Journal of Electroanalytical Chemistry 767 (2016) 141–152

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

# Novel chelating agent assisted dual doped spinel via sol–gel method for lithium rechargeable batteries

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ARTICLE INFO

*Article history:*
Received 21 December 2015
Received in revised form 10 February 2016
Accepted 17 February 2016
Available online 18 February 2016

*Keywords:*
Multi doping
Sol–gel method
Margaric acid
Differential capacity
Li-ion battery

ABSTRACT

$LiMn_2O_4$ and $LiCu_xAl_yMn_{2-x-y}O_4$ ($x = 0.50$; $y = 0.05$–$0.50$) powders have been synthesized via sol–gel method for the first time using Margaric acid as chelating agent. The synthesized samples have been used to physical and electrochemical characterization such as thermo gravimetric analysis (TG/DTA), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and electrochemical characterization viz., electrochemical galvanostatic cycling studies, electrochemical impedance spectroscopy (EIS) and differential capacity curves ($dQ/dE$). XRD patterns of $LiMn_2O_4$ and $LiCu_xAl_yMn_{2-x-y}O_4$ confirm high degree of crystallinity with better phase purity of synthesized materials. FESEM images of parent $LiMn_2O_4$ depict the most of the particles that are in 0.5 μm while $LiCu_{0.5}Al_{0.05}Mn_{1.45}O_4$ powders exhibiting ice-cube surface morphology with good agglomerated less particle size of 50 nm. TEM images of spinel $LiMn_2O_4$ and $LiCu_{0.5}Al_{0.05}Mn_{1.45}O_4$ corroborate that all the synthesized particles are nano-sized with uniform spherical and cloudy particle morphology. $LiMn_2O_4$ samples calcined at 850 °C deliver the high discharge capacity of 130 mA h g$^{-1}$ in the first cycle while $LiCu_{0.5}Al_{0.05}Mn_{1.45}O_4$ samples deliver 120 mA h g$^{-1}$ during the first cycle. Inter alia all the dopant compositions investigated, $LiCu_{0.5}Al_{0.05}Mn_{1.45}O_4$ delivers the stable cycling performance of 119 and 115 mA h g$^{-1}$ in the 5th and 10th cycle with low capacity fade of 0.1 and 0.1 mA h g$^{-1}$ cycle$^{-1}$ corresponding to columbic efficiency of 99 and 99%.

## 1. Introduction

Spinel $LiMn_2O_4$ has been zeroed in on attractive and promising cathode materials for lithium-ion batteries owing to its high voltages, proper $Mn^{3+}/Mn^{4+}$ redox potential, high energy densities and high power densities. Lithium-ion batteries are much dependent on cathode material insertion–de-insertion processes. $LiMn_2O_4$, $LiCoO_2$ are used as commercial positive cathode materials for various applications and high-voltage spinel cathode materials are also used for various energy-storage devices. Among all the positive materials used for lithium-ion battery applications, $LiMn_2O_4$ is an apt cathode material for rechargeable lithium-ion batteries, owing to its low cost, easily availability, environmentally benign nature, non-toxicity, and ease of synthesis while comparing with other layered oxides such as $LiCoO_2$ and $LiNiO_2$. [1–3]. However, specific capacity of undoped $LiMn_2O_4$ decreases gradually upon the repeated cycling carried out at elevated temperature [4,5]. It is well known that the capacity fading is caused due to several factors such as Jahn–Teller distortion, two-phase unstable reaction [2], slow dissolution of manganese into the electrolyte [6], lattice instability [7], and particle size distribution [8,9]. In order to overcome the problem of Jahn–Teller distortion for achieving the high capacity retention, several researchers have investigated lithium rich spinels with various divalent, trivalent and tetravalent-doped ions such as Cr, Fe, Zn, Cu, Ga, Co, Al, Ni and Ti [10]. Ohzuku et al. [8] and Lee et al. [11] have reported earlier that partial doping of cations is effective in suppressing the capacity fade upon the cycling. Moreover, the capacity fade of $LiMn_2O_4$ is often happened much in 3 V region which can be completely suppressed by doping selenium with $LiMn_2O_4$ [12]. Low temperature synthesis methods viz., sol–gel [13,14] chemical precipitation [15] hydrothermal and pechini process [16] have been used to obtain cathode materials with expected physical and electrochemical properties for using in lithium-ion batteries. $LiMn_2O_4$ and Zn, Co, Ni and In substituted $LiMn_2O_4$ have been synthesized via facile sol–gel method to improve the electrochemical and structural properties of $LiMn_2O_4$ spinel based on electrode materials for Li-ion batteries [17]. The present work highlights that much efforts are taken carefully to synthesize, physical and electrochemical characterization of $LiMn_2O_4$ and $LiCu_xAl_yMn_{2-x-y}O_4$ ($x = 0.50$; $y = 0.05$–$0.50$) via sol–gel method

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http://dx.doi.org/10.1016/j.jelechem.2016.02.026
1572-6657/© 2016 Published by Elsevier B.V.

