



Suppressing capacity fading and voltage decay of Li-rich layered cathode material by a surface nano-protective layer of CoF₂ for lithium-ion batteries



Shaokun Chong^a, Yuanzhen Chen^a, Wuwei Yan^a, Shengwu Guo^a, Qiang Tan^a, Yifang Wu^b, Tao Jiang^a, Yongning Liu^{a,*}

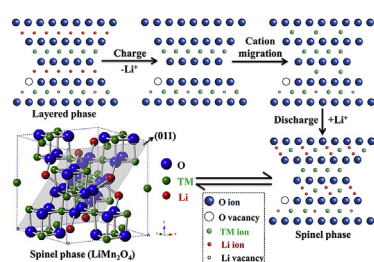
^a State Key Laboratory for Mechanical Behavior of Materials, School of Material Science and Engineering, Xi'an Jiaotong University, Xi'an, 710049, PR China

^b Northwest Institute for Nonferrous Metal Research, Xi'an, 710016, PR China

HIGHLIGHTS

- Nano-CoF₂ is firstly coated on Li_{1.2}Ni_{0.2}Mn_{0.6}O₂ via a wet chemistry method.
- 0.5% CoF₂-coated sample delivers the improved initial coulombic efficiency of 86.2%.
- Excellent stability of capacity and voltage are observed for 1.0% CoF₂-coating.
- The mechanisms of serious fading of capacity and voltage are discussed in details.
- Structure transition is suppressed by CoF₂ nano-coating evidenced by TEM analysis.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 8 July 2016

Received in revised form

2 September 2016

Accepted 6 September 2016

Keywords:

Lithium-ion battery
Cathode material
CoF₂ coating layer
Capacity fading
Voltage decay

ABSTRACT

Li-rich layered oxides have been regarded as valuable cathode materials for high energy density lithium-ion batteries. However, high initial irreversible capacity, bad rate capability, as well as serious capacity fading and voltage decay hinder their commercial application. In this paper, a nano CoF₂ protective layer is coated on the surface of Li_{1.2}Ni_{0.2}Mn_{0.6}O₂ via a facial wet chemistry method. A high initial discharge capacity of 264.4 mAh g⁻¹ is obtained for 0.5% CoF₂-coated sample and 259.1 mAh g⁻¹ for 1% CoF₂-coated sample owing to the suppression of irreversible release of O₂ and the contribution of electrochemical conversion of CoF₂/LiF. Furthermore, 1% CoF₂-coated sample exhibits the excellent rate capability of 167.5 mAh g⁻¹ at 5 C rate, the superior cycling stability with the capacity retention of 241.0 mAh g⁻¹ and the ameliorative voltage drop of 0.312 V at 0.1C after 100 cycles. The enhanced rate performance as well as stability of capacity and voltage can be attributed to the nano coatings which inhibit the electrolyte-electrode side reaction, enhance the electrochemical kinetics and mitigate structure transition from layered to spinel phase.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

To meet more demanding requirements for portable electronics, electric vehicles and hybrid electric vehicles, rechargeable lithium-

* Corresponding author.

E-mail address: ynliu@mail.xjtu.edu.cn (Y. Liu).

ion secondary batteries (LIBs) have been urged for much higher energy density and power density, outstanding safety and long cycle life [1,2]. Li-rich Mn-based layered cathode material is one of the most promising candidates for LIBs due to its higher initial discharge capacity, over 250 mAh g⁻¹, compared to other cathode materials [3,4], such as LiMO₂ (M = Ni, Co and Mn), LiFePO₄, and LiMn₂O₄. However, several shortcomings hinder the practical commercialization: (i) the low initial coulombic efficiency caused by the irreversible O₂ release; (ii) the inferior rate performance associated with lower electronic conductivity; (iii) severe capacity fading and voltage decay resulting from a fast phase transformation from layered to spinel upon cycling [5–8].

Surface coating has been considered as a facile and effective method to improve the electrochemical performances of cathode materials, because the coating layers can avoid direct contact between the electrode and the electrolyte to suppress the side reactions and mitigate the surface structure transformation from layered to spinel. Thus far, four series of compounds, such as oxides (ZrO₂, P₂O₅, Al₂O₃, Cr₂O₃, Sb₂O₃, MoO₃, MgO, MnO₂, Sm₂O₃, TiO₂) [6,9–17], metal fluoride (CaF₂, AlF₃, FeF₃) [18–21], metal phosphate (AlPO₄, Li₃PO₄) [22,23], and other Li-ion extraction/insertion materials (Li₂TiO₃, Li₄Ti₅O₁₂, Li₃VO₄, LiVO₃, LiAlO₂) [24–30], have been employed to coat the active materials.

