

Short communication

Performance improvement of LiCoO_2 by molten salt surface modificationYing Bai, Hongjun Shi, Zhaoxiang Wang^{*}, Liquan Chen*Laboratory for Solid State Ionics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China*

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Abstract

The surface of commercial LiCoO_2 was modified by molten salt method. The structure and electrochemical and thermal performances of the MgCl_2 -treated LiCoO_2 were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), X-ray photoelectron spectroscopy and galvanostatic cycling. It is found that surface modification improves the structural and thermal stability as well as the rate performance of LiCoO_2 . These improvements were attributed to the formation of homogeneous solid solution on the surface of the LiCoO_2 particle.

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Keywords: Surface modification; Molten salt; Performance improvement; Lithium ion batteries**1. Introduction**

LiCoO_2 is the most commercialized cathode material for lithium ion batteries because of its favorable features such as high energy density, low self-discharge rate and excellent cycle life. However, its available specific capacity remains only *ca.* 140 mAh g^{-1} in a practical battery, only roughly half of its theoretical capacity (274 mAh g^{-1}). Higher capacity can be obtained by charging the material to higher potentials ($>4.2 \text{ V}$ *versus* Li^+/Li). Nevertheless, this will lead to severe structural deterioration due to irreversible phase transitions [1] and obvious electrolyte decomposition because of the formation of strong oxidizing oxygen at deep delithiation states [2].

Elemental substitution has proved an effective method to improve the structural stability of the cathode materials. However, the improvement of the structural stability was realized at the expense of specific capacity [3–8].

Surface chemistry is of great importance to the performance of the electrode [9]. Recent studies show that coating the LiCoO_2 particles with oxides such as Al_2O_3 [10,11], MgO [12], ZrO_2 [13], TiO_2 [13], SnO_2 [14], CeO_2 [15], ZnO [16], P_2O_5 [17] and

SiO_2 [18] helps to suppress capacity fading at deep charge states ($>4.2 \text{ V}$). Many researchers try every effort to coat the LiCoO_2 surface as compactly as possible because it was believed that the coating layer helps to avoid the direct contact between the electrolyte and the active cathode material and, therefore, the reaction between them. Our previous studies [19,20], on the other hand, indicated that even compact coating cannot prevent the corrosion of LiCoO_2 by the acidic electrolyte. Surface coating increases the acidity of the electrolyte by forming Lewis acids via interaction with the electrolyte rather than scavenges the acidic species in the electrolyte. Previous studies also indicated that the solid solution formed near the surface of LiCoO_2 during electrochemical cycling for MgO -coated LiCoO_2 and during LiAlO_2 -coating on LiMn_2O_4 [21] improved the structural stability of the cathode materials.

Molten salt method is one of the simplest means to prepare pure and stoichiometric multi-component oxide powders. The molten salts, characteristic of low melting point but high decomposition temperature, work as solvent or reacting species or sometimes both [22,23]. This method has found applications in synthesis of electrode materials [24–27] at rather low temperatures and in a short time because the diffusion of the ions is much quicker in the molten salt than in the solid. We believe that this method can also be used to modify the surface chemistry of LiCoO_2 by controlling the temperature, time and other

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Table 1
Molar proportions of the chemicals in molten salt process

	MgCl ₂ ·6H ₂ O	LiCoO ₂	LiOH·H ₂ O
I	5	85	10
II	10	75	15
III	15	65	20
IV	20	55	25

conditions of the molten salt reaction. In this work, we improve the performances of commercial LiCoO₂ by bathing it in MgCl₂ molten salt to form a homogeneous modification layer.

2. Experimental

MgCl₂·6H₂O (99.0%, Beijing Shuanghuan Chemical Reagent Company), LiOH·H₂O (98.0%, Guangdong Longxi Chemicals) and commercial LiCoO₂ (Nippon Chemicals, battery grade; ~5 μm in diameter) were carefully mixed in a mortar at the required ratios (Table 1). LiOH·H₂O was used here to increase the Li content in the molten salt so as to compensate the lost lithium due to concentration difference in and out of the LiCoO₂ particles. The mixture was transferred to a muffle furnace when the temperature of the latter reached 750 °C. It was taken out after 2 h and cooled down outside the furnace to room temperature. The mixture was then washed with distilled water and filtered three times. Finally, the precipitates were heated

at 100 °C for more than 12 h. Surface-modified LiCoO₂ was thus obtained. For comparison, the commercial LiCoO₂ was also annealed in the same way as the above samples.

