Available online at www.sciencedirect.com
ScienceDirect
Materials Chemistry and Physics 104 (2007) 479–482
MATERIALS CHEMISTRY AND PHYSICS
www.elsevier.com/locate/matchemphys

Synthesis and characterization of Cr-doped $LiMn_{2-x}Cr_xO_4$ ($x = 0.1$–0.4) cathode for Li-ion battery

K. Suryakala, G. Paruthimal Kalaignan *, T. Vasudevan

Department of Industrial Chemistry, Alagappa University, Karaikudi 630003, Tamilnadu, India

Received 31 May 2006; received in revised form 3 March 2007; accepted 8 April 2007

Abstract

$LiMn_{2-x}Cr_xO_4$ cathode materials were prepared by sol–gel method. The structure and electrochemical properties of $LiMn_{2-x}Cr_xO_4$ ($x = 0.1$, 0.2, 0.3 and 0.4) cathode materials for lithium ion batteries were studied by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscope (TEM), cyclic voltammetry and galvanostatic charge–discharge tests. The cathodes with different Cr in contents $LiMn_{2-x}Cr_xO_4$ ($x = 0.1$, 0.2, 0.3 and 0.4) were synthesized and showed a single-phase spinel structure without any impurity. The amount of Cr has a large consequence on the electrochemical characteristics. The total discharge capacities were increased with the Cr content and all of them have good cycle stability.

Keywords: Lithium-ion batteries; Cathode; Cr doping; Sol–gel method; XRD; TEM

1. Introduction

Lithium rechargeable batteries offer the highest energy density of all rechargeable battery systems [1] and give various applications ranging in size from portable electronic devices to zero emission vehicles (ZEV) [1,2]. The requirements for advanced lithium rechargeable batteries include high energy and power density, reversibility and cyclability, safety, limited environmental impact and low cost [1,2]. Improved performance is achieved with new or improved anodes, electrolytes or cathodes [1–4]. Three classes of materials $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$ compounds have been developed as cathode materials for Li-ion batteries. $LiMn_2O_4$ is a very promising cathode material with economical and environmental advantages over the layered compounds such as $LiCoO_2$and $LiNiO_2$. Especially, the good thermal stability of $LiMn_2O_4$ is a positive factor for its use in batteries for electric vehicles [5]. However, $LiMn_2O_4$ shows severe capacity fading with cycling at room and high temperatures. It was reported that the capacity fading mechanism at room temperature was related to the Jahn–Teller distortion caused by Mn^{3+} Jahn–Teller ions [6]. The cycling performance of $LiMn_2O_4$ at room temperature was enhanced by the partial substitution of Mn in $LiMn_2O_4$ with transition metals (Co, Cr, Ni, Fe, Ti and Zn) [7–12]. The poor cycling behaviour can be improved by cation and anion substitution, and also surface passivation treatment of $LiMn_2O_4$ [13–15].

Now, partial substitution of manganese, with other metal elements into $LiM_xMn_{2-x}O_4$ (M = Co, Mg, Cr, Ni, Fe, Al, Ti and Zn) has been suggested [16–19]. In the case of small amount of substitution, the dopant reduces the initial capacity at the 4 V plateau slightly, but improves the cycle-life of the spinel greatly. An extensive amount of substitution shows a significant decrease in capacity at the 4 V plateau [20]. In this present work, the spinel $LiMn_{2-x}Cr_xO_4$ has been prepared via a sol–gel method. The structure and morphologies of the products have been investigated. Via a serial of electrochemical tests, the electrochemical characteristics of the spinel $LiMn_{2-x}Cr_xO_4$ with different Cr contents are discussed in detail.

