

# Improvement of electrochemical stability of $\text{LiCoO}_2$ cathode by a nano-crystalline coating

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## Abstract

A nano-crystalline MgO coating was formed on the surface of  $\text{LiCoO}_2$  particle via a sol-gel method. MgO coating can improve the cycling stability of  $\text{LiCoO}_2$  significantly. After the 40th cycle a discharge capacity of more than 120 mAh/g was remained for 1 mol% MgO-coated  $\text{LiCoO}_2$ , while only 13 mAh/g for pristine  $\text{LiCoO}_2$  when both charged up to 4.7 V. During heat treatment and charge/discharge process,  $\text{Mg}^{2+}$  in coatings will diffuse into  $\text{LiO}_2$ -layers of  $\text{LiCoO}_2$ , which does not cause any detectable shift in X-ray diffractometer (XRD) peak positions, but does impact the XRD peak intensity due to the aberrance of (003) plane.  $\text{Mg}^{2+}$  ions existing in  $\text{LiO}_2$ -layers will stabilize the lattice structure of  $\text{LiCoO}_2$ , hence improve the cycling performance of  $\text{LiCoO}_2$  cathode. More MgO coating on  $\text{LiCoO}_2$  is detrimental to the electrochemical properties of  $\text{LiCoO}_2$  cathode, probably due to the electrochemical inactivity of MgO particles.

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## 1. Introduction

There is a pressing need for high-specific power, high-specific energy and high-safety battery systems suitable for use in portable electric device and power tools, electric vehicles and spacecraft. Due to their excellent properties such as high voltage, high energy density, and durable cycle charge characteristics, lithium-ion batteries have so far attracted most attentions. Currently, lithium-ion batteries have captured a large share of the rechargeable battery market.

The active cathode material of a secondary lithium battery is a host compound into/from which lithium ions can be reversibly inserted/extracted over a large composition range [1]. Transition metal oxides, such as  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$  and  $\text{LiMn}_2\text{O}_4$  [2–7], have found application as positive electrode materials for high power application through their high potentials (ca. 4 V versus Li). In recent years, significant effort has been made to optimize the electrochemical properties of these three materials, besides the identification of completely new materials suitable for the use as positive electrodes in rechargeable lithium batteries.

$\text{LiCoO}_2$ , with  $R\bar{3}m$   $\alpha\text{-NaFeO}_2$  layered structure, is considered the most stable cathode of these three materials when the  $\text{Li}/\text{Li}_{1-x}\text{CoO}_2$  cell is cycled within limited composition range ( $0 < x < 0.5$ ), and thus being used widely in various applications. However, its electrochemical properties degrade rapidly when more Li-ion is extracted from the host lattice in the overcharge occasion. Many works have been reported to improve the cycling stability of  $\text{LiCoO}_2$  by doping or coating some inactive material into/on its particles [8–12]. Al, Mg, Sn and their corresponding oxides are generally considered the promising candidates for improving the cycling performance of  $\text{LiCoO}_2$  cathode [10–16]. However, different results have been observed when incorporating Mg into  $\text{LiCoO}_2$  lattice [10,17]. Mg dopants were reported to have no effect on the capacity retention of  $\text{LiCoO}_2$ , except the reinforcement in electronic conductivity due to the appearance of  $\text{Co}^{4+}$  charge compensators [10]. While other works showed the significant improvement of Mg-doping on the cycling stability of  $\text{LiCoO}_2$  that is used as the cathode in secondary lithium-ion battery [17]. The effect of Mg-doping on the capacity retention of  $\text{LiCoO}_2$  is, virtually, associated with the Mg distribution between the layers of  $\text{LiCoO}_2$  lattice structure [17]. The replacement of Co by Mg in  $\text{CoO}_2$ -layers has a positive effect on the

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capacity retention; however, Mg dopants in  $\text{LiO}_2$ -layers do not influence the cycling stability. In respect of surface modification, MgO-coated  $\text{LiCoO}_2$  exhibits obviously improved electrochemical stability even though charged up to 4.7 V [16,17]. MgO coated on the particle surface of  $\text{LiCoO}_2$  appears to have no impact on the lattice parameters of pristine  $\text{LiCoO}_2$ , no changes being detectable in X-ray diffraction (XRD) patterns before and after coating, although small amounts of  $\text{Mg}^{2+}$  ions were believed to have diffused into the lattice of  $\text{LiCoO}_2$ . Further, to the best of our knowledge, there is limited report concerning the effect of coating quantity on the electrochemical properties of  $\text{LiCoO}_2$ .

