Enhanced Electrochemical Performances of Cobalt-Doped Li$_2$MoO$_3$ Cathode Materials

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Abstract: Co-doped Li$_2$MoO$_3$ was successfully synthesized via a solid phase method. The impacts of Co-doping on Li$_2$MoO$_3$ have been analyzed by X-ray photoelectron spectroscopy (XPS), X-ray powder diffraction (XRD), scanning electron microscope (SEM), and Fourier transform infrared spectroscopy (FTIR) measurements. The results show that an appropriate amount of Co ions can be introduced into the Li$_2$MoO$_3$ lattices, and they can reduce the particle sizes of the cathode materials. Electrochemical tests reveal that Co-doping can significantly improve the electrochemical performances of the Li$_2$MoO$_3$ materials. Li$_2$Mo$_{0.90}$Co$_{0.10}$O$_3$ presents a first-discharge capacity of 220 mAh·g$^{-1}$, with a capacity retention of 63.6% after 50 cycles at 5 mA·g$^{-1}$, which is much better than the pristine samples (181 mAh·g$^{-1}$, 47.5%). The enhanced electrochemical performances could be due to the enhancement of the structural stability, and the reduction in impedance, due to the Co-doping.

Keywords: Li$_2$MoO$_3$; Co-doping; cathode materials; Li ion battery

1. Introduction

Recently, the development of high-capacity cathode materials has become a hot topic in the field of Li-ion batteries. Mn-based Li-rich layer oxides $x$ Li$_2$MnO$_3$·(1 − $x$)LiMO$_2$ (0 < $x$ < 1.0, M = Mn, Ni, Co, etc.) were proposed as potential cathode materials, due to their high discharge capacities of above 280 mAh·g$^{-1}$, and thus, the structure stability of the Li$_2$MnO$_3$ component [1–8]. Unfortunately, numerous reports have indicated that the drawbacks of Li$_2$MnO$_3$-based composites, such as low initial Coulombic efficiency, a fast decline in capacity, and potential safety hazards, were difficult to overcome, which severely restricted their practice applications [9–11]. Thus, much attention has been paid to find other transition metals instead of Mn, to build new Li$_2$MO$_3$ (M = Ru, Ir, Mo, etc.)-based materials for next generation Li–ion batteries in recent years [12–15].

Li$_2$MoO$_3$ as a type of Li-rich layer cathode material with alternating Li layers and randomly distributed [Li$_{1/3}$Mo$_{2/3}$] layers, has attracted much research interest [15–21]. The previous studies verified that Li$_2$MoO$_3$ promised a high theoretical capacity of up to 339 mAh·g$^{-1}$, and a near-absence of oxygen evolution [17,18], which supported Li$_2$MoO$_3$ as a candidate to replace Li$_2$MnO$_3$ in constructing Li-rich cathode materials. However, the poor cycling stability and rate capability of the Li$_2$MoO$_3$ material, owing to its low conductivity and irreversible phase transition, hinders its practical application. Hence, it is necessary to find a suitable modification method to improve the performance of the Li$_2$MoO$_3$ material.

At present, only a few studies about on modifying Li$_2$MoO$_3$ have been reported [19–21]. Ceder’s group constructed a solid solution between Li$_2$MoO$_3$ and LiCrO$_2$ for cathode materials [19].
The Li$_2$MoO$_3$–LiCrO$_2$ cathode materials presented not only high-discharge capacities, but also great cycling stabilities over the 10 cycles. In our previous study, carbon-coated Li$_2$MoO$_3$ composites were successfully prepared, and they achieved much lower impedances and better electrochemical performances than bare Li$_2$MoO$_3$ [21]. Cobalt doping has been considered to be a facile and effective method in enhancing the electrochemical performances, since it can improve structure stability and reduce the impedance of cathode materials [22–26]. In this paper, cobalt was selected to improve the electrochemical performances of Li$_2$MoO$_3$ for the first time. The structural characteristics and electrochemical performances of Li$_2$Mo$_{1-x}$Co$_x$O$_3$ are presented here.

