



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

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

A new coating for improving the electrochemical performance of cathode materials

E.V. Makhonina ^{a,*}, A.E. Medvedeva ^a, V.S. Dubasova ^b, V.V. Volkov ^{a,c},
Yu. A. Politov ^a, I.L. Eremenko ^a

^a N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky pr., Moscow, 119991, Russia

^b Scientific Research Institute of Electrical Carbon Products, per. Gorki 1, Electrougli, Moscow Region, 142455, Russia

^c Brookhaven National Laboratory, Upton, New York, 11973, United States

ARTICLE INFO

Article history:

Received 13 October 2015

Received in revised form

16 February 2016

Accepted 18 February 2016

Available online 12 March 2016

Keywords:

Li-ion battery

Cathode material

Epitaxial coating

Alumina

Carbon

ABSTRACT

The layered $\text{LiNi}_{0.40}\text{Mn}_{0.40}\text{Co}_{0.20}\text{O}_2$ compound was synthesized and modified with a mixed alumina–carbon coating by a simple soft chemical route. The simultaneous presence of alumina and carbon on the surface of coated samples was proved by ICP-AES, chemical analysis, XP spectroscopy, SEM microanalysis and local electron diffraction. For the first time, we show that the alumina epitaxial layer is formed on basal {001} facets of cathode grains, whereas side-view facets, like {010}, remain free from crystalline $\alpha\text{-Al}_2\text{O}_3$, thus leaving them easy for Li-ion diffusion into cathode structure. An amorphous carbon film was used here for better conductivity of the coating layer and prevention of the electrical contact loss between cathode grains. Electrochemical tests revealed that the mixed alumina-carbon coating applied on $\text{LiNi}_{0.40}\text{Mn}_{0.40}\text{Co}_{0.20}\text{O}_2$ stabilizes the surface structure and improves the cycling performance (3–4.5 V) and rate capability of cathodes on their basis compared with the pristine and alumina-coated $\text{LiNi}_{0.40}\text{Mn}_{0.40}\text{Co}_{0.20}\text{O}_2$ samples.

© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Lithium-ion batteries (LIBs) now dominate the energy storage market for portable electronic devices. However, their widespread use as high-energy storage devices for electric and hybrid vehicles requires further improvement in their energy density, safety, and operation time. It concerns first of all cathode materials playing the most important role in battery electrochemical performance. Layered compounds of the $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ family are promising candidates for the

positive electrode of high-energy LIBs due to their high discharge capacity and relative thermal and structural stabilities. In 2001, Ohzuku and Makimura [1] were the first who proposed the $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ compound as a new cathode material to replace LiCoO_2 . Nearly at the same time, $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ compounds were described by the Dahn research group [2]. Despite a great number of studies on these materials during past years, these compounds still have relatively low energy densities for above applications and poor cycling and thermal stability. One of the ways to solve these problems is to protect the surface of materials. Different

* Corresponding author. Tel.: +7 495 6338516.

E-mail address: elenamakhonina@mail.ru (E.V. Makhonina).

<http://dx.doi.org/10.1016/j.ijhydene.2016.02.091>

0360-3199/© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

compounds can be used for this purpose [3–10], among them aluminum oxides [11–15]. Various mechanisms were proposed to explain better capacity retention for alumina-coated cathode materials. It is usually believed that such alumina-based coatings can improve the surface stability of cathode materials by suppressing detrimental chemical side reactions between an electrode surface and electrolyte by acting as the physical barrier or/and as a scavenger for hydrogen fluoride and water [12–15]. According to [12], the alumina coating obtained by atomic layer deposition decreased the impedance rise observed during battery cycling. One of the purposes for a cell impedance rise during cycling is the failure of electron-conducting network. A thick insulating particle coating can increase particle–particle contact resistance. In the present study, $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ compound was synthesized and coated with a new alumina–carbon mixed coating produced by a simple soft chemical route. We believed that inclusion of carbon in the coating composition can compensate for impedance growth and prevent a loss of the electrical contact between particles. The electrochemical behavior of $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ material protected by mixed alumina–carbon coating was compared here with that of pristine and alumina-coated $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ samples. We also tried to elucidate the role of the coating layer by using a local electron diffraction analysis.

