



Performance improvement of LiCoO₂ by MgF₂ surface modification and mechanism exploration



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ABSTRACT

LiCoO₂ cathode material synthesized by a sol-gel method is modified by different contents of MgF₂ via simple chemical deposition. The structure and morphology of pristine and MgF₂-coated LiCoO₂ are investigated by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and high resolution transmission electron microscopy (HRTEM). It is found that the homogeneous MgF₂ surface modification does not change the bulk structure of LiCoO₂. The effects of MgF₂ on the electrochemical behaviors of LiCoO₂ are studied. Comparatively, 1 wt.% MgF₂-coated LiCoO₂ exhibits the best electrochemical performances. Cyclic voltammetry (CV) results confirm that MgF₂ surface coating decreases the electrode polarization and improves the structural stability of LiCoO₂ during cycling. The results of electrochemical impedance spectroscopy (EIS) and Fourier transform infrared (FTIR) for pristine and 1 wt.% MgF₂-coated LiCoO₂ further demonstrates that modification layer suppresses the undesirable growth of solid electrolyte interface (SEI) film, which greatly contributes to the improved electrochemical performances after surface modification. Differential scanning calorimetry (DSC) tests show that MgF₂ coating also improves the thermal stability of LiCoO₂ electrode.

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1. Introduction

Lithium ion batteries (LIBs) have become the dominant power sources for portable electronic devices. Most recently, the fast development of hybrid electric vehicles (HEVs), electrical vehicles (EVs) and energy storage apparatus set higher and higher demand on their energy sources [1,2]. To meet the requirements of higher capacity and longer cycle life for LIBs, many researchers are focusing on the development of the cathodes working at higher potentials, including traditional electrode materials [3].

As the most commercialized cathode material for LIBs, LiCoO₂ is typically charged up to 4.2 V versus Li⁺/Li and delivers a specific capacity of 140 mAh g⁻¹, although it has a high theoretical capacity of 274 mAh g⁻¹. In order to obtain higher capacity, it needs to be charged above 4.2 V [4–6].

However, the capacity fading of LiCoO₂ is quite pronounced under elevated upper cutoff voltage. Some research groups reported that the poor cycling performance above 4.2 V is attributed to structural instability and/or irreversible phase transition from a hexagonal phase to a monoclinic phase with accompanying volume

change of ~2.6% along *c*-axis [7,8], which causes the accumulation of stress and propagation of microfractures in positive electrode, resulting in fast capacity decay with cycling [2,9].

Surface modification of LiCoO₂ with metal oxides and metal phosphates such as Al₂O₃, MgO, ZnO, ZrO₂, AlPO₄, FePO₄ and YPO₄ has been approved to successfully improve its cycling performance at higher voltage [10–12]. Sun *et al.* observed AlF₃ on the surface of Al₂O₃ coated active material with time of flight secondary ion mass spectrometry (ToF-SIMS) [13]. Bai *et al.* reported that the conversion of YPO₄ to YF₃ even happened in chemical storage of YPO₄ coated LiCoO₂ [14]. Inspired by their pioneering work, Lee *et al.* coated AlF₃ and LaF₃ on the surface of LiCoO₂, effectively improves the electrochemical performances of LiCoO₂ [15]. Enlightened by the previous studies, metal fluorides are most likely to be the ultimate products which make genuine contribution in repeated electrochemical cycling, and the improvement mechanism by metal fluoride modification has not been thoroughly elucidated up to now.

MgF₂ is widely applied in the design and development of various optical thin films and multilayer photonic crystals for its properties including high hardness, good thermal stability, low refractive index, higher transmissivity in the ultraviolet, visible and infrared range, low absorption and wide bandgap. Cho *et al.* coated MgF₂ on the surface of LiCoO₂ through dry-coating method and obtained

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improved electrochemical performances, which were attributed to the reduced side reactions with electrolytes based on electrochemical impedance spectroscopy (EIS) analysis [16]. In their work, the coating process was quite complex and highly dependent on apparatus. Besides, the optimum proportion of MgF_2 in the coated cathode was not provided [16]. Lee *et al.* characterized the electrochemical properties of pristine and MgF_2 coated LiCoO_2 films, and contributed the electrochemical performance improvement of LiCoO_2 film to the protective effect MgF_2 coating layer only based on the analysis of Co dissolution [17]. In both of these two previous works, the influence of MgF_2 on the LiCoO_2 has not been comprehensively evaluated and the improvement mechanism has not been intensively explored yet.

In this paper, LiCoO_2 was modified by MgF_2 via simple chemical deposition, which is workable in practical application. The comparison of electrochemical performances show that electrode of LiCoO_2 coated by 1 wt.% MgF_2 exhibits the optimal cycling stability. Besides, it is found that the thermal stability of LiCoO_2 electrode has been improved by MgF_2 surface modification. Further, the mechanism for the improvements has also been intensively studied.

2. Experimental

2.1. Sample preparation

LiCoO_2 cathode material was synthesized by a sol-gel method. In a typical experiment, certain amount of lithium nitrate, cobalt nitrate and citric acid with molar ratio of 1:1:3.15 were separately put into three beakers and dissolved in distilled water to form transparent solutions with stirring. Next, the solutions were homogeneously mixed and the pH value was adjusted to 7.0 by slowly adding ammonia solution, followed by stirring at 80°C for 5 h to form a sol. The sol was then thoroughly dried to form corresponding gel at 120°C for 12 h. Afterwards, the gel was annealed at 750°C for 4 h in air and naturally cooled down to room temperature, finally yielding black powder of LiCoO_2 .