2. Materials and Methods

2.1. Preparation of the Li$_2$Mo$_{1-x}$Co$_x$O$_3$ Powder

The pristine and Co-doped Li$_2$MoO$_3$ powders were synthesized via a solid reaction method, as shown in Figure 1. Firstly, stoichiometric amounts of Li$_2$CO$_3$ (>99.7%, Sinopahrm Medicine, Shanghai, China), MoO$_3$ (>99.5%, Aldrich, Shanghai, China), and 2CoCO$_3$·3Co(OH)$_2$ (>99.5%, Aldrich, Shanghai, China) were homogeneously mixed by ball milling, and then calcinated at 873 K for 24 h under air, to obtain the precursor. Li$_2$CO$_3$ was added in at 10% excess to compensate Li volatilization. After that, the obtained precursor was reduced in a stream of flowing 5%H$_2$/95%N$_2$ at 973 K for 48 h to prepare Li$_2$Mo$_{1-x}$Co$_x$O$_3$.

![Figure 1. Flow chart of the process for preparing Li$_2$Mo$_{1-x}$Co$_x$O$_3$.](image)

2.2. Physical Characterization

X-ray powder diffraction (XRD) was carried out by using a PhilipsX’ Pert PW3050/60 diffractometer (PANalytical. B. V, Lelyweg, the Netherlands), with a scan rate of 0.02° per second, by Cu–K$_\alpha$ radiation (λ = 1.5406 Å). X’pert Highscore software (PANalytical. B. V, Lelyweg, the Netherlands) was used for Rietveld refinement. The morphologies of the samples was determined by a HITACHI S-4800 field-emission high-resolution scanning electron microscope (SEM) (Hitachi, Tokyo, Japan). X-ray photoelectron spectroscopy (XPS) was detected on a ESCALAB250Xi (ThermoFisher, Waltham, America). Fourier transform infrared spectroscopy (FTIR) was detected on a Nicolet6700 (ThermoFisher, Waltham, America) in the wave range of 4000–400 cm$^{-1}$ with a high resolution of 4 cm$^{-1}$.

2.3. Electrochemical Tests

The electrochemical performances were tested through CR2032-type coin cells (HF-Kejing, Hefei, China). Cathodes were prepared by mixing 70 wt % Li$_2$Mo$_{1-x}$Co$_x$O$_3$, 20 wt % acetylene carbon black and 10 wt % polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP) solution. The slurry was cast evenly onto a stainless steel sheet, and dried in a vacuum oven (Suopuyiqi, Shanghai, China) at 120 °C for 12 h. Lithium metal and Celgard 2400 were used as the anode and separator, respectively. A concentration of 1 mol·L$^{-1}$ LiPF$_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (volume ratio: 1:1) solution was adopted as the electrolyte. The coin cells were assembled in an argon-filled
glove box, and measured on a Land CT2001A system (LANHE, Wuhan, China) in galvanostatic mode at 30 °C. Electrochemical impedance spectroscopy (EIS) was tested using an electrochemical station (CHI660B) (Chenhua, Shanghai, China) in $10^{-2}$ Hz–10 MHz, with a voltage amplitude of 5 mV. Cycliation at a scanning speed of $10^{-1}$ mVc voltammetry (CV) was performed with the same electrochemical at s$^{-1}$.

