



Short communication

Electrochemical performance and thermal stability of LiCoO₂ cathodes surface-modified with a sputtered thin film of lithium phosphorus oxynitride

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ARTICLE INFO

Article history:

Received 3 February 2010

Received in revised form 4 June 2010

Accepted 8 June 2010

Available online 8 July 2010

Keywords:

Lithium cobalt oxide

Cathode

Thin film

Thermal stability

Lithium-ion battery, Lithium phosphorus oxynitride

ABSTRACT

A lithium phosphorus oxynitride (LiPON) glass-electrolyte thin film is coated on a lithium cobalt oxide (LiCoO₂) composite cathode by means of a radio frequency (RF) magnetron sputtering method. The effect of the LiPON coating layer on the electrochemical performance and thermal stability of the LiCoO₂ cathode is investigated. The thermal stability of the delithiated LiCoO₂ cathode in the presence of liquid electrolyte is examined by differential scanning calorimetry (DSC). It is found that the LiPON coating, improves the rate capability and the thermal stability of the charged LiCoO₂ cathode. The LiPON film appears to suppress impedance growth during cycling and inhibits side-reactions between delithiated LiCoO₂ and the electrolyte.

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1. Introduction

In recent years, lithium-ion batteries have attracted considerable attention from the viewpoint of safety because of their extensive applications. Many safety-related incidents can be attributed to the rapid exothermic reactions of the electrode materials, especially delithiated cathode materials, with liquid electrolytes [1–3]. Most approaches to suppress such exothermic reactions have been based on either the development of thermally-stable cathode materials [4,5] or the surface coating of cathodes [6–12]. The surface coating of the active materials is a complex and expensive wet chemical solution process that can also result in the degradation of electrochemical performance in terms of specific capacity and rate capability.

As an alternative to these two methods, it is suggested that the deposition of a protective film on composite electrodes might be a novel approach to control the interfacial reaction between the active materials in the cathode and the liquid electrolytes, while also ensuring that the electrode materials have the required electrochemical performance.

Lithium phosphorous oxynitride (LiPON) is well known as a stable and relatively high ionic-conducting solid electrolyte [13,14]. Therefore, a LiPON thin film deposited on a cathode might function

as a protective layer that prevents the reaction between the cathode and the electrolyte and improves the thermal stability of the cathode.

In the present study, LiCoO₂ is chosen as the active material for the cathode and a LiPON thin film is deposited on the LiCoO₂ composite electrode using a sputtering method. The effects of LiPON thin-film deposition on the electrochemical performance and thermal stability of the LiCoO₂ composite electrode are investigated.

2. Experimental

An LiCoO₂ composite electrode was prepared by mixing active cathode material (LiCoO₂), carbon black, and polyvinylidene fluoride (PVDF) binder in N-methyl pyrrolidone (NMP). The mixture was coated on an aluminum foil. LiPON thin film was deposited by radio frequency (RF) magnetron reactive sputtering of a Li₃PO₄ target in a nitrogen gas atmosphere. The surface morphology of the pristine and LiPON-coated electrodes was observed by means of scanning electron microscopy (SEM).

For the evaluation of electrochemical performance, a solution of 1 M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by volume, provided by Ukseung Chemical Co., Ltd., Korea) was used as an electrolyte. A coin-type half-cell was assembled with a lithium-foil counter electrode. The cells were charged and discharged in the voltage range of 3.0–4.2, and 3.0–4.5 V, respectively using a current of 0.2C at 30 °C.

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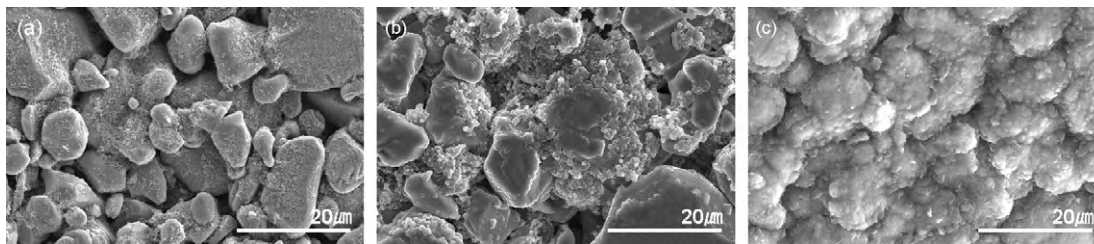


Fig. 1. FE-SEM images of (a) pristine LiCoO₂ electrode, and (b) 0.3- and (c) 0.5-μm-thick LiPON-coated LiCoO₂ electrode.