To prepare MgF_2 -coated LiCoO_2 , ammonium fluoride (Aldrich) and magnesium nitrate nonahydrate (Aldrich) were separately dissolved in distilled water. After that, the as-prepared LiCoO_2 powder was added into the magnesium nitrate nonahydrate solution in

which the pH value was also adjusted to 7.0. The molar ratio of Mg to F was adjusted to be 1:2 and the amount of MgF_2 in the solution varied from 0 wt.%, 0.5 wt.%, 1 wt.% and 3 wt.%. The solution containing LiCoO_2 was constantly stirred at 80°C for 5 h and repeatedly filtered by distilled water. Finally, the obtained powders were heated at 400°C for 5 h in air.

2.2. Physical characterizations

The X-ray diffraction (XRD) patterns of the as-prepared LiCoO_2 samples were measured on Bruker D8 Advance diffractometer (Bruker, Germany) with $\text{Cu K}\alpha$ radiation of $\lambda \sim 0.15418$ nm. In addition, the structural parameters were refined by the Rietveld method from XRD data with a 2θ range from 10° to 130° using the Full-proof software. Morphological characterizations were carried out on a field emission scanning electron microscopy (FESEM) (JEOL 7001F). Electron diffraction spectroscopy (EDS) mapping was measured to determine the element distribution together with SEM in large field of view. The image of high resolution transmission electron microscopy (HRTEM) was collected on JEOL JEM 2010 equipment to investigate the sample microstructure. The inductively coupled plasma (ICP) analysis was performed on Thermo Fisher ICP 6300 to determine the exact chemical compositions of the samples. Fourier transform infrared (FTIR) measurements were performed on Nicolet AVATAR360. Differential scanning calorimetry (DSC) analysis was carried out on TA Q600 by sealing the charged cathode (4.5 V at galvanostatic 0.1 C) in an Al crucible in dry Ar and heated from 100 to 350°C at a rate of 5°C min^{-1} .

2.3. Electrochemical characteristics

The working electrodes were fabricated by compressing the mixture of 84 wt.% active materials (pristine, 0.5 wt.%, 1 wt.%, 3 wt.% MgF_2 -coated LiCoO_2), 8 wt.% acetylene black (Super-P, MMM Carbon) and 8 wt.% binder (polyvinylidene fluoride, PVDF), which were all dissolved in N-methyl-pyrrolone (NMP) on an aluminum foil. After thoroughly dried, the films were cut into electrode sheets (8×8 mm²) as working electrodes. 1 M LiPF_6 dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with volume ratio of 1:1 was used as electrolyte. The assembly process was

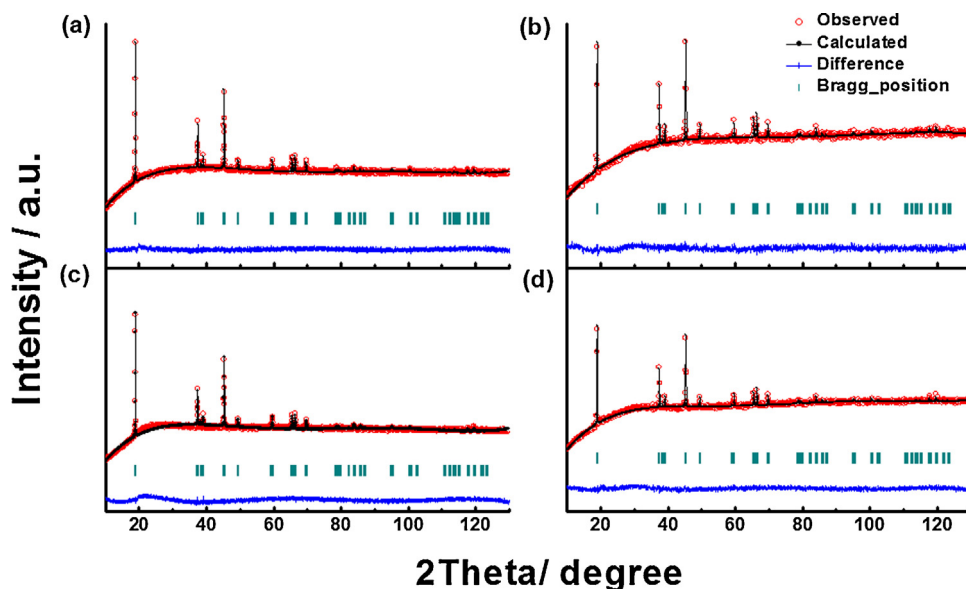


Fig. 1. Refined XRD patterns of pristine (a), 0.5 wt.% (b), 1 wt.% (c) and 3 wt.% (d) MgF_2 -coated LiCoO_2 samples, which demonstrate that the collected XRD patterns show slightly difference with the simulated ones as confirmed to hexagonal LiCoO_2 phase.

conducted in an argon-filled glove-box with H_2O and O_2 content less than 1 ppm.

Before electrochemical tests, the batteries were sufficiently aged to ensure good soakage. The cells were charged and discharged on a battery tester (NEWARE CT-3008W-5V1 mA, China) between 3.0 and 4.5 V (*versus* Li^+/Li). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) investigations were performed on an electrochemical workstation with three electrode systems (CHI660C, Shanghai). The CV curves were recorded between 3.0 and 4.5 V at a scan rate of 0.05 mV s^{-1} . The EIS measurements were performed over a frequency range from 100 kHz to 5 mHz.

