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Porous Zn/ZnO and Zn/ZnO/NiO nanosystems for potential application in Li-ion batteries

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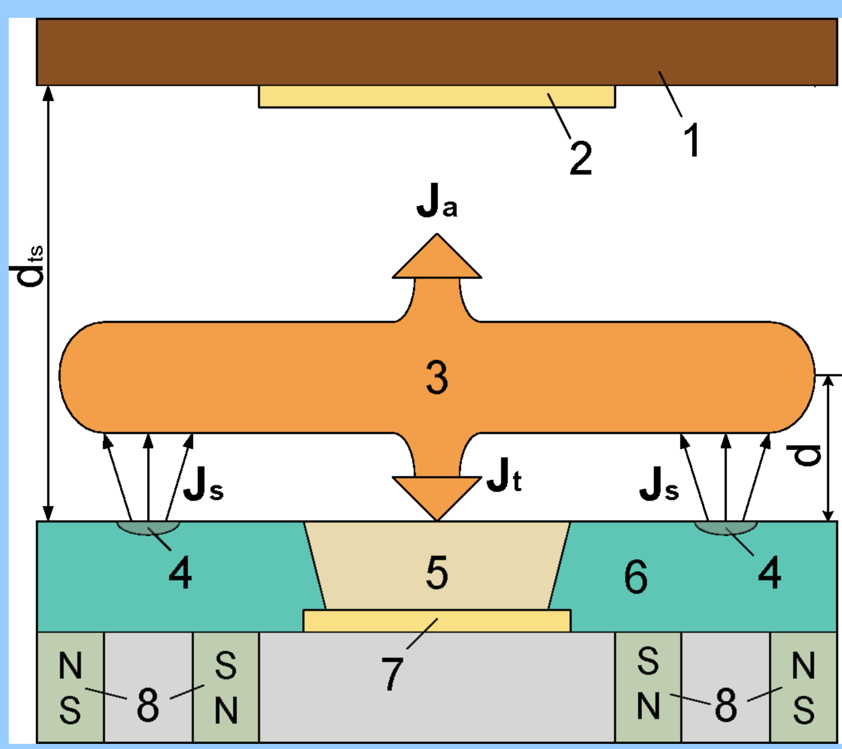
Abstract Over the past two decades, rechargeable lithium-ion batteries have been widely used as energy source for various types of modern electronics. In order to satisfy an increasing demand for batteries with higher energy densities, many researches have been devoted to the study of new electrode materials or the development of new nanostructures. It is known, that the size of the particles and their size distribution are important electrochemical parameters. Different metal oxides have significant prospects for applications as electrodes of efficient lithium-ion batteries. Among them are mainly tin oxide, zinc oxide, oxides of 3d-transition metals (Fe, Co, Ni, and Cu) or composite oxide materials. Thus, the aim of the proposed work is to develop the methods for producing composites, on the basis of ZnO/NiO nanosystems, and to study their structural-morphological characteristics and some features of charge transfer.

Near-equilibrium condensation conditions



1 - anode with heating substrate holder;
2 - substrate in the direct flows;
3 - diffusive source of the substance;
4 - erosion zone;
5 - hollow cathode;
6 - metal target;
7 - substrate in the reverse flows;
8 - magnetic system.