In this paper, nano-crystalline MgO was coated on the particle surface of commercial  $\text{LiCoO}_2$  by a sol-gel method. The changes in lattice structure of  $\text{LiCoO}_2$  before and after coating was observed in the XRD patterns. The electrochemical stability of  $\text{LiCoO}_2$  was remarkably improved by a surface coating of nano-crystalline MgO. The effect of coating amount of MgO on the cycling stability of  $\text{LiCoO}_2$  is also examined.

## 2. Experimental

Commercial  $\text{LiCoO}_2$  with particle size ranging from 8 to 10  $\mu\text{m}$  was used as pristine material, and  $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  was used as coating reagent.  $\text{LiCoO}_2$  powder was initially dispersed into ethanol containing the desired amount of  $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  by using a blender and followed by an ultrasonic stirring for 10 min, then dried with a rotary evaporator under reflux condition. The residue as-obtained was heat-treated at 650 °C in air for 4 h to decompose the organic radicle and thus create a MgO coating layer on the particle surface of  $\text{LiCoO}_2$ . The coating amount of MgO on  $\text{LiCoO}_2$  powders was 1, 2 and 3.8 mol%, respectively.

The X-ray phase analysis was performed on the  $\text{LiCoO}_2$  powders before and after coating using a D/MAX-RB X-ray diffractometer with Ni-filtered  $\text{Cu K}\alpha$  radiation. The surface morphology of  $\text{LiCoO}_2$  powder coated and uncoated with MgO was observed by scanning electron microscope (SEM, S250-II).

To prepare the electrodes for the electrochemical characterization, the MgO-coated  $\text{LiCoO}_2$  powders were mixed with carbon black and PVDF in the weight ratio of 85:10:5. The mixture was rolled into a thin sheet of uniform thickness from which 6 mm diameter pellets were cut. Electrochemical cells were assembled in Ar-filled glove box with metallic lithium foil as the counter electrode, Cellgard 2300 as the separator and 1M  $\text{LiPF}_6$  (Merck, battery grade) in ethyl carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume ratio) as the electrolyte. The cell was left aged for at least 6 h after assembly before galvanostatically cycled between 3.3 V and various charge cutoff voltages on LAND cyler (Wuhan, China).

## 3. Results and discussion

$\text{LiCoO}_2$  is the best commercial cathode material so far for secondary lithium-ion battery owing to its excellent electrochemical properties.  $\text{LiCoO}_2$  displays an ordered rock-salt structure, in which Co and Li separately occupy the two octahedral positions in the (1 1 1) cubic planes (3a and 3b sites), thus leading to the formation of distinct  $\text{LiO}_2$  and  $\text{CoO}_2$ -layers. Li-ions can be intercalated/deintercalated into/from the  $\text{CoO}_2$  layer reversibly under electrochemical driving force in a limited extent [4]. When the cell is over-charged more Li-ions will be extracted, which will cause the reordering of O atoms in the lattice structures and thus resulting in the destruction of the layered structure of  $\text{LiCoO}_2$ . Consequently, the cycle stability is deteriorated. Therefore, an effective way to improve the rechargeability of the cathode material is to make its structure more flexible. It has been reported [16,18] that the degradation of  $\text{LiCoO}_2$  cathode material is related to its surface defects or surface chemistry. Therefore, coating the surface of  $\text{LiCoO}_2$  by an appropriate substance is probably a good method to improve its electrochemical properties by modifying its surface structural characteristics. Fig. 1 presents the variation of specific discharge capacity with the number of cycles for  $\text{LiCoO}_2$  coated with 1, 2 and 3.8 mol% MgO, respectively. As a comparison, the discharge capacity of pristine  $\text{LiCoO}_2$  is also given here. The cutoff voltage for the first 10 cycles is from 3.3 to 4.25 V, the second 10 cycles is from 3.3 to 4.5 V and the third 10 cycles is from 3.3 to 4.7 V. When cycled at 3.3–4.25 V, MgO-coated  $\text{LiCoO}_2$  shows a relatively lower specific discharge capacity compared with that of pristine  $\text{LiCoO}_2$ . With the increase of the coating amount of MgO, the discharge capacity of MgO-coated  $\text{LiCoO}_2$  decreases. Nevertheless, the discharge capacity of  $\text{LiCoO}_2$  coated with 1 mol% MgO is very close to that of pristine  $\text{LiCoO}_2$  except the initial capacity. The initial discharge capacity of 1 mol% MgO-coated sample is apparently lower