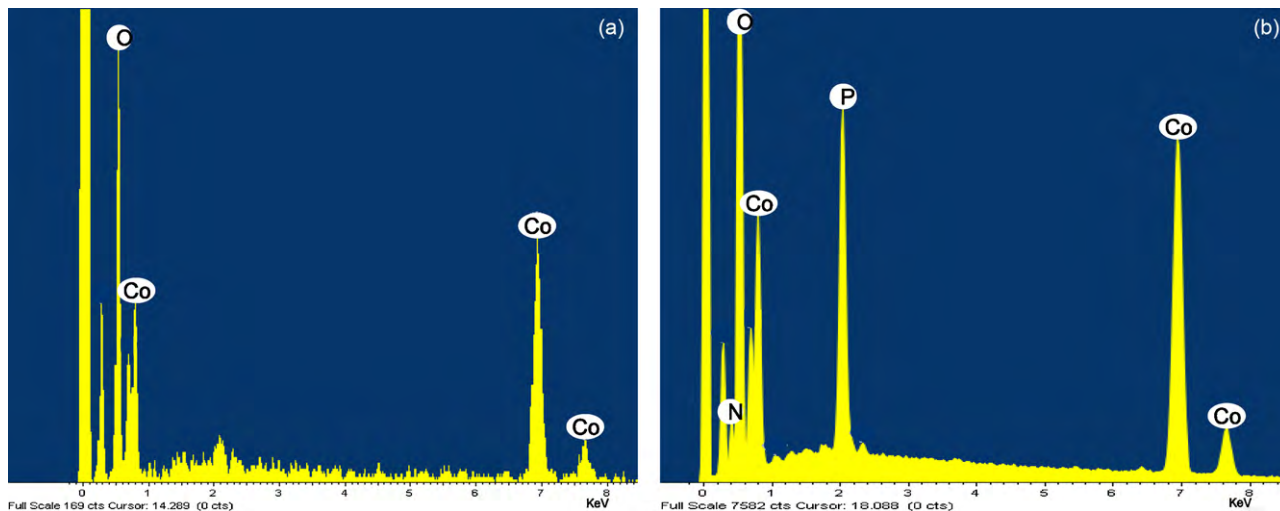


Fig. 2. EDX results of (a) pristine LiCoO₂ electrodes and (b) LiPON-coated LiCoO₂ electrode.