3. Results and discussion

3.1. Physical characteristics

Fig. 1 shows the XRD patterns of pristine and MgF_2 -coated LiCoO_2 powders. All the powders are confirmed to be well-defined

Table 1

Structural parameters of the pristine and MgF_2 -coated LiCoO_2 powders.

Sample	a (Å)	c (Å)	Volume ($\text{\AA}^3$)	c/a
pristine	2.814(4)	14.046(9)	96.35	4.9911
0.5 wt.% MgF_2	2.814(2)	14.045(6)	96.33	4.9910
1 wt.% MgF_2	2.814(5)	14.044(2)	96.34	4.9899
3 wt.% MgF_2	2.814(2)	14.045(5)	96.33	4.9909

hexagonal $\alpha\text{-NaFeO}_2$ structure with a space group of $R\bar{3}m$ [18]. No diffraction peaks can be assigned to the MgF_2 phase in the obtained XRD patterns. Rietveld refinement is performed to obtain the structural parameters of the samples, and the results are listed in Table 1. The unit cell parameter a , an indication of the metal-metal distance within the (001) layer [19], displays negligible variations after surface coating. Besides, the c/a value reveals the extent of trigonal distortion [19]. As shown in Table 1, a high c/a value 4.99, which is desirable for better hexagonal structure for layered compounds [20], also remains the same. The high c/a values and the

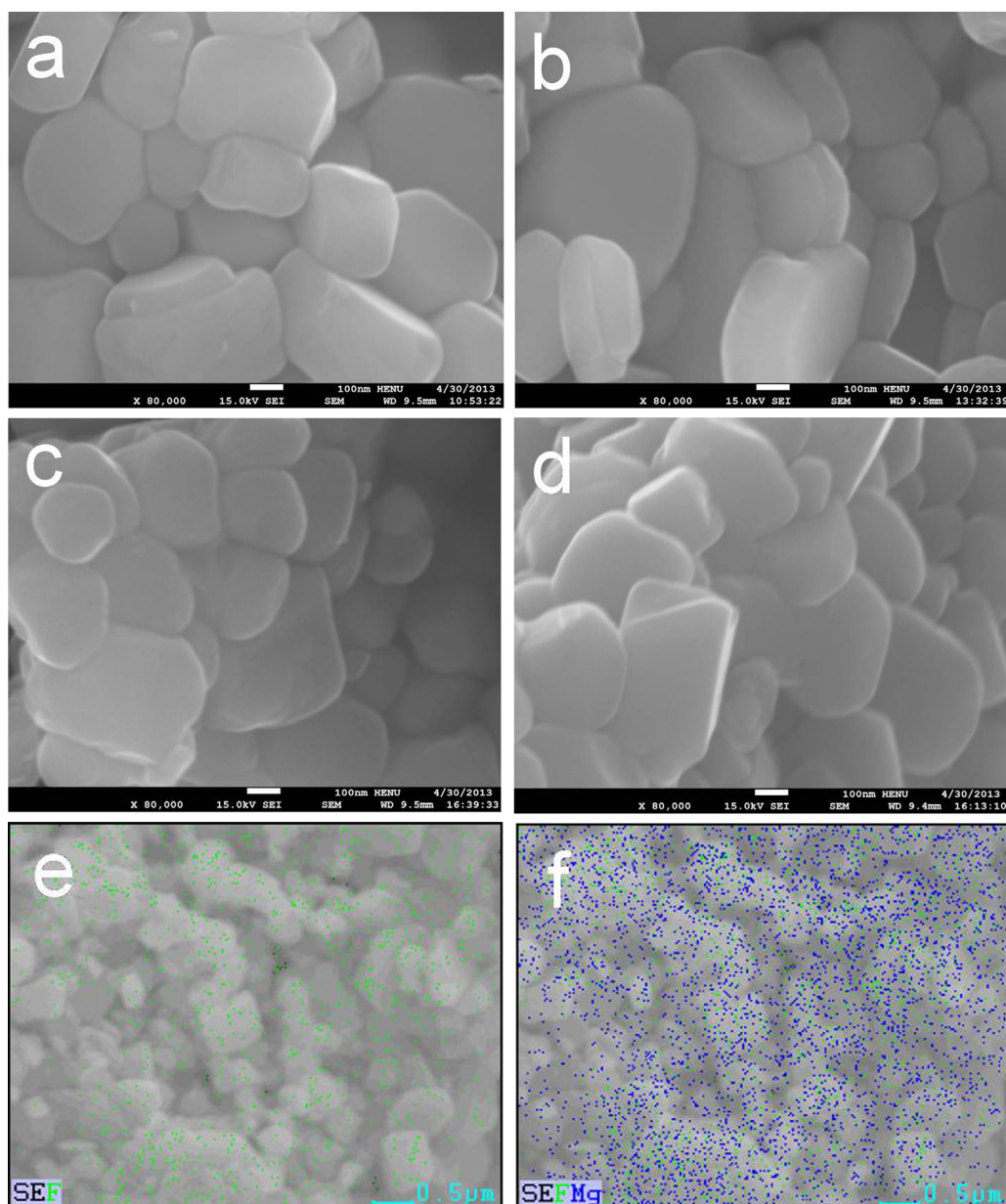


Fig. 2. Surface morphologies of pristine (a) 0.5 wt.% (b) 1 wt.% (c) and 3 wt.% (d) MgF_2 -coated LiCoO_2 and EDS mappings of F (e) and Mg (f) for 1 wt.% MgF_2 -coated LiCoO_2 .

