

LaF₃ surface-modified LiCr_{0.05}Mn_{1.95}O₄ cathode material with improved high-temperature performances for lithium-ion batteries

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Abstract The LaF₃ surface-modified LiCr_{0.05}Mn_{1.95}O₄ samples were synthesized by co-precipitation method and characterized by high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray detector (EDX). HAADF-STEM and EDX observations showed that LaF₃ deposited on the surface of LiCr_{0.05}Mn_{1.95}O₄ particles. When tested as the cathode materials for lithium-ion battery, the LaF₃-modified LiCr_{0.05}Mn_{1.95}O₄ exhibited significantly improved cyclic and rate performances at high temperature (55 °C). Electrochemical impedance spectrum analyses demonstrated that the surface of LiCr_{0.05}Mn_{1.95}O₄ modified by LaF₃ was much more stable during the electrochemical process and could greatly facilitate the charge–transfer reaction, which may be attributed to the protection of active material by LaF₃ from the HF attack.

Keywords LiMn₂O₄ · LaF₃ · Modification · Electrochemical performance · Lithium-ion battery

Introduction

Rechargeable lithium-ion batteries (LIBs) have become very important in electronic devices as well as in electric vehicles and hybrid electric vehicles. Among many cathode materials for LIB, LiMn₂O₄ spinel has been considered as one of most promising candidates due to its high working voltage, good

safety, low cost, abundance and non toxicity [1–4]. However, poor electrochemical performances at high temperature limit its wide application to some extent. The poor high-temperature performances can be ascribed to several possible factors, such as the choice and purity of the electrolyte and the operating voltage window of the cells.

Many experiments showed that Li₂Mn₂O₄ will be formed when the Li_xMn₂O₄ spinel electrodes' (0 ≤ x ≤ 2) excessive discharge is below 3.0 V, in which a large crystallographic (Jahn–Teller) distortion was responsible for the capacity loss [5–10]. Non-equilibrium localized formation of Li₂Mn₂O₄ at the particle surface has also been observed, particularly under high-rate conditions above 3 V, which can result in subsequent disproportionation reactions to yield Mn(II) and Mn(IV) products. The soluble Mn²⁺ ions can be transported across the electrolyte to the anode where they are deposited, resulting in capacity fade. At present, cation substitution (Li, Sm, Mg, Al, Cr, etc.) at the Mn site is demonstrated to stabilize the lattice structure and improve electrochemical performances of spinel LiMn₂O₄ [11–15].

In the electrolyte, a small amount of water can react with fluoride-based electrolyte, generating hydrofluoric acid (HF), which accelerates the decomposition of LiMn₂O₄ and Mn²⁺ dissolution, especially at high temperature. In order to overcome these shortcomings, surface coating or modification of LiMn₂O₄ is suggested to protect Mn³⁺ from dissolution in the electrolyte. Up to now, many oxides such as Al₂O₃, ZnO, ZrO₂ and TiO₂ have been used to modify the surface of spinel LiMn₂O₄ [16, 17]. However, few researches about the fluorides surface-modified LiMn₂O₄ have been reported [18]. Considering that those protective oxides will transform into a stable fluoride layer by reacting with HF in the electrolyte during the electrochemical process, a better effect may be achieved if the surface of LiMn₂O₄ is directly modified by metal fluorides.

In this paper, in order to overcome the structure distortion of LiMn₂O₄ and assault from the electrolyte, we focus on

