

Short communication

Direct carbon-black coating on LiCoO₂ cathode using surfactant for high-density Li-ion cell

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Abstract

Direct carbon-black coating of the cathode material using a surfactant increases the capacity of a Li-ion cell by ~10% compared with using bare LiCoO₂. The coating method comprises two steps: (i) dispersion of aggregated carbon black using orotan[®]—a polyacrylate dispersant; (ii) carbon-black coating of the cathode material using a gelatin—an amphoteric surfactant. This technology reduces the carbon content in the electrode without sacrificing the cycle-life performance of the cell, and also improves the rate capability of the Li-ion cell. Moreover, the direct carbon-black-coated cathode exhibits excellent capacity recovery and restricted expansion of the cell thickness compared with a bare cathode during storage at 85 °C.

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1. Introduction

The market for Li-ion cells has rapidly expanded due to the increase in demand for mobile electronics, such as notebook-PCs, PDAs, mobile phones and camcorders. Total sales of the cells in 2002 have been reported to be over 6.5 billion dollars, and are expected to be more than 10 billion dollars in 2005 [1]. The capacity of Li-ion cells has also been increasing by over ~8% every year, along with a decrease in cell thickness [1]. This has been made possible by using a composite-cathode material with a larger particle-size distribution, a smaller weight portion of the binder and a conducting agent, as well as thinner electrode substrates of Al and Cu. At present, most cathode electrodes in Li-ion cells consist of 2 wt.% carbon black, 2 wt.% binder, and 96 wt.% cathode material. Therefore, the only means to increase the cell capacity is to replace the active materials with those of higher capacity, or to blend such materials with LiCoO₂

(for the cathode) or graphite (for the anode). Several candidates such as LiNi_{1-x-y}Mn_xCo_yO₂ for the cathode, and SnO₂ or Si for the anode have been proposed, but the overall power of the cell is lower due to the reduced working voltage [2–15].

Surfactants consist of hydrophobic (water-hating) and hydrophilic (water-liking) groups, and the surfactant head groups (S) and inorganic precursors (I) can be templated by electrostatic interactions, such as coulomb interactions, hydrogen bonding, and covalent bonding [16,17]. Very limited types of surfactants can, however, be used in Li-ion cells. The reason is that the surfactants must be totally dissolved in a solvent, and those with Na⁺ or K⁺ ions should be excluded. Also, the surfactant not deteriorate the electrochemical properties of the cells, such as cycle-life and storage performance at high temperature. Among the various types of surfactants, amphoteric surfactants promise to be the best candidates for use in Li-ion cells, since they have been reported to be electrochemically stable up to 4.4 V [18].

In this paper, a direct carbon-black coating has been applied to the cathode using an amphoteric-gelatin surfactant

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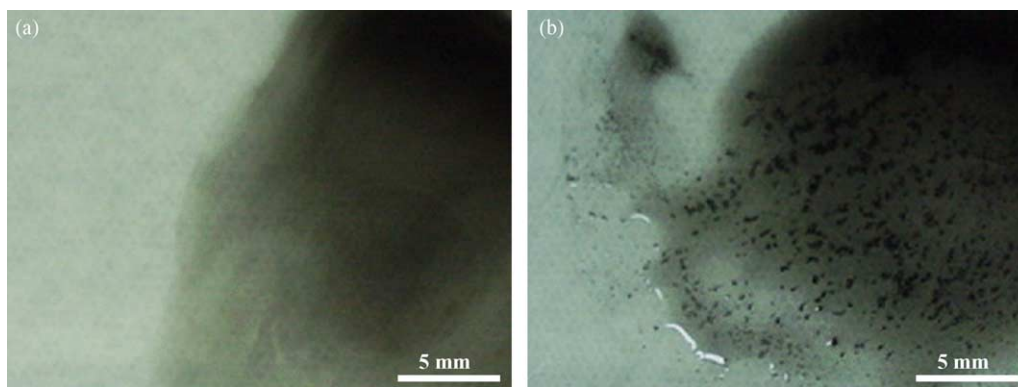


Fig. 1. Photographs of (a) dispersed Super P carbon black using the orotan[®] solution, and (b) dispersed carbon black without using orotan[®] solution.

to fabricate a high-density Li-ion cell. By this method, the volumetric density and rate capability are improved without sacrificing electrochemical performance, compared with a conventional cell using bare LiCoO₂.

