

Short communication

## Performances and thermal stability of $\text{LiCoO}_2$ cathodes encapsulated by a new gel polymer electrolyte

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### Abstract

A unique approach for improving the thermal stability of delithiated  $\text{LiCoO}_2$  cathodes has been presented, which is based on the encapsulation of  $\text{LiCoO}_2$  by a new cyano-substituted polyvinylalcohol (cPVA)-based gel polymer electrolyte. In a bid to maximize the effect of encapsulation, the cPVA-based gel polymer electrolyte was applied to the  $\text{LiCoO}_2$  cathode with a predetermined degree of porosity. Through this new process, the gel polymer electrolyte is expected to locate preferentially onto the  $\text{LiCoO}_2$  at well-controlled thickness, with the overall porous structure of the modified cathode being little influenced. Due to the presence of cyano ( $-\text{CN}$ ) groups, the cPVA shows high dielectric constant ( $\epsilon = 15$  at 1 kHz at 20 °C), which is thus expected to enhance the Li-salt dissociation, leading to the excellent ionic conductivity (around 7 mS cm at 25 °C). Under the assumption that the  $\text{LiCoO}_2$  could be fully covered with the cPVA, the encapsulated thickness is calculated around 10 nm, which was further evidenced by the FE-SEM results. Meanwhile, compared to the pristine  $\text{LiCoO}_2$  cathode ( $\Delta H = 413 \text{ J g}^{-1}$ ), the modified  $\text{LiCoO}_2$  cathode exhibited the superior thermal stability ( $\Delta H = 31 \text{ J g}^{-1}$ ) and also presented the satisfactory C-rate performances and cyclability. Such a remarkable enhancement in the thermal stability and the electrochemical performances has been discussed on the basis of the morphology of the modified  $\text{LiCoO}_2$  cathode and the electrochemical properties of the cPVA-based gel polymer electrolytes.

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**Keywords:** Battery;  $\text{LiCoO}_2$ ; Gel polymer electrolyte; Thermal stability; Encapsulation

### 1. Introduction

With pursuing larger capacity and higher performances of lithium ion secondary batteries, their safety has been issued as a major concern. The main cause for many safety-related incidents is known to be related with vigorous exothermic reaction between delithiated cathode active materials and liquid electrolytes [1–3]. Many efforts to suppress the exothermic reaction have been carried out, which have mainly focused on the development of stable structured-cathode active materials or the modification of cathode active materials by inorganic coating or the addition of new electrolytes [4–9]. However, most of them have been accompanied by the loss of other electrochemical performances, including the decreased capacity and the poor C-rate (charge/discharge) capability. Therefore, a completely new solution that can achieve the safety enhancements with little losing the electrochemical performances is needed.

It has been well known that a gel polymer electrolyte tends to show better safety characteristics than a conventional liquid electrolyte, while exhibits excellent electrochemical performances due to its high ionic conductivity [10–15]. Up to now, most applications of gel polymer electrolytes have been focusing on a function as a kind of separator locating between an anode and a cathode, however, which has not given satisfactory results for improving the safety problems, because gel polymer electrolytes have acted only as an ion-conducting separator, not as an effective protective layer to control the interfacial reaction of cathode active materials. In this study, a gel polymer electrolyte is employed as a coating material for  $\text{LiCoO}_2$  active materials, instead of a physical separator. In a bid to maximize the effect of introducing the gel polymer electrolyte onto the surface of  $\text{LiCoO}_2$  active materials, a unique approach is suggested [18], which comprises of, as a first step, the preparation of a  $\text{LiCoO}_2$  cathode with a predetermined degree of porosity and then the treatment of the  $\text{LiCoO}_2$  cathode by the gel polymer electrolyte. Through this new process, it is possibly expected that the gel polymer electrolyte can locate preferentially onto the  $\text{LiCoO}_2$  active materials at well-controlled thickness, with

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the overall porous structure of the cathode being little influenced. The detailed experimental procedure was described in the Section 2.

As a cathode, the most widely used  $\text{LiCoO}_2$  was chosen and a new gel polymer electrolyte, cPVA (cyano ( $-\text{CN}$ )-substituted polyvinylalcohol) was introduced as a coating material [18]. The presence of  $-\text{CN}$  groups enables the cPVA to present high dielectric constant ( $\epsilon = 15$  at 1 kHz at  $20^\circ\text{C}$ ) that is believed to possibly enhance the Li-salt dissociation when it is plasticized with liquid electrolytes, which leads to the superior ionic conductivity (around  $7 \text{ mS cm}^{-1}$  at  $25^\circ\text{C}$ ). This value is remarkably high, considering the previous publications [10–15] that the ionic conductivities of traditional gel polymer electrolytes have been reported to be around  $1 \text{ mS cm}^{-1}$ .