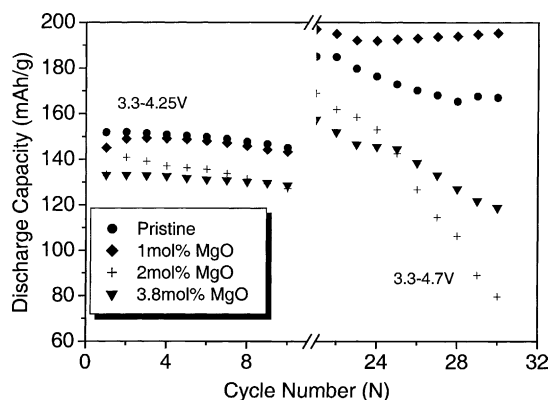


Fig. 1. Plots of specific discharge capacities of pristine  $\text{LiCoO}_2$  and  $\text{LiCoO}_2$  coated with 1, 2 and 3.8 mol% MgO, respectively, as a function of the cycle number for the first 30 cycles. The cutoff voltage for the first 10 cycles is 3.3–4.25 V, the second 10 cycles 3.3–4.5 V and the third 10 cycles 3.3–4.7 V.

than that of the pristine  $\text{LiCoO}_2$ , and also somewhat lower than itself on the second cycle, which can be attributed to the insulation of MgO on the surface to both the electrons and the  $\text{Li}^+$  ions [16]. From the second cycle on, the difference in discharge capacity between the pristine  $\text{LiCoO}_2$  and 1 mol% MgO-coated  $\text{LiCoO}_2$  becomes unobvious and negligible. This is deemed to be due to the migration of  $\text{Mg}^{2+}$  ions from the MgO shell into the core of the underlying  $\text{LiCoO}_2$  during the charge and discharge cycling. More MgO coating may lower the discharge capacity of  $\text{LiCoO}_2$  cathode, most likely resulting from the electrochemical inactivity of MgO and the lower solid solution concentration of MgO in  $\text{LiCoO}_2$  lattice. The more accumulation of MgO on the surface of  $\text{LiCoO}_2$  particle will hinder the diffusion of  $\text{Li}^+$  ions into/from  $\text{LiCoO}_2$  cathode.

With increasing the charge cutoff voltage, the effect of MgO coating on the electrochemical properties of  $\text{LiCoO}_2$  becomes more remarkable, as illustrated in Fig. 1. The discharge capacity of  $\text{LiCoO}_2$  coated with 1 mol% MgO when charged/discharged between 3.3 and 4.7 V is more than 190 mAh/g, higher than that of pristine  $\text{LiCoO}_2$ . Furthermore, a more stable cycling performance is obtained for 1 mol% MgO-coated  $\text{LiCoO}_2$  compared to that of pristine  $\text{LiCoO}_2$ , as evidenced in Fig. 2. Excessive MgO on  $\text{LiCoO}_2$  particle is apparently unfavorable to the improvement of cycle-reversibility of  $\text{LiCoO}_2$  cathode. It is worthwhile to note that the electrochemical performance of the sample coated with 2 mol% MgO is even worse than that of the sample coated with 3.8 mol% MgO. The reason is not yet clear so far.

