

Mg-Doped high voltage LiCoO₂ for high performance lithium-ion batteries

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Abstract—Further increasing the voltage is the most efficient means of acquisition to obtain lithium cobalt oxide with high specific capacity, but the irreversible phase transition of LiCoO₂ at high voltage leads to poor electrochemical performance. In this paper, a 4.6V high voltage stable lithium cobalt oxide cathode material was achieved by simple high temperature solid-phase synthesis method doped with different contents of Mg elements. Under the condition of Mg content of 0.02, the specific capacity of discharge is 222.7 mAh/g at 0.5C, and the capacity retention rate is 93% after 50 cycles of 1C, showing good electrochemical performance.

1. Introduction

At present, the energy density of lithium-ion batteries is primarily constrained by the cathode material.

In order to further increase the energy density of the battery, it is very important to develop high-voltage, high-capacity cathode materials. Among various cathode materials, lithium cobalt oxide (LCO) exhibits a high theoretical density and a theoretical specific capacity of 274 mAh/g. However, the charging voltage for lithium cobalt oxide in the industry is limited to 4.2 V, which corresponds to a specific capacity range of 140-160 mAh/g. When lithium cobalt oxide is charged to a higher working cut-off voltage, more Li⁺ can be extracted during cycling, thereby effectively increasing the specific capacity. However, a higher cut-off voltage (>4.45 V) would lead to irreversible phase transition and collapse of the layered structure, degrading the cycle performance. Doping modified LCO is a common method to improve the electrochemical performance. Through the doping of hetero elements during the synthesis process, the main structure of the material can be stabilized and the cycle stability can be enhanced.

Mg element has been proven to effectively improve the electronic conductivity of lithium cobalt oxide, and can improve the problem of insufficient insulating state of LCO in the state of high lithium concentration. In this study, LCO with varying Mg contents were synthesized using a high-temperature solid-state method. This approach not only enhanced the high-voltage stability and rate performance of LCO, but also provided a facile

and efficient route for preparing high-voltage LCO cathodes.

2. Experimental section

2.1 Material synthesis

The precursors Li₂CO₃, Co₃O₄, and MgO were weighed according to the molar ratio Li:Co:Mg=1.05:1:0, 1.05:1:0.01, 1.05:1:0.02, 1.05:1:0.03, respectively named as LCO, Mg=0.01, Mg=0.02, Mg=0.03. Excessive 5% lithium source was used to compensate the loss of Li in solid phase sintering. The above-mentioned samples were ball milled for 1 hour, then placed in the ultrasonic cell disruptor for 10 minutes, and then the samples were transferred to the muffle furnace and sintered at 1000 °C for 10 hours to obtain the final product.

2.2 Electrochemical measurements

The active material, conductive agent (Super P) and binder (PVDF) are ground into a uniform slurry with N-methylpyrrolidone (NMP) as the solvent according to the mass ratio of 8:1:1, and coated on the aluminum foil with the average active material loading density of 2.0 ± 0.1 mg cm⁻², and then dried and cut into 14mm diameter wafers. The wafers were used as the positive electrode and lithium metal as the negative electrode to assemble CR2025 coin cells. Neware instrument (CT-4008T) was used for galvanostatic charge-discharge test of coin cells, and the electrochemical workstation (CHI600E) was used for EIS and CV tests.

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3. Test Results and Discussions

In order to analyze the crystal structure of the Mg-doped LCO material, X-ray diffraction analysis was performed on each sample. The XRD patterns of LCO with varying Mg doping content are presented in Fig. 1. It can be seen from the figure that all the synthesized samples crystallize in the hexagonal $R\bar{3}m$ space group, and the diffraction peaks of the samples are consistent with the LCO standard PDF card (JCPDS No. 50-0653) consistent, and no other heterogeneous peaks were exhibited, indicating that all samples are typical α -

NaFeO₂ structures. The clear separation of (006)/(102) and (018)/(110) peaks indicates that the synthesized materials are well-ordered and highly crystalline layered structures. In addition, according to the Bragg equation, the (003) diffraction peak of the Mg-doped LCO cathode materials are shifted to the lower angle, which can be attributed to the widening of the (003) interplanar spacing, indicating that the lattice parameter increased. The widening of the c-axis widens the diffusion channel of lithium ions, reduces the diffusion barrier and migration resistance of lithium ions, and facilitates their rapid intercalation and extraction between layers.

