



## Full Length Article

# Enhanced high-voltage cycling stability and rate capability of magnesium and titanium co-doped lithium cobalt oxides for lithium-ion batteries

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## ARTICLE INFO

## Keywords:

Lithium-ions battery  
Cathode material  
LiCoO<sub>2</sub>  
Mg and Ti co-doping  
Synergistic effect

## ABSTRACT

To improve the high-voltage cycling stability and rate capability, the Mg<sup>2+</sup> and Ti<sup>4+</sup> co-doping strategy is firstly proposed to modify the LiCoO<sub>2</sub> cathode material. The synergistic effect of co-doping with Mg<sup>2+</sup> and Ti<sup>4+</sup> ions on the structure, morphology and high-voltage electrochemical performance of LiCoO<sub>2</sub> is investigated. For the co-doped sample, the introduction of Mg<sup>2+</sup> and Ti<sup>4+</sup> ions can efficiently optimize the particle size distribution and reduce the aggregation behavior. Compared with the undoped and single-doped samples, the Mg<sup>2+</sup> and Ti<sup>4+</sup> co-doped LiCoO<sub>2</sub> sample presents better high-voltage cycling stability and rate capability due to the fact that the Mg<sup>2+</sup> and Ti<sup>4+</sup> ions co-doping can make full use of the respective advantages of Mg<sup>2+</sup>-doping and Ti<sup>4+</sup>-doping. When cycled at 1.0 C, the co-doped sample exhibits an initial discharge capacity of 179.6 mAh g<sup>-1</sup> in the voltage range of 2.75–4.5 V. After 100 cycles, the capacity retention of this sample can reach up to 82.6%. Moreover, the co-doped sample shows better rate performance with high discharge capacity of 151.4 mAh g<sup>-1</sup> at 5.0 C. These outstanding results may be attributed to the suppressed phase transition, decreased charge transfer resistance, improved thermal stability, enhanced electrical conductivity and uniform particle size distribution of the Mg<sup>2+</sup> and Ti<sup>4+</sup> co-doped LiCoO<sub>2</sub> sample.

## 1. Introduction

Among commercialized cathode materials, layered LiCoO<sub>2</sub> has been regarded as the most popular cathode material for lithium-ion batteries (LIBs). This material can demonstrate excellent cycling stability with practical discharge capacity of 140 mAh g<sup>-1</sup> when charged to 4.2 V [1]. However, such capacity performance can hardly meet the increasing requirement in high energy density for next-generation lithium-ion batteries. For layered LiCoO<sub>2</sub>, the theoretical specific capacity is 274 mAh g<sup>-1</sup>, but the actual discharge capacity in commercial Li-ion batteries only reach up to approximately 60% of the theoretical value. In order to enhance the capacity performance, many researchers attempt to solve this problem by raising the charge voltage. Unfortunately, the high charge voltage always results in the rapid capacity fading upon cycling. This undesirable result can be attributed to many causes, such as phase transition, cobalt dissolution and particle cracking [2–7].

Up to now, many researchers have made many efforts to stabilize

the structure of LiCoO<sub>2</sub> at high voltage [8–18]. Among various modification methods, bulk doping has been widely considered as effective methods to enhance the structural stability. Dopants are usually metal ions (Al<sup>3+</sup>, Mg<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Ti<sup>4+</sup>, Zr<sup>4+</sup>, etc.) and metalloid cation (B<sup>3+</sup>, Si<sup>4+</sup>, etc.) due to the expectation of occupying Co<sup>3+</sup> sites [19–32]. Among these elements, magnesium is cheap, light and abundant. The previous research results show that the Mg-doping can not only enhance the electrical conductivity of LiCoO<sub>2</sub>, but also promote the insulator-to-conductor transition in early deintercalation process [20,33]. Moreover, compared with other cation doping, the capacity reduction caused by Mg-doping (–130 mAh g<sup>-1</sup> when x = 1 in LiCo<sub>1-x</sub>Mg<sub>x</sub>O<sub>2</sub>) is much smaller [34]. However, it should be noted that the ability of Mg-doping to stabilize LiCoO<sub>2</sub> structure is deficient [35]. For layered LiCoO<sub>2</sub>, doping with Mg<sup>2+</sup> ions will raise the average oxidation state of cobalt, which is undesirable to enhance the high-voltage cycling performance. According to existing literature [36], such undesirable result can be solved by introducing equal amount of tetravalent cations in the crystal structure of LiCoO<sub>2</sub>. Yu et al. have found that the Ti-

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<https://doi.org/10.1016/j.apsusc.2018.07.091>

Received 19 March 2018; Received in revised form 5 June 2018; Accepted 11 July 2018