2. Experimental

Cr-doped $LiMn_{2-x}Cr_xO_4$ [$x = 0.1$, 0.2, 0.3 and 0.4] spinel cathode material for lithium ion batteries was prepared by sol–gel method. The solution for sol–gel method was obtained by dissolving stoichiometric ratios of $(CH_3COO)_2Mn{\cdot}4H_2O$, $LiNO_3{\cdot}3H_2O$ and $Cr(NO_3)_3{\cdot}9H_2O$ (99%) in distilled water and mixed well with citric acid [$C(OH)(COOH)(CH_2COOH)_2$] in distilled water. The resulting precursor solution was evaporated at 80 °C under constant stirring for 6 h. The evaporation increases the viscosity of the solution and further heating leads to the formation of polymeric resin. Thus, prepared

* Corresponding author. Tel.: +91 4565 228836; fax: +91 4565 225202.
E-mail address: kalaignan@yahoo.com (G.P. Kalaignan).

0254-0584/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2007.04.004

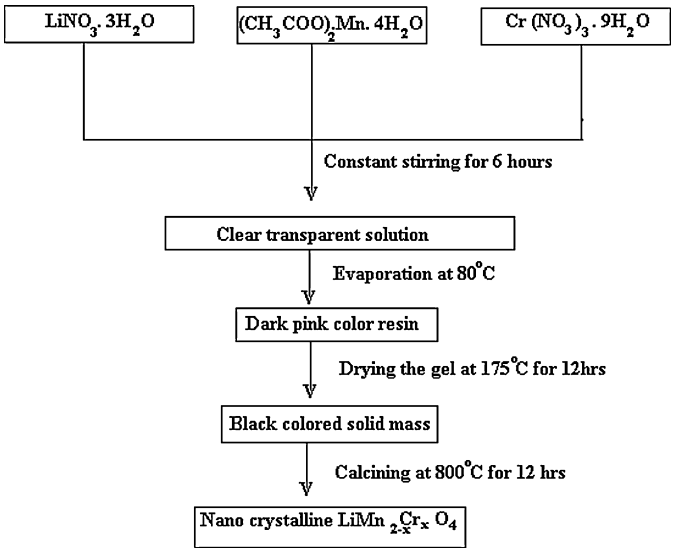

Fig. 1. Schematic representation for the preparation of nanocrystalline $LiMn_{2-x}Cr_xO_4$.

polymeric resin was further heated at 175 °C for 12 h to set polymeric intermediates with solid mass nature. It was calcined at 800 °C for 10 h, the polymeric intermediates caused the decomposition of organic derivatives due to the combustion and led to the formation of nano crystalline $LiMn_{2-x}Cr_xO_4$ powder by citric acid through sol–gel route as given in Fig. 1.

Synthesis of $LiMn_{2-x}Cr_xO_4$ powder by citric acid assisted sol–gel route was investigated through XRD (JOEL model JDX 8030 X-ray diffractometer using Cu Kα radiation), Scanning Electron Microscope (Philips scanning electron microscopy) and transmission electron microscope (TEM, JEM–2010) to identify the structural co-ordination and crystalline phase.

The electrochemical performance of the as-prepared powder electrodes was estimated using two-electrode coin type cell (2032) with lithium foil as the reference electrode. All testing electrodes were prepared by coating the slurry of a mixture (composed of 80 wt% active cathode powders, 10 wt % conducting agent (acetylene black) and 10 wt% binders (polyvinylidene fluoride) onto a copper foil current collector. After drying in air at 80 °C for 4 h, the electrodes were pressed under 20 MPa for 1 min, and then dried at 120 °C for 24 h in a vacuum drier. The weight of the active materials in the electrode sheet was 10 mg cm^{-2}. The cells were assembled in Argon filled glove box. The electrolyte was 1 M $LiClO_4$ in the mixture of ethylene carbonate (EC) and propylene carbonate (PC) with mass ratio being 1:1. A polypropylene (PP) film (Cellgard 2300) was used as the separator. Galvanostatic charge–discharge tests were conducted on a WPG instrument, South Korea battery program-control test system with the cut-off voltages of 3 and 5 V (versus Li/Li^+) under a specific current density (a nominal specific capacity of 120 mAh g^{-1} was assumed to convert the current density into charge rate). The cyclic voltammogram (CV) test was performed on EG&G PARC model 6310, Electrochemical Impedance Analyzer coupled with M398 software at room temperature with a scan rate of 0.1 mV s^{-1}.

