



Electrochemical investigation of Li-excess layered oxide cathode materials/mesocarbon microbead in 18650 batteries



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ABSTRACT

The electrochemical performance of the 18650 lithium-ion batteries for layered Li-excess oxide $\text{Li}_{1.144}\text{Ni}_{0.136}\text{Co}_{0.136}\text{Mn}_{0.544}\text{O}_2$ (LNCMO) cathode material and mesocarbon microbead (MCMB) anode material is investigated. The battery shows an excellent rate capability with the capacity of 227 mAh g^{-1} at 8 C-rate (the cut-off voltage is 4.5 V). Furthermore, it exhibits excellent cycle performance that the capacity retention over 300 cycles in the voltage ranges of 2.5–4.5 V (vs. MCMB) and at 0.2 C-rate is about 85%. Although the medium voltage of the battery greatly reduces during the first 30 cycles, it keeps stable in the following cycles. The mechanisms of the capacity fade and voltage decay are also studied based on energy dispersive spectrometry, X-ray photoelectron spectroscopy, charge-discharge curves, and dQ/dV plots.

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1. Introduction

Nowadays, lithium-ion batteries (LIBs) as power sources are becoming increasingly important for plug-in hybrid electric vehicles (PHEVs) or electric vehicles (EVs) [1–3]. It is known that the commercial cathode materials such as LiCoO_2 , LiMn_2O_4 , and LiFePO_4 used in portable electronic devices have low energy density of 140–160 Wh kg^{-1} [2]. To achieve high energy density over 250 Wh kg^{-1} , intensive attention has been drawn to study Li-excess layered transition metal oxides cathode materials, e.g. $\text{Li}[\text{Li}_{(1/3-2x/3)}\text{Ni}_x\text{Mn}_{(2/3-x/3)}]\text{O}_2$ or $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiMO}_2$ (M = Ni, Co, Mn etc.), which is due to their ultrahigh specific capacity of above 250 mAh g^{-1} , low cost, and intrinsic thermal safety [4–8]. On the other hand, these materials might be as a suitable lithium source for the pre-lithiation of carbonaceous anode in lithium-ion capacitors or hybrid energy storage devices [9,10]. However, they suffer from several inner obstacles [11–14]: (i) large initial irreversible capacity loss of 40–100mAh g^{-1} , (ii) poor rate capability, and (iii) capacity fade and voltage decay during cycling, all of which have seriously restricted their large-scale application.

To overcome these restrictions, a number of approaches such as new synthesis methods [15,16], surface modifications with metal oxides [5,17] and phosphates [5,18], and doping other metals [19,20] have been intensively explored. Most of these studies

fabricated half cells with lithium metal as anode. However, lithium metal is not competent for anode material as a result of the formation of Li dendrites during the cycling process [21,22]. For this reason, some other optional anode materials, such as titanium anode [23,24], alloys [25] and carbon materials [26], have taken it over to exert their respective superiorities in full cells. Recently, Kang *et al.* [23] have evaluated the electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}/0.5\text{Li}_2\text{MnO}_3-0.5\text{LiNi}_{0.44}\text{Mn}_{0.31}\text{Co}_{0.25}\text{O}_2$ cells, which delivered a high specific capacity (> 200 mAh g^{-1}) at 1 C-rate after 100 cycles. However, the working voltage range of this cell was between 0.05 V and 3.25 V, which is difficult to meet the requirements of high energy density.