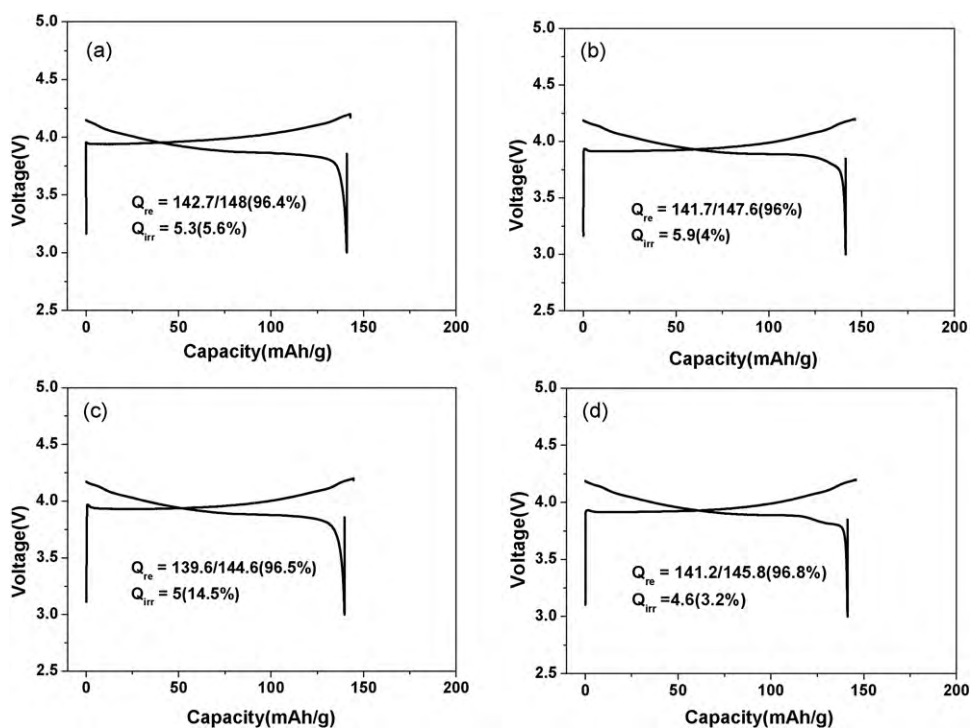


Fig. 3. Charge–discharge curves between 3.0 and 4.2 V for pristine and LiPON-coated LiCoO₂ electrodes at first cycle. (a) Pristine LiCoO₂ electrode, and (b) 0.3-, (c) 0.5- and (d) 0.75-μm-thick LiPON-coated LiCoO₂ electrode.

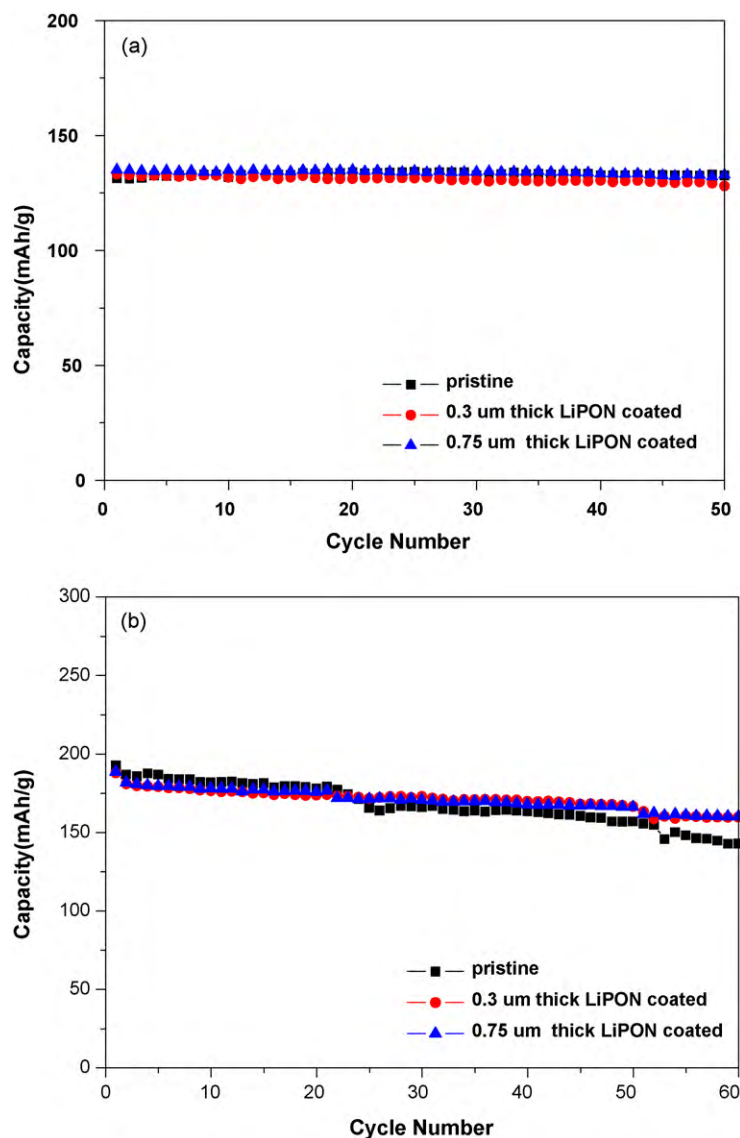


Fig. 4. Cycle performances of pristine and LiPON-coated LiCo₂ electrodes in different voltage ranges: (a) 3.0–4.2 V and (b) 3.0–4.5 V.

