Improving the Cycling Stability of LiCoO₂ at 4.5 V by Mg Doping and Graphite Coating

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Abstract. Mg doping and graphite coating are applied to the LCO materials at the same time, thereby improving the structural stability of the LCO and the electrode conductivity at the same time. cLCO-0.02Mg displays the best cycle performance with a high capacity of 146.2 mAh/g after 60 cycles, corresponding to the 79% capacity retention of the initial discharge capacity. And cLCO-0.02Mg displays the best rate performance among the three samples with a high capacity of 41.1 mAh/g at 5 C. Mg doping helps to improve the structure stability, resulting in improving the cycle stability. Graphite coating enhances the electronic conductivity among the LCO particles, indicating a lower internal resistance, thereby resulting in the cycling performance improved.

1. Introduction

Li-ion batteries (LIBs) have been urged for high energy density, high rate capability, and long cycling stability, with increasing energy storage demands in portable electronic devices, electrical vehicles, and grid [1-3]. The most direct way to increase energy density is to choose electrode materials with a high capacity and/or a high working voltage [1,4-8]. LiCoO₂ (LCO) remains the best cathode material in the portable electronic domain, benefiting from its with high redox potential, high specific capacity and high cycle-life [9-12]. However, the actual specific capacity of LCO can only reach 140 mAh/g, corresponding to the reversible deintercalation/intercalation of 0.55 Li per LCO, and the upper cut-off voltage of 4.2 V vs. Li/Li⁺ [1,11-13]. The specific capacity and energy density of the LCO electrode can be effectively improved by increasing the cut-off potential of the LCO electrode. However, the cycling stability of LCO is relatively poor ascribed to its inferior structural stability and interface stability when the cut-off potential is increased to 4.5 V [1]. Therefore, great efforts have been made to modify the interface stability between LCO and the electrolyte at 4.5 V, in order to enhance the working potential of LIBs and achieve a higher energy density.

Doping can effectively improve the stability of the LCO structure, thereby improving the cycle stability of the LCO. In addition, some element doping can effectively improve the electronic conductivity of the LCO, resulting in reducing the LCO polarization resistance and improving the rate performance [14-17]. Some studies have shown that proper Mg doping can increase the electrical conductivity of LCO material from 1 × 10⁻³ S/cm to 0.5 S/cm without changing the crystal structure. This is mainly because 2Co³⁺ → Co⁴⁺ + Mg²⁺, resulting in causing electron holes [14-16]. In addition, Mg²⁺ can form Mg-O bonds with oxygen, which are stronger than Li-O bonds, indicating that the structure of LCO is more stable, and the cycle stability of LCO is higher [16]. However, if the doping ratio is too high, Li⁺ in the LCO structure will partially occupy the Co site, resulting in serious ion mixing and affecting the structural stability of LCO materials [17]. The porous powder electrode...
contributes to the infiltration of the electrolyte, reduces the Li diffusion distance, and enhances the release of the electrode's capacity. However, this cannot hinder the side reaction between the LCO electrode and the electrolyte, thereby generating the solid electrolyte interphase (SEI) film on the surface of the active material. The conductivity of the SEI film is relatively poor, resulting in increasing the polarization resistance between the electrode and the electrolyte, and reducing the cycle stability and the rate performance.

In this paper, Mg doping and graphite coating are applied to the LCO materials at the same time, thereby improving the structural stability of the LCO and the electrode conductivity at the same time. This makes the cycle stability and rate performance of the LCO improved. The effect of Mg doping and graphite coating on the performance of LCO was studied by electrochemical performance test. At the same time, the impedance of the electrodes before and after the cycle was studied by EIS test, and the mechanism of graphite coating and Mg doping was analysed.

2. Formatting the title, authors and affiliations

2.1. The preparation of LCO active materials

The preparation of LiCo_{1-x}Mg_{x}O_{2} (LCO-xMg) active materials was realized by traditional high temperature solid phase method. The raw materials which were Li_{2}CO_{3} (Aladdin, 99%), Co_{3}O_{4} (Aladdin, 99%), and Mg(OH)_{2} (Aladdin, 99%), were weighed according to the stoichiometric ratio (1.05 : 1-x : x, x = 0.01, 0.02, 0.03, 0.04). The raw materials are ground in an agate mortar for 1 hour. The mixture and absolute ethanol were sealed in an agate ball tank fitted with an agate ball, and followed by grounding in a planetary ball mill (QM3SP2, Nanjing NanDa Instrument Plant, China) for 5 hours at 400 rpm. After that, the slurry was poured into a beaker, placed in a blast drying oven, and dried at 100 °C for 5 hours to obtain the precursor powder. The precursor powder was heated at 750 °C for 6 h and calcined at 900 °C for 12 h.