Experimental

Synthesis

$\text{LiOH}\cdot\text{H}_2\text{O}$ (99+%, by Fluka), $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ (98+%, by Acros Organics), $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ (99+%, by Acros Organics), and $\text{MnSO}_4\cdot \text{H}_2\text{O}$ (99+%, by Acros Organics) were used as starting reagents. $\text{LiNi}_{0.40}\text{Mn}_{0.40}\text{Co}_{0.20}\text{O}_2$ (LNMC) materials were synthesized by reaction of $\text{LiOH}\cdot\text{H}_2\text{O}$ with a mixed precursor. The precursor was obtained by co-precipitation of the freshly recrystallized sodium carbonate hydrate $\text{Na}_2\text{CO}_3\cdot 10\text{H}_2\text{O}$ as a precipitator and a solution of metal sulfates in appropriate amounts at the total salt concentration of 2.0 mol L^{-1} . The synthesis was carried out under CO_2 atmosphere. The pH value, reaction temperature, and the stirring speed were controlled at 7.5, 50°C , and 1000 ppm, respectively. The carbonate precursor was washed with deionized water and dried at 120°C in an argon flow. After that, the precursor was thoroughly mixed with $\text{LiOH}\cdot\text{H}_2\text{O}$ (at the Li: precursor molar ratio of 1.02). The mixture was heated at 480°C for 5 h and annealed at 900°C for 12 h in air.

Coating procedure

Samples with mixed alumina–carbon coatings (LNMC-AC) were obtained using the reaction of hydrolysis of aluminum isopropoxide (99.3%, The Merck); the hydrolysis was performed under water deficiency condition. The Al_2O_3 concentrations obtained were in the range of 0.25–1.0 wt%. The solids obtained this way were heat treated in several stages. The last stage was an annealing of samples under an argon flow to carbonize the rest of organic species. To obtain alumina-coated samples (LNMC-A), hydrolysis of the aluminum isopropoxide

was carried out using a water excess. This sample was annealed only in air.

Characterization

Powder X-ray diffraction (XRD) measurements were performed using a Bruker D8 Advance diffractometer (Cu $K\alpha$ radiation, 45 kV/250 mA). The diffraction data were collected in the $\Theta/2\Theta$ scan mode at 0.02° step widths over a 2Θ range from 10° to 80° . The morphology and microstructure of bare and coated samples were studied using scanning electron microscopy (SEM) (Carl Zeiss NVision-40 workstation equipped with an Oxford Instruments INCA ENERGY (EDX) X-ray analysis system) and high-resolution transmission electron microscopy (HR-TEM, JEM 2100, JEOL).

Metal contents in compounds under study were determined by the inductively coupled plasma atomic emission spectroscopy (ICP-AES) with an IRIS Advantage “Thermo Jarrell Ash” spectrometer. The X-ray photoelectron (XP) spectroscopy measurements were performed using a Physical Electronics ESCA system PHI5500. The high-resolution XP spectra were obtained with Al $K\alpha$ radiation (1486.6 eV) in constant pass energy mode in 0.125 eV step increments. Binding energies were calibrated relative to adventitious carbon at 284.9 eV. The peak positions were determined by approximation. The atomic element concentrations were determined by the relative-sensitivity factor method with the PC ACCESS ESCA V7.2c program package. The carbon content in coated samples was determined by using a EuroEA3000 CHNS-O Elemental Analyzer.

Electrochemical measurements

The electrochemical performance of the cathodes based on compounds under this study was evaluated with the use of coin-type cells at 25°C . Cathodes were prepared by mixing of LNMC, LNMC-A, and LNMC-AC materials with carbon black and polyvinylidene difluoride (PVDF) in the wt% ratio of 93.5:3.2:3.3 in N-methylpyrrolidone. The cathode slurry was cast onto an aluminum foil current collector and dried at 120°C . The active mass loading ranged from 12 to 14 mg/cm^2 . The negative electrode was a lithium foil. An electrolyte solution was 1 M LiPF_6 in the mixture of ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate in the weight ratio of 1:1:1. The cycling was carried out galvanostatically in three steps. The cells were cycled first three times between 3.0 and 4.3 V, then three times between 3.0 and 4.4 V, and finally between 3.0 and 4.5 V. A current 0.5 mA (6 mA g^{-1}) was used in these three steps. In the rate capability tests, all cells were charged at the constant current density of 10 mA g^{-1} and discharged at current densities up to 500 mA g^{-1} (5 C) in the range of 3.0–4.5 V.

Results and discussion

The metal contents, including aluminum in the LNMC, LNMC-AC, and LNMC-A samples were determined by ICP-AES. Close values of alumina concentrations were obtained by SEM microanalysis. These concentrations were too small to be

Download English Version:

<https://daneshyari.com/en/article/1277042>

Download Persian Version:

<https://daneshyari.com/article/1277042>

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