

Electrochemical and electron microscopic characterization of thin-film LiCoO_2 cathodes under high-voltage cycling conditions

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Abstract

Thin-film LiCoO_2 batteries using the Lipon electrolyte exhibit excellent cycleability up to 4.4 V. With the enhanced voltage limit for repeatable cycling, the thin-film cathode delivers a specific capacity of 170 mAh/g, which is 22% higher than that for previous LiCoO_2 cathodes cycled to 4.2 V. No evidence of grain fracture was detected by transmission electron microscopy (TEM) in the cathode layer after cycling to 4.4 V. When cycled to >4.4 V, capacity fades and cell resistance increases more rapidly, attributed to the onset of a phase transition at >4.4 V. Fracture of grains was observed by TEM in the cathode layer after cycling to 5 V. Nanocrystalline films show better cycleability to 5 V than films with a larger grain size.

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1. Introduction

LiCoO_2 is the most widely used cathode material in rechargeable Li batteries. It has a specific capacity of 140 mAh/g between 3.0 and 4.2 V versus Li. Reversible delithiation of Li_xCoO_2 is typically limited to $x = 0.5$, corresponding to ≈ 4.2 V. The capacity fades rapidly when cycled to >4.2 V, generally attributed to mechanical failure associated with structural changes at $x < 0.5$ [1]. Microstructural damage has been previously observed using transmission electron microscopy (TEM) in composite powder cathodes after cycling to 4.35 V [2]. To increase the capacity and energy density utilization of the cathode, efforts have been made to improve the cycling stability above 4.2 V by surface treatment or doping of LiCoO_2 powders [3–5].

In this paper, we show that LiCoO_2 thin films obtained by sputtering exhibit excellent capacity retention when cycled up to 4.4 V. We also report the electrochemical properties of completely delithiated CoO_2 obtained by charging the battery to 5.0 V. Electrochemical characterization was performed on solid-state thin-film batteries using an amorphous lithium phosphorus oxynitride (Lipon [6]) as the electrolyte. As the Lipon film is electrochemically stable up to 5.5 V at

room temperature [7], capacity fade due to electrolyte decomposition is avoided in this study. After cycling tests, we used TEM to directly examine the cathode films on a local, microscopic scale.

2. Experimental

Thin-film batteries with LiCoO_2 cathodes were fabricated as previously reported [8]. Cathode films were deposited by radio frequency (RF) magnetron sputtering of LiCoO_2 targets in Ar atmosphere and annealed at 800 °C for 2 h in O_2 . The cathode area was 1 cm², and the thickness was 1.2 ± 0.1 μm. The grain size of the film was 0.3 ± 0.1 μm, determined by X-ray diffraction (XRD) and scanning electron microscopy [9]. XRD analysis showed that the cathode film had a low degree of texturing. The electrolyte was 1.5 μm-thick Lipon film deposited by RF magnetron sputtering of a Li_3PO_4 target in N_2 . Thermally vapor-deposited Li metal of 3 μm thickness was used as the anode. Au and Ni films deposited on polycrystalline Al_2O_3 substrates were used as the cathode and anode current collectors, respectively.

Electrochemical characterization of the batteries was performed at 25 °C using a Maccor series 4000 battery test system. Cycling tests were performed at 5–1000 μA/cm² with various charge cutoff voltages of 4.2–5.0 V. Discharge

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cutoff voltage was fixed at 3.0 V. For each cycle, the batteries were charged to the cutoff voltage at a given current density and then held at the cutoff voltage until the current decreased to $<1 \mu\text{A}/\text{cm}^2$.

After the cycling tests, cross-section specimens of the batteries were examined by TEM. The specimens were prepared as detailed elsewhere [9]. A Hitachi HF-2000 cold field emission gun TEM operating at 200 kV accelerating voltage and equipped with a double-tilt holder was used for imaging and selected-area electron diffraction (SAD). Bright-field imaging was recorded using the central transmitted beam only. The specimen was placed in a liquid nitrogen cooled specimen holder to minimize damage during the TEM session.

