

# THERMAL INDUCED CHANGES IN CRYSTAL STRUCTURE AND ELECTRONIC STATES OF LI-ION CATHODE MATERIALS BASED ON LI-Mn-O-S SYSTEM

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Sulphur substitution of oxygen in  $\text{LiMn}_2\text{O}_4$  spinel destroyed the ideal symmetry of  $\text{MnO}_6$  octahedrons. In consequence, the phase change at about room temperature is strongly retarded, manifested by lowering heat of the transition and hysteresis of the temperature dependence of electrical conductivity. The optimal conditions for preparation of sulphur substituted spinel  $\text{LiMn}_2\text{O}_{4-y}\text{S}_y$  have been determined.

**Keywords:** DSC, electrical conductivity, Li-ion batteries, oxysulphide spinel, phase transition, TG

## Introduction

Currently used in high power Li-ion batteries cathode materials, like  $\text{LiCoO}_2$  and  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ , are toxic and expensive [1, 2]. Alternative to them,  $\text{LiMn}_2\text{O}_4$  spinel reveals similar reversible electrochemical capacity being cheaper and environmental friendly material. Hence, many papers was devoted to this spinel and related systems [1–4], which are considered as promising materials for electric vehicles (EV) or hybrid electric vehicles (HEV) [5]. Commercialization of cathode materials based on  $\text{LiMn}_2\text{O}_4$  system is delayed mainly because of their structural instability. The stoichiometric  $\text{LiMn}_2\text{O}_4$  shows a reversible phase transition from cubic (Fd3m) to orthorhombic (Fddd) structure near room temperature [6], which causes fading of the electric capacity of the cathode materials in consecutive cell cycling.

This phase transition is related to the Jahn–Teller distortion of high-spin  $\text{Mn}^{3+}$  ions located in high symmetry ( $\text{O}_h^7$ ) sites [7, 8] and specific charge ordering in manganese sublattice [9–11]. Stabilization of the high temperature structure (cubic phase) may be performed by partially substitution of  $\text{Mn}^{3+}$  ions by 3d metal ions (Cr, Fe, Ni, Co) [12, 13],  $\text{Al}^{3+}$  [14] ions or excess of  $\text{Li}^+$  ions [15–17]. But, these modifications can seriously decrease of  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ratio due to the necessary charge compensation in crystal lattice and in consequence causes a remarkable decrease in 4V capacity.

We have previously proposed another modification of the spinels by isoelectronic partial substitution with sulphur of oxygen atoms in anionic sub-

lattice [18, 19]. Such a modification appeared satisfactory sufficient to avoid the Jahn–Teller effect and in consequence to suppress the RT phase transition.

The goal of this work is to reveal the changes in crystal structure and electrical properties during thermal treatment of the sulphur modified lithium–manganese spinels and to optimize the conditions of their preparation.

## Experimental

A set of sulphur modified lithium–manganese spinels  $\text{LiMn}_2\text{O}_{4-y}\text{S}_y$  ( $0.00 \leq y \leq 0.5$ ) were obtained by the sol–gel method described elsewhere [18–20]. The samples were calcined within temperature range 300–800°C in the air for 6–24 h and quenched, to obtain materials with different properties and defect structure. Thermal stability in the air of the sulphur modified lithium–manganese spinels at the temperatures above 800°C was determined using MS-TG method in another paper [18]. The crystal structure was confirmed by X-ray powder diffraction technique on PW3710 Philips X’Pert apparatus using  $\text{CuK}_{\alpha 1}$  ( $\lambda = 0.154178$  nm) radiation with a graphite monochromator [19]. The local structure of  $\text{MnO}_6$  polyhedrons was determined by Raman spectroscopy [20].

The thermogravimetric analysis (TG) coupled with mass spectrometry analysis (MS-TG/DTG/SDTA) experiments was performed in Mettler-Toledo 851<sup>e</sup> apparatus in 150  $\mu\text{L}$  platinum crucibles under flow of air (80  $\text{mL min}^{-1}$ ), within temperature range 25–1000°C with heating rate equal to

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5°C min<sup>-1</sup>. The simultaneous evolved gas analysis (EGA) was performed during the experiments by joined on-line quadruple mass spectrometer (QMS) (Thermostar-Balzars).

The differential scanning calorimetry (DSC) experiments were performed in Mettler-Toledo 821<sup>e</sup> calorimeter equipped with intracooler Haake in 40 μL aluminum crucibles under constant flow of argon (80 mL min<sup>-1</sup>) within temperature range -40–+60°C with the cooling and heating equal to 10°C min<sup>-1</sup>.

