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on Fundamental and Applied Aspects of
Physical Chemistry

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CONTENT

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THE SYNTHESIS AND CHARACTERIZATION OF $ZnMn_2O_4$ IN AN AQUEOUS SOLUTION OF $ZnCl_2$

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ABSTRACT
This work provides the synthesis and characterization of $ZnMn_2O_4$ that may be a potential replacement for the hazardous cathode materials used in commercial Li-ion batteries, as well as the examination of its electrochemical properties in an aqueous solution of $ZnCl_2$. Due to the fact that commercial Li-ion batteries contain toxic and flammable electrolyte, there is a need for their replacement with less harmful substance.

INTRODUCTION
This work aims to design an ecological Zn-ion battery using the glycine nitrate procedure by which sub-micron sized particles are obtained. $ZnMn_2O_4$, according to the data reported, has a stable capacity in both aqueous and organic electrolytes. Zhang *et al.* examined $ZnMn_2O_4$ as the cathode material in 3M aqueous solution of $Zn(CF_3SO_3)_2$. The measurement by galvanostatic charge and discharge gave a capacity of 150 mAh g^{-1} with a capacity retention of 94% after 500 cycles at rate of 500 mA g^{-1}. Sheklar *et al*. examined the electrochemical properties of $ZnMn_2O_4$ as an anode in 1M $NaClO_4$ dissolved in 1:1 (v/v) mixture of ethylene carbonate with diethyl carbonate. The measurement was performed by galvanostatic charge and discharged obtaining the capacity of 170 mAh g^{-1} with the retention of 1000 cycles at rate of 100 mA g^{-1}. This work provides the synthesis, crystallographic and morphological analysis as well as the electrochemical properties of the material in the aqueous solution of zinc salt.

METHODS
The glycine nitrate combustion method was applied to synthesize $ZnMn_2O_4$. The solutions of 1M $Mn(NO_3)_2x6H_2O$ and $Zn(NO_3)_2x6H_2O$ in stoichiometric ratio were mixed and glycine was added (glycine/NO_3=1.2). The solution was combusted at 200ºC until complete combustion, and thereafter annealed for four hours at 800ºC in air.

XRPD data are collected using the Rigaku Ultima IV powder diffractometer with Ni-filtered Cu Kα radiation in the interval of 4 to 90º 2θ with the step of 0.02 º (scanning speed 2º min^{-1}). The unit cell refinement was performed using the Le Bail full pattern profile fitting method [3] implemented in FullProf software [4].

The sample morphology was analyzed using the scanning electron microscope (Tescan VEGA TS 5130MM) operating at 20 kV accelerating voltage.

Cyclic voltammetry was performed using the Gamry PCI4/300 Potentiostate/Galvanostate at the polarization rate 10 and 50 mV s^{-1}. The three electrode system was used (a counter electrode was platinum, reference SCE, and working electrode was glossy carbon electrode on which was pasted

cathode material, carbon black as well as polyvinildiendifluoride in ratio 85:10:5). The paste was obtained according to reference [5]. The measurement was performed at 25 ºC.

RESULTS AND DISCUSSION

The diffractogram calculated shows a good agreement with the data reported in the literature [6] and shown in **Fig. 1**; the pattern is refined to the $I4_1/amd$ space group with lattice parameters: a= b= 5.7185(8) Å, c= 9.268(2) Å.

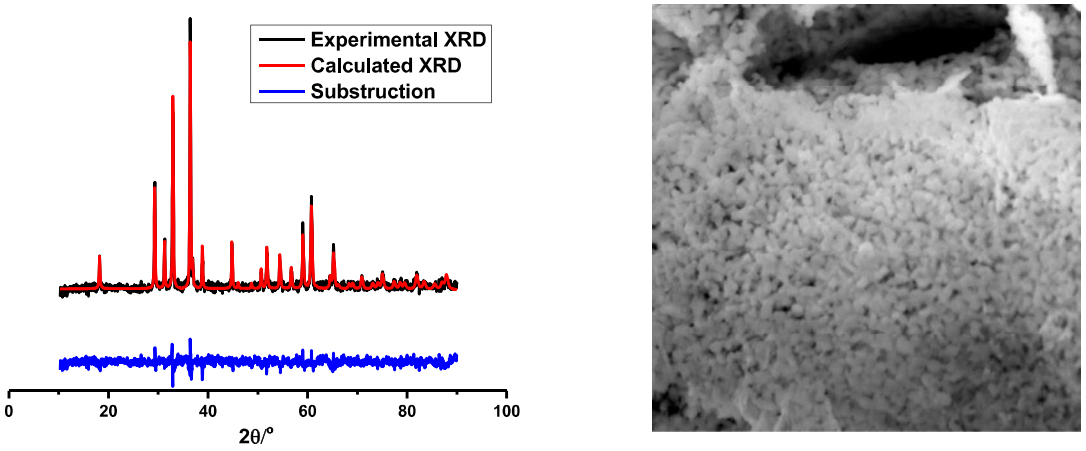

Figure 1. a) refined XRD pattern of the material synthesized, **b)** SEM micrographs at magnification of 10 000x