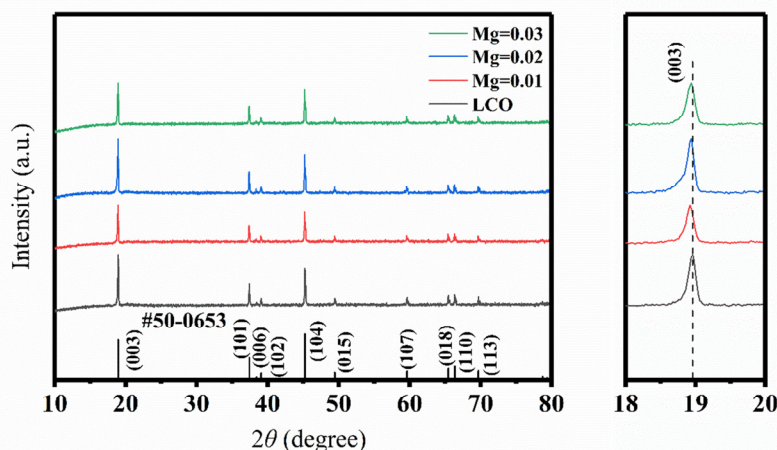


Fig.1 XRD patterns of LCO with different content of Mg doped

Fig.2a-2d shows the SEM images of Mg-doped samples with different contents. Fig.2a shows that the particle distribution of the unmodified sample is not uniform, and the particle size gap between the large particles and small particles is obvious, accompanied by obvious agglomeration. In Fig.2b, it can be found that the particle distribution is relatively more uniform, but there is still some agglomeration phenomenon. In Fig.2c-2d, the distribution of LCO is uniform, no excessive large particles are observed, and the morphology is relatively regular. Therefore, it can be concluded that the incorporation of Mg is beneficial to the growth process of grains, effectively reduces the electrochemical polarization of the material, and promotes the capacity retention during cycling.

Fig.2e-2f are the initial charge and discharge curves of samples with different doping amounts. It can be found that the curves of all samples are similar, but the charge-discharge curves of the unmodified sample and the sample with Mg doping amount of 0.01 in Fig.2e and

Fig.2f have obvious fluctuation near 4.2 V, while the curves of samples with Mg doping amount of 0.02 and 0.03 are relatively smoother. The LCO undergoes a series of phase transitions during charge and discharge, in which the "hexagonal - monoclinic - hexagonal" phase transition occurs when it releases close to 50% of the lithium ions, which corresponds to the fluctuating part of the curve in Fig.2e and Fig.2f. In the process of interconversion between the hexagonal and monoclinic phases, the crystal structure will change and since this process is not completely reversible, it will lead to a decrease in the performance of the LCO cathode material. In Fig.2e, the unmodified LCO has obvious monoclinic phase transition, while the sample with Mg doping amount of 0.01 in Fig.2f also failed to completely suppress the phase transition, while the sample with Mg doping amount of 0.02 (Fig.2g) and 0.03 (Fig.2h) could effectively inhibit the phase transition, indicating that the proper doping amount of Mg can improve the cycle performance of LCO.

