



Short communication

Electrochemical performance of SrF₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cathode materials for Li-ion batteriesJiangang Li^a, Li Wang^b, Qian Zhang^a, Xiangming He^{a,b,*}^a School of Chemical Engineering, Beijing Institute of Petrochemical Technology, Beijing 102617, PR China^b Institute of Nuclear & New Energy Technology, Tsinghua University, Beijing 100084, PR China

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ABSTRACT

SrF₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cathode materials with improved cycling performance over 2.5–4.6 V were investigated. The structural and electrochemical properties of the materials were studied using X-ray diffraction (XRD), scanning electron microscope (SEM), charge–discharge tests and electrochemical impedance spectra (EIS). The results showed that the crystalline SrF₂ with about 10–50 nm particle size is uniformly coated on the surface of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ particles. As the coating amount increased from 0.0 to 2.0 mol%, the initial capacity and rate capability of the coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ decreased slightly owing to the increase of the charge-transfer resistance; however, the cycling stability was improved by suppressing the increase of the resistance during cycling. 4.0 mol% SrF₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ showed remarkable decrease of the initial capacity. 2.0 mol% coated sample exhibited the best electrochemical performance. It presented an initial discharge capacity of 165.7 mAh g⁻¹, and a capacity retention of 86.9% after 50 cycles at 4.6 V cut-off cycling.

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1. Introduction

Recently, LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ has been considered to be one of the most attractive cathode materials due to its high capacity, safety and low cost. It presents a high specific capacity of ~160 mAh g⁻¹ over 2.5–4.4 V, moderate thermal behavior at charged state, and good cycleability even at 5 C rate [1–4]. In addition, the high power pulse capability and the accelerated aging test of C/LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cells show that LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ is more suitable for lithium-ion batteries in the HEV application [4].

When charged up to 4.6 V, LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ can deliver a capacity of ~184 mAh g⁻¹, however its capacity fading becomes more serious than that over 2.5–4.4 V [5]. In addition, our experiment showed that when charged up to 4.6 V, the C/LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cell swelled markedly due to more gas generation. The electrolyte decomposition is speculated to be main reason for the deteriorated performance.

The surface coating has been proved to be an effective method to reduce the electrolyte decomposition on surface of cathode materials. Metal oxides, such as Al₂O₃, ZrO₂, ZnO, TiO₂ and SiO₂, have

been reported to be effective materials for this purpose for the coating of LiMn₂O₄, LiCoO₂, LiNiO₂ etc. [6–14]. To improve the cycling performance, the surface treatment of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ with TiO₂ has been investigated in our previous study [15]. Most of the metal oxides coating materials such as Al₂O₃, ZrO₂, ZnO and SiO₂, cannot remain stable under the corrosion of HF [16–18]. Considering that the Al₂O₃ coating layer acted as a HF scavenger, which leads to the less decomposition of the cathode particle by forming AlF₃ on the surface of Al₂O₃ coating layer, Sun et al. [17] firstly reported the effect of surface modification of LiCoO₂ by AlF₃ on electrochemical performance at higher cut-off voltage up to 4.5 V. The AlF₃ coating layer, which reduces the formation of LiF films that increases the cathode/electrolyte interfacial impedance, suppresses Co dissolution by covering LiCoO₂ surface from HF attack, and improves the capacity retention of LiCoO₂ at 4.5 V cut-off cycling. AlF₃ coating for the improvement of the electrochemical properties of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ [18] and LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ [19] has also been reported. However, AlF₃ coating is carried out by precipitation method at 80 °C [17–19], and this is inconvenient. However, SrF₂, with better stability in HF, should be an alternative fluoride coating material, because SrF₂ coating by precipitation method can be carried out at room temperature due to its insolubility in cold water [16]. Our research showed that SrF₂ coating can improve the cycling performance of LiMn₂O₄ at elevated temperatures by reducing the electrolyte decomposition and also suppressing Mn dissolution by covering LiMn₂O₄ surface from HF attack [20].