2. Experimental

Since Super P carbon black consists of aggregated chunks, it must be broken into submicron-sized particles in order to be effectively coated on LiCoO₂ cathode powder (with an average particle size of $\sim 10 \mu\text{m}$, and a BET surface area of $0.2 \text{ m}^2 \text{ g}^{-1}$). It is known that orotan[®] is the most effective surfactant (polyacrylate dispersant) for dispersing carbon black, and is widely used for carbon coatings in the display industry [19]. Three grams of orotan[®] powder was mixed with 30 g of Super P carbon black in 500 ml of distilled water, and then ball-milled for 2 h. The carbon black with orotan[®] gave a good dispersion in water without forming aggregates, as shown in Fig. 1(a). By contrast, the carbon-black chunks without orotan[®] do not disperse well, despite ball-milling (Fig. 1(b)).

To coat the dispersed carbon black on the cathode material (200 g), 2 g of gelatin was dissolved in 30 ml of distilled water

at 50 °C for 10 min, and then poured into 900 ml of distilled water. Gelatin was coated on the dispersed carbon black when the carbon-dispersed orotan[®] solution was added. The pH of gelatin had to be adjusted to near its isoelectric point of $\text{pH} \cong 4\text{--}5$ by using acetic acid so that the carbon could be coated directly on the cathode particle [16]. At the isoelectric point, the $-\text{COOH}$ end-group in gelatin dissociated to $-\text{COO}^-$, and thus a dehydration reaction occurred with the OH^- group created on the LiCoO₂-particle surface and resulted instantly in a carbon-black coating on the cathode powder. The carbon-coated LiCoO₂ powders then sank to the bottom of the beaker, usually within 30 s. A miniature process for carbon coating on LiCoO₂ powders is shown in Fig. 2. After filtering, the powders were dried at 300 °C for 2 h. Scanning electron microscopy (SEM) showed that the surface morphology of the carbon-coated LiCoO₂ was distinctly different from that of bare LiCoO₂ (Fig. 3).

The capacity of the Li-ion cell was designed to be 700 mA h or 800 mA h at 0.2 C rate, with an anode:cathode dimensional ratio of 1.08. Micro-beads carbon fibre (MCF) synthetic graphite was used as the anode material. The weight percentage of the composite-cathode electrode (LiCoO₂: Super P carbon black: binder) was 96:2:2 and 97:1:2, respectively, for bare and carbon-coated LiCoO₂. The cell size

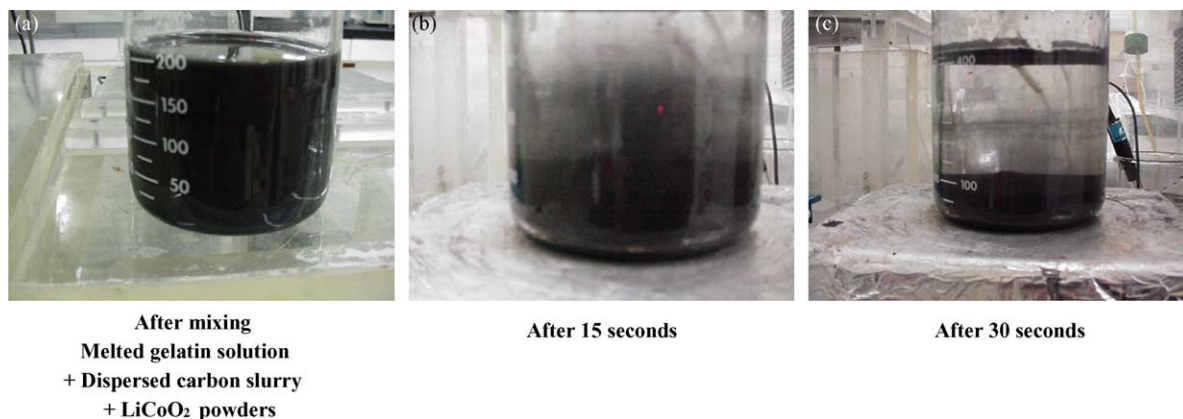


Fig. 2. Photographs of gelatin solution mixed with dispersed carbon black and LiCoO₂ powders as a function of time: (a) just after mixing solution; (b) after 15 s; and (c) after 30 s.

