



Improved electrochemical performance of LiMn_2O_4 cathode material by Ce doping



M. Michalska ^{a,*}, D.A. Ziótkowska ^{b,c}, J.B. Jasiński ^b, P.-H. Lee ^d, P. Ławniczak ^e,
B. Andrzejewski ^e, A. Ostrowski ^e, W. Bednarski ^e, S.-H. Wu ^d, J.-Y. Lin ^f

^a Institute of Electronic Materials Technology, Wólczyńska 133, 01-919, Warsaw, Poland

^b Conn Center for Renewable Energy Research, University of Louisville, Louisville, KY, 40292, USA

^c University of Warsaw, Faculty of Physics, Pasteura 5, 02-093, Warsaw, Poland

^d Department of Materials Engineering, Tatung University, No. 40, 3rd Section, Zhongshan North Road, Taipei 104, Taiwan

^e Institute of Molecular Physics Polish Academy of Sciences, Smoluchowskiego 17, 60-179, Poznań, Poland

^f Department of Chemical Engineering, Tatung University, No. 40, 3rd Section, Zhongshan North Road, Taipei 104, Taiwan

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ABSTRACT

Lithium manganese oxide nanopowders doped with Ce ions are synthesized using modified sol-gel method and the effect of annealing atmosphere (air vs. nitrogen) on the structure, morphology, and phase composition is studied thoroughly. Electrochemical testing is conducted to evaluate the effect of annealing atmosphere on electrochemical performance. The X-ray diffraction indicates the cubic spinel structure for all the obtained samples. The lattice parameter is observed to slightly decrease with increasing concentration of Ce^{3+} ions substituting Mn^{3+} ions from 8.230 to 8.228 Å and from 8.227 to 8.224 Å for air annealing and for nitrogen-air annealing, respectively. A limited solubility of cerium in LiMn_2O_4 is also observed, as small amounts of cerium dioxide is detected on the surface of $\text{LiMn}_{2-x}\text{Ce}_x\text{O}_4$ grains and confirmed by XPS analysis of cerium which shows only the spectrum of Ce^{4+} ions. Electrochemical testing is conducted to evaluate the effect of annealing atmosphere on electrochemical performance. It is shown that annealing in nitrogen and then in air results in excellent capacity retention with minimal, 4–8% capacity loss after 150 cycles. $\text{LiMn}_{1.99}\text{Ce}_{0.01}\text{O}_4$ samples prepared that way display better high rate performance in comparison with pristine LiMn_2O_4 .

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1. Introduction

Lithium manganese oxide of spinel structure is an attractive candidate for a positive electrode material in lithium ion batteries and supercapacitors [1–8]. This is partially due to its non-toxicity, low cost and ease of preparation. LiMn_2O_4 (LMO) has high discharge potential (4.1 V vs. Li metal) compared to layered lithium cobalt (LiCoO_2) or lithium nickel (LiNiO_2) oxides and is environmentally friendly. However, LiMn_2O_4 electrodes suffer from a capacity fading during charge-discharge cycles, at higher voltages of around 4.1 V (vs. Li/Li^+), especially at elevated temperature (50–60 °C), which restricts their use in commercial Li-ion batteries.

The capacity fading originates from a cooperative Jahn-Teller transition from cubic to hexagonal structure, which causes strains and fracturing, and from Mn loss caused by disproportional reaction $2\text{Mn}^{3+} \rightarrow \text{Mn}^{4+} + \text{Mn}^{2+}$ followed by Mn^{2+} dissolution into the electrolyte [1–9].

A surface coating or thin surface film such as metallic [10–17], carbon [10–12,18–20] or ceramic oxides [10–12,21–24] on LMO grains can prevent the direct contact between the electrolyte solution and the electrode material, as well as help to improve structural stability and suppress phase transitions. A substitutional doping with other divalent or trivalent metals at the Mn sites (16d octahedral sites in spinel structure) or a formation of the high concentration of Mn^{4+} ions on the surface of LiMn_2O_4 particles reduces the Jahn-Teller distortion and improves the stability of the material during cycling [25–29]. Doping with various metals, including transition metals, such as Fe [30], Co [31], Ni [32], or non-transition ones, such as Al [33–35], Mg [36,37], has

* Corresponding author.

E-mail addresses: monika.michalska83@gmail.com (M. Michalska), jacek.jasinski@louisville.edu (J.B. Jasiński).

been extensively explored with Mn-substitution at concentrations ranging from 0.5 up to 25% at. There have been also reports suggesting alternative strategies, such as substituting rare-earth elements into manganese sites. Despite their large binding energy and ionic radius, the rare-earth elements reduce the Mn content, increase the average valence of Mn ions, stabilize the cubic structure, and suppress the Jahn–Teller distortion [38–47]. Arumugam et al. have reported that by using sol-gel method with succinic acid as a complexing agent, $\text{LiCe}_x\text{Mn}_{2-x}\text{O}_4$ ($x = 0–0.1$) could be obtained with improved structural stability, high reversible capacity and enhanced electrochemical performances. They have demonstrated 91% of capacity retention after 100th cycles at 1C rate of discharge, as well as 123 and 113 $\text{mAh} \cdot \text{g}^{-1}$ for 1st and 100th discharge capacities, respectively for $\text{LiCe}_{0.05}\text{Mn}_{1.95}\text{O}_4$ [46]. Sun et al. have synthesized spinel powders of $\text{LiMn}_{2-x}\text{RE}_x\text{O}_4$ (RE = La, Ce, Nd, Sm $0 \leq x \leq 0.1$) by solid-phase reaction and have shown capacity retention of 97, 93, 95 and 94% after 100th cycles for $\text{LiMn}_{1.9}\text{RE}_{0.1}\text{O}_4$ with RE = La, Ce, Nd, Sm, respectively [38].