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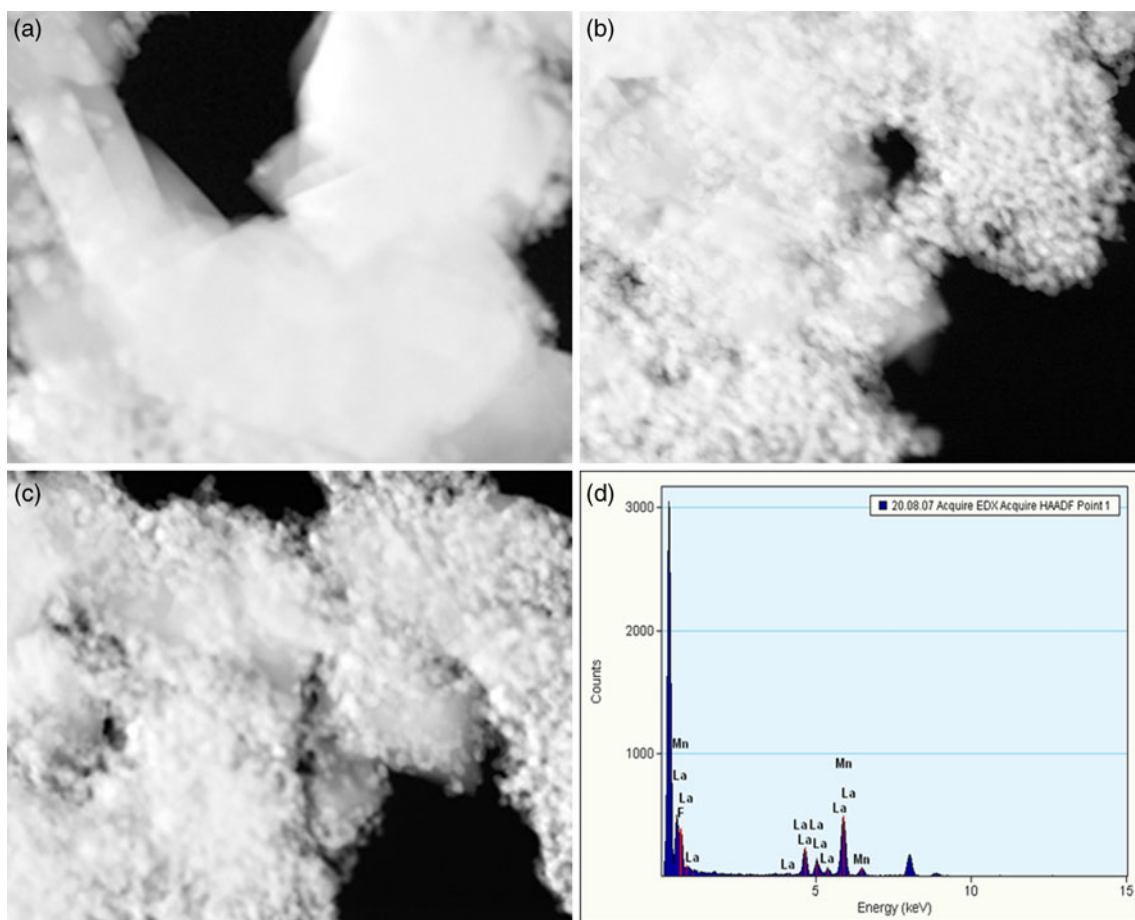


Fig. 1 HAADF-STEM images of **a** pristine, **b** 1.0 wt% LaF_3 modified, **c** 2.0 wt% LaF_3 modified and **d** EDX figure

LaF_3 surface-modified $\text{LiCr}_{0.05}\text{Mn}_{1.95}\text{O}_4$ electrode materials. The structural and electrochemical properties of the as-prepared samples were investigated.

Experiment

The pristine $\text{LiCr}_{0.05}\text{Mn}_{1.95}\text{O}_4$ sample is a commercial product of Huilong Technology Co., Ltd., in Yuxi. To prepare the surface-modified materials, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and NH_4F and $\text{LiCr}_{0.05}\text{Mn}_{1.95}\text{O}_4$ are dissolved in distilled water; the specific process is $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{LiCr}_{0.05}\text{Mn}_{1.95}\text{O}_4$ are dissolved in distilled water with continuous stirring for 2 h at 80°C ; 1 mol NH_4F is dissolved in 1 L distilled water, added to the mixture at the rate of 3 ml/min and continuously stirred for 2 h at 80°C ; the composition of LaF_3 in the modified cathode materials was 0.5, 1.0 and 2.0 wt%, respectively. Subsequently, the mixture was filtered and dried at 90°C for 5 h; then, the obtained powder was heated at 400°C for 5 h, and the surface-modified cathode materials are gotten.

The microstructure of the powder was obtained using a high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM). For measuring the

electrochemical properties, the electrochemical cells consisting of $\text{LiCr}_{0.05}\text{Mn}_{1.95}\text{O}_4$ as positive electrode, Li metal as the negative electrode and the electrolyte was 1 M LiPF_6 dissolved in a 1:1 (volume ratio) mixture of ethylene carbonate and dimethyl carbonate, and Celgard 2400 membrane as the

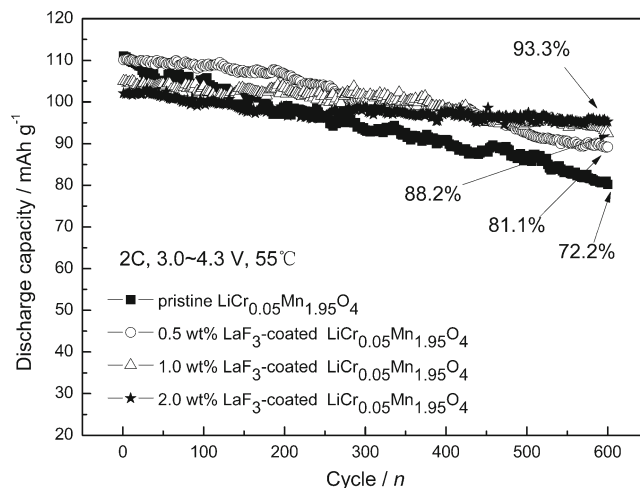


Fig. 2 The cyclic performance of pristine and LaF_3 -modified $\text{LiCr}_{0.05}\text{Mn}_{1.95}\text{O}_4$ electrodes at 55°C

