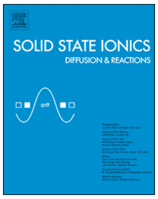
Solid State Ionics 324 (2018) 7–12

Contents lists available at ScienceDirect

Solid State Ionics

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



Stabilized structural and electrochemical properties of $LiNi_{0.5}Mn_{1.5}O_4$ via ZrF_4 nanolayer modification for Li-ion batteries

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ARTICLE INFO

Keywords:
Lithium ion batteries (LIBs)
High voltage
Surface modification
Electrochemical performance

ABSTRACT

Uniform and thin ZrF_4 nanolayer with diverse contents are successfully coated on the surface of spinel-structured $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) material with $Fd\bar{3}m$ space group via a simple co-precipitation process. The morphologies and structures of the as-prepared samples are studied by X-ray diffraction (XRD), Raman, scanning electron microscopy (SEM), energy dispersive spectrometric (EDS) analyses and high resolution transmission electron microscopy (HRTEM). Electrochemical measurements demonstrate that a desirable capacity retention of 95.5% could be obtained for 2 wt% ZrF_4-surface modified LNMO after 120 cycles, much greater than that of 80.1% for the pure material. Meanwhile, 2 wt% ZrF_4 modified sample shows superior rate performance, which delivers a high capacity of 106 mAh g^{-1} at 2C. Intensive electrochemical impedance spectroscopy (EIS) and Fourier transform infrared (FTIR) analyses indicate that ZrF_4 surface modification is effective in stabilizing the electrode/electrolyte interface at high voltage, through averting the direct contact and depressing the undesirable side reactions between cathode and electrolyte. The ZrF_4 surface modification on LNMO proposed herein, with a facile and repeatable strategy, provides a perspective in enhancing surface structural stability as well as electrochemical reversibility for electrode functionalization.

1. Introduction

Lithium ion batteries (LIBs) have attracted more and more interest in power sources, such as electric vehicles (EVs) and hybrid electric vehicles (HEVs), due to their large energy densities [1]. So far, however, LIBs have to be improved in terms of safety and longevity, especially in the aspect of energy density to meet the demands of current applications [2]. A way is to elevate the working voltage of positive electrode, since the potential of commercial anode is close to that of lithium metal. Among cathode materials, $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) has been extensively studied due to its high voltage plateau (~ 4.7 V vs. Li/Li^+) and high energy density (~650 Wh kg^{-1}) [3, 4]. On the other hand, as a derivative of $LiMn_2O_4$ (LMO), LNMO retains the spinel structure and three-dimensional ion channel, which are beneficial to the transfer of lithium ions [5].

Despite these advantages, the practical application of this material is still challenged due to electrolyte decomposition and side reactions on the interface of cathode/electrolyte at high voltage [6, 7]. Therefore, great efforts have been paid to develop of electrolyte resisting high cutoff voltages in recent years [8]. As an alternative, the interface of cathode/electrolyte could be stabilized to enhance the properties of LNMO material. In this regard, many strategies have been proposed, such as morphological design [9–13], surface coating [14–18] and bulk material doping [19–23]. Among them, moderate surface modification is a feasible way to improve the electrochemical performances of LNMO by inhibiting the decomposition of electrolyte and HF corrosion [24].

Cho et al. [25] utilized thin-film metal oxides (ZrO_2, Al_2O_3, TiO_2, B_2O_3) to modify layered $LiCoO_2$, and established that the phase change was significantly impeded by ZrO_2 with high fracture toughness. Thackeray et al. [26] reported that ZrO_2, served as a stabilizing medium, successfully modified spinel $LiMn_2O_4$ and contributed to improving electrochemical properties. They also found that ZrO_2 could scavenge HF in $LiPF_6$-based electrolyte to generate ZrF_4. Thus the surface of $LiMn_2O_4$ was protected from HF attack. Analogously, ZrO_2 is applied to surface modification of other electrode materials for the similar mechanism [27–29]. Actually, ZrF_4 has been already investigated as modification material on the surface of cathode materials, such as $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ [30] and $Li_4Ti_5O_{12}$ [31], which contributed to enhancing performances. Inspired by the previous literatures [30, 31], in this study, ZrF_4 is utilized to coat the surface of LNMO material. The purpose of this work aims to improve the electrochemical properties of LNMO by ZrF_4 modification. Moreover, the investigation focuses