To investigate the thermal stability of the delithiated cathodes, the cells were pre-cycled three times in the coin cell and the cycling was interrupted at the charged state. The charged cells were disassembled in a glove-box, and the electrodes (without removal of the electrolyte) were then loaded on to a high-pressure chromenickel steel pan with a gold-plated copper seal. The DSC measurements were performed in a DSC 200 F3 (NETZSCH, Germany) at a heating rate of 10 °C min⁻¹. Electrochemical impedance spectroscopy measurements were performed on cells in the charged state of 4.2 and 4.5 V using an impedance analyzer (IM6e Zahner Elektrik). The amplitude of the a.c. signal was 5 mV, and the frequency range was from 10 mHz to 1 MHz.

3. Results and discussion

Scanning electron micrographs of the original and LiPON-coated LiCo₂ electrodes are shown in Fig. 1. The LiCo₂ particles are encapsulated with fine deposits, especially when the thickness of the deposited film is above 0.5 μm, at which time the electrode surface is homogeneously covered with the deposits. It may be noted that estimation of the thickness of the deposited film is based

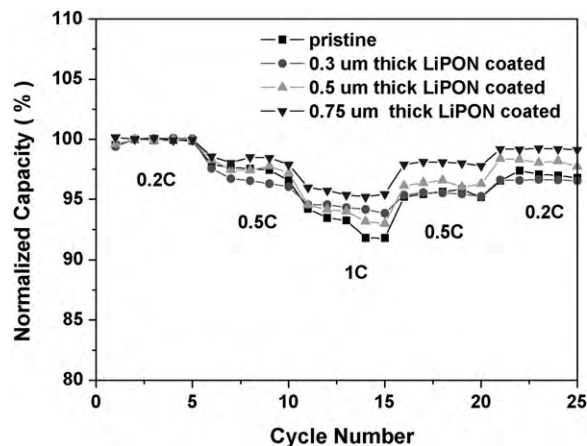


Fig. 5. Rate performance of pristine and LiPON-coated LiCo₂ electrodes at different rates: 0.2C, 0.5C, and 1C.

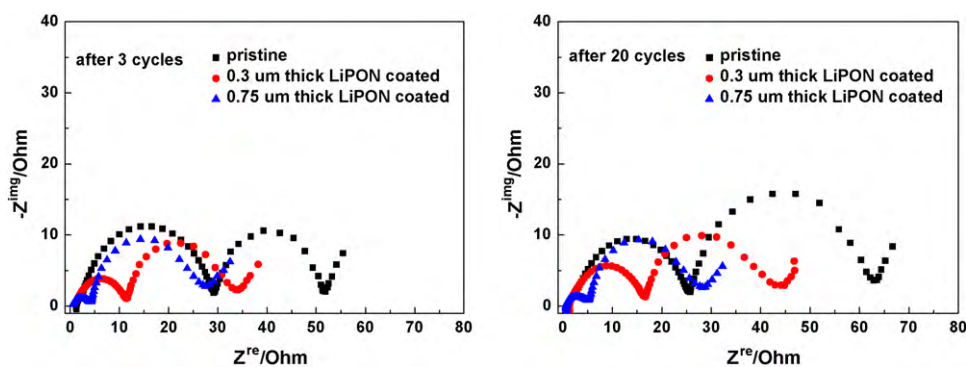


Fig. 6. Nyquist plots of pristine LiCoO₂ and 0.3- and 0.75- μ m-thick LiPON-coated LiCoO₂ electrodes at charged state after 3 and 20 cycles in range of 3.0–4.2 V.

on the thickness of the film deposited on a silicon wafer under similar conditions. EDAX data for the original and LiPON-coated electrodes are shown in Fig. 2, in which additional N and P peaks are observed with the LiPON-coated electrode. The deposited films that were sputtered from the Li₃PO₄ target in N₂ process gas represent the typical ion-conducting behaviour of LiPON, as inferred from impedance measurements using a blocking electrode system with a Pt/LiPON/Pt sandwich structure (not shown).

