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Electrochemical Performance Improvement of Li_2MnO_3 Cathode Materials by MgF_2 Coating

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Abstract: Cathode material Li_2MnO_3 has received more and more attention owing to its high theoretical capacity (459 $mAh \cdot g^{-1}$). However, the low initial coulombic efficiency and the poor cycle stability hamper its practical application in lithium-ion batteries. Herein, we investigated the crystal structure and electrochemical performance of Li_2MnO_3 by introducing MgF_2 coating layer. The results indicated that the conversion of partial layer Li_2MnO_3 to spinel phase induced by MgF_2 coating could reduce the initial irreversible capacity and improve the first cycle efficiency. The initial coulombic efficiencies of the 0.5wt.%, 1.0wt.%, and 2.0wt.% MgF_2-coated electrodes were 70.1%, 77.5% and 84.9%, respectively, compared with 57.7% of the pristine cathode. The charge-discharge curves showed that the 1.0wt.% MgF_2-modified Li_2MnO_3 delivered the highest charge and discharge capacities, and exhibited the best cycle stability. The capacity retention rate of the 1.0wt.% MgF_2-coated sample was 81% after the 40th cycles, which was much higher than that of the pristine sample (53.6%). The electrochemical impedance spectroscopic data revealed that the MgF_2 coating reduced the rapid deposition of the resistive component and improved the cycle stability of the electrodes.

Key words: Li_2MnO_3 cathode; MgF_2 coating; cycle stability; coulombic efficiency
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Lithium-ion batteries have been regarded as the most promising electrochemical energy storage system, and used in electric vehicles and portable electronic devices[1-3]. In order to meet the requirement of high energy density, the development of cathode materials with superior electrochemical performance and environmental friendly has become the focus of lithium-ion batteries[4-7]. Manganese (Mg)-based lithium (Li)-rich layered compounds as cathode materials are safer, less toxic and cheaper than cobalt (Co) or nickel (Ni)-based layered compounds. Therefore, Mg-based Li-rich layered compounds have received more attention as cathode materials in lithium-ion batteries[8-11]. The Mg-based Li-rich layered compound is characterized by an irreversible high voltage platform above 4.5 V during the first charge. This platform is formed by the removal of "Li_2O" from Li_2MnO_3[12-13]. Mg-based Li-rich layered compounds have high initial discharge capacity owing to the activation of Li_2MnO_3, but the cycle performance is poor. Therefore, it would be beneficial to understand the properties of this type layered compound by re-examination in the properties of the Li_2MnO_3 material.

The main problem with Li_2MnO_3 is the poor electronic conductivity and the irreversible loss of oxygen, making the structure unstable. Oxygen release during the first charging process results in an irreversible structural change that reduced the coulombic efficiency of the first cycle and accelerated the capacity decay during cycling[14]. The common methods of improving Li_2MnO_3 performance are surface coating and element doping. Yanhong Xiang[15] synthesized the $Li_2Mn_{0.9}Al_{0.1}O_3$ compounds. The results showed that the doping of Al could slow the capacity decay and improve the rate performance. However, Loraine Torres-Castro[16] used Al instead of the Li site to imoprove the properties of the Li_2MnO_3 material. The data showed that the spinel phase was gradually

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formed with the increase of Al content, and the binding energy of the sample was decreased, which improved the electrochemical properties of the material. Toshiyuki Matsunaga[17] prepared Ni-doped Li_2MnO_3 materials. With the increasing of Ni metal, the number of active Li ions increased, which resulted in high charge and discharge capacities. Lilong Xiong et al. used Na-doped[18] or Mg-doped[19] Li-site to modify Li_2MnO_3 cathode. They deemed that Na or Mg doping could significantly improve the cycle stability and rate performance of the material. In addition, the Mg modification brought the energy density of the Li_2MnO_3 material to a new height (944 $Wh \cdot kg^{-1}$) compared with 747.1 $Wh \cdot kg^{-1}$ of Li_2MnO_3 without Mg modification. Surface modification can hinder the reaction between electrolyte and electrode, alleviate the rapid growth of the unfavorable solid electrolyte interphase (SEI) film, and improve the electrochemical performance. Hui Liu[20] investigated surface-modified $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ materials with NH_4HF_2 coating, indicating that this coating caused chemical precipitation of Li in Li_2MnO_3 material. This method effectively enhanced the electrochemical properties of Li-rich Mn-based materials. Yang-Kook Sun[21] prepared AlF_3-coated $Li[Li_{0.19}Ni_{0.16}Co_{0.08}Mn_{0.57}]O_2$. The results indicated that a part of Li_2MnO_3 in the material was converted into spinel structure, which effectively improved the electrode rate performance and lithium storage capacity.