3. Results and discussion

Fig. 1 shows the charge–discharge curves of a cell cycled at $0.1 \text{ mA}/\text{cm}^2$ in various voltage ranges. The corresponding differential capacity plots (inset) clearly shows two peaks “a” and “b”, associated with hexagonal \leftrightarrow monoclinic phase transitions at compositions around $\text{Li}_{0.5}\text{CoO}_2$ [10]. The height of the peaks and the depth of the minimum are a qualitative indicator of the degree of Li/vacancy ordering in the monoclinic phase [11,12]. They do not change greatly with cycling (20 cycles in each voltage range), indicating that the degree of Li/vacancy ordering remains nearly constant when cycled up to 4.5 V. Note that another peak starts

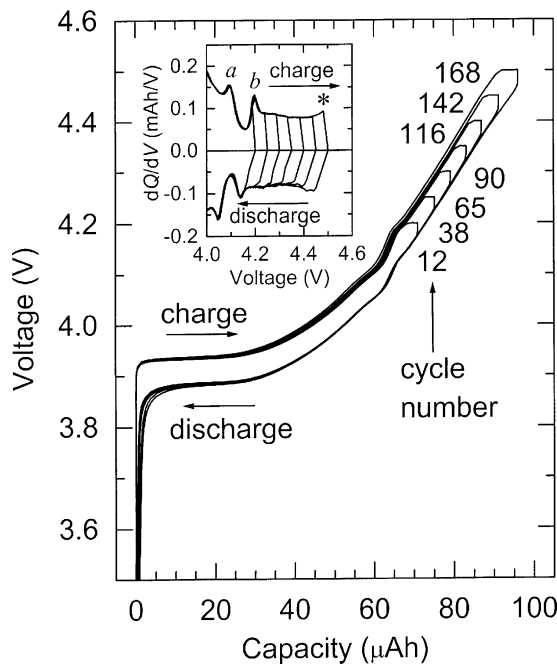


Fig. 1. Charge–discharge curves with the various charge cutoff voltages of 4.2, 4.25, 4.3, 4.35, 4.4, 4.45, and 4.5 V. The discharge cutoff voltage was fixed at 3.0 V. All the cycles were performed at $0.1 \text{ mA}/\text{cm}^2$. Inset shows the corresponding differential capacity plots during charge and discharge. Refer to the text regarding the peak denotations.

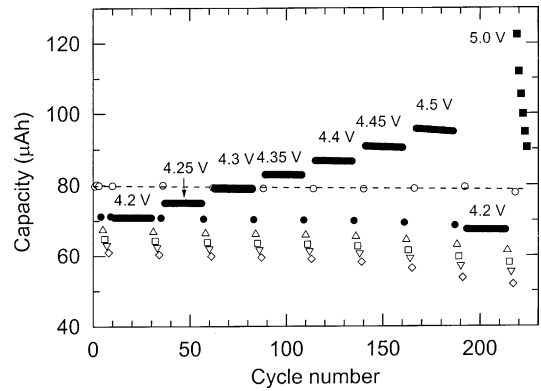


Fig. 2. Discharge capacities with the various charge cutoff voltages of 4.2, 4.25, 4.3, 4.35, 4.4, 4.45, 4.5, and 5.0 V. The discharge cutoff voltage was fixed at 3.0 V (\bullet , $0.1 \text{ mA}/\text{cm}^2$ with various charge cutoff voltages; \blacksquare , $0.01 \text{ mA}/\text{cm}^2$ between 3.0 and 5.0 V; \circ , \triangle , \square , ∇ , and \diamond correspond to 0.005, 0.3, 0.5, 0.7, and $1.0 \text{ mA}/\text{cm}^2$ between 3.0 and 4.2 V, respectively).

to develop at $>4.4 \text{ V}$ (marked as “*”), which will be discussed below.

