Electrochimica Acta 56 (2011) 4791–4796

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Improvement of structural and electrochemical properties of commercial $LiCoO_2$ by coating with LaF_3

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ARTICLE INFO

Article history:
Received 10 December 2010
Received in revised form 4 March 2011
Accepted 4 March 2011
Available online 12 March 2011

Keywords:
Lithium-ion battery
Cathode material
Surface modification
LaF_3 coating
Overcharge tolerance

ABSTRACT

Commercial $LiCoO_2$ has been modified with LaF_3 as a new coating material. The surface modified materials were characterized by X-ray diffraction (XRD), transmission electronic microscopy (TEM), field emission scanning electron microscopy (FE-SEM), auger electron spectroscopy (AES) and galvanostatic charge–discharge cycling. The LaF_3-coated $LiCoO_2$ had an initial discharge specific capacity of 177.4 mAh g^{-1} within the potential ranges 2.75–4.5 V (vs. Li/Li^+), and showed a good capacity retention of 90.9% after 50 cycles. It was found that the overcharge tolerance of the coated cathode was significantly better than that of the pristine $LiCoO_2$ under the same conditions – the capacity retention of the pristine $LiCoO_2$ was 62.3% after 50 cycles. The improvement could be attributed to the LaF_3 coating layer that hinders interaction between $LiCoO_2$ and electrolyte and stabilizes the structure of $LiCoO_2$. Moreover, DSC showed that the coated $LiCoO_2$ had a higher thermal stability than the pristine $LiCoO_2$.

1. Introduction

Layered $LiCoO_2$ has been the dominant cathode material for commercial Li-ion batteries since 1991 because of its ease of production, high operating potential, low self-discharge rate and high reversibility below 4.2 V (vs. Li/Li^+) [1–3]. However, its available specific capacity in practical batteries is only about 140 mAh g^{-1}, roughly half of its theoretical capacity (274 mAh g^{-1}). In order to obtain a higher capacity from $LiCoO_2$, it must be charged above 4.2 V (vs. Li^+/Li) but this would lead to a rapid capacity loss thought to be caused by side reactions with the electrolyte at high potentials as well as structural instability [3–8]. To enhance the electrochemical stability of $LiCoO_2$ at upper cutoff potential, partial substitution of Co by other metals in $LiCoO_2$ has been shown to be an effective method of improving the structural stability of the cathode materials. However, such improvements in structural stability have been realized at the expense of specific capacity [9,10].

As an alternative approach, there has been extensive research into coating of $LiCoO_2$ with various metal oxides in order to enhance their electrochemical properties and structural stability [11–15], however, most of the metal oxides as coating materials such as Al_2O_3, ZnO, ZrO_2, cannot remain stable under the corrosion of HF from the electrolyte.

In this work, LaF_3 has been introduced as a new coating material for the $LiCoO_2$ cathode for the first time. On the one hand, lanthanum is an effective coating element in the form of lanthanide oxide which possesses good thermal stability, increases the maximum current carrier capacity and supports high potential, to improve the electrochemical performance of the cathode material [16,17]. On the other hand, fluorine in the form of fluorides such as AlF_3, as a surface coating material, has successfully improved the electrochemical performance of the cathode material, which could be attributed to the reduction of the structural change of active material from HF attack by a thin AlF_3 coating layer preventing the highly delithiated cathode from being directly contacted with liquid electrolyte [18–20]. LaF_3 has been used as chemical sensors because of its high chemical stability and ionic conductivity, but it has not been introduced as surface coating material for cathode material in lithium-ion batteries. In this study, we report a study of the structure, morphology, overcharge behavior and thermal stability of LaF_3-coated $LiCoO_2$ material.

