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Introduction

Lithium (Li) ion batteries composed of a LiCoO₂ cathode and a graphite anode are the dominating power sources for commercial 3C electronic devices at present. In order to extend the endurance of devices, the capacity of LiCoO₂ cathode as the capacity-limited component in the batteries must been enhanced. Theoretically, LiCoO₂ can deliver a capacity of 274 mA h g⁻¹ after entire lithium ions extract out.¹ Nevertheless, its practical capacity is usually limited to only 137 mA h g⁻¹ corresponding to Li_{1-x}CoO₂ (x = 0.5) with the cut-off voltage of 4.2 V in order to maintain the good structure stability and compatibility with nonaqueous electrolyte. A higher specific

Spinel MgAl₂O₄ modification on LiCoO₂ cathode materials with the combined advantages of MgO and Al₂O₃ modifications for high-voltage lithium-ion batteries[†]

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In order to improve the electrochemical performance of LiCoO₂ cathode in a high-voltage range of 3.0-4.5 V, spinel MgAl₂O₄ has been modified on the surface of LiCoO₂ particle by a facile high-temperature solid state reaction. The structure and morphology of the MgAl₂O₄-modified LiCoO₂ are investigated in comparison with the pristine, Al₂O₃-modified and MgO-modified LiCoO₂. The MgAl₂O₄ modification is highly conformal and uniform just similar as the Al₂O₃ modification, while the MgO modification is not uniform. In terms of electrochemical performance as a high-voltage cathode material, the MgAl₂O₄modified LiCoO₂ delivers an initial discharge capacity of 184 mA h q^{-1} between 3.0 V and 4.5 V at 0.1C $(1C-rate = 160 \text{ mA g}^{-1})$ and a capacity retention of 96.8% after 70 cycles at 1C rate. There is a significant improvement on high-voltage cycling stability for the MgAl₂O₄-modified LiCoO₂ since the capacity retention of the pristine LiCoO₂ is only 38.7% after 70 cycles. Moreover, the MgAl₂O₄-modified LiCoO₂ exhibits an enhanced rate capability. Compared with the Al₂O₃ modification and the MgO modification, spinel MgAl₂O₄ modification has the combined advantages of Al₂O₃ and MgO modifications on improving the electrochemical performance of the LiCoO₂ cathode for high-voltage applications. The modified spinel MgAl₂O₄ layer can effectively protect the charged Li_{1-x}CoO₂ cathode from structural collapse and impede the oxidation decomposition of the electrolyte for the high-voltage application of LiCoO₂

capacity can be gained by charging to a high voltage over 4.2 V, but worse cycling stability need be overcome. At higher voltages than 4.2 V, serious side reactions between the charged $\text{Li}_{1-x^{-}}$ CoO₂ (1 > *x* > 0.5) cathode and nonaqueous electrolyte components cause the structural collapse of Li_{1-x} CoO₂ cathode and the serious oxidative decomposition of the electrolyte.^{2,3}

To achieve the high-voltage application of LiCoO₂, many efforts have been made by either electrolyte reformulation or LiCoO₂ modification. Surface modification with metal oxides (e.g., Al₂O₃,⁴⁻⁷ MgO,^{8,9} ZrO₂ (ref. 10 and 11)) has been widely reported as a facile and effective way to the high-voltage application of LiCoO₂ cathode materials. It is reported that a "zerostrain" LiCoO₂ cathode can be obtained by the surface modification with a thin layer of a high-fracture-toughness metal oxides, which can suppress the lattice constant changes and phase transitions of LiCoO₂ during high-voltage cycling.^{12,13} Most recently, it is proposed that the surface modification could lead to improvement of the structural stability at the surface region of LiCoO2.14 Moreover, the modified layer can provide a physical barrier to suppress the interfacial side reactions between the charged LiCoO₂ and the electrolyte, which is also important for stabilizing the LiCoO2 surface.¹⁵ Therefore, the crystal structure and conductivity of the modified materials, the

