



Synthesis and characterization of advanced high capacity cathode active nanomaterials with three integrated spinel-layered phases for Li-ion batteries



Emrah Bulut ^{a, *}, Mustafa Can ^b, Mahmut Özacar ^a, Hatem Akbulut ^c

^a Department of Chemistry, Sakarya University, 54187 Serdivan, Sakarya, Türkiye

^b Vocational School of Arifiye, Sakarya University, 54580 Arifiye, Sakarya, Türkiye

^c Department of Metallurgical and Materials Engineering, Sakarya University, 54187 Serdivan, Sakarya, Türkiye

ARTICLE INFO

Article history:

Received 2 November 2015

Received in revised form

18 January 2016

Accepted 6 February 2016

Available online 9 February 2016

Keywords:

Electrode materials

Energy storage materials

Composite materials

Nanostructured materials

Doped manganese spinel

Spinel-layered composite materials

ABSTRACT

Mesoporous cathode active materials that included undoped and separated Cu^{2+} and Co^{3+} doped spinels were prepared. The “doped spinel-layered-Li-rich spinel” composite nanoparticles within the three integrated phased ($\text{LiM}_{0.02}\text{Mn}_{1.98}\text{O}_4\text{—Li}_2\text{MnO}_3\text{—Li}_{1.27}\text{Mn}_{1.73}\text{O}_4$; where M is Cu^{2+} and Co^{3+}) were synthesized by a microwave assisted hydrothermal synthesis. These materials were investigated with X-Ray powder Diffraction spectroscopy (XRD), Scanning Electron Microscopy (SEM and FE-SEM), High Resolution Transmission Electron Microscopy (HR-TEM), galvanostatic cycling at 0.1C and 0.5C rates, Cyclic Voltammetry (CV), and Electrochemical Impedance Spectroscopy (EIS). The effects of the calcination temperature and the partial substitution of Mn^{3+} in the spinel by Cu^{2+} and Co^{3+} , and onto the spinel structure were investigated with XRD. The lattice parameters of the spinel structured compounds were calculated from the XRD data using the Williamson-Hall equation. However, the morphological changes, which depended on the calcination temperature, were examined by SEM, FE-SEM and HRTEM. Furthermore, the two other phases which were different from $\text{LiM}_{0.02}\text{Mn}_{1.98}\text{O}_4$ had a great impact on the electrochemical performance over the potential range of the 3–5 V. At the 0.1C rate, the first discharge capacities of undoped and Cu^{2+} , Co^{3+} doped materials were 577, 285, 560 mAh/g respectively. After 50 cycles at 0.5C rate, we achieved 96.2%; 52.5%; 95.4% capacity retention for the undoped and Cu^{2+} , Co^{3+} doped materials respectively.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Rechargeable lithium ion batteries are the most intensively studied subjects in regard to energy storage devices. The energy requirements of portable consumer products such as smart phones, tablet computers, and laptops, are usually provided by lithium ion batteries. At the same time, the most important application areas for lithium ion batteries are electric vehicles and smart grids. However, further improvements, in terms of energy and power densities, are still required in order to make lithium ion batteries suitable for application in these sectors. An increase in energy density requires novel, advanced chemistries based on high

performance electrode materials. Spinel LiMn_2O_4 cathode active material is an attractive option for rechargeable lithium batteries due to its low self-discharge and cost, higher operative voltage (3–4 V range), abundant and environmentally benign nature, and ease of preparation, when compared to other layered oxides [1–5].

However, the main disadvantage of LiMn_2O_4 spinel as a cathode material is its capacity fading during the charge–discharge processes of the lithium-ion batteries. The main reason for this disadvantage is Jahn-Teller distortion due to the Mn^{3+} dissolution in the electrolyte [6–8]. Substituting the Mn^{3+} ions that exist in the spinel structure with small amounts of divalent [9–14] and trivalent [15–18] cations seems to be a promising strategy for the prevention of the Mn^{3+} dissolution.