3. Results and Discussion

3.1. Characteristics of the as-Prepared $\text{Li}_2\text{Mo}_{1-x}\text{Co}_x\text{O}_3$

Figure 2a and b shows the XPS spectra of Co 2p$_{3/2}$ in $\text{Li}_2\text{Mo}_{0.90}\text{Co}_{0.10}\text{O}_3$, and the corresponding precursor. The peak of Co 2p$_{3/2}$ in the precursor is at 779.8 eV (Figure 2a) with a weak satellite at 789.9 eV. This satellite peak is 10.1 eV above Co 2p$_{3/2}$, corresponding diamagnetic Co$^{3+}$ ($S = 0$), which is very consistent with the XPS result reported for LiCoO$_2$ [27]. After the reduction by hydrogen at a high temperature, the original satellite disappears, and a new intense satellite appears at 784.4 eV, as shown in Figure 2b. Compared with the original satellite, the new satellite is 4.1 eV higher than the core level line (780.3 eV), corresponding to high-spin Co$^{2+}$ ($S = 3/2$) compounds, indicating that the valence state of the Co element will be reduced from Co$^{3+}$ to Co$^{2+}$ after reduction processing under hydrogen [28]. Figure 2c and d show that the XPS spectra of Mo in $\text{Li}_2\text{MoO}_3$ and $\text{Li}_2\text{Mo}_{0.90}\text{Co}_{0.10}\text{O}_3$. The peak at around 230.1 eV is assigned to Mo$^{4+}$ 3d$_{5/2}$, and the peak at around 232.6 eV is assigned to Mo$^{6+}$ 3d$_{5/2}$. Obviously, after cobalt doping, the peak intensity of Mo$^{6+}$ 3d$_{5/2}$ rises, and the peak intensity of Mo$^{4+}$ 3d$_{5/2}$ decreases, indicating an increased amount of Mo$^{6+}$.

![Figure 2](image_url)

Figure 2. XPS spectra of Co in (a) the doped precursor, and (b) $\text{Li}_2\text{Mo}_{0.90}\text{Co}_{0.10}\text{O}_3$ and the XPS spectra of Mo in (c) $\text{Li}_2\text{MoO}_3$ and (d) $\text{Li}_2\text{Mo}_{0.90}\text{Co}_{0.10}\text{O}_3$.

Figure 3a shows the XRD patterns of the synthesized $\text{Li}_2\text{Mo}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0, 0.05, 0.10, 0.15$). Except the sample with $x = 0.15$, all samples match well with the $\alpha$-NaFeO$_2$ structure, which could be indexed to $\text{Li}_2\text{MoO}_3$ (see Figure 3a). When the Co content adds up to 0.15, the characteristic peaks of the impurity phase Li$_4$MoO$_5$ and Co appear. The splitting of the (006)/(101) peaks at 36°, reflecting that the layer structure weakens with the increase of Co content, indicating that Co-doping increases the disorder of the cations. Rietveld refinements for $\text{Li}_2\text{Mo}_{1-x}\text{Co}_x\text{O}_3$ were carried out, to obtain more information from XRD (see Figure 3b,c). The a(b)-parameters are increased, and c-parameters are
were stored in the air for 7 days before the FTIR test. Obviously, both samples present a similar FTIR spectrum while the peaks at 1480, 1420, 830 and 817 cm⁻¹ were assigned to Li₂CO₃, which could be attributed to Li₂MoO₃ and Li₂MoO₄, respectively. These species are believed to be the reaction products between of Li₂MoO₃, CO₂ and O₂, revealing that both samples are partially decomposed in air. No peaks related to Li₂MoO₃ are detected in the FTIR spectra, which may contribute to the shorter storage time compared with the previous report [16].

Figure 3. (a) XRD patterns, (b) a(b)-parameters in the lattice, (c) c-parameters, and (d) unit cell volume of the synthesized Li₂Mo₁₋ₓCoₓO₃ (x = 0, 0.05, 0.10).

In order to observe the impacts of Co-doping on the particle morphologies of the samples, the SEM images of Li₂Mo₀.₉₀Co₀.₁₀O₃ (x = 0, 0.05, 0.10) were examined (see Figure 4). The particle sizes of the pristine Li₂MoO₃ present a wide distribution range from 1 to 3 μm (see Figure 4a), whereas the doped samples show smaller particles with more uniform distributions in the range of 200–300 nm (see Figure 4b,c). The results suggest that the addition of Co affects the morphology, and decreases the particle size of cathode materials. Particle growth may be restricted by lattice distortion of Li₂MoO₃ due to the replacement of Mo by Co. Similar phenomena have also been observed by some other groups [29,30]. Ma, J. et al. studied the stability of Li₂MoO₃ in air [16]. Their results verified that Li₂MoO₃ easily adsorbed O₂ and thus was partially oxidized to Li₂MoO₄. Meanwhile, the CO₂ in air also reacted with Li₂MoO₃ to produce Li₂CO₃, which consumed the Li ions near the surface and produced MoO₃ [16]. In order to investigate the effects of Co-doping on the stability of Li₂Mo₀.₁₋ₓCoₓO₃ in air, FTIR spectra of Li₂MoO₃ and Li₂Mo₀.₀₅Co₀.₁₀O₃ were carried out (see Figure 5). The samples were stored in the air for 7 days before the FTIR test. Obviously, both samples present a similar FTIR spectra. The peaks at 446, 497, 559 and 698 cm⁻¹ are assigned to Li₂MoO₃, which is consistent with the previous study [16]. While the peaks at 1480, 1420, 830 and 817 cm⁻¹ could be attributed to Li₂CO₃ and Li₂MoO₄, respectively. These species are believed to be the reaction products between of Li₂MoO₃, CO₂ and O₂, revealing that both samples are partially decomposed in air. No peaks related to MoO₃ are detected in the FTIR spectra, which may contribute to the shorter storage time compared with the previous report [16].