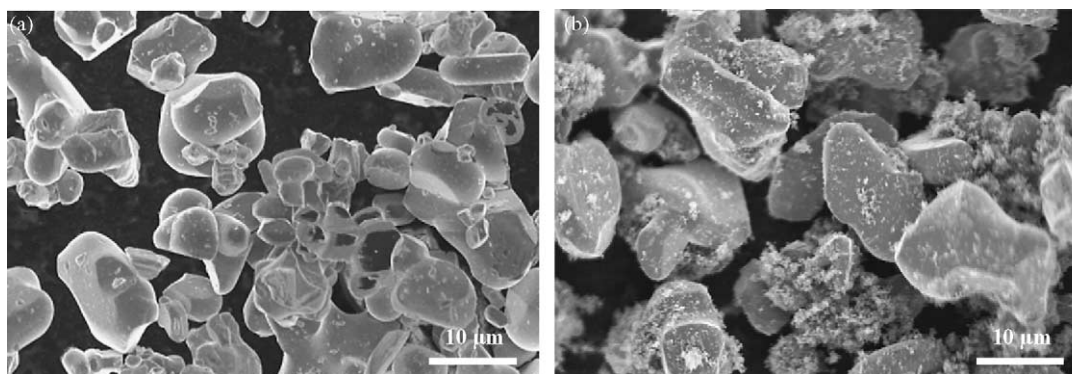


Fig. 3. SEM images of (a) bare LiCoO₂ with average particle size of ~10 μm, and (b) 1 wt.% carbon-coated LiCoO₂ using carbon-dispersed orotan[®] solution and gelatin.

Table 1
Comparison of volumetric capacities in Li-ion cells using bare or carbon-coated LiCoO₂ electrode materials

	Bare LiCoO ₂ (Carbon content: 2 wt.%)	2 wt.% Carbon-coated LiCoO ₂	1 wt.% Carbon-coated LiCoO ₂
Maximum-electrode density (g cm ⁻³)	3.5	3.7	3.9
Discharge capacity of LiCoO ₂ in Li-ion cell (mA h g ⁻¹)	145	145	145
Volumetric capacity (mA h cm ⁻³)	508	537	566

was 40 mm × 3.4 mm × 62 mm (width × thickness × length). A mixture of ethylene carbonate and diethyl carbonate (EC/DEC) with 1 M LiPF₆ was used as the electrolyte, and all the cells contained 2.1 g of electrolyte. Detailed information of the electrode fabrication is described elsewhere [20]. To measure the cell thickness at every 50 cycles, the cells were charged to 4.2 V with a constant current at the rate of 1 C, rate followed by holding at 4.2 V until the applied current decreased to 30 mA. The cell thickness was measured during storage at 85 °C after fresh cells were initially cycled at the rate of 0.2 C rate between 4.2 and 2.75 V for 1 cycle, and charged to 4.2 V at 0.2 C. The charged cells were then stored in a hot oven at 85 °C and the cell thickness was measured after 4, 24, 48, 72, and 96 h storage. To check the capacity recovery of the cells with bare or carbon-coated cathodes, the cells charged to 4.2 V were stored at 85 °C for 24 h, and cooled to room temperature. The cells were then discharged to 2.75 V at the rate of 0.2 C rate.