LiMn_2O_4 spinel was traditionally prepared with a solid-state direct reaction at high temperatures [19,20]. Within the last few decades, nanostructured materials have become of great interest due to their outstanding features. Most of the nanostructured

* Corresponding author.

E-mail addresses: ebulut@sakarya.edu.tr (E. Bulut), mstfacan@gmail.com (M. Can), nmozacart@hotmail.com, mozacar@hotmail.com (M. Özacar), akbulut@sakarya.edu.tr (H. Akbulut).

electrode materials are synthesized by low-temperature treatment processes such as soft chemicals [21], sol–gel [22,23], the Pechini process [24], the microwave synthesis route [25], and hydrothermal methods [26,27]. The crystalline nature and particle size of the product can be controlled by a hydrothermal synthesis. Also, the materials can be synthesized at lower temperatures than with the conventional solid state route.

Recently, nanostructured materials have been synthesized rapidly and easily by microwave (MW) dielectric heating. The dipole–dipole interactions occur as a result of the interactions of the polar molecules with the electromagnetic field. This dipolar polarization results in microwave dielectric heating. MW provides many advantages such as a higher reaction rate, novel phases and morphologies, homogeneous volumetric heating, and energy savings, when compared to conventional heating methods [28,29].

In the present study, we first aimed to synthesize the cation doped spinel $\text{LiM}_{0.02}\text{Mn}_{1.98}\text{O}_4$ (M: Cu^{2+} , Co^{3+}) cathode active nanoparticles by the microwave hydrothermal method in order to enhance the electrochemical performance of the spinel cathode active materials. However, we noticed the other phases (Li_2MnO_3 and Li-rich spinel $\text{Li}_{1.27}\text{Mn}_{1.73}\text{O}_4$) work progresses. Then, the efficiency of these phases in relation to the electrochemical performance was investigated, and the advanced three integrated phased ($\text{LiM}_{0.02}\text{Mn}_{1.98}\text{O}_4$ – Li_2MnO_3 – $\text{Li}_{1.27}\text{Mn}_{1.73}\text{O}_4$; where M is Cu^{2+} and Co^{3+}) cathode active materials with enhanced specific capacity were obtained. The cathode active nanoparticles were produced by microwave irradiation with ease, and were characterized structurally and electrochemically.

2. Experimental section

The synthesis chemicals; LiNO_3 , $\text{Mn}(\text{CH}_3\text{COO})_2$, $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, were purchased from Sigma–Aldrich. The components and chemicals for the CR 2016 button cells; acetylene black, Polyvinylidene fluoride (PVDF), N,N-Dimethylformamide (DMF), and 1 M LiPF_6 electrolyte solution in ethylene carbonate-dimethyl carbonate (EC-DMC 1:1 in volume), were purchased from the MTI Corporation.

2.1. Synthesis of three integrated phased cathode active nanoparticles

The microwave-assisted hydrothermal synthesis was performed by a CEM Mars microwave oven, which can generate 1600 W of output power by a dual magnetron device with a 2.45 GHz frequency microwave radiation. The stoichiometric amounts (1:1.98:0.02) of LiNO_3 , $\text{Mn}(\text{CH}_3\text{COO})_2$ and doping reagent ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ or $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) were dissolved in 50 mL of deionized water. The resulting mixture was transferred into Teflon lined vessels. The reaction was carried out for an hour at 160 °C, and the temperature was controlled via the temperature probe which was in the autoclave. The resulting precipitate was dried at 80 °C for 12 h. The final powders were heat-treated within a temperature range of 500–700 °C for 3 h.

2.2. Structural and morphological characterization

All the samples of the crystalline structures of undoped and Cu^{2+} , Co^{3+} doped, were identified by a X-ray powder diffraction (XRD) spectrometer (Rigaku D/Max 2200) equipped with graphite monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The operation voltage and current were 40 kV and 40 mA respectively. The diffracted intensities were recorded from 10° to 90°, 2 θ angles. The chemical analysis was carried out by an inductively coupled plasma optic emission spectrometry (ICP-OES). The morphological

characterizations were performed by scanning electron microscopes (field emission FE-SEM: FEI Quanta FEG 450 and SEM: JEOL JSM-6060 LV) and a high resolution transmission electron microscope (HRTEM: JEOL 2100 JEM) operated at 20 kV. The lattice parameters of the spinel structured compounds were calculated from the XRD data using a Williamson–Hall equation [30].