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doping can enormously improve the stability of LiCoO<sub>2</sub> [28,29]. The Ti<sup>4+</sup>-doped LiCoO<sub>2</sub> sample demonstrates excellent cycling stability and outstanding rate performance at 4.4 V voltage. By comprehensive considering of the respective improvement of Mg-doping and Ti-doping, we attempt to combine the advantages of Mg-doping and Ti-doping to more effectively enhance the high-voltage cycling performance of LiCoO<sub>2</sub>. In this work, we successfully synthesized the layered LiCo<sub>0.98</sub>MO<sub>2</sub> (M = Co<sub>0.02</sub>, Mg<sub>0.02</sub>, Ti<sub>0.02</sub>, Mg<sub>0.01</sub>Ti<sub>0.01</sub>) samples by citric acid-assisted sol-gel method. The synergistic effect of co-doping with Mg<sup>2+</sup> and Ti<sup>4+</sup> ions on the structure, morphology and high-voltage electrochemical performance of LiCoO<sub>2</sub> was investigated in detail.

## 2. Experimental

The Mg<sup>2+</sup> and Ti<sup>4+</sup> ions co-doped LiCo<sub>0.98</sub>Mg<sub>0.01</sub>Ti<sub>0.01</sub>O<sub>2</sub> sample has been synthesized by sol-gel method. Firstly, stoichiometric lithium hydroxide monohydrate and citric acid monohydrate were added into deionized water to form a solution. The mixed solution of cobalt acetate and magnesium nitrate was added dropwise into the above solution under constantly stirring at 55 °C. And then, the ethanol solution of butyl titanate was added dropwise into the mixed solution. Next, adding ammonia water to manipulate the pH of the obtained solution to about 7.0. The achieved solution was evaporated at 85 °C to get a wet purple gel. After dried at 105 °C for 24 h in oven, the purple gel was sintered at 450 °C for 6 h in air. Subsequently, the decomposed gel precursor was ground in mortar and sintered at 900 °C for 12 h in air to get the black product. For comparison, the un-doped LiCoO<sub>2</sub>, LiCo<sub>0.98</sub>Mg<sub>0.02</sub>O<sub>2</sub> and LiCo<sub>0.98</sub>Ti<sub>0.02</sub>O<sub>2</sub> samples were synthesized by the same sol-gel process.

In order to confirm the crystal structures, X-ray diffraction (XRD, Bruker DX-1000, Cu Kα radiation) was carried out. The surface morphology of bare and modified samples were identified by scanning electron microscopy (SEM, JEOL JSM-6360LV) and the chemical or oxidation state was measured by X-ray photoelectron spectroscopy (XPS, ESCALAB 250XI). The thermal stability of all samples was investigated by the thermogravimetric analysis (TGA, Q500) under air atmosphere at a heating rate of 10 °C per min. For electrochemical evaluation, the working electrodes were obtained by using obtained samples as active materials. Lithium foil and polypropylene membrane were used as anode material and diaphragm, respectively. 1 M LiPF<sub>6</sub> in a mixture (V<sub>DMC</sub>:V<sub>EMC</sub>:V<sub>EC</sub> = 1:1:1) was used as the electrolyte. Electrochemical measurements were carried out by using LAND CT2001A. Electrochemical impedance spectra (EIS) and cyclic voltammogram (CV) were studied by CS-350 electrochemical workstation. The electron conductivity of all samples was investigated by Four-point probe device (RTS-9).

## 3. Results and discussion

To identify the influence of doping with Mg<sup>2+</sup> and Ti<sup>4+</sup> ions on the structure of LiCoO<sub>2</sub>, XRD characterization is carried out on the LiCo<sub>0.98</sub>MO<sub>2</sub> (M = Co<sub>0.02</sub>, Mg<sub>0.02</sub>, Ti<sub>0.02</sub>, Mg<sub>0.01</sub>Ti<sub>0.01</sub>) samples, and the corresponding XRD patterns are shown in Fig. 1a. The characteristic diffraction peaks of these samples are consistent with the standard diffraction peaks of LiCoO<sub>2</sub> (JCPDS No. 75-0532), indicating that all these samples possess the typical α-NaFeO<sub>2</sub> structure with R-3m space group. Moreover, it can be seen that the separation of (0 0 6)/(0 1 2) peaks and (0 1 8)/(1 1 0) peaks is very obvious, which suggests the formation of well-ordered layered structure of all these samples [37]. Fig. 1b shows the magnified (0 0 3) peak of these samples. Compared with the undoped sample, the (0 0 3) peaks of all the doped samples shift slightly to lower angle, indicating that doping with Mg<sup>2+</sup> or Ti<sup>4+</sup> ions can enlarge the lattice parameter. Table 1 lists the accurate values of lattice parameters calculated from the XRD patterns. The values of lattice parameter a and c varies with doping with Mg<sup>2+</sup> or Ti<sup>4+</sup> ions, which agrees with the analysis result from Fig. 1b. This effect can be

explained by the bigger radius of dopant ions ( $r_{\text{Mg}^{2+}} = 0.72 \text{ \AA}$ ,  $r_{\text{Ti}^{4+}} = 0.61 \text{ \AA}$ ,  $r_{\text{Co}^{3+}} = 0.54 \text{ \AA}$ ) [20,38]. These results indicate that the introduction of Mg<sup>2+</sup> and Ti<sup>4+</sup> ions can extend the two-dimensional channel of lithium ions, which is beneficial to the intercalation and deintercalation process of lithium ions. As a result, the Mg<sup>2+</sup> and Ti<sup>4+</sup> ions doped LiCoO<sub>2</sub> samples may show good electrochemical performance.