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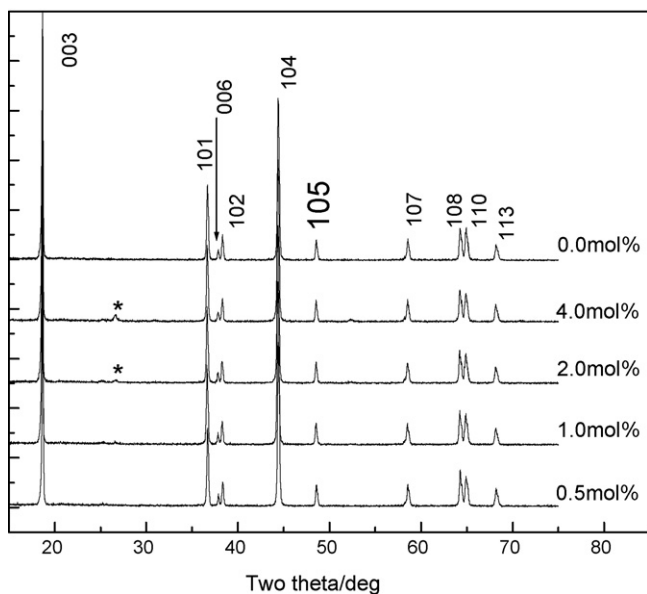


Fig. 1. XRD patterns of the SrF₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ samples (* SrF₂).

In this study, surface coating of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ by SrF₂ was attempted to improve the cycleability at 4.6 V cut-off cycling. The effect of coating amount on the structural and electrochemical performance of the spherical LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ was investigated.

2. Experimental

The spherical LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ was prepared by a controlled co-precipitation. To prepare the SrF₂-coated sample, as-prepared

LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ powders were suspended in the Sr(NO₃)₂ alcohol solution, followed by the addition of NH₄F alcohol solution with drops into the suspension solution. The molar ratio of Sr to F was fixed to 2 and the amounts of SrF₂ in the solution were set to 0.5, 1.0, 2.0, and 4.0 mol% of the LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ powders, respectively. After the solutions containing the cathode powders were constantly stirred at 60 °C for 2 h, the coated powders were filtrated and heated at 400 °C under N₂ for 5 h before further processing.

Powder X-ray diffraction (XRD7000) was used to characterize the structure of the powders. Particle morphology of the powders was observed using a scanning electron microscope (SEM; HITACHI-s3500). The electrochemical characterization was performed using CR2032 coin-type test cells. The cell consisted of a cathode with the composition of 88 wt.% active materials, 6 wt.% carbon black, and 6 wt.% PVDF, a lithium metal anode separated by a Celgard 2400 microporous film. The electrolyte was 1.15 mol L⁻¹ LiPF₆/EC+DMC+DEC (3:3:1, v/v/v). The charge–discharge tests were galvanostatically performed over 2.5–4.6 V at different current densities. The electrochemical impedance spectra (EIS) tests were conducted using electrochemical workstation (IM6ex) in the frequency range 100 KHz to 10 mHz with an ac signal amplitude of 5 mV.

3. Results and discussion

Fig. 1 shows XRD patterns of the pristine and SrF₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ powders. The pristine powders are confirmed to be well-defined single phase with order layered structure. The lattice parameters *a* and *c* of the sample are determined to be 2.860 and 14.249 Å, respectively. These data match well with the values observed by Ohzuku and Makimura (*a* = 2.867 Å and *c* = 14.246 Å) [1] and Shaju et al. (*a* = 2.864 Å and *c* = 14.233 Å) [2]. It is obvious that all of the SrF₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ samples show similar lines