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coverage ratio of the modified layer on $LiCoO_2$ are very important to modify the $LiCoO_2$ cathode materials for high-voltage Liion batteries. Recently, modification with Li^+ -ion conductors on high-voltage cathode materials has attracted greater interests because of the advantageous combination of both physical barrier and Li^+ -ion conduction.¹⁶⁻¹⁸

Both Al₂O₃ and MgO modified layers have been demonstrated to improve the cycling stability of LiCoO₂ at a highvoltage range. It was previously reported that Al₂O₃ modification inhibited the volume change of the LiCoO₂ lattice,⁴ and MgO modification provided Mg²⁺ ions as pillars to stabilize the layered structure of $\text{Li}_{1-x}\text{CoO}_2$ (1 > x > 0.5) by diffusing into Co and Li sites during heat treatment.8 Seldom literatures reported the effect of Al₂O₃ and MgO co-modification on the electrochemical performance of LiCoO₂ cathode in a high-voltage range. Recently, spinel MgAl₂O₄ has been incorporated into the cathode composite materials and solid electrolytes as a promising Li⁺ ion conductor for applications in Li-ion batteries.¹⁹⁻²³ In this work, we investigate the effect of spinel MgAl₂O₄ modification on LiCoO₂ cathode by comparison with Al₂O₃ and MgO modifications. Our results show that spinel MgAl₂O₄ modification has combined advantages of Al₂O₃ and MgO modifications on improving the electrochemical performance of the LiCoO₂ cathode for high-voltage applications.

Experimental

Materials synthesis

All the starting materials were purchased from commercial sources and used without further purification. Commercial LiCoO₂ powders were obtained from Chinese company as the pristine and used for surface modification. To prepare MgAl₂O₄modified LiCoO₂ powders, the LiCoO₂ powders were dispersed into distilled water. Then, Al(NO₃)₃·9H₂O and Mg(NO₃)₂·6H₂O with the molar ratio of 2:1 were poured into the solution. The mass ratio of LiCoO₂ versus the final received MgAl₂O₄ was controlled to be 99:1. After stirring for 10 min, 2% NH₃·H₂O solution was dropped into the solution to adjust pH value to 8. After stirring for another 1 h, the suspension was dried at 60 °C and 120 °C to receive dry powders. The MgAl₂O₄-modified LiCoO₂ powders were finally obtained after heat-treatment at 800 °C for 6 h in air. For comparison, the Al₂O₃, MgO-modified LiCoO₂ powders were prepared at a similar procedure. The mass of the modified Al₂O₃ and MgO was controlled to be 1% of the final products. Herein, the content of 1% is the optimal in terms of the electrochemical performance.

Physical characterization

The crystal structures of the pristine LiCoO₂, MgAl₂O₄, Al₂O₃ and MgO-modified LiCoO₂ samples were characterized by X-ray diffraction (XRD) using a diffractometer (D/MAX2500 V, Cu Kα radiation). The XRD patterns were recorded from 10° to 70° (2 theta), and an internal standard of silicon powders were used to confirm the peak shifts. Rietveld refinement of 1% MgAl₂O₄modified LiCoO₂ was carried out by using GSAS software. Morphologies of the pristine LiCoO₂ and Al₂O₃, MgO, MgAl₂O₄- modified LiCoO₂ were observed by field-emission scanning electron microscopy (FE-SEM, Hitachi SU8020) and high resolution transmission electron microscopy (HRTEM, JEM-2100F). X-ray photoelectron spectroscopy (XPS, ESCALAB250) was used to characterize the surface state of various LiCoO₂ powders, and the depth profiles of Al and Mg in the 1% MgAl₂O₄-modified LiCoO₂ were analysed on the electron spectroscopy for chemical analysis (ESCA) instrument (ESCALAB250).