2. Experimental

2.1. Synthesis of materials

Commercial $LiCoO_2$ with an average particle size of 10 μm was obtained from Beijing Easpring Material Technology Co. Ltd. The required amount of $LiCoO_2$ (10 g) was first suspended in distilled water with vigorous agitation, and acetic acid was added drop by drop into the mixture to adjust the pH value at 5.5. The amount of

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doi:10.1016/j.electacta.2011.03.017

LaF_3 in the solution was 0.5 mol% of the $LiCoO_2$ powders. A solution containing $La(NO_3)_3$ (0.1674 g) was then slowly added drop-wise to the suspension. At the same time, a solution containing NH_4F (0.0611 g) was added drop-wise. The suspension was subsequently aged at room temperature with vigorous agitation for 1 h. The final powder was filtered and dried at 100 °C for 12 h, and subsequently heat-treated in a furnace at 400 °C for 5 h in air.

2.2. Characterization of materials

The particle morphologies of the products were observed by means of a field emission scanning electron microscope (FE-SEM) (JSM-7500F). X-ray powder diffraction (XRD) measurements were obtained on a Rigaku D/MAX-1A diffractometer operated at 40 kV and 30 mA in the 2θ range 10–70° with Cu-K_α radiation ($\lambda = 0.15406$ nm). Transmission electronic microscopy (TEM) was carried out on a Hitachi H-800 instrument for investigating the microstructure of the samples. Auger electron spectroscopy (AES) (ULVAC-PHI, AES-PHI 700) was used to examine the spatial distribution of constituent ions in the coated particles. Co dissolution content of the sample after storage in electrolyte for 7 days at 55 °C was examined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Shimadzu ICPS-7500).

Electrochemical behavior during charge–discharge cycles was examined using a two-electrode test cell with lithium foil as the negative electrode. A positive electrode was made by coating a paste of the active material, acetylene black and a polyvinylidene fluoride (PVDF) binder (90:5:5 wt%) on an aluminum-foil collector. The positive film was subjected to roll pressing and electrodes of 1.2 mm diameter were punched out. The positive electrodes were dried at 120 °C for 12 h in a vacuum oven. Coin-type cells (CR 2032) were assembled in an argon filled glove box with an electrolyte of 1 mol dm^{-3} $LiPF_6$ in EC-EMC-DMC (1:1:1 volume ratio) solution and a Celgard 2400 separator. The electrochemical data were collected using a LAND CT2001A test system within the potential range 2.75–4.3, 2.75–4.5 or 2.75–4.7 V (vs. Li/Li^+) at a constant current density of 0.2 mA cm^{-2}.

The thermal stabilities of the pristine and LaF_3-coated $LiCoO_2$ were studied using differential scanning calorimetry (DSC) (PerkinElmer Pyris 1). The coin cell was first galvanostatically charged to 4.5 V at a constant current and then opened in a dry room. The measurement was performed in a nitrogen atmosphere at a heating rate of 10 °C min^{-1}.

3. Results and discussion

After precipitation of a solution containing $La(NO_3)_3$ and a solution of NH_4F, the precipitate was dried at 100 °C, and subsequently heat-treated in a furnace at 400 °C for 5 h in air. The XRD pattern of the product was shown in Fig. 1, and the pure phase of the synthesized LaF_3 material calcined at 400 °C for 5 h in air could be indexed to the JCPDS No.74-1324 pattern, which it does not show any additional peaks about the lanthanum oxides.

The XRD patterns of the pristine and LaF_3-coated $LiCoO_2$ are shown in Fig. 2. It was confirmed that both materials can be indexed in the hexagonal-type space group $R\bar{3}m$. The XRD pattern of the LaF_3-coated $LiCoO_2$ material does not show any additional peaks other than those of $LiCoO_2$. This is presumably because the content of is low and LaF_3 forms only a thin film on the surface of $LiCoO_2$. The lattice parameters were calculated by a least square method from Fig. 2. The calculated lattice parameters of the LaF_3-coated $LiCoO_2$ were $a = 0.2816$ nm and $c = 1.4079$ nm, respectively. The values are close to those of pristine, $a = 0.2816$ nm, $c = 1.4072$ nm, indicating that the LaF_3 was not incorporated into the host structure since no changes were seen in the structure.