The microstructure of the obtained powder was examined by scanning electron microscopy (SEM) using Philips XL 30 apparatus combined with EDS spectrometer LINK-ISIS.

Electrical conductivity was measured on pellets pressed by hydraulic press (5 tons) using ac (33 Hz) 4-probe method within temperature range of -40–+55°C. To improve the electrical contact between sample and electrodes a silver paste with acrylic resin was used.

## Results and discussion

The results of thermogravimetric analysis (TG) of the sulphur substituted spinels are presented in Fig. 1. For comparison, the TG curves of pure lithium–manganese spinels calcined at 300°C (Li<sub>0.96</sub>Mn<sub>1.92</sub>O<sub>4</sub>) and 800°C (LiMn<sub>2</sub>O<sub>4</sub>) were added. Thermal decomposition of the sulphided spinels LiMn<sub>2</sub>O<sub>4-y</sub>S<sub>y</sub> obtained by sol–gel method and calcined at 300°C occurs in four stages. The mass loss up to 150°C is related to water evolution from the sample, probably from small amount of impurity phase Li<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O, what was reported previously [18, 19]. The second one, taking place between 150–780°C, is related to a slow oxygen evolution with rearrangement of the spinel structure and disappearance of the cations defects (similarly to behaviour observed for the Li<sub>0.96</sub>Mn<sub>1.92</sub>O<sub>4</sub>). The cationic defected spinel structure is typical for the materials obtained by the low temperature sol–gel

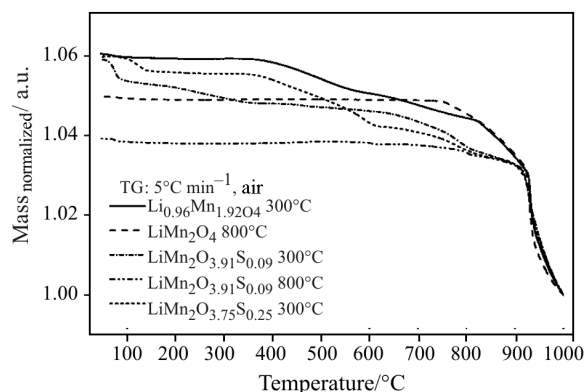
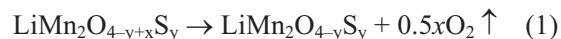
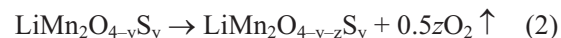


Fig. 1 TG curves of the sulphided spinels

method. In a close packed spinel lattice the presence of cations defects is observed as real excess of oxygen. This transformation may be described by the following reaction (1):

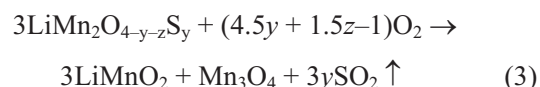


At higher temperature (780–910°C) the slight oxygen evolution due to formation of anionic defects were observed (2):



The formation of such oxygen vacancies was previously observed for Li<sub>0.96</sub>Mn<sub>1.92</sub>O<sub>4</sub> and LiMn<sub>2</sub>O<sub>4</sub> spinels [8]. Moreover, this effect was much more intensive what suggests that during substitution the sulphur ions replace only the mobile oxygen ions.

Above 910°C the fast decomposition of the spinel, the oxides separations and sulphur dioxide evolution took place (3) [18]:



During thermal treatment of the spinel samples sintering of the crystallites occurs what can be easily observed on SEM images presented in Fig. 2. The sintering process is not desirable because it can decrease the surface of the cathode material and increase the grains size. This affects the good properties of the sol–gel obtained materials, but subsequent thermal treatment increases the electrical conductivity in result of better arrangement of the spinel structure. These two opposite effects have to be optimized.

The structural stability of the sulphided spinels is presented in Fig. 3. The observed heat effects during heating and cooling cycles are related to the first order phase transition (cubic ↔ orthorhombic) in the spinel structure. The sulphur substitution into oxygen sublattice provides stabilization of the regular spinel structure in comparison to stoichiometric LiMn<sub>2</sub>O<sub>4</sub> spinel. However, the heat effects related to the phase change are still present. Lowering of the calcination time from 24 to 6 h provides further stabilization of the structure as well as lowering of the calcination temperature. The sulphur substituted spinel LiMn<sub>2</sub>O<sub>4-y</sub>S<sub>y</sub> obtained by calcination at 650°C for 6 h was stable and showed no heat effects on DSC curves (Fig. 3).