Electrochemical measurement

The electrochemical properties of various LiCoO₂ cathode materials were evaluated in Li||LiCoO2 CR2032-type coin cells. The LiCoO₂ electrodes for the coin cell assembly are prepared as follows: (1) a slurry containing LiCoO₂ material with or without modification, acetylene black, and polyvinylidene fluoride (PVDF) with the mass ratio of 84 : 8 : 8 was formed in N-methyl-2-pyrrolidinone (NMP); (2) the slurry was cast onto an aluminum current collector with a controlled thickness; (3) a LiCoO2 laminate was received after NMP removal by vacuum drying at 70 °C; (4) the laminate was punched into discs (Φ 14 mm) as the LiCoO₂ electrodes. Microporous polypropylene membrane was used as separator. Highly pure lithium foil was used as the counter electrode and reference electrode in the Li||LiCoO₂ coin cell. The electrolyte was 1 M LiPF₆/ethylene carbonate (EC) + ethyl methyl carbonate (DMC) (1 : 1 w/w). The coin cells using various LiCoO2 electrodes were assembled in an Ar-filled glove box (MBraun). The cell performance of the Li||LiCoO₂ cells using the pristine LiCoO₂ and Al₂O₃, MgO, MgAl₂O₄-modified LiCoO₂ was evaluated on a LANHE multichannel battery cycler. In a typical activation procedure, all the cells were initially cycled twice between 3.0 and 4.5 V at 0.1C rate $(1C = 160 \text{ mA g}^{-1})$. Then the cycling tests were performed at a current rate of 1C in the constant current-constant voltage (CC-CV) charge mode and constant current (CC) discharge mode between 3.0 and 4.5 V. The electrochemical impedance spectra (EIS) of the Li||LiCoO₂ cells at the 100% state of charge (SOC) were measured on a CHI 604D electrochemical workstation (Chenhua Instruments Co. Ltd). The frequency range and potential perturbation were set from 100 kHz to 0.01 Hz and 10 mV, respectively.

Results and discussion

Structure and morphology

The XRD patterns of the pristine $LiCoO_2$ and the modified $LiCoO_2$ samples are shown in Fig. 1. From Fig. 1a, all the strong diffraction peaks except the peak at 28.5° (from the internal standard Si) can be indexed to the hexagonal phase with space group $R\bar{3}m$ (JPCDS card no. 50-0653). No diffraction peak corresponding to Al_2O_3 , MgO and MgAl₂O₄ can be clearly observed in the modified samples owing to their low content of 1%. Even though all the 1% Al_2O_3 , MgO and MgAl₂O₄ modifications do not greatly affect the crystal structure of $LiCoO_2$, the (003) peak at around 19° displays a distinct shift in every modified $LiCoO_2$ sample in Fig. 1b. The left shift to a smaller degree means the increase of the lattice parameters and the swelling of the lattice



Fig. 1 XRD patterns (a) and magnified (003) peaks (b) of the pristine $LiCoO_2$ and the 1% Al_2O_3 , MgO, MgAl₂O₄-modified $LiCoO_2$ samples; magnified XRD patterns (c) of the pristine $LiCoO_2$ and 1%, 10% MgAl₂O₄-modified $LiCoO_2$ samples; and Rietveld refinement patterns (d) of 1% MgAl₂O₄-modified $LiCoO_2$.

volume, which is in agreement with the previous literatures.^{7,8} During high-temperature surface modification, Mg²⁺ and Al³⁺ cations could partially dope into the LiCoO₂ lattice from the modified layer.²⁴ Since the ionic size of Al³⁺ (0.535 Å) is smaller than that of Mg^{2+} (0.720 Å), Al^{3+} diffuses into the LiCoO₂ lattice more easily than Mg^{2+} . That is the reason for the order of the (003) peak position: MgO modification $< MgAl_2O_4$ modification < Al₂O₃ modification. This is also consistence with mostly recent viewpoint that modification species can be incorporated at grain boundaries into the LiCoO2 surface and lead to reversible structural changes.14 In order to confirm the formation of spinel MgAl₂O₄, Fig. 1c shows the magnified XRD patterns of the 10 wt% MgAl2O4-modified LiCoO2 sample compared with the pristine and the 1 wt% MgAl₂O₄-modified LiCoO₂. The full-range XRD patterns can be found in ESI (Fig. S1[†]), which shows that no peak of MgAl₂O₄ is observed due to the low quantity unless the amount increases to 10 wt%. From the magnified XRD patterns in Fig. 1c, the existence of spinel MgAl₂O₄ is confirmed by the peak at 37° ,²¹ which corresponds to the (311) plane of MgAl₂O₄ lattice. The Rietveld refinement patterns of the 1% MgAl₂O₄-modified LiCoO₂ shown in Fig. 1d further prove the existence of spinel MgAl₂O₄ in the 1% MgAl₂O₄-modified LiCoO₂ and the real content of spinel MgAl₂O₄ is about 0.6%.

