CaF$_2$-coated Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ as cathode materials for Li-ion batteries

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**Abstract**

Li-rich cathode material Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ is prepared by a sol–gel method and coated with CaF$_2$ layer via a wet chemical process. The pristine and CaF$_2$-coated samples are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). An amorphous nanolayer coating of CaF$_2$ is obtained on the surface of layered pristine material. The CaF$_2$-coated Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ material exhibits excellent electrochemical performance. The initial coulombic efficiency is enhanced to 89.6% with high initial discharge capacity of 277.3 mAh g$^{-1}$ after CaF$_2$ coating. Galvanostatic charge–discharge tests at 0.2 C display faster activation of Li$_2$MnO$_3$ phase and higher capacity retention of 91.2% after 80 cycles for CaF$_2$-coated material. Meanwhile it also shows higher rate capability with the capacity of 141.5 mAh g$^{-1}$ at the 3 C-rate and stable cyclic performance above 190 mAh g$^{-1}$ after 100 cycles at the 1 C-rate. The analysis of $dQ$/$dV$ plots and electrochemical impedance spectroscopy (EIS) indicates that the obvious improvement of CaF$_2$ coating is mainly attributed to the accelerated phase transformation from layered phase to spinel phase and stable electrolyte/electrode interfacial structure due to the suppression of the electrolyte decomposition.

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1. Introduction

Lithium ion battery with high energy density and high power density has been considered as the promising power sources for electric vehicles (EV) and hybrid electric vehicles (HEVs) [1,2]. However, the conventional cathode materials, such as LiCoO$_2$, LiMn$_2$O$_4$ and LiFePO$_4$, cannot meet the requirements of high energy density due to its limited specific capacity. Recently, Li-rich Mn-based layered solid-solution system Li$_2$Mn$_{2-y}$Ni$_y$O$_2$ (M = Co, Ni, Mn)$_{1/2}$Ni$_{1/2}$, Mn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$) has drawn much attention for its higher capacity over 250 mAh g$^{-1}$ with significantly reduced cost and toxicity compared to the LiCoO$_2$ cathode [3,4]. Different from conventional cathode materials, Li-rich cathode materials exhibit a long voltage plateau at about 4.5 V in the first charging process, corresponding to the delithiation process accompanied with oxidation of O$^2-$ and subsequent evolution of oxygen gas [5–7]. This process is regarded as the activation of electrochemical inactive Li$_2$Mn$_3$O$_5$ phase and responsible for the unusually high discharge capacity. However, several drawbacks hinder extensive commercial application of Li-rich cathode materials. The first problem is the huge irreversible capacity loss (ICL) in the first cycle which is attributed to the extraction of Li$_2$O followed by an elimination of the oxide ion vacancies from the structure during the first charge, leading to fewer insertion–extraction sites of lithium ions in the discharge process [8]. Furthermore, poor cyclic performance and rate capability due to complicated structural evolution and formation of solid–electrolyte interfacial (SEI) layer at higher potential are also practical problems to solve urgently.

One common approach to improve the electrochemical performance of the Li-rich cathode material is to modify the cathode surface with materials inert against the electrolyte. Surface modified (1–z)Li[Li$_{1/3}$Mn$_{2/3}$]O$_2$–zLi[Li$_{0.55}$Ni$_{0.35}$]Co$_{0.1}$O$_2$ with series of metal oxide, such as Al$_2$O$_3$, ZnO, ZrO, CeO$_2$, show lower ICL in the first cycle and higher discharge capacity than pristine samples [9]. Double-layer surface modified Li[Li$_{0.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$]O$_2$, reported by Manthiram, exhibits better rate capability and capacity retention [8,10]. In recent years, AlF$_3$ is considered to be one of the most promising coating materials to improve electrochemical performance of Li-rich cathode, due to its high stability [11–15]. The existence of the AlF$_3$ coating layer is believed to suppress the HF corrosion which is responsible for better cycle stability. Furthermore, it is also proposed that AlF$_3$ could induce the phase transformation of the Li-rich cathode, from layered phase to spinel phase, which is beneficial for rate performance [13]. In this paper, CaF$_2$ was first introduced and utilized as the coating material for Li-rich cathode Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ to further investigate the role of metal fluoride coating. Compared to AlF$_3$, CaF$_2$ shows better thermal stability and equally inert behavior in electrolyte
A comparison of pristine and CaF$_2$-coated Li-rich cathode Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ on structure and electrochemical performance was conducted. As cathode of lithium ion battery, the CaF$_2$-Coated Li-rich Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ demonstrates higher capacity retention, rate capability and more stable cyclic performance.