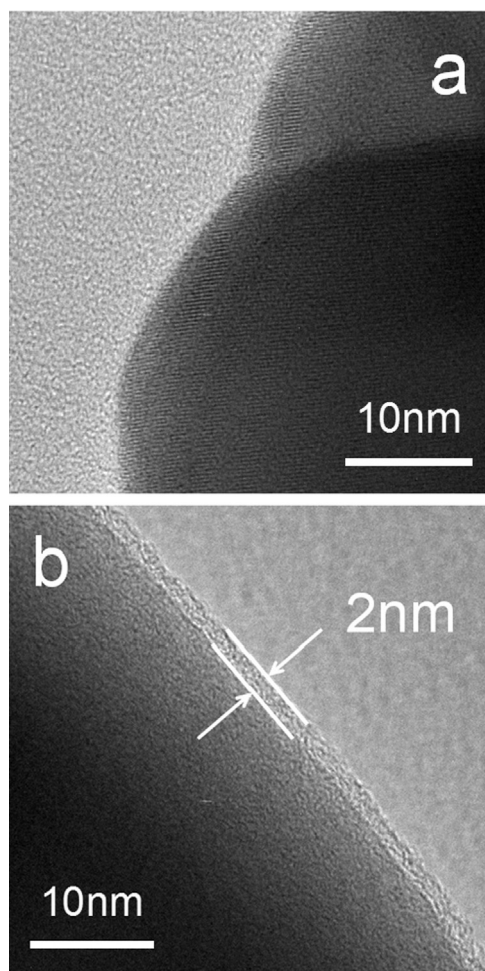


Fig. 3. TEM of (a) pristine and (b) 1 wt.% MgF_2 -coated LiCoO_2 .

well-resolved splitting of the XRD peaks assigned to the pairs of Miller indices (006)/(102) and (108)/(110) in all the compounds are good indications of a nearly perfect hexagonal layered structure [21]. No obvious change of the lattice parameters could be observed among the four samples, implying that the structure of LiCoO_2 remains unchanged after MgF_2 surface modification.

SEM images of the pristine and MgF_2 -coated LiCoO_2 are shown in Fig. 2. The particles of pristine LiCoO_2 are uniformly distributed, with smooth and clean surface, as can be observed in Fig. 2(a). The particle size keeps unchanged after surface modification with different contents of MgF_2 (Fig. 2(b)–(d)). Careful investigation indicate that the surfaces and edges gradually become obscure with increasing amount of coating, showing a thin layer outside LiCoO_2 exists after MgF_2 modification. Fig. 2(e) and (f) present the EDS mapping images for 1 wt.% MgF_2 -coated LiCoO_2 . It is clearly observed that F and Mg are evenly distributed, indicating that the MgF_2 layer deposited outside the LiCoO_2 particle surface is homogeneous.

To directly observe the microstructure of MgF_2 coating layer, TEM images were recorded and compared. Fig. 3 reveals the TEM images of the pristine and 1 wt.% MgF_2 -coated LiCoO_2 . It is apparent that the pristine LiCoO_2 is well crystallized, with lattice fringe extending to the grain boundary (Fig. 3(a)). The crystal orientation can be clearly viewed along (003), corresponding with the XRD results. Not surprisingly, the 1 wt.% MgF_2 -coated LiCoO_2 material (Fig. 3(b)) exhibits an amorphous and uniform modification layer with thickness of about 2 nm on the surface. This modification layer

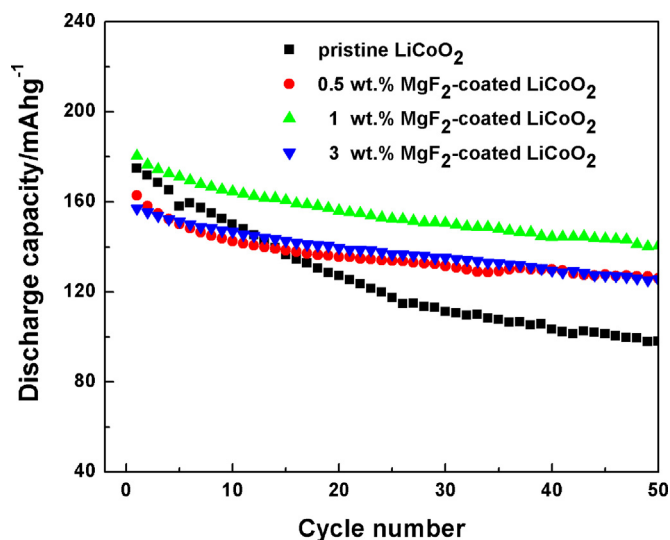


Fig. 4. Comparison of capacity retentions for pristine and MgF_2 -coated LiCoO_2 between 3.0 and 4.5 V at 0.2 C rate.

of MgF_2 will separate the direct contact between the electrode and electrolyte and thus suppress side reaction(s).

ICP analysis was also conducted to determine the exact content of MgF_2 in the coated materials. It shows that the actual contents of MgF_2 are 0.39 ± 0.01 , 0.76 ± 0.01 and 2.35 ± 0.01 wt.% for 0.5, 1 and 3 wt.% MgF_2 -coated LiCoO_2 . Nevertheless, we still call 0.5, 1 and 3 wt.% MgF_2 -coated LiCoO_2 in the following discussion.