Fig. 2 shows SEM images of the pristine $LiCoO_2$ and 1 wt% Al_2O_3 , MgO, MgAl_2O_4-modified $LiCoO_2$ samples. The surface of the pristine $LiCoO_2$ (Fig. 2a) is quite smooth and clean, but some stuff can be found on the surfaces of the Al_2O_3 , MgO, MgAl_2O_4-modified $LiCoO_2$ particles shown in Fig. 2b–d. Quite different from the loose connection between the modified MgO and the $LiCoO_2$ particle (Fig. 2c), the tight connections between the modified Al_2O_3 or MgAl_2O_4 with the $LiCoO_2$ particle are



Fig. 2 SEM images of (a) the pristine $LiCoO_2$; (b) Al_2O_3 -modified $LiCoO_2$; (c) MgO-modified $LiCoO_2$; (d) and MgAl_2O_4-modified $LiCoO_2$ at high magnification (×5.0k).

shown clearly in Fig. 2b and d. Since Al^{3+} ion (0.535 Å) has the smaller size than Mg^{2+} ion (0.720 Å), it is reasonable for more Al³⁺ diffusion from Al₂O₃ and MgAl₂O₄ into the LiCoO₂ lattice than Mg²⁺ from MgO during the high-temperature treatment, which enhances the connection between the modified material and the LiCoO₂ bulk. The tight connection between the modified material and the LiCoO₂ bulk means a pretty stable and conformal surface modification. It is indicative of that the Al₂O₃ and MgAl₂O₄ modifications have the higher coverage ratios than the MgO modification, and thus more effectively suppress the structural collapse of LiCoO2 and interfacial side reactions between the charged cathode and the electrolyte. In order to check the uniformity of the MgAl₂O₄ modification layer, EDS mapping was further performed and the results are shown in Fig. 3. It is clearly shown that the elements O, Al and Mg are uniformly dispersed on the surface of the MgAl₂O₄-modified LiCoO₂. That means the elements Mg and Al in the MgAl₂O₄modified LiCoO₂ sample are uniformly distributed, illustrating that the MgAl₂O₄ modification is quite uniform and conformal.

In order to observe the thickness of the surface modification layer in the MgAl₂O₄-modified LiCoO₂, Fig. 4 shows the HRTEM images of a MgAl₂O₄-modified LiCoO₂ particle. The modification layer (translucent) has the thickness of around 10 nm and the lattice fringe of *ca.* 0.244 nm is consistent with the interplanar distance of (311) planes of spinel MgAl₂O₄. The dark region shows the (006) planes of layered LiCoO₂ crystal with the fringe of *ca.* 0.234 nm. Fig. 4 also clearly shows that the modification layer is tightly attached on the surface of LiCoO₂, which is beneficial to adequately suppress the interfacial side reactions between the charged LiCoO₂ and the electrolyte.

