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The thermal stability of fully charged and discharged $LiCoO_2$ cathode and graphite anode in nitrogen and air atmospheres

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ABSTRACT

The thermogravimetric (TG) and differential thermal analysis (DTA) were used to investigate the thermal stability of fully charged and discharged $LiCoO_2$ cathode and graphite anode in nitrogen and air atmospheres. The results showed that the weight of charged and discharged $LiCoO_2$ cathode samples exhibited an obvious decrease between 100 and 120 °C in two atmospheres. The exothermic decomposition reaction of fully charged $LiCoO_2$ cathode occurred at 250 °C in two atmospheres. A small decomposition reaction of the discharged $LiCoO_2$ cathode occurred at 300 °C. When the temperature of samples was elevated to 600 °C, the weight of fully charged and discharged $LiCoO_2$ cathode in air atmosphere did not change; while the weight of samples in nitrogen atmosphere decreased. This was because the Co_3O_4 as the decomposition product of the cathodes could be reduced to CoO by the carbon black above 600 °C in N_2 atmosphere. The solid electrolyte interphase (SEI) film of fully charged and discharged graphite anode was decomposed at 100–120 °C in two atmospheres, and the weight loss of fully charged graphite anode at 100–120 °C was obviously less than that of the fully discharged graphite anode. When the samples were heated to 300 °C, there was no fierce exothermic reaction for the lithiated graphite anode in N_2 atmosphere, whereas an exothermic reaction in air atmosphere occurred rapidly.

1. Introduction

Lithium rechargeable batteries possess the advantages of long cycle life, high energy density and high voltage as compared with other secondary batteries [1,2]. Lithium-ion batteries are widely used in portable electronic devices and their electrochemical performance has been improved greatly. However, the safety of batteries is still the main concern of both consumers and manufacturers in the hybrid electric vehicle applications. The concern becomes more severe when the batteries work under abusive conditions such as high temperatures, high charge and discharge rates, and overcharge. More energy the batteries store, potentially more hazardous they will be. The main reason for firing and explosion of lithium-ion batteries can be attributed to rapid exothermic reactions of the electrode materials with the electrolyte components, which occur in batteries under abusive conditions, especially at high temperatures and overcharge. These reactions are known to be exothermic and can produce much heat and gas, which result in high pressure and temperature exceeding the enduring limits of the batteries [3–8].

It is well known that fully charged $LiCoO_2$ cathode materials with the electrolyte in lithium-ion batteries are unstable, and are easy to be decomposed to release oxygen at elevated temperatures. The evolved oxygen can then react with the organic solvent in the electrolyte (e.g. EC, DEC, EMC, DMC, etc.), which generates much heat [8–18]. The thermal stability of Li_xCoO_2 is affected by the type, particle size and concentration of the electrolyte salts, which strongly depend on the content of the electrolyte [12]. It is also well known that the fully lithiated graphite anode is unstable, which is attributed to the fact that the intercalated lithium can react with the electrolyte at the elevated temperature [16,19–22]. So far, almost all the studies on the thermal stability of Li_xCoO_2 and lithiated graphite anode are limited to the effects of the electrolyte. This is due to the fact that the electrolyte not only can react severely with the lithiated graphite anode at high temperature, but can also react easily with the O_2 evolved from the charged cathode. There are no studies on the effects of the atmosphere on the thermal stability of Li_xCoO_2 cathode and graphite anode. The atmosphere is an important factor which could significantly influence the thermal stability of Li_xCoO_2 and lithiated graphite. During the production

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process of batteries, although various measures have been taken to drive out the air in the batteries, it is inevitable that some air still exists in the batteries. Therefore, the analysis of the thermal stability of charged and discharged $LiCoO_2$ cathode and graphite anode in N_2 and air atmospheres is necessary for understanding the reaction mechanisms relating to safety. In this work, the thermal stability of charged and discharged $LiCoO_2$ cathode and graphite anode in N_2 and air atmospheres were investigated, and the effect of O_2 on the thermal stability of $LiCoO_2$ cathode and graphite anode was also examined.

2. Experimental

Lithium-ion batteries (model-463446, which was 4.6 mm thick, 34 mm wide and 46 mm long) were assembled. The batteries used $LiCoO_2$ as the cathode, graphite as the anode and polyethylene as a separator. The nominal capacity of the batteries was designed to be 800 mAh according to the theoretical specific capacity (274 mAh/g) and the actually available (reversible) specific capacity (137 mAh/g) of $LiCoO_2$. The $LiCoO_2$ cathodes consisted of 90 wt.% $LiCoO_2$, 5 wt.% conductive carbon black and 5 wt.% poly(vinylidene fluoride) (PVDF), and the graphite anodes consisted of 91 wt.% composite graphite, 6 wt.% styrene-butadiene rubber (SBR) and 3 wt.% carboxymethyl cellulose (CMC). 1 M $LiPF_6$ in a 1:1:1 (in mass) mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethylene methyl carbonate (EMC) (1 M $LiPF_6$/EC + DMC + EMC) was used as the electrolyte. The mass of pure $LiCoO_2$ of each battery was calculated, and the designed capacity of the graphite anodes and electrolyte was 2% larger than that of the $LiCoO_2$ cathodes, which could make the capacity of the $LiCoO_2$ cathodes being used completely. The preparation and injection of the electrolyte were conducted in an argon filled glove box.

