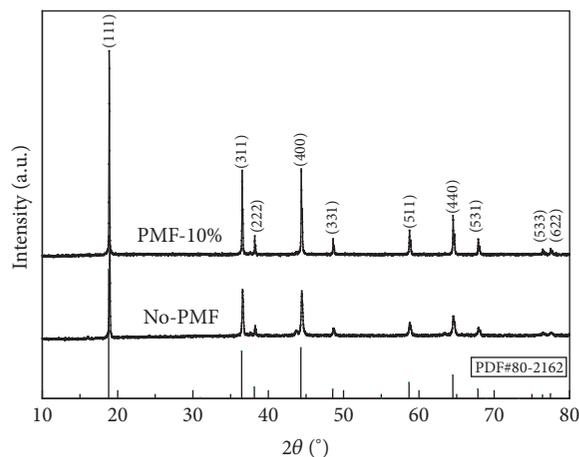


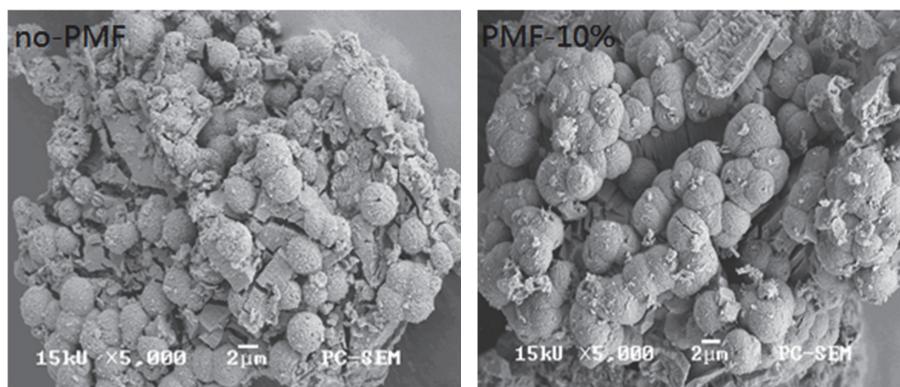
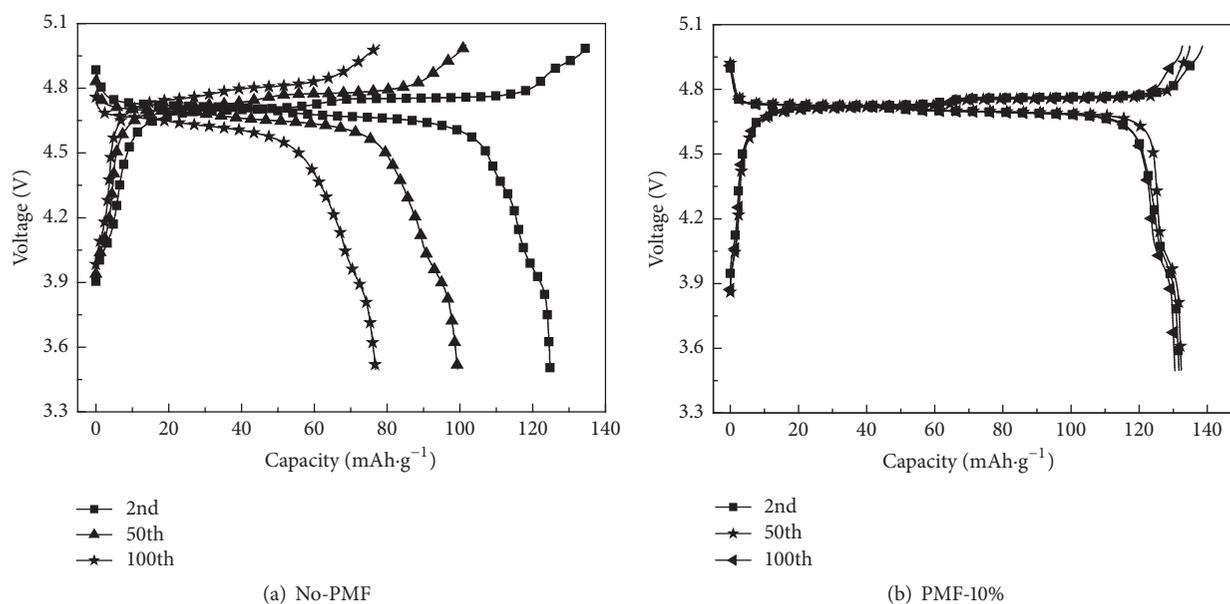
FIGURE 1: XRD patterns of prepared LiNi_{0.5}Mn_{1.5}O₄.

of samples increases after the PMF carbon coating. The degree of sphericity drops gradually.