3.2. Electrochemical characteristics

The influence of MgF_2 coating layer on the capacity retention of LiCoO_2 in the range of 3.0–4.5 V at a current rate of 54.8 mA g^{-1} (0.2 C) is compared in Fig. 4. Apparently, pristine LiCoO_2 suffers fast capacity decay with cycling. It releases an initial discharge capacity of 175 mAh g^{-1} , while after 50 cycles, it sharply decreases to 98 mAh g^{-1} , with capacity retention of only 56%. As can be clearly observed in Fig. 4, MgF_2 surface modification greatly improves the cyclability of LiCoO_2 . Comparatively, 1 wt.% MgF_2 coating is the most effective in improving the cycling performance of LiCoO_2 . The initial discharge capacity is about 180 mAh g^{-1} , which still remains 141 mAh g^{-1} after 50 cycles, with high capacity retention of 80%. The cycling performance gets worse when the MgF_2 content increases from 1 wt.% to 3 wt.%, implying that excessive MgF_2 coating plays a negative role in the transportation of Li^+ , which could be attributed to the intrinsic chemical and electrochemical inactivity of it.

Fig. 5 shows the discharge capacities of pristine and 1 wt.% MgF_2 -coated LiCoO_2 cells at various current densities between 3.0 and 4.5 V. The discharge capacity of pristine LiCoO_2 drops dramatically with increasing current. Comparatively, 1 wt.% MgF_2 -coated LiCoO_2 delivers higher discharge capacities and shows slower capacity decay at high current, indicating that MgF_2 coating effectively improves the rate performance of LiCoO_2 . Furthermore, the discharge capacity can be completely recovered when the current density is reset to 0.2 C, implying that the 1 wt.% MgF_2 -coated LiCoO_2 electrode experienced high rate cycling still retains good electrochemical reversibility and structural stability.

When the cell is charged to a higher potential, larger amount of Co^{3+} will convert to Co^{4+} in LiCoO_2 structure. If the cathode material is exposed to electrolyte, the strong oxidizing Co^{4+} will attack the carbonate groups of the solvent due to their nucleophilic properties and are easily reduced to Co^{3+} or Co^{2+} [22]. Simultaneously, Co^{4+} ions are capable of oxidizing alkyl carbonates to produce CO_2

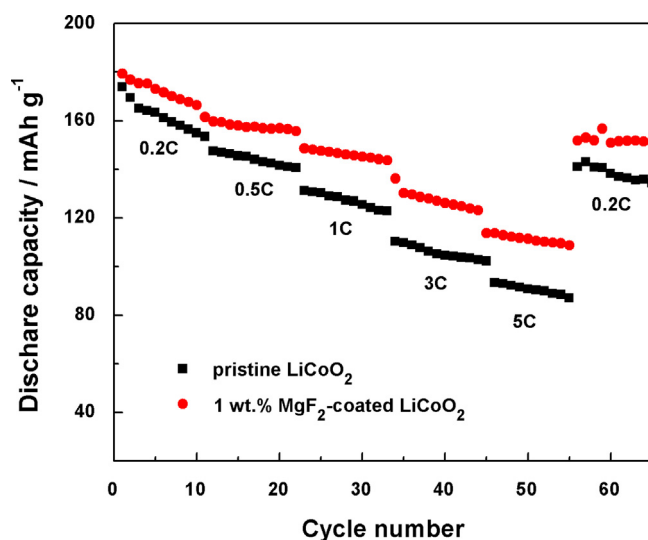


Fig. 5. Comparison of rate performances for pristine and 1 wt.% MgF₂-coated LiCoO₂.

Table 2
Redox potentials and D-Values of pristine and MgF₂-coated LiCoO₂.

Cycle number	Redox potential (V)		D-Value (V) ^a	
	pristine	1 wt.% MgF ₂	pristine	1 wt.% MgF ₂
1st	3.92/3.87	3.93/3.89	0.05	0.04
	4.08/4.05	4.07/4.05	0.03	0.02
	4.17/4.14	4.17/4.15	0.03	0.02
2nd	3.94/3.86	3.94/3.88	0.08	0.06
	4.09/4.05	4.08/4.05	0.04	0.03
	4.18/4.14	4.18/4.13	0.04	0.03

^a D-value: difference between redox pairs.

[22], resulting in the formation of various organic species at the interfaces [23]. Accordingly, these surface films may be the main sources for impedance increasing [16] and main reason for capacity decay [24]. It is confirmed that the coating layer of MgF₂ efficiently prevented the dissolution of Co⁴⁺ and successfully protected the surface of the electrode from the reactive electrolyte [17]. The uniform MgF₂ coating layer herein can effectively prevent Co⁴⁺ from direct contact and reaction with the electrolyte, which contributes to the stabilization of LiCoO₂ and decreases the side reactions in cycling. This partly explains the enhanced capacity retentions in Figs. 4 and 5.

