



Silver/carbon nanotube hybrids: A novel conductive network for high-rate lithium ion batteries



Fangdong Zhou^{b,c}, Kehui Qiu^{a,*}, Gongchang Peng^c, Li Xia^{b,c}

^a Institute of Materials Science and Technology, Chengdu University of Technology, Chengdu 610059, China

^b College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059, China

^c Chengdu Jingyuan New Materials Technology Co., Ltd., Chengdu 610100, China

ARTICLE INFO

Article history:

Received 5 September 2014

Received in revised form 29 October 2014

Accepted 12 November 2014

Available online 15 November 2014

Keywords:

Lithium ion battery

$\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$

Carbon nanotube

Ag additive

Electrochemical performance

ABSTRACT

$\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2/\text{Ag}$ composite cathodes are synthesized by a thermal decomposition method and multi-walled carbon nanotubes are uniformly introduced into the composites through ball mixing. A composite electrically conductive network consisting of CNTs and Ag is obtained to improve the conductivity of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ material. By comparing with the pure $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and cathode modified by CNTs or Ag, the as-obtained $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2\text{-CNT/Ag}$ electrode exhibits the best rate capability (120.6 mAh/g at 5C) and cycle performance (134.2 mAh/g at 1C with a capacity retention of 94.4% over 100 cycles). With the construction of 3D spatial conductive network, the novel hybrid CNT/Ag demonstrates itself a promising strategy to improve Li storage performance for lithium ion batteries.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Because of the serious environmental problems coupled with high fuel prices, substantial efforts have been exerted to develop chemical energy storages such as Li-ion batteries to effectively store extra energy [1,2]. And continuous breakthroughs in electrode materials provide the driving force for the significant improvement in the current Li-ion batteries [3,4]. The layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material developed by Ohzuku and Makimura, has been extensively investigated because of its higher reversible capacity, stable structure, lower cost and safety [5,6]. However, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ also has the problems of a low-rate capacity, a low-electronic conductivity, and cation mixing, which are all required to be solved [7–9].

Research into the improvement of the performance of the cathode materials has managed to overcome these drawbacks, such as (1) ionic substitution [10,11], (2) surface coating [12–15], (3) and mixing the electrode material with conducting additives to improve its conductivity [16,17]. Typically, carbon blacks (CBs) are introduced to the active materials to enhance the electrical conductivity of the cathodes in Li-ion battery industry. However, CBs could not construct a robust and interconnected conductive

network at a low loading content because the small-diameter particles tended to aggregate [18].

Recently, carbon nanotubes (CNTs) have become a hotspot in lithium ion battery research owing to their large surface area and excellent electrical conductivity ($> 10^3 \text{ S cm}^{-1}$ for multiwalled nanotubes), which can improve the electrochemical properties of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ [19,20]. The one-dimensional (1D) CNTs can function as conductive bridges to enhance the electron transfer efficiency among the active materials and reduce the inner resistance of the cathodes. Meanwhile, in order to improve the electrical conductivity and lower the polarization of electrodes, there were some researches mixing cathode materials with Ag powders and achieved improved electrochemical performance [21,22]. However, the combination of CNTs and Ag as conductive additive of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathodes has not been explored.

In this paper, a hybrid conductive network consisting of CNTs and Ag was introduced into $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode and a uniform distribution of each element was achieved through ball milling. The 3D spatial CNT/Ag network was fabricated to promote the possible short and long range electron pathways among the nanoparticles. In addition, because of carbon's Li-ion battery inactive property, with partial replacement of carbon into Ag as conductive agent, it can improve the energy efficiency of the Li-ion batteries. The electrochemical performance, structure, morphology and electrochemical impedance spectroscopy of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2\text{-CNT/Ag}$ composites were investigated.

* Corresponding author.

2. Experimental

The $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM) was prepared by the conventional co-precipitation method similar to the previous publications [23,24]. The $[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{OH}$ precursors were synthesized by a co-precipitation method using nickel, cobalt and manganese sulfate as starting materials. The prepared powders were then mixed with excess amount of lithium carbonate (10% excess). The mixtures were grounded in a crucible, then heated in air at 980°C for 10h, and followed by slowly cooling to room temperature.

The first type of composite cathode consisted of NCM and Ag, at a weight ratio of 97:3. The NCM powders and AgNO_3 aqueous solution were mixed in distilled water to obtain a suspension. The suspension was stirred vigorously with a planetary ball mill for 2 h and then dried at 100°C to evaporate the water. After that, the prepared precursor powders were heated in a furnace at 450°C for 1h in air atmosphere to obtain the observed samples.

The second type of cathode contained NCM/Ag composites and MWCNTs conductive additives. The MWCNTs (supplied by Chengdu Organic Chemicals Co., Ltd.) with a diameter of 10–20 nm, a length of 10–30 μm and specific area of $\sim 200\text{m}^2/\text{g}$ were used in this work. Since the MWCNTs with a bundle-type shape are not easy to disperse in a viscous slurry, the MWCNTs were dispersed in N-methylpyrrolidinone (NMP) with a concentration of 9.3 wt% by ball milling for 2h as conductive pastes. The NCM/Ag composites were then added to the prepared pastes at a weight ratio of 9.3:1. After ball milling again for 2h and drying at 120°C for 12h in a vacuum oven, MWCNTs were homogeneously distributed in the composite cathodes. CNT/NCM mixture with a weight ratio of 1:100 was also prepared to construct composite cathode for comparison.