Figure 3 shows the 2nd, 50th, and 100th charge and discharge curves of carbon coated LiNi_{0.5}Mn_{1.5}O₄ at the rate of 0.5 C. The specific discharge capacity of LiNi_{0.5}Mn_{1.5}O₄ increased after PMF carbon coating at around 4.7 V voltage plateau. The 2nd cycle specific discharge capacity raised from 125.1 mAh·g⁻¹ (no coating) to 131.7 mAh·g⁻¹ (after coating). After 100 discharge and charge cycles, the specific discharge capacity of carbon coated LiNi_{0.5}Mn_{1.5}O₄ was 130 mAh·g⁻¹, and even the corresponding capacity retention was 98.8%. And yet the specific discharge capacity of no coated LiNi_{0.5}Mn_{1.5}O₄ was 88.9 mAh·g⁻¹, and the corresponding capacity retention was 71.1%. The discharge and charge curves indicate that the PMF carbon coating reduces the electrode polarization after repeatedly charging and discharging cycle which suggests that PMF coating was in favour of improving the discharge and charge performance of lithium nickel manganese oxide materials. Another reason might be that the PMF carbon coating prevents the Mn³⁺ dissolving in the process of charging and discharging, thereby reducing the fading rate of discharge capacity [20, 21].

Figure 4 shows the 2nd, 50th, and 100th charge and discharge curves of carbon coated LiNi_{0.5}Mn_{1.5}O₄ at the rate of 10 C. The specific discharge capacity of LiNi_{0.5}Mn_{1.5}O₄ declines sharply after PMF carbon coating at high rate discharge. The 2nd cycle specific discharge capacity decreased from 117.9 mAh·g⁻¹ (before coating) to 110.6 mAh·g⁻¹ (after coating). The PMF carbon coating hinders the Li⁺ ionic conduction at high rate discharge and charge. But the corresponding capacity retention was greatly improved after PMF carbon coating. The 100th cycle specific discharge capacity of carbon coated LiNi_{0.5}Mn_{1.5}O₄ was 105.4 mAh·g⁻¹, and even the corresponding capacity retention was 95.2%. And yet the specific discharge capacity of no coated LiNi_{0.5}Mn_{1.5}O₄ was 85.4 mAh·g⁻¹, the corresponding capacity retention was 69.1%.

Figure 5 shows the CV curves of the PMF carbon coated LiNi_{0.5}Mn_{1.5}O₄ electrode. In the full range view of CV curves,

FIGURE 2: FE-SEM images of prepared $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.FIGURE 3: The charge and discharge curves of prepared $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at 0.5 C.

one pair of redox peaks around 4 V ($\text{Mn}^{3+}/\text{Mn}^{4+}$) and two pairs of well separated strong redox peaks at 4.6–4.8 V can be observed in CV curve of no carbon coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode. The two strong redox peaks indicate a two-stage ($\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{3+}/\text{Ni}^{4+}$) Li^+ extraction from or insertion into the spinel framework [22]. For PMF carbon coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode, the peaks around 4 V should weaken obviously. This indicates that the Mn^{3+} ions dissolution amount of the PMF carbon coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is smaller than no carbon coating [23]. The presence of Mn^{3+} in the LMNO material plays an important role in the capacity retention [9]. And the two redox peaks of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with 10 wt.% PMF carbon coating are overlapped to a broad peak. The cyclic voltammetry curves of the PMF carbon coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material exhibit smaller potential intervals that indicated higher electrode reaction reversibility and lower polarization. The PMF carbon coating would

effectively restrain the Mn^{3+} stripping and the side reaction between positive electrode active material and electrolyte at high voltage.

Figure 6 depicts the electrochemical impedance spectroscopy of the electrode obtained after the first cycle of charge. The semicircle at high frequency (>100 Hz) in EIS spectra reflects the contact resistances between the active materials and electrolyte or current collector [24]. The significant improvements in electric conductivity for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode could therefore be attributed to the PMF carbon coating [25].