X-ray diffraction (XRD) was carried out on a Holland X'Pert Pro MPD X-ray diffractometer equipped with a monochromatized Cu Kα radiation (λ = 1.5418 Å). The morphology of the samples was observed on a Hitachi S-4000 scanning electron microscope (SEM). Inductively coupled plasma (ICP) was conducted on ICP-8000 (Shimadzu Co.) to determine the atomic ratio of the samples.

Descriptions of the electrode preparation and button-type test cell assembly can be found in Ref. [19]. The cells were charged and discharged on a LAND BT1-10 battery tester between 2.5 V *versus* Li⁺/Li and various charge cut-off potentials. The ac impedance measurements were performed using an IM6e (Zahner Electric) impedance analyzer over a frequency range from 100 kHz to 5 mHz.

Differential scanning calorimetry (DSC) analysis was carried out on NETSCH STA 449 C in air by sealing the charged cathode sheet in an Al crucible in dry Ar and heated from 25 to 500 °C at a rate of 5 °C min^{−1}.

3. Results and discussion

Fig. 1 illustrates the morphologies of commercial and molten salt-treated LiCoO₂. It is seen that the surface of the 5% (not

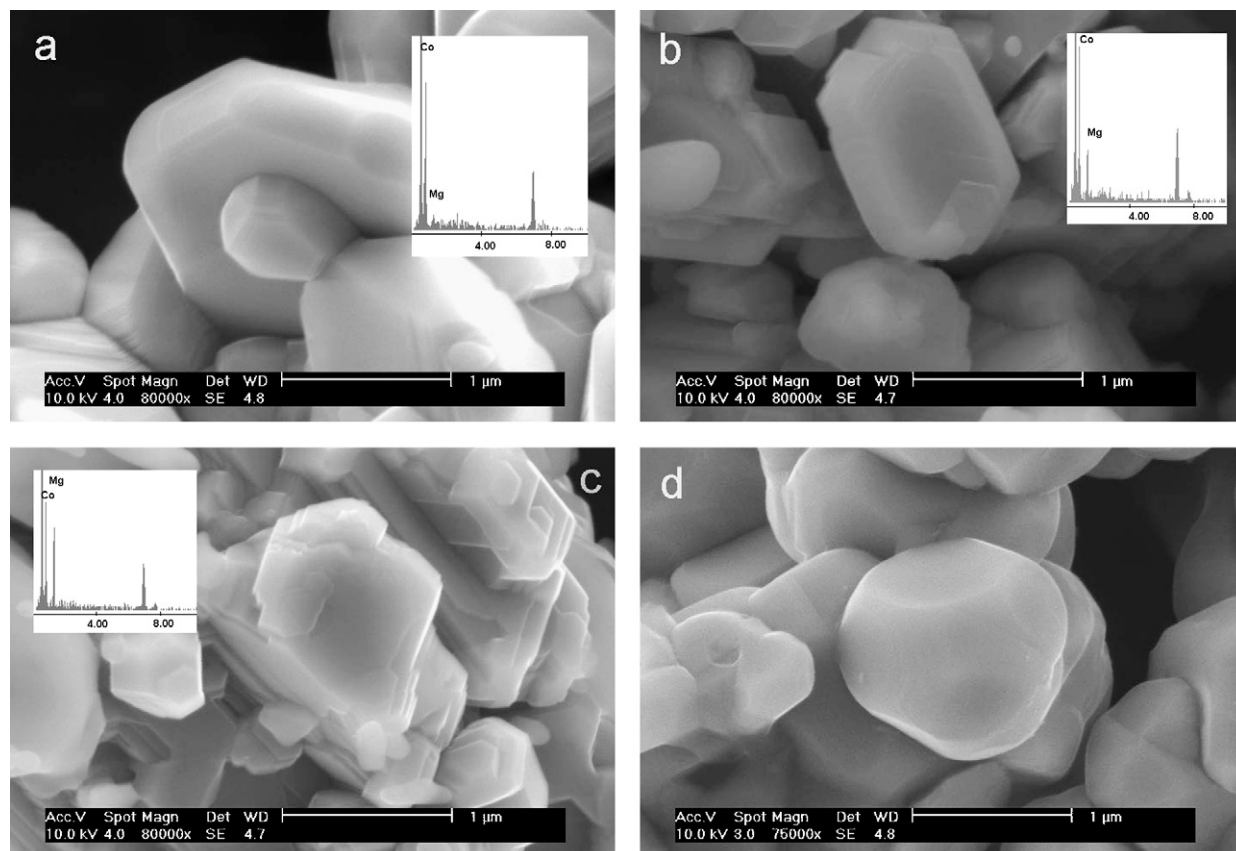


Fig. 1. Surface morphology of: (a) 10%, (b) 15%, (c) 20% MgCl₂ treated and (d) commercial LiCoO₂ (the insets are the corresponding EDAX patterns of the surface-modified LiCoO₂).

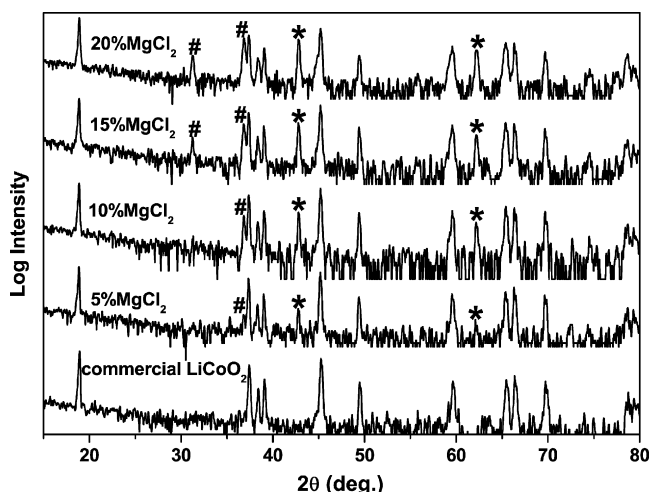