The prepared LCO-xMg and graphite powder were weighed according to the mass ratio of 8:1, and mixed in an agate mortar for 1 hour. The mixture and absolute ethanol were sealed in an agate ball tank fitted with an agate ball, and followed by grounding in a planetary ball mill (QM3SP2, Nanjing NanDa Instrument Plant, China) for 5 hours at 300 rpm. After that, the slurry was poured into a beaker, placed in a blast drying oven, and dried at 80 °C for 5 hours to obtain the materials by graphite coating (cLCO-xMg).

2.2. Battery assembling

The electrodes were prepared by spreading well-mixed commercial LCO powders (active materials, 80 wt%), acetylene black (conducting additive, 10 wt%) and PVDF (binder, 10 wt%) on the surface of aluminium (Al) foil (~ 20 μm). The electrodes and separators (polypropylene, Celgard 2400) were dried in vacuum overnight at 110 °C and 50 °C, respectively. LCO/Li half-cells were assembled in a glovebox filled with argon. The electrochemical properties of samples were tested in 2032 coin cells equipped with a lithium metal anode electrode. The electrolyte solution was 1 M LiPF_{6}/EC : DMC : EMC (v/v/v = 1 : 1 : 1) and all the cells were fabricated in an Ar filled glove box. A Celgard® 2400 microporous polypropylene membrane was used as a separator.

2.3. Characterizations

The structural analysis of samples was performed by X-ray diffraction (XRD) using CuKα radiation. The surface morphology of samples was observed by scanning electron microscopy. The electrochemical impedance spectroscopy (EIS) of the samples were studied by Princeton VersaSTAT 3F electrochemical analyzer. The amplitude voltage was 10 mV and the frequency range were from 0.1 Hz to 100 kHz. Cycling tests were performed between 3.0 V and 4.5 V at charge-discharge rates of 0.2 C at room temperature by the battery test equipment (NEWARE CT-3008).
3. Formatting the text

3.1. Mg doping

Figure 1 shows the XRD diffraction patterns of LiCo$_{1-x}$Mg$_x$O$_2$ ($x=0.01,0.02,0.03,0.04$). As shown in Figure 1(a), the characteristic diffraction peaks of these samples are consistent with the diffraction peaks of standard high-temperature layered LiCoO$_2$ (JCPDS No. 75-0532). As can be seen from Figure 1(b), the (003) patterns of LiCo$_{1-x}$Mg$_x$O$_2$ ($x=0.01,0.02,0.03,0.04$) samples are magnified. The diffraction peak obviously shifts to left with increasing $x$, which is mainly because the atomic radius of Mg ($r_{Mg^{2+}}=0.72$ Å) is larger than that of Co ($r_{Co^{3+}}=0.54$ Å). This means that Mg substituting Co are incorporated into the LCO crystal structure.

The benefit of Mg doping is demonstrated by the remarkable improvement of the cycle stability of the LCO cathode as shown in Figure 2. The cycle performances of LCO-xMg cathode materials were tested in the voltage range of 3.0 V - 4.5 V, and at the charge-discharge rate of 0.2 C at room temperature. The initial discharge capacity of the samples is about 185 mAh/g. As the number of cycles increases, the specific capacity begins to decrease. After 60 cycles, the specific capacity of LCO is only 17.8 mAh/g, and the retention rate is only 9.5%. In contrast, the cycle stability of LCO cathode doped by Mg are significantly improved, and the capacity retention rate are over 55% after 60 cycles. LCO-0.02Mg displays the best cycle performance with a high capacity of 115.2 mAh/g, corresponding to the 62.2% capacity retention of the initial discharge capacity. This is mainly because Mg$^{2+}$ can form Mg-O bonds with oxygen, which are stronger than Li-O bonds, indicating a more stable structure [16]. However, if the doping ratio is too high, Li$^+$ in the LCO structure will partially occupy the Co site, resulting in serious ion mixing and affecting the structural stability of LCO materials [17]. Therefore, the proper doping ratio helps to improve the structure stability, resulting in improving the cycle stability.
Figure 2. Cycle performances of LCO-xMg samples at 0.2 C

3.2. Graphite Coating
The XRD diffraction patterns of LCO, cLCO, and cLCO-0.02Mg samples are shown in Figure 3. The characteristic diffraction peaks of these samples are consistent with the diffraction peaks of standard high-temperature layered LiCoO$_2$ (JCPDS No. 75-0532), indicating that graphite coating does not affect the structure of the LCO cathode materials.

