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SYNTHESIS AND STRUCTURE OF $LIMN_{2-X}ZN_XO_4$ THROUGH ULTRASONIC SPRAY PYROLYSIS

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Abstract

Ultrasonic spray pyrolysis method was used for the synthesis of quaternary spinel oxide $LiMn_{2-x}Zn_xO_4$ ($x \approx 0.08$) powder, without additional annealing. Aqueous solutions of metal nitrates were atomized at a frequency of 1.7 MHz by the ultrasonic nebulizer. Aerosol was introduced in the horizontal electric furnace at the temperature of 1073 K. The crystal structure of the as-prepared powder was revealed by X-ray powder diffraction and identified as a single spinel phase with Fd3m space group. Particle morphology was determined by scanning electron microscopy (SEM).

Introduction

$LiMn_2O_4$ spinel is environmentally acceptable and low cost material which has attracted much attention as a promising cathode material for lithium-ion batteries [1, 2]. The major limitation of $LiMn_2O_4$ in battery applications is capacity fading upon electrochemical cycling. The largest improvements of the cycle life have been achieved by the substitution for some of the manganese by other metal cations (Li^+, Ni^{2+}, Al^{3+}, Co^{2+}, Zn^{2+}, Cr^{3+}) [3]. This substitution increases the average oxidation state of the remaining manganese and produces more robust spinels with better capacity retention, but somewhat lower initial capacity.

In this paper we demonstrate the possibility to prepare quaternary spinel oxide $LiMn_{1.92}Zn_{0.08}O_4$ by using an ultrasonic spray pyrolysis method, without additional annealing. The structural and morphological properties of such synthesized material are presented.

Experimental

Starting solution was an aqueous solution of $LiNO_3$ (Laphoma), $Mn(NO_3)_2$ (Merck), and $Zn(NO_3)_2$ (Merck) p.a. chemicals, mixed in such a ratio to achieve the stoichiometry of $LiMn_{1.92}Zn_{0.08}O_4$. The total metal concentration was 0.98 mol/dm^3. This solution was atomized at a frequency of 1.7 MHz by the ultrasonic nebulizer. The generated mist, with the average droplet diameter of approximately 2.5 μm, was carried to the horizontal electric furnace by air, with a flow rate of 0.5 dm^3/min. The effective heating length of the reaction tube was 0.6 m with the

maximum temperature of 1073 K in the middle of the furnace. The residence time of droplets/particles inside the furnace and in the maximum temperature zone was 65 s and 6 s, respectively, assuming the air flow rate and droplet velocities to be equal. The heating rate of droplets/particles was 15 °C/s. The precipitated powder was collected from a quartz glass tube at the outlet of the reactor.

X-ray diffraction data were collected on a Philips PW 1050 diffractometer with Cu-K$\alpha_{1,2}$ radiation (Ni filter) at the room temperature. Measurements were done in 2θ range of 10-100° with scanning step width of 0.02° and 10 s time per step. Crystal structure refinement was based on the Rietveld full profile method [4] using the Koalariet computing program. This program is appropriate for processing the data obtained from the samples with dominant microstructure parameters [5].

SEM was performed on a JEOL JSM-5300, with electron energy of 20 keV.

Results and Discussion

X-ray powder diffraction patterns were used for the structural analysis of the synthesized samples. The refinement results show that $LiMn_{1.92}Zn_{0.08}O_4$ powder is well crystallized as single-phase spinel. The structure of $LiMn_{1.92}Zn_{0.08}O_4$ has been refined in the space group Fd3m (O_h^7) in well-known spinel type with following crystallographic positions: Li^+ ions in special crystallographic position 8*a* [0,0,0] with local symmetry $\bar{4}$3m, Mn^{3+} and Mn^{4+} ions in special crystallographic position 16*d* [5/8,5/8,5/8] with local symmetry 3m, and O^{2-} in special crystallographic position 32*e* [x,x,x] with local symmetry 3m. The observed and calculated X-ray diffraction profiles are given in Figure 1, while main results of the final Rietveld refinements are presented in Table 1. Throughout the refinements the model with Zn in the tetrahedral (8*a*) site was applied. The inclusion of Zn on the tetrahedral site is in common with many spinel systems, resulting from the tendency of Zn to be four-coordinated and then to occupy this site. In addition, one of the peaks of the diffraction pattern, namely (220) at 2θ = 30.708°, is allowed in the space group Fd-3m, but its appearance is sensitive to the presence of dopant ions on the Li^+ (8*a*) tetrahedral site. It should be emphasized that lattice parameter of $LiMn_{1.92}Zn_{0.08}O_4$ (a=8.2324(3) Å) is appreciably reduced comparing to $LiMn_2O_4$ (a= 8.2410(1) Å) synthesized under the same conditions [6].