Fig. 2. Logarithm-scaled XRD patterns of LiCoO₂ before and after molten salt process at 750 °C for 2 h (*MgO, #Co₃O₄).

shown) and 10% MgCl₂-treated LiCoO₂ is very clean and smooth, without any radicals, very similar to that of commercial LiCoO₂ annealed at 750 °C. However, the inset EDAX patterns demonstrate the existence of Mg on the LiCoO₂ surface. With increasing content of MgCl₂, the content of Mg increases and the LiCoO₂ surface becomes rough.

Fig. 2 shows the XRD patterns of LiCoO₂ before and after molten salt treatment. Besides hexagonal LiCoO₂, diffraction peaks of MgO and Co₃O₄ are observed after MgCl₂ processing. MgO is believed to be the reaction product between MgCl₂ and LiOH at high temperature while Co₃O₄ derives from LiCoO₂ when some lithium of the latter is lost. Calculation indicates that molten salt treatment does not lead to obvious changes in the lattice parameters of LiCoO₂. This is true even when the content of MgCl₂ increases to 20%. This means that the MgO and Co₃O₄ are formed at or near the surface of the LiCoO₂ particles but the hexagonal structure of bulk LiCoO₂ remains unchanged. More MgO and Co₃O₄ are detected when the content of MgCl₂ increases.

Table 2 shows the atomic ratios of Co, Li and Mg in the surface-modified LiCoO₂. It is clear that the loss of lithium ion is rather severe due to its content difference in and out of the LiCoO₂ particle. More lithium is lost when the MgCl₂ content increases.