decreased, with a rise of Co-doping content. Notably, the variations of cell parameters are negligible while x is higher than 0.10 considering the fitting error, which indicates that the solubility limit of Co is around x = 0.10. Moreover, the values of c/a drop with the increase of the Co-doping content, which indicates that Co-doping increases the disorder of Li₂MoO₃ materials. As indicated in the above XPS results, the valence of cobalt should be +2 in the samples. Its radius (0.745 Å) is very similar to that of Li⁺ (0.76 Å), which may result in the increase of disorder. Figure 3d exhibits the unit cell volume of the pristine and the Co-doped Li₂MoO₃. Clearly, the unit cell volume increases with the rise of the Co-doping contents, which could be related to the replacement of Mo⁴⁺ (0.65 Å) by Co²⁺ (0.745 Å).

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which may be attributed to the rise of inert impurities of Li$_4$.

Present the discharge capacities of 86, 121, 140 and 52 mAh·g$^{-1}$ in the voltage range of 1.5–4.5 V at 5 mA·g$^{-1}$.

3.2. Electrochemical Performances

Figure 6 compares the initial charge-discharge profiles of pristine and Co-doped samples in the voltage range of 1.5–4.5 V at 5 mA·g$^{-1}$. The samples present initial discharge capacities of 181, 213, 220 and 165 mAh·g$^{-1}$, respectively. When the doping content is 0.05 and 0.10, the first discharge capacities of Co-doped samples are higher than that of the pristine sample. It also can be found the first discharge capacity decreases obviously while x = 0.15. What’s more, voltage difference between charge and discharge profiles of Li$_2$Mo$_{0.90}$Co$_{0.10}$O$_3$ is much smaller than that of pristine Li$_2$MoO$_3$, indicating that Co-doping can effectively suppress the polarization and enhance reversibility of Li$_2$MoO$_3$ materials. Notable that the charge behaviors with two regions for Co-doped Li$_2$MoO$_3$ cathode materials are similar to that for the pristine sample in the first charge-discharge process, which may relate to the delithiation reaction corresponding to the oxidation of the Mo ions in the 1.5–3.7 V region and a Li$_2$MoO$_3$-Li$_{0.91}$MoO$_3$ two phase reaction in the 3.7–4.5 V region [17].

Figure 7 shows the cycling performances of pristine and Co-doped samples between 1.5 and 4.5 V at 5 mA·g$^{-1}$. It is clearly seen that Li$_2$Mo$_{0.95}$Co$_{0.05}$O$_3$ and Li$_2$Mo$_{0.90}$Co$_{0.10}$O$_3$ deliver much higher discharge capacity than that of pristine sample. After 50 cycles, pristine and Co-doped sample present the discharge capacities of 86, 121, 140 and 52 mAh·g$^{-1}$ with the capacity retentions of 47.5%, 56.8%, 63.6% and 31.5%, respectively. Clearly, the cycling stability of pristine is poor. However, while increasing cobalt content to 0.05 and 0.10, the discharge capacity and cycling stability are significantly improved. With a further increase of Co content, the discharge capacity and cycling stability reduce, which may be attributed to the rise of inert impurities of Li$_4$MoO$_5$ and Co. Li$_4$MoO$_5$ delivers poor electrochemical performances because of its low electron conduction, low Coulombic efficiency and critical irreversible phase transition [31]. In addition, Co shows ignorable specific capacity above
Therefore, the appearance of Co and $\text{Li}_4\text{MoO}_5$ in the sample has negative effects on the electrochemical performance of $\text{Li}_2\text{MoO}_3$. $\text{Li}_2\text{Mo}_{0.95}\text{Co}_{0.05}\text{O}_3$ possesses the highest discharge capacity and the best capacity retention, which indicates the amounts of dopant will be important for the electrochemical performances of $\text{Li}_2\text{MoO}_3$.