Fig. 2 shows the discharge capacity of the cell in various voltage ranges. The cell exhibits excellent cycleability with a capacity fade rate of $<0.02\%$ per cycle when cycled up to 4.4 V. By increasing the charge cutoff voltage from 4.2 to 4.4 V, the utilization of capacity and energy density increased by 22% (170 mAh/g) and 26% (690 mWh/g), respectively, at $0.1 \text{ mA}/\text{cm}^2$. Such a high degree of capacity retention is remarkable for LiCoO_2 in the high-voltage range. In a previous work using LiCoO_2 powders of $\approx 10 \mu\text{m}$ particle size [4], the capacity dropped by 53% after 50 cycles between 2.75 and 4.4 V at $0.5C$ rate ($1C = 140 \text{ mA}/\text{g}$). In the present work, a thin-film battery lost only 2% of the initial capacity after 100 cycles between 3.0 and 4.4 V at $0.1 \text{ mA}/\text{cm}^2$, corresponding to $1.4C$ rate (see Fig. 3). Clearly, our thin-film cathodes exhibits far better capacity retention than traditional powder cathodes when cycled to 4.4 V. We attribute the excellent cycleability of our thin-film batteries to small grain size of the cathode film and the stability of the Lipon electrolyte.

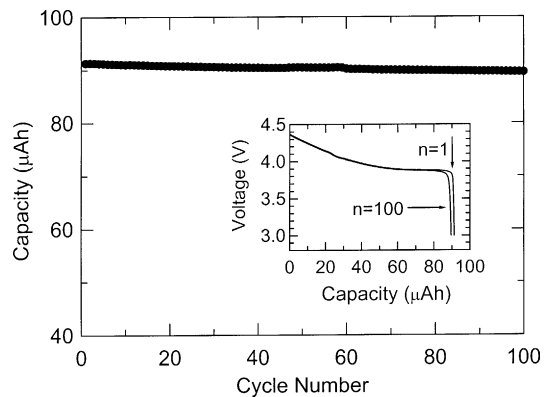


Fig. 3. Discharge capacities between 3.0 and 4.4 V at $0.1 \text{ mA}/\text{cm}^2$. Inset shows the discharge curves for the first ($n = 1$) and 100th ($n = 100$) cycles.

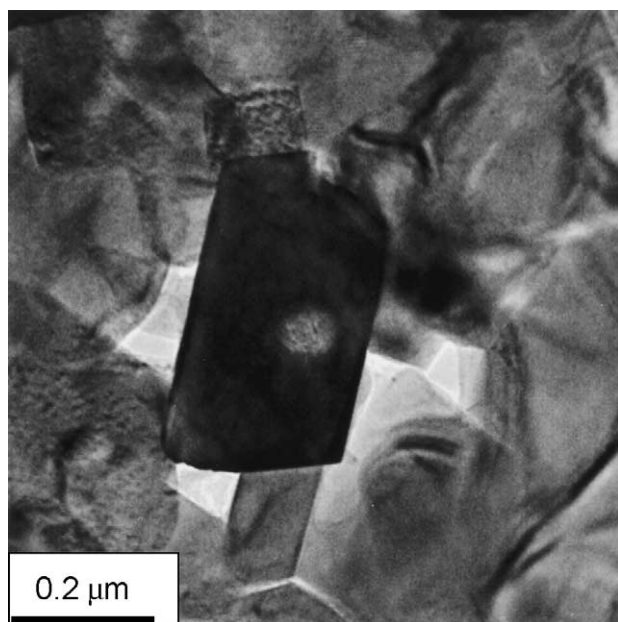


Fig. 4. TEM bright-field image of the LiCoO_2 cathode layer after cycling 188 times in various voltage ranges with the charge cutoff voltage up to 4.5 V.