Usually, MgF_2 is stable in the electrolyte of lithium-ion batteries. Here, we report that the improved electrochemical performance of Li_2MnO_3 materials by surface modification. In this work, Li_2MnO_3 samples with the surface-coated MgF_2 were prepared in an attempt to improve the cycle stability. The role of MgF_2 coating in the electrochemical performance of Li_2MnO_3 at room temperature has been investigated.

1 Experimental

1.1 Reagents and Instruments

The reagents used in this work and their parameters are listed in Tab. 1.

Tab. 1 Main chemical reagents

Reagent	Purity	Manufacturer
$LiCH_3COO \cdot 2H_2O$	AR	Aladdin
$Mn(CH_3COO)_2 \cdot 4H_2O$	AR	Aladdin
$MgCl_2$	AR	Aladdin
NH_4F	AR	Aladdin
$C_6H_8O_7 \cdot H_2O$	AR	Aladdin

The names, models and sources of the equipments involved in this work are listed in Tab. 2.

1.2 Experimental Method

The pristine Li_2MnO_3 sample was synthesis by solgel method. Stoichiometric amounts of $LiCH_3COO \cdot 2H_2O$ and $Mn(CH_3COO)_2 \cdot 4H_2O$ were dissolved in deionized water to form metal ions solution. The citric acid solution was added to the above metal ions solution with constant stirring, and then this mixed solution was evaporated at 80 °C to obtain a viscous gel. Next, the gel was dried completely at 120 °C for 10 h. Finally, the resultant precursor was heated to 500 °C for 4 h. To prepare the MgF_2-coated Li_2MnO_3, NH_4F and $MgCl_2$ were dissolved in deionized water,

Tab. 2 Main instruments

Name	Model	Factory
Electronic balance	ALC-210.4	ACCULRB sartorius group
Blast drying oven	101	Beijing Guangming Medical Co., Ltd.
Tube furnace	TCW-32B	Yixing Opry Furnace Industry
Magnetic heating stirrer	DF-101S	Zhengzhou Changcheng Branch Industry and Trade Co., Ltd.
LAND test system	CT2001A	Wuhan Landian Electronics Co., Ltd.
Electrochemical workstation	CHI660A	Shanghai Zhenhua Instrument Company

respectively. Afterwards the obtained Li_2MnO_3 powder was added in the $MgCl_2$ solution, and then the NH_4F solution was added with continuous stirring. The weight ratios of MgF_2 to Li_2MnO_3 powder were 0.5%, 1.0%and 2.0%, respectively. The solution was dried at 80 °C in an oven. The obtained MgF_2-coated Li_2MnO_3 powder was heated at 400 °C for 3 h in air.

The phase structure was analyzed by X-ray diffraction (XRD) using Cu K_α radition. The scanning range was $10° \leqslant 2\theta \leqslant 80°$ and the scanning rate was $8° \cdot min^{-1}$. Scanning electron microscope (SEM) was used to analyze the morphology and particle size of the samples. Energy-dispersive spectroscope (EDS) was employed in combination with SEM to roughly determine the element content of powder. The active material was mixed with polyvinylidene fluoride and conductive carbon black in a mass ratio of 80:10:10 and stirred with N-methylpyrrolidone to form slurry. The slurry was coated into the Al foil current collector and dried thoroughly at 80 ℃ in an oven. The CR2032 type cells consisted of Li metal anode and cathode separated by a polypropylene film were assembled in an argon-filled glove box. The electrolyte solution was 1 $mol \cdot L^{-1}$ $LiPF_6$-DMC/EC (1:1 by volume) that purchased from DouDou Chemical Company. The charge-discharge measurements were carried out in LAND CT2001A test system in the voltage range from 2.0 to 4.8 V. The data of electrochem ical impedance spectroscope (EIS) was collected on an electrochemical workstation in the frequency range from 100 kHz to 0.1 Hz.