![Figure 6](image1.png)

**Figure 6.** The initial charge–discharge profiles of the synthesized $\text{Li}_2\text{Mo}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0, 0.05, 0.10, 0.15$) between 1.5 and 4.5 V at 5 mA·g$^{-1}$.

![Figure 7](image2.png)

**Figure 7.** Cycling performances of the synthesized $\text{Li}_2\text{Mo}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0, 0.05, 0.10, 0.15$) between 1.5 and 4.5 V at 5 mA·g$^{-1}$.

The comparison of rate capabilities between the pristine and Co-doped $\text{Li}_2\text{MoO}_3$ with current density from 5 mA·g$^{-1}$ to 20 mA·g$^{-1}$ is evaluated in Figure 8. The $\text{Li}_2\text{Mo}_{0.90}\text{Co}_{0.10}\text{O}_3$ possesses a higher discharge capacity of 218 mAh·g$^{-1}$ at 5 mA·g$^{-1}$ and 137 mAh·g$^{-1}$ at 20 mA·g$^{-1}$ than pristine $\text{Li}_2\text{MoO}_3$ material (180 mAh·g$^{-1}$ at 5 mA·g$^{-1}$ and 71 mAh·g$^{-1}$ at 20 mA·g$^{-1}$). The difference of discharge capacities between $\text{Li}_2\text{MoO}_3$ and $\text{Li}_2\text{Mo}_{0.90}\text{Co}_{0.10}\text{O}_3$ increases from 38 mAh·g$^{-1}$ to 66 mAh·g$^{-1}$ with a rise of current density from 5 mA·g$^{-1}$ to 20 mA·g$^{-1}$. When the current density returns to 5 mA·g$^{-1}$, the discharge capacity of $\text{Li}_2\text{Mo}_{0.90}\text{Co}_{0.10}\text{O}_3$ could reach up 155 mAh·g$^{-1}$, while that of pristine $\text{Li}_2\text{MoO}_3$ only lefts 104 mAh·g$^{-1}$. The above results suggest that Co-doping significantly enhances the rate capability of $\text{Li}_2\text{MoO}_3$. 
with electrode polarization. Hence, the conclusion can be drawn that Co-doping can reduce the polarization of Li$_2$MoO$_3$. In contrast, the capacity of Li$_2$Mo$_{0.90}$Co$_{0.10}$O$_3$ could reach up to 155 mAh·g$^{-1}$ at 5 mA·g$^{-1}$ and 71 mAh·g$^{-1}$ at 20 mA·g$^{-1}$, while that of pristine Li$_2$MoO$_3$ only lefts 104 mAh·g$^{-1}$ and 66 mAh·g$^{-1}$ at 20 mA·g$^{-1}$, respectively. The above results suggest that Co-doping significantly enhances the rate capability of Li$_2$MoO$_3$.

To further analyze the kinetic behaviors of the pristine and Co-doped samples, EIS measurements of Li$_2$MoO$_3$ and Li$_2$Mo$_{0.90}$Co$_{0.10}$O$_3$ were carried out and the results are presented in Figure 10. Both EIS plots display similar shapes (see Figure 10a), which are fitted through the equivalent circuit (see Figure 10c) and the fitting results are listed in Table 1. In the equivalent circuit, $R_f$ is related to Li$^+$ diffusion in the SEI film, $R_q$ is corresponding to the charge transfer resistance at electrolyte-electrode interface and $R_s$ is considered to be ohmic resistance. As can be seen from Table 1, the $R_s$ and $R_f$ of both samples change slightly. In contrast, the $R_f$ of Li$_2$MoO$_3$ is significantly reduced due to the Co-doping. The Li$_2$Mo$_{0.90}$Co$_{0.10}$O$_3$ presents the $R_f$ of 105.70 Ω, which is far below the pristine Li$_2$MoO$_3$ (478.75 Ω). The $R_f$ is major part to the total electrode impedance, and its reduction reveals that Co-doping is very effective in enhancing the conductivity of Li$_2$MoO$_3$.
beneficial to enhance the kinetic behaviors of Li$_2$MoO$_3$. In addition, the Li$^+$ ion diffusion coefficients ($D_{Li^+}$) were estimated by the following formula:

