Materials Research Bulletin 73 (2016) 362–368

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Improving thermal and electrochemical performances of $LiCoO_2$ cathode at high cut-off charge potentials by MF_3 (M=Ce, Al) coating

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ARTICLE INFO

Article history:
Received 1 June 2015
Received in revised form 9 September 2015
Accepted 15 September 2015
Available online 24 September 2015

Keywords:
Surfaces
Electrochemical properties
Energy storage
Electrochemical measurements
Microstructure
Interfaces
Inorganic compounds
Oxides

ABSTRACT

Surface coating of $LiCoO_2$ remained one of the efficient methods to enhance its electrochemical and thermal performances, especially at high cut-off potential. In this work, MF_3 (M = Ce, Al) coated $LiCoO_2$ was synthesized via co-precipitation method followed by a solid state reaction at 400 °C. The morphology and structure of the modified cathode material were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and transmission electron microscopy (TEM). The results show that the fluoride compound MF_3 is successfully coated on the surface of $LiCoO_2$ cathode particles with an average layer thickness about 12 nm and 40 nm for AlF_3 and CeF_3, respectively.

The electrochemical tests show that the AlF_3-coating layer significantly enhances the cycling performance of $LiCoO_2$ cathode material, even at high cut-off potential. While the bare $LiCoO_2$ cathode displays fast fading at 4.6 V vs. Li^+/Li cutoff potential, the surface-modified electrode exhibits the great capacity of 160 mAh g^{-1} with excellent capacity retention on several cycles.

We concluded that the electrochemical and the thermal enhancement at high potential are ascribed to the presence of MF_3 coating layer which prevent the side reaction during the charge discharge process, alleviate the attack by the acidic electrolyte and reduce the damage of electrode structure.

1. Introduction

Lithium ion batteries have attracted considerable interest because of the promising application ranging from electronic devices, to the electric and hybrid vehicles or space applications. Total sales of the cells in 2013 have been reported to be over 17.5 billion dollars, and are expected to be more than quadruple by 2020 [1].

Since the first Li-ion battery commercialized by Sony, layered $LiCoO_2$ is still the most widely used commercial cathode material because of its high electronic conductivity, excellent cycling performances, low self-discharge rate and excellent capacity retention below 4.2 V (vs. Li/Li^+), reasonable rate capability and feasible recycling from spent batteries [2–4].

In spite of a high theoretical specific capacity of 274 mAh g^{-1}, the practical reversible capacity of $LiCoO_2$ is limited to only 140 mAh g^{-1} or less when cycled between 3.0 and 4.2 V (vs. Li/Li^+) in order to maintain a reasonable cycling stability [5]. By charging to higher voltage such as 4.5 V, the capacity of the cell will increase by about 20%. Cobalt dissolution, structural changes, and oxidative decomposition of the electrolyte produce a dramatic increase in the capacity fade at the higher potentials. These instabilities can be addressed by coating the LiCoO2 powders with metal oxide coatings with thicknesses of 100–1000 Å.

The modification of surface properties of the cathode materials by coating its particles with some metal oxides recognized as one of the reliable techniques. The advantage of this technique is that the side reactions on the surface with electrolyte are avoided and the structural breakage of $LiCoO_2$ during charge discharge cycling can be lessened [6].

Many research groups have proposed various modifications in an attempt to enhance the electrochemical and structural stabilities of LiCoO2 at high cutoff voltages

To overcome this problem, many approaches are adopted in the literature, either by the modification of the $LiCoO_2$ particle surface with a metal oxide [7–9] or fluorine compounds [10,11], or either by the partial substitution of Co by other metals in $LiCoO_2$ [12].

There are many suitable coating materials, such as metal oxides (MgO [13,14], Al_2O_3 [15,16], CeO_2 [17], SnO_2 [18], SiO_2 [19], ZrO_2 [20,21], ZnO [22,23], TiO_2 [24] . . . etc.) and metal phosphate like $AlPO_4$ [25–28] and $FePO_4$ [29]. The results demonstrated promising increases in the discharge capacity reversibility upon cycling;

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http://dx.doi.org/10.1016/j.materresbull.2015.09.020
0025-5408/

however, the resulting thermal properties remained unimproved due to the intrinsic structural instability of the parent $LiCoO_2$ at a highly delithiated state and most of the metal oxides as coating materials cannot remain stable under the corrosion of HF from the electrolyte (degradation of $LiPF_6$ salt).

In recent years, fluorine in the form of metal fluorides such as AlF_3 [30,31], CaF_2 [32], MgF_2 [33], LaF_3 [34], CeF_2 [35], FeF_3 [36] is considered to be one of the most promising coating materials to improve electrochemical performance of cathode, due to its high stability. This could be attributed to the reduction of the structural change of active material from HF attack by a thin coating layer preventing the direct contact between delithiated cathode and liquid electrolyte.

Several different mechanisms have been suggested for the improvement of electrochemical stability of cathode material by metal oxide coating, such as: (1) reduction of “electrolyte–electrode” interactions; (2) formation of the solid solution between metal oxides and layered oxides near the particle surface; (3) creation of stable grain boundaries by formation of composite two-phase cathodes; (4) improving of thermal stability of oxides in delithiated state.

In this paper, we have attempted to synthesize MF_x (M = Al, Ce)-coated $LiCoO_2$ particles by precipitation method. The effect of coating on the structural, electrochemical and thermal properties was investigated in detail. The CeF_3-coated $LiCoO_2$ cathode material exhibits the highly enhanced cycling performance and rate capability compared with the pristine at high cut off voltage (4.5 V). The thermal properties are enhanced compared with standard $LiCoO_2$.

