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Capacity fading of pulsed-laser deposited HT-$LiCoO_2$ films cycled in $LiClO_4$/PC

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Abstract

Well-crystallized HT-$LiCoO_2$ films with preferential *c*-axis orientation were prepared by pulsed-laser deposition using stoichiometric $LiCoO_2$ targets. The cyclicability of the deposited HT-$LiCoO_2$ films was evaluated using constant current (CC) and pulse discharge (PD) cycling. X-ray diffraction, Raman spectroscopy and scanning electron microscopy were performed to characterize the changes in the structure and morphology of the HT-$LiCoO_2$ films before and after cycling. The films delivered an initial discharge capacity of 40 μAh μm^{-1} cm^{-2} and the discharge capacity decreased to 22.4 after 100 constant current cycles, due to the following three effects which occurred simultaneously: (a) mechanical failure, (b) dissolution of cation ions and (c) transformation of HT-$LiCoO_2$ to spinel phase (Co_3O_4 or $LiCo_2O_4$). Under PD cycling, the discharge capacity of the films decreased quickly from about 39 to 9 μAh μm^{-1} cm^{-2} after only five cycles. The faster capacity fading in PD cycling may be induced by significant increase in inhomogeneous lithium intercalation, while the underlying mechanisms under PD cycling may be the same with those under CC cycling.

Keywords: $LiCoO_2$; Capacity fading; Pulsed-laser deposition

1. Introduction

Recently, capacity fading mechanism of cathode materials in lithium ion battery is of increasing interest due to its growing power-demanding and durable applications, in which life-time prediction and capacity fading prevention are crucial [1]. Although many new cathode materials with attractive properties have been developed, α-$NaFeO_2$-type $LiCoO_2$ (referred to as HT-$LiCoO_2$ thereafter) in which lithium and cobalt ions reside in alternating layers of octachedral sites in a nearly cubic close-packed oxygen sublattice [2], is currently the most widely used cathode materials for commercial lithium ion batteries because of its high operating potential, good reversibility and ease of fabrication. HT-$LiCoO_2$ is generally quite stable upon lithium intercalation/deintercalation and can deliver a practical specific capacity of 140 mAh g^{-1} (3–4.2 V versus Li/Li^+) which is about half of its theoretical capacity, although it experiences a series of phase transformations involving lithium ordering within its octahedral layers and change of crystal symmetry [3,4]. In spite of its superior electrochemical properties, capacity loss of the HT-$LiCoO_2$ cathode upon cycling has been observed to different degrees in all of the lithium ion battery systems. It is therefore of great importance to explore the capacity decay mechanism for the HT-$LiCoO_2$ cathode.

So far, capacity fading of HT-$LiCoO_2$ powder in lithium ion battery is considered to originate mainly from the following three effects [5]: (a) mechanical failure, (b) dissolution of cation ions and (c) transformation of HT-$LiCoO_2$ to electrochemically inert phase. Unfortunately, the above effects are not widely and equally recognized yet. There also exists some controversy over the transformation of HT-$LiCoO_2$ to electrochemical inert phase. Gabrisch et al. [6] believed that the formation of the lithiated spinel phase $Li_{1+y}Co_2O_4$ on the surface of HT-$LiCoO_2$ cycled in $LiClO_4$/PC should be responsible for the capacity fading, while Aurbach et al. [7] claimed the

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electrochemical inert phase to be Co_3O_4 when it was cycled in $LiPF_6$/EC + EMC.

HT-$LiCoO_2$ films, prepared by either magnetron sputtering [8] or pulsed-laser deposition (PLD) [9], have been demonstrated to be a prototype cathode for thin film microbattery. It may also serve as an ideal electrode to study the intrinsic properties of HT-$LiCoO_2$ because it is free of conducting additive and binder, thus any possible influence of carbon black and binder can be excluded [10,11]. It is expected that investigation on cyclic behavior of the HT-$LiCoO_2$ film will not only reveal the capacity fading mechanism of HT-$LiCoO_2$ films in liquid electrolyte, but also be helpful to clarify the detailed capacity fading mechanism of the HT-$LiCoO_2$ powder electrode. To the best of our knowledge, however, there is no such information available yet. In this paper, capacity fading behavior of pulsed-laser deposited HT-$LiCoO_2$ films cycled in $LiClO_4$/PC has been investigated using two kinds of cycling methods, namely constant current cycling and pulse discharge cycling, since capacity fading may vary with cycling conditions and pulse discharge is commonly demanded in many applications.

2. Experimental

The HT-$LiCoO_2$ films were deposited on platinum metallized silicon (PMS) substrates, Pt(100 nm)/Ti(50 nm)/Si, by PLD using sintered stoichiometric $LiCoO_2$ pellets as the targets. A KrF excimer laser (248 nm, Lambda Physik 210i) was used as the light source. The beam of 0.03 cm^2 in size was focused on the target at an incident angle of 45° with repetition frequency of 10 Hz and average energy of 250 mJ per pulse. The distance between the target and substrate was 50 mm. The substrate temperature was maintained at 600 °C. Oxygen partial pressure (PO_2) was kept at 0.6 mbar. The deposition duration was 60 min for all the samples unless specified and the typical thickness of as-deposited $LiCoO_2$ films was measured to be about 530 nm by examining the fractured cross-section of these films using scanning electron microscopy (SEM). The base pressure of the chamber for all depositions was below 10^{-2} mbar.

