

# Structural and electrochemical characterization of sulphur-doped lithium manganese spinel cathode materials for lithium ion batteries

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## ABSTRACT

Nanosized  $\text{LiMn}_2\text{O}_4$  and  $\text{LiMn}_2\text{O}_{3.99}\text{S}_{0.01}$  powders were prepared using a modified sol-gel method followed by calcination at 300 °C and further calcination at 650 °C in air. The high-temperature calcination was required to receive improved structural and electrical properties of the spinels. X-ray powder diffraction showed that for samples calcined at 650 °C, single phase materials of *Fd-3m* symmetry with nanoparticles size of ~50 nm were obtained. The  $\text{LiMn}_2\text{O}_4$  spinel showed the phase transition at about room temperature, but the effect was strongly diminished with the substitution of sulphur for oxygen in the spinel structure. Electrochemical results on 2032 coin-type cells reveal that slight substitution of sulphur in the  $\text{LiMn}_2\text{O}_4$  enhances the electrochemical performance and cell cycleability. The sulphided cathode material in which the capacity retention after 50 cycles is around 99% displays good rate capability, even at higher current densities.

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## 1. Introduction

Lithium manganese oxides (LMO) are still considered to be the most serious alternative cathode materials for rechargeable lithium ion batteries [1–5]. They may replace the commercially used layered cobalt oxide  $\text{LiCoO}_2$  and its derivatives, which are toxic and expensive. The  $\text{LiMn}_2\text{O}_4$  spinel is more abundant, cheaper, environmental friendly and has similar practical capacity (about  $140 \text{ mAhg}^{-1}$ ) to currently used materials [6–8]. However, previous studies [9–12] identified that stoichiometric  $\text{LiMn}_2\text{O}_4$  shows considerable capacity fading on cycling associated with reversible phase transition from cubic (*Fd-3m*) to orthorhombic (*Fddd*) crystal structure near room temperature [13]. This transition is related to the Jahn–Teller distortion of high spin  $\text{Mn}^{3+}$  ions [14]. In order to improve structural properties of  $\text{LiMn}_2\text{O}_4$  spinel materials and achieve better rate capability, several methods have been investigated so far. Among them, partial substitution of  $\text{Mn}^{3+}$  ions by other metal ions, such as  $\text{Co}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Li}^+$ , etc. [15–18], synthesis of cation deficient (oxygen rich) spinels [19,20], modification of oxygen sublattice by isoelectronic partial substitution with sulphur [21,22] and many others.

This work reports the structural and electrochemical characteristics of nanosized sulphided lithium manganese spinel material synthesized

by the modified sol-gel method [20,23]. For comparison, stoichiometric  $\text{LiMn}_2\text{O}_4$  spinel was also synthesized and investigated.

## 2. Experimental

$\text{LiMn}_2\text{O}_4$  and  $\text{LiMn}_2\text{O}_{3.99}\text{S}_{0.01}$  spinels were synthesized by a xerogel type sol-gel method using aqueous solutions of lithium and manganese acetates and ammonium sulphide. Ammonia as the alkalinizing agent was also added to the solution. The syntheses were carried out with an argon flow to prevent uncontrolled oxidation of the  $\text{Mn}^{2+}$  ions. Condensation of the formed soles was performed at 90 °C for 3–4 days, and then, the obtained xerogels were calcined in air for 24 h at 300 °C with a heating rate of  $1 \text{ °C}\cdot\text{min}^{-1}$ . Additional high-temperature calcination at 650 °C for 6 h in air with heating rate of  $5 \text{ °C}\cdot\text{min}^{-1}$ , followed by quenching, was performed to obtain better crystallized samples with optimized electrical properties.

The crystal structure of the resulting materials was investigated by X-ray powder diffraction (XRD) on BRUKER D2 PHASER using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.154184 \text{ nm}$ ) in the range of 10–80° (2 $\theta$ ) with a step of 0.02°. The phase identification of the XRD pattern was performed using structural data from the ICDD database. A Rietveld refinement has been accomplished using XPowder program and structural data from AMCSD database. The average crystallite size was estimated from the integral width of (111) reflection of the cubic spinel using Scherrer's equation. To determine the existence of sulphur in  $\text{LiMn}_2\text{O}_{3.99}\text{S}_{0.01}$  compound, an elemental analysis was conducted using EURO EA 3000 Elemental Analyzer (EuroVector). Differential scanning calorimetry experiments (DSC) were performed in Mettler-Toledo 821<sup>e</sup>

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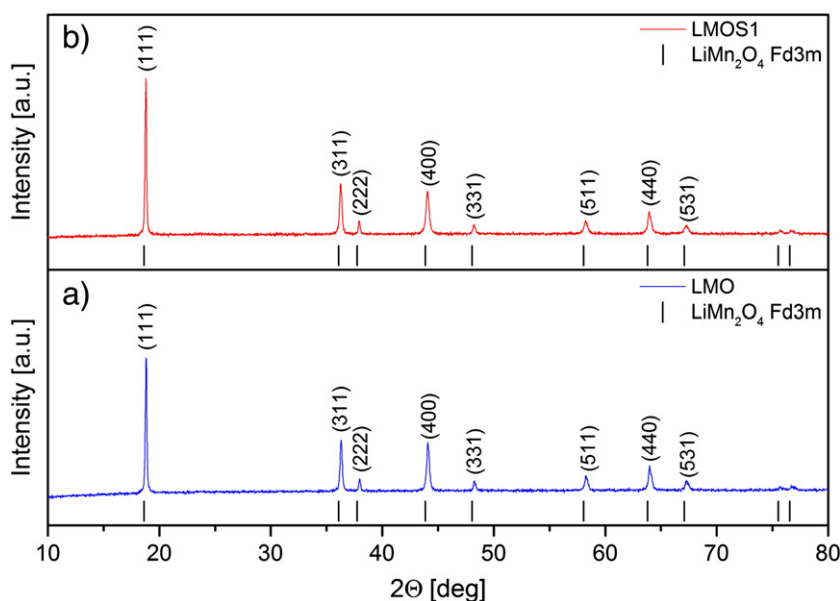


Fig. 1. X-ray diffraction patterns of  $\text{LiMn}_2\text{O}_4$  (a) and  $\text{LiMn}_2\text{O}_{3.99}\text{S}_{0.01}$  (b) spinels calcined at  $650\text{ }^\circ\text{C}$ .