2 Results and Discussion

The XRD patterns of the MgF_2-coated and pristine Li_2MnO_3 materials are shown in Fig. 1. The characteristic peaks of all the samples were basically consistent with the standard lines of the monoclinic layered structure Li_2MnO_3 (PDF No. 84-1634, space group C2/m). As can be seen in Fig. 1, the 1.0wt.% and 2.0wt.% MgF_2-coated materials had the characteristic peak belonging to spinel structure around 37°, indicating that the MgF_2 coating induced the transformation of Li_2MnO_3 from layered structure to spinel structure. No diffraction peaks associated with MgF_2 were observed in the MgF_2-coated Li_2MnO_3 samples, indicating that this coating layer was not presented as a crystalline phase. This might probably be caused by the low heat treating temperature of 400 °C, which is not sufficient for MgF_2 to form a crystalline coating layer[22-23].

The morphology and particle size of the MgF_2-coated and pristine Li_2MnO_3 particles are shown in Fig. 2. Evidently, the surface morphology of the Li_2MnO_3 partic les modified by MgF_2 was changed. With the increasing amount of MgF_2, most of the surfaces were covered by the coating film. The

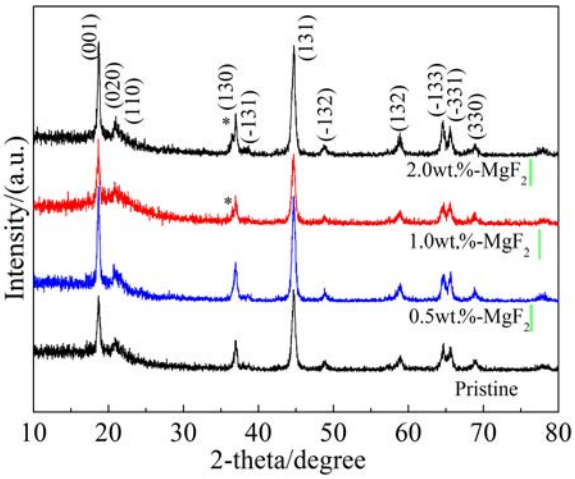

Fig. 1 X-ray diffraction patterns of the pristine and different MgF_2-coated Li_2MnO_3 samples

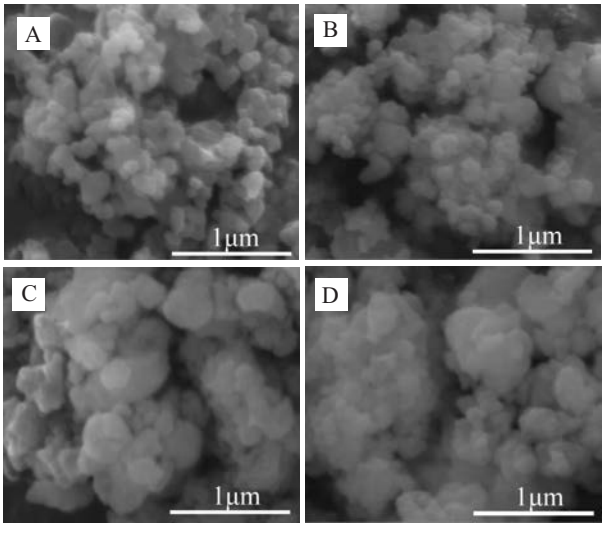

Fig. 2 SEM images of (A) the pristine, (B) 0.5wt.%, (C) 1.0wt.%, and (D) 2.0wt.% MgF_2-coated Li_2MnO_3 samples

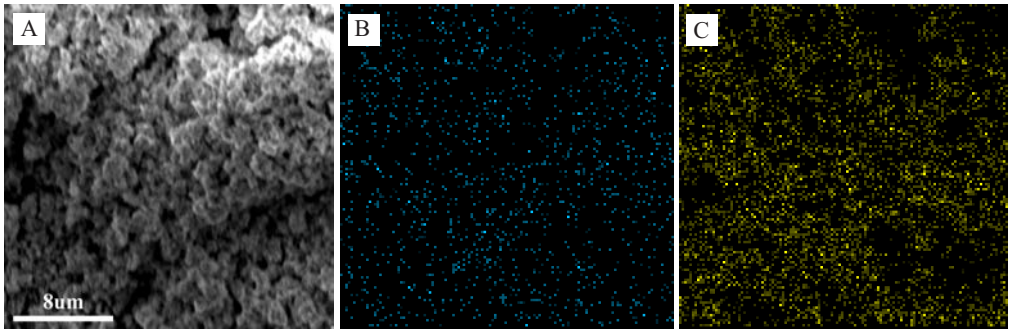

Fig. 3 SEM image (A) and the corresponding EDS mapping images of 1.0wt.% MgF_2-coated Li_2MnO_3 for (B) Mg and (C) F elements