In this study, the effect of cPVA-based gel polymer electrolytes on the thermal stability of the delithiated  $\text{LiCoO}_2$  cathode and the cell performances such as the C-rate capability and the cyclability has been discussed on the basis of the novel morphology of the modified  $\text{LiCoO}_2$  cathode and the electrochemical properties of the cPVA-based gel polymer electrolytes.

## 2. Experimental

A typical  $\text{LiCoO}_2$  cathode was prepared by combining polyvinylidene fluoride (PVdF) binder, and carbon black in N-methyl pyrrolidone (NMP) with  $\text{LiCoO}_2$  active materials. The prepared  $\text{LiCoO}_2$  cathode was modified by dipping it into the cPVA (cyano ( $-\text{CN}$ )-substituted polyvinylalcohol,  $M_w = 80,000 \text{ g mol}^{-1}$ ,  $[-\text{CN}]/([-\text{CN}] + [-\text{OH}]) = 0.88$ ) solution for a determined time of 10 min to allow the complete penetration of the solution into the pores of cathode, where acetone was chosen as a solvent for the cPVA [18]. The cPVA concentration in the solution was fixed at 1 wt%. After complete evaporation of the acetone, the loaded amount of the cPVA in the modified  $\text{LiCoO}_2$  cathode was measured. Schematic illustration on the coating procedure is presented in Fig. 1.

The morphology of the modified  $\text{LiCoO}_2$  was observed with a field emission scanning electron microscopy (FE-SEM, JEOL

Ltd., Japan). The aluminum-pouched cells with the pristine cathodes or the modified cathodes were assembled using the lithium ion polymer battery technology of the LG Chem [19]. The cells were activated by injecting the liquid electrolytes (1 M  $\text{LiPF}_6$  in carbonate mixtures, Mitsubishi chemical.). The C-rate (charge/discharge) capability of cells was examined with changing a discharge rate from 0.2 C ( $=152 \text{ mA g}^{-1}$ ) to 1 C ( $=760 \text{ mA g}^{-1}$ ) at a constant charge rate of 0.5 C ( $=380 \text{ mA g}^{-1}$ ). For the DSC measurements, the cells were charged to 4.2 V at a charge rate of 0.2 C. The cells were then disassembled in a dry room to remove the charged cathodes containing the liquid electrolytes. Approximately 10 mg of the charged cathodes was cut and hermetically sealed into an aluminum sample pan. The DSC measurements were carried out under nitrogen atmosphere with a heating rate of  $5 \text{ K min}^{-1}$ .

## 3. Results and discussion

The morphology of the modified  $\text{LiCoO}_2$  is compared with that of the pristine one. It is apparently observed that the  $\text{LiCoO}_2$  was encapsulated with the thin cPVA layer, where the coated thickness appears to be far below 100 nm (Fig. 2(b)). The amount of the loaded cPVA in the cathode is observed to be 0.55 g per 100 g of  $\text{LiCoO}_2$  by measuring the weight change of the cathode. It was already informed that the specific surface area of the  $\text{LiCoO}_2$  is  $0.4 \text{ m}^2 \text{ g}^{-1}$  and its true density is  $5.1 \text{ g cc}^{-1}$ , while the density of the cPVA is  $1.2 \text{ g cc}^{-1}$ . Under the assumption that the  $\text{LiCoO}_2$  could be fully covered with the cPVA, the encapsulated thickness is calculated around 10 nm, which seems to be quite consistent with the FE-SEM results. The small pores formed between the  $\text{LiCoO}_2$  active materials in Fig. 2(b) may come from the phase inversion occurred during the formation of cPVA layer, which is commonly observed in the preparation of micro-porous membranes [16].

The effect of encapsulation of  $\text{LiCoO}_2$  by the cPVA on the cell performances such as the C-rate (charge/discharge) capability and the cyclability is investigated. Fig. 3 presents that there is little difference in the C-rate capability and the cyclability over 350

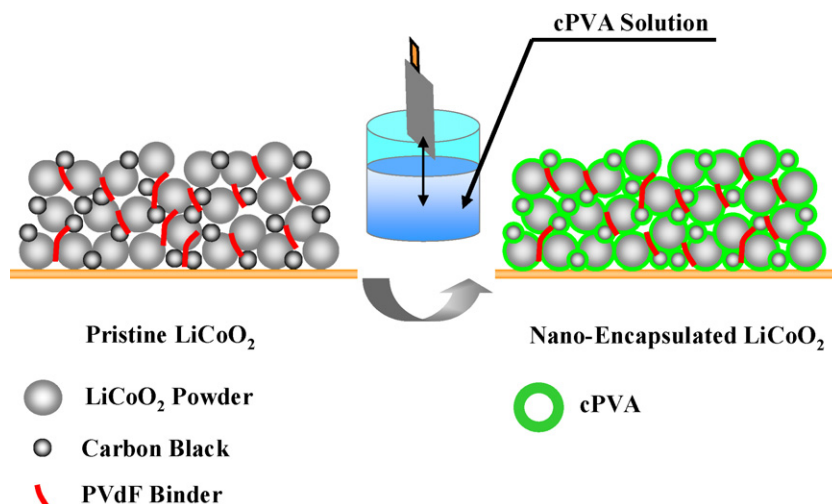


Fig. 1. Schematic illustration on modification procedure of  $\text{LiCoO}_2$  cathode by cPVA.