LiMn_2O_4 spinel has been mainly synthesized by conventional solid state methods [48–50]. However, some other synthetic routes have been recently investigated, including a modified sol-gel (Pechini) technique, which seems appropriate for the preparation of nanocrystalline cathode materials. As a solution-based method, it offers a possibility of molecular level mixing of starting materials and thus a high degree of homogeneity with small particle size and high surface area can be attained [51–55].

Here, we demonstrate the application of the modified sol-gel approach for the efficient substitution of cerium ions into manganese sites in LiMn_2O_4 and improved electrochemical performance of LMO after Ce doping. The effect of the annealing atmosphere on structural and electrochemical properties of resulting $\text{LiMn}_{2-x}\text{Ce}_x\text{O}_4$ ($0 \leq x \leq 0.03$) samples was investigated. All powders were extensively characterized using several complementary techniques such as: X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and electron paramagnetic resonance (EPR). The influence of Ce doping on the electrochemical and electrical performances was examined.

2. Experimental part

2.1. Synthesis of $\text{LiMn}_{2-x}\text{Ce}_x\text{O}_4$ ($0 \leq x \leq 0.03$) powders

Highly pure manganese acetate tetrahydrate ($\text{C}_4\text{H}_6\text{O}_4\text{Mn} \cdot 4\text{H}_2\text{O}$, CHEMPUR, purum p.a., 99%), lithium acetate dihydrate ($\text{C}_2\text{H}_3\text{O}_2\text{Li} \cdot 2\text{H}_2\text{O}$, Sigma-Aldrich, $\geq 97\%$), cerium (III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich, 99.99%), citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, purum p.a., 99.5%, Avantor Performance Materials Poland S.A.), acetic acid ($\text{C}_2\text{H}_4\text{O}_2$, CHEMPUR, 99.5%) were used to synthesize $\text{LiMn}_{2-x}\text{Ce}_x\text{O}_4$ ($0 \leq x \leq 0.03$) nanopowders.

Stoichiometric amounts of manganese and lithium acetates and cerium nitrate were dissolved in deionized water separately. Solutions were mixed together and then citric with acetic acids were added. The metal to citric acid ratio was 1:1. The acetic acid was used as a second chelating agent, the ratio of citric to acetic acids was 1:0.25. During formation of spinel structure the condensations reaction occurs, between citric and acetic acids. Also the acetic acid is used to provide synthesis in acidic solution. The prepared solutions were then evaporated until gels were obtained. The resulting gel precursors were dried at 150 °C for few hours in the air. The xerogels (pre-dried powders) were heated in the one- or two-stage processes. In the first method, the xerogel was heated in air atmosphere only (A) at 300 °C for 7 h and then at 700 °C for 5 h. In a two-stage process, the xerogel was heated at temperature 300 °C for 7 h and then at 700 °C for 5 h in: 1) nitrogen (B) and afterwards in 2) air atmosphere (BA). The heating rate for each step of annealing was 5 °C/min. The flowchart of the synthesis is presented in Fig. 1.

The sample labeled LMO-A was a pure LiMn_2O_4 powder. The Ce-doped samples were labeled as LMO-CeX-Y, where X = 1,2,3 corresponded to nominal Mn:Ce molar composition ratio of 1.99:0.01, 1.98:0.02 and 1.97:0.03, respectively, and Y indicated annealing in air only (A), in nitrogen only (B), and in nitrogen and then in air (BA), respectively.

2.2. Material characterizations

The crystal structure of all obtained powders was analyzed using X-ray powder diffraction (XRD). XRD patterns were acquired

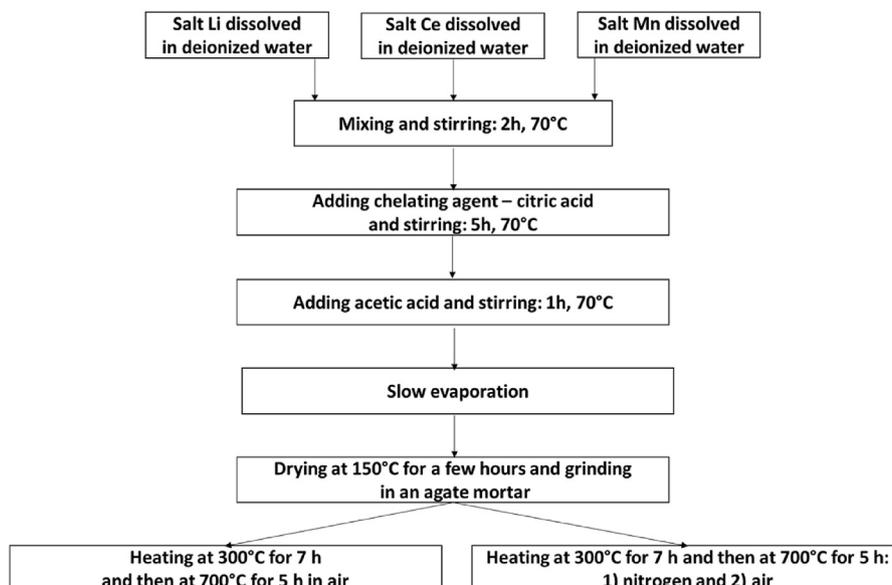


Fig. 1. A flowchart of modified sol-gel method to synthesize $\text{LiMn}_{2-x}\text{Ce}_x\text{O}_4$ where $0 \leq x \leq 0.03$.

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