4. Conclusions

PMF carbon coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was prepared as the 5 V cathode materials of lithium ion batteries for the first time. PMF carbon coating increases the crystallinity of

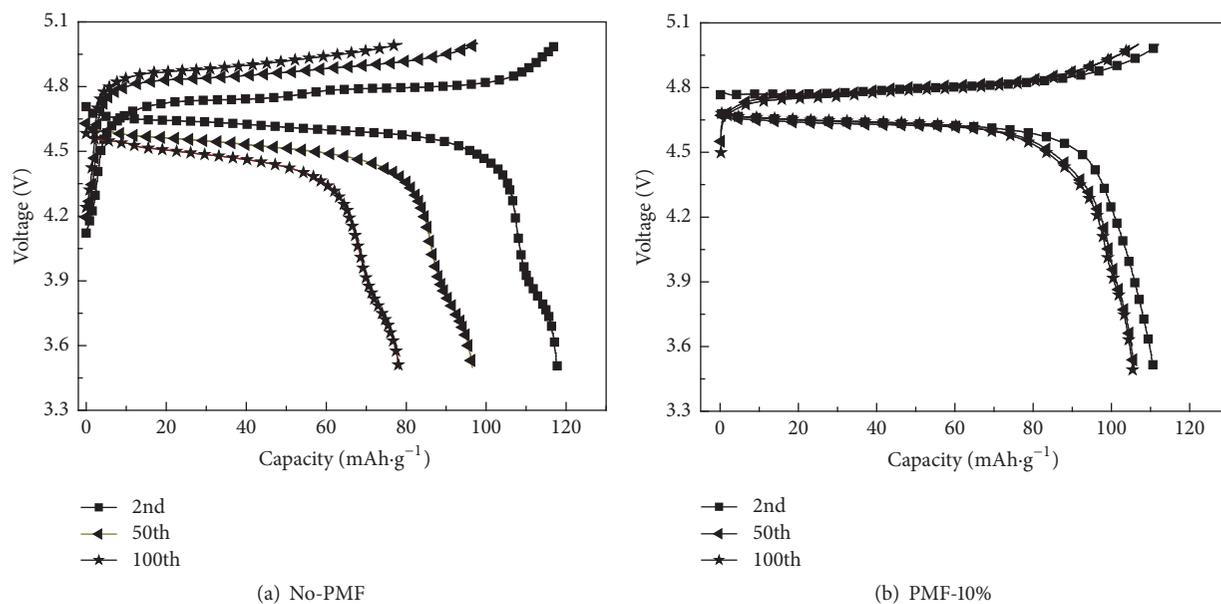


FIGURE 4: The charge and discharge curves of prepared $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at 10 C.

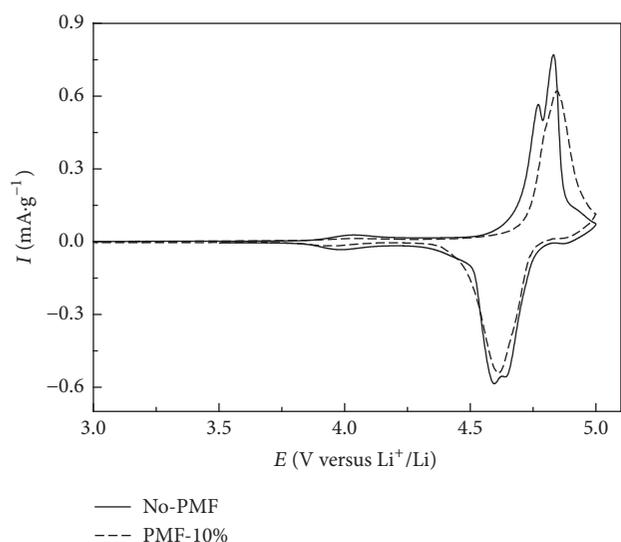


FIGURE 5: Cyclic voltammogram curves of prepared $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