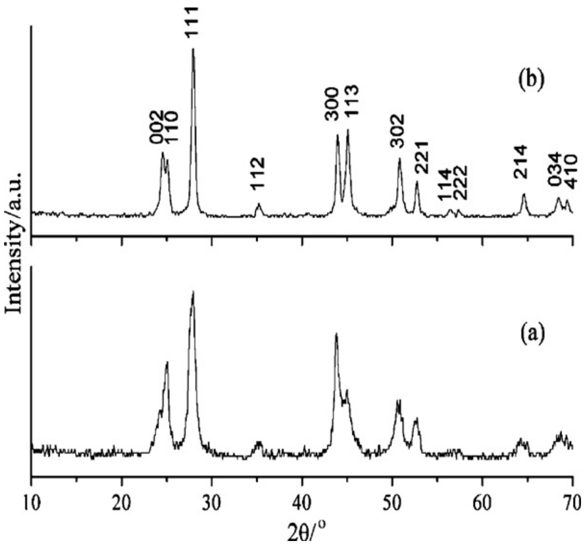

Fig. 1. XRD patterns of the LaF_3 calcined at (a) 100 and (b) 400 °C for 5 h in air.

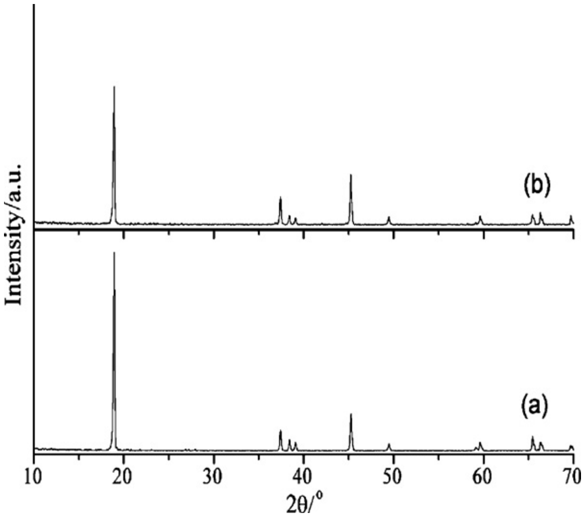

Fig. 2. XRD patterns of (a) the pristine $LiCoO_2$ and (b) LaF_3-coated $LiCoO_2$ calcined at 400 °C for 5 h in air.

Fig. 3 shows TEM images of the pristine and coated $LiCoO_2$. The pristine material shows a very smooth edge lines, and there is no other layer on the surface in Fig. 3a. The coating material formed a coating layer with a thickness of about 10 nm around the $LiCoO_2$ particle shown in Fig. 3b. FE-SEM images of the pristine and coated $LiCoO_2$ particles are shown in Fig. 4. A smooth and clean surface was observed on pristine $LiCoO_2$ particle at high magnification in Fig. 4a. After coated with LaF_3, the change of coated particle morphology is obvious even at low magnification in Fig. 4b, which is more obvious at high magnification. The differences of pristine $LiCoO_2$ and coated $LiCoO_2$ in the images, we could conclude that the surface of the $LiCoO_2$ is covered with a coating thin film.

AES was carried out to examine the spatial distribution of La atoms near the surface of the coated particles, and the results are shown in Fig. 5. It can be clearly seen that Co is hardly detected on the top surface of the coated $LiCoO_2$ particles. The La concentration on the top surface of the coated $LiCoO_2$ particles is initially very high, decreases sharply before a depth of about 9 nm, and Co shows the opposite trend to the La concentration, as shown in Fig. 5. Therefore, the thickness of LaF_3 coating layer is about 9 nm. The result is consistent with that of the TEM. The La levels off at a depth of