It is known that formation of layered LiMO₂-type structure usually results from the size difference between the LiO₆ octahedra and the MO₆ octahedra. Therefore, the large cations preferentially occupy the lithium site if the layered LiMO₂ material is Li-deficient. As the radius of Mg²⁺ (0.072 nm) is very close to that of the Li⁺ (0.076 nm), the Mg²⁺ ions tends to enter

the interslab of LiCoO₂ to occupy the Li sites [28], resulting in the formation of Li–Mg–Co–O solid solution near the surface of LiCoO₂ particle. Clearly dissolution of Li⁺ from LiCoO₂ in the molten salt accelerates the migration of Mg²⁺ into its interslab. Therefore, a thin layer of solid solution is formed at or near the surface of Li-deficient LiCoO₂, though Kweon et al. [29] and Kweon and Park [30] reported that only a small amount of Mg²⁺ can diffuse into the well-crystallized Li_xNi_{1–y}Co_yO₂ and LiSr_{0.002}Ni_{0.9}Co_{0.1}O₂ at 750 °C for 10 h. Because of the controlled reaction time, we believe that only a thin layer of solid solution Li_{1–y}Mg_yCoO₂ is formed near the surface of the LiCoO₂ particles. Therefore, no traces of solid solution are detected with XRD.

Surface-sensitive X-ray photoelectron spectroscopy (XPS) was employed to find out any differences in the electronic structure before and after molten salt treatment to commercial LiCoO₂. However, no obvious changes were observed in the binding energies of Co2p and O1s because the binding energies of Co2p in different cobalt oxides are similar to each other (ref. 780.2 eV in CoO, 779.9 eV in Co₂O₃ and 780.2 eV in Co₃O₄). Comparison of the integrated peaks indicates that the intensity ratio of Li1s *versus* Co3p decreases while the intensity ratio of Mg2p *versus* Co3p increases after molten salt treatment. This can be evidence for the formation of surface solid solution (Li_{1–x}Mg_xCoO₂) on LiCoO₂ (Fig. 3).

The formation of a surface solid solution is expected to improve the performance of LiCoO₂ material. Fig. 4a shows the charge/discharge profiles of the commercial and MgCl₂-treated LiCoO₂. The discharge plateau of commercial LiCoO₂ is rather steep in the first cycle but becomes flat in the subsequent cycles. The capacity retention of these two materials can be seen more clearly in Fig. 4b. The 750 °C annealed commercial LiCoO₂ has an initial discharge capacity of 131 mAh g^{–1}. Its capacity reaches 143 mAh g^{–1} after eight cycles. In the subsequent cycles, however, its capacity quickly degrades. It fades to 110 mAh g^{–1} after 60 cycles, corresponding to a capacity retention of 84%. In contrast, the discharge capacity of

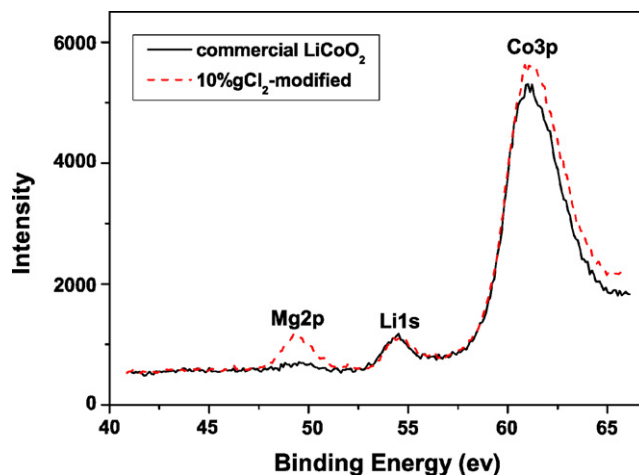


Fig. 3. Comparison of the X-ray photoelectron spectra of Li1s, Mg2p and Co3p on commercial LiCoO₂ simply annealed at 750 °C/2 h in air and bathed in molten MgCl₂ at 750 °C/2 h.