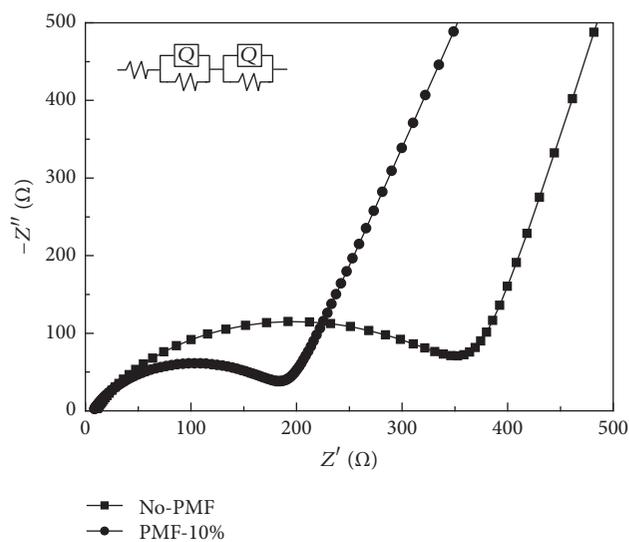


FIGURE 6: EIS spectra of prepared $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The as-prepared $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has the cubic face-centered spinel structure with a space group of $\text{Fd}3\text{m}$. The PMF carbon coating greatly promotes electrochemical performance and reduces the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode polarization in the process of charging and discharging. The cycle life of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was significantly improved by PMF carbon coating, especially at high rate discharging and charging.

Competing Interests

The authors declare that they have no competing interests.

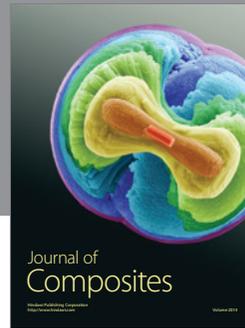
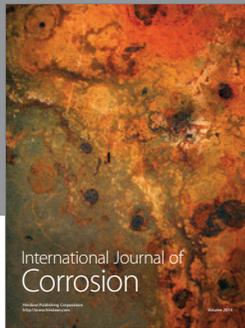
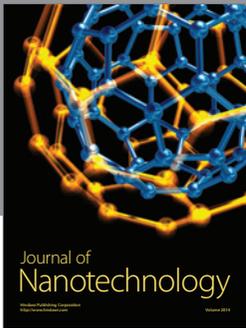
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References

- [1] R. Santhanam and B. Rambabu, "Research progress in high voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material," *Journal of Power Sources*, vol. 195, no. 17, pp. 5442–5451, 2010.