$$J_a \approx J_s(d/d_{ts}) \quad \text{and} \quad J_t \approx J_s(1-dd_{ts})$$

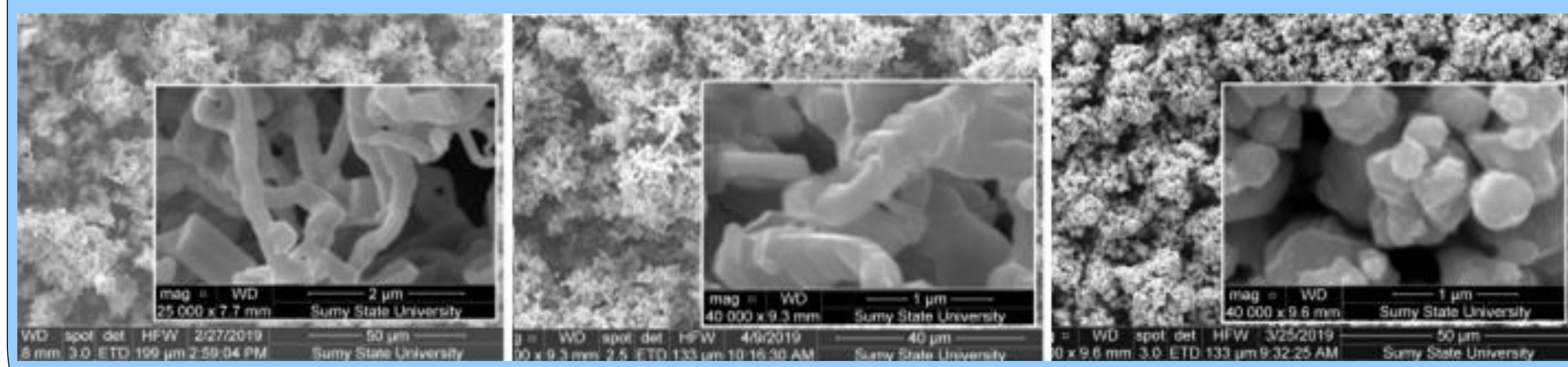
$$\Delta\mu = (\Omega_v - \Omega_c)(P - P_e) + (s_v - s_c)\Delta T$$

$$\Delta\mu, \xi \geq 0 \Rightarrow P, n, J_c \downarrow \quad T \uparrow \quad E_d \downarrow$$

Stages of nanocomposites formation

First stage

At the first stage, porous Zn systems have been formed under near-equilibrium stationary conditions. Prior to obtaining Zn porous systems, two-layer contact pads based on Cr and Au were deposited on laboratory glass substrates using two magnetron sputterer. Depending on the thechnological conditions three types of porous Zn layers were obtained on the contact pads.

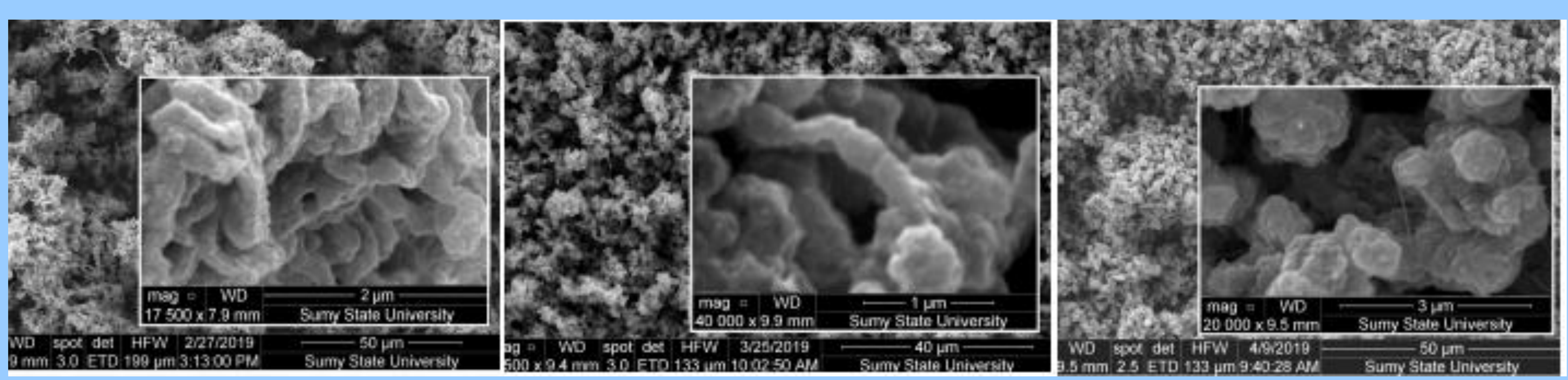


SEM images of Zn porous layers having different morphologies

Formation of Zn/ZnO nanocomposites

Second stage

Formation of Zn/ZnO nanosystems has been performed using two different methods. In the first case, reactive magnetron sputtering of Zn in a mixture of argon and oxygen (Ar 70%, O2-30%) at a temperature of 240 ˚C was used. The second variant of Zn/ZnO nanosystems formation is based on the surface layer oxidation of previously obtained porous Zn layers. The process of partial oxidation was carried out in an air atmosphere at a temperature of 350 ˚C for 0.5 hours.

