Journal of ELECTRONIC MATERIALS, Vol. 42, No. 6, 2013
DOI: 10.1007/s11664-013-2588-x

Synthesis, Structure, and Electrochemistry of Sm-Modified $LiMn_2O_4$ Cathode Materials for Lithium-Ion Batteries

ABDALLA M. KHEDR,[1,3] MORSI M. ABOU-SEKKINA,[1] and FOUAD G. EL-METWALY[1,2]

1.—Chemistry Department, Faculty of Science, Tanta University, Medical Campus, El-Bahr Street, Tanta, Egypt. 2.—Chemistry Department, Faculty of Science, Gazan University, Gazan, Kingdom of Saudi Arabia. 3.—e-mail: abkhedr2010@yahoo.com

Spinel lithium manganese oxide and a series of $Sm/LiMn_2O_4$ spinels with different Sm additive contents (x = 0.02%, 0.05%) were prepared for the first time via a coprecipitation method for rechargeable lithium-ion batteries. X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive analysis of x-rays (EDAX), infrared (IR), and electron spin resonance spectral studies as well as various electrochemical measurements were used to examine the structural and electrochemical characteristics of $LiMn_{2-x}Sm_xO_4$ (x = 0.00%, 0.02%, 0.05%). XRD and SEM studies confirmed the nano materials size for all prepared spinels. From cyclic voltammetry studies, in terms of peak splitting, electrochemical active surface area, and intensity of the peaks, the $LiMn_{1.98}Sm_{0.02}O_4$ sample possesses better electrochemical performance compared with the $LiMn_{1.95}Sm_{0.05}O_4$ sample. Hence, limited addition of a rare-earth dopant is preferable to obtain better efficiency. Direct-current (DC) electrical conductivity measurements indicated that these samples are semiconducting and their activation energies decrease with increasing rare-earth Sm^{3+} content.

Key words: Nano lithium manganates, Sm^{3+} doping, electrical properties

INTRODUCTION

Electrical rechargeable lithium-ion batteries have achieved significant commercial success as the most promising portable energy source in electronic products such as laptop computers and cellular phones, mainly due to their high working voltage, high energy density, and long life. Currently, $LiCoO_2$, $LiNiO_2$, and $LiMn_2O_4$ are the main cathode materials for lithium-ion batteries. Among these, spinel $LiMn_2O_4$ and its derivatives are considered as the materials with the greatest potential, ascribed to the merits of low material cost, rich abundance of Mn resources, low toxicity of Mn ion, and environmentally friendly nature.[1–4] However, the severe capacity fading of the spinel $LiMn_2O_4$ during charge–discharge cycling limits its application in commercial lithium-ion batteries.[5] This phenomenon can be attributed to various reasons such as Jahn–Teller distortion due to the Mn^{3+} ion, dissolution of manganese into electrolyte, loss of crystallinity during cycling, and electrolyte decomposition at high-potential regions.[6–8] Recently, several investigations have been carried out to overcome such capacity fading by doping the spinel with several cations (such as Ag, Al, Co, Cr, Ni, Fe, etc.[9–12]) or by surface modification of $LiMn_2O_4$ with different materials (such as TiO_2, MgO, $LiAlO_2$, Al_2O_3, etc.[13–16]). Meanwhile, high electronic conductivity is very important for good performance of $LiMn_2O_4$ electrodes in lithium-ion secondary batteries. Usually, carbon is used as the conductive agent added to the cathode material to form an electrode with relatively good electronic conductivity, but the carbon will reduce the energy efficiency because of its inactive Li battery property.[17–20] During recent years, there has been some research dealing with silver deposition on electrode materials such as $LiFePO_4$,[21,22] $LiCoO_2$,[20] and $Li_4Ti_5O_{12}$,[19,23,24] which

(Received November 1, 2012; accepted March 21, 2013; published online April 23, 2013)