3. Results and discussion

The volumetric capacities of Li-ion cells prepared from bare LiCoO₂ with 2 wt.% carbon content, 2 wt.% carbon-coated LiCoO₂, and 1 wt.% carbon-coated LiCoO₂ are listed in Table 1. The discharge capacities of LiCoO₂ were obtained from the anode/cathode dimensional ratio of 1.08, and are not normally affected by the ratio up to 1.15. The carbon-black coating enhances the packing density of the composite-cathode electrode when the maximum electrode density is obtained from the yield point where the electrode does not disintegrate on simply folding. From the discharge capacity

of LiCoO₂ and the electrode density, the volumetric density of the cell with 1 wt.% carbon-coated LiCoO₂ has the highest value of 566 mA h cm⁻³. Based on this result, practical cells were assembled using bare LiCoO₂ or 1 wt.% carbon-coated LiCoO₂. The rate capabilities of bare LiCoO₂ with 2 wt.% carbon content or 1 wt.% carbon-coated LiCoO₂ are shown in Fig. 4(a) for Li-ion cells adjusted to the same capacity (700 mA h). The Li-ion cell with 1 wt.% carbon-coated LiCoO₂ displays enhanced voltage profiles and rate capabilities. In addition, despite of the reduced carbon content, the cell gives a similar cycle-life performance to that with 2 wt.% carbon content, as shown in Fig. 4(b).

To investigate further the effect of surfactant on the long-term stability of the Li-ion cell, the cells containing bare or carbon-coated cathodes were charged to 4.2 V after every 50 cycles and the variation in cell thickness at room temperature was measured, as shown in Fig. 5. The cells exhibit quite similar swelling behaviour with increasing number of cycles. The variation of cell thickness and Co dissolution during storage at 85 °C are shown in Fig. 6. The initial cell thickness at 4.2 V was ~3.5 mm. After storage at 85 °C for 96 h, the thickness of the cell with a carbon-coated cathode increases only up to 5.4 mm, while that for the cell with a bare cathode swells to 6.4 mm (Fig. 6(a)). This is because the carbon coating may prevent electrolyte decomposition with accompanying gas evolution at the cathode/electrolyte interface. In addition, any residual surfactants may be removed by filtering and firing at 300 °C. Otherwise, these residuals may prove detrimental to the cycle-life and through cell swelling due to the generation of gas from the decomposition of surfactants at high voltage. In summary, these results show that the carbon-black coating can reduce the carbon content in

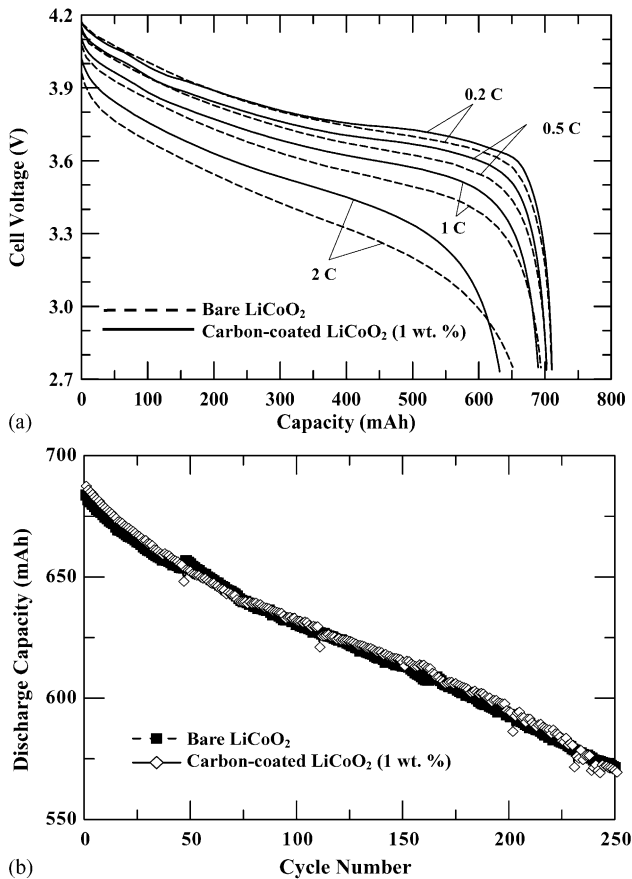


Fig. 4. (a) Rate capabilities of Li-ion cells using bare (dotted line), and 1 wt.% carbon-coated LiCoO₂ (solid line). The cell capacity was designed to 700 mAh, and the charge rate was fixed at 1 C (=700 mA). (b) Plots of discharge capacity vs. the cycle number for Li-ion cells using bare or 1 wt.% carbon-coated LiCoO₂. The charge and discharge rates are fixed at 1 C.