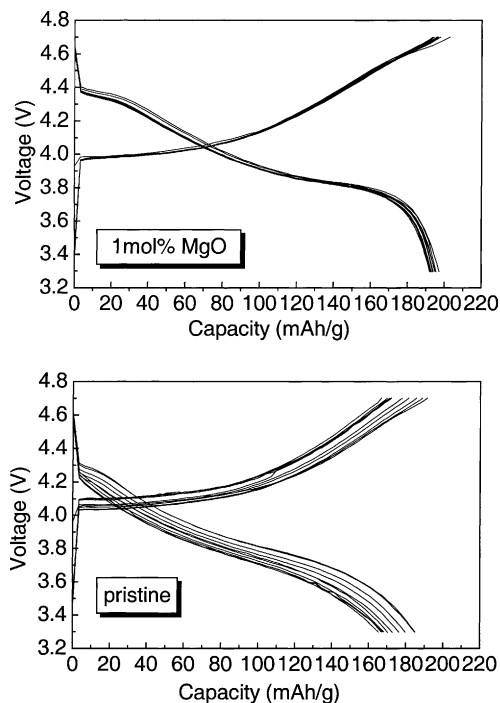


Fig. 2. Charge and discharge curves of pristine  $\text{LiCoO}_2$  and 1 mol% MgO-coated  $\text{LiCoO}_2$  cycled between 3.3 and 4.7 V during 20th–30th cycles.

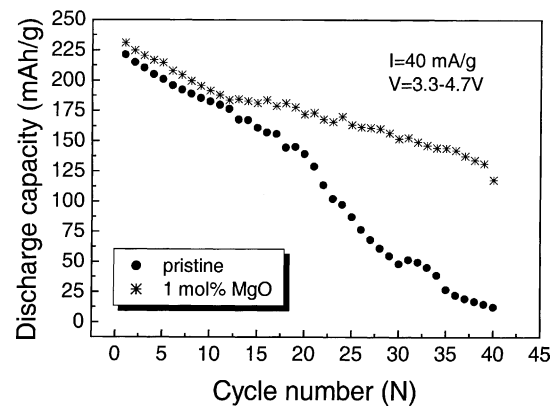


Fig. 3. Cycling stability curves of pristine  $\text{LiCoO}_2$  and 1 mol% MgO-coated  $\text{LiCoO}_2$ . The cells were charged and discharged at a constant current of 40 mA/g of the active material in the potential ranges of 3.3–4.7 V.

To give further evidence for the improvement of MgO coating on the cycling stability of  $\text{LiCoO}_2$ , 1 mol% MgO-coated  $\text{LiCoO}_2$  and pristine  $\text{LiCoO}_2$  were cycled between 3.3 and 4.7 V from the beginning. Fig. 3 shows the discharge capacities of the pristine  $\text{LiCoO}_2$  and 1 mol% MgO-coated  $\text{LiCoO}_2$  as a function of the cycle number. One can see that the cycling stability of  $\text{LiCoO}_2$  is improved significantly by MgO coating when it was charged to a high upper limiting voltage. After the 40th cycle a discharge capacity of more than 120 mAh/g still remained for 1 mol% MgO-coated  $\text{LiCoO}_2$ , but only 13 mAh/g for pristine  $\text{LiCoO}_2$ . It is interesting to note that during the first 12 cycles the discharge capacities of pristine  $\text{LiCoO}_2$  and 1 mol% MgO-coated  $\text{LiCoO}_2$  exhibit the similar values, and the decreases in the capacity also show the nearly same tendency. Thereafter, the pristine  $\text{LiCoO}_2$  degrades very rapidly with cycling, while the MgO-coated  $\text{LiCoO}_2$  fades tardily. This can be ascribed to the stabilizing effect of MgO coating on the surface structure of  $\text{LiCoO}_2$  particles.

