



Effects of multi-dopants (Zn and Ho) in stabilizing spinel structure for cathode materials in lithium rechargeable batteries—Novel chelated sol-gel synthesis



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ABSTRACT

Multi-doped spinels, namely LiMn_2O_4 and $\text{LiZn}_x\text{Ho}_y\text{Mn}_{2-x-y}\text{O}_4$ ($x=0.10-0.18$; $y=0.02-0.10$), for use as cathode materials for lithium-ion rechargeable batteries were synthesized via sol-gel method, using lauric acid as the chelating agent, to obtain micron-sized particles. The physical properties of the synthesized samples were investigated using differential thermal analysis, Fourier-transform infrared spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy, energy-dispersive X-ray analysis, and electrochemical methods. XRD showed that LiMn_2O_4 and $\text{LiZn}_x\text{Ho}_y\text{Mn}_{2-x-y}\text{O}_4$ have high degrees of crystallinity and good phase purities. The SEM images of LiMn_2O_4 showed an ice-cube morphology with particles of size 1 μm . Charge-discharge studies showed that undoped LiMn_2O_4 delivered the discharge capacity of 124 mA h/g with coulombic efficiency of 95% during the first cycle, whereas doped spinels delivered discharge capacities of 125, 120, and 127 mA h/g in the first cycle with coulombic efficiencies of 96%, 91%, and 91%, respectively.

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Introduction

Lithium-ion batteries are attracting much attention for potential applications such as electric vehicles and energy-storage systems, because of their high voltages, high energy densities, and good power densities at fast charge-discharge rates. Lithium-ion batteries are dependent on cathode material insertion-deinsertion processes. LiCoO_2 is used as a commercial positive cathode material for various applications, and high-voltage spinel cathode materials are also used for various energy-storage devices. Among the positive materials used for lithium-ion battery applications, LiMn_2O_4 is an appropriate cathode material for rechargeable lithium-ion batteries, because of its low cost, ready availability, environmentally benign nature, non-toxicity, and ease of synthesis compared with other layered oxides such as LiCoO_2 and LiNiO_2 (Tarascon et al., 1994; Gummow, de Kock, & Thackeray, 1994; Thackeray et al., 1992). However, the specific capacity of pure spinel, LiMn_2O_4 , decreases gradually on repeated cycling at elevated temperatures

(Xia, Zhou, & Yoshio, 1997; Pistoia, Antonini, Rosati, & Zane, 1996). Capacity fading is caused by several factors such as Jahn-Teller distortion, two-phase unstable reactions (Gummow et al., 1994), slow dissolution of manganese into the electrolyte (Jang, Shin, & Oh, 1996), lattice instability (Yamada, 1996), and the particle size distribution (Ohuzuku, Takeda, & Iwanaga, 1999; Song, Ikuta, Uchida, & Wakihara, 1999). Studies to overcome the problem of Jahn-Teller distortion for delivering high-capacity retention with stable cycling performances have been performed on lithium-rich spinels doped with various multi-, tri-, and tetra-valent-ions such as Cr, Fe, Zn, Cu, Ga, Co, Al, Ni, and Ti (Iqbal & Zahoor, 2007; Ohuzuku et al., 1999; Lee, Hong, Jang, Sun, & Oh, 2000); it has been reported that partial doping with cations is effective in depressing capacity fading on repeated cycling. LiMn_2O_4 capacity fading mainly occurs in the 3 V region, and can be completely suppressed by selenium-doped LiMn_2O_4 (Park, Park, Sun, & Nahm, 2000). Low-temperature synthetic methods such as sol-gel (Bach, Henry, Baffier, & Livage, 1990; Ferreira-Ramos, 1995), chemical precipitation (Barboux, Tarascon, & Shokoohi, 1991), hydrothermal, Pechini method (Liu, Farrington, Chaput, & Dunn, 1996), and ultrasonic spray pyrolysis methods (Park, Oh, Myung, & Sun, 2004) have been used to obtain cathode materials with desired physical and electrochemical properties for use in lithium-ion batteries. In this paper, we report the facile synthesis of lauric acid (chelating agent) assisted multi-doped spinels,

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i.e., LiMn_2O_4 and $\text{LiZn}_x\text{Ho}_y\text{Mn}_{2-x-y}\text{O}_4$ ($x=0.10-0.18$; $y=0.02-0.10$) via sol-gel synthesis despite its large ionic radius (0.89 Å) makes Ho(III) appropriate for use in cathode materials for lithium-ion rechargeable batteries.