To increase the working voltage window in full cells, the appropriate choice is using carbon materials as anodes due to their low working voltage vs. Li^+/Li (about 0.1 V). It is generally assumed that the high irreversible capacity loss of the both electrode during the initial cycle could be counterbalanced each other in theory [26]. From this idea, the cell consisting of $0.4\text{Li}_2\text{MnO}_3-0.6\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ cathode and hard carbon anode was fabricated [26]. However, this cell only delivered a specific discharge capacity of 105 mAh g^{-1} with initial coulombic efficiency of 71%, of which the reason is that the hard carbon has low initial reversible capacity and coulombic efficiency. It is conformed that to counterbalance for both electrodes each other during the initial cycle is not achieved in practice. This is possibly that partial lithium in Li-excess layered oxide electrode cannot react with electrolyte to form solid electrolyte interphase (SEI) protective layer on the hard carbon electrode surface, but participates in side

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reactions at high potential [27]. In contrast, MCMB graphite was widely applied in LIBs [28,29], due to its high initial coulombic efficiency (> 90%), relatively large reversible capacity (> 320 mAh g⁻¹), and good rate capability. In this regard, the full cell of LNCMO/MCMB is supposed to have better electrochemical performance.

In this study, we selected Li-excess layered oxide Li_{1.144}Ni_{0.136}Co_{0.136}Mn_{0.544}O₂ cathode material with a rechargeable capacity of 280 mAh g⁻¹ to fabricate the LNCMO/MCMB 18650 battery. The electrochemical performance of the battery, including the charge-discharge curves, cycling stability, medium voltage and rate capability, were evaluated in detail.

2. Experimental

2.1. Preparation

Li-rich layered oxide with a nominal formula Li_{1.144}Ni_{0.136}Co_{0.136}Mn_{0.544}O₂ was synthesized through solid-state reaction between Li₂CO₃ and (Ni_{1/6}Co_{1/6}Mn_{4/6})CO₃ powders. The mole ratio between them was set to 0.7. The mixed precursor was firstly pre-treated at 500 °C for 5 h and then calcined at 850 °C for 15 h. The detail procedure of the (Ni_{1/4}Co_{1/4}Mn_{4/6})CO₃ precursor was carried out as below: an aqueous solution containing NiSO₄·6H₂O, CoSO₄·7H₂O, and MnSO₄·5H₂O with a concentration of 2.0 mol L⁻¹ was pumped into a continuously stirring tank reactor (CSTR); at the same time, 2 M Na₂CO₃ solution and 0.2 M NH₄OH solution were separately added into the reactor. The co-precipitation temperature was held at 60 °C, and the pH value was fixed to 8.0. The resulting (Ni_{1/6}Co_{1/6}Mn_{4/6})CO₃ powders were washed several times by pure water to remove residual Na⁺, and dried in a vacuum oven at 80 °C for more than 20 h.

2.2. Characterizations

Powder X-ray diffraction (XRD) measurements were performed on a German Bruker D8 Advanced X-Ray Diffractometer with Cu K α radiation at a voltage of 40 kV and a current of 40 mA. Field emission scanning electron microscopy (FESEM) images were acquired on a FEI Quanta 250 FEG microscope, equipped with energy dispersive spectrometry (EDS). EDS and elemental mapping were used to demonstrate the existence and distribution of manganese on the anode electrode after several cycles. X-ray photoelectron spectroscopy (XPS) measurements were conducted using an AXIS Ultra DLD spectrometer with Al-K α (1253.6 eV) radiation.

2.3. Electrochemical measurements

Electrochemical properties of LNCMO cathode materials and MCMB anode materials were measured after assembling them into coin cells (type CR2032) in an argon-filled glove box, respectively. The cathode was prepared by casting a slurry of the active material (LNCMO, 80 wt%), conductive graphite (Super P, 10 wt%, SCM Industrial Chemical Co., LTD), and polyvinylidene fluoride binder (PVDF, 10 wt%, Solvay) in N-methyl-2-pyrrolidone (NMP) on aluminum foil. The anode was fabricated by casting a slurry of commercial MCMB (80 wt%, BTR, Shenzhen), 10 wt% conductive graphite (10 wt%) and carboxymethyl cellulose binder (CMC, 10 wt%, Wealthy, Suzhou) on copper foil; Celgard 2502 was utilized as separator. Lithium metal was employed as counter electrode. A mixture of ethylene and dimethyl carbonate (3:7 vol ratio) with LiPF₆ (1 M) was used as electrolyte (Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd.). The cells were galvanostatically charged-discharged on a LAND-CT2001A battery test system (Jinnuo Wuhan Co., Ltd., P. R. China).