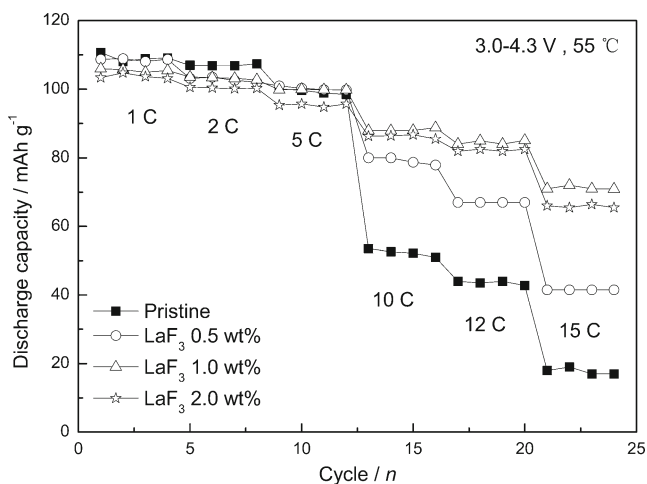


Fig. 3 Rate capability of pristine and LaF₃-modified LiCr_{0.05}Mn_{1.95}O₄ electrodes at 55 °C

separator between cathode and anode. The cathode was the mixture of 85 wt% active material, 8.0 wt% acetylene black and 7.0 wt% poly-vinylidene fluoride dissolved in 1-methyl-2-pyrrolidinone (NMP), which was spread on a 14-mm-diameter aluminium foil and heated to 120 °C for 12 h in vacuum; the electrode thickness is about 20 μm. The cells were assembled in an argon-filled glove box. The constant current constant voltage charge model (CC-CV) cycling was performed between 3.0 and 4.3 V with 1 C (148 mA g⁻¹) rate on the LandCT2001A made in China; the rate performance was performed between 3.0 and 4.3 V with different currents (1 C, 2 C, 5 C, 10 C, 15 C), and electrochemical impedance spectroscopy (EIS) was tested on a PARSTAT 2273 made in the USA. After the cells were at the fully charged state (4.3 V), the impedance spectra were recorded potentiostatically by applying an AC voltage of 5 mV amplitude over the frequency range from 10⁵ to 0.05 Hz.

Results and discussion

Figure 1 presents the typical HAADF-STEM images of the pristine and LaF₃-modified LiCr_{0.05}Mn_{1.95}O₄ powders. The

pristine particles exhibit a smooth surface, while the surfaces of the modified particles are covered with thin nanolayers, which are determined to be LaF₃ on the basis of EDX analysis (Fig. 1d). From the results of the HAADF-STEM and EDX, it can be concluded that the LaF₃-modified layer is successfully formed on the surface of LiCr_{0.05}Mn_{1.95}O₄.

Figure 2 shows the cyclic performance of pristine and LaF₃-modified LiCr_{0.05}Mn_{1.95}O₄ electrodes at 55 °C. It is even more important that the cycle ability at high temperature is remarkably improved with the introduction of LaF₃-modified layers. For example, the pristine LiCr_{0.05}Mn_{1.95}O₄ merely retains 72.2 % of its initial capacity after 600 cycles with 1 C rate. However, the capacity retentions are 81.1, 88.2 and 93.3 % for 0.5, 1.0 and 2.0 wt% LaF₃-modified samples, respectively. This great enhancement can be ascribed to the fact that the LaF₃-modified layers prevent direct contact between the LiCr_{0.05}Mn_{1.95}O₄ active material and the acidic electrolyte, suppressing the tendency for Mn dissolution in the electrolyte.

Figure 3 shows the rate capability of the pristine and LaF₃-modified samples at 55 °C. When the moderate rates (1–5 C) are adopted, no obvious difference can be identified between the pristine and LaF₃-modified samples. When the rate increases to around and above 10 C, the discharge capacity of the pristine LiCr_{0.05}Mn_{1.95}O₄ decreases rapidly as compared to that of the low rates, and only 15.6 % of the 1 C capacity is obtained at 15 C. Meanwhile, the LaF₃ surface modification markedly improves the high-rate performance of LiCr_{0.05}Mn_{1.95}O₄ since the capacity retentions at 15 C are 38.2, 67.1 and 64.5 % for the 0.5, 1.0 and 2.0 wt% LaF₃ samples, respectively.

