



Versatile Coating of Lithium Conductive Li_2TiF_6 on Over-lithiated Layered Oxide in Lithium-Ion Batteries



Wonchang Choi^a, Anass Benayard^b, Jin-Hwan Park^b, Junho Park^b,
Seok-Gwang Doo^b, Junyoung Mun^{b,c,*}

^a Center for Energy Convergence, Korea Institute of Science and Technology, Hwarangno 14gil-5, Seongbuk-gu, Seoul 136-791, Korea

^b Battery group, Energy Lab, Samsung Advanced Institute of Technology, Samsung Electronics, Giheung-gu, Youngin-si, Gyeonggi-do 446-712, Korea

^c Department of Energy and Chemical Engineering, Incheon National University, 12-1, Songdo-dong, Yeonsu-gu, Incheon 406-840, Korea

ARTICLE INFO

Article history:

Received 22 August 2013

Received in revised form

23 November 2013

Accepted 26 November 2013

Available online 11 December 2013

Keywords:

lithium titanium fluoride
coating
over-lithiated layered oxide
lithium-rich cathode
thermal stability

ABSTRACT

We demonstrate an easy and versatile approach to modify a cathode-surface with a highly lithium-ion conductive layer by coating it with Li_2TiF_6 . The thin and homogeneous Li_2TiF_6 coating is introduced onto an over-lithiated layered oxide (OLO, namely $\text{Li}_{1.17}\text{Ni}_{0.17}\text{Co}_{0.1}\text{Mn}_{0.56}\text{O}_2$) surface via simple co-precipitation at ambient temperature by using Li_2CO_3 and H_2TiF_6 aqueous solutions. The lithium-conductive fluoride coating is expected to effectively suppress the undesired electrochemical and thermal interfacial reactions involving the OLO, which is critical in improving cycle performance and thermal stability. After Li_2TiF_6 surface modification, the coated OLO materials showed high rate capability as well as long cyclability and improved thermal stability. The crystalline structure and surface microstructure of the prepared OLOs were investigated by X-ray diffraction, transmission electron microscopy, and X-ray photoelectron spectroscopy. Ultimately, the performances of the assembled lithium ion batteries were thoroughly investigated by electrochemical methods and thermal analysis.

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1. Introduction

Lithium-ion batteries (LIBs) have attracted a lot of attention because they are one of the most promising power sources for electric vehicles (EV) owing to their high energy density and long cycle lives [1]. However, the energy density of LIBs is still not sufficient for range-extended EVs, which can travel over several hundreds of kilometers after charging. Therefore, many researchers have investigated the fabrication of LIB systems with improved energy density to satisfy the needs of those EVs. Since LIBs were introduced and commercialized by adopting graphite anodes and LiCoO_2 cathodes, anode candidates such as Si and Sn have been proposed to supply high energy density by electrochemically accommodating large amounts of lithium ions in their crystal structures. However, only a few kinds of high-energy-density cathodes have been introduced owing to the limitations of cathode crystal structures [1,2].

Since J. Dahn proposed the first lithium-rich cathode materials, $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_{4+z}$, there have been numerous studies on $(1-x)\text{Li}_2\text{MnO}_{3-x}$ and LiMO_2 ($M=\text{Ni}, \text{Co}, \text{or Mn}$) materials (over-lithiated layered oxide, OLO) reporting that OLO contains Li_2MnO_3 as a solid solution or nanocomposites in the layered structure [3–5].

Conventional layered cathodes like $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ and LiCoO_2 consist of layers of lithium, transition metal, and oxygen. The oxygen layers distinguish the layers of lithium and transition metal. Meanwhile, as OLOs can take up additional reversible lithium ions in the transition metal layer to introduce a large number of lithium ions in the crystal structure, they have been developed for high-energy-density LIBs [4,6–9]. Although conventional layered cathodes usually operate within a potential under 4.3 V (vs. Li/Li^+), OLOs have to be charged to a high potential beyond 4.4 V (vs. Li/Li^+) to utilize lithium ions in the transition metal layer of Li_2MnO_3 . This high cut-off potential accelerates surface failure phenomena, which include electrolyte decompositions, oxygen evolutions, and irreversible phase transitions to an inactive phase [4,10,11].