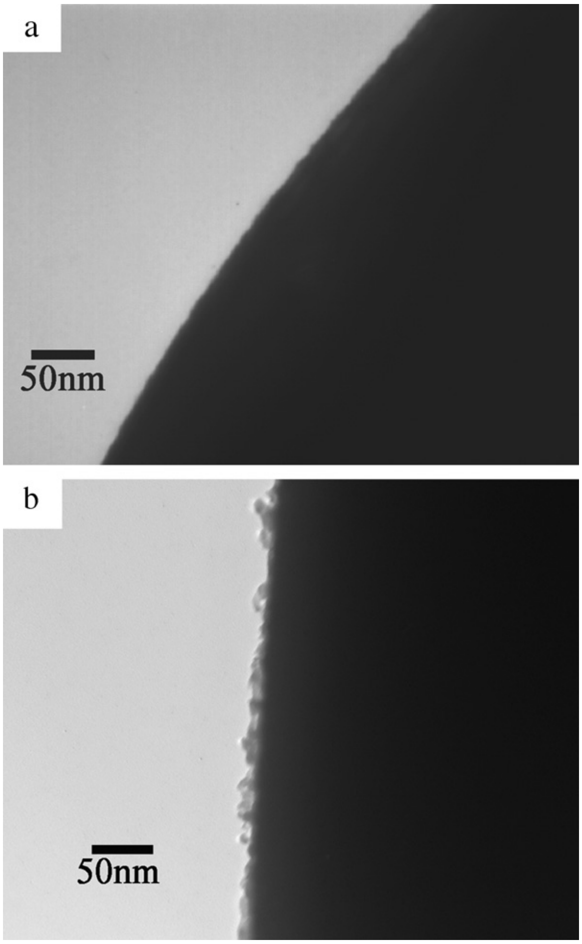

Fig. 3. TEM images of the (a) pristine and (b) coated $LiCoO_2$ powders.

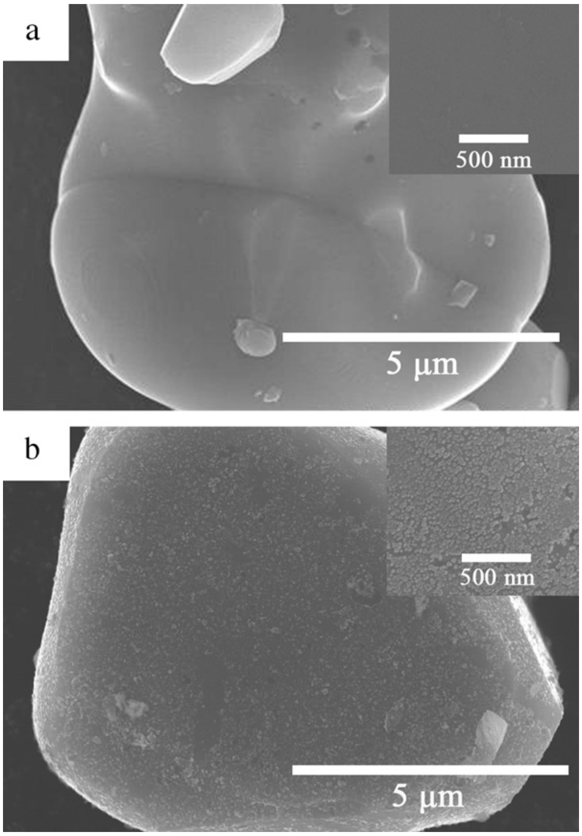

Fig. 4. FE-SEM images of the (a) pristine and (b) coated $LiCoO_2$ powders. The inset is the corresponding FE-SEM image of the cathode surface at high magnification.

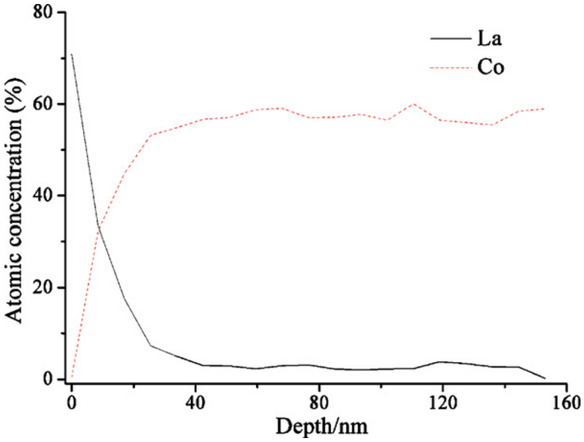

Fig. 5. Depth profiles of coated $LiCoO_2$ particle determined by AES.

about 40 nm, as shown in Fig. 5. The result implies that the coating elements diffuse into the bulk $LiCoO_2$ during calcination process to form an doped $LiCoO_2$ phase with a thickness of about 31 nm.