The suggested reasons for the capacity fade of pristine  $\text{LiCoO}_2$  are the cobalt dissolution reactions and/or the mechanical failure of the electrode material when the cell is charged above 4.2 V [15,18–20]. Cumulative stresses inside the particles induce their fracture. Coating a film on the surface of  $\text{LiCoO}_2$  particles may prevent the direct contact of the active core material with the acidic electrolyte and further avoid the dissolution of the  $\text{Co}^{4+}$  ions [15,16]. In our experiments, this seems not to be the main reason for the improvement of cycling stability as the discharge capacity of the initial 12 cycles hardly changes for the two kinds of  $\text{LiCoO}_2$ . What contributes to the cycling stability of MgO-coated  $\text{LiCoO}_2$  is considered to be the structure stabilizing effect of MgO. A transmission electron microscopy study by Gabrisch et al. [21] indicated that the layered structure of  $\text{LiCoO}_2$  would partially transform to a cubic spinel structure during cycling, especially on the surface of particles. They suggested that this spinel phase formation could be responsible in part for the irreversible capacity

fade. With respect to our experiments, MgO on the surface of LiCoO<sub>2</sub> particle will be activated during cycling owing to its nano-size and its high specific surface area (as described below). The activated Mg<sup>2+</sup> ions will easily diffuse into the interslab space (LiO<sub>2</sub> layer) of LiCoO<sub>2</sub> and take the sites of Li<sup>+</sup> ions, thus stabilize the structure of the active material. More Mg<sup>2+</sup> ions may migrate into the lattice of LiCoO<sub>2</sub> as the cycle continues and the structure of LiCoO<sub>2</sub> thus being gradually stabilized. The phase transformation on the surface of LiCoO<sub>2</sub> particle from layered structure to spinel structure will be suppressed. As a result, the cycling performance of LiCoO<sub>2</sub> is improved progressively.

This claim can be confirmed by the comparison of Fig. 1 with Fig. 3. The cycle-reversibility of 1 mol% MgO coated LiCoO<sub>2</sub> during the first 10 cycles is even worse when charged up to 4.7 V directly (Fig. 3), compared to that of the third 10 cycles when charged to 4.7 V stepwise (Fig. 1). This can be elucidated by the kinetic diffusion of Mg<sup>2+</sup> ions into the lattice of LiCoO<sub>2</sub>. For the sample charged to 4.7 V stepwise, Mg<sup>2+</sup> ions will diffuse into the LiO<sub>2</sub> layers of LiCoO<sub>2</sub> particles gradually during the first (charged to 4.25 V) and second (charged to 4.5 V) 10 cycles before charged to 4.7 V, as a result of which, the surface structure of LiCoO<sub>2</sub> particles is stabilized progressively upon the cycling on. Consequently, a good cycle-reversibility during the third 10 cycles for the sample is expected even being charged up to 4.7 V. However, for the sample charged directly up to 4.7 V from the beginning of charge–discharge cycling, Mg<sup>2+</sup> ions can not migrate into lattice of underlying LiCoO<sub>2</sub> immediately and sufficiently during the first several cycles due to the kinetic reasons of diffusion. Therefore, the surface structure of LiCoO<sub>2</sub> particle cannot be stabilized thoroughly at the beginning of cycling, thus the discharge capacity exhibits a relatively fast degradation. With cycling on, more Mg<sup>2+</sup> is incorporated into the lattice of LiCoO<sub>2</sub>, the surface structure of LiCoO<sub>2</sub> particles being stabilized and the cycle-reversibility also, thereby, being improved after the first 12 cycles, as evidenced in Fig. 3.