2. Experimental

2.1. Preparation and characterization

The Li-rich layered oxide, Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ was synthesized by a sol–gel process with citric acid as chelating agent. Stoichiometric amounts of Li(CH$_3$COO)$_2$·2H$_2$O, Ni(CH$_3$COO)$_2$·4H$_2$O and Mn(CH$_3$COO)$_2$·4H$_2$O were dissolved in distilled water and stirred continuously. The ratio of metal: chelating agent was 1:1. After adjusting the pH value to 7–8 with ammonium hydroxide, the solution was evaporated at 80 °C until a viscous violet gel emerged. The gels were then dried in a vacuum oven at 120 °C for 12 h. The precursor powders were decomposed at 450 °C for 5 h. The obtained powders were compressed in the form of circular pellets and calcined at 900 °C for 12 h in air to obtain the final product.

A chemical deposition method was used to obtain CaF$_2$-coated Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$. The as-prepared Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ powders was immersed in the Ca(NO$_3$)$_2$ dilute aqueous solution. Then the solution was heated to 80 °C and stirred vigorously. NH$_4$F dilute solution was then added into the solution drop by drop. The molar ratio of Ca to F was controlled to be 1:2, and the designed amount of CaF$_2$ was 2 wt.% of the Li-rich layered oxide. Continuous stirring was performed till the mixed solution was evaporated to dryness. The obtained powders were heated at 450 °C in the flowing nitrogen for 4 h to obtain the CaF$_2$-Coated Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$.

The structure of the as-prepared powders was confirmed by X-ray diffraction (XRD, Bruker D8 Advance, Cu Kα radiation, λ = 1.5406 Å) with a range of 2θ from 10° to 80° at a scan rate of 1 min$^{-1}$. The morphology and composition of the samples were investigated by scanning electron microscopy (SEM, JEOL JSM-6390) and field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800) equipped with an energy-dispersive X-ray spectrometer (EDX). The CaF$_2$ coating layer was analyzed by transmission electron microscopy (TEM, JEM-2100F).

2.2. Electrochemical measurements

The working electrodes were consisted of 70 wt.% as-prepared powders, 20 wt.% carbon conductive agents (super P) and 10 wt.% polytetrafluoroethylene (PTFE) and compressed onto the aluminum nets. The total mass of the active electrode material is about 4–5 mg and the electrode surface area is 0.785 cm$^2$ (Φ10 mm). The electrodes were dried overnight at 80 °C in a vacuum oven prior to use. The A metallic lithium foil was used as an anode, 1 M LiPF$_6$ in ethylene carbonate (EC)–dimethyl carbonate (DMC)–diethyl carbonate (DEC) (1:1:1 in volume) was used as the electrolyte, and a polypropylene micro-porous film (Celgard 2300) served as the separator. Coin-type (CR2032) half-cells were assembled in an argon-filled glove box (Mikrouna, Superstar 1220/750/900). The galvanostatic discharge–charge measurements were performed on battery test system (Land CT2001A, Wuhan Jinnuo Electronic Co. Ltd.) between 2.0 and 4.8 V (vs. Li$^+$/Li) at different rates at room temperature. EIS measurements were performed on an electrochemical workstation (CH Instrument 660A, CHI Company). Impedance spectra of the pristine and CaF$_2$-coated samples were tested at the open circuit potential before charge and after cycle test, respectively. The amplitude of the AC signal was 5 mV over a frequency range from 100 kHz to 10 mHz. The EIS results were simulated using ZPVIEW software.