Experimental

Synthesis of cathode material

Multi-doped pristine spinels LiMn_2O_4 and $\text{LiZn}_x\text{Ho}_y\text{Mn}_{2-x-y}\text{O}_4$ ($x=0.10-0.18$; $y=0.02-0.10$) for use as cathode materials for lithium-ion rechargeable batteries were synthesized via a sol-gel method, using a chelating agent. Fig. 1 shows a flow chart of the synthetic procedure. Stoichiometric amounts of lithium and manganese acetates, and zinc and holmium acetates as dopants, were combined with 10 ml of slightly heated ethanol (for dissolution), and dissolved independently in triple-distilled water. The solutions were thoroughly mixed until they were completely homogeneous. The solution was stirred continuously with gentle heating, and 1 M lauric acid was added drop-wise to allow chelation to take place. The solution pH was maintained between 5 and 6, and the solution was slowly heated until a viscous gel was obtained. The foamy mass was dried in an oven at 110°C overnight. The precursor was ground well using a mortar and pestle to obtain a fine powder with good homogeneity. A small amount of the gel was examined using thermogravimetric/differential thermal analysis (TG/DTA) to

ascertain its thermal behavior, and the remainder of the sample was calcined at 850°C for 6 h. For thermal analysis, the precursors were heated in a nitrogen atmosphere at $10^\circ\text{C}/\text{min}$ to 850°C . All the calcined samples were characterized using TG/DTA, X-ray diffraction (XRD—PANalytical, Netherlands, Model: PW3040/60 X'pert PRO) Fourier-transform infrared (FTIR—Nicolet 5DX-FTIR spectroscope, Thermo Electron Corporation, USA) spectroscopy, scanning electron microscopy (SEM—HITACHI S-3000H, Japan, Magnification: $30\times-300,000\times$, resolution, 3.5 nm at 25 kV high vacuum mode), transmission electron microscopy (TEM—FEI, The Netherlands, Model, Tecnai 20 G2 (FEI make, Resolution, Line-1.8 Å, Point-2.40 Å), energy-dispersive X-ray spectroscopy (EDXA—was attached with SEM), and galvanostatic charge-discharge cycling studies (Won-tech, Model WBCS3000, South Korea).

Coin cell fabrication

Coin cells with a 2016 configuration were assembled in an argon-filled glove box (MBraun, Germany) using lithium foil as the anode, Celgard 2400 as the separator, 1 M solution of LiPF_6 in a 50:50 (v/v) mixture of ethylene carbonate and diethylene carbonate as the electrolyte, and the synthesized material as the cathode. The cathode was prepared by slurry coating a mixture comprising the synthesized compound, carbon black, and poly(vinylidene fluoride) binder in *N*-methyl-2-pyrrolidone solution mixed in a

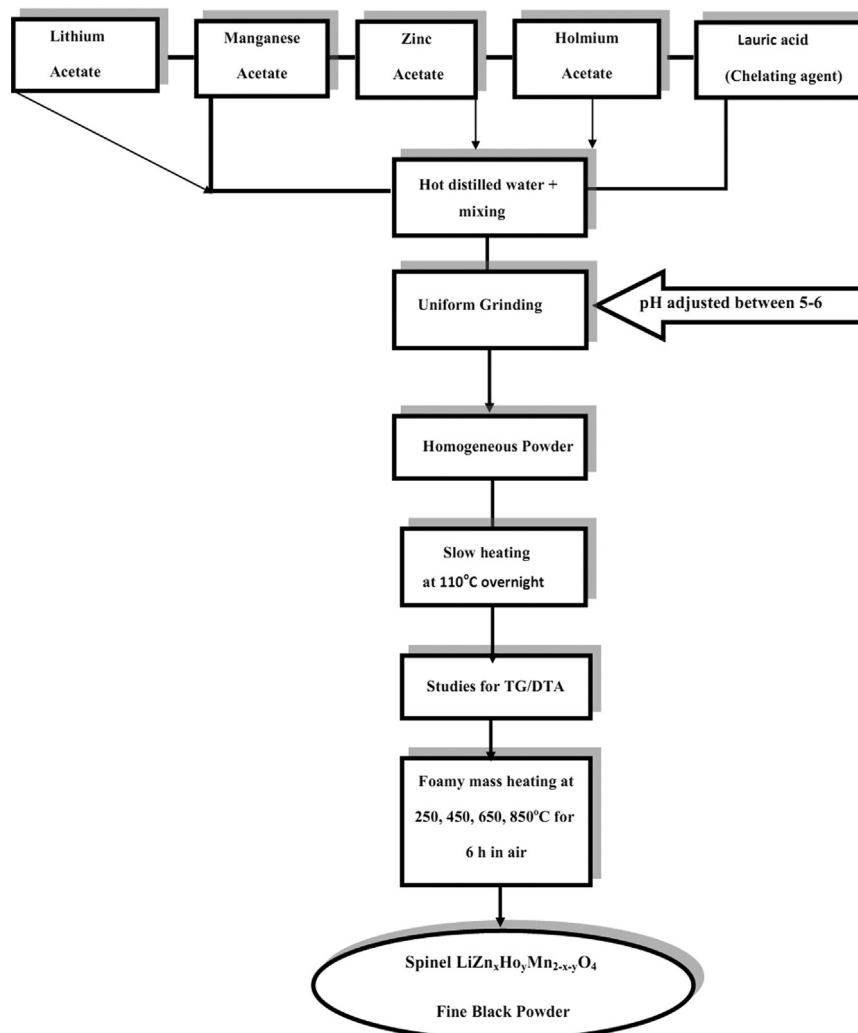


Fig. 1. Flow chart for synthesis of $\text{LiZn}_x\text{Ho}_y\text{Mn}_{2-x-y}\text{O}_4$ by sol-gel method using lauric acid as chelating agent.

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