Charge–discharge curves for the original and LiPON-coated LiCoO₂ electrodes on the first cycle are presented in Fig. 3. The reversible capacity and the initial irreversible capacity appear to be the same. In addition, there exists only a slight difference in capacity retention during cycling between 3.0 and 4.2 V (Fig. 4(a)). On the other hand, when the upper cut-off voltage is raised to 4.5 V, the discharge specific capacity of the pristine LiCoO₂ shows a significant fading in capacity with cycling, while the LiPON-coated LiCoO₂ shows much less fading as seen in Fig. 4(b). The enhanced overcharge behaviour of LiPON-coated LiCoO₂ may be attributed to the coating layer prohibiting direct contact of the active material with the electrolyte and thus preventing dissolution of the cobalt. The rate performance of the original and the LiPON-coated LiCoO₂ electrodes is illustrated in Fig. 5. The cells are charged galvanostatically to 4.2 V at a current of 0.2C but discharged to 3.0 V at different current densities. It is seen that the LiPON-coated LiCoO₂ electrode has lower capacity fading than the pristine one. When the C-rates are applied in a descending order, i.e., 1.0, 0.5 and 0.2C, the LiPON-coated LiCoO₂ electrode, especially the one with the 0.75- μ m-thick LiPON deposition, exhibits good reversibility in discharge capacity, whereas the pristine electrode gives considerably reduced discharge capacities at a given C-rate.

In order to elucidate the improved rate performance and cycleability of the LiPON-coated LiCoO₂ electrode, electrochemical impedance spectra (EIS) analysis was carried out. Figs. 6 and 7 show the Nyquist plots of pristine LiCoO₂ and the 0.3- and 0.75-

μ m-thick LiPON-coated LiCoO₂ electrodes at a charged state after 3 and 20 cycles in the range of 3.0–4.2 and 3.0–4.5 V, respectively. All the spectra consist of two well-defined semicircles, followed by a short linear portion. The semicircle observed in the high-frequency domain is attributed to the impedance due to the Li-ion migration through the surface film that covers the active material (R_f), and that in the low-frequency domain is attributed to the charge-transfer resistance (R_{ct}) [15,16]. Both the surface layer resistance and the charge-transfer resistance of the LiCoO₂ electrode are significantly reduced by LiPON coating. In particular, for the 0.75- μ m-thick LiPON-coated LiCoO₂ electrode, there is little increase in R_f and R_{ct} even after cycling in voltage range of 3.0–4.5 V. On the other hand, for the pristine LiCoO₂ electrode, R_{ct} increases after 20 cycles and a dramatic increase is observed after cycling in the 3.0–4.5 V range. The results indicate that an ion-conducting LiPON film enhances lithium-ion migration through the interface between the surface of LiCoO₂ particles and the electrolyte, and suppresses the surface reaction between the electrode surface and the electrolyte during cycling. This leads to the improved rate capability of the LiPON-coated electrode. Therefore, in the case of LiPON-coated electrode with a homogeneous coating film, the LiPON coating layer has an important role as a surface film on the active material, in that it suppresses the impedance growth during cycling.

It is important to study the thermal stability of delithiated cathodes because this parameter has a crucial effect on the thermal stability of lithium-ion batteries. The DSC curves of the pristine electrode and the LiPON-coated electrode charged to 4.2 and 4.5 V, respectively, are given in Figs. 8 and 9. The exothermic peak heat flow and the total heat generation between 100 and 400 °C are reduced by coating a LiPON film on the pristine LiCoO₂ electrode. When the electrodes are charged to 4.5 V, the temperature of the major exothermic peak of LiPON-coated electrodes is slightly higher than that of pristine electrode. Because the exothermic heat observed in the pristine LiCoO₂ cathode is known to be due to