3. Results and discussion

3.1. Structure and morphology of pristine and CaF$_2$-coated Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$

XRD patterns of pristine and CaF$_2$-coated Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ are shown in Fig. 1(a) and (b) respectively. All the diffraction peaks of both samples, except weak peaks between 2θ = 20–25°, are indexed to α-NaFeO$_2$ hexagonal type structure with a space group symmetry of R3 m. Clear separation of adjacent peaks of (006)/(012) and (108)/(110) indicates that the samples have a well crystalline layered structure. Weak peaks located between 2θ = 20–25° show the presence of monoclinic Li$_2$MnO$_3$ phase with a space group symmetry of C$\bar{2}$/m. These peaks are attributed to the short-range Li–Mn cation ordering in the transition metal layers [18,19]. The low intensity results from the disorder of LiMn$_6$ clusters with addition of Ni and Co [20]. There is no peak indexed to CaF$_2$ in XRD patterns, resulting from the low quantity and poor crystalline of coating CaF$_2$ material.

SEM images and EDX patterns are shown in Fig. 2. Both pristine and CaF$_2$-coated samples exist as particles of 200–400 nm with little agglomeration (Fig. 2(a) and (b)), indicating no difference in morphology after CaF$_2$ coating. At a high magnification, we can clearly see that the surface of CaF$_2$-coated samples becomes rough (Fig. 2(c)). In order to prove the homogeneity of the coating, EDS test is carried out on CaF$_2$-coated samples and the results show the presence of Ca and F elements besides O, Mn, Ni, Co elements (Fig. 2(d)).

Fig. 3 shows TEM images of pristine and CaF$_2$-coated samples. The pristine sample has a clear grain edge while the coated sample has a much rougher edge (Fig. 3(a) and (b)). Both samples exhibit continuous interference fringe spacing of 0.47 nm corresponding to the (001) and (003) lattice fringes of the monoclinic Li$_2$MnO$_3$ and hexagonal layered LiMO$_2$ phase. A clear boundary separates the 2–7 nm thick amorphous coating layer from the bulk crystalline phase in Fig. 3(d), indicating that CaF$_2$ coating was successful achieved on the surface of Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$.

3.2. Electrochemical properties of pristine and CaF$_2$-coated Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$

The initial galvanostatic charge–discharge profiles of pristine and CaF$_2$-coated Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ material at 0.05 C
Fig. 2. Low magnification SEM images of (a) pristine and (b) CaF$_2$-coated Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$; (c) high magnification SEM images and (d) EDX patterns of CaF$_2$-coated Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$.

Fig. 3. TEM images of (a) pristine and (b) CaF$_2$-coated Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ and HRTEM images of (c) pristine and (d) CaF$_2$-coated Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$.

$\text{(1 C = 250 mA g}^{-1}\text{)}$ are presented in Fig. 4. Both samples show a long plateau at about 4.5 V during the first charge process. The mechanism of the 4.5 V plateau is complicated and most researchers speculate that it is related to the removal of oxygen with further delithiation and migration of transition metal ions from the surface to the bulk [5,21]. The initial charge curve of CaF$_2$-coated sample shows a shorter plateau compared to pristine sample, leading to lower initial charge capacity (362.9 mAh g$^{-1}$ for pristine sample and 319.0 mAh g$^{-1}$ for CaF$_2$-coated sample). This can be attributed to the strong F–O bonds which suppress the oxygen
Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ at pristine and others, while inactive are decomposed on curves indexed to the spinel phase of lithium manganese oxide and the phase transformation from layered structure to spinel structure can increase initial coulombic efficiency, similar to AlF$_3$ coating effect reported by Sun et al. [13]. The results indicate that CaF$_2$ coating on Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ cathode material increases the initial coulombic efficiency and induces the phase transformation at a low current density.