In order to explore the mechanism of electrochemical performance improvement of MgF₂ coating layer on LiCoO₂, CV profiles were collected and presented in Fig. 6. For pristine LiCoO₂, a well-defined current redox at 3.92/3.87 V with a long tail is observed in the initial cycle, corresponding to the complex solid-solution reaction. The oxidation peaks at 3.92, 4.08 and 4.17 V are generally treated as phase transitions from O3-O2 (hexagonal-monoclinic) and O2-O1 (monoclinic-hexagonal) [25–28]. In the 2nd cycle, a redox appears at 3.94/3.86 V with degradation compared with the 1st cycle. For 1 wt.% MgF₂-coated LiCoO₂, all redox couples at 3.93/3.89 V, 4.07/4.05 V and 4.17/4.15 V can be clearly distinguished, with narrow and sharp peaks, indicating fast lithium diffusion and better structural reversibility. The improved structural stability of cathode material can be ascribed to the physical separation by MgF₂ layer between electrolyte and electrode material, plausibly preventing the dissolution of Co⁴⁺ ions and further enhancing the structural stability.

It is widely accepted that the difference between redox pairs (D-value) relates to the degree of polarization [29]. Table 2 compares the D-values of pristine and 1 wt.% MgF₂-coated LiCoO₂

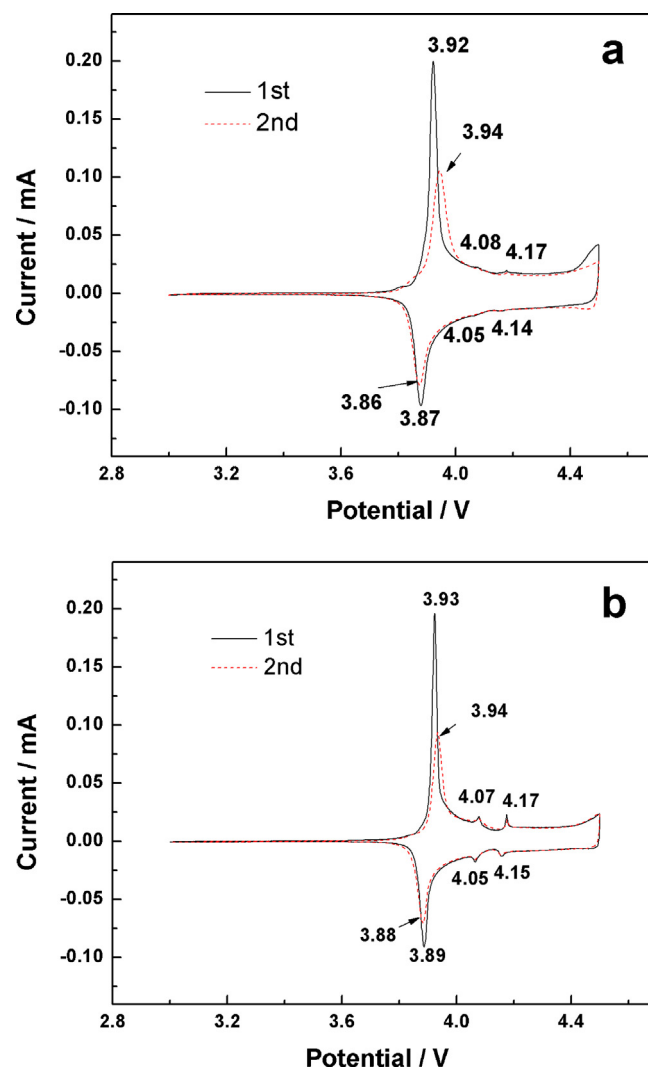


Fig. 6. Cyclic voltammograms of pristine (a) and 1 wt.% MgF₂-coated LiCoO₂ (b).

Table 3
R_{sf} data of the pristine and 1 wt.% MgF₂-coated LiCoO₂ electrodes.

Cycle number	1st	5th	10th	20th
R _{sf} (Ω)				
pristine	80.5	280.4	306.8	372.4
1 wt.% MgF ₂	81.4	134.2	150.1	235.3

electrodes for each redox in the first two cycles. Unexceptionally, the D-values of 1 wt.% MgF₂-coated LiCoO₂ are smaller than those of pristine electrode, implying that MgF₂ surface modification effectively decreases the electrode polarization. Surprisingly, as a chemical and electrochemical inactive material, the MgF₂ coating layer outside bulk LiCoO₂ plays a positive role in surface ion transportation, which will be further explored and explained in the following EIS and FTIR analysis.

AC impedance curves of the pristine and 1 wt.% MgF₂-coated LiCoO₂ electrodes were measured after the cells at fully charged state (4.5 V) were aged for two days to reach equilibrium. The impedance behaviors of the pristine and 1 wt.% MgF₂-coated LiCoO₂ electrodes at different cycles are presented in Fig. 7. As widely accepted, the semicircle in high frequency region of Nyquist plot is attributed to the resistance of solid electrolyte interface (SEI) film (R_{sf}) that covers cathode particles [30], which is fitted and compared in Table 3. The R_{sf} for the 1 wt.% MgF₂-coated LiCoO₂ in the first cycle is a little higher than that for pristine LiCoO₂,