An electrochemical test is conducted with a constant charge/discharge current density of 0.2 mA cm^{-2} in the different upper cutoff potential. Typical charge/discharge curves of the pristine and LaF_3-coated $LiCoO_2$ cathode are shown in Fig. 6. The initial discharge specific capacities of the pristine $LiCoO_2$ (152.8 mAh g^{-1}) is slight higher than that of the LaF_3-coated $LiCoO_2$ (150.7 mAh g^{-1}) cathode within the potential range 2.75–4.3 V, as shown in Fig. 6. The capacity retention of LaF_3-coated $LiCoO_2$ within the potential range 2.75–4.3 V is 96.6% after 50 cycles which is much higher than the corresponding value for the pristine $LiCoO_2$. Rate capability is an important and desirable feature in secondary battery applications. Fig. 7 shows the rate capability and cyclability of the pristine and LaF_3 coated $LiCoO_2$ between 2.75 and 4.3 V at various C-rates. It was clearly observed that the LaF_3-coated electrode has better rate capability than the pristine $LiCoO_2$.

In order to further study the overcharge behavior of the cathode, the upper charge cutoff potential was increased to 4.5 and 4.7 V, respectively. Cycle-life plots of the pristine and LaF_3-coated $LiCoO_2$ cathode in the different upper cutoff potential are presented in Fig. 8. The initial discharge specific capacity of LaF_3-coated $LiCoO_2$ within the potential range 2.75–4.5 V is 177.4 mAh g^{-1}, and the capacity retention is 90.9% after 50 cycles, much higher than that of the pristine $LiCoO_2$ (62.3%). In addition, the discharge curve for the LaF_3-coated $LiCoO_2$ electrodes at the later stage are slightly higher than that of the pristine $LiCoO_2$, which may be contributed that a resistive coating layer exists on the surface of LaF_3-coated $LiCoO_2$ particle. Sun et al. have also reported the similar result [18–20]. The initial discharge specific capacity of LaF_3-coated $LiCoO_2$ within the potential range 2.75–4.7 V is 232.6 mAh g^{-1}, slightly higher than the value (221.3 mAh g^{-1}) for the pristine $LiCoO_2$. Zhao et al. have also reported that $LiCoO_2$ charged at higher upper charge cutoff potential has a lower discharge specific capacity than that of coated cathodes [13]. This suggests that the LaF_3 coating layer, like other coating materials, stabilizes the structure of $LiCoO_2$ and allows more Li ions to be intercalated into the cathode during the discharge process. At the upper charge cutoff potential of 4.7 V, the discharge specific capacity of the pristine $LiCoO_2$ shows a dramatic fading in capacity with cycling, while LaF_3-coated $LiCoO_2$ shows much less fading in capacity. After 30 cycles, the discharge specific capacity