The cyclic performances of pristine and CaF$_2$-coated samples are investigated at a higher current density of 0.2 C to suppress the decomposition of electrolyte. The first three discharge curves of both samples at 0.2 C are exhibited in Fig. 5. The charge processes are also performed at 0.2 C. The discharge capacity of both samples increase gradually during the first three cycles. This is attributed to the stretch of the plateau under 3.5 V, illuminating that it takes several cycles to activate the Li$_2$MnO$_3$ phase completely at 0.2 C. However, the changes of discharge capacity and discharge curves are steeper for pristine samples, showing more inactive component left after initial charge process. While for CaF$_2$-coated samples, the initial discharge capacity is much closer to the others, indicating that CaF$_2$ coating can accelerate the activation of Li$_2$MnO$_3$ phase during the initial charge process at a higher charge current density. The cyclic performances of both samples at 0.2 C are shown in Fig. 6. After a few activating cycles, the discharge capacity of both samples reaches the maximum, 259 mAh g$^{-1}$ for pristine Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ material and 250 mAh g$^{-1}$ for CaF$_2$-coated Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ material. Yet after 80 cycles the discharge capacity of the pristine material is only 155 mAh g$^{-1}$ while the CaF$_2$-coated material still has a discharge capacity of 228 mAh g$^{-1}$. The capacity retention rate with respect to the maximum of discharge capacity is 59.8% for pristine samples and 91.2% for CaF$_2$-coated samples. High capacity retention rate of fluoride-coated conventional layered cathode is usually attributed to the protection of coating layer which prevents the inner oxide from reacting with HF in the electrolyte. However, some researchers recently reported that AlF$_3$ coating on Li-rich cathode can have a great effect on the bulk structure of cathode, especially on the phase transformation [13,14]. Thus the mechanism of good cyclic performance of CaF$_2$-coated Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ could be more complicated. To compare the structural changes of both samples during galvanostatic charge-discharge tests at 0.2 C, corresponding differential capacity vs. voltage (dQ/dV) plots are shown in Fig. 7. The results indicate that CaF$_2$ coating can not only suppress the oxygen evolution during the initial charge process [22,23], but also enhance the discharge capacity and cycling stability of the Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ cathode material.
investigated. We choose the third cycle as reference to ignore the different activation rates during the initial two cycles. The \(dQ/dV\) plots of the third cycle are shown in Fig. 7(a). The peaks over 3.6 V are attributed to the oxidation and reduction of \(\text{Co}^{3+}/\text{Co}^{4+}\) and \(\text{Ni}^{2+}/\text{Ni}^{4+}\). The reduction of \(\text{Mn}^{4+}\) in the layered \(\text{MnO}_2\) component created after \(\text{Li}_2\text{MnO}_3\) activation occurs at 3.3–3.4 V. The plots of \(\text{CaF}_2\)-coated samples show a shift to lower potential at oxidation peaks and a shift to higher potential at reduction peaks, indicating a smaller polarization after \(\text{CaF}_2\) coating. The \(dQ/dV\) plots of the 50th cycle are presented in Fig. 7(b). The area under curves is much larger for \(\text{CaF}_2\) coated material, consistent with its good capacity retention. The intensity of reduction peak at about 3.3 V is decreased obviously and a new reduction peak appears below 3.0 V corresponding to spinel-like phase of lithium manganese oxide. This phenomenon keeps in line with the mechanism of phase transformation due to migration of transition metal ions from the transition metal layer to the lithium layer during cycles [24–27]. In the \(dQ/dV\) plot of \(\text{CaF}_2\)-coated sample, the new reduction peak is much stronger than the reduction peak at 3.3 V, indicating little layered phase of lithium manganese oxide left after 50 cycles. On the contrary, the reduction peak at 3.3 V remains stronger than the reduction peak below 3.0 V for pristine samples. The results illustrate that \(\text{CaF}_2\) coating could accelerate the phase transformation of activated \(\text{Li}_2\text{MnO}_3\) phase during charge-discharge processes. The faster phase transformation can be associated to the larger amount of inactive \(\text{O}_2\) molecules and more stable interfacial structure due to the presence of mitigating fluoride layer. Though the phase transformation is usually regarded as a drawback to cause capacity deterioration, some researchers consider spinel-like phase to be a framework structure for stable cycling [13,26]. However, the increase of spinel-like phase reduces the average discharge voltage, leading to lower power density and obvious hysteresis upon cycles in the full cell [28].