- [2] H.-S. Fang, Z.-X. Wang, X.-H. Li, H.-J. Guo, and W.-J. Peng, "Exploration of high capacity $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ synthesized by solid-state reaction," *Journal of Power Sources*, vol. 153, no. 1, pp. 174–176, 2006.
- [3] Y. Qian, Y. Deng, Z. Shi, Y. Zhou, Q. Zhuang, and G. Chen, "Sub-micrometer-sized $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spheres as high rate cathode materials for long-life lithium ion batteries," *Electrochemistry Communications*, vol. 27, pp. 92–95, 2013.
- [4] J.-H. Kim, N. P. W. Pieczonka, Z. Li, Y. Wu, S. Harris, and B. R. Powell, "Understanding the capacity fading mechanism in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /graphite Li-ion batteries," *Electrochimica Acta*, vol. 90, pp. 556–562, 2013.
- [5] D. Liu, J. Han, and J. B. Goodenough, "Structure, morphology, and cathode performance of $\text{Li}_{1-x}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ prepared by coprecipitation with oxalic acid," *Journal of Power Sources*, vol. 195, no. 9, pp. 2918–2923, 2010.
- [6] Y.-C. Jin and J.-G. Duh, "Nanostructured $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode material synthesized by polymer-assisted co-precipitation method with improved rate capability," *Materials Letters*, vol. 93, no. 2, pp. 77–80, 2013.
- [7] L. Wang, D. Chen, J. Wang, G. Liu, W. Wu, and G. Liang, "Synthesis of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode material with improved electrochemical performances through a modified solid-state method," *Powder Technology*, vol. 292, pp. 203–209, 2016.
- [8] J. Hassoun, K.-S. Lee, Y.-K. Sun, and B. Scrosati, "An advanced lithium ion battery based on high performance electrode materials," *Journal of the American Chemical Society*, vol. 133, no. 9, pp. 3139–3143, 2011.
- [9] J. Xiao, X. Chen, P. V. Sushko et al., "High-performance $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Spinel controlled by Mn^{3+} concentration and site disorder," *Advanced Materials*, vol. 24, no. 16, pp. 2109–2116, 2012.
- [10] J. Deng, Y. Xu, L. Xiong, L. Li, X. Sun, and Y. Zhang, "Improving the fast discharge performance of high-voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel by Cu^{2+} , Al^{3+} , Ti^{4+} tri-doping," *Journal of Alloys and Compounds*, vol. 677, no. 8, pp. 18–26, 2016.
- [11] G. Liu, Y. Du, W. Liu, and L. Wen, "Study on the action mechanism of doping transitional elements in spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$," *Electrochimica Acta*, vol. 209, pp. 308–314, 2016.
- [12] S. Wang, P. Li, L. Shao et al., "Preparation of spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and Cr-doped $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode materials by tartaric acid assisted sol-gel method," *Ceramics International*, vol. 41, no. 1, pp. 1347–1353, 2015.
- [13] Y. S. Lee, Y. K. Sun, S. Ota, T. Miyashita, and M. Yoshio, "Preparation and characterization of nano-crystalline $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ for 5 V cathode material by composite carbonate process," *Electrochemistry Communications*, vol. 4, no. 12, pp. 989–994, 2002.
- [14] H. B. Yao, Y. Xie, G. J. Han, and D. M. Jia, "Enhanced electrochemical performance of the cathode material $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ embedded by CNTs," *Journal of Materials Science: Materials in Electronics*, vol. 26, no. 3, pp. 1780–1783, 2015.
- [15] X. Li, W. Guo, Y. Liu, W. He, and Z. Xiao, "Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as superior electrode materials for lithium-ion batteries: ionic liquid assisted synthesis and the effect of CuO coating," *Electrochimica Acta*, vol. 116, no. 1, pp. 278–283, 2014.
- [16] T. Hwang, J. K. Lee, J. Mun, and W. Choi, "Surface-modified carbon nanotube coating on high-voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes for lithium ion batteries," *Journal of Power Sources*, vol. 322, no. 8, pp. 40–48, 2016.
- [17] A. Vijn, F. Hoffmann, and M. Fröba, "Thermal conversion to form $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$: Influence of precursors and supporting carbon template materials," *Thermochimica Acta*, vol. 638, pp. 138–150, 2016.
- [18] Y. Wei, C. Shengzhou, and L. Weiming, "Oxygen reduction on non-noble metal electrocatalysts supported on N-doped carbon aerogel composites," *International Journal of Hydrogen Energy*, vol. 37, no. 1, pp. 942–945, 2012.
- [19] Y.-J. Gu, Y. Li, Y.-B. Chen, and H.-Q. Liu, "Comparison of Li/Ni antisite defects in Fd-3 m and $\text{P4}_3\text{32}$ nanostructured $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode for Li-ion batteries," *Electrochimica Acta*, vol. 213, no. 9, pp. 368–374, 2016.
- [20] H. Wang, Z. Shi, J. Li et al., "Direct carbon coating at high temperature on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode: unexpected influence on crystal structure and electrochemical performances," *Journal of Power Sources*, vol. 288, no. 8, pp. 206–213, 2015.
- [21] G. Jia, C. Jiao, W. Xue et al., "Improvement in electrochemical performance of calcined $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{GO}$," *Solid State Ionics*, vol. 292, no. 9, pp. 15–21, 2016.
- [22] L. Zhou, D. Y. Zhao, and X. W. Lou, " $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ hollow structures as high-performance cathodes for lithium-ion batteries," *Angewandte Chemie International Edition*, vol. 124, no. 1, pp. 243–245, 2012.
- [23] J. Liu and A. Manthiram, "Understanding the improved electrochemical performances of Fe-substituted 5 V spinel cathode $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$," *Journal of Physical Chemistry C*, vol. 113, no. 33, pp. 15073–15079, 2009.
- [24] Q.-C. Zhuang, T. Wei, L.-L. Du, Y.-L. Cui, L. Fang, and S.-G. Sun, "An electrochemical impedance spectroscopic study of the electronic and ionic transport properties of spinel LiMn_2O_4 ," *The Journal of Physical Chemistry C*, vol. 114, no. 18, pp. 8614–8621, 2010.
- [25] T. Yang, N. Zhang, Y. Lang, and K. Sun, "Enhanced rate performance of carbon-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode material for lithium ion batteries," *Electrochimica Acta*, vol. 56, no. 11, pp. 4058–4064, 2011.



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