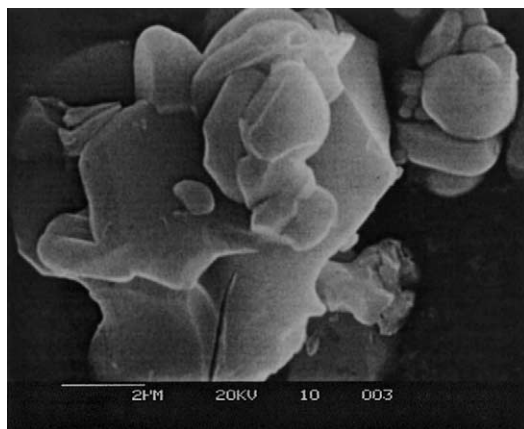


Fig. 4. Morphology of pristine LiCoO<sub>2</sub> observed under SEM.

Figs. 4 and 5 show the morphologies of pristine LiCoO<sub>2</sub> and MgO-coated LiCoO<sub>2</sub> particles. A smooth and clean surface was observed on pristine LiCoO<sub>2</sub> particles, while, lots of nano-sized MgO beads (have been identified by EDAX, not shown here) appeared on the surface of MgO-coated LiCoO<sub>2</sub> particles. With the coating amount of MgO increasing, the distribution of the small beads on the surface of LiCoO<sub>2</sub> particle tends denser, whereas, the size of MgO beads keeps constant. The surface free energy of these MgO beads is very high due to its nanometer size; hence they quite easily migrate into the lattice of LiCoO<sub>2</sub> during the heat treatment of coating preparation and the cycling process, and thus resulting in the stabilization of layered LiCoO<sub>2</sub>.

The X-ray diffraction patterns of pristine LiCoO<sub>2</sub> and MgO-coated LiCoO<sub>2</sub> are compared in Fig. 6. The patterns contain all the major diffraction peaks for LiCoO<sub>2</sub>. There is almost no apparent change in XRD profiles between pristine LiCoO<sub>2</sub> and 1 mol% MgO-coated LiCoO<sub>2</sub>, no peaks related to MgO detectable in XRD pattern of 1 mol% MgO-coated LiCoO<sub>2</sub>, which is consistent with the results reported in

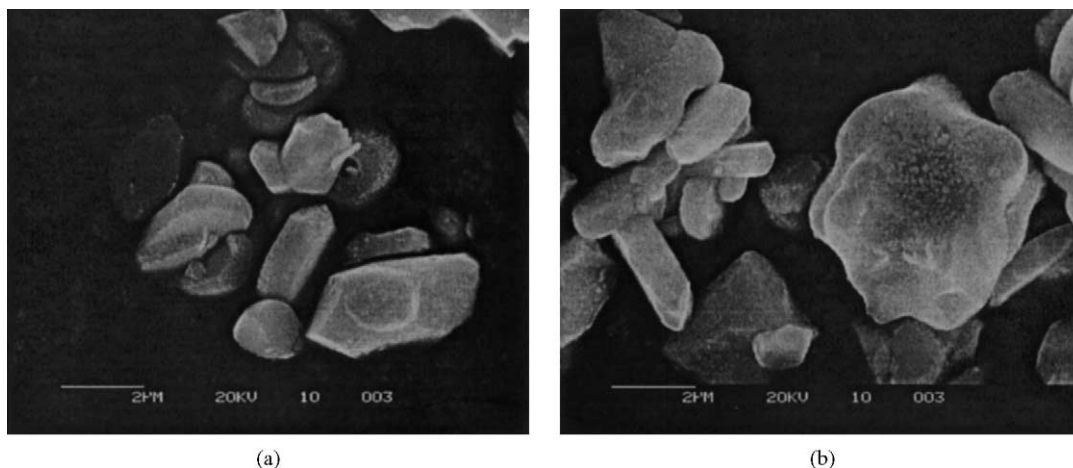


Fig. 5. SEM photographs of LiCoO<sub>2</sub> coated with 1 mol% (a) and 3.8 mol% (b) MgO.