Table 2

Atomic ratios of LiCoO₂ after molten salt processing

MgCl ₂ content (%)	Co	Li	Mg
10	1	0.88	0.13
15	1	0.78	0.22
20	1	0.66	0.35

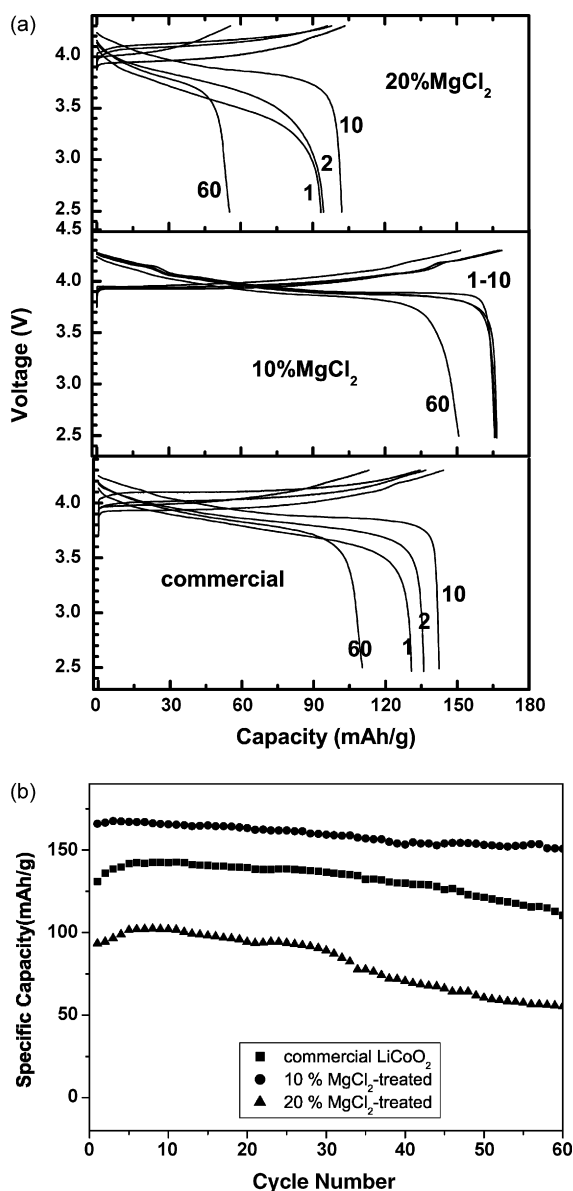


Fig. 4. Charge/discharge profiles: (a) and cycle number dependence of the discharge specific capacity and (b) of commercial LiCoO₂ annealed at 750 °C, 10 and 20% MgCl₂-processed LiCoO₂ cycled between 2.5 and 4.3 V at 0.2 mA.

the 10% MgCl₂-treated LiCoO₂ is high (166 mAh g⁻¹) in the initial cycling. In the subsequent cycles, this capacity further increases, reaching its maximum, 167 mAh g⁻¹, after six cycles. This value keeps fairly stable in the subsequent cycling processes. The capacity fades from 166 mAh g⁻¹ in the 1st cycle to 151 mAh g⁻¹ in the 60th cycle, corresponding to a capacity retention of 91%, indicating the improved structural reversibility of the surface-modified LiCoO₂ at deep delithiation states. However, excess addition of MgCl₂ (20%) decreases the capacity and deteriorates the reversibility of the material.

Usually the exothermic temperature becomes low when the cathode material is charged to a high voltage. This will lead to safety problems when the battery is overcharged or otherwise abused. Fig. 5 compares the DSC traces of commercial (before and after 750 °C/2 h annealing) and 10% MgCl₂-treated

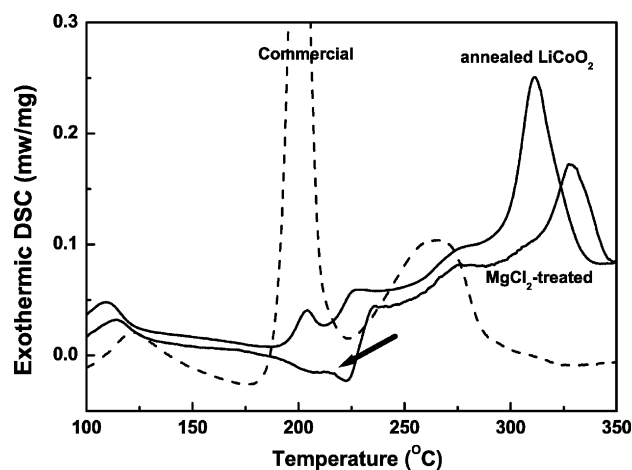


Fig. 5. DSC traces of commercial before (6.6 mg) and after (7.2 mg) 750 °C/2 h processed and 10% MgCl₂-treated LiCoO₂ (5.9 mg) charged to 4.7 V (the arrow is for the exothermic peak of 10% MgCl₂-modified LiCoO₂).

