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Thickness-tunable polyimide nanoencapsulating layers and their influence on cell performance/thermal stability of high-voltage $LiCoO_2$ cathode materials for lithium-ion batteries

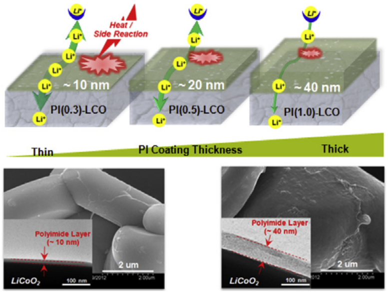
Jang-Hoon Park [a], Ju-Hyun Cho [a], Eun-Ho Lee [a], Ju-Myung Kim [a], Sang-Young Lee [b,*]

[a] *Department of Chemical Engineering, Kangwon National University, Chuncheon, Kangwondo 200-701, Republic of Korea*
[b] *Interdisciplinary School of Green Energy, Ulsan National Institute of Science and Technology (UNIST), Ulsan 689-798, Republic of Korea*

HIGHLIGHTS

- ► Thickness-tunable polyimide nanoencapsulating layer is introduced on $LiCoO_2$ surface.
- ► Effect of PI coating thickness on high-voltage cell performance is explored.
- ► PI encapsulating layer is featured with nanometer-thick, large surface coverage.
- ► PI coating thickness of 10 nm imparts well-balanced coating effects on 4.4 V $LiCoO_2$.
- ► Beneficial coating effects can be optimized by tuning PI coating thickness.

GRAPHICAL ABSTRACT



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ABSTRACT

We have previously demonstrated polyimide (PI) gel polymer electrolyte (GPE)-based nanoencapsulation as a new surface modification strategy for high-voltage cathode materials. In this study, in an endeavor to attain a more comprehensive understanding of the PI GPE-based surface modification, effects of structural variation of PI encapsulating layers (specifically, focusing on PI coating thickness) on cell performance and thermal stability of high-voltage (4.4 V) $LiCoO_2$ are investigated. Herein, PI coating thickness is tuned between approximately 10 and 40 nm by varying polyamic acid (synthesized from pyromellitic dianhydride/oxydianiline) concentration of coating solutions. As PI coating thickness is increased, discharge C-rate capability of cells is deteriorated due to undesired rise of ionic and electronic resistance of thick PI coating layers. On the other hand, thick PI encapsulating layers are effective in mitigating interfacial exothermic reaction between delithiated $LiCoO_2$ and liquid electrolyte. Notably, among the various PI coating thicknesses, average thickness of 10 nm imparts well-balanced enhancement in cell performance and thermal stability. These results demonstrate that structural fine-tuning (particularly, coating thickness) of PI encapsulating layers, acting as ion-conductive protective conformal thin films, plays a significant role in optimizing their beneficial coating effects on high voltage $LiCoO_2$.

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* Corresponding author. Tel.: +82 33 250 6338; fax: +82 33 251 3658.
E-mail address: sangyounglee87@gmail.com (S.-Y. Lee).

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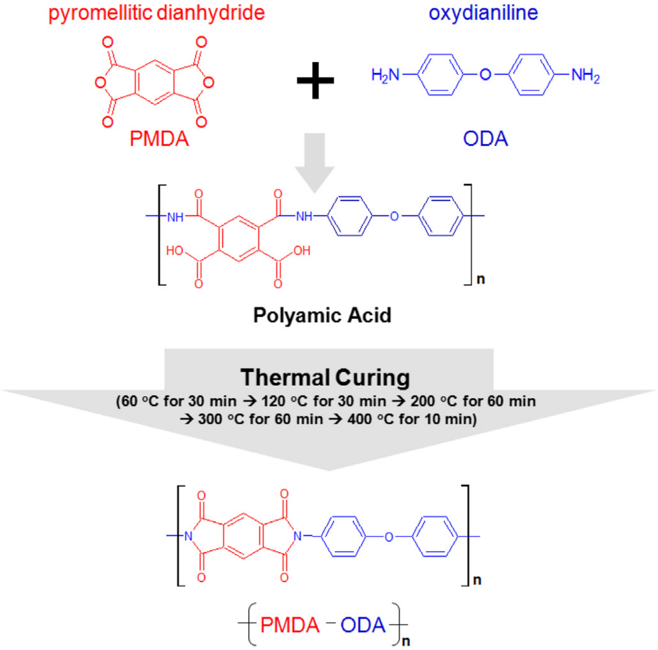

Fig. 1. Chemical structures of pyromellitic dianhydride (PMDA)/oxydianiline (ODA) polyamic acid and resulting polyimide (PI). Detailed information on a stepwise imidization process is also provided.

