Electrochimica Acta 261 (2018) 565–577

Contents lists available at ScienceDirect

Electrochimica Acta

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

Enhanced rate performance and high potential as well as decreased strain of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ by facile fluorine modification

Shuo Zhou, Guixin Wang*, Wenjie Tang, Yao Xiao, Kangping Yan

College of Chemical Engineering, Sichuan University, Chengdu, 610065, China

ARTICLE INFO

Article history:
Received 30 October 2017
Accepted 26 December 2017
Available online 28 December 2017

Keywords:
$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$
PTFE
Fluorine modification
Electrochemical performance
Strain analysis

ABSTRACT

Fluorine is interesting for improving the electrochemical performance of current electrode materials, but the preparation process faces challenges because of the difficult homogeneous mixing of powders. A facile novel strategy of surface fluorine modification using polytetrafluoroethylene (PTFE) emulsion at low temperature, where the powders are easy to be homogeneously mixed and evenly covered by fluorine polymer, has been proposed to enhance the electrochemical performance of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ material. Though the initial discharge capacities of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_{2-y}F_y$ (y = 0.02, 0.05, 0.08) are slightly decreased at 0.1C, the capacity retention ratios at higher current densities, higher potential and elevated temperatures are improved compared to that of the pristine one. Among the samples with different fluorine contents, $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_{1.95}F_{0.05}$ exhibits the best performance, and the average discharge capacity fade rate in one cycle and the residual stress after 50 cycles at 1.0 C, as well as the discharge capacity after 10 cycles at 4.0 C are respectively about 0.03%, 10.3 MPa, 129.5 mAh g^{-1}, while the corresponding values of the pristine samples are around 0.12%, 29.4 MPa, and 99.7 mAh g^{-1}, respectively. After 50 cycles at 1.0 C between 2.8 and 4.7 V, $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_{1.95}F_{0.05}$ improves the capacity retention ratio and the discharge capacity of the pristine sample from 80.0% to 90.4%, and from 156.7 to 176.3 mAh g^{-1}, respectively. The electrode reaction process and fluorine modification mechanisms have been discussed using various techniques. This method is easily achievable and may be used to modify other powder materials via a simple solid-solution mixing and an in-situ surface modification.

1. Introduction

The extensive applications of electric vehicles (EV), hybrid electric vehicles (HEV) and large-scaled energy storage systems need more and more high energy and safe lithium-ion batteries (LIBs) [1]. As a significant component of LIBs, cathode plays a key role in determining electrochemical performance, safety performance and service life in some degree [2]. Thus, cathode materials with unique properties, such as high capacity, good cyclability and environmental compatibility, have become one of the focuses for improving the performances of current batteries [3,4]. Among various cathode materials, a series of Li–Ni–Co–Mn–O materials with different metal compositions have attracted great interests because of the advantages like high energy density, low toxicity and low cost [5,6]. However, Li–Ni–Co–Mn–O materials still have some disadvantages, such as poor thermal stability, cycling performance, and high-temperature performance, which hinders their comprehensive applications [7].

In order to improve the electrochemical performance and safety property of Li–Ni–Co–Mn–O materials, many measures have been taken, including surface coating and bulk doping. Cyclic retention and rate capability can be enhanced by surface coating, which prevents the direct contact and the side reactions between electrode and electrolyte [8]. Compared to surface coating, ion doping can not only alter the valence states of both transition metals and oxygen by charge compensation, but also alter the distance of both lithium and transition metal layers, resulting in enhanced electronic and lithium ion conductivity of host materials [7]. Therefore, various ions, such as transition-metal ions [9,10], Na^+ [11], Mg^{2+} [12], and Zr^{4+} [13], have been adopted to dope Li–Ni–Co–Mn–O materials to improve structural stability. Al and/or Mg substitution for Ni can improve the structural stability at the cost of a slight discharge capacity sacrifice [14]. A small quantity of Cr substitution for Ni in $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ material can improve electrochemical performance without reducing the reversible capacity [15].

---

* Corresponding author.
E-mail addresses: guixin66@scu.edu.cn, guixinwang1@gmail.com (G. Wang).

https://doi.org/10.1016/j.electacta.2017.12.159
0013-4686/

However, such cation doping site is difficult to be controlled because several transition metals with different oxidation states coexist in the transition metal layer. Compared to cation doping, anion modification is relatively easy to be implemented, which is from only one anion O^{2-} in the material. The structure in Li-rich layered cathode material is more flexible after sulfur modification for oxygen because the electronegativity of S^{2-} is lower than that of O^{2-} [16]. As for the element with the lowest electronegativity in current elemental periodic table, F has a high reaction activity, and can form Li–F by attacking Li–O in Li–Ni–Co–Mn–O materials to enhance capacity retention, stability, and safety performance [7]. The reasons for the improvement are that fluorine modification can help to form more stable solid permeable interface (SPI) film and decreases the cell impedance for Li^+ diffusion by forming LiF on the surface of electrodes during charging/discharging process [17,18]. Unfortunately, the fluorine resources in current studies are main solids (LiF and NH_4F), which is difficult to control the homogenous distribution of the fluorine in the material [7].

Herein, an effective and facile method of surface fluorine modification has been supplied by using industrial PTFE emulsion at low temperature, which can make the uniform mixing and in-situ particle surface modifying possible. In comparison with that of the pristine $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$, the modified materials deliver higher capacity retention at 25 °C and 50 °C, better rate performance, wider working potential window, and lower strain.