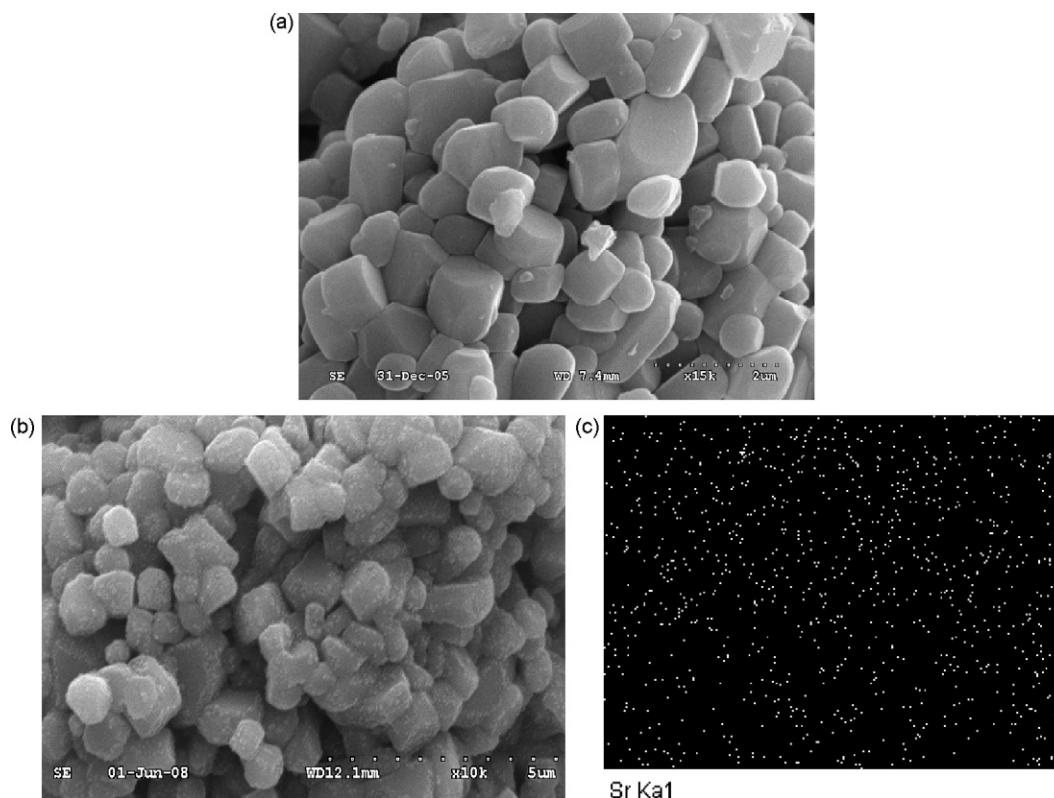


Fig. 2. SEM images of (a) pristine, (b) SrF₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ powders, (c) EDAX spectra dot map of Sr on the LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ particle.

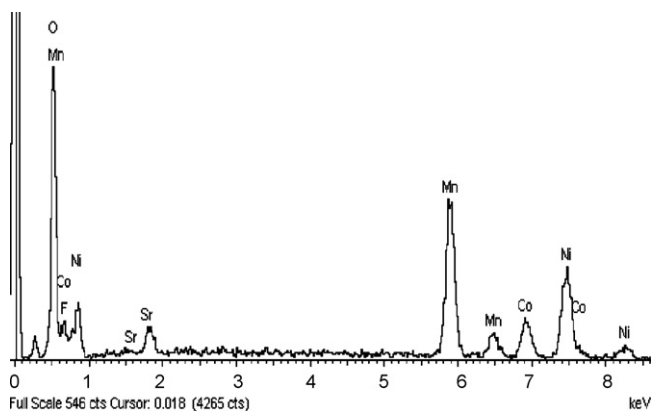


Fig. 3. EDAX spectrum of the SrF₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ powders.

as that of the pristine one. The SrF₂ lines can be detected when the coating amounts over 2.0 mol%. However, the lattice parameters of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ show no detectable changes before and after coating, indicative of that the coating does not affect the structure of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂, and SrF₂ exists as a separate crystalline phase on the LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ particle surface.