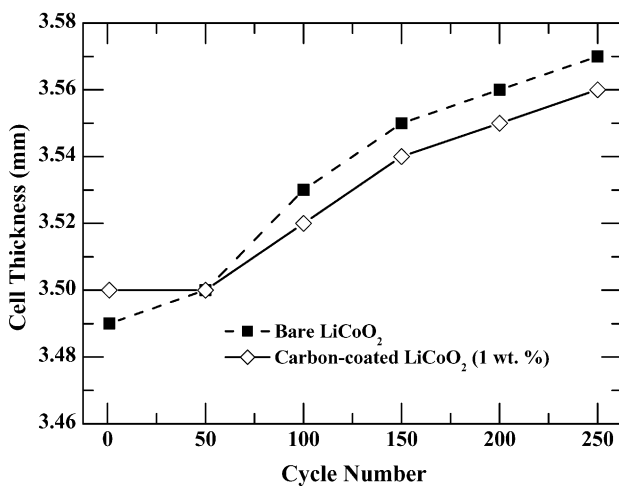


Fig. 5. Plots of cell thickness as a function of cycle number. To measure thickness at every 50 cycles, both cells containing bare or carbon-coated LiCoO₂ are charged to 4.2 V.

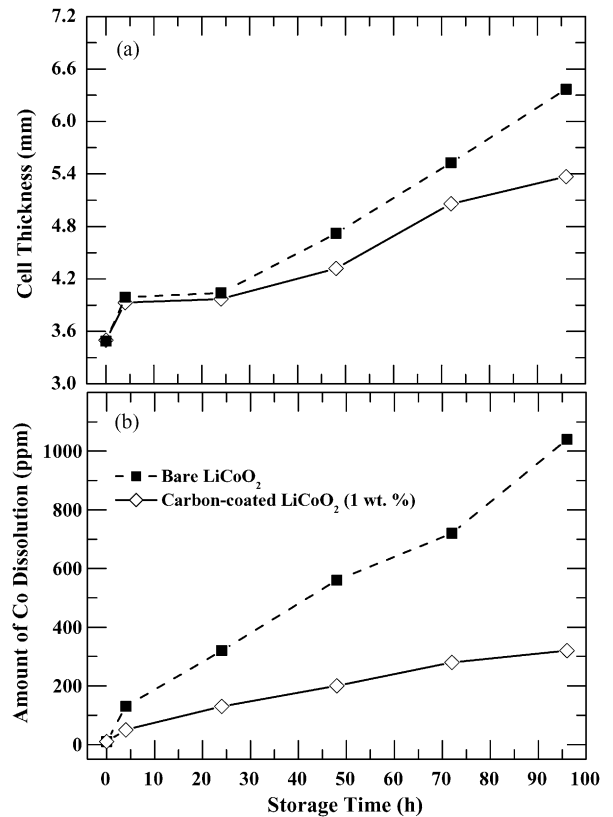


Fig. 6. (a) Variation of cell thickness during storage at 85 °C. (b) Amount of Co dissolution during storage at 85 °C. All cells are charged to 4.2 V before storage.

the composite-cathode electrode without sacrificing cycle-life.

In addition, the cell containing the carbon-coated cathode shows notably suppressed Co dissolution in the electrolyte. The dissolved Co concentration from the carbon-coated cathode is 320 ppm in the electrolyte, after storage for 96 h at 85 °C, while that from the bare cathode is 1050 ppm, as shown in Fig. 6(b). Similar effects have been observed for the metal-oxide-coated LiCoO₂, which greatly reduced the Co dissolution at 90 °C storage [21]. These results show that the carbon-black coating greatly diminishes the reactivity between the charged cathode and the electrolyte, even at high temperature. The discharge-capacity recovery of cells after storage at 85 °C for 24 h is presented in Fig. 7. The cell with a bare cathode shows ~8% higher capacity loss than the carbon-coated cathode. The initial discharge capacities of the cells containing bare or carbon-coated cathodes were 710 mAh at room temperature (Fig. 4(a)). The capacity recovery after storage at 85 °C for 24 h is enhanced due to the suppression of both Co dissolution and electrolyte decomposition by the carbon-black coating. Cobalt dissolution into solution is coupled with the release of lithium and oxygen and this results in structural degradation of LiCoO₂ [22]. Enhanced capacity recovery of the carbon-coated cathode demonstrates that the carbon-black coating plays a key role