In order to reduce the undesirable behavior, surface modification with electrochemically inert materials can successfully block surface deteriorations by preventing direct contact between the electrolyte and the electrode. In particular, many researchers have developed cathodes covered by simple metal fluorides owing to their high chemical stability, which is derived from strong ionic bonding between the metal and fluoride ions because of the high electron negativity of the fluoride ions [6–8]. However, these simple metal fluorides affect the surface resistance of the electrodes owing to additional resistance from suppression of lithium transportation through the coatings. Therefore, the development of lithium-ion-conducting coatings has been highly pursued to improve surface

* Corresponding author.

E-mail address: junyoung.mun@gmail.com (J. Mun).

lithium conductivity. Among the fluoride materials, lithium metal fluorides such as Li_2TiF_6 , Li_3AlF_6 , and Li_3FeF_6 exhibit high lithium conductivity because they have channels in their crystal structures through which lithium ions can easily move [12–15].

The coating on the electrode materials is generally prepared in the following order: first, intermediate material is co-precipitated from solution in which precursors are dissolved; second, coating materials such as Al_2O_3 and AlF_3 [16,17] are heat treated at over 300°C to make them stable. However, the additional heat treatment process can cause thermal breakdown of the cathode structure and increase the preparation cost of the material.

Accordingly, we report a detailed investigation into Li_2TiF_6 -coated OLOs. The Li_2TiF_6 coating was quite simply executed even at ambient temperature by ion exchange, using H_2TiF_6 and Li_2CO_3 to modify the surface characteristics on the OLO with a robust and lithium conductive coating. After the coating, the OLO crystal structure, OLO surface characteristics, and electrochemical performance of resulting lithium-ion batteries and their thermal stability were studied. Our results showed that the Li_2TiF_6 coating greatly improved thermal stability as well as rate capability and cyclability.

2. Experimental

Li_2TiF_6 was synthesized by a simple co-precipitation method using a 60 wt% aqueous solution of H_2TiF_6 (Aldrich) and Li_2CO_3 (Aldrich) (1:1 mol ratio). The obtained powder was filtered, washed thoroughly with de-ionized water, and then dried at 120°C for 1 day to eliminate residual water. 10 g of the prepared Li_2TiF_6 was stirred vigorously in an electrolyte, 10 mL of 1.3 M LiPF_6 in ethylenecarbonate:diethylcarbonate:ethylmethylcarbonate (3:5:2 vol%, Panaxetec), for 1 h at 60°C . Subsequently, the electrolyte was filtered through a PTFE membrane (DISMIC-25JP, Advantec) with 200-nm pores to remove undissolved salts. The filtered electrolyte was then analyzed by an inductively coupled plasma-atomic emission spectrometer (ICP-AES; ICPS-8100, Shimadzu) to check the amount of dissolved titanium ions.

OLO ($\text{Li}_{1.17}\text{Ni}_{0.17}\text{Co}_{0.1}\text{Mn}_{0.56}\text{O}_2$) was prepared by oxalate co-precipitation with heat treatment at 900°C for 12 h in air [18]. To prepare the Li_2TiF_6 -coated OLO, OLO was mixed and ground homogeneously with Li_2CO_3 by pestle and mortar with the addition of a small amount (approximately 25 wt% to OLO) of H_2O and ethanol (1:1 vol%) mixture. A 60 wt% H_2TiF_6 solution was dropped into the slurry mixture of OLO, Li_2CO_3 , and solvent. The amount of coating material was set to 0.2, 0.5, 0.7, 1 and 3 wt% of OLO by controlling the sum of Li_2CO_3 and H_2TiF_6 . The prepared OLO samples were also washed thoroughly with de-ionized water. The microstructure of the prepared OLO samples was investigated by transmission electron microscopy (TEM; Tecnai F20, Philips), X-ray diffraction (XRD; X'pert Pro, PANalytical), and X-ray photoelectron spectrometer (XPS; Quantum 2000 scanning ESCA microprobe, Physical Electronics).