MgF_2-coated particles tended to aggregate to form large particles, and the corners and edges became blurred. The MgF_2 coating could inhibit the contact between the electrolyte and the particles, and prevent the dissolution of Mn^{3+}. Fig. 3(B-C) displays the EDS mapping images of 1.0wt.% MgF_2-coated sample from Fig. 3(A). It can be seen from Fig. 3(B-C) that Mg and F elements were uniformly distributed in the surface. As shown in Fig. 4, the 1.0wt.% MgF_2-coated Li_2MnO_3 surface (A) revealed a uniform film compared to the pristine sample surface (B), confirming that the surface of Li_2MnO_3 was successfully coated with MgF_2 film.

Fig. 5(A) exhibits the initial charge-discharge curves of the pristine and MgF_2-coated Li_2MnO_3 cathodes at 0.1 C (20 $mA \cdot g^{-1}$) rate. Similar to the previously reported Li_2MnO_3 electrode, all the samples showed a significant charging platform around 4.5 V, which corresponds to the "Li_2O" extraction from the Li_2MnO_3 lattice structure[12-13]. However, the width of this platform was decreased as the amount of MgF_2 coating increased, and when the amount of MgF_2 coating increased to 2.0wt.%, the electrode had a very short voltage platform and capacity was only 129 $mAh \cdot g^{-1}$. In addition, the modified sample showed a voltage platform at 2.8 V, which is feature of the spinel phase ($LiMn_2O_4$)[24-25], and the platform became more and more obvious as the amount of MgF_2 coating increased. It indicates that the MgF_2 coating induced the transition of the layered structure to the spinel structure, agreed with the XRD data.

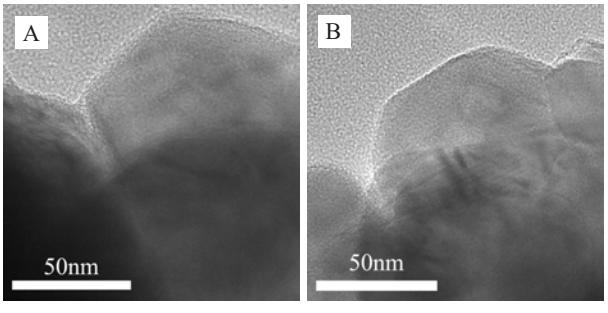

Fig. 4 TEM images of (A) the pristine Li_2MnO_3 and (B) 1.0wt.% MgF_2-coated Li_2MnO_3

The cycle performance curves of the MgF_2-coated and pristine Li_2MnO_3 cathodes are presented in Fig. 5(B). As we can see from the discharge curve, there was a sequential phase transformation: monoclinic C2/m → tetragonal I41 → cubic spinel[26]. It was clear from Fig. 4(B) that the capacity retention rate of the MgF_2-modified electrode was higher than that of the pristine electrode. Capacity retention values were 65% for 0.5wt.%, 81% for 1.0wt.%, and 72.2% for 2.0wt.% MgF_2-modified cathodes, compared with 53.6% for the pristine cathode. In addition, owing to the formation of a large number of spinel phases, the discharge capacity tended to be increased and then decreasd as the amount of MgF_2 increased. The reason why the cycle performance of the MgF_2-modified electrodes was enhanced is that the spinel structure might be stably circulated[27] and the MgF_2 coating could avoid the contact between the electrolyte and the particles[28].