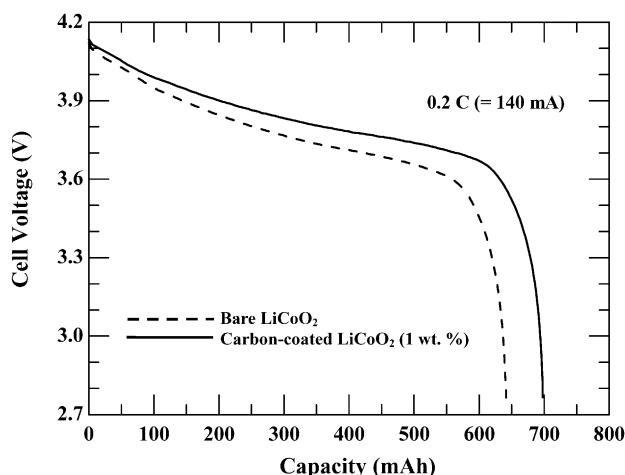


Fig. 7. Plots of capacity recovery after storage at 85 °C for 24 h. Cells with bare or carbon-coated cathodes were initially cycled with charge and discharge rates of 1 and 0.2 C, respectively, at room temperature. Initial discharge capacity is 710 mA h for each cell (as shown in Fig. 4(a)).

in reducing the reactivity between the charged cathode and the electrolyte.

The rate capabilities of bare LiCoO₂ with 2 wt.% carbon content and 1 wt.% carbon-coated LiCoO₂ are given in Fig. 8 for a cell designed to have the maximum capacity. The carbon-coated LiCoO₂ powder allows an increase in the fraction of the cathode content in the composite-cathode slurry and in the coating thickness of the composite-cathode electrode. Therefore, the carbon-coated LiCoO₂ improves the cell capacity, compared with the conventional bare LiCoO₂. The discharge capacity of the Li-ion cell increases from 700 mA h (with bare LiCoO₂) to 800 mA h (with carbon-coated LiCoO₂). The enhanced rate capability (Fig. 8) may be attributed to an improvement in the electrical contact between the cathode particles that is caused by the uniform carbon-black coating.

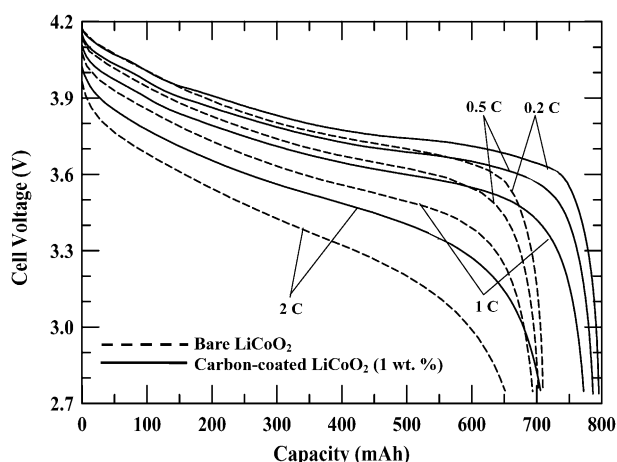


Fig. 8. Plots of rate capabilities of Li-ion cells using bare (dotted line) and 1 wt.% carbon-coated LiCoO₂ (solid line). Cells are designed to give maximum capacity. The charge rate is fixed at 1 C (=700 mA for bare LiCoO₂, and 800 mA for 1 wt.% carbon-coated LiCoO₂).

4. Conclusions

A direct carbon-black coating on the cathode material makes it possible to fabricate a composite-cathode electrode with lower carbon content without sacrificing electrochemical performance. In addition, the carbon-black coating improved the voltage profile of the cell, compared with a to the conventional cell using bare LiCoO₂. These results correlate with the suppression of Co dissolution and electrolyte decomposition. Consequently, the direct carbon-black coating enables fabrication of high-density Li-ion cell.

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