The formation and charge/discharge tests were performed by the BS-9300 lithium-ion battery tester. Since the most recent industrial formation process constitutes only one cycle, the experimental batteries in this work also first underwent one cycle of charge/discharge for the formation. The batteries were charged with a constant current of 40 mA (0.05C) to 3.00 V, 80 mA (0.1C) to 3.85 V, and 160 mA (0.2C) to 4.20 V, followed by holding the voltage at 4.20 V until the current dropped to 8 mA (0.01C), and then discharged at 400 mA (0.5C) to 2.75 V of the cut-off voltage. After the formation, all batteries were charged and discharged two times between 2.75 and 4.20 V at a current of 400 mA (0.5C), which could stabilize the performance of batteries. The batteries with similar properties were chosen as the studied batteries. Some batteries were fully charged, and the others were fully discharged. The charged and discharged batteries were transferred to the glove box and then dissembled. The lithiated graphite was taken from the surface of anodes and the charged $LiCoO_2$ cathode from the surface of cathodes in the charged batteries. The de-lithiated graphite and discharged $LiCoO_2$ cathode were also taken from the fully discharged batteries. All the samples were rinsed with DMC to remove the electrolyte from the surface of the materials. Then, the samples were dried in the glove box antechamber for 2 h to remove the residual DMC. After the samples were dried, an appropriate amount of the samples (about 10 mg) were set in a stainless steel pan and were covered (not sealed) fitly by a circular stainless steel plate. The stainless steel pan with the samples was taken out from the glove box and introduced into the furnace of the TG-DTA immediately to conduct the TG-DTA experiments.

Some fully charged and discharged $LiCoO_2$ cathodes were heated from room temperature to different temperatures at 10 °C min^{-1} in air and N_2 atmospheres and the temperatures were kept for 1 h, and then the samples were cooled to room temperature.

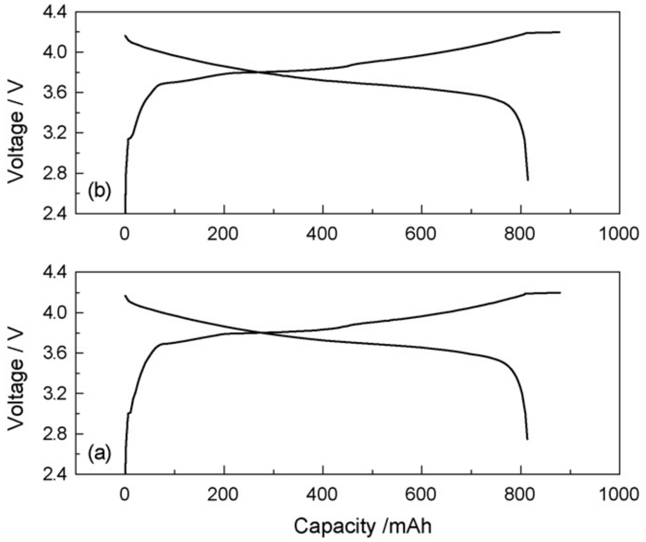

Fig. 1. The first charge and discharge curves for two batteries.

The X-ray diffraction (XRD) patterns of the pure $LiCoO_2$ and thermally treated fully discharged $LiCoO_2$ and fully charged $LiCoO_2$ were obtained by a PANAlytical X'Pert powder diffractometer using Co Ka radiation with an angular range of 10–90°(2θ) and a step of 0.02°(2θ) at room temperature. The structural parameters were calculated from the XRD patterns by using the MDI Jade 5.0 profile matching refinement method.

The thermogravimetric (TG) and differential thermal analysis (DTA) analyses for the $LiCoO_2$ cathode, graphite anode, conductive blank carbon and PVDF were conducted by using a Rigaku Thermo Plus TG8120 system. The stainless steel pan with samples was introduced into the furnace of the TG-DTA, and then the $LiCoO_2$ cathode, conductive black carbon and PVDF were heated to 800 °C at a rate of 10 °C min^{-1} and the graphite anode was heated to 450 °C at a rate of 5 °C min^{-1} under a nitrogen or air flow with Al_2O_3 as the reference material.

3. Results and discussion

The theoretical specific capacity of $LiCoO_2$ is 274 mAh/g and the available (reversible) specific capacity of $LiCoO_2$ is 137 mAh/g. However, the actual specific capacity of $LiCoO_2$ in commercial lithium-ion batteries depends on the material compositions of the anode, cathode, electrolyte and separator etc. Fig. 1 shows the first charge and discharge curves for two batteries. The capacities of the first charge and discharge of battery *a* are respective 879.10 and 813.19 mAh, and the capacities of battery *b* are respective 877.97 and 814.40 mAh. So the coulombic efficiency of these two batteries in the first cycle is 92.50% and 92.75%, respectively, which indicates that the electrochemical performance of these two batteries is quite similar. Thus, these two batteries can be used as the studied batteries. The mass of pure $LiCoO_2$ of batteries *a* and *b* is 5.819 and 5.823 g, respectively. So the actually available (reversible) specific capacity of $LiCoO_2$ in battery *a* is 139.75 mAh/g, and for battery *b* it is 139.85 mAh/g. After the formation, all the batteries were charged and discharged two times between 2.75 and 4.20 V at a current of 400 mA (0.5 C) to stabilize the performance of the batteries. The coulombic efficiency of these two batteries is over 99.70% in the two cycles. So it is reasonable to conclude that the coulombic efficiency is almost 100% if the batteries are cycled between 2.75 and 4.20 V. During the experiments, the battery *a* was fully charged and battery *b* was fully discharged, and then they were transferred into