We examined a thin-film cathode by TEM after cycling up to 4.5 V. The cycling history of the cell (i.e. voltage range, number of cycles, current density) was identical with that shown in Fig. 2 with a similar cycling behavior. Fig. 4 shows that the cathode grains are not fractured and are in good contact with surrounding grains. No evidence of grain fracture was detected by TEM examination of ≈ 400 grains in the cathode layer. The absence of fractured and isolated grains explains the excellent capacity retention of the thin-film cathodes shown above. For composite powder cathodes of $\approx 1.1 \mu\text{m}$ particle size, approximately 20% of the particles examined were fractured after 50 cycles to 4.35 V [2].

Fig. 5 shows that capacity fade and cell resistance increase are both more rapid when the charge cutoff voltage is >4.4 V. We believe that this behavior is originated by the onset of a phase transition at >4.4 V, as indicated by the peak “*” in Fig. 1. In order to confirm the occurrence of a phase

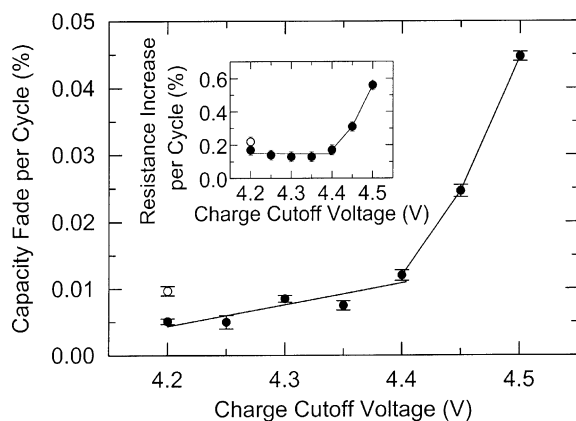


Fig. 5. Capacity fade per cycle determined by linear regression in each voltage range (20 cycles). Inset shows the increase in cell resistance per cycle.

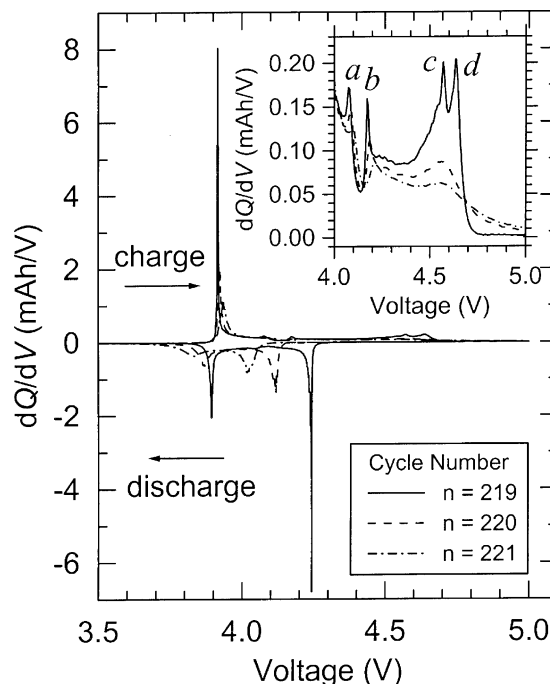


Fig. 6. Differential capacity plots of the first three cycles at $10 \mu\text{A}/\text{cm}^2$ between 3.0 and 5.0 V.

transition at >4.4 V, we cycled the cell between 3.0 and 5.0 V at $10 \mu\text{A}/\text{cm}^2$. Not surprisingly, the capacity fades rapidly in this voltage range (see Fig. 2). Fig. 6 shows the differential capacity plots for the first three cycles between 3.0 and 5.0 V. Two peaks appear above 4.5 V, marked as “c” and “d”, respectively, during the first charge to 5.0 V. The peak “c”, starting to develop at >4.4 V, is associated with a two-phase reaction that induces an abrupt change in the c parameter by 3.2% [13]. Such abrupt structural changes of the cathode may increase resistance of the cathode or interface. A previous study indicated that increase in resistance of thin-film LiCoO_2 batteries is mainly due to increases in the resistance of the interface [8].