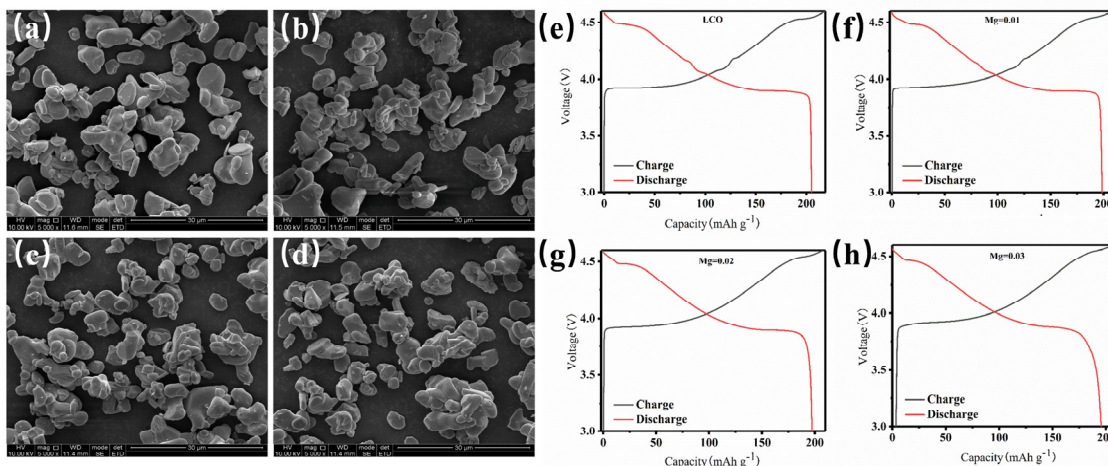


Fig.2 SEM images of Mg-doped samples with different contents (a-d); initial charge-discharge curves of Mg-doped LCO with different contents at 1C rate (e-h)

The discharge specific capacities of the unmodified LCO and the active materials doped with different proportions of Mg at different rates were compared, and the results are shown in Fig.3a. The discharge specific capacity of the modified sample under relatively high current conditions of 2 C, 5 C, and 10 C (1 C=150 mAh/g) are significantly better than that of the unmodified sample, indicating that the incorporation of Mg can significantly improve the capacity of LCO at high rates. When the doping amount of Mg is 0.02, the discharge specific capacity reaches 222.7, 212.6, 197.2, 168.1, 126.7 mAh/g at the current density of 0.5, 1, 2, 5, 10 C. The discharge specific capacities of the unmodified LCO are 218.8, 200.1, 173.1, 130.4, 50.8 mAh/g at current densities of 0.5, 1, 2, 5, and 10 C. The sample with Mg=0.02 has a great improvement on the rate performance of LCO.

The cycle stability test was carried out on LCO with different Mg doping amounts. The test voltage range was 3.0-4.6 V, the charge and discharge current density was 1

C, and the test temperature was constant temperature 25 °C. From Fig.2e, it can be seen that the first-cycle specific capacity of unmodified LCO reaches 205.3 mAh/g, while the first-cycle specific capacity of modified LCO will decrease to a certain extent, and continues to decrease with the increase of doping amount, because the active material ratio of LCO will decrease after Mg doping, which will affect the release of the specific capacity of the positive electrode material. However, after fifty cycles, the specific capacities of Mg-doped samples are significantly increased compared with unmodified LCO, which are 142.0, 161.9, 183.6 and 175.5 mAh/g, respectively. The sample with the value of 0.02 retains 93% of its initial capacity after fifty cycles, much higher than the 69.2% of unmodified LCO. In combination with the rate performance, the capacity retention rate of the sample with this doping amount is also the highest, indicating that the optimal doping amount of Mg is 0.02.

