



Preparation and characterization of 18650 $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2/\text{graphite}$ high power batteries

Yan-Bing He^{a,*}, Zhi-Yuan Tang^a, Quan-Sheng Song^a, Hui Xie^a, Quan-Hong Yang^a,
Yuan-Gang Liu^b, Guo-Wei Ling^a

^a Department of Applied Chemistry, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

^b McNair Technology Co., Ltd., Dongguan, Guangdong 523700, China

ARTICLE INFO

Article history:

Received 21 April 2008

Received in revised form 20 June 2008

Accepted 23 June 2008

Available online 3 July 2008

Keywords:

Layered $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$

High power batteries

Electrochemical performance

Discharge rate

Temperature

ABSTRACT

The commercial 18650 $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2/\text{graphite}$ high power batteries were prepared and their electrochemical performance at temperatures of 25 and 50 °C was extensively investigated. The results showed that the charge-transfer resistance (R_{ct}) and solid electrolyte interface resistance (R_{sei}) of the high power batteries at 25 °C decreased as states of charge (SOC) increased from 0 to 60%, whereas R_{ct} and R_{sei} increased as SOC increased from 60 to 100%. The discharge plateau voltage of batteries reduced greatly with the increase in discharge rate at both 25 and 50 °C. The high power batteries could be discharged at a very wide current range to deliver most of their capacity and also showed excellent power cycling performance with discharge rate of as high as 10 C at 25 °C. The elevated working temperature did not influence the battery discharge capacity and cycling performance at lower discharge rates (e.g. 0.5, 1, and 5 C), while it resulted in lower discharge capacity at higher discharge rates (e.g. 10 and 15 C) and bad cycling performance at discharge rate of 10 C. The batteries also exhibited excellent cycle performance at charge rate of as high as 8 C and discharge rate of 10 C.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

There are many studies about high power lithium-ion batteries used as power sources for hybrid electric vehicles (HEVs) and power tools [1,2]. At present, the applications of lithium-ion batteries in the HEV systems and power tools are limited by their cycling performance, thermal abuse characteristics, and high cost. The LiCoO_2 cathode materials show high energy density and excellent cycling stability, but they also have some disadvantages such as poor thermal stability, inferior overcharge characteristics, and environmental pollution problems. These disadvantages limit the use of LiCoO_2 materials in large capacity and high power lithium-ion batteries [3–8].

The cathode materials of spinel LiMn_2O_4 and olivine LiFePO_4 exhibit excellent overcharge characteristics and good thermal stability, which make them promising for the use in large capacity and high power lithium-ion batteries. However, there are also some limitations for spinel LiMn_2O_4 and olivine LiFePO_4 . It is well known that the energy density of the two materials is lower than that of LiCoO_2 . For the spinel LiMn_2O_4 , another obstacle is its poor structure stability during the battery cycling process, espe-

cially during the operation at elevated temperatures. Meanwhile, LiMn_2O_4 -based cathode also suffers from significant capacity loss and impedance increase, which is attributed to Mn dissolution induced by HF in the electrolyte [9–12]. For LiFePO_4 , the synthesis process is usually difficult and time-consuming. The LiFePO_4 is characterized by the low conductivity, mainly resulted from the low lithium-ion diffusion rate and low electronic conductivity [13,14]. Moreover, the preparation and coating of LiFePO_4 slurry on an aluminum foil collector are also difficult.

Layered $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ materials, which possess large specific capacity and excellent safety characteristics due to much lower heat generation, are very promising for use as the positive electrode in lithium-ion batteries. The layered $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ materials can be synthesized by various methods [15–25]. The electrochemical performance of these materials was mainly investigated by using coin cells. It is well-known that the safety performance of layered $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ is better than that of LiCoO_2 [3,26], making it suitable to be used as cathode materials for commercial lithium-ion high power batteries [27]. However, so far there are few studies on the preparation and electrochemical performance of commercial $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2/\text{graphite}$ high power batteries.