To further understand the effect of LaF₃ modification on the cycle and high-rate performances of LiCr_{0.05}Mn_{1.95}O₄ cathode material, EIS analyses are carried out on each cell of 100 % SOC (4.3 V) after the 1st and 100th cycle, respectively. The Nyquist plots of pristine LiCr_{0.05}Mn_{1.95}O₄ and LaF₃-modified samples are presented in Fig. 4. All the plots in Fig. 4a consist of one semicircle in the high-frequency region, one capacitive arc in the middle frequency and the straight sloping line in the low-frequency region. The high-frequency semicircle is

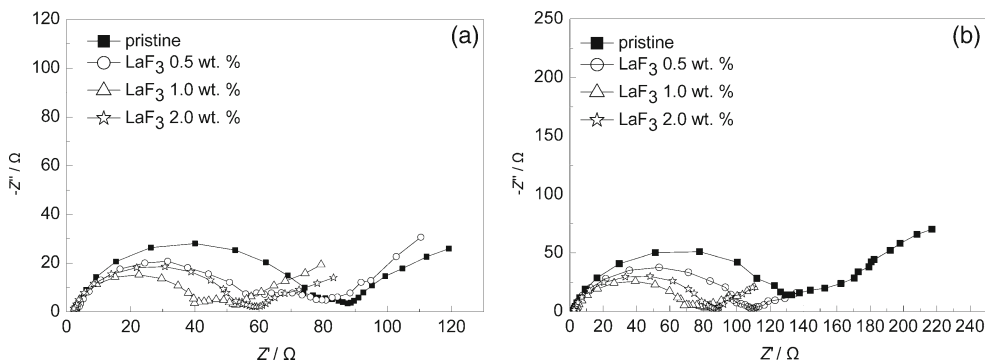


Fig. 4 Nyquist plots of pristine and LaF₃-modified LiCr_{0.05}Mn_{1.95}O₄ samples at 100 % SOC. **a** 1st cycle and **b** 100th cycle

attributed to the charge–transfer reaction, the middle frequency loop is due to the solid electrolyte interface layer, and the inclined line is Warburg impedance (W) which is used to model semi-infinite diffusion in the bulk cathode material [18]. It is clear in Fig. 4a that the LaF₃-modified samples have smaller charge–transfer resistance (R_{ct}) values than the pristine LiCr_{0.05}Mn_{1.95}O₄, indicating a faster electrochemical reaction on the LaF₃-modified spinel electrode. After the 100th cycle, the value of R_{ct} for pristine powders greatly increases from 70 to 128 Ω (Fig. 4b). However, the increase of the R_{ct} value for each LaF₃-modified electrode after the 100th cycle is relatively smaller, e.g. the value of R_{ct} for 1 wt% LaF₃-modified electrode increases from 40 to 65 Ω . Since the electrochemical reaction happened on the interface between the active material and the electrolyte, the smaller changes in the value of R_{ct} during the cycles imply a more stable surface of the LaF₃-modified LiCr_{0.05}Mn_{1.95}O₄, suggesting the protection of active material by LaF₃ from the HF attack.

Conclusions

The LaF₃ surface-modified LiCr_{0.05}Mn_{1.95}O₄ samples are synthesized by co-precipitation method. HAADF-STEM and EDX observations illustrate that LaF₃ deposited on the surface of LiCr_{0.05}Mn_{1.95}O₄ particles. When tested as the cathode materials for LIB, the LaF₃-modified LiCr_{0.05}Mn_{1.95}O₄ exhibits significantly the improved cyclic and rate performances at a relatively high temperature (55 °C). The capacity retentions are 81.1, 88.2 and 93.3 % for LaF₃-modified electrode materials with 0.5, 1.0 and 2.0 wt%, respectively, after 600 cycles, while that of the pristine is only 72.2 %. The capacity retention at the 15 C rate of the pristine powders is only 15.6 % relative to that at 1 C rate. However, the capacity retentions are 38.2, 67.1 and 64.5 % for electrode materials with 0.5, 1.0 and

2.0 wt%, respectively. EIS analysis demonstrates that the surface of LiCr_{0.05}Mn_{1.95}O₄ modified by LaF₃ is much more stable during the electrochemical process and could greatly facilitate the charge–transfer reaction, which may be attributed to the protection of active material by LaF₃ from the HF attack.

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