1. Introduction

As applications of lithium-ion batteries are vigorously expanding into newly emerging fields such as (hybrid) electric vehicles and power grids, development of new cathode active materials capable of offering large reversible capacity is strongly demanded [1–5]. Among various cathode materials, $LiCoO_2$ (LCO) has been most widely used in commercial lithium-ion batteries owing to the ease of manufacturing procedure and well-balanced electrochemical performance. Meanwhile, in an effort to increase the capacity of LCO, charging cells above a conventional cut-off voltage of 4.2 V has been extensively investigated [6–10]. However, raising the charge cut-off voltage entails confronting formidable challenges related to deterioration of cell performance (particularly, cyclability) and thermal stability. These problems are mainly due to undesirable interfacial side reactions between the delithiated LCO and liquid electrolytes, where liquid electrolytes are highly prone to electrochemical decomposition at high voltage conditions. Hence, it is no doubt that interfacial control between the LCO and liquid electrolyte is crucially important in the development of high-voltage cells.

One promising attempt to resolve these challenges of the high-voltage LCO is the surface modification of LCO with inorganic materials such as Al_2O_3 [8,9], ZrO_2 [10], ZnO [11], $AlPO_4$ [12], and AlF_3 [13,14]. Unfortunately, these inorganic materials, although they are effective in suppressing the interfacial side reactions, tend to be discontinuously deposited on LCO surface and behave as an

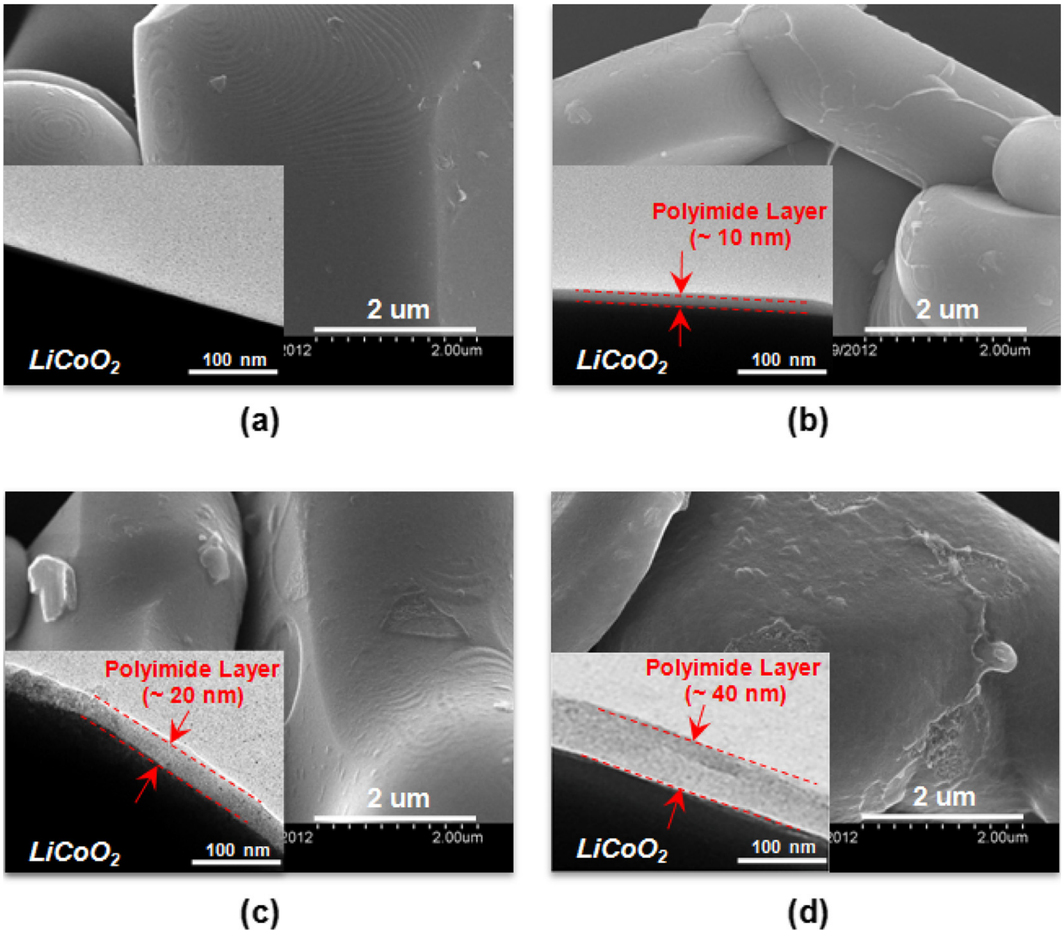

Fig. 2. FE-SEM photographs of: (a) pristine LCO; (b) PI(0.3)-LCO; (c) PI(0.5)-LCO; (d) PI(1.0)-LCO. Insets are TEM photographs of pristine LCO and various PI-LCO samples.