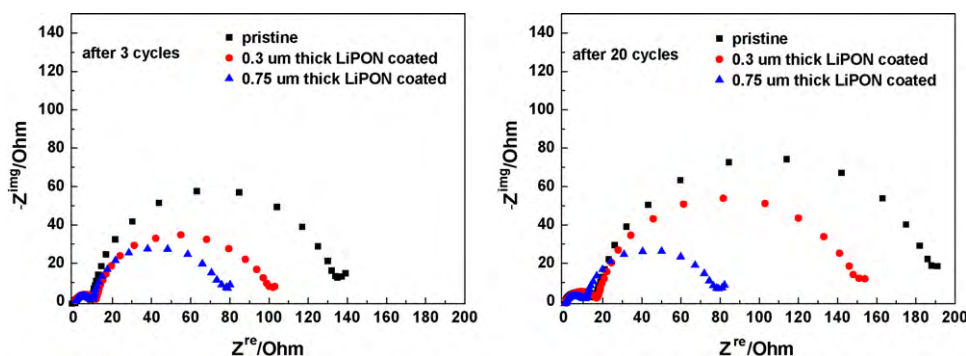


Fig. 7. Nyquist plots of pristine LiCoO₂ and 0.3- and 0.75- μ m-thick LiPON-coated LiCoO₂ electrodes at charged state after 3 and 20 cycles in range of 3.0–4.5 V.

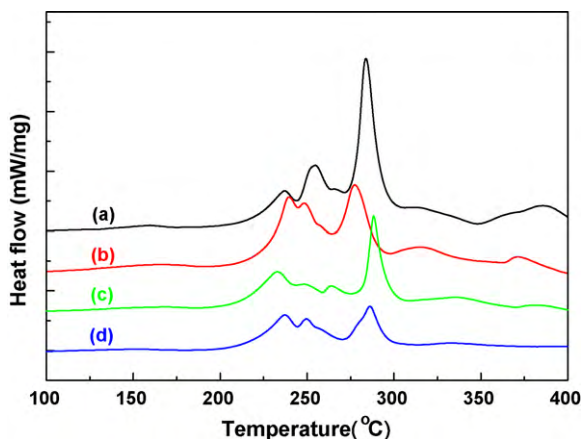


Fig. 8. DSC curves of (a) pristine LiCoO₂ electrode, and (b) 0.3-, (c) 0.5-, and (d) 0.75- μ m-thick LiPON-coated LiCoO₂ electrode. Cells were charged to 4.2 V before DSC measurements.

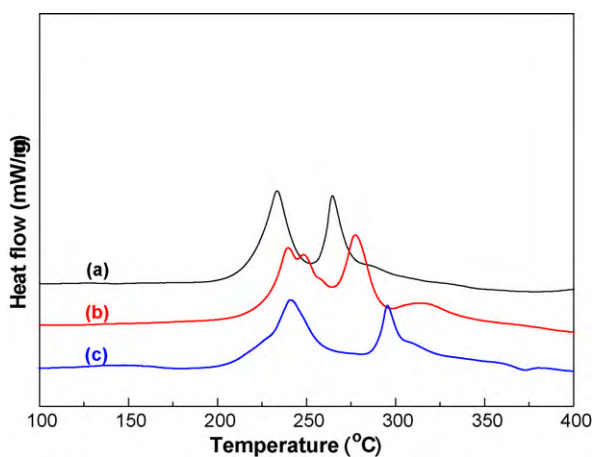


Fig. 9. DSC curves of (a) pristine LiCoO₂ electrode, and (b) 0.3-, (c) 0.75- μ m-thick LiPON-coated LiCoO₂ electrode. Cells were charged to 4.5 V before DSC measurements.

the reaction between the delithiated LiCoO₂ and the liquid electrolyte [1–3], it is concluded that the LiPON coating layer might be suppressing the exothermic reaction by separating the delithiated LiCoO₂ and the electrolyte solution, thus decreasing heat generation.

4. Conclusions

A solid electrolyte film, LiPON, has been coated on the surface of a LiCoO₂ composite cathode by RF magnetron sputtering. The ion-conducting LiPON film enhances lithium-ion migration through the interface between the surface of LiCoO₂ particles and the electrolyte and suppresses the surface reaction between the electrode surface and electrolyte during cycling. Therefore, the deposition of an ion-conducting LiPON film appears to be an effective method to improve the electrochemical performance in terms of cycleability and rate capability, as well as the thermal stability of the charged LiCoO₂ cathode.

Acknowledgements

This work was supported by LG Chemical Ltd. and a grant from the Energy Efficiency & Resources of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) funded by the Korea Government, Ministry of Knowledge Economy (2008EEL11P070000).

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