LiCoO₂ charged to 4.7 V. It is seen clearly that after 750 °C/2 h processing, the exothermic reaction temperature of LiCoO₂ charged to 4.7 V is delayed from 194 °C for the annealed commercial LiCoO₂ to 204 °C for the MgCl₂-treated LiCoO₂. In addition, the exothermic amount is sharply reduced. Therefore, 10% MgCl₂ treatment also improves the thermal stability of the material at charged state.

Indeed the rate performance and cycling performance of commercial LiCoO₂ can be enhanced by simple heat treatment because the insulating impurities such as Li₂CO₃ on LiCoO₂ is eliminated during this process, as Chen and Dahn [33] reported. However, the same authors also pointed out that heat treatment alone cannot improve the thermal stability of LiCoO₂. Fig. 6 compares the FTIR spectra of commercial LiCoO₂ before and after heat treatment at 750 °C for 2 h. The FTIR spectra of commercial LiCoO₂ and LiCoO₂ annealed in air at 750 °C for 2 h are almost the same to each other, indicating that surface species on long-term stored commercial LiCoO₂ is very low. The FTIR spectra of commercial MgO and Co₃O₄ are also presented for reference. Clearly MgO and Co₃O₄ are observed on the surface of the MgCl₂-molten salt processed LiCoO₂. That is, the FTIR spectrum of LiCoO₂ annealed in 10% MgCl₂ at 750 °C for 2 h can be regarded as a simple addition of the weighed spectra of MgCl₂, Co₃O₄ and LiCoO₂. No other species/phases are recognizable. Therefore, the improved structural stability (including the improved cycling performance and the thermal stability) should be attributed to the surface modification though we believe that the surface impurities on commercial LiCoO₂ can be removed during the molten salt treatment.

The above results show that molten salt processing is effective in improving the structural stability of LiCoO₂. This improvement is attributed to the pillaring effect of the Mg²⁺ ions in the interslab. Poullierie et al. [28] believed that the existence of Mg²⁺ in LiNiO₂ hinders the collapse of the hexagonal structure at the end of the charge process. Analogously, oxidation of the Co³⁺ ions induces a local collapse of the interslab space in the Li_{1-x}CoO₂ system, making it difficult for the lithium ions to diffuse and re-intercalate. In the Li_{1-x-y}Mg_yCoO₂, however, the

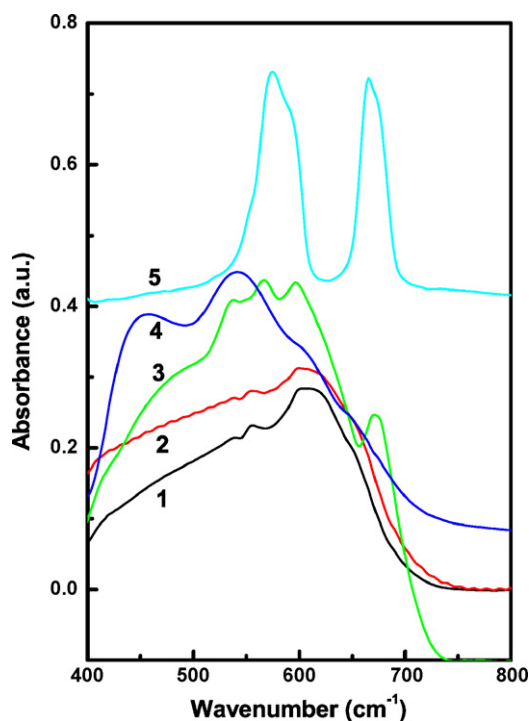


Fig. 6. Comparison of the FTIR spectra of commercial LiCoO_2 (1), LiCoO_2 annealed at 750°C for 2 h in air (2), LiCoO_2 annealed in 10% MgCl_2 at 750°C for 2 h (3), and commercial Co_3O_4 (4) and MgO (5).