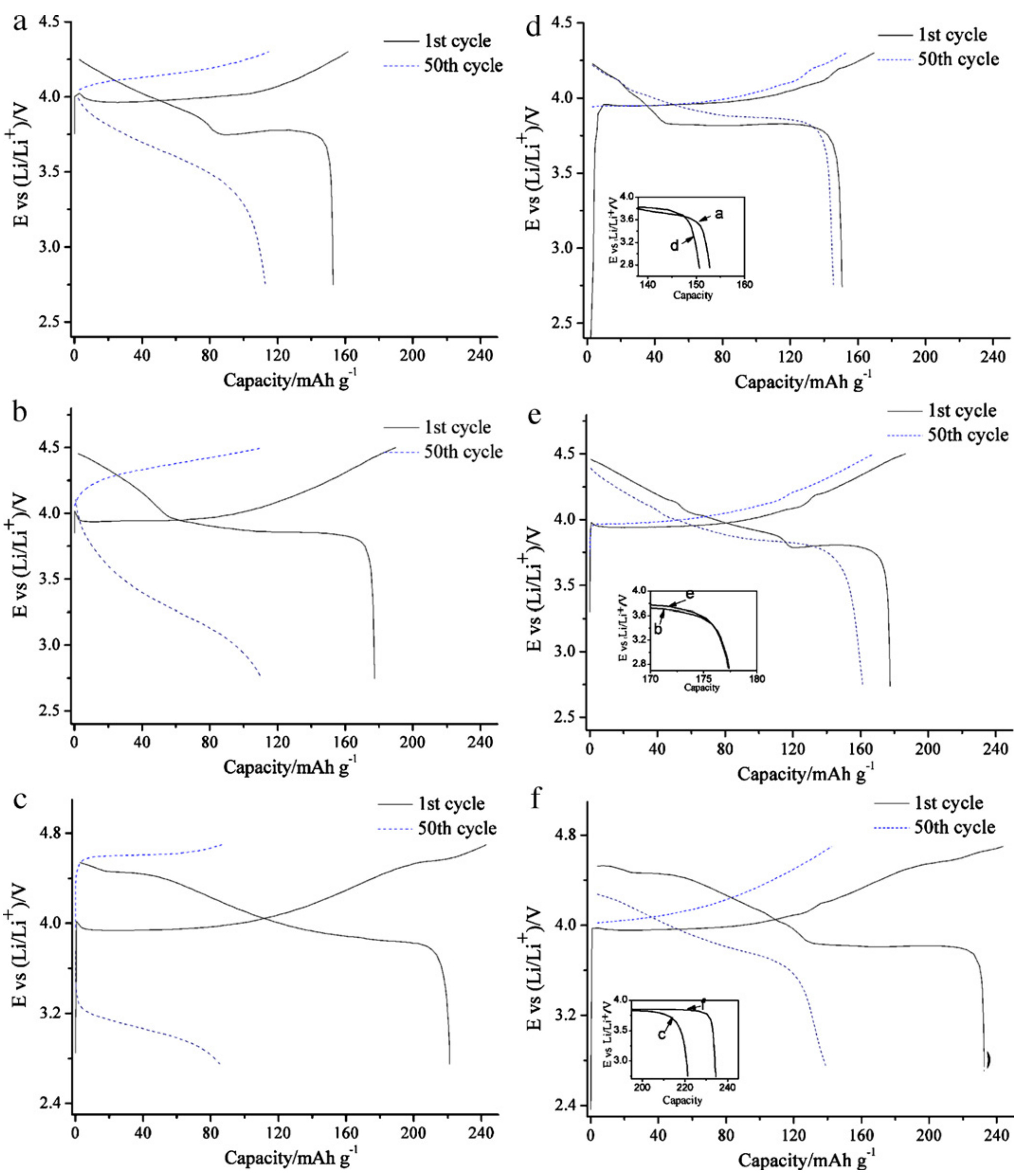

Fig. 6. The charge/discharge curves of the pristine (a–c) and LaF_3-coated $LiCoO_2$ (d–f) within different potential ranges: (a and d) 2.75–4.3 V, (b and e) 2.75–4.5 V and (c and f) 2.75–4.7 V. The inset is the discharge curves of the pristine (a–c) and LaF_3-coated $LiCoO_2$ (d–f) at the later stage for the discharge process.

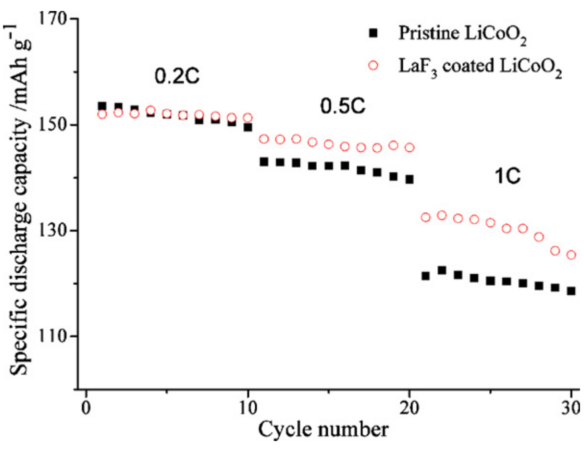

Fig. 7. Rate capability of the pristine and LaF_3-coated $LiCoO_2$ between 2.75 and 4.3 V.