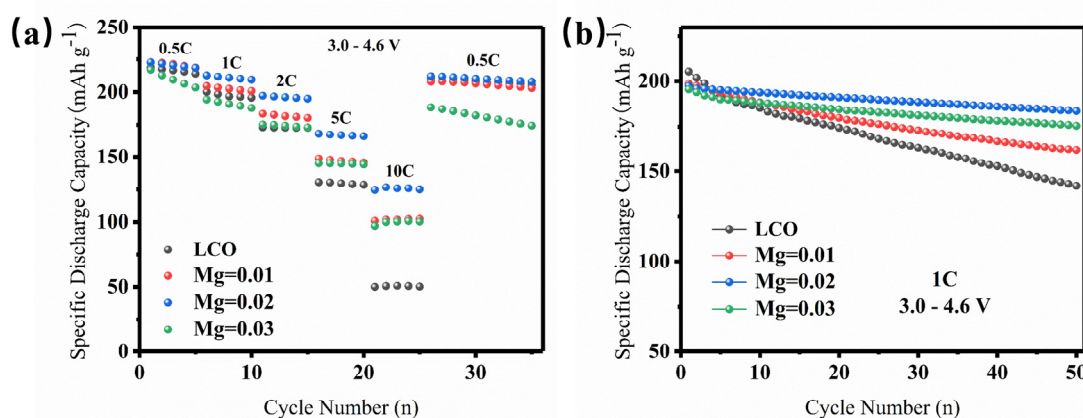


Fig.3 Rate (a) and cycle (b) stability test of LCO with different Mg doping amounts

Fig.4 shows the AC impedance spectra and equivalent circuit diagrams of samples with different amounts of Mg doping before and after cycling, and the impedance data obtained by fitting. In general, the AC impedance spectrum of LCO after cycling consists of three parts.

The semicircle observed in the high frequency region corresponds to the SEI resistance (R_{sei}) of the material,

while the semicircle seen in the intermediate frequency range represents charge transfer resistance (R_{ct}), and finally, a straight line is observed in the low frequency region which corresponds to Warburg impedance (W_1). As depicted in Fig.4a, the doped sample exhibits a significantly lower charge transfer resistance compared to the unmodified sample, which can be attributed to the effective enhancement of electronic conductivity by Mg

ions. It can be observed in Fig.4b that the unmodified LCO has a large R_{sei} and R_{ct} after fifty cycles, while the doped sample is significantly reduced, which shows that the Mg element is beneficial to ensure the low electrochemical impedance of the material after the charge-discharge process, which corresponds to the excellent cycling stability of the modified sample. The low SEI resistance and charge transfer resistance are conducive to the rapid transport of electrons, promote the charge transfer kinetics, and improve the electrolyte contact, so that LCO can release the specific capacity better and improve its rate performance, which is consistent with the rate performance test results.

Cyclic voltammetry (CV) tests were performed for unmodified samples and samples with doping of 0.02, including test curves before the cycle and after fifty cycles. As shown in Fig.4a and Fig.4b, the test voltage range is 3-4.6V, and the scanning rate is 0.1mV/s. It can

be seen in Fig.4a that there are multiple redox peaks between 4.0-4.2V. According to the voltage of monoclinic phase transition, it can be inferred that the peaks pointed by the arrows in the figure are the LCO undergoing "hexagonal- The process of monoclinic-hexagonal phase transition. The monoclinic phase transition seems to be reversible, but each cycle will bring a certain expansion and contraction to the lattice, so that the stress will continue to accumulate and seriously affect the cycle stability of the material. The CV curve after fifty cycles shows that the monoclinic phase transition still exists, and the capacity of the material drops significantly. It can be observed in Fig.4d that the curve is very smooth, the incorporation of Mg suppresses the occurrence of monoclinic phase transition, and the intensity of the redox peak is not seriously weakened after fifty cycles, indicating that the impurities bring better structural stability to LCO.