SEM imaging revealed the irregular to prismatic shaped bridged particles composing the partly porous microstructure **Fig. 1.b**. Taking into account submicroscopic dimensions of particles and their coalescence a high specific surface may be predicted to zinc ions absorption, but their coalescence will affect to zinc ion insertion, and, consequently, to a capacity amount. The material's electrochemical properties are tested by cyclic voltammetry.

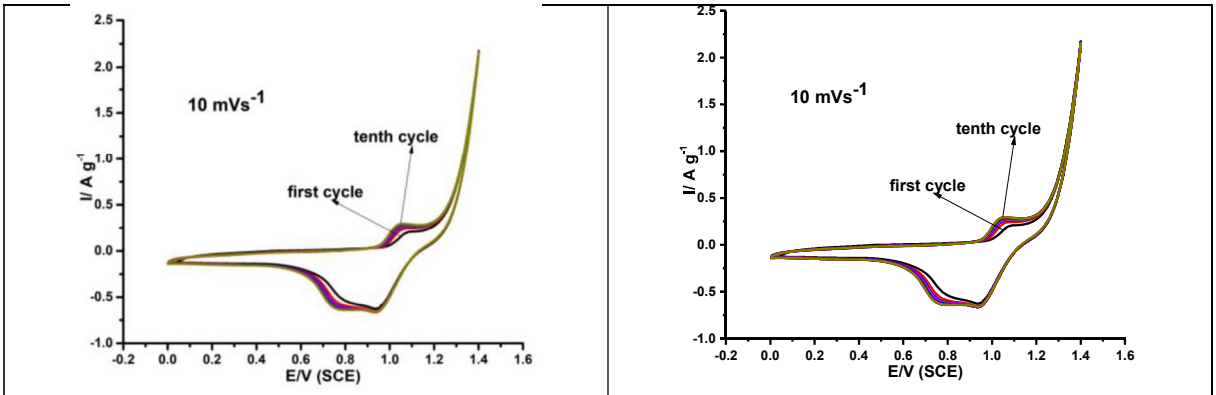

Figure 2. Cyclic voltamogrammes of $ZnMn_2O_4$ in $ZnCl_2$ solution at polarization rates of **a)** 10 mV s^{-1} **b)** 50 mV s^{-1}

Low, however, a stable capacity may be observed from **Fig. 2 a) and b)**. The average discharge capacity for 10 mV s^{-1} amounting to 10.33 mAh g^{-1}, as well as 4.1 mAh g^{-1} for 50 mV s^{-1} are low

compared to the theoretical capacity of the material, 224 mAh g^{-1}. Lower distance of the peaks for a lower rate means that the process of insertion and de-insertion of zinc ions is more reversible compared to a higher rate. The consequence is that distinction of anode and cathode peaks is higher for the higher rate (0.26V) compared to the lower rate (0.11V), as may be observed from **Fig 2.** In practice, these results show that the material may be used for low rates as well as for high rates. The reason for low capacity lies in the fact that the coalescence of the sub-micron particles gave rise in the total particle specific surface area reduction, thus amount of the inserted Zn ions is reduced. Zinc ions may be inserted and de-inserted only through the opened surface part of the particles. Since the low capacity values, the research needs to be directed to improve this disadvantage by doping the material with different metal, or using different salt aqueous solution.

CONCLUSION

This work presents the results of characterization of $ZnMn_2O_4$ cathode material synthesized using the glycine nitrate procedure. This material was characterized by XRPD showing the lattice parameters obtained were in a good agreement with the data reported in literature. The morphological characterization predicted a low capacity, due to the presence of sub-micron particles and their coalescence, that was proven by cyclic voltammetry, in the aqueous solution of $ZnCl_2$. Owing to the results obtained, the material might be used for both low and high rates. Research should be continued in order to improve the capacity by doping the material with some other ion, or using an aqueous solution of some other salt.

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