Composite electrodes were fabricated with the active materials, Denka black and polyvinylidene fluoride (PVdF, Solvay), in the ratio of 94:3:3 wt% on Al foil. The loading level of the composite electrode were controlled in the range of 8–9 mg cm^{-2} . 2032 coin-type cells were assembled with the composite electrodes (1.2 cm diameter), lithium foil, and polypropylene separators (Celgard). Galvanostatic charge/discharge cycling was made with the coin-type cells in the potential range of 4.6–2.5 V (vs. Li/Li^+) at 1 C (1 C = 230 mA g^{-1}) after cycling (potential range of 4.7–2.5 V and 0.05 C) at 25°C .

For analysis using a differential scanning calorimeter (DSC; Q2000, TA Instruments), the composite electrodes were delithiated to 4.6 V (vs. Li/Li^+) after 10 cycles and then disassembled from the coin cells in an Ar-filled glove box. The obtained electrode (approximately 3 mg of the cathode) was assembled in a

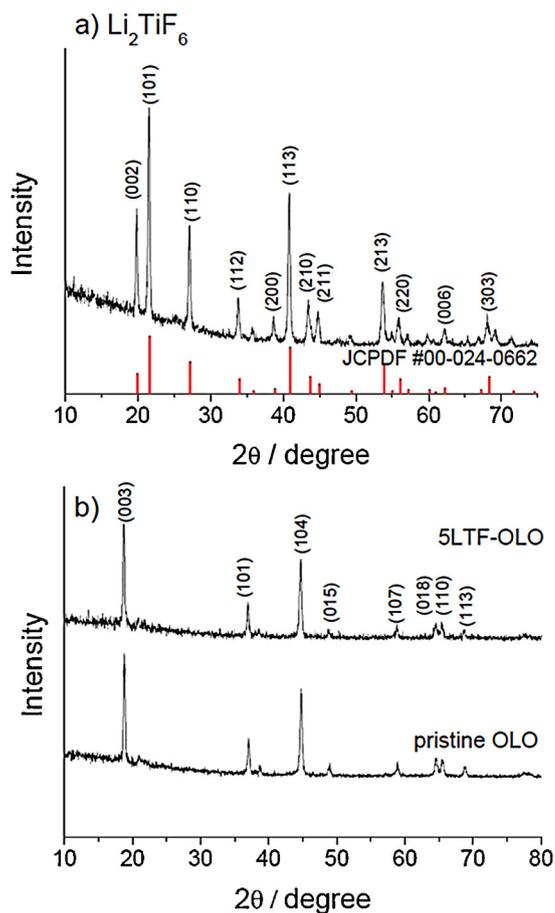


Fig. 1. XRD patterns of prepared (a) Li_2TiF_6 and (b) OLO cathode powders. Bottom: $\text{Li}_{1.17}\text{Ni}_{0.17}\text{Co}_{0.1}\text{Mn}_{0.56}\text{O}_2$; top: 5LTF-OLO.

hermetically sealed DSC pan without additional treatment. The measurement was conducted at a heating rate of $10^\circ\text{C min}^{-1}$ under a N_2 atmosphere.

3. Results and discussion

When the mixture of Li_2CO_3 and H_2TiF_6 solution was prepared to make Li_2TiF_6 , they reacted very quickly with the formation of CO_2 bubbles and became blurry within 1 min after the reagents were mixed. White powders were obtained after the rapid reactions and examined to confirm the structure by XRD. Fig. 1a shows the XRD pattern of the synthesized Li_2TiF_6 . The major XRD peaks of the co-precipitated white powder corresponded highly with Li_2TiF_6 data on the JCPDF #00-024-0662 card. The prepared Li_2TiF_6 was highly crystalline, with strong diffraction peaks from (101) and (113) and a distinct peak from (006). Therefore, we conclude that Li_2TiF_6 was synthesized successfully at the ambient temperature without additional heat treatment. The process of Li_2TiF_6 coating on OLO was also conducted at room temperature without further heat treatment, just like the preparation of Li_2TiF_6 powder. After the OLO surface was coated with 0.5 wt% of Li_2TiF_6 (5LTF-OLO) through the simple coating process discussed above, its crystal structure did not change from that of the pristine OLO (Fig. 1b). The room-temperature Li_2TiF_6 coating sequence did not affect the structural integrity of the OLO for energy storage and conversion. However, the XRD peaks of Li_2TiF_6 were not observed after the coating process because the amount of coating material was too small to exhibit their crystal peaks on XRD patterns.

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