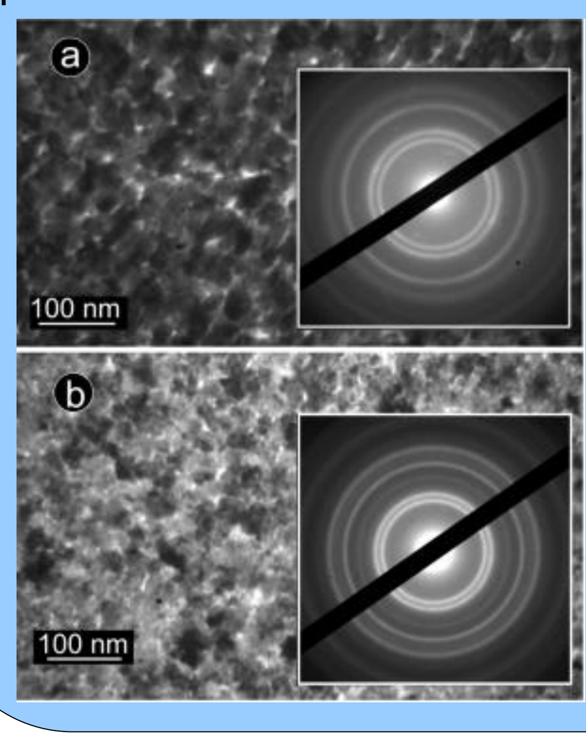


Structural and morphological characteristics of Zn/ZnO condensates after partial oxidation of Zn porous layers

Formation of Zn/ZnO/NiO nanocomposites

Third stage

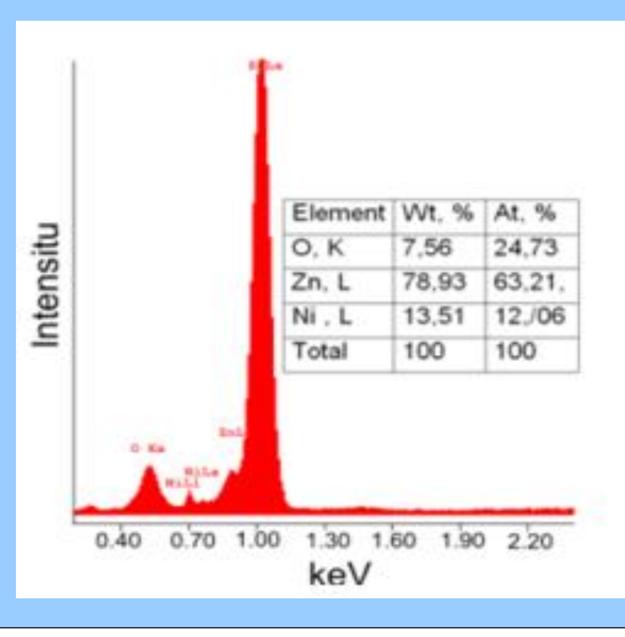
At the last stage, the nickel oxide film was deposited by means of magnetron reactive deposition in an oxygen-argon medium. The following technological parameters were used: the composition of the working mixture (35% O_2 and 65% Ar), the working gas pressure ~ 1.5 Pa, the substrate temperature ~ 240 ˚C and the power of the magnetron sputterer ~ 80 W.



TEM results
NiO (a)
ZnO (b)