2.3. CR 2016 button cell preparation and electrochemical characterization

The CR 2016 button cells were produced for electrochemical characterization. The electrode material was prepared by mixing 76 wt% of cathode active material $\text{LiM}_{0.02}\text{Mn}_{1.98}\text{O}_4$ (M: Co^{3+} , Cu^{2+}), 9 wt% acetylene black, and 15 wt% PVDF. This powder mix was transformed into a homogeneous slurry by adding DMF. Then the slurry was spread onto the Al foil and dried at 120 °C under a vacuum for 12 h. The CR 2016 button cell construction was carried out in an argon-filled glove box (M Braun Model Unilab). The Li foils were used as anode. A microporous polypropylene film was used as a separator between the electrodes. The electrolyte was a 1 M LiPF_6 solution in EC-DMC (1:1 in volume). The polypropylene separator was soaked in the electrolyte. The galvanostatic cycling tests were carried out with a MTI battery tester using CR 2016 button cells. The initial charge and discharge tests were carried out at a constant current density over the potential range of 3–5 V vs. Li/Li+. The Electrochemical Impedance Spectroscopy (EIS) and Cyclic Voltammogram (CV) data was collected via a CHI 660C Electrochemical Workstation.

3. Results and discussion

3.1. Structural and morphological characterization

The actual stoichiometry of the as-prepared sample was analyzed with an ICP-OES spectrometer. The stoichiometry of the $\text{LiM}_{0.02}\text{Mn}_{1.98}\text{O}_4$ – Li_2MnO_3 – $\text{Li}_{1.27}\text{Mn}_{1.73}\text{O}_4$ composite cathodes was determined as Li:Mn:Co:Cu = 4.27:4.71:0.02:0.02. Also metal ion contents of the $\text{LiM}_{0.02}\text{Mn}_{1.98}\text{O}_4$ (M: Cu^{2+} and Co^{3+}) compound in the composite cathode are shown in Table S1 (supporting information). The experimental ratios of Mn:Co:Cu in all the samples are in good agreement with the nominal value of 1.98:0.02:0.02. The microwave irradiated hydrothermal synthesis caused a decreased reaction time for the formation of $\text{LiM}_{0.02}\text{Mn}_{1.98}\text{O}_4$ (M: Cu^{2+} , Co^{3+}). The powder XRD patterns of the undoped materials that calcined at different temperatures are shown in Fig. 1 (See supplementary

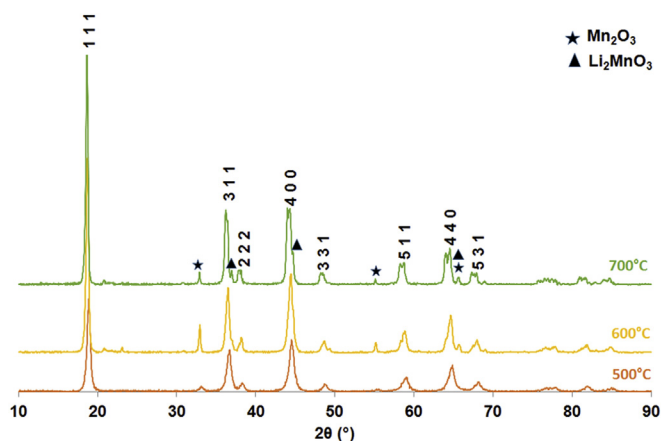


Fig. 1. XRD patterns of undoped cathode active nanoparticles calcined at different temperatures.

Download English Version:

<https://daneshyari.com/en/article/1606272>

Download Persian Version:

<https://daneshyari.com/article/1606272>

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