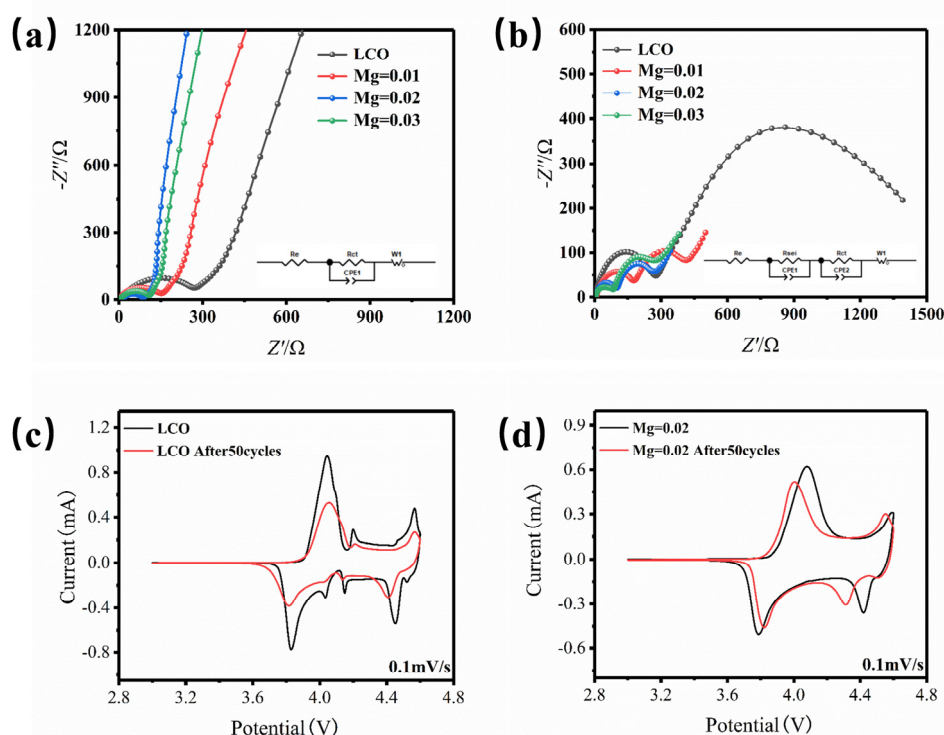


Fig.4 Electrochemical impedance diagrams before (a) and after (b) cycling of samples with different amounts of Mg doping ; cyclic voltammetry tests of LCO (a) and Mg=0.02 (b) before and after cycling

168.1, 126.7 mAh/g at current densities of 0.5, 1, 2, 5, and 10 C, respectively, which is significantly improved compared with the unmodified LCO.

4. Conclusion

Based on the results and discussions presented above, the conclusions are obtained as below:

(1) Mg doping widens the (003) interplanar spacing of LCO, and the widening of the c-axis facilitates the rapid intercalation and extraction of lithium ions between layers.

(2) The doping of Mg can effectively suppress the monoclinic phase transition of LCO during cycling, and further improve the high voltage cycle stability of LCO. After 50 cycles, the capacity retention rate of the sample with 0.02 Mg doping is 93%, which is significantly improved compared with 69.2% of unmodified LCO.

(3) The specific discharge capacity of the sample with Mg doping amount of 0.02 is 222.7, 212.6, 197.2,

Acknowledgments

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References

1. Cheng T, Ma Z, Qian R, et al. Achieving stable cycling of LiCoO₂ at 4.6 V by multilayer surface

- modification[J]. *Advanced Functional Materials*, 2021, 31(2): 2001974.
2. Wang L, Ma J, Wang C, et al. A novel bifunctional self-stabilized strategy enabling 4.6 V LiCoO₂ with excellent long-term cyclability and high-rate capability[J]. *Advanced Science*, 2019, 6(12): 1900355.
 3. Lyu Y, Wu X, Wang K, et al. An overview on the advances of LiCoO₂ cathodes for lithium-ion batteries[J]. *Advanced Energy Materials*, 2021, 11(2): 2000982.
 4. Kong W, Zhang J, Wong D, et al. Tailoring Co3d and O2p band centers to inhibit oxygen escape for stable 4.6 V LiCoO₂ cathodes[J]. *Angewandte Chemie International Edition*, 2021, 60(52): 27102-27112.
 5. Chen S X, Wang C W, Zhou Y, et al. Co/Li-dual-site doping towards LiCoO₂ as a high-voltage, fast-charging, and long-cycling cathode material[J]. *Journal of Materials Chemistry A*, 2022, 10(10): 5295-5304.