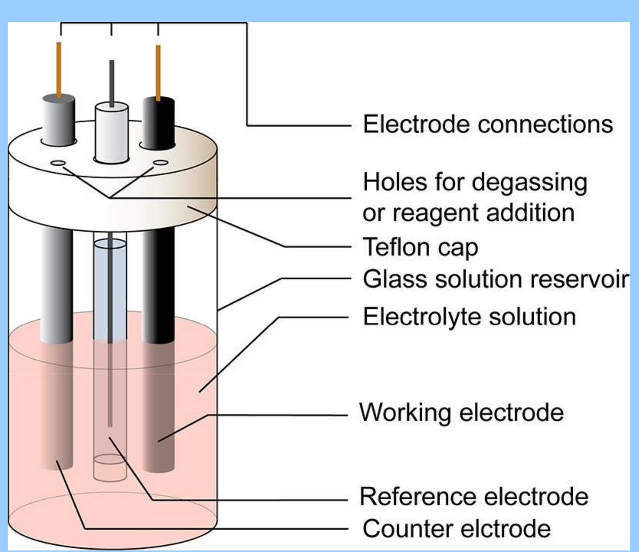
Zn/ ZnO/NiO

Elemental composition

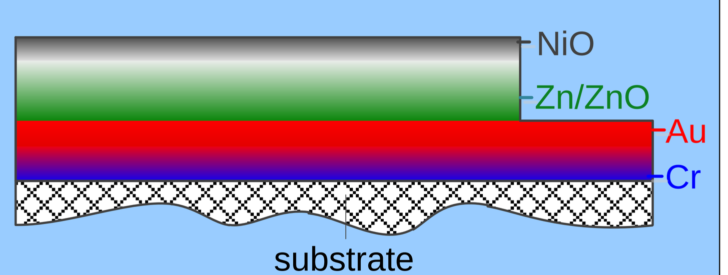


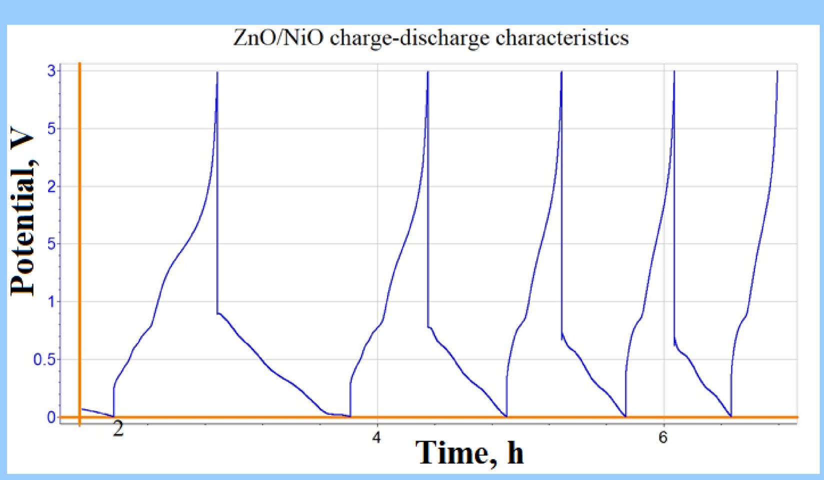
Element	Wt, %	At, %
O, K	7,56	24,73
Zn, L	78,93	63,21,
Ni , L	13,51	12,/06
Total	100	100

Electrochemical tests



Schematic representation of the cross-section of multilayer structure Cr/Au/Zn/ZnO/NiO





Electrochemical reactions on anode surface:

$ZnO + 2Li^+ + 2e^- = Li_2O + Zn$
$Zn + Li^+ + e^- = LiZn$
$NiO + 2Li^+ + 2e^- = Ni + LiO_2$

Conclusions

The work presents the physical principle and methodological features of the formation technology of two-layer Zn/ZnO and three-layer Zn/ZnO/NiO porous systems. At first, the structure formation mechanism of porous Zn systems under near-equilibrium stationary conditions is described together with some aspects of the technological process control using self-organization of the condensed vapors small supersaturations. Then, the subsequent oxidation and formation of ZnO nanosystems was carried out. At the final stage, NiO thin film was deposited on the ZnO layer surface. The possibility of reducing the total resistance of the multilayer systems by means of the incomplete oxidation of Zn basic porous layers or by depositing ZnO and NiO films has been shown, which is important for the practical application of the obtained layers to create electrodes of lithium-ion batteries. The phase and elemental compositions, as well as the structural and morphological characteristics of the Zn/ZnO and Zn/ZnO / NiO layers, have been optimized using scanning and transmission electron microscopy, energy-dispersive X-ray spectroscopy and X-ray phase analysis.

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