2. Experimental

2.1. Materials synthesis

Powders of $(Ni_{0.6}Co_{0.2}Mn_{0.2})(OH)_2$ and $LiOH \cdot H_2O$ (molar ratio of 1:1.05) were completely mixed, using alcohol as the dispersing agent by a planetary ball milling at 180 rpm for ~4 h. The milled precursor was preheated at 550 °C in air for ~4 h in a muffle oven and further calcined at 750–850 °C in air for ~12 h. The fluorine modified $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ samples were prepared by mixing the as-obtained $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ with required amounts of 60% of PTFE emulsion in purified water at 25 °C to form a homogeneous viscous slurry, and drying the mixed material at 100 °C for 1 h in air and further heating at 600 °C for 1 h in argon. Consideration of the low PTFE addition, the fluorine content in the samples is marked as theoretical value. Three samples with various fluorine contents, i.e. $Li(Ni_{0.6}Co_{0.2}Mn_{0.2})O_{1.98}F_{0.02}$, $Li(Ni_{0.6}Co_{0.2}Mn_{0.2})O_{1.95}F_{0.05}$ and $Li(Ni_{0.6}Co_{0.2}Mn_{0.2})O_{1.92}F_{0.08}$ are marked as F2, F5 and F8, respectively.

2.2. Materials characterization

In order to detect the composition and crystal structure of the samples, X-ray diffraction (XRD) technique was carried out, using Cu-Kα radiation in the range from 10 to 80° at a scan rate of 0.04° s^{-1} on a Philips X'Pert pro MPD machine. To investigate the reaction process, thermal analysis was performed from ~50 to ~800 °C at a ramp rate of 10 °C/min under argon on a NETZSCH STA 449C instrument. The morphology and the particle size were observed, using scanning electron microscopy (SEM, JEOL JSM-7500F, Japan), and the elemental composition on the surface of the samples were analysed via energy dispersion spectrum (EDS). The chemical composition of the as-synthesized materials was detected by FTIR on a Thermo NICOLET 6700 machine and X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi)

2.3. Electrochemical evaluation

The as-synthesized materials for electrochemical characterization were well mixed with 10 wt% of conductive additive of super P and 7 wt% of commercial PVDF binder in NMP solvent to form a homogeneous viscous slurry to coat a cleaned aluminium foil using a doctor blade. After being dried at 100 °C, the aluminium foils loaded with active materials were cut into 1.2 cm^2 wafers which were further dried at 100 °C under vacuum for 12 h before using as the working electrodes. The loading density of the active material in one electrode is about 0.93 mg/cm^2. CR2025 coin cells were assembled by sandwiching a Celgard 2300 microporous separator between the working electrode and the counter and reference electrodes of lithium disc in an argon-filled glove box. The electrolyte was 1.0 M $LiPF_6$ in a mixture of ethyl carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) (1:1:1 in vol., Shenzhen Capchem Chemicals Co. Ltd., China).

Galvanostatic charge/discharge cycling tests were carried out under different current rates and working temperatures on a Neware battery-testing instrument (Shenzhen Neware Technology Ltd., China). Electrochemical Impedance Spectroscopy (EIS) measurements were conducted in the frequency range from 100 kHz to 0.01 Hz with a sinusoidal excitation voltage of 10 mV, and the impedance curves were fitted well using Zsimpwin and Zview softwares. Cyclic voltammetry (CV) technique was used in the voltage window of 2.8–4.3 V to investigate the electrode reaction processes after different cycles. Both EIS and CV tests were carried out on an electrochemical workstation consisting of a PAR 273A potentiostat/galvanostat and a signal recovery model 5210 lock-in-amplifier controlled by a Powersuit software (Princeton Applied Research, USA).

2.4. Stress-strain tests

The stress-strain and electrochemical testing system, along with the detailed testing method, has been supplied in our previous work [19,20]. Both cycling process and stress-strain tests of the cells proceed simultaneously.

3. Results and discussion

3.1. TG-DSC analysis

To obtain the possible reaction temperature for fluorine modification, thermodynamic analysis was conducted in Argon with a heating rate of 10 °C/min, and the simultaneous thermogravity (TG) and differential scanning calorimetry (DSC) plots of the dried mixture of $Li(Ni_{0.6}Co_{0.2}Mn_{0.2})O_2$ and PTFE (in a mass ratio of about 100:1), are supplied in Fig. 1. There are three key stages of mass

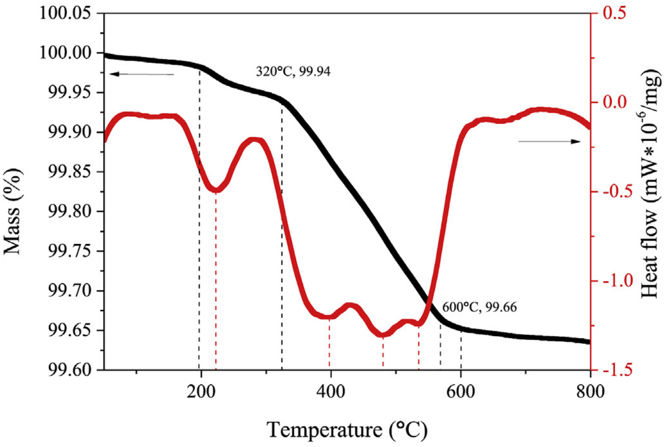

Fig. 1. Thermal analysis of stoichiometric mixture of $Li(Ni_{0.6}Co_{0.2}Mn_{0.2})O_2$ and PTFE.