electrochemically inactive Mg^{2+} ions work as pillars and suppress the collapse of the CoO_2 interslab. The Mg^{2+} ions in the interslab do not hinder the lithium diffusion because they have similar ionic size as the Li^+ ions. These Mg^{2+} ions have another effect. They suppress the dissolution of the highly oxidized Co^{4+} from the 2D lithium layer to the electrolyte because the $\text{Mg}-\text{O}$ bonding is stronger than the $\text{Co}-\text{O}$ bonding, thus alleviate the electrolyte decomposition due to attack of the oxidizing Co^{4+} ions.

Fig. 4 also demonstrates the remarkable polarization of commercial LiCoO_2 . This polarization explains the low charge/discharge capacity of commercial LiCoO_2 . However, as MgO is electron- and ion-insulating and electrochemically inactive, coating MgO on the surface of LiCoO_2 particle will increase its polarization. This is contradictory to the observed low polarization of surface-modified LiCoO_2 . An explanation is that the Mg^{2+} ions migrate into the lattice of Li -deficient LiCoO_2 during cycling and the thickness of the solid solution near the surface of LiCoO_2 is increased. Tukamoto and West [31] reported that doping Mg^{2+} in LiCoO_2 creates more Co^{4+} ions and enhances the conductivity of LiCoO_2 as well as its structural stability. Meanwhile, Li^+ vacancies are generated to balance the excess covalence, greatly enhancing the conductivity of LiCoO_2 and resulting in the decrease of polarization of the system, beneficial for the Li^+ transportation [31].

Fig. 7 exhibits the rate performance of commercial and 10% MgCl_2 -treated LiCoO_2 at 25°C . The cells are charged galvanostatically to 4.5 V at a current of 0.1 mA but discharged to 2.5 V at different current densities. It is seen that the capacity of commercial LiCoO_2 decreases sharply with increasing current density.

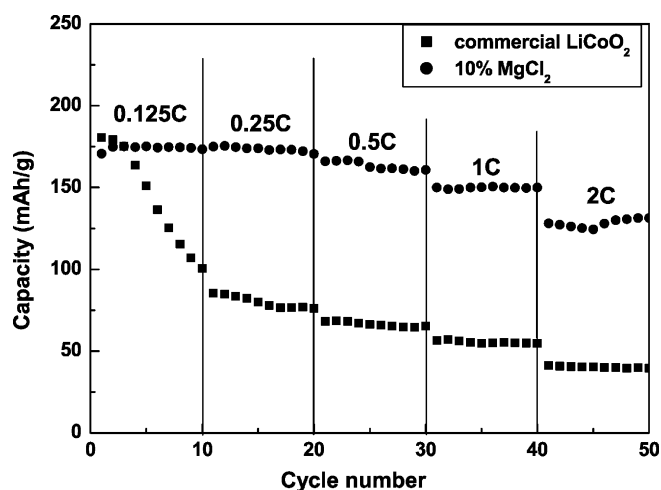


Fig. 7. Comparison of the rate performances of commercial and 10% MgCl_2 -treated LiCoO_2 at different current densities ($1\text{C} = 190\text{ mAh g}^{-1}$).