Tab. 3 presents the initial capacity and coulom

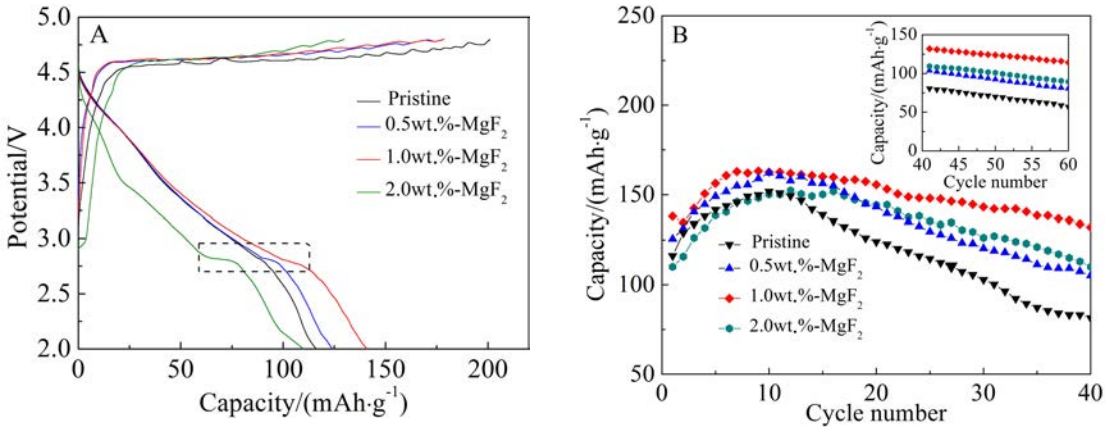

Fig. 5 (A) The initial charge-discharge curves and (B) the cycle performance curves of the pristine and MgF_2-coated Li_2MnO_3 samples

bic efficiency for the MgF_2-coated and pristine Li_2MnO_3 electrodes. Compared with the pristine electrode, the 0.5wt.% and 1.0wt.% MgF_2-coated electrodes exhibited an increased discharge capacity, that may be owing to the combination of the stabilized electrolyte/cathode interface and partial spinel structure induced by MgF_2 coating. As the amount of MgF_2 increased, the first cycle efficiency increased gradually. The first cycle efficiencies of different modified electrodes were higher than that of the pristine electrode. During the first charging period, the "Li_2O" which was removed from the Li_2MnO_3 above 4.5 V could not be re-inserted, resulting in irreversible capacity loss. The conversion of partial Li_2MnO_3 induced by MgF_2 coating to $LiMn_2O_4$ might reduce the initial irreversible capacity and improve the first cycle efficiency.

As shown in Fig. 6, three consecutive cyclic voltammograms of the pristine Li_2MnO_3 and MgF_2-coated Li_2MnO_3 electrodes were obtained at a scanning rate of 0.1 mV·s^{-1}. During the initial charging of the pristine Li_2MnO_3 sample, no anodic peak was observed around 4.0 V. However, this characteristic peak of spinel phase ($LiMn_2O_4$) appeared in the subsequent cycle with the weak intensity. Contrastly, the characteristic peak of spinel phase was observed at the first cycle as the MgF_2 amount increased, indicating that this coating could induce a phase transition from layer to spinel[18,29]. The oxidation peak around 4.5 V was connected to the removal of "Li_2O" from the Li_2MnO_3 material. Owing to the formation of layered $LiMnO_2$ ($Li + MnO_2 \rightarrow LiMnO_2$), a cathodic peak around 3.2 V was observed during the discharging for all the samples[30]. A reduction peak at 2.8 V, which is feature of the spinel phase[20-21], was observed, and its intensity gradually became stronger with the increasing MgF_2 amount, which is consistent with the evolution of the discharge platform.

Tab. 3 Initial charge and discharge capacities, and the first cycle efficiency of the pristine and MgF_2-coated Li_2MnO_3 electrodes cycled between 2.0 and 4.8 V at a current density of 20 mA·g^{-1}

Li_2MnO_3 sample	Charge capacity/(mAh·g^{-1})	Discharge capacity/(mAh·g^{-1})	First cycle efficiency/%
Pristine	200.9	116.1	57.7
0.5wt.%-MgF_2	178.2	125.6	70.1
1wt.%-MgF_2	178.5	138.2	77.5
2wt.%-MgF_2	129.7	110	84.9