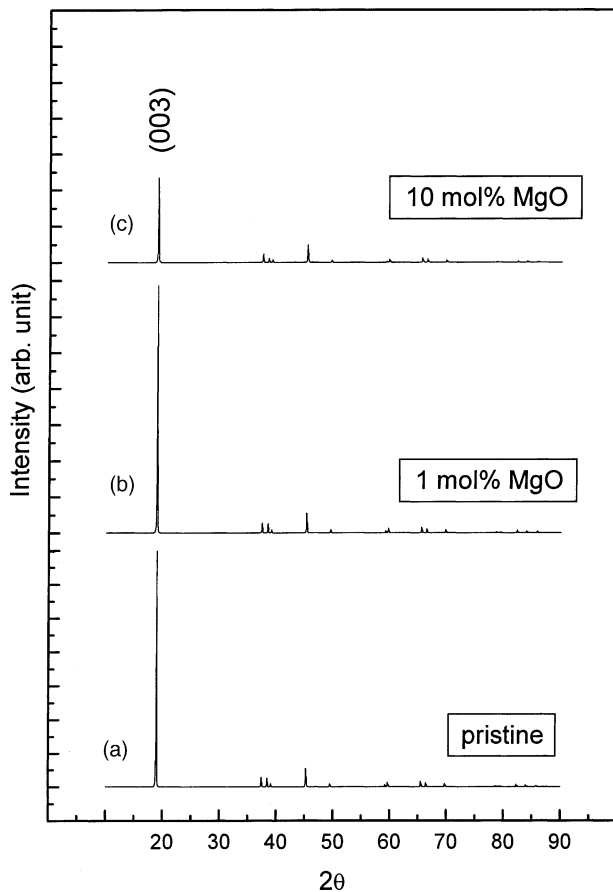


Fig. 6. XRD patterns of pristine LiCoO<sub>2</sub> (a) and LiCoO<sub>2</sub> coated with 1 mol% (b) and 10 mol% (c) MgO, respectively.

literatures [15,17]. There is every possibility that the amount of MgO coated on the surface of LiCoO<sub>2</sub> goes beyond the measurement precision of XRD. In order to get circumstantial evidence on the identity of diffusion of Mg<sup>2+</sup> ions into the lattice of layered LiCoO<sub>2</sub> and to gain an insight into if MgO reacts with underlying LiCoO<sub>2</sub>, LiCoO<sub>2</sub> was coated with 10 mol% MgO, followed by the identical heat treatment the previous coating samples have ever taken. Its XRD pattern is shown in Fig. 6c. It is apparent that although no deviation is detected in characteristic peak positions between pristine LiCoO<sub>2</sub> and 10 mol% MgO-coated LiCoO<sub>2</sub>, a remarkable change in (003) peak intensity has exhibited. The (003) peak of 10 mol% MgO-coated LiCoO<sub>2</sub> tends to much weak compared to that of pristine LiCoO<sub>2</sub>. Furthermore, some small diffraction peaks due to MgO were identified in the enlarged XRD profiles of 10 mol% MgO-coated LiCoO<sub>2</sub> powder, but no other impurity peaks emerged, as evidenced in Fig. 7. This indicates that no chemical reaction occurs between LiCoO<sub>2</sub> and MgO.

Peak intensity in XRD patterns depends on many factors. The multiplicity factor is one of the important elements that affect the intensity of power line. In powder diffraction all net planes with an equal value of  $1/d_{hkl}$  contribute to the same powder line. The number of contributing reflec-

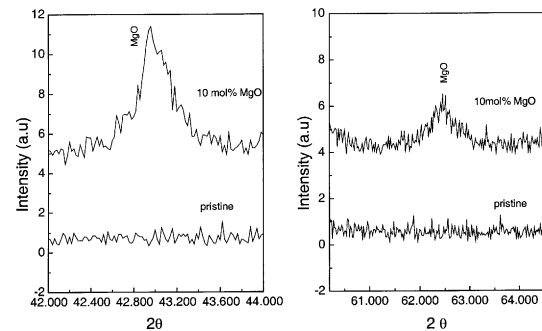


Fig. 7. Comparison of XRD patterns in some extents for pristine LiCoO<sub>2</sub> and LiCoO<sub>2</sub> coated with 10 mol% MgO, indicating the existence of MgO on particle surface of LiCoO<sub>2</sub>.

