The role of SnO_2 surface coating in the electrochemical performance of $Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ cathode materials

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HIGHLIGHTS

- The good conductive SnO_2 is used as the coating layer.
- SnO_2-coated cathode shows an improvement electrochemistry performance.
- The improved material shows the minimum amounts of transition metal dissolution.
- Ex-XRD patterns confirm that the improved material has a better layered structure.
- The coating layer plays an effective role in protecting the electrode from etching.

ARTICLE INFO

ABSTRACT

The manganese metal ions and other transition metal ions in lithium manganite cathode materials will be dissolved into the electrolyte during cycling and storage at charged state, leading to severe capacity fading. Herein, the SnO_2-coated $Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ cathode material is prepared successfully by a simple organic liquid-phase method. The data of inductive coupled plasma-atomic emission spectroscopy and ex-XRD suggest that the coating layer can effectively suppress the dissolution of metal ions, which maintains the stability of main structure. The value of the charge transfer impedance is 35.49 Ω cm^2 for LLMO-Sn1 after 50 cycles, while the LLMO is 123.30 Ω cm^2. The LLMO-Sn1 has the highest discharge capacity of 214.0 mAh·g^{-1} after 150 cycles in half cell and exhibits the capacity retention of 86.8% after 150 cycles in full-cell. The decomposition reaction peak of LLMO-Sn1 appears at 250.1 °C.

1. Introduction

Since the first commercialization of lithium-ion secondary battery by Sony Corporation in 1991, the lithium-ion secondary batteries have been widely used in our daily life. New demands are proposed for lithium-ion batteries to satisfy large scale equipment, such as higher energy density, lower price, etc. In this aspect, lithium-rich layered manganese based materials are very attractive, due to the high discharge capacity [1—3], low cobalt content, and high operating voltage.

Since layered Li_2MnO_3 ($Li[Li_{1/3}Mn_{2/3}]O_2$) and $LiMO_2$ have a similar structure, the lithium-rich layered manganese based materials can be described as $xLi_2MnO_3·(1−x)LiMO_2$ (M = Mn, Co, Ni, Fe, etc.) or lithium-rich layered solid solution $Li[Li_xM_{1−x}]O_2$ (M = Mn, Co, Ni, Fe, etc.), in which the Li_2MnO_3 compound is able to support the stability of the unit crystal cell [4]. Although the lithium-rich layered manganese based materials can deliver a high discharge capacity of more than 250 mAh·g^{-1} at a high charging voltage (4.8 V, vs Li/Li$^+$), it will undergo a large irreversible capacity loss (ICL) at first cycle, which is attributed to the extraction of the lithium as "Li_2O" from the Li_2MnO_3 compound with oxide ion vacancies elimination in the lattice [5,6]. The oxygen evolved from the Li_2MnO_3 compound has been demonstrated by Bruce et al. [7]

directly in the *in-situ* differential electrochemical mass spectrometry. Furthermore, the catalytic side reaction between the electrolyte and the electrode surface can lead to an successive formation of a non-conducting solid electrolyte interface layer, which accelerate the structure transformation of cathode materials, resulting in the decrease of capacity [8,9]. In addition, the dissolution of manganese ions from cathode electrode, which is induced by the HF acid generated by fluorinated anions (PF_6^-) and protons [10], will also contribute a severe capacity fading [11] and a voltage fading [12].

Many efforts have been tried to improve the electrochemical performance of lithium-rich layered manganese based materials, such as surface modification [8,13—16], ions doping to replace transition metal ions [17], Li^+ ions [18] and oxygen ions in the materials [19]. Among these efforts, the surface modification has been proved to be an effective way to enhance the stability of electrolyte/electrode interface and improve the electrochemical performance of lithium-rich layered manganese based materials. SnO_2 with a good electronic conductibility has been used as a coating layer to improve the electrochemical performance of $LiCoO_2$ [20], $LiFePO_4$ [21], and $LiMn_{1.5}Ni_{0.5}O_4$ [22]. Zhu et al. [16] has reported the lithium-rich layered manganese based materials with a $SnO_{2-x}F_x$ coating layer showed an excellent cyclability. However, the pure SnO_2 phase as the coating layer has not been systematically investigated. Meanwhile, the introduction of fluorine increases the complexity of operation.

In this paper, a good conductive SnO_2 coating layer is formed on the surface of $Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ (LLMO) by an organic liquid phase method. The surface modified material shows an excellent long-life cycling and good rate performance. Even in the full-cell (LLMO/graphite) tests, the material with SnO_2 coating layer (LLMO-Sn1) also exhibit a good cycle retention rate. The data of inductive coupled plasma-atomic emission spectroscopy (ICP-AES) confirm that the coating layer is quite effective in inhibiting the dissolution of transition metal ions, especially for the manganese and nickel ions. Thus, the degradation of the cathode is suppressed, to improve the stability of cathode material. The data of ex-X-ray diffraction indicate the LLMO-Sn1 sample has a better layered structure after 100 cycles at 1C rate.