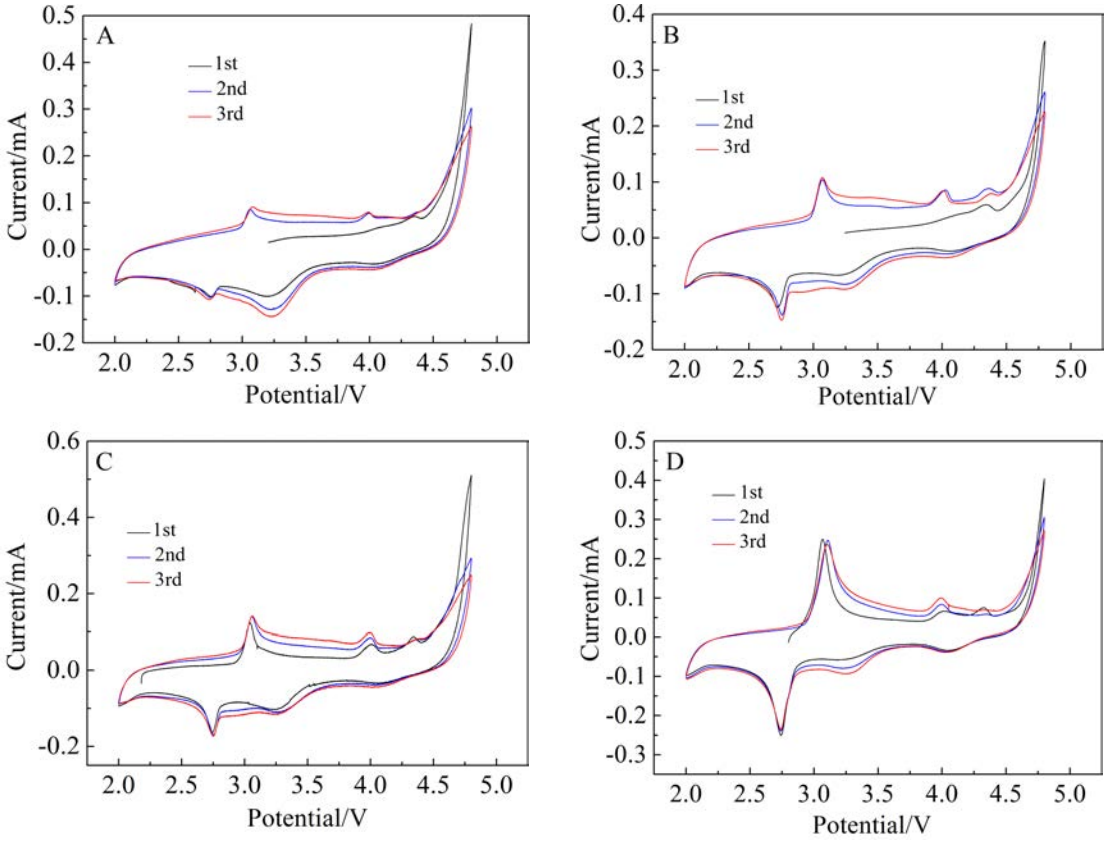

Fig. 6 Cyclic voltammograms of (A) Li_2MnO_3, (B) 0.5wt.%MgF_2-Li_2MnO_3, (C) 1.0wt.%MgF_2-Li_2MnO_3 and (D) 2.0wt.%MgF_2-Li_2MnO_3 in the voltage range of 2.0 ~ 4.8 V with a scan rate of 0.1 mV·s^{-1}