The oxidation states of the Co and O elements in the pristine LiCoO₂ and three modified LiCoO₂ samples were investigated by XPS as shown in Fig. 5. The Co 2p peaks for the pristine and modified LiCoO₂ shown in Fig. 5a included a 2p1/2 peak at around 780 eV and a 2p3/2 peak at around 795 eV.² The modified LiCoO₂ samples show a shift in the Co 2p1/2 peak by 0.1-0.3 eV toward a higher binding energy than the pristine, which indicates that the Co bonding environment in the surface of the modified samples has a small change.⁷ Similar change can also be found in O 1s peaks as shown in Fig. 5b. The O 1s peak at 529.3 eV is assigned to O^{2-} ions in the O_3 layered structure of LiCoO₂, and the higher binding energy for the O 1s peak in the modified LiCoO₂ samples is attributed to the Al/Mg substitution in Co site on the particle surface.² The O 1s peak at 531.3 eV is difficult to be speculated but should be due to the free oxygen/ adsorbed oxygen.25 In the modified LiCoO2 samples, the



Fig. 3 EDS maps for MgAl₂O₄-modified LiCoO₂ particles.

MgAl₂O₄ modification reveals the slight differences on both the Co 2p and O 1s peaks from the Al₂O₃ modification and MgO modification. More interestingly, the lower intensities for the Co 2p peak and the O 1s peak at 531.3 eV for the MgAl₂O₄ modified LiCoO₂ suggest that the MgAl₂O₄ modification is more uniform than the MgO modification, which is accordance with the SEM results shown in Fig. 2. Fig. 5c and d show the depth profiles of Al and Mg elements in the 1% MgAl₂O₄-modified LiCoO₂. At an etch level of 0 nm, the peak at 73 eV in Fig. 5c is ascribed to the binding energy of Al 2p.5 The intensity of the Al 2p peak greatly decreases at the level of 10 nm and that peak completely disappeared at the level of 50 nm, which indicates that Al is just present on the surface region of the MgAl₂O₄ modified LiCoO₂. Similarly as the depth profiles of Al 2p, the intensity of the Mg 2p peak at 49 eV in Fig. 5d²⁶ drops obviously from the etch level of 0 nm to 10 nm.

Electrochemical properties

Electrochemical properties of the pristine $LiCoO_2$ and Al_2O_3 , MgO, MgAl_2O_4-modified $LiCoO_2$ were evaluated in the Li|| $LiCoO_2$ coin-cells. Fig. 6 shows initial, 10th, 40th and 70th



Fig. 4 HRTEM images of a MgAl₂O₄-modified LiCoO₂ particle.

charge-discharge curves of the pristine LiCoO₂ and Al₂O₃, MgO, MgAl₂O₄-modified LiCoO₂ cells between 3.0 and 4.5 V, respectively. From the initial voltage profiles in Fig. 6a, the pristine and MgO-modified LiCoO₂ display slightly higher discharge capacity than the Al₂O₃ and the MgAl₂O₄ modified LiCoO₂. Moreover, the latter two have higher charge voltage plateau, especially for the Al₂O₃-modified sample, which corresponds to the high electrochemical polarization. Cyclic voltammograms (CVs) results also clearly indicate that the Al_2O_3 and the MgAl₂O₄ modified LiCoO₂ samples exhibit higher electrochemical polarization in ESI (Fig. S2[†]). At the 10th cycle (Fig. 6b), the MgO and MgAl₂O₄-modified LiCoO₂ samples deliver the higher discharge capacities than the pristine and the Al_2O_3 -modified LiCoO₂ samples. However, the pristine LiCoO₂ shows both fast capacity fading and voltage fading at the 40th cycle (Fig. 6c), which is just similar as previous literatures.^{3,6,27} Different from the Al₂O₃ and MgAl₂O₄-modified LiCoO₂, the MgO-modified LiCoO₂ experiences a visible capacity fading from 180 mA h g^{-1} at the 10th cycle to 160 mA h g^{-1} at the 40th cycle. Furthermore, at the 70th cycle shown in Fig. 6d, the MgOmodified LiCoO2 exhibits a serious capacity fading to 120 mA h g^{-1} , along with a big voltage plateau drop. The MgAl₂O₄-modified LiCoO₂ shows higher capacity than the others at the 70th



Fig. 5 XPS spectra (a, b) of the pristine $LiCoO_2$ and Al_2O_3 , MgO, MgAl_2O_4-modified $LiCoO_2$ samples, and the depth profiles of Al (c) and Mg (d) elements in the 1% MgAl_2O_4-modified $LiCoO_2$.