Fig. 6 shows that the differential capacity is nearly zero above 4.7 V during the first charge, indicating that LiCoO_2 is completely delithiated, forming CoO_2 [13]. During the following discharge, 92% of the capacity was recovered. Two differential capacity peaks are observed during discharge. The major peak at higher voltage is attributed to two-phase reaction of CoO_2 and Li_xCoO_2 , and the minor peak at lower voltage (≈ 3.9 V) to two hexagonal Li_xCoO_2 phases. In Ref. [13], composite powder cathodes exhibited only one voltage plateau at 4.35 V during discharge. As the two-phase reaction at ≈ 3.9 V is a signature of LiCoO_2 [11], the presence of the ≈ 3.9 V peak in Fig. 6 suggests that the present thin-film cathode deteriorates to a lesser extent than the previous powder cathodes after the complete delithiation.

After 6 cycles to 5.0 V as shown in Fig. 2, the cathode film was examined by TEM. Cracks were observed in approximately 5% of the grains examined. Fig. 7 shows a bright-field image of a fractured grain (see the arrow). A single

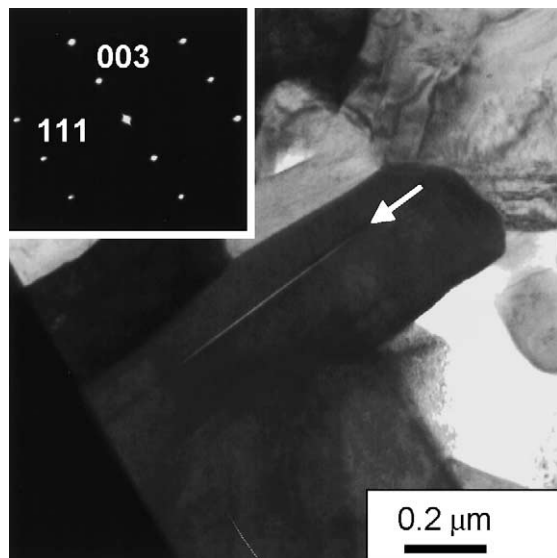


Fig. 7. TEM bright-field image and single crystal SAD pattern (zone axis: $[1\bar{1}0]$). The arrow indicates a crack.

crystal SAD pattern was obtained from the fractured grain. Indexing of the SAD pattern (zone axis: $[1\bar{1}0]$) indicates that fracture of the grain is perpendicular to the c -axis of LiCoO_2 . All of the cracks observed were along the plane normal to the c -axis. The cracks were also nearly normal to the film plane. These results suggest that fracture occurs as result of the anisotropic structural changes combined with in-plane stresses developed in the film during cycling.

To date, there has been no report on extended cycling of LiCoO_2 to ≥ 5.0 V. It is known that fine grain or particle size generally improves cycling stability against mechanical failure associated with a large dimensional change [14]. Nanocrystalline cathode films are thus of interest for possible use under high-voltage cycling conditions. We fabri-

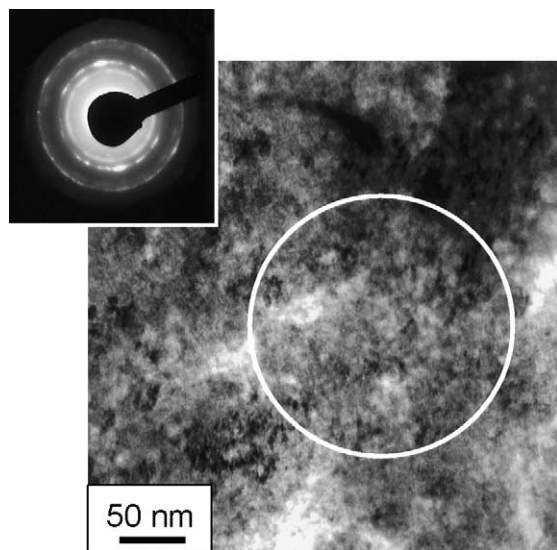


Fig. 8. TEM bright-field image of a nanocrystalline cathode film. The SAD pattern was obtained from the cathode region indicated by the circle.