Fig. 2 shows the morphologies of the pristine and 2.0 mol% SrF₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ powders. The crystal faces and edges existing on the surface of the pristine LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ are very clear. In comparison, surface morphologies of the SrF₂-coated sample become smooth and blurry, and most of the crystal faces and edges are covered by fine SrF₂ particles with about 10–50 nm particle size. Fig. 2c clearly reveals that Sr is uniformly distributed on the surface of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ particles. Fig. 3 shows energy-dispersive analysis by X-ray (EDAX). It was also readily observed that Sr existed on the surface of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ particles.

Fig. 4 shows the first charge–discharge curves for the pristine and of SrF₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ electrodes over 2.5–4.3 V. The pristine spherical LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ presents a discharge capacity of 152.9 mAh g⁻¹. However, the discharge capacities of SrF₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ samples decrease as the coating amounts increase. They are 151.2, 148.3, 146.1 and 138.6 mAh g⁻¹ for 0.5, 1.0, 2.0 and 4.0 mol% SrF₂-coated samples, respectively. The discharge capacity decreases slightly with the increase of coating amount to 2 mol%, but decreases remarkably to 138.6 mAh g⁻¹ as the coating amount up to 4 mol%. In addition, SrF₂ coating also leads

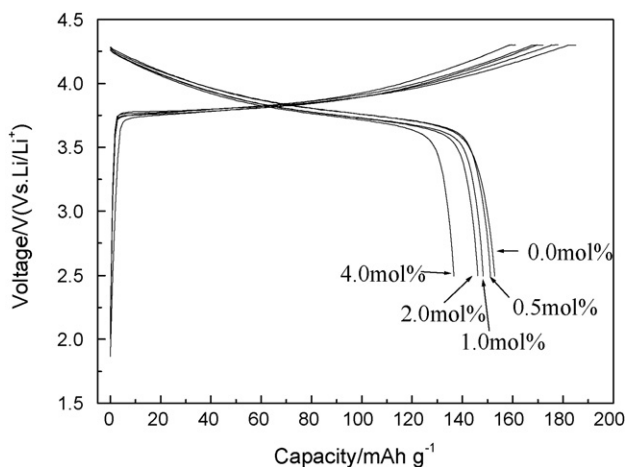


Fig. 4. The first charge–discharge curves for the pristine and various amounts of SrF₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ electrodes over 2.5–4.3 V.

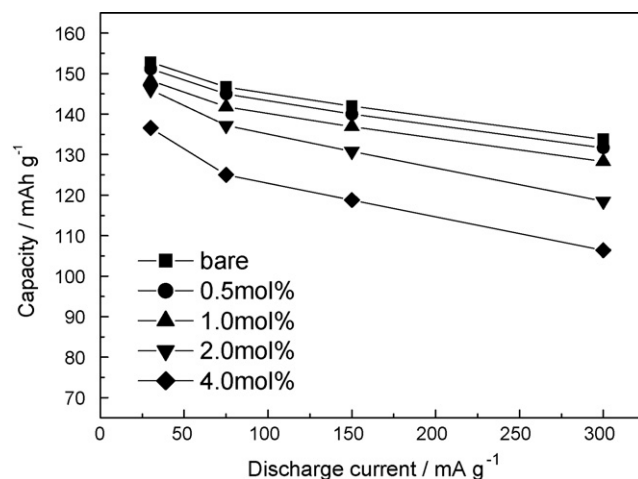


Fig. 5. The capacity as function of discharge current for the bare and various amounts of SrF₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ electrodes over 2.5–4.3 V.

to the reduction of the rate capability, as shown in Fig. 5. With the increase of the SrF₂ coating amount, the polarization (voltage difference between the charge and the discharge curves) increases. Because the SrF₂ is inactive, we speculate that the coating may increase the contact resistance of inter-particles and the charge-transfer resistance, leading to the decrease of the capacity and rate capability. Because the increase in polarization of the electrode is consistent with the decrease of discharge capacity and rate capability, we speculate that the decrease of discharge capacity and rate capability of SrF₂-coated samples is related to the increase of electrochemical resistance. Because of low capacity of 4.0 mol% SrF₂-coated sample, further studies on cycling performance is carried out only for 0.0–2.0 mol% SrF₂-coated sample.