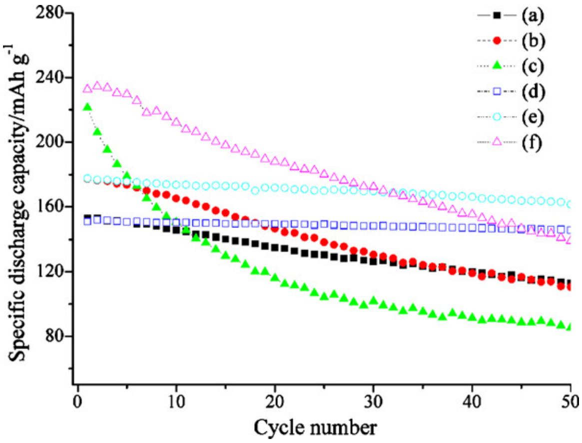

Fig. 8. Comparison of the cyclabilities of the pristine (a–c) and LaF_3-coated $LiCoO_2$ (d–f) cycled in different potential ranges: (a and d) 2.75–4.3 V, (b and e) 2.75–4.5 V and (c and f) 2.75–4.7 V.

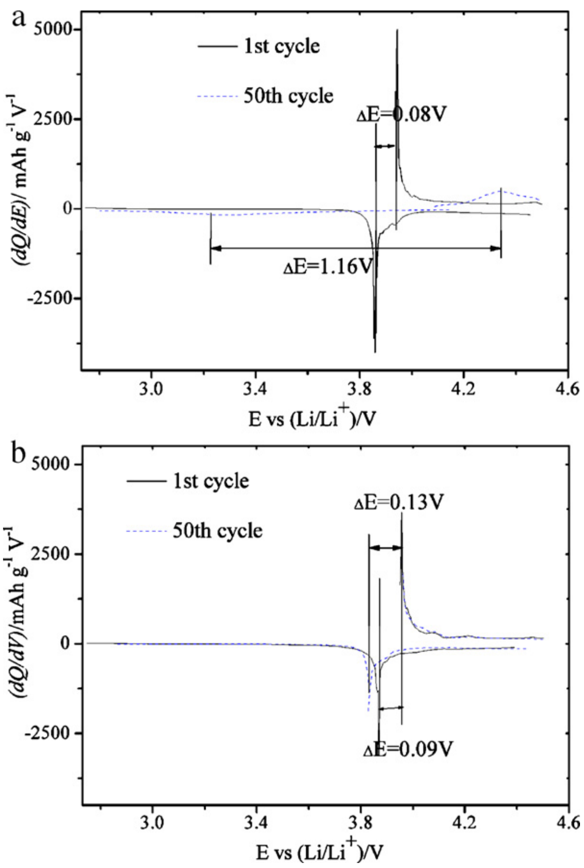

Fig. 9. dQ/dV vs. potential curves of (a) the pristine and (b) LaF_3-coated $LiCoO_2$ in the potential range of 2.75–4.5 V.

of the coated cathode is as high as 172.3 mAh g^{-1}, while that of the pristine cathode is only 101.6 mAh g^{-1}, as shown in Fig. 8. The enhanced overcharge behavior of the LaF_3-coated $LiCoO_2$ may be attributed to the improvement of the structural stability of active core material from HF attack by a thin LaF_3 coating layer preventing the highly delithiated cathode from being directly contacted with liquid electrolyte and thus preventing dissolution of the cobalt. To analyze the Co dissolution behavior in the product, the pristine $LiCoO_2$ (0.50 g)and LaF_3-coated $LiCoO_2$ (0.50 g) positive electrodes were immersed in 30 mL electrolyte solution for 7 days at 55 °C, and the Co content was determined by ICP-AES. The ICP analysis results for the pristine and LaF_3-coated $LiCoO_2$ dissolution have shown that the amount of Co dissolution from the pristine $LiCoO_2$ (0.25 mg) was much higher than that of LaF_3-coated $LiCoO_2$ (0.051 mg). The result illustrates that LaF_3-coated $LiCoO_2$ can effectively reduce the Co dissolution into the electrolyte.