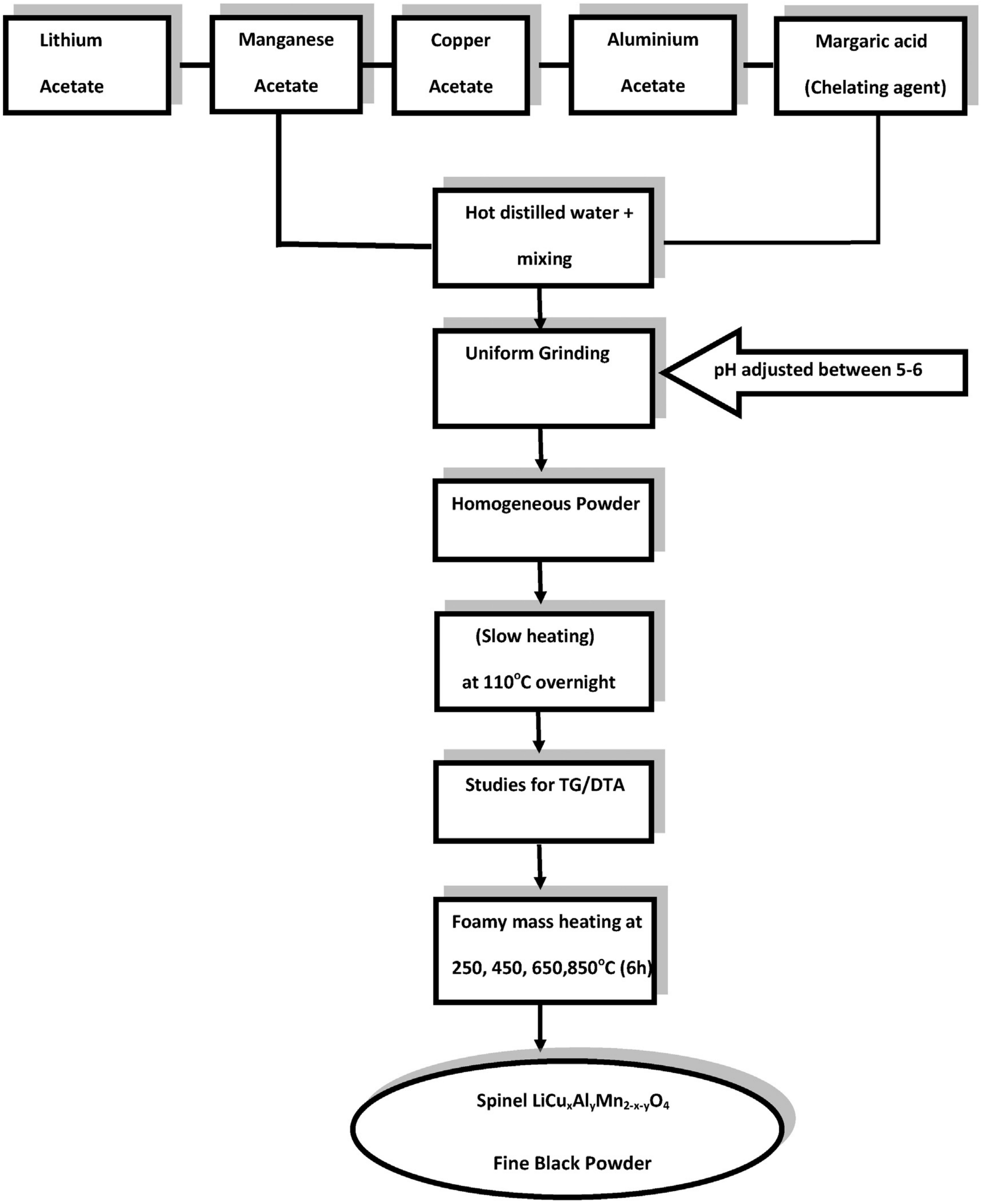

**Fig. 1.** Flow chart for synthesis of $LiCu_xAl_yMn_{2-x-y}O_4$ by sol–gel method using Margaric acid as chelating agent.

using Margaric acid as new chelating agent for the exploration of this facile synthesis methods with good electrochemical performance.

## 2. Experimental

$LiMn_2O_4$ and $LiCu_xAl_yMn_{2-x-y}O_4$ ($x = 0.50$; $y = 0.05$–$0.50$) powders have been synthesized via sol–gel method using Margaric acid as chelating agent. Fig. 1 depicts the flow chart of the synthesis procedure. Stoichiometric amounts of acetates of lithium, manganese, and the dopant salts such as acetate of copper and aluminum were dissolved independently in triple-distilled water. The chelating agent (Margaric acid) is dissolved slowly in heating ethyl alcohol gently. After dissolving all the salts gently, it will be mixed with chelating agent. A small amount of precursor has been taken for TG/DTA analysis in order to understand the thermal behavior and the rest of the sample is calcined at 850 °C for 6 h. For thermal analysis, the precursors are heated in air atmosphere at 10 °C/min to 850 °C. All the calcined samples are subjected for physical characterization using the thermo gravimetric/differential thermal analysis (TG/DTA–Seiko Exstart 6000, Japan), X-ray diffraction (XRD–Bruker D2 Phaser desktop, Cu source, AXS, Karisruhe, Germany), Fourier-transform infrared spectroscopy (FTIR–Tensor 27, Bruker (Germany), field-emission scanning electron microscopy (FESEM–JEOL, Model–JSM-7000F (Japan), transmission electron microscopy (TEM–JEOL, JEM–ARM 200F, Japan), energy dispersive X-ray analysis (EDAX–JEOL, Model–JSM-7000F, Japan) and galvanostatic charge–discharge cycling studies (Won-A-Tech–Model, WBCS 3000, South Korea),