With the increase of coating amount of SrF₂ from 0 to 2.0 mol%, the discharge capacity and rate capability of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ decrease slightly, but the cycleability of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ is improved, as shown in Fig. 6. When charge–discharged between 2.5 and 4.6 V for 50 cycles, the uncoated sample shows very fast capacity fading, and only 79.3% of its initial capacity remains. However, 2.0 mol% SrF₂-coated sample exhibits the best electrochemical performance. It presents an initial discharge capacity of 165.7 mAh g⁻¹, and a capacity retention 86.9% after 50 cycles.

In order to elucidate the change in electrochemical properties after SrF₂ coating, EIS analysis of the composite electrodes

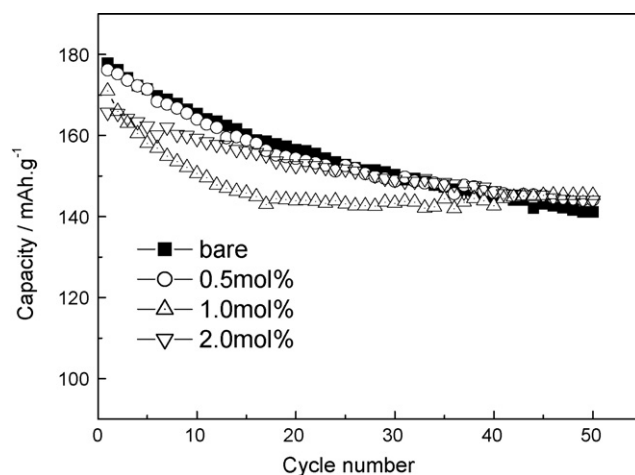


Fig. 6. Cycling performance of SrF₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ samples.