Electrochemical measurements were performed using the three-electrode beaker-type cell (Teflon beaker) on an Autolab PGSTAT 30 in an argon-filled glove box with the content of oxygen and moisture less than 2 ppm. Both the counter and reference electrode were lithium (battery grade) and the prepared $LiCoO_2$ film, with an area of 1 cm^2 exposed to the electrolyte solution, was served as the work electrode. The electrolyte used was 1 M $LiClO_4$ in propylene carbonate (PC) (battery grade, water content: 30 ppm). Constant current cycling was carried out at a constant charge and discharge current of 10 μA cm^{-1} between 3.2 and 4.2 V. Pulse discharge cycling was conducted by charging the cell at a constant current of 5 μA cm^{-1} to 4.2 V and then discharging the cell using small potentiostatic steps of 50 mV from 4.2 to 3.8 V. Relaxation time for each potential step was 30 min. The typical residual current at the end of each step was observed to less than 1 μA cm^{-1}. To reveal the effect of PD cycling, the HT-$LiCoO_2$ film was evaluated under CC condition before PD cycling and after every five PD cycles and then compared with CC cycled sample.

The morphology and microstructure of the films were characterized by SEM, X-ray diffraction (XRD), Raman spectroscopy and transmission electron microscopy (TEM) using an FE-SEM, LEO 1530VP, Philips X'pert diffractometer with a Cu Kα radiation, Renishaw RM3000 Raman spectroscope and Philips CM20, respectively. Raman spectra were collected using a 514.5 nm line from an argon ion laser (5.8 mW) with typical collection duration of 60 s. For laser sensitive samples, Raman spectra were recorded with collection duration of 30 s and 24% of the laser power. Specimens for TEM observation were prepared by depositing HT-$LiCoO_2$ films on PMS substrates for 15 min and dispersing scraps from these HT-$LiCoO_2$ films onto copper-grid-supported carbon films. The cycled HT-$LiCoO_2$ films were discharged to 3.2 V versus Li/Li$^+$, rinsed using acetone and ethanol in sequence and then dried before characterization.

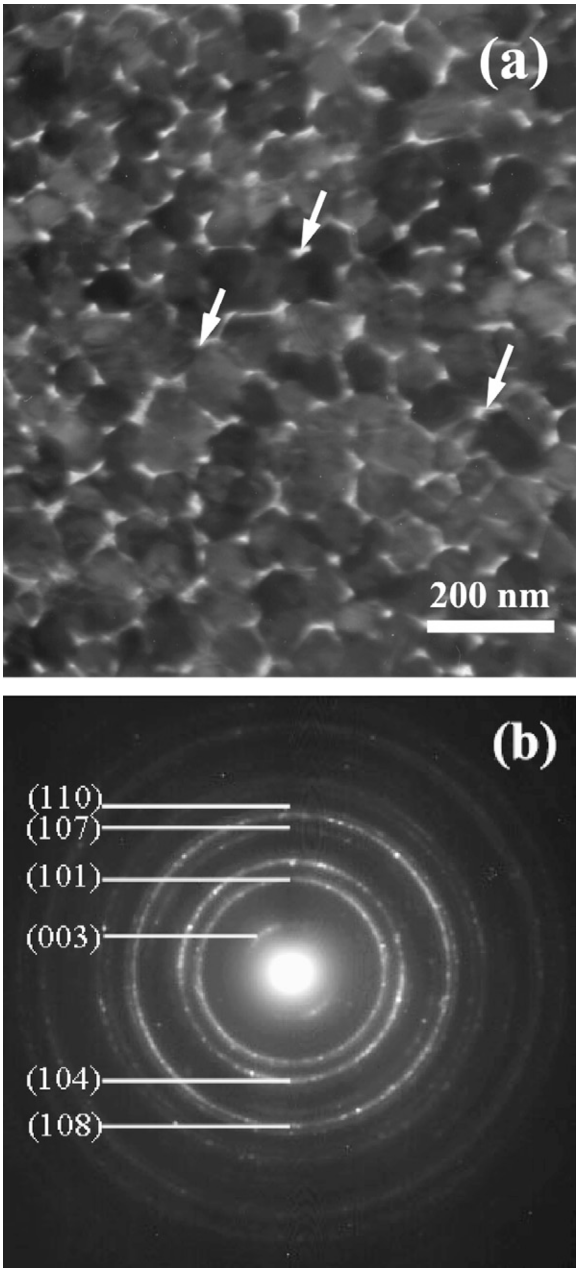

Fig. 1. TEM micrographs of $LiCoO_2$ films prepared by PLD with deposition duration of 15 min: (a) bright field image and (b) selected area electron diffraction (SAED) pattern.

3. Results

3.1. Microstructure and capacity fading of the PLD-deposited $LiCoO_2$ films

The bright field TEM image and selected area electron diffraction (SAED) pattern of $LiCoO_2$ films prepared by 15 min deposition is shown in Fig. 1(a and b). As it shows, the film consists of grains with a uniform size distribution and the average grain size is about 100 nm. It means that the film has a nano-structure feature. It is noted that there are many voids, as indicated by the arrow, in the film. Apart from the hexagonal HT-$LiCoO_2$, no other impurity phases can be identified from