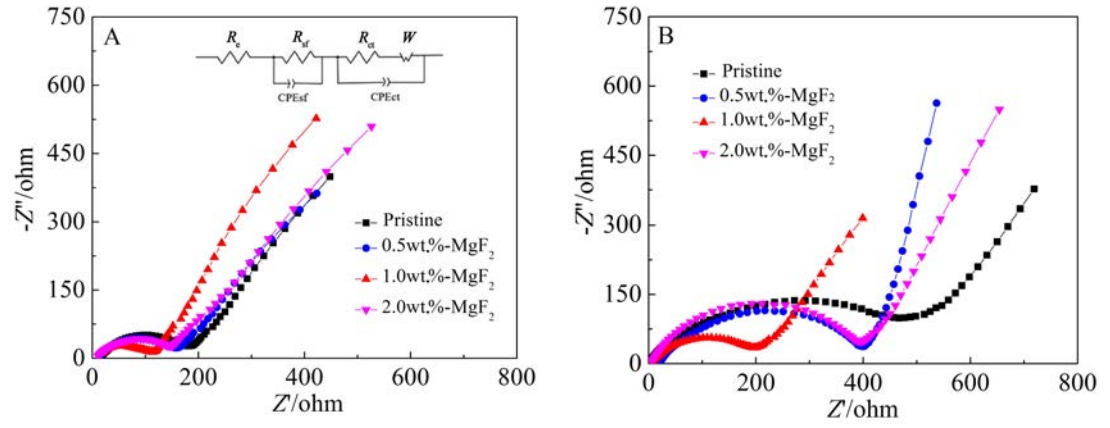

Fig. 7 Nyquist plots of the pristine and MgF_2-coated Li_2MnO_3 samples: (A) before the cycle and (B) after the 40th cycle

The alternating current (AC) impedance spectra of the MgF_2-coated and pristine Li_2MnO_3 electrodes, and the equivalent circuit are presented in Fig. 7. In the equivalent circuit (the inset in Fig. 7(A)), W, R_e, R_{ct} and R_{sf} represent the Warburg impedance of lithium ion diffusion, the resistance of liquid electrolyte, charge transfer resistance and electrode surface film resistance, respectively. The semicircle in the high frequency region of Nyquist plot could elucidate R_{sf}, and the fitted values are compared in Tab. 4. As we can see from Tab. 4, the MgF_2-modified electrodes showed lower R_{sf} value than the pristine electrode before the cycle. However, the R_{sf} value of the pristine electrode increased significantly faster than those of

Tab. 4 The fitted R_{sf} values of the pristine and MgF_2-coated Li_2MnO_3 electrodes

R_{sf}	Pristine	0.5wt.%-MgF_2	1wt.%-MgF_2	2wt.%-MgF_2
0	180.8	157.8	108	146
40th	424.9	406.3	195.4	352.2

the MgF_2-coated electrodes after the 40th cycles, indicating that MgF_2 coating could reduce the interface impedance. Since the MgF_2 coating alleviated the rapid growth of the SEI film[31-32], thereby, enhancing the cycle stability of the modified material.

3 Conclusions

The pristine and MgF_2-coated Li_2MnO_3 electrodes were prepared by the sol-gel method. The results showed that the presence of MgF_2 coating could induce the partial layer structure of the material to the spinel structure, which improved the initial coulombic efficiency and cycle stability of the Li_2MnO_3 material. The capacity retention rate of the 1.0wt.% MgF_2-coated Li_2MnO_3 sample reached 81% after the 40th cycles, while that of the pristine Li_2MnO_3 sample was only 53.6%. In addition, this coating could prevent the Li_2MnO_3 particles from directly contacting the electrolyte, reducing the dissolution of Mn^{3+} and the oxidation of the electrolyte. The results presented in this work suggested that the MgF_2 surface modification might be practically applicable to lithium-rich layered compounds to improve their electrochemical performance.

Acknowledgements

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富锂层状正极材料 Li_2MnO_3 的表面改性及其电化学性能研究

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摘要: Li_2MnO_3 正极材料具有较高的理论容量(459 $mAh\cdot g^{-1}$),不仅安全无毒还能够大大降低电池的制造成本,从而受到越来越多的关注. 然而,较低的首圈库仑效率和较差的循环性能妨碍了其在锂电池中的实际应用. 在此,作者研究了 MgF_2 涂层对 Li_2MnO_3 正极材料的电化学性能. 结果表明,MgF_2 涂层诱导部分层状 Li_2MnO_3 向尖晶石相转化,从而降低了首圈不可逆容量,提高库仑效率. 重量比为 0.5%、1.0%和 2.0%的 MgF_2 涂层电极的初始库仑效率分别为 70.1%、77.5%和 84.9%,而原始电极仅为 57.7%. 充放电曲线表明,1.0wt.%MgF_2 涂层改性的 Li_2MnO_3 具有最高的充放电容量和最佳的循环稳定性. 40 个循环后1.0wt.%MgF_2 涂层样品的容量保持率为 81%,远高于原始样品的容量保持率(53.6%). 电化学阻抗谱结果表明 MgF_2 涂层减少了不利成分的快速沉积,并改善了电极的循环稳定性.

关键词: Li_2MnO_3 正极材料;氟化镁涂层;循环稳定性;库仑效率