cycle. The cycling performance of the pristine LiCoO2 and Al2O3, MgO, MgAl₂O₄-modified LiCoO₂ was shown in Fig. 7. Clearly, the discharge capacity of the pristine LiCoO₂ drops to 72 mA h g^{-1} after 70 cycles, with the capacity retention of 42% (vs. the capacity of the 3rd cycle). Although the MgO-modified LiCoO₂ has the higher discharge capacity at the first twenty cycles than the others, a fast capacity fading leads to the capacity of only 115 mA h g^{-1} after 70 cycles with the capacity retention of 63%. Herein, the MgO modification can improve the capacity but has invisible effect on enhancing the cycling stability, which is in accordance with the Shim's result.8 However, both the Al₂O₃ and MgAl₂O₄-modified LiCoO₂ samples show the excellent cycling stability with the capacity retention over 96% after 70 cycles. Especially, the MgAl₂O₄-modified LiCoO₂ has not only the excellent cycling stability and also the highest capacity. The enhanced electrochemical performance of the MgAl₂O₄-modified LiCoO₂ is mainly attributed to both the uniform modification layer (Fig. 2d) and Mg²⁺/Al³⁺ dopings on the surface of LiCoO₂ particles (Fig. 1b). The uniform MgAl₂O₄ layer can effectively prevent the oxidation decomposition of the electrolyte and Co⁴⁺ dissolution into the electrolyte at high voltages.^{6,8}

These results clearly indicate that the MgAl₂O₄ modification exhibits the combined advantages of the Al₂O₃ modification on cycling stability and the MgO modification on capacity improvement. In addition, in our study the 1% MgAl₂O₄ modification is better than 0.5% and 2% modification (Fig. S3 in ESI[†]). The optimal composition of MgAl₂O₄ means the appropriate thickness of the modification layer. It is vital to not only provide vigorous protection for LiCoO₂ from the electrolyte corrosion (resulting in Co⁴⁺ dissolution), but also allow Li⁺ ion transport fluently (lower impedance).

Fig. 8 shows rate capabilities of the pristine $LiCoO_2$ and Al_2O_3 , MgO, MgAl_2O_4-modified $LiCoO_2$ samples between 3.0 and 4.5 V. After two formation cycles at 0.1C, all the cells were charged at a rate of 0.5C and discharged at incremental rates from 0.5 to 5C followed by recovering back to 0.5C. In the case of the pristine $LiCoO_2$, its discharge capacity rapidly drops with increasing the current rates and even at the same rate the capacity fades fast, just similar as the cycling performance shown in Fig. 7. The three modified $LiCoO_2$ samples exhibit the enhanced rate capability, presumably due to the positive effect of Mg^{2+}/Al^{3+} surface dopings on increasing ionic conductivity.



Fig. 6 Charge and discharge curves of the pristine $LiCoO_2$ and Al_2O_3 , MgO, MgAl_2O_4-modified $LiCoO_2$ at (a) the first cycle; (b) the 10th cycle; (c) the 40th cycle and (d) the 70th cycle.





Fig. 7 Cycling performance at the current rate of 1C and coulombic efficiency of the pristine $LiCoO_2$ and Al_2O_3 , MgO, MgAl_2O_4-modified $LiCoO_2$.

Fig. 8 Rate capability of the pristine the pristine $LiCoO_2$ and $Al_2O_3,$ MgO, $MgAl_2O_4\text{-modified }LiCoO_2.$

The Al₂O₃-modified LiCoO₂ delivers the capacities of 168 mA h g^{-1} at 1C, 157 mA h g^{-1} at 2C and 133 mA h g^{-1} at 5C. Similar as their higher capacities shown in Fig. 7, the MgO and MgAl₂O₄-modified LiCoO₂ samples show higher rate capabilities than the Al₂O₃-modified LiCoO₂. Both the MgO and MgAl₂O₄-modified

 $LiCoO_2$ samples deliver the capacity of 158 mA h g⁻¹ at 5C. In addition, when the current rate returns back to 0.5C, the discharge capacities of all the modified samples can be restored. The enhanced rate capability of the MgAl₂O₄-modified LiCoO₂ is possibly due to high Li⁺ ion conductivity of the MgAl₂O₄ layer.