$$D_{Li^+} = \frac{R^2T^2}{2A^2F^4C_{Li^+}^2\sigma^2}$$  \hspace{1cm} (1)

$R$, $T$, $A$, $F$ and $C_{Li^+}$ are the gas constant, the absolute temperature, the area of the electrode surface, the Faraday’s constant and the molar concentration of Li ions, respectively [7]. The $\sigma$ corresponding to the Warburg factor could be calculated by the $Z'/\omega^{-0.5}$ (see Figure 10b) and the following formula:

$$Z' = R_f + R_{cl} + \sigma\omega^{-0.5}$$  \hspace{1cm} (2)

The improving trend in the values of $D_{Li^+}$ is very similar to the reducing trend in the values of $R_{cl}$. The pristine and Co-doped Li$_2$MoO$_3$ deliver the Li$^+$ ion diffusion coefficients of $3.89 \times 10^{-17}$ and $1.94 \times 10^{-16}$ cm$^2$ s$^{-1}$, respectively. As we can see, the Li$^+$ ion diffusion coefficients of Li$_2$MoO$_3$ have an obvious growth due to the Co-doping. These results clearly indicate that Co-doping significantly improves the kinetics behavior of Li$^+$ and reduces the impedance of Li$_2$MoO$_3$, which is responsible for the better rate capability and cycling stability of Li$_2$Mo$_{0.90}$Co$_{0.10}$O$_3$.

![Figure 10](image_url)

Figure 10. (a) EIS plots of Li$_2$MoO$_3$ and Li$_2$Mo$_{0.90}$Co$_{0.10}$O$_3$ after 20 cycles between 1.5 and 4.5 V at 5 mA g$^{-1}$, (b) $Z'$ vs. $\omega^{-0.5}$ at low frequency of EIS plots and (c) equivalent circuit model.

| Samples                      | $R_s$/$\Omega$ | $R_d$/$\Omega$ | $R_{cl}$/$\Omega$ | $D_{Li^+}$ (cm$^2$ s$^{-1}$) |
|------------------------------|----------------|----------------|-------------------|-----------------------------|
| Li$_2$MoO$_3$                | 6.21           | 32.73          | 478.75            | $3.89 \times 10^{-17}$      |
| Li$_2$Mo$_{0.90}$Co$_{0.10}$O$_3$ | 5.89           | 25.79          | 105.70            | $1.94 \times 10^{-16}$      |

To investigate the structural transformation of the samples during charge-discharge process, XRD patterns of Li$_2$MoO$_3$ and Li$_2$Mo$_{0.90}$Co$_{0.10}$O$_3$ after 20 cycles are exhibited in Figure 11. There are notable differences in the structure of Li$_2$MoO$_3$ before and after cycling. For pristine Li$_2$MoO$_3$ material, the strongest diffraction peak transfers from (003) to (104) and ratio of (003)/(104) drops to 0.65 after cycling, which could be indexed into the Li-insufficient structure [17]. This Li-insufficient structure contributes to the partially reversible migration of the Mo ions and the partial recovery of the Mo$_3$O$_{13}$ clusters during charge-discharge processes, leading to irreversible capacity loss and poor cycling stability. In contrast, ratio of (003)/(104) of Li$_2$Mo$_{0.90}$Co$_{0.10}$O$_3$ after cycling can maintain at 0.83, which is much better than the pristine Li$_2$MoO$_3$ after cycling. It indicates that Co-doping can effectively enhance the structural stability during charge-discharge process.
material, and thus benefit for its application.

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