2. Experiment

$Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ cathode materials were synthesized by a liquid-phase method [23]. Stoichiometric amounts of $MnSO_4 \cdot 4H_2O$ (≥99.0%, AR, Sinopharm Chemical Reagent Co. Ltd), $CoSO_4 \cdot 7H_2O$ (≥99.0%, AR, Sinopharm Chemical Reagent Co. Ltd), $NiSO_4 \cdot 6H_2O$ (≥99.0%, AR, Sinopharm Chemical Reagent Co. Ltd) were dissolved into 150 ml deionized water. 50 ml ethanol (AR, Sinopharm Chemical Reagent Co. Ltd) was added into the mixed metal salt solution. After stirred 1 h, the 200 ml NH_4HCO_3(AR, Sinopharm Chemical Reagent Co. Ltd) solution was dropped into the mixed metal salt solution to form a suspension. The powder was collected through filtration after 1 h at 10 °C, then dried in a vacuum oven at 80 °C. The obtained powder was heated at 500 °C for 5 h and obtained a black powder. The black powder mixed well with $LiOH \cdot H_2O$ (3 wt% excess, ≥95.0%, AR, Sinopharm Chemical Reagent Co. Ltd) was calcined at 480 °C for 4 h and at 800 °C for 12 h in air. The final material was $Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$, which was denoted as LLMO. The heating rate was 5 °C min^{-1}.

Adequate amount of $SnCl_4 \cdot 5H_2O$ (≥99.995%, metals basis, Aladdin) was dissolved into a 200 ml ethanol, then, 0.5 g LLMO powder was added. After ultrasonically treated for 1 h, the $NH_3 \cdot H_2O$ (GR, Sinopharm Chemical Reagent Co. Ltd) solution was added to form a precipitate. After a centrifuging process, the precipitation was heated at 500 °C for 5 h in air, resulting in LLMO-Sn. According to the weight ratios of SnO_2/LLMO, two samples were

synthesized, which were named as LLMO-Sn1 (1 wt% SnO_2) and LLMO-Sn3 (3 wt% SnO_2) (Table 1), respectively. The pure SnO_2 was also prepared in this way without adding the LLMO powders. All the reagents have not been further purified.

The Rigaku Ultima IV (Rigaku Corporation) using Cu-Kα radiation was used to determine the crystal structures of all materials. The data were collected in the range of 2 theta values between 10° and 90° at an interval of 0.02° and then analyzed using PDXL-2 analysis software. The S-4800 (Hitachi Corporation) was used to determine the morphologies of all materials. Elemental mappings of all materials were carried out on the energy dispersive X-ray detector (EDX, the accessory of S-4800). Transmission electron microscopies (TEM) were performed on the JEM-2100 (JEOL). The inductive coupled plasma-atomic emission spectroscopy (ICP-AES) was used to determine the elemental compositions of materials.

Electrochemical performances of materials in this paper were tested through the CR2032-type coin cells. The 1.0 M $LiPF_6$ in mixed organic solution of ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC) (1:1:1, volume ratio) was used as the electrolyte. Celgard 2400 was used as the separator to separate the positive and negative electrodes. The slurry was composed of the active material, acetylene and polyvinylidene fluoride (PVDF) with the weight ratio of 8:1:1 in *N*-methyl-2-pyrrolidone (NMP). The slurry was coated onto the aluminum foil to get the electrode sheet. The electrode sheet was dried at 80 °C in vacuum for overnight. All the coin cells were assembled in the Ar-filled glovebox (Mbraun, Germany). Each of the active materials for all cells was controlled at about 2.5 mg. In the half-cell, the lithium metal foil was the anode, while in the full-cell, the graphite (Rightful Technology Co. Ltd, China) served as the anode.

The charge/discharge tests were carried out galvanostatically on a Land CT2001A (Wuhan, China) battery testing system at 25 °C between 2.0 V—4.8 V. For charge/discharge cycling performances, the current of 125 mA g^{-1} was used as 0.5 C. The rate performances were carried out at rates ranging from 0.1 C to 5 C. The electrochemical performances of full-cells were performed at rate of 0.1 C between 1.95 V—4.75 V.

The thermal stability of electrode in the electrolyte mentioned above was measured by the DSC/TG (STA 449 F3 Jupiter Netzsch) from 100 °C to 300 °C. Details of the treatment are described as follows: 1) cells were cycled for one circle at the rate of 0.1 C, and then charged to 4.8 V, held for 2 h; 2) cells were disassembled in an Ar-filled glove box to get charged cathode films; 3) the films were respectively immersed and washed in the DMC and naturally dried in the glove box; 4) the electrode materials stripped from the cathode and the electrolyte were respectively put into in a stainless steel crucible at the ratio of 10 μL electrolyte per 1 mg electrode material.

In the full-cell, the deposition amount of metal ions on the anode was calculated by ICP-AES. Firstly, full-cells were cycled for 50 circles at 0.5C rate between 1.95 V—4.75 V, and then discharged to 1.95 V at the 50th circle. Secondly, all full-cells were disassembled to obtain the anode, the separator and the cell cases. All of these were rinsed by deionized water. All of them were respectively put into a 25 ml color comparison tube containing 6 M HCl water solution. The solution was tested by ICP-AES, obtaining the dissolution amount of transition metal ions.

Table 1
The gram of $SnCl_4 \cdot 5H_2O$ used for the coating purpose.

Sample name	Amount of $SnCl_4 \cdot 5H_2O$/g	Amount of LLMO/g
LLMO-Sn1	0.0116	0.5
LLMO-Sn3	0.0349	0.5