In this paper, the layered $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ material was synthesized through a soft chemical process with a subsequent heat treatment. The commercial 18650 $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2/\text{graphite}$

* Corresponding author. Tel.: +86 769 83015365.

E-mail address: hezuzhang.2000@163.com (Y.-B. He).

high power batteries were prepared and their electrochemical performance was studied. The high power batteries show excellent rate-discharge and cycling performance.

2. Experimental

The layered structure $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ was synthesized by the co-precipitation method as follows. 0.25 M aqueous solution of the metal nitrates was prepared with a cation ratio of Ni:Co:Mn = 1:1:1. The preparation of $M(\text{OH})_2$ ($M = \text{Ni, Co, Mn}$) was achieved by slowly dripping the nitrate solution and 0.5 M NaOH solution synchronously into a glass reactor with continuous stirring. The pH value of the reactant solution was adjusted by ammonia and was kept at 11. The $M(\text{OH})_2$ precipitate was filtered, washed, dried and mixed with stoichiometric amount of $\text{LiOH}\cdot\text{H}_2\text{O}$. The mixed powder was ground in an automatic grinder and was pressed into pellets. The pellets were initially heat-treated at 500°C for 5 h for the impregnation of LiOH into the matrix. The product was then cooled and re-ground, and the obtained pellets were heat-treated at 1000°C for 12 h, followed by quenching to room temperature.

X-ray diffraction (XRD) patterns of the samples were obtained by a PANalytical X'Pert powder diffractometer using $\text{Co K}\alpha$ radiation in an angular range of $10\text{--}90^\circ$ (2θ) with a 0.02° (2θ) step. The structural parameters were calculated by using the MDI Jade 5.0 profile matching refinement method for the XRD diagrams. The microstructure and morphology of the prepared powders was observed by using an environment scanning electron microscope (Philips XL-30 ESEM).

18650 lithium-ion batteries (18 mm in diameter and 65 mm in height) were assembled. The nominal capacity of the batteries was designed to be 1300 mAh. The batteries used the prepared layered $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ as cathodes, graphite as anodes, and polyethylene as separator. The $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ cathodes consisted of 86 wt% $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$, 9 wt% conductive graphite, and 5 wt% poly(vinylidene fluoride) (PVDF). The graphite anodes consisted of 91 wt% composite graphite, 6 wt% styrene-butadiene rubber (SBR), and 3 wt% carboxymethyl cellulose (CMC). 1 M LiPF_6 in a 1:1:1 mixture of ethylene carbonate, dimethyl carbonate and ethylene methyl carbonate (1 M $\text{LiPF}_6/\text{EC} + \text{DMC} + \text{EMC}$) was used as the electrolyte.

Positive electrodes were obtained by coating the mixing slurry of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ active material, conductive graphite, and PVDF onto an aluminum foil collector. The loading amount of the cathode material on each side of the electrodes was about 10 mg cm^{-2} . Negative electrodes were prepared by coating the mixing slurry of composite graphite, SBR and CMC onto a copper foil. The loading amount of the anode material on each side of the electrodes was about 5 mg cm^{-2} . The injection of the electrolyte was conducted in an argon filled glove box.

The formation, rate-discharge and cycle performance tests of batteries were performed by using the BS-9300 and BS-9366 lithium-ion battery testers. Since the most recent industrial formation process includes only one cycle, the experimental batteries in this study also underwent one cycle of charge-discharge for formation. The batteries were charged with a constant current of 65 mA (0.05 C) to 3.00 V, 130 mA (0.1 C) to 3.85 V, and 260 mA (0.2 C) to 4.20 V, respectively, followed by holding the voltage at 4.20 V until the current dropped to 13 mA (0.01 C), and then the batteries were discharged at 650 mA (0.5 C) to a cut-off voltage of 2.75 V. After formation, all batteries were charged and discharged three times between 2.75 and 4.20 V at 650 mA (0.5 C) to stabilize the performance of batteries. The rate-discharge and cycle performance of batteries was examined between 2.75 and 4.20 V at temperatures of 25 and 50°C . The surface temperature of batteries was recorded

during the rate-discharge performance testing. A type-K thermal couple was attached to the center of the largest face of the batteries to record the temperature change.