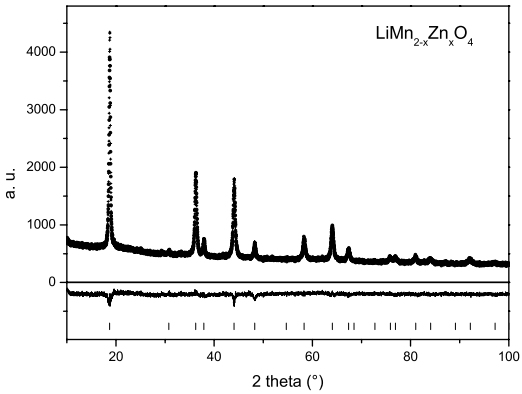


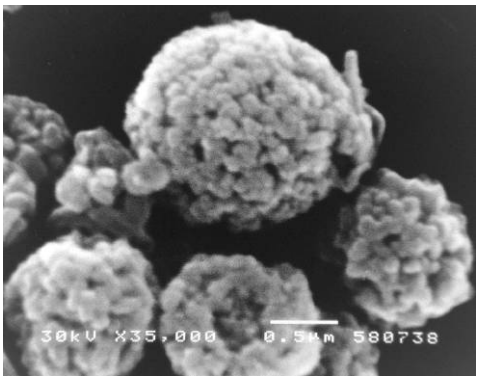
Fig. 1. The observed (•), calculated (-), and difference (bottom) X-ray diffraction data of $LiMn_{1.92}Zn_{0.08}O_4$ taken at room temperature. Vertical markers bellow the diffraction pattern indicate positions of possible Bragg reflections.

This is probably due to the increase in the average oxidation state of the manganese (average oxidation state 3.5) upon substitution of some Mn ions with Zn^{2+} ions, since the ionic radii of tetrahedral Li^{+} and Zn^{2+} are very similar, 0.73 and 0.74 Å, respectively.

Table 1. The final results of the structural refinement for $LiMn_{1.92}Zn_{0.08}O_4$

Lattice parameters [Å]	a = 8.2324(3)
Primitive cell volume [$Å^3$]	V = 139.48(4)
Mean crystallite size [Å]	660(20)
Microstrain [%]	0.51(1)
Strain [%]	0.13(1)
Free coordinates O^{2-}	u = 0.3849(4)
Li^{+} crystall. position occ.	N_{Li} (8a) =1-0.09(1)
R factors [%]	R_B = 4.5

Also, microstrain and strain parameters are reduced comparing to $LiMn_2O_4$. Strain parameter is in connection with Jahn-Teller distortion. Introduction of Zn to spinel structure impede Jahn-Teller distortion since it is dependent on the amount of Mn^{3+} ions. Reduced microstrain in comparison with $LiMn_2O_4$ means that more stable spinel structure was obtained.



Scanning electron microscopic image of the sample are shown in Figure 2. The particles are spherical in shape and non-agglomerated, showing porous microstructure. When metal nitrates melt at low temperature (in this case $Zn(NO_3)_2 \cdot 6H_2O$, Tm=45°C), before the decomposition, molten salt retain solvent and porous particles appear.

Fig. 2. SEM image of $LiMn_{1.92}Zn_{0.08}O_4$

Conclusion

In summary, well-crystallized single-phased spinel $LiMn_{1.92}Zn_{0.08}O_4$ can be readily obtained by an ultrasonic spray pyrolysis. The structural refinement confirmed the presence of Zn^{2+} ion on the tetrahedral sites of the spinel. The synthesized powder had spherical particle morphology and non-agglomerated particles, with porous surface appearance.

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