As reported, the cyclability is enhanced by ZrO₂, MoO₃, MgO and TiO₂ coating, respectively, for the reason that the coating layer efficiently alleviates the side reaction between the active material and the electrolyte [6,13,14,17]. Among these coating materials, 2 wt% MgO-coated sample delivers the highest capacity retention of 96.4% after 100 cycles, while it suffers decreased initial capacity, unsolved problems of rate property and voltage decay [14]. In addition, it has been reported that surface coating by CaF₂, AlF₃, and AlPO₄ on active materials, respectively, improves both stability of capacity and rate performance for stable electrolyte-electrode interfacial structure and good Li-ion conductivity [18,20,22]. For instance, the capacity retention of AlF₃-coated sample is 98% after 50 cycles, higher than LNMO of 93% in a voltage range of 2.0–4.6 V, and the rate capability is measured to be 127.5 mAh g⁻¹ at 5 C [20]. Furthermore, coating with Li-ion extraction/insertion material (such as LiAlO₂) has been also an important approach to increase the initial coulombic efficiency for a much higher reversible capacity of 257.6 mAh g⁻¹ on account of more available sites for insertion of extracted Li-ion from coating layer, besides enhance the cyclability (the capacity retention of 101.6% after 50 cycles) and rate performance (88.3 mAh g⁻¹ at 10C) [30]. Nevertheless, the above-mentioned surface coating materials display little effect on the voltage decay upon long term cycling. Recently, a highly ordered mesoporous Al₂O₃/polyacene double shelled coating suppresses the voltage fading with the retention of 3.14 V after 100 cycles [10]. Also, FeF₃ of which theoretical capacity is 712 mAh g⁻¹, was used to coat the Li-rich cathode materials, and the results reveals a higher reversible capacity of 291.8 mAh g⁻¹, enhanced rate performance of 170.3 mAh g⁻¹ at 5 C, improved slightly cyclability with the capacity retention rate of 89.14% after 60 cycles. However, the FeF₃ coating layer will lower the operating voltage because of the low reaction potential (2.7 Versus Li/Li⁺) of the conversion reaction though it decreases the voltage decay, which will reduce the energy density [21]. Therefore, it is necessary to study a novel coating materials, whose functions consist of protecting the surface of active materials against the electrolyte attacks, improving the electronic and Li-ion conductivity, possessing the electrochemical activity and restraining structure transformation, to optimize the integrated electrochemical properties of Li-rich cathode materials.

In this paper, CoF₂ with a high theoretical capacity of 600 mAh g⁻¹ [31,32], was in situ nano-synthesized and employed to coat Li_{1.2}Ni_{0.2}Mn_{0.6}O₂ (LNMO) via a facile wet chemistry method.

What is more, CoF₂ can react with two Li-ions to generate a product of LiF at an operating potential of 2.854 V during discharge process [31–33], which provides a CoF₂/LiF protective layer on LNMO surface upon cycling. It is shown that CoF₂ nano-coating layer not only restrains the surface of active material deterioration, improves the electrochemical kinetics, but also delays the phase transition from layered to spinel structure. Thus, high reversible initial discharge capacity, outstanding rate property, as well as splendid stability of capacity and voltage have been displayed.

2. Experimental

2.1. Material preparation

Li_{1.2}Ni_{0.2}Mn_{0.6}O₂ cathode material was synthesized via a typical combustion method with Li, Ni, Mn acetates and citric acid as starting reagents. Stoichiometric amounts of C₂H₃O₂Li·2H₂O with 5 wt% excess, C₄H₆NiO₄·4H₂O and C₄H₆MnO₄·4H₂O (Sinopharm Chemical Reagent) were dissolved in ethanol with vigorous stirring to form solution A, and C₆H₈O₇·H₂O (Sinopharm Chemical Reagent) was dissolved in ethanol to get solution B. The molar ratio of metal and citric acid was 1:1. Then solution A and solution B were instilled separately into 100 ml ethanol solution under continuous mechanical stirring at 80 °C. Afterwards the solution was evaporated until a white gel emerged and further dried at 110 °C for 12 h to obtain precursor. Finally the mixture was precalcined at 450 °C for 5 h in air to eliminate the organic substances and further heated at 900 °C for 5 h in air to obtain LNMO powders.

CoF₂ was coated on the surface of LNMO powder using a wet chemistry method, as schematically illustrated in Fig. 1. A desire amount of LNMO was dispersed in the CoCl₂ dilute aqueous solution under ultrasonic treatment for 30 min. Then the NH₄F aqueous solution was dropped into the above solution at a rate of 1 ml/min under continuous stirring and the molar ratio of Co to F was controlled to be 1:2. After that, the mixture was stirred forcefully at 80 °C till the solution was evaporated to dryness, and subsequently heated at 400 °C for 5 h in argon atmosphere to obtain the CoF₂-coated LNMO. Samples were synthesized with 0.1 wt%, 0.5 wt% and 1.0 wt% CoF₂ coating amount and are named as CF-0.1, CF-0.5 and CF-1.0, respectively.

2.2. Material characterization

The crystal structure of as-prepared powder was characterized by X-ray diffraction (XRD, UltimaIV-185, Rigaku) with Cu K α radiation operating at 40 kV and 40 mA over a range of 10–80°. The powder morphology was observed by field-emission scanning electron microscopy (FESEM, JSM-6390). Elemental distribution mapping of sample coated by CoF₂ was collected by an energy-dispersive X-ray spectrometer (EDS). Transmission electron microscopy (TEM, JEOL JEM-2100CX) was used to study the microstructure of samples. X-ray photoelectron spectra (XPS, Axis Ultra, Kratos) measurement was carried out by Thermo Fisher Scientific ESCALAB with monochromatic Al K α radiation (h ν = 1486.6 eV).

2.3. Electrochemical test

The cathode electrode was prepared by coating an aluminum foil with a slurry, which was composed of active material, acetylene black and polyvinylidene fluoride (PVDF) with a weight ratio of 80:10:10 in *N*-methyl pyrrolidinone (NMP). After that the aluminum foil was dried overnight at 100 °C in a vacuum oven and punched into disk with ϕ 12 mm. The mass loading for active material was

Download English Version:

<https://daneshyari.com/en/article/5150123>

Download Persian Version:

<https://daneshyari.com/article/5150123>

[Daneshyari.com](https://daneshyari.com)