Figure 3. XRD patterns of LCO, cLCO, and cLCO-0.02Mg samples

As shown in Figure 4, the cycle performances of LCO, cLCO, and cLCO-0.02Mg samples at room temperature are displayed. The voltage range is 3.0 V - 4.5 V, and the charge-discharge rate is 0.2 C. LCO samples with graphite coating show the cycling performances enhanced. During the first 20 cycles, both cLCO and LCO samples show the same capacity decay trend, but the capacity decay of cLCO-0.02Mg samples is relatively flat. This may be because of the structural stability caused by Mg doping. The cLCO-0.02Mg displays the best cycle performance with a high capacity of 146.2 mAh/g after 60
cycles, corresponding to the 79% capacity retention of the initial discharge capacity. In addition, the discharge capacity of cLCO-0.02Mg is higher than that of LCO-0.02Mg, indicating that a highly conductive graphite coating helps to enhance the further release of capacity.

The rate performances of LCO, cLCO, and cLCO-0.02Mg from 0.2 C to 5 C are displayed in Figure 5. As the discharge rate increases, the decay rate of the discharge capacity increases, which is mainly affected by polarization and internal resistance of the cells. As expected, due to the high electronic conductivity, graphite coating provides many specific channels for e⁻ transportation form LiCoO₂ to the current collector, leading to more capacity release. Particularly, cLCO-0.02Mg displays the best rate performance among the three samples with a high capacity of 41.1 mAh/g at 5 C. However, LCO exhibits poor rate performance, almost no discharge capacity at 5 C. This is mainly because Mg²⁺ can form Mg-O bonds with oxygen, which are stronger than Li-O bonds, indicating a more stable LCO structure [16], and graphite coating enhances the electronic conductivity among the LCO particles, meaning the lower internal resistance.

3.3. EIS Testing
EIS testing is often used to analyse the internal resistance of the battery to further analyse the battery failure mechanism. As shown in Figure 6, the EIS plots of LCO, LCO-0.02Mg, and cLCO-0.02Mg with
The different cycle are demonstrated, and the equivalent circuit model of the cells is displayed. Here, $R_e$, $R_{sei}$, and $R_{ct}$ mean the ionic resistance of the electrolyte, the surface layer resistance, and the charge-transfer resistance, respectively. The $R_{sei}$ and $R_{ct}$ of LCO, LCO-0.02Mg, and cLCO-0.02Mg with the different cycle are summarized in Table 1. $R_{ct}$ of LCO increases rapidly with the charge-discharge cycles, but $R_{ct}$ of LCO-0.02Mg and cLCO-0.02Mg are relatively low. The differences we observed in EIS measurements strongly suggest that graphite coating enhances the electronic conductivity among the LCO particles, indicating a lower internal resistance, thereby resulting in the cycling performance improved.

| Sample          | $R_{sei}$ (Ω) After 1 cycle | $R_{sei}$ (Ω) After 20 cycles | $R_{sei}$ (Ω) After 50 cycles | $R_{ct}$ (Ω) After 1 cycle | $R_{ct}$ (Ω) After 20 cycles | $R_{ct}$ (Ω) After 50 cycles |
|-----------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| LCO             | 128.4                       | 74.3                        | 34.7                        | 237.3                       | 660.9                       | 979.6                       |
| LCO-0.02Mg      | 114.3                       | 65.0                        | 42.9                        | 190.0                       | 328.3                       | 421.6                       |
| cLCO-0.02Mg     | 95.1                        | 68.5                        | 23.8                        | 154.4                       | 309.4                       | 349.1                       |

3.4. SEM
The stability of the sample structure directly affects the performance of the battery. Figure 7 shows SEM images of LCO and cLCO-0.02Mg before and after cycling. As can be seen from (a) and (c) of Figure 7, the LCO particles after cycling shows obvious pulverization. However, cLCO-0.02Mg still exists as particles and is not pulverized (Figure 7 (b) and (d)). The differences we observed in SEM measurements strongly suggest that Mg doping helps to improve the structure stability, resulting in improving the cycle stability.
Figure 7. SEM images of LCO and cLCO-0.02Mg before and after cycling. (a) LCO and (b) cLCO-0.02Mg before cycling; (c) LCO and (d) cLCO-0.02Mg after cycling.

4. Conclusion
Mg doping and graphite coating are applied to the LCO materials at the same time, thereby improving the structural stability of the LCO and the electrode conductivity at the same time. Mg doping helps to improve the structure stability, resulting in improving the cycle stability. Graphite coating enhances the electronic conductivity among the LCO particles, indicating a lower internal resistance, thereby resulting in the cycling performance improved. cLCO-0.02Mg displays the best cycle performance with a high capacity of 146.2 mAh/g after 60 cycles, corresponding to the 79% capacity retention of the initial discharge capacity. And cLCO-0.02Mg displays the best rate performance among the three samples with a high capacity of 41.1 mAh/g at 5 C. Doping and coating are both used to modify the other high-voltage cathode materials, which helps to increase the energy density of batteries.

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