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https://doi.org/10.1016/j.ssi.2018.06.001
Received 10 May 2018; Received in revised form 29 May 2018; Accepted 1 June 2018
0167-2738/

on exploring fundamental improvement mechanism of ZrF_4 and paves a way to realizing rational surface functionalization for the convenience of LNMO application.

2. Experimental section

2.1. Material synthesis

The LNMO material was synthesized via a sol-gel method. Stoichiometric amounts of lithium acetate ($CH_3COOLi{\cdot}4H_2O$), nickel acetate ($Ni(CH_3COO)_2{\cdot}4H_2O$), manganese acetate ($Mn(CH_3COO){\cdot}4H_2O$) and citric acid were dissolved in ultrapure water separately. After dissolved completely, $Ni(CH_3COO)_2{\cdot}4H_2O$, $CH_3COOLi{\cdot}4H_2O$ and citric acid were added slowly into $Mn(CH_3COO){\cdot}4H_2O$ solution successively with vigorous stirring. The mixture was heated at 80 °C until the solvent was evaporated to form a wet gel. Meanwhile, the PH value was kept to 6.5 through adding ammonia aqueous solution during the gelation process. The wet gel was dried at 120 °C for 24 h to form a dry gel. The resulting powder was heated at 500 °C for 6 h after full grinding, followed by another calcination at 820 °C for 14 h to obtain the LNMO spinel material.

LNMO sample was coated by different amounts of ZrF_4 via a precipitation method. Certain amount of $Zr(NO_3)_4{\cdot}5H_2O$ and LNMO powders with different ratios were homogeneously dispersed in ultrapure water with continuous stirring for 2 h. Meanwhile, NH_4F powder was also dissolved in ultrapure water, in which the molar ratio of Zr and F sources was set to be 1:4. Whereafter, the latter solution was slowly dripped into the above LNMO mixture. The resulting solution was filtered repeatedly with ultrapure water after thoroughly mixed, followed by drying at 80 °C for 12 h in an oven and post-calcination treatment at 400 °C for 4 h in Argon atmosphere. Finally, 1 wt%, 2 wt% and 3 wt% ZrF_4-coated LNMO powders (nominal proportions) were obtained.

2.2. Physical characterizations

X-ray diffractometry (XRD, Bruker, Germany) of the samples were collected using Cu K source (λ ~0.15418 nm) in the 2θ range of 10° ~ 130° with a step size of 0.02°. The particle morphology images of the samples were recorded on a scanning electron microscope (SEM, JEOL JSM-7001F). Energy dispersive X-ray spectroscopy (EDS, APOLLO X silicon drift X-ray detector) was performed to analyze the element distribution of materials on surface. Raman spectra (Raman, RM-1000, Renishaw) were recorded with wavenumber range from 200 to $1000\ cm^{-1}$. Fourier transform infrared (FTIR) measurements were carried out using an AVATAR360 FTIR spectrometer within the region of $400–4000\ cm^{-1}$. Inductively coupled plasma spectrometer (ICP, Thermo Fisher ICAP 6300) was employed to determine the element composition of the as-prepared materials.

2.3. Electrochemical measurements

The cathode was prepared by casting the mixed slurry of 80% active materials, 10% carbon black and 10% binder (a mixture of polyvinylidene difluoride (PVDF) and N-methyl-2-pyrrolidone (NMP)) onto an aluminum foil. The electrode slice was pressed at a pressure of 10 MPa after the slurry was dried at 120 °C for 24 h in a vacuum oven. The standard CR2032 coin-type cells were assembled in an argon-filled glove box (H_2O, $O_2 < 1\ ppm$) using lithium sheet as counter electrodes, Celgard 2400 separators, and 1 M $LiPF_6$ in the mixture of ethylene carbonate ($C_3H_4O_3$)/dimethyl carbonate ($(C_2H_5O)_2CO$) (EC/DMC). The cells were cycled in a potential range of 3.5–4.9 V on a LAND CT2001A (Wuhan, China) battery tester at room temperature. The electrochemical impedance spectroscopy (EIS) of the coin cell was measured with CHI660E electrochemistry work station (Shanghai, Chenhua) over the frequency range of 5 mHz–100 kHz.