Fig. 9 Electrochemical impedance spectra (EIS) of the pristine $LiCoO_2$ and Al_2O_3 , MgO, MgAl_2O_4-modified $LiCoO_2$ at full discharge (a) after 2 cycles; (b) after 70 cycles.

To further understand the effect of the MgAl₂O₄ modification on the electrochemical performance of LiCoO₂, EIS results of the Li||LiCoO₂ cells using the pristine LiCoO₂ and Al₂O₃, MgO, MgAl₂O₄-modified LiCoO₂ materials are compared in Fig. 9. The Nyquist plots of the cells after 2 cycles (Fig. 9a) and 70 cycles (Fig. 9b) are composed of two semicircles in the highto-medium frequency range and an inclined line in the low frequency range, similar as previously reported.11,13,28-30 The inset equivalent circuit in Fig. 9a is used to fit the Nyquist plots. The semicircle in the high frequency range (>20 Hz) can reflect the impedance (R_{sf}) for Li⁺ ion migration through the solidelectrolyte interphase (SEI) films which occur both on the cathode and Li anode,^{31,32} where the frequencies are shown as labelled. Considering that the same electrolyte and highlypurity Li metal were used, the differences on the SEI film impedances are attributed to the different LiCoO₂ cathodes. The semicircle in the medium frequency range and the inclined line represent the charge transfer impedance (R_{ct}) and the Warburg impedance (W), respectively. In Fig. 9a, the Al_2O_3 modified LiCoO₂ exhibits the higher interface impedance than

the pristine LiCoO₂, which is consistent with previous literatures.⁶ However, both the MgO and MgAl₂O₄-modified LiCoO₂ samples have the slightly smaller interface impedance than the pristine LiCoO2. The difference on the interface impedances is one of the main reasons for the difference on the capacity of the modified or unmodified LiCoO₂ cathode materials, as proposed previously.^{3,29} After 70 cycles (Fig. 9b), the Al₂O₃ and MgAl₂O₄modified LiCoO₂ samples experience negligible increases on the interface impedance as well as the charge transfer impedance. These results strongly suggest that both the Al₂O₃ and $MgAl_2O_4$ modifications are so stable that the oxidation decomposition of the electrolyte on the charged LiCoO₂ can be effectively suppressed and the structure of LiCoO₂ bulk keeps stable. However, the MgO-modified LiCoO2 shows a distinct increase on interface impedance, even though its increase is not as rapid as that of the pristine LiCoO₂. Moreover, the full plot parts of the pristine and the MgO-modified LiCoO₂ samples in the inset of Fig. 9b (the region with low impedance values) mean much higher charge transfer impedances than the Al₂O₃ and MgAl₂O₄-modified LiCoO₂ samples. That means the MgO surface modification could not essentially stabilize the surface structure of the LiCoO₂ against the electrolyte at high-voltage cycling. Herein, the charge transfer impedances are not discussed. Nevertheless, the change on the interface impedances of various LiCoO₂ samples are in consonance with their cycling stabilities shown in Fig. 7. In summary, the MgAl₂O₄ modification has the combined advantages on the high conductivity of the MgO modification and excellent stability of the Al₂O₃ modification.

Conclusions

Spinel MgAl₂O₄ modification has been successfully carried out on the surface of LiCoO₂ cathode material, and the modification layer is conformal and fairly uniform. The MgAl₂O₄ modification layer shows the positive effects of combining the Al₂O₃ modification on the cycling stability and the MgO modification on the conductivity. Therefore, the MgAl₂O₄-modified LiCoO₂ exhibits excellent cycling stability and rate capability at high voltages up to 4.5 V. Such results indicate that the MgAl₂O₄ spinel is a good modification material for LiCoO₂ cathode for high-voltage Li ion batteries.

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