The phase structures and morphologies of the composite cathodes were analyzed by using an X-ray diffraction (XRD, Dmax/1200, Rigaku) with Cu $K\alpha$ radiation ($\lambda=15.406\text{nm}$), a scanning electron microscope (SEM, JEOL-7500F) and a transmission electron microscope (TEM, JYT 011–1996) operated at 200.0 KeV.

To evaluate the electrochemical performances of the composite cathodes, two-electrode coin cells (Type CR2032) were used. Positive electrodes were prepared by coating a slurry of as-prepared composite cathodes, carbon black and polyvinylidene fluoride (PVDF) binder (94.4:2.5:3.1 (wt.%)) onto Al foil collector. The cells were assembled in an argon-filled glove box using Li foil as the anode, microporous polyethylene sheet (Celgard 2400) as the separator, and LiPF_6 (1.0molL^{-1}) dissolved in ethylene carbonate/dimethyl carbonate (1:1) as the electrolyte. The charge/discharge testing was performed using Neware multichannel battery cycler over a voltage range of 3.0–4.25 V at different currents. The cyclic voltammetry (CV) were carried out at a sweep rate of 0.2 mV/s between 2.5 and 4.6 V (vs Li/Li^+). Electrochemical impedance spectroscopy (EIS) were collected using a CHI660D impedance analyzer by applying an AC voltage of 5 mV amplitude in the 100kHz–10mHz frequency range.

3. Results and Discussion

Powder XRD patterns of the pure $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ with CNT/Ag conductive additives were shown in Fig. 1. Both of the patterns were indexed to the hexagonal $\alpha\text{-NaFeO}_2$ structure with a space group of R3m according to the XRD data file (PDF card number 87-1564). The sharp and well-defined diffraction peaks indicates the prepared compounds were well-crystallized. No impurity was detected in the XRD pattern of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ -CNT/Ag sample except the strongest characteristic Ag (111) peak which could be found between the (006) and (012) peaks. It is hard to identify other characteristic Ag peaks

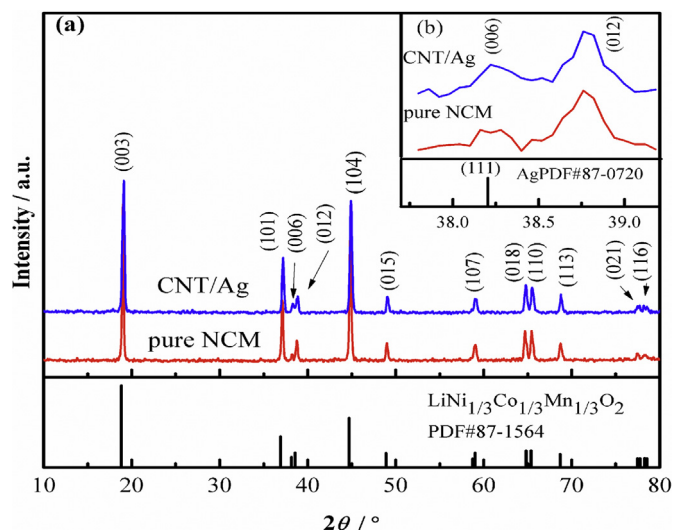


Fig. 1. (a) XRD patterns of the pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, and the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ -CNT/Ag composite, (b) local view of (a) in the 2θ range of 37.5° – 39.5° .

and the presence of CNTs as the amount of additives is relatively small. The calculated lattice constants (a and c) for both $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ -CNT/Ag ($a=28.57\text{nm}$ and $c=142.27\text{nm}$) and the pure $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ($a=28.51\text{nm}$ and $c=14.219\text{nm}$) were similar, which suggested that Ag additive is just dispersed on the surface of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particles instead of entering the structure.

The surface morphologies of the pure $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and the CNT/Ag modified $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode studied by SEM and TEM were shown in Fig. 2. The prepared samples were spherical aggregates composed of the primary particles with a diameter of 25–200 nm in Fig. 2a and Fig. 2b. A uniform distribution of Ag powders on the surface of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particles could be confirmed by the energy dispersive spectroscopy (EDS) which was presented in Fig. 2d. The EDS spectrum of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ -CNT/Ag composites corresponded to the circle area of the SEM image in Fig. 2c. The dispersed Ag powders could promote the efficiency of electron transfer across the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particles in short range due to its low resistance. However, the small diameter Ag particles could not cover the surface of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particles to form a conductive layer, which limited its attachment to the cathode (Fig. 2f). As shown in Fig. 2c and Fig. 2e, most CNTs connected with $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particles and uniformly extended throughout the composite cathode. A 3D spatial conductive network was formed by the interconnected CNTs around the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particles which could serve as long range pathways. Accordingly, with the combination of conductive Ag and CNTs employed as electron pathways, it is an excellent method to achieve high conductivity and make full use of the electrochemical potential of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$.

To compare the conductivity of the composite cathodes and the pure $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, the electrochemical impedance spectroscopy (EIS) measurements are carried out in this work. As shown in Fig. 3, all the EIS curves consist of a semicircle in the high frequency region and a straight line at low frequency region. A dramatic decrease in the area of the semicircle, which is attributed to the resistance of charge transfer (R_{ct}) [25], is observed for the composite electrodes compared to $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode. The high-frequency intercept at the Z' axis corresponds to ohmic resistance (R_s), which is referred from electrolyte. A simulated electric circuit used to fit the spectra is shown in the inset. The parameters R_f and CPE1 correspond to the surface layer resistance

Download English Version:

<https://daneshyari.com/en/article/184804>

Download Persian Version:

<https://daneshyari.com/article/184804>

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