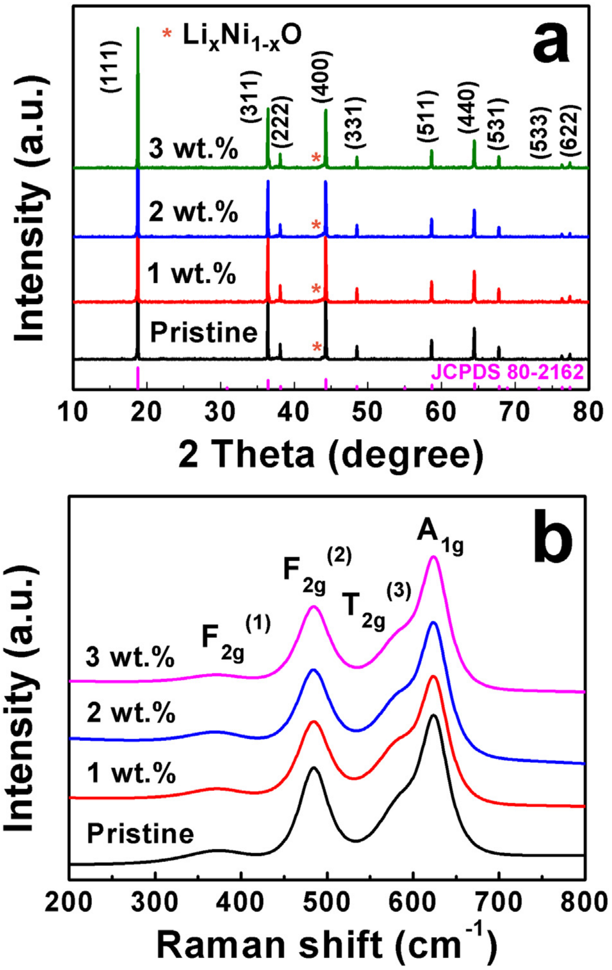

Fig. 1. XRD patterns (a) and Raman spectra (b) of the pristine and ZrF_4-coated spinel LNMO.

3. Results and discussion

3.1. Physical characteristics

Fig. 1a presents the XRD profiles of the pristine and ZrF_4-surface modified LNMO samples. Apparently, all these samples display prominent diffraction lines with similar feature, which could be well assigned to a typical spinel phase with $Fd\bar{3}m$ space group (JCPDS No. 80-2162) [32]. The discernible minor peak at $2\theta = 43°$ could be indexed to $Li_{1-x}Ni_xO$ [33], which is a rock-salt impurity phase generated under annealing treatment with temperature over 750 °C [34]. It implies that a fraction of Mn^{4+} ions reduce to Mn^{3+} to remain charge conservation with the impurity formation, which is also the characteristic of the disordered phase [35]. Moreover, no diffraction peaks for ZrF_4 could be observed, indicating that the amount of ZrF_4 is too low to be detected. Diffraction peaks of ZrF_4 appear in the XRD pattern (Fig. S1, in Supporting Information) when the modification content is enhanced to 20 wt%, coinciding with the annealing temperature repeated previously [36]. The result manifests that rather thin ZrF_4 coating layers are generated with quite low crystallinity for 1 wt%, 2 wt% and 3 wt% ZrF_4 modified LNMO. XRD refinement profiles of LNMO before and after ZrF_4 modification are observed in Fig. S2, and the calculated parameters are shown in Table 1. The results indicate that the lattice parameter and cell volume remain unchanged after ZrF_4-surface modification, reflecting the negligible structure influence from low content ZrF_4.

Raman analysis is performed to further ascertain the component and