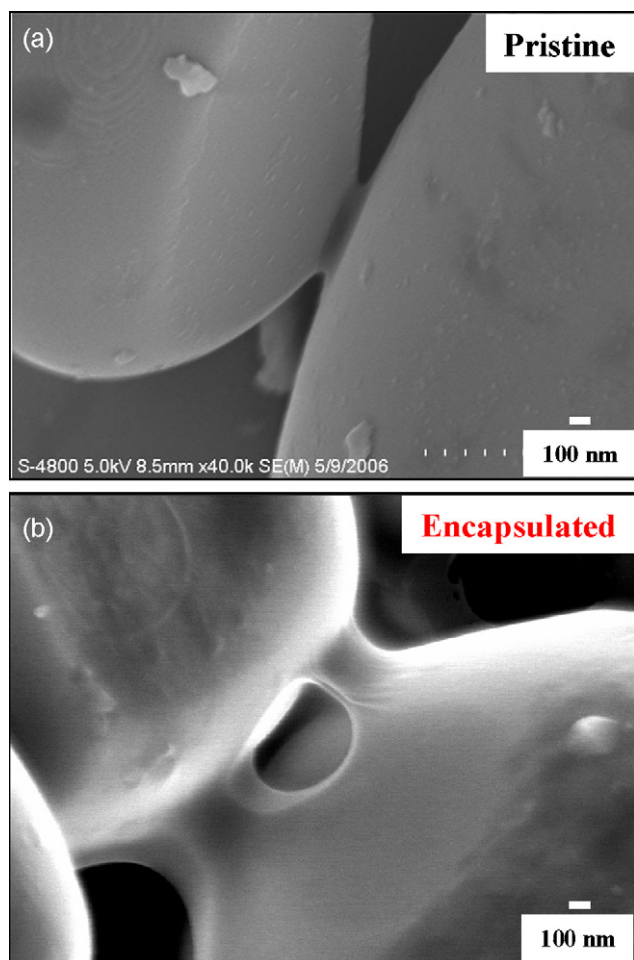


Fig. 2. Scanning electron micrographs of LiCoO<sub>2</sub>: (a) pristine and (b) cPVA-modified.

cycles between the pristine cathode and the modified cathode, which indicates that the cPVA-encapsulation barely deteriorates the cell performances. From the viewpoint of ion transport, the only difference between the two cathodes is the presence of the cPVA-based gel polymer electrolyte locating on the surface of the LiCoO<sub>2</sub>. Considering the previous observations that the cPVA layer presents the thickness of around 10 nm and the ionic conductivity of  $7 \text{ mS cm}^{-1}$ , the ion transport in the modified cathode is expected to be little affected by the presence of cPVA-based gel polymer electrolyte. Furthermore, from Fig. 2(b), it has been already observed that the overall porous structure of the cathode has been little affected even after the cPVA treatment, which enables the efficient uptake of liquid electrolytes into the pores of cathodes and thus also contributes to the favorable ion conduction in the cathode. Therefore, the satisfactory electrochemical performances of cells could be attributed to both the high ionic conductivity of cPVA-based gel polymer electrolytes and the well-preserved porous structure of the modified LiCoO<sub>2</sub> cathode.

Fig. 4 presents the DSC thermograms of the pristine cathode and the modified cathode charged to 4.2 V. The pristine LiCoO<sub>2</sub> cathode exhibits a traditional behavior, i.e., the large exothermic peaks ( $\Delta H = 413 \text{ J g}^{-1}$ ) between 100 and 300 °C,