Table 1

Chemical composition, lattice constant, average crystallites size and textural properties of nanosized  $\text{LiMn}_2\text{O}_4$  and  $\text{LiMn}_2\text{O}_{3.99}\text{S}_{0.01}$  spinels.

Sample	Nominal composition	Lattice constant [nm]	Average crystallites size [nm]	Surface BET area [ $\text{m}^2 \cdot \text{g}^{-1}$ ]	Pore volume [ $\text{cm}^3 \cdot \text{g}^{-1}$ ]	Average pore diameter [nm]
LMO	$\text{LiMn}_2\text{O}_4$	$0.8227 \pm 0.0002$	48	2.7	0.010	14
LMOS1	$\text{LiMn}_2\text{O}_{3.99}\text{S}_{0.01}$	$0.8259 \pm 0.0002$	48	4.5	0.018	16

microcalorimeter equipped with intracooler Haake in aluminum crucibles under constant flow of argon ( $80\text{ ml} \cdot \text{min}^{-1}$ ) within a temperature range of  $-25$  to  $+55\text{ }^\circ\text{C}$  with the cooling and heating rate equal to  $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$ . Multipoint nitrogen adsorption–desorption measurements were conducted at about  $-196\text{ }^\circ\text{C}$  on a Micromeritics 3Flex surface area analyzer. The prepared products were evacuated at appropriate conditions before analysis. The specific surface area was calculated according to the Brunauer–Emmett–Teller (BET) method. The Barrett–Joyner–Halenda (BJH) method was applied to determine the pore size distribution and estimate a pore volume and an average pore diameter. The electrical conductivity (EC) studies were carried out using the 4-probe *ac* method within temperature range of  $-20$  to  $+40\text{ }^\circ\text{C}$ . The powder samples were placed in a glass tube between the parallel gold circular electrodes and pressed by a screw-press until the measured resistance of the sample did not change. The electrical conductivity obeys the Arrhenius law  $\sigma = \sigma_0 \cdot \exp\left(\frac{-E_a}{k_B T}\right)$  where  $\sigma_0$  is the pre-exponential factor,  $E_a$  is the activation energy and  $k_B$ , the Boltzmann constant. The slope of the plot in the  $\ln\sigma$  vs.  $1000 \cdot T^{-1}$  coordinates enabled the determination of the activation energy.

The electrochemical tests of the synthesized powders were performed in CR2032 coin-type cells. The test cells were made of a cathode and a lithium metal anode separated by a microporous polypropylene film (Celgard 2325) and a porous glass microfiber filters (Whatman GF/F). The cathodes were prepared by mixing 80 wt.% of active material with 10 wt.% of carbon black and 10 wt.% of polyvinylidene fluoride (PVDF) binder in *N*-methylpyrrolidone (NMP) solvent. The fabricated slurry was then coated on an aluminum foil to form the working electrodes of  $1.44\text{ cm}^2$  area. The typical loading of active materials in the assembled cells was around 2.5 mg. The electrolyte was a 1 M solution of  $\text{LiPF}_6$  in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 in weight). The assembly process was carried out in an

argon-filled glove box with both  $\text{H}_2\text{O}$  and  $\text{O}_2$  levels less than 0.1 ppm. The galvanostatic charge/discharge cycling tests (CELL TEST) were conducted at various current densities between 3.0 and 4.5 V on an ATLAS 0961 MBI multichannel battery tester at room temperature. The electrochemical impedance spectroscopy (EIS) measurements were carried out at an open circuit potential (OCP) of the cells on a potentiostat/galvanostat AUTOLAB PGSTAT302N/FRA2 by applying 0.1 V amplitude in the frequency range from 100 kHz to 0.1 Hz. The impedance data were then fitted using Nova 1.8 program.

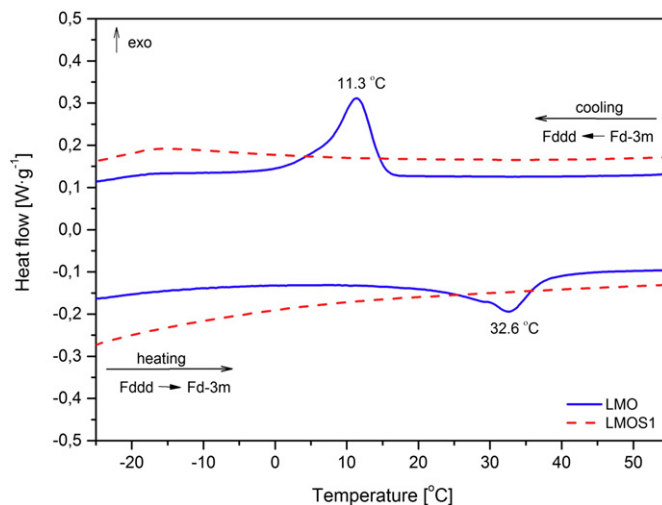


Fig. 2. Differential scanning calorimetry results of LMO and LMOS1 samples calcined at  $650\text{ }^\circ\text{C}$ .

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