tions is determined by the crystal system and the Miller indices  $hkl$  of the reflecting net planes [22]. During the heat treatment of MgO-coated LiCoO<sub>2</sub>, Mg<sup>2+</sup> ions quite likely diffuse into LiO<sub>2</sub>-layer due to the similar ionic radius of Mg<sup>2+</sup> (0.72 Å) with Li<sup>+</sup> (0.76 Å) and the nanometer size of MgO coated on the surface of LiCoO<sub>2</sub> particle, as illustrated in Fig. 5. The difference in electrovalence between Mg<sup>2+</sup> and Li<sup>+</sup> will yield some aberrance in LiO<sub>2</sub> layer and thus lower the ordering of LiO<sub>2</sub> layer, which is assigned to be (003) plane [23], when compared to pristine LiCoO<sub>2</sub> crystalline. The tiny aberrance in LiO<sub>2</sub> layer may not impose detectable effect on the lattice parameters of LiCoO<sub>2</sub> (no detectable peak position change), whereas it is considered to be responsible for the change in XRD peak intensity because the ordering level will affect the multiplicity factor in XRD detection. It is reasonable to demonstrate that with the coating amount of MgO on LiCoO<sub>2</sub> particle increasing, the Mg<sup>2+</sup> ions migrated into LiCoO<sub>2</sub> lattice increase, thus the impact of Mg<sup>2+</sup> ions on the peak intensity of XRD profile becomes more significant. Thereby, 1 mol% MgO coating corresponds to no detectable change in XRD patterns, while 10 mol% MgO coating corresponds to a significant decrease in peak intensity of (003) plane of LiCoO<sub>2</sub>. The migration of Mg<sup>2+</sup> into LiO<sub>2</sub>-layer will increase the attraction power between CoO<sub>2</sub> slabs owing to its high electrovalence, thus stabilize the structure of LiCoO<sub>2</sub>, and eventually improve the cycling stability of LiCoO<sub>2</sub> especially charged to a high voltage.

However, when more Mg<sup>2+</sup> ions migrate into the LiO<sub>2</sub> layers as increasing the coating quantity of MgO, the lattice structure, especially the LiO<sub>2</sub> layer structure, may be severely distorted as evidenced in the XRD results of LiCoO<sub>2</sub> powders coated with different amounts of MgO. The aberrance of lattice structure tends to more significant for delithiated MgO-coated LiCoO<sub>2</sub> when charged up to 4.7 V. This excessive aberrance is considered to be harmful to the structure stability (corresponding to the cycle-reversibility) although a certain amount of Mg<sup>2+</sup> can stabilize the lattice structure and so improve the cycle-reversibility of LiCoO<sub>2</sub>, as indicated in Fig. 1.

#### 4. Conclusion

MgO coating can improve the cycling stability of LiCoO<sub>2</sub> remarkably. During heat treatment and charge/discharge process, Mg<sup>2+</sup> ions in coatings will diffuse into LiO<sub>2</sub>-layers of LiCoO<sub>2</sub>, which does not cause any detectable shift in peak positions of XRD profiles, but does impact the XRD peak intensity due to the aberrance of (003) plane. Mg<sup>2+</sup> ions existing in LiO<sub>2</sub>-layers will stabilize the structure of LiCoO<sub>2</sub>, hence improving the cycling performance of LiCoO<sub>2</sub> cathode. A 1 mol% MgO on the LiCoO<sub>2</sub> particle surface can improve its cycling stability effectively, especially under the overcharged conditions. More MgO coating on LiCoO<sub>2</sub>, however, is not only unfavorable for the improvement of discharge capacity but also very detrimental to the cycling stability of LiCoO<sub>2</sub> cathode, probably due to the electrochemical inactivity of MgO particles.

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