2. Experimental

2.1. Preparation of MF_3 coated $LiCoO_2$ materials

$LiCoO_2$ powder was prepared by employing Co_3O_4 (Managem group S.A. product) and Li_2CO_3 powders as starting materials. The both reagents were mixed in the mole ratio of 1:1.05 and fired in an oxygen stream for 14 h at 900 °C. Excess Li_2CO_3 was used to compensate for the loss of Li during firing. The obtained $LiCoO_2$ was used for MF_3 coating as presented in the flow chart in Fig. 1.

In the preparation of AlF_3 and CeF_3-coated $LiCoO_2$, aluminum nitrate nonahydrate, cerium nitrate octahydrate and ammonium fluoride were separately dissolved in distilled water firstly. To coat $LiCoO_2$ with AlF_3, $LiCoO_2$ powder was dispersed in the solution containing aluminum nitrate and stirring for 5 h to obtain a homogeneous suspension. Then, the stoichiometric amount of ammonium fluoride was added drop by drop to the mixture under heating at 80 °C. After precipitation, the mixture was stirred constantly at 100 °C for 4 h until evaporation of solvent.

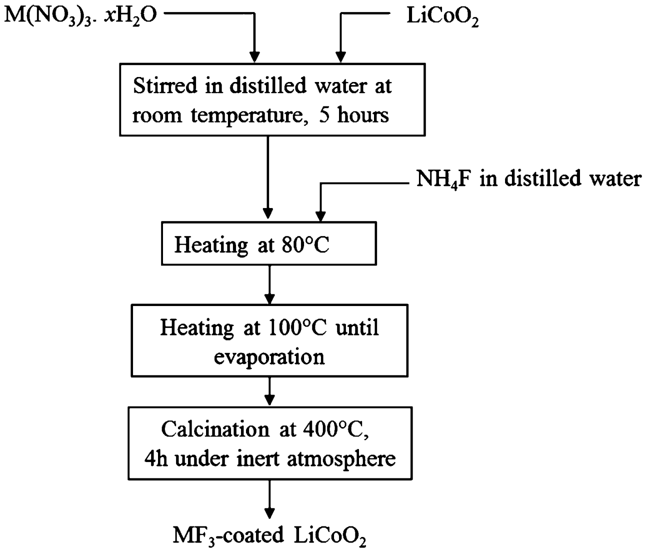

Fig. 1. Flow chart for the MF_3-coated $LiCoO_2$ (M = Al or Ce) cathode materials prepared by a ceramic process

The resulting powders were heat-treated in a furnace at 400 °C for 4 h under inert atmosphere to avoid the formation of oxide.

2.2. Physical characterization

The X-ray diffraction (XRD, Philips X-pert) with monochromatic Cu-Kα radiation was employed to identify the crystal structure of the powders in the 2θ range from 10 to 60°, with a step size of 0.03°. Structural parameters, such as lattice constants and intensity ratio, were calculated by Dopowder program.

Scanning electron microscope (SEM, FEI) and transmission electron microscope (TEM, TECNAI G2/FEI) were used to observe the micromorphology of the powders and the status of coating layer. Energy dispersive spectroscopy (EDS) was employed to analyse the surface composition and the element content of powders.

The thermal stability of bare and coated-$LiCoO_2$ materials was evaluated by differential scanning calorimeter (Perkin Elmer DSC 8000) using a temperature scan rate of 3 °C/min. The cells were charged to 4.6 V at 400 μA (40 mA g^{-1}) and then disassembled in the glove box. The cathode materials were recovered from the current collector after removing the remained electrolyte. Samples of 3–5 mg were collected in a stainless steel sealed pan with a gold plated copper seal. The weight was constant in all cases, indicating that no leaks occurred during the experiments.

2.3. Electrochemical characterization

Electrochemical characterizations of all the synthesized materials were performed using a CR2430 coin cell fabricated in a glove box (Jacomex, SA) under an Argon atmosphere. The cell consisted of the synthesized material as the cathode and a metallic lithium anode separated by a polypropylene micro-porous film (Celgard 2300) as separator with 1 M $LiPF_6$ dissolved in EC:DMC (1:1 by volume) as the electrolyte.

For cathode fabrication, the prepared powders were mixed with 15 wt.% of black carbon and 10 wt.% of polyvinylidene fluoride (PVDF) in N-methyl pyrrolidinone until slurry was obtained. The blended slurries were cast onto an aluminum current collector by a doctor blade method, and the electrode was dried at 125 °C for 3 h in vacuum before the fabrication of the cell. All the organic solvents and electrolyte were of battery grade.

Galvanostatic charge/discharge testing was performed at different potential range between 3 V and 4.6 V and at a current density of 40 mA g^{-1} on an Arbin BT 2000 battery tester.

3. Results and discussion

3.1. X-ray diffraction and refinement parameters

The X-ray diffraction (XRD) patterns of bare $LiCoO_2$, AlF_3-coated $LiCoO_2$ and CeF_3-coated $LiCoO_2$ powders are given in Fig. 2.

The main peaks confirmed that both materials can be indexed in the hexagonal-type space group $R\bar{3}m$. The XRD pattern of the CeF_3-coated $LiCoO_2$ material shows additional peaks attributed to cerium oxide CeO_2. This is presumably because the content of CeF_3 is high (2% mol) and its excess doesn't form only a thin film on the surface of $LiCoO_2$ but also an aggregate of cerium oxide. The lattice