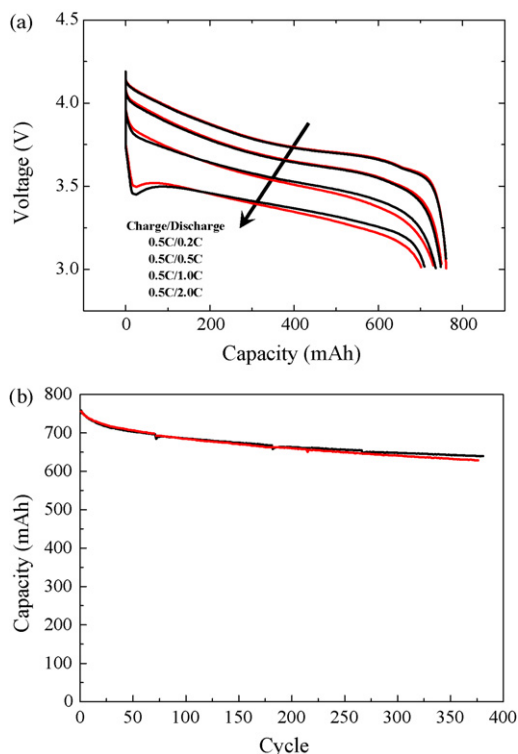


Fig. 3. (a) Discharge profiles and (b) cyclability of cells for pristine LiCoO<sub>2</sub> cathode (black-line) and cPVA-modified LiCoO<sub>2</sub> cathode (red-line). The discharge-rate performances were examined with changing a discharge rate from 0.2 C ( $=152 \text{ mA g}^{-1}$ ) to 2.0 C ( $=1520 \text{ mA g}^{-1}$ ) at a constant charge rate of 0.5 C ( $=380 \text{ mA g}^{-1}$ ). The charge/discharge rate for cyclic performance is fixed at 1.0 C/1.0 C ( $=760 \text{ mA g}^{-1}$ ). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

which is known to be due to vigorous reaction between the delithiated LiCoO<sub>2</sub> active materials and the liquid electrolytes [1–3]. On the other hand, the noticeable decrease of exothermic heat ( $\Delta H = 31 \text{ J g}^{-1}$ ) is observed for the modified LiCoO<sub>2</sub> cathode, which indicates that the cPVA locating onto the LiCoO<sub>2</sub> is effective in suppressing the exothermic reaction. It is possibly expected that the modified LiCoO<sub>2</sub> would encounter the gel polymer electrolyte rather than directly the violent liquid elec-

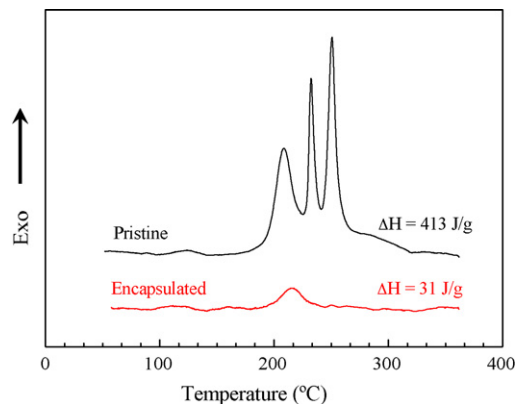


Fig. 4. DSC thermograms of exothermic reaction between delithiated LiCoO<sub>2</sub> active materials and electrolytes. The cells were charged to 4.2 V at a charge rate of 0.2 C. The DSC measurements were carried out under nitrogen atmosphere with a heating rate of  $5 \text{ K min}^{-1}$ .

trolyte, which suggest that they may go through the less vigorous exothermic reaction. Furthermore, considering the previous publications [17] that the cyano groups are known to easily form a kind of coordinated complexes with transition metal ions such as cobalt, nickel, and so on, it is assumed that the cobalt cations in the LiCoO<sub>2</sub> could interact with the –CN groups of cPVA-based gel polymer electrolytes, which might influence the structural stability of the delithiated LiCoO<sub>2</sub> as well as the surface reaction with the liquid electrolytes. The details on the interfacial phenomena between the delithiated LiCoO<sub>2</sub> and the cPVA-based gel polymer electrolytes will be further investigated in the next study.

This is, to the best of our knowledge, the first report that has improved the thermal stability of delithiated LiCoO<sub>2</sub> cathode by introducing the gel polymer electrolyte as a nano-scaled coating layer for LiCoO<sub>2</sub>.

#### 4. Conclusion

The encapsulation of LiCoO<sub>2</sub> by the cPVA-based gel polymer electrolyte has been successfully carried out. Compared to the pristine cathode ( $\Delta H = 413 \text{ J g}^{-1}$ ), the modified cathode exhibited much safer thermal stability ( $\Delta H = 31 \text{ J g}^{-1}$ ), with maintaining the excellent C-rate capability and the cyclability. This novel morphology and the possible formation of coordinated complexes between the –CN groups of cPVA and the cobalt cations of LiCoO<sub>2</sub> are considered as key factors for significantly suppressing the exothermic reaction in the delithiated cathode. Meanwhile, the preserved porous structure in the modified cathode and the excellent ionic conductivity of the

cPVA-based gel polymer electrolytes are believed to contribute to the satisfactory C-rate capability and cyclability.

Further works will be focused on the more comprehensive understanding of the interfacial phenomena between the delithiated LiCoO<sub>2</sub> and the cPVA-based gel polymer electrolytes and finally the practical cell safety tests such as hot-oven preservation will be conducted and correlated with the DSC results.

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