2.4. Battery tests

18650 lithium-ion batteries (18 mm in diameter and 65 mm in height) were assembled. The capacity of the batteries was nominally designed to be 1800 mAh corresponding to the specific capacity of the half cell. The batteries used Li-excess layered LNCMO as cathode, MCMB graphite as anode, and polyethylene as separator. The positive electrodes consisted of 90 wt% LNCMO, 4 wt% conductive graphite, 2 wt% SFG-6 (SCM Industrial Chemical Co., LTD), 2 wt% CNTs (Cnano, Beijing) and 2 wt% PVDF. The loading amount of the cathode material on each side of the electrode was about 12 mg cm⁻². The negative electrode consisted of 90.5 wt% MCMB graphite, 2 wt% conductive graphite, 3 wt% SFG-6, and 2.5 wt% styrene-butadiene rubber (SBR, Jinbang Power Source Co., LTD), 2 wt% CMC. The loading amount of the anode material on each side of the electrode was about 10 mg cm⁻². A certain amount of electrolyte was injected in an argon filled glove box.

The formation, rate capability and cycle performance tests of batteries were performed by using LAND-CT2001B battery test systems. For the formation process, the experimental batteries in this study underwent one cycle of charge-discharge. The batteries were charged with a constant current of 80 mA (0.05 C) for 4 h, 160 mA (0.1 C) for 2 h, and 320 mA (0.2 C) for 3 h, respectively, followed by holding the voltage at 4.4 V or 4.5 V until the current dropped to 80 mA (0.05 C), while the batteries were discharged at 160 mA (0.1 C) to a cut-off voltage of 2.5 V. After formation, all batteries were charged and discharged under the voltage of 2.5–4.4 V or 2.5–4.5 V at 160 mA (0.1 C) or 320 mA (0.2 C) to perform the cycling performance of batteries using the constant-current constant-voltage (CC-CV) protocol. And the fully discharged batteries at 150th cycle at 0.1 C-rate were disassembled in a glove box to evaluate the dissolution of the transition metal. To avoid the loss of the transition metal, the obtained anode electrode, without rinsing by using DMC, were used for further EDS and XPS analyses to determine the dissolution of the transition metal on the cathode electrode. The rate capabilities of batteries were also examined at the charge rate of 160 mA (0.1 C) under the voltage of 2.5–4.4 V and 2.5–4.5 V using the CC-CV protocol. The surface temperature of batteries was recorded during the rate-discharge performance testing. A type-K thermal couple was attached to the center of the largest face of the batteries to record the temperature change.

3. Results and Discussion

Fig. 1 shows XRD pattern of the layered LNCMO cathode material. Its main reflections are well consistent with the basis of a hexagonal R-3m unit cell, while the weak superlattice reflections between 20° and 30° are ascribed to the characteristic of honeycomb ordering of LiMn₆ cation in the transition metal layer [30].

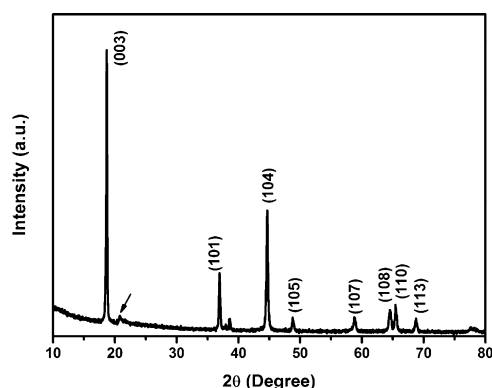


Fig. 1. XRD pattern of Li-excess layered LNCMO cathode materials.

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