Fig. 2 shows the SEM images of the LiCo<sub>0.98</sub>MO<sub>2</sub> (M = Co<sub>0.02</sub>, Mg<sub>0.02</sub>, Ti<sub>0.02</sub>, Mg<sub>0.01</sub>Ti<sub>0.01</sub>) samples. As we can see from Fig. 2a, the undoped LiCoO<sub>2</sub> sample consists of irregular particles with uneven particle size distribution. The smallest particle size is only 1.0 μm, while the biggest particle size can reach up to about 10 μm. Such result of undoped sample is distinct when compared with those modified samples which demonstrate more regular particles with reduced particle size in Fig. 2b–d. But visible difference can be found as the Mg-doped sample still contains large particle and the Ti-doped sample exhibit severe aggregation behavior. By contrast, the co-doped sample presents most uniform particle size and reduces the particle aggregation. These results indicate that the substitution of Mg<sup>2+</sup> and Ti<sup>4+</sup> ions for partial cobalt ions efficiently optimize the particle size distribution and reduce the aggregation behavior to some extent, which agree with the previous research results [28,39]. Regular and smaller-sized particles shorten the diffusion distance of Li<sup>+</sup> and thus reduce the electrochemical polarization, which contributes to its electrochemical properties.

In order to characterize the chemical and oxidation state of each element in the modified material, X-ray photoelectron spectroscopy (XPS) is carried out. Fig. 3 shows the XPS spectra of Li1s, Co2p, Mg1s, Ti2p and O1s in the LiCo<sub>0.98</sub>Mg<sub>0.01</sub>Ti<sub>0.01</sub>O<sub>2</sub> sample. As shown here, the spectrum of Li1s, Co2p and O1s presents well-defined characteristic binding energy peaks, which matches completely with reported studies [40,41]. It is noticeable that the Co2p spectrum is split to two components (Co2p<sub>3/2</sub> and Co2p<sub>1/2</sub>) due to spin orbital interactions, and two satellite peaks resulted from ligand-to-metal charge transfer are clearly observed [42,43]. As shown in Fig. 3b, the characteristic peak of Co2p<sub>3/2</sub> component is observed at 779.8 eV with a satellite peak at 789.8 eV, and the characteristic peak of Co2p<sub>1/2</sub> component is observed at 794.9 eV with a satellite peak at 804.9 eV. This result indicates that Co element is in trivalent state which is in good agreement with previous works [40,42–45]. In Fig. 3c the Mg1s peak is assigned to 1303.2 eV, which corresponds to the divalent state of Mg ions. And in Fig. 3d the Ti2p peaks for Ti<sup>4+</sup> ions reveal a Ti2p<sub>3/2</sub> peak at 457.98 eV and a Ti2p<sub>1/2</sub> peak at 463.68 eV. These binding energy positions are in good agreement with previous research results and further confirm that introducing equal amount of Mg and Ti ions does not alter the oxidation of cobalt [46–49].

The thermal behavior of the LiCo<sub>0.98</sub>MO<sub>2</sub> (M = Co<sub>0.02</sub>, Mg<sub>0.02</sub>, Ti<sub>0.02</sub>, Mg<sub>0.01</sub>Ti<sub>0.01</sub>) is investigated by thermogravimetric analysis (TGA). According to previous study, the weight loss of LiCoO<sub>2</sub> material mainly comes from the evaporation of absorbed species and loss of oxygen at elevated temperature [50,51]. As shown in Fig. 4, all samples demonstrate weight loss rate less than 1% with increasing temperature. However, the co-doped sample exhibiting more slowly quality decreasing rate, indicating the improved thermal stability caused by co-doping with Mg<sup>2+</sup> and Ti<sup>4+</sup> ions.

Four-point probe method is carried out on the electrodes of all samples and the results are shown in Fig. 5 [52]. It can be obviously found that all modified samples demonstrate apparently improved electrical conductivity due to the introduction of Mg<sup>2+</sup> or Ti<sup>4+</sup>, or both. But compared with other modified samples, Mg-doped sample exhibits the highest electrical conductivity, which indicates the apparent improvement on electrical conduction ability caused by Mg-doping. In particular, although Ti-doping cannot bring as much improvement as Mg-doping dose, the co-doped sample exhibits similar electrical conductivity to Mg-doped sample. This result suggests that Mg<sup>2+</sup> as dopants effectively enhance the electrical conduction ability of LiCoO<sub>2</sub>, and such visible enhancement is also brought by co-doping

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