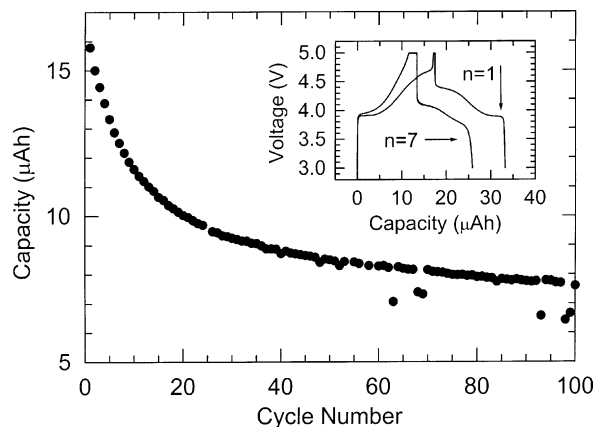


Fig. 9. Discharge capacities between 3.0 and 5.0 V at $10 \mu\text{A}/\text{cm}^2$. Inset shows the charge-discharge curves for the first ($n=1$) and seventh ($n=7$) cycles.

cated and cycled nanocrystalline LiCoO_2 cathode films. The cathode area was 1 cm^2 , and the thickness was $0.15 \mu\text{m}$. Details of fabrication of nanocrystalline cathode films will be published elsewhere. Fig. 8 shows a ring-type SAD pattern from the cathode region indicated by the circle of $\approx 200 \text{ nm}$ diameter, indicating that the cathode film is nanocrystalline. Based on TEM imaging at higher magnifications (not shown here), it is estimated that the grain size is $\sim 10 \text{ nm}$. Fig. 9 shows the discharge capacity with cycling between 3.0 and 5.0 V at $10 \mu\text{A}/\text{cm}^2$. Over the first 7 cycles, the capacity dropped by 20%, and the cell resistance increased rapidly (see inset). These results indicate that the charge cutoff voltage should be limited to $< 5 \text{ V}$ for the nanocrystalline LiCoO_2 films as well. However, nanocrystalline films do exhibit better cycleability than films with larger grains. In Fig. 9, the capacity fade rate decreases with cycling and finally saturates at 0.2% per cycle. This contrasts with the results shown in Fig. 2. Further studies are necessary to investigate the electrochemical properties and microstructural changes of nanocrystalline LiCoO_2 films during cycling.

4. Conclusions

Thin-film LiCoO_2 batteries using the Lipon electrolyte exhibit excellent capacity retention when cycled up to 4.4 V. The capacity fade rate when cycled to 4.4 V was $< 0.02\%$ per cycle at $0.1 \text{ mA}/\text{cm}^2$. By extending the voltage limit from the typical 4.2 V cutoff to 4.4 V, the utilization of capacity and energy density increases by 22% (170 mAh/g) and 26% (690 mWh/g), respectively. The cycling stability of thin-film batteries is attributed to small grain size of the cathode film and the stability of the Lipon electrolyte. No evidence of grain fracture was detected by TEM. Upon cycling to $> 4.4 \text{ V}$, the capacity fades and the cell resistance increases more rapidly, attributed to the onset of a phase transition at $> 4.4 \text{ V}$. Fracture occurs when the cathode film is cycled to 5 V, as observed by TEM. Nanocrystalline films show better

cycleability when charged to 5 V than films with larger grains. The present study exemplifies the usefulness of thin films in developing LiCoO₂ batteries with higher capacity and energy density by enhancing the high-voltage cycling stability.

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