Fig. 9 shows the profiles of dQ/dV vs. potential for the pristine and LaF_3-coated $LiCoO_2$ cathode within the potential range of 2.75–4.5 V at the 1st and 50th cycle, respectively. It is observed that the oxidation–reduction peaks of the pristine $LiCoO_2$ are centered at 3.94 and 3.86 V at the first cycle, respectively, and the peaks are narrow and sharp, as shown in Fig. 9a. However, after 50 cycles, it is shown that the peaks become so broader that the plateau almost disappears, and shift to 4.38 and 3.22 V, respectively. For LaF_3-coated $LiCoO_2$ cathode in Fig. 9b, the oxidation–reduction peaks corresponding to the phase transition during charge–discharge process are centered at 3.96 and 3.87 V at the first cycle, respectively, are narrow and sharp, whereas after 50 cycles, the oxidation peak almost never moves and the reduction peak only shifts to 3.83 V, and both peaks are still narrow and sharp. Moreover, the potential gap (ΔV) of pristine $LiCoO_2$ is increased from 0.08 V to 1.16 V, while that of LaF_3-coated $LiCoO_2$ is increased by only 0.04 V. Since the charge–discharge plateaus strongly depend on the structure of the cathode, based on the above results, we could draw a conclusion that the LaF_3 coating layer is very helpful to stabilize the structure of the $LiCoO_2$ cathode during the charge–discharge process in a wider potential range.

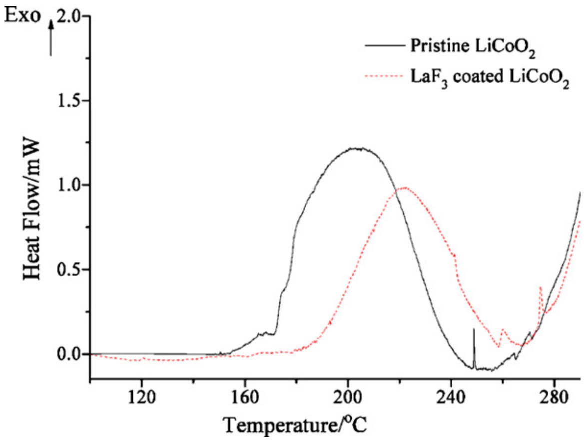

Fig. 10. DSC scans of the pristine and coated $LiCoO_2$ cathodes after charging to 4.5 V. The scan rate was 10 °C/min.

The exothermic decomposition reaction is the most important factor affecting the thermal stability of Li-ion batteries. DSC measurements were performed in order to study the thermal stability of the cathodes, and the results are shown in Fig. 10. The pristine $LiCoO_2$ had a large exothermic peak at about 206 °C, and the enthalpy of reaction of the pristine $LiCoO_2$ is 27.5 J g^{-1}. However, thermal stability of the LaF_3-coated $LiCoO_2$ was improved more obviously; its DSC profile exhibited a relatively small peak about 218 °C with the enthalpy of 14.3 J g^{-1}. The enhanced thermal stability of the coated $LiCoO_2$ compared with the pristine $LiCoO_2$ could be attributed to the thin LaF_3 coating layer preventing the highly oxidized positive electrode particles coming into direct contact with the electrolyte solution, thereby reducing the exothermic reaction.

4. Conclusions

Commercial $LiCoO_2$ has been successfully coated with a layer of LaF_3. The LaF_3-coated $LiCoO_2$ exhibited high capacity retention of 90.9% after 50 cycles within the potential range 2.75–4.5 V compared with the 62.3% capacity retention for the pristine $LiCoO_2$. The LaF_3-coated $LiCoO_2$ showed an excellent overcharge tolerance and structure stability during the high upper cutoff potential. Furthermore, the LaF_3 coating could be significantly reduce the Co dissolution from $LiCoO_2$ and improve thermal stability of $LiCoO_2$. Therefore, LaF_3 has considerable potential as a new coating material to give enhanced overcharge tolerance and thermal stability of $LiCoO_2$ cathode material.

Acknowledgments

This work was supported by the opening funds of State Key Lab of Chemical Resource Engineering, the Nature Science Foundation of Liaoning Province (Grant No. 20082187). The authors wish to acknowledge Dr. Guoming Liu for fruitful discussions.

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