The measurements of the electrical conductivity are presented in Fig. 4. The obtained results are in good accordance with DSC results. However, the sulphur stabilized spinels shows unfortunately lower electrical conductivity. An improvement can be achieved also by lowering of the calcination time to 6 h and the temperature to 650°C. Such material provides quite acceptable electrical conductivity. More-

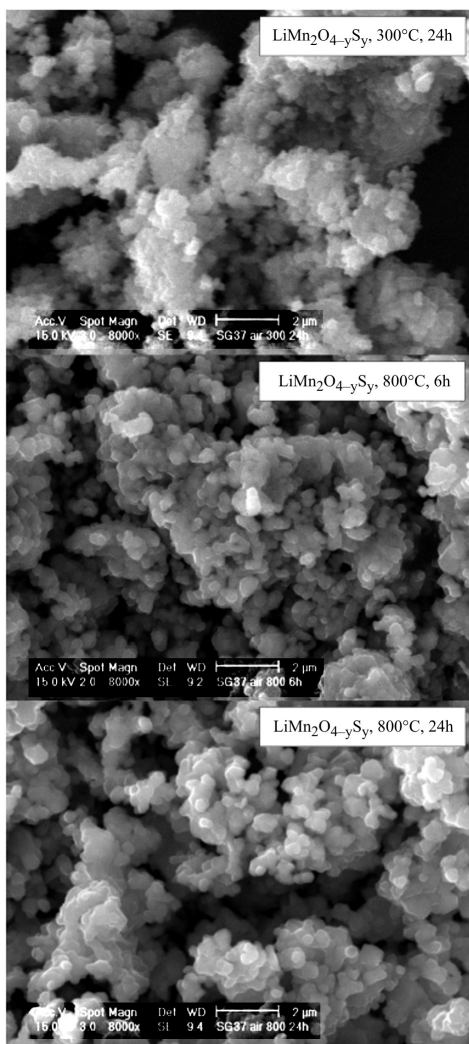


Fig. 2 SEM micrographs of the sulphidated spinels

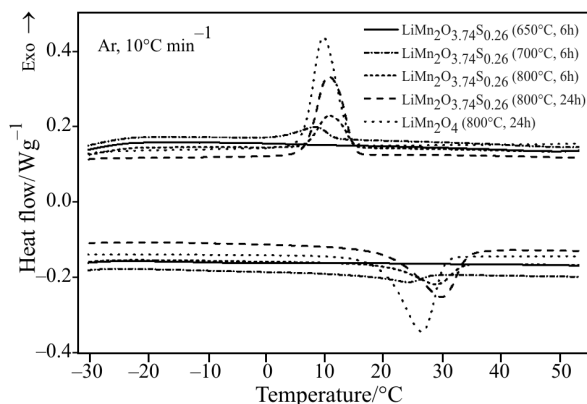


Fig. 3 DSC curve of the sulphidated spinels

over, this material reveals the lowest activation energy equal 0.30 eV, even in relation to  $\text{LiMn}_2\text{O}_4$  spinel ( $E_a=0.32$  eV). We hope that new synthesized C/ $\text{LiMn}_2\text{O}_{4-y}\text{S}_y$  composites will help in achievement of the material with fully satisfied electrical conduc-

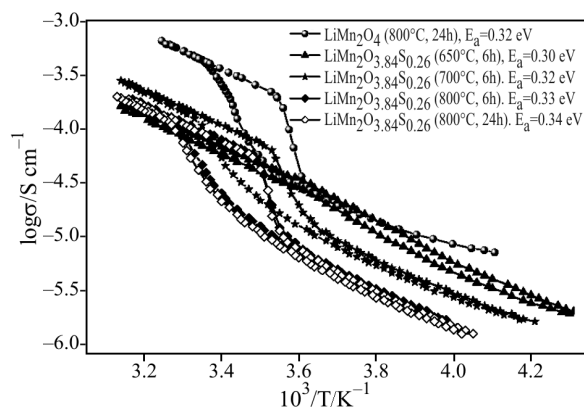


Fig. 4 Electrical conductivity of sulphidated spinels

tivity. The first results obtained on a model C/ $\text{Al}_2\text{O}_3$  system are very promising [21].

## Conclusions

The sol-gel method followed by thermal treatment at  $650^\circ\text{C}$  for 6 h allows obtaining  $\text{LiMn}_2\text{O}_{4-y}\text{S}_y$  spinel with stable structure showing no RT phase transition. Activation energy of electrical conductivity is low enough but the conductivity needs further improvement. Covering of the spinel grains by conductive carbon should help in this improvement.

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