The electrochemical working station (Gamry Instrument model PCI 4-750) was used to measure the electrochemical impedance spectrum (EIS) of the 18650 $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2/\text{graphite}$ high power batteries. It was necessary that one nickel lead was welded on the cathode and the other on the anode of 18650 battery shell before the EIS testing. Then the batteries were connected with the electrochemical working station to test the EIS of batteries. The EIS of batteries with different states of charge (SOC) at a temperature of 25°C was measured at the open circuit voltage (OCV) of the batteries with $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ cathodes as the working electrode and graphite anodes as both the reference and counter electrodes. To describe SOC of the batteries, we defined it as the ratio of the charging capacity at a specific point to the capacity obtained at 25°C by charging at 0.5 C from the fully discharged state to 4.2 V. For the measurement of the impedance at various SOC, the experiments were started from the fully discharged state. The batteries were charged at 0.5 C to a specific SOC and kept for 0.5 h in the oven with a temperature of 25°C to reach a stable OCV. The impedance was measured by applying a 5 mV of ac oscillation with the frequency ranging from 100 kHz to 0.01 Hz. This procedure was repeated until the batteries were fully charged.

3. Results and discussion

Fig. 1 shows the XRD patterns of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ materials, such as as-prepared one, the discharged one (2.75 V) and the charged one (4.2 V). In all cases, the observed diffraction lines can be indexed based on the $R\text{-}3m$ space group and are consistent with the layered structure of $\alpha\text{-NaFeO}_2$. The 3d metals (Ni, Co, and Mn) are supposed to be randomly distributed on the (3b) crystallographic position, whereas the lithium atoms occupy the (3a) sites between the metallic slabs. The hexagonal lattice parameters for the respective materials are $a = 2.8719\text{ \AA}$, $c = 14.2628\text{ \AA}$ for the as-prepared $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$; $a = 2.8633\text{ \AA}$, $c = 14.3017\text{ \AA}$ for $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ cathode discharged to 2.75 V; and $a = 2.8240\text{ \AA}$, $c = 14.4892\text{ \AA}$ for $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ cathode charged to 4.2 V. An expansion of the c parameter and a shrinkage a parameter of the delithiated material are observed as compared with the fully lithiated material.

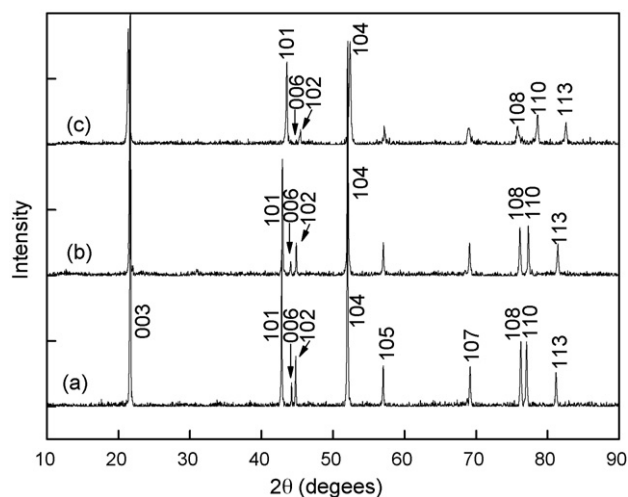


Fig. 1. XRD patterns of: (a) as-prepared $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$; (b) $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ discharged to 2.75 V and (c) $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ charged to 4.2 V.

Download English Version:

<https://daneshyari.com/en/article/1294444>

Download Persian Version:

<https://daneshyari.com/article/1294444>

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