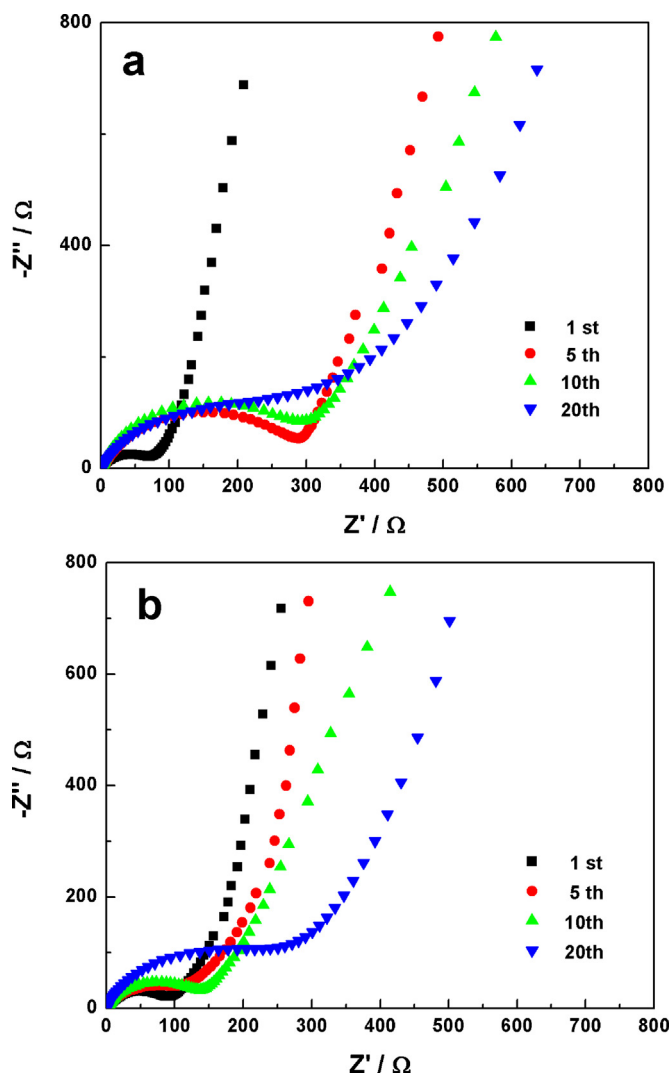


Fig. 7. Families of Nyquist plots for pristine (a) and 1 wt.% MgF₂-coated LiCoO₂ (b).

which may be resulted from the insulating nature of MgF₂ coating layer on LiCoO₂. For both electrodes in Fig. 7 (a) and (b), the R_{sf} increase distinctly with cycling, which could be attributed to the increasingly precipitation of surface film. For the electrode of pristine LiCoO₂, the R_{sf} values in cycling increase more faster than those of 1 wt.% MgF₂-coated LiCoO₂, indicating less resistive component is deposited on the surface of coated LiCoO₂ in electrochemical cycling.

To further compare the growth of SEI film for the two electrodes, the evolutions of the impedances with cycling are demonstrated in Fig. 8. For the pristine LiCoO₂, the R_{sf} of the 20th cycle is about 5 times than that of the first cycle, while the R_{sf} of 1 wt.% MgF₂-coated LiCoO₂ increase very little. Aurbach et al. reported that the precipitation of surface film on LiCoO₂ positive electrode increases the electrode impedance and thereby deteriorates the capacity [31]. The pristine LiCoO₂ particles are covered with surface film, which is mainly composed of decomposition of electrolyte [32,33]. However, the MgF₂ layer protects the electrode surface against HF attack. The smaller R_{sf} is in favor of rapid electrochemical reactions and may result in better electrochemical performance of the active materials [34]. In this work, MgF₂ coating layer helps to alleviate the dissolution of Co⁴⁺ and diminish the precipitation of resistive components. Compared with the pristine LiCoO₂, the 1 wt.% MgF₂-coated LiCoO₂ exhibits smaller R_{sf} , which partly explains

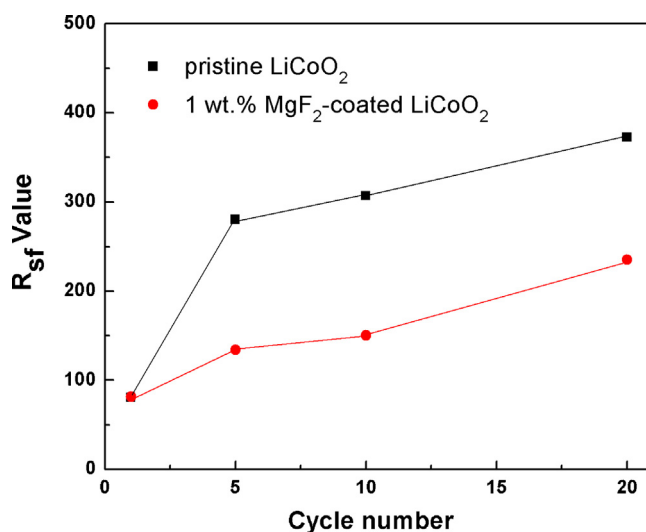


Fig. 8. Comparison of surface film resistance for the cells after different cycles.

the improved electrochemical performances after MgF₂ coating in Figs. 4 and 5.

Fig. 9 presents the FTIR spectra of pristine and 1 wt.% MgF₂-coated LiCoO₂ before and after cycling. Two vibrations at 615 and 525 cm⁻¹ are apparent in all the four profiles, which could be ascribed to the asymmetric stretching of Co-O bonds in CoO₆ octahedrons and the bending modes of O-Co-O bonds [35], respectively. A weak band at 1634 cm⁻¹ is attributed to the ambient O-H vibration. Compared Fig. 9(a) and (c), no characteristic vibration corresponding to Mg-F appears after MgF₂ surface modification, which possibly derives from its low content. As can be observed in Fig. 9(b) and (d), new absorption peaks appear after 10 cycles. Based on the previous literatures [36–42], detailed assignments of all the new absorption peaks are listed in Table 4, wherein all the seven absorption peaks can be assigned to certain components of SEI. Strictly, the absorption peaks at 615 cm⁻¹ for pristine and 1 wt.% MgF₂-coated LiCoO₂ after 10 cycles have been normalized in Fig. 9(b) and (d) to compare the intensities of new absorption peaks. Obviously, it is clear that 1 wt.% MgF₂ coating layer effectively suppresses the growth of the SEI film, which is consistent with the EIS results in Figs. 7 and 8. The MgF₂ hinders the