The comparison of high rate capability between \(\text{CaF}_2\)-coated and pristine samples is exhibited in Figs. 8 and 9. The cyclic performance at various rates from 0.1 C to 3 C for each 5 cycles are shown in Fig. 8. No major change in discharge capacity is observed at 0.1 C for both samples. Yet the capacity difference between the \(\text{CaF}_2\)-coated cathode and the pristine cathode increases gradually with the rate value. At the 3 C-rate, the discharge capacity of \(\text{CaF}_2\)-coated cathode is 141.5 mAh g\(^{-1}\) while that of pristine cathode is only 85 mAh g\(^{-1}\). The better cyclic stability for \(\text{CaF}_2\)-coated cathode at the 1 C-rate is exhibited in Fig. 10. The initial discharge capacity of \(\text{CaF}_2\) coated sample at 1 C reaches 216 mAh g\(^{-1}\) in contrast to 172 mAh g\(^{-1}\) for pristine sample. After 100 cycles, the discharge capacity of 191 mAh g\(^{-1}\) still remains for the \(\text{CaF}_2\)-coated sample. While for the pristine sample, the discharge capacity is lower than 130 mAh g\(^{-1}\) in the 100th cycle.

To investigate the origin of the improved electrochemical performance of \(\text{CaF}_2\)-coated sample, EIS patterns of both samples were performed. The measurements were carried out before charge and
after 30 cycles at 0.2 C. The experimental results were fitted with the equivalent circuits inset in Fig. 10. An intermediate-frequency semicircle and a low-frequency tail are observed in Fig. 10(a). The intermediate-frequency semicircle is related to charge-transfer resistance (Rct) while the low-frequency tail is associated with Li+ ion diffusion process in the solid phase of electrode. After 30 cycles, an additional high-frequency semicircle, ascribed to formation of the passivating surface film upon cycling, is observed in Fig. 10(b). The fitted results show obviously decreased Rct values after CaF2 coating. Before charge, the Rct value of pristine cathode is 154.8 Ω while the CaF2-coated cathode exhibits much smaller Rct value of 75.1 Ω. After 30 cycles, Rct values of both samples decrease dramatically, resulted from electrochemical activation [14,29,30]. The Rct value of pristine cathode is 44.6 Ω in contrast to 15.3 Ω for CaF2-coated cathode after cycle test. As mentioned above, CaF2 acts as a role of buffer layer to reduce the activity of extracted oxygen species. Consequently oxidation of electrolyte and degradation of electrolyte/electrode interface are suppressed effectively by CaF2 coating, which leads to decreased Rct value and improved electrochemical performance.

4. Conclusion

The present paper shows distinguishable effects of CaF2 coating for the Li-rich cathode material Li1.2Mn0.54Ni0.13Co0.13O2. Through a sol–gel method and wet chemical process, an amorphous CaF2 layer with a thickness of 2–7 nm is successfully coated on the surface of the pristine sample. Compared with the pristine Li1.2Mn0.54Ni0.13Co0.13O2, the CaF2-coated sample has the obviously improved electrochemical performance. The coulombic efficiency of the first charge–discharge process is enhanced from 76.0% to 86.3% after CaF2 coating with almost unchanged discharge capacity of 277.3 mAh g⁻¹ at 0.05 C. The CaF2-coated sample exhibits superior capacity retention rate of 91.2% at 0.2 C after 80 cycles. Furthermore, a discharge capacity of 141.5 mAh g⁻¹ is obtained at 3 C and 190 mAh g⁻¹ remains after 100 cycles at 1 C for the CaF2-coated sample, much higher than the pristine sample. The excellent initial coulombic efficiency, cyclic stability and rate capability can be attributed to the suppression of electrolyte decomposition, stable electrolyte/electrode interfacial structure and accelerated phase transformation from the initial layered phase to spinel phase. Therefore, we believe that the obtained CaF2-coated Li1.2Mn0.54Ni0.13Co0.13O2 should be one of ideal candidates for expansion of Li-ion battery technology in electric vehicles and hybrid electric vehicles.

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