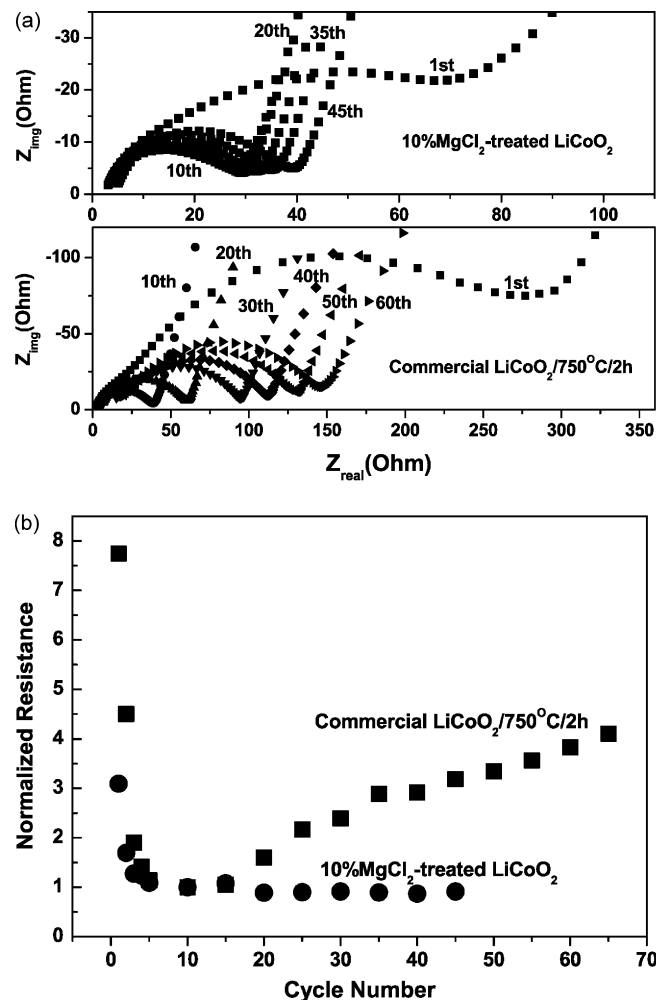


Fig. 8. Comparison of the dependence of: (a) Nyquist plots and (b) the normalized impedance of commercial and 10% MgCl_2 -treated LiCoO_2 with cycling numbers (the unexpectedly large impedance of the first cycle of commercial LiCoO_2 electrode arises from fitting error because the semicircles of the first cycle is rather irregular).

On the contrary, the capacity decrease of the 10% MgCl_2 -treated LiCoO_2 is much slower with increasing current density. The improvement of rate performance is attributed to the enhanced conductivity of the 10% MgCl_2 -treated LiCoO_2 .

In order to understand the improved rate performance of the surface-modified LiCoO_2 , the Li/LiCoO_2 cell was aged for 2 days to reach equilibrium before the ac impedance spectra were recorded (Fig. 8a). The semicircle in the high-frequency region of the Nyquist plot is mainly the contribution of the solid electrolyte interphase (SEI) on the electrode [32]. It is seen that the impedance of the commercial LiCoO_2 electrode increases sharply with cycling while that of the 10% MgCl_2 -treated LiCoO_2 increases very slowly.

As the commercial LiCoO_2 and the 10% MgCl_2 -treated LiCoO_2 are different electrodes, their impedances cannot be quantitatively compared directly. Therefore, the impedance of each electrode after 10 cycles at discharge state is defined as 1 (normalized). The evolutions of the impedance of these two materials with cycling are compared in Fig. 8b. The impedance of commercial electrode increases monotonously with cycling while that of the 10% MgCl_2 -treated LiCoO_2 increases very little. Chen and Dahn [33] pointed out that impedance growth was responsible for the rapid capacity fading of LiCoO_2 cycled to 4.5 V versus Li^+/Li . These facts partially explain the good capacity retention of 10% MgCl_2 -treated LiCoO_2 (Fig. 4) and insure the excellent rate performance of the materials (Fig. 7). Enhanced structural stability is another reason for the improved reversibility of the surface-modified material.

4. Conclusions

The electrochemical and thermal performances of commercial LiCoO_2 are significantly improved by modifying its surface via molten-salt treatment. The migration of Mg^{2+} ions into the lattice of Li^+ deficient LiCoO_2 during molten salt processing and during electrochemical cycling takes important roles. The formation of surface solid solution stabilizes the structure of LiCoO_2 , alleviates the reaction between oxidizing $\text{Li}_{1-x}\text{CoO}_2$ (charged LiCoO_2) and the electrolyte, suppresses the Co^{4+} dissolution at charged state and enhances the conductivity of, at least, the surface layer. The molten salt method is superior to the traditional coating method in surface modification because a solid solution can be formed during annealing and the coating layer is homogeneous.

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