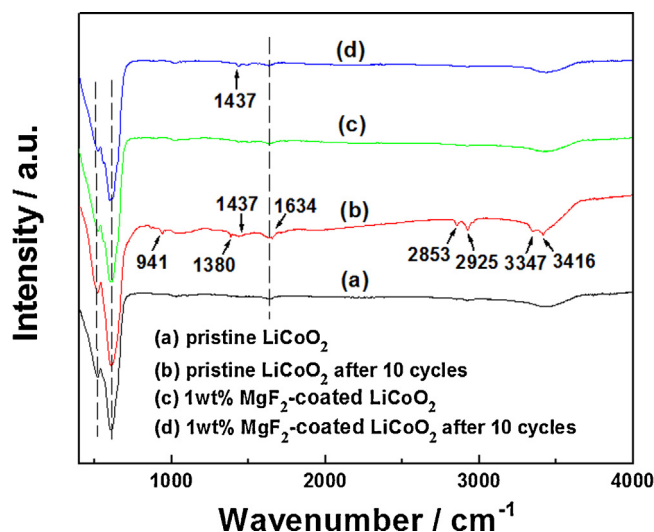


Fig. 9. FTIR spectra of the bare and 1 wt.% MgF₂-coated LiCoO₂.

Table 4
New infrared peaks and the corresponding identifications.

Peak position	Assignment
941	=C–H, characteristic of PEO [36] 1380 COO [−] bending [37–39]
1437	Li ₂ CO ₃ , CH, CH ₃ asym. bend of SEI [36,40]
2853	C–H stretching [41]
2925	C–H stretching [41]
3347	Structural OH groups [42]
3416	Structural OH groups [42]

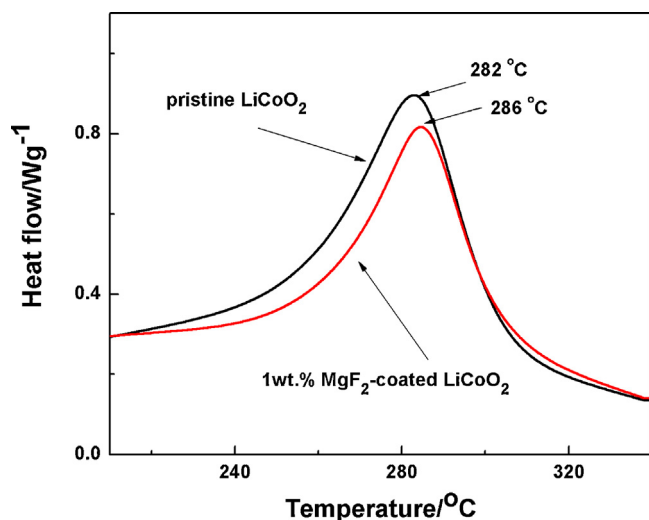


Fig. 10. DSC traces of pristine and 1 wt.% MgF₂-coated LiCoO₂ electrodes at charged state of 4.5 V at a heating rate of 5 °C min^{−1}.

decomposition of the electrolyte at the particle surface in repeated cycling, thus inhibits the growth of SEI film.

Thermal stability of electrodes materials is important to large-scale commercial applications of LIBs and the superior thermal stability of electrode will greatly contribute to desirable thermal stability of a cell. DSC measurement was performed to compare the thermal stabilities of delithiated pristine and 1 wt.% MgF₂-coated LiCoO₂ materials (Fig. 10). For 1 wt.% MgF₂-coated LiCoO₂, the exothermic peak shifts to a higher temperature of 286 °C compared with 282 °C for the pristine material. On the other hand, the amount of exothermic heat released is smaller in comparison with that of pristine electrode. Peak fitting to the DSC traces demonstrates that the integrated area of the exothermic peak is 85% that of pristine LiCoO₂ for the 1 wt.% MgF₂-coated material.

The DSC results showed significant exothermic reaction delay and heat reduction after MgF₂ surface coating, indicating the lowered reactivity with the electrolyte. This implies that the crucial factor governing the exothermic reaction is the interfacial reaction with the electrolyte and cathode. It is also believed that the strong-bonded nature of Mg–F contributes to a strong resistance to the reaction with the electrolyte, and MgF₂ has been reported to be thermally stable [43].

4. Conclusions

Different contents of MgF₂ were coated on as-prepared LiCoO₂ via simple chemical deposition method. Experimental results show that 1 wt.% MgF₂-coated LiCoO₂ cathode exhibits the optimal electrochemical performances. The homogeneous MgF₂ surface coating layer on LiCoO₂ separates the direct contact between electrolyte and high active electrode in deep charged state, thus alleviates the invasion of high oxidation Co⁴⁺ and inhibits the fast growth of SEI layer in cycling. As a result, the structural stability, cycling

capability and thermal stability of LiCoO₂ are greatly enhanced, even at high cutoff voltage of 4.5 V. Surface modification by MgF₂ is an effective way to improve the electrochemical performances and thermal stability of LiCoO₂ at high cutoff voltage.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2014.04.155>.

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