3. Results and discussions

3.1. X-ray diffraction

Fig. 2 shows the XRD patterns of $LiMn_{2-x}Cr_xO_4$ powders. The crystal phase of all the samples are identified from the XRD data to be an ordered spinel structure indexed by cubic *Fd-3m* and no other minor products are detected. This fact indicates that the Mn site in $LiMn_2O_4$ is completely substituted by Cr doing. For $LiMn_{1.9}Cr_{0.1}O_4$ the lattice parameter and unit cell volume are $a = 8.2163$ Å and $V = 554.663$ Å, respectively. With increasing the amount of Cr the lattice parameter decreases gradually.

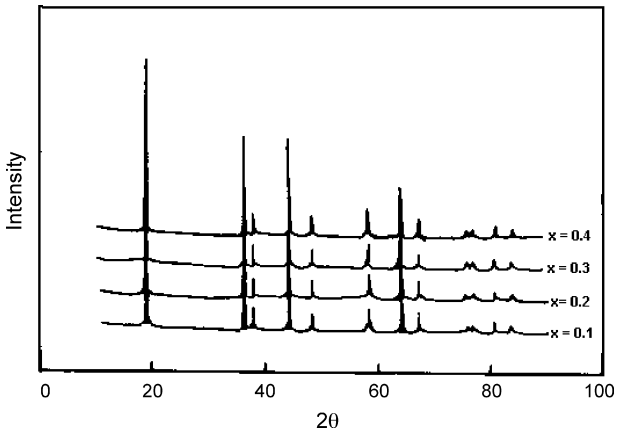

Fig. 2. X-ray diffraction pattern of $LiMn_{2-x}Cr_xO_4$ powder.

When the Cr content reaches 0.4, the lattice parameter is only 8.1679 Å. This decrease is due to the increase in the concentration of Mn^{4+} ions in the spinel structure as Mn^{3+} ions are substituted by Cr^{3+} ions.

3.2. SEM and TEM

All the samples were synthesized under the same processing conditions as described in Section 2 by only changing the stoichiometric compositions of the corresponding starting materials.

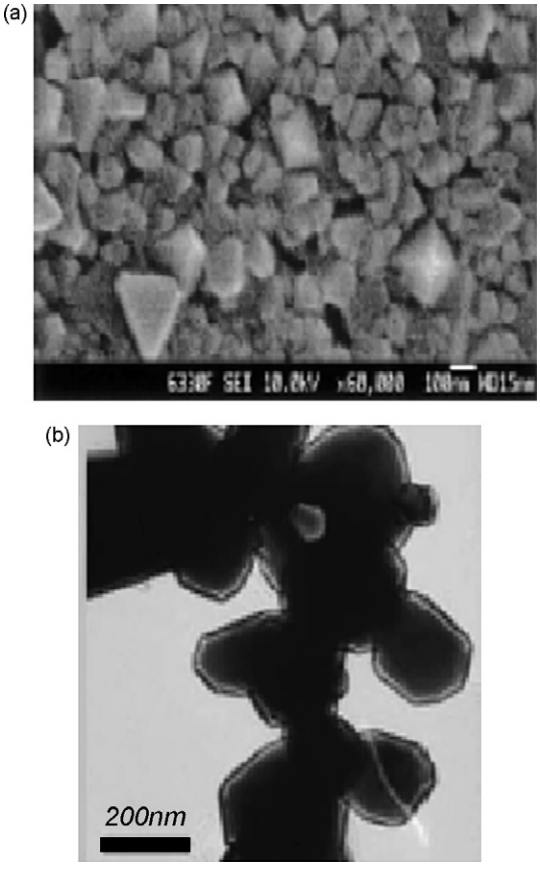

Fig. 3. Images of $LiMn_{2-x}Cu_xO_4$ powders prepared by citric acid assisted sol–gel method: (a) SEM and (b) TEM.