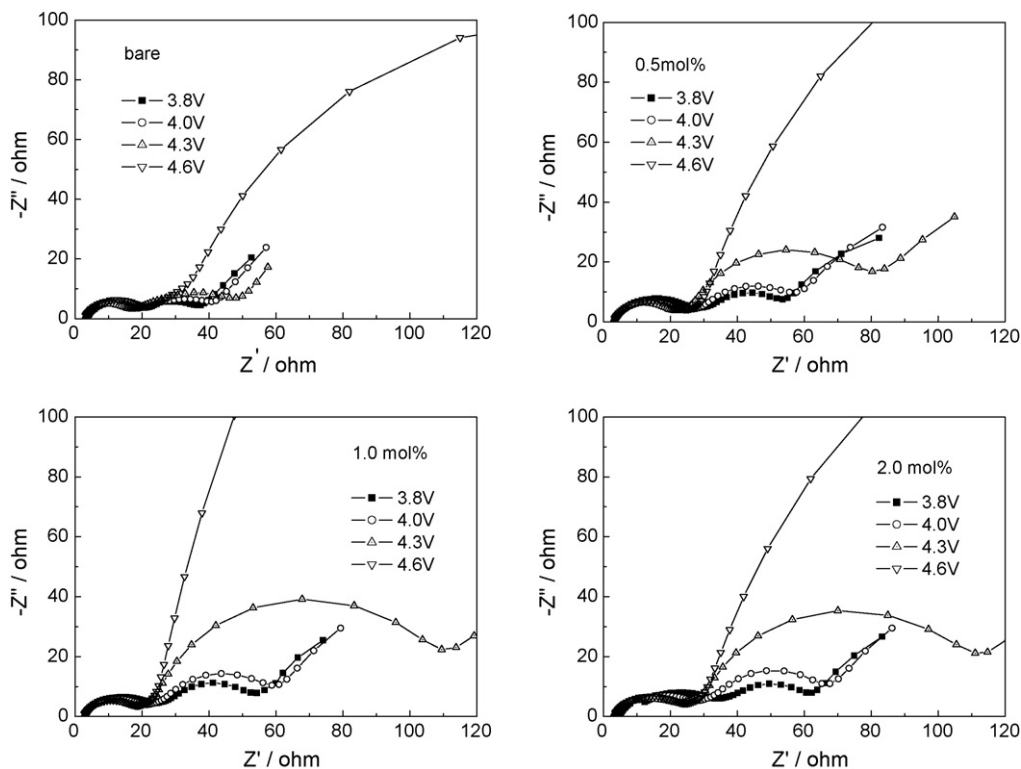


Fig. 7. EIS spectra of SrF₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ samples.

is carried out. Fig. 7 shows the Nyquist plots of the pristine LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ and the 0.5, 1.0 and 2.0 mol% SrF₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ samples at different charged state, respectively. A semicircle is observed for all samples in the high frequency domain, and its origin is ascribed to the lithium ion migration through the interface between the surface layer of the particles and the electrolyte. The calculated surface layer resistance (R_f) data are shown in Fig. 8. The increase of the coating amount leads to the increase of R_f in the case of below 4.3 V, which can be ascribed to the inactivity of the SrF₂. However, R_f changes from about 14 to 22.5 Ω for the pristine LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ when charged to 4.6 V. It is obviously larger than that of SrF₂-coated samples. The surface layer comes from the reaction between electrolyte and the

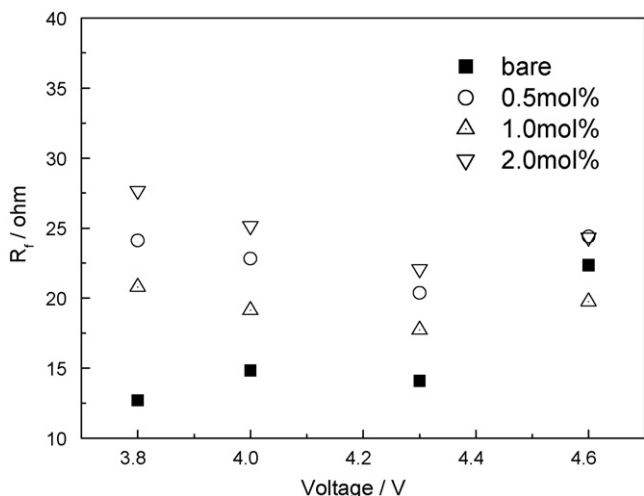


Fig. 8. Surface layer resistance (R_f) of SrF₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂.

electrode surface. The reaction can be accelerated at higher voltage due to instability of the delithiated electrode surface, and leads to the increase of R_f . Although the increase of R_f is not so big, the surface reaction between electrolyte solution and the electrode surface during long-term cycling still can lead to the worsening of the electrochemical properties of active electrode materials, because that common electrolytes in use today decompose at high voltages, forming insoluble products which exhaust Li⁺ content in electrodes, blocking the pores of the electrodes, resulting in the impedance increase and gas generation in the cell [21–24]. Fig. 9 shows the Nyquist plots of the pristine and 2.0 mol% SrF₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ charged to 4.6 V at the 2nd and 50th cycles. After 50 cycles, R_f resistance rises from 22 to 54 Ω for the pristine LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ electrode, while this resistance rises only from 24 to 39 Ω for the 2.0 mol% SrF₂-coated electrode. The results show that SrF₂ coating can reduce the surface reaction between electrolyte and the electrode surface during long-term cycling.

In addition, a depressed semicircle appears for all samples in the relatively low frequency region, whose origination could simply be assigned to the charge-transfer resistance (R_{ct}). It can be seen in Fig. 7 that SrF₂ coating layer has remarkable influence on the charge-transfer resistance. More the SrF₂ coating, more the R_{ct} increases. The SrF₂ coating increases the charge-transfer resistance, leading to the decrease of the capacity and rate capability of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂. Especially, as shown in Fig. 9, the increase in charge-transfer resistance of the pristine LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ at 4.6 V is much larger than that of 2.0 mol% SrF₂-coated sample during cycling. The charge-transfer resistance of the pristine LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ is about 300 Ω at 2nd cycle, but it dramatically increases to about 820 Ω at 50th cycle. On the other hand, the increase of R_{ct} for the 2.0 mol% SrF₂-coated electrode is unobvious during cycling. The results indicate that SrF₂ coating on the surface of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ can effectively suppress the increase of charge-transfer resistance during cycling in 2.5–4.6 V.

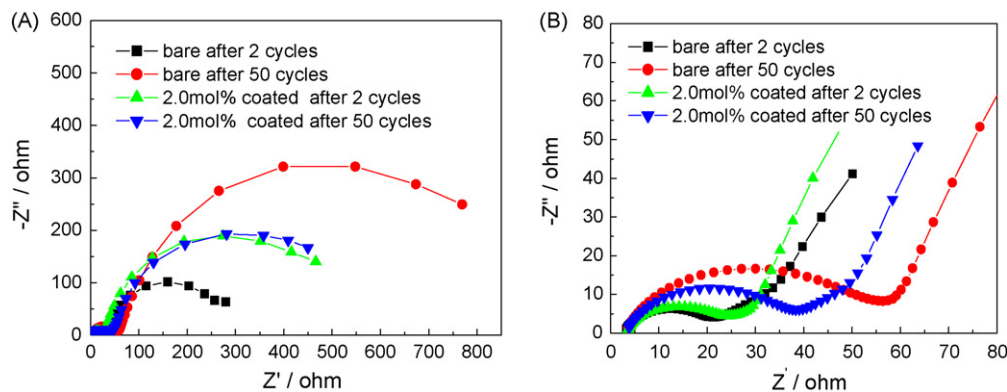


Fig. 9. EIS spectra of (A) bare and SrF₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ samples charged to 4.6 V at different cycles of the 2nd and 50th, (B) expanded view of (A).

The abrupt increase in charge-transfer resistance of the LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ during cycling has been reported, and considered as main reason for capacity fading [25,26]. ZrO₂ coating [25] and LiF addition [26] have been reported to effectively suppress the increase in charge-transfer resistance, and improve the cycling performance of LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂. The improved cycling behavior of the AlF₃-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ [18] and LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ [19] materials is also attributed to the stable interfacial resistance between the cathode and the electrolyte. Because AlF₃ is very resistant to HF solution, the reason for the stable interface between the cathode and the electrolyte is suggested to be that the AlF₃ coating layer acts as a stabilizer and hence protects the oxide structure from damage during long-term cycling. In this study, SrF₂ coating on the surface of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ can effectively suppress the increase of total resistance (especially in the charge-transfer resistance) during cycling in 2.5–4.6 V, which contributes to the improved cycling performance. It is speculated that the stable interface between the cathode and the electrolyte is also attributed to the SrF₂ coating layer acting as a stabilizer, because SrF₂ is also very resistant to HF solution. The stability of SrF₂ coating layer on improving the cycling performance of LiMn₂O₄ at elevated temperatures has been proved in our previous work [20].

4. Conclusions

SrF₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ were prepared at room temperature. The crystalline SrF₂ with about 10–50 nm particle size uniformly distributes on the surface of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ particles. The coating leads to the slight decrease of both initial capacity and rate capability owing to the increase in charge-transfer resistance, but it improves the cycling performance over 2.5–4.6 V by suppressing the increase of total resistance (especially in the charge-transfer resistance) during cycling. The study has demonstrated that 2.0 mol% SrF₂-coated sample exhibits the best electrochemical performance. It presents an initial discharge capacity of 165.7 mAh g⁻¹, and 86.9% of initial capacity retention after 50 cycles. Therefore, the electrochemical properties of a pristine LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cathode, which has many advantages over commercial LiCoO₂, can be further enhanced by a 2.0 mol% SrF₂ coating.

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