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ELECTROCHEMICAL SYNTHESIS OF ZnO NANOPARTICLES DURING ANODIC DISSOLUTION OF ZINC IN ALCOHOLS SOLVENTS

ELEKTROCHEMICZNA SYNTEZA NANOCZĄSTEK ZnO NA DRODZE ANODOWEGO ROZTWARZANIA CYNKU W ROZPUSZCZALNIKACH ALKOHOLOWYCH

Studies of the effect of the kind of alcohol, electrolyte concentration and water on the anodic dissolution of zinc and the nature of dissolution products were performed. The dissolution products were analyzed by spectroscopic methods (SEM/EDS, XPS and UV-vis) and X-ray diffraction. These studies have shown that the process of anodic dissolution of zinc in alcohol electrolytes (methanol and ethanol) in the presence of water (1-5% vol.), is a simple way to obtain ZnO nanoparticles.

Keywords: zinc, anodic dissolution, organic solvents, nanoparticles ZnO

Przeprowadzono badania wpływu rodzaju alkoholu, stężenia elektrolitu oraz zawartości wody na proces anodowego roztwarzania cynku i charakter tworzących się produktów roztwarzania w obszarze wysokich potencjałów. Do identyfikacji produktów anodowego roztwarzania wykorzystano spektroskopowe techniki badawcze (SEM/EDS, XPS, UV-vis) oraz metodę dyfrakcji rentgenowskiej. Badania te wykazały że proces anodowego roztwarzania cynku w alkoholowych elektrolitach (metanolowych i etanolowych) w obecności wody (1-5% obj.), jest prostym sposobem otrzymywania nanocząstek ZnO.

1. Introduction

Zinc oxide particles are used for many applications in the rubber and paint industries, catalysis and the production of varistors etc. Ultrafine ZnO particles are very transparent, and are used in the production of sunscreens, paints, varnishes plastics and cosmetics, especially for broad UV-A and UV-B blocking.

Morphology and properties of ZnO nanoparticles depend on their synthesis method. Until now, various techniques have been used for the preparation of ZnO particles, e.g. high temperature hydrothermal synthesis [1-3], laser heating [4] or high temperature decomposition method [5]. However, the high temperature methods are unfavourable because of high energy consumption. In contrast to these processes, the solution – based route has been recently wide developed [6-9] due to low temperature and large scale production of nanocrystalline ZnO. The electrochemical methods in different electrolytes were also used in a synthesis of ZnO nanoparticles and films [10-14].

Recently we have shown that colloidal solution of ZnO was formed as a result of anodic dissolution of zinc in ethanolic solution of LiCl, containing 1 to 5% vol. of water [15-17].

In the presented work, the influence of kind of alcohol solvent, anions and water content on anodic dissolution of zinc and forming of the final products (ZnO nanoparticles) has been investigated.

2. Experimental

Samples of zinc (99.9% Zn) were polished progressively from a 600 grit finish to a 1600 grit paper. Before electrochemical treatment electrodes were cleaned in anhydrous ethanol. Anodic properties of zinc were investigated using PGZ301 Voltalab potentiostat by means of potentiodynamic techniques. Investigations were performed at room temperature in anhydrous solutions of LiCl and LiClO₄, with methanol and ethanol solvent and in electrolytes containing 1-5% H₂O. The electrolytes

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have been deaerated by dried argon. The Ag/AgCl electrode was used as reference electrode.

The products of anodic dissolution were analysed by use of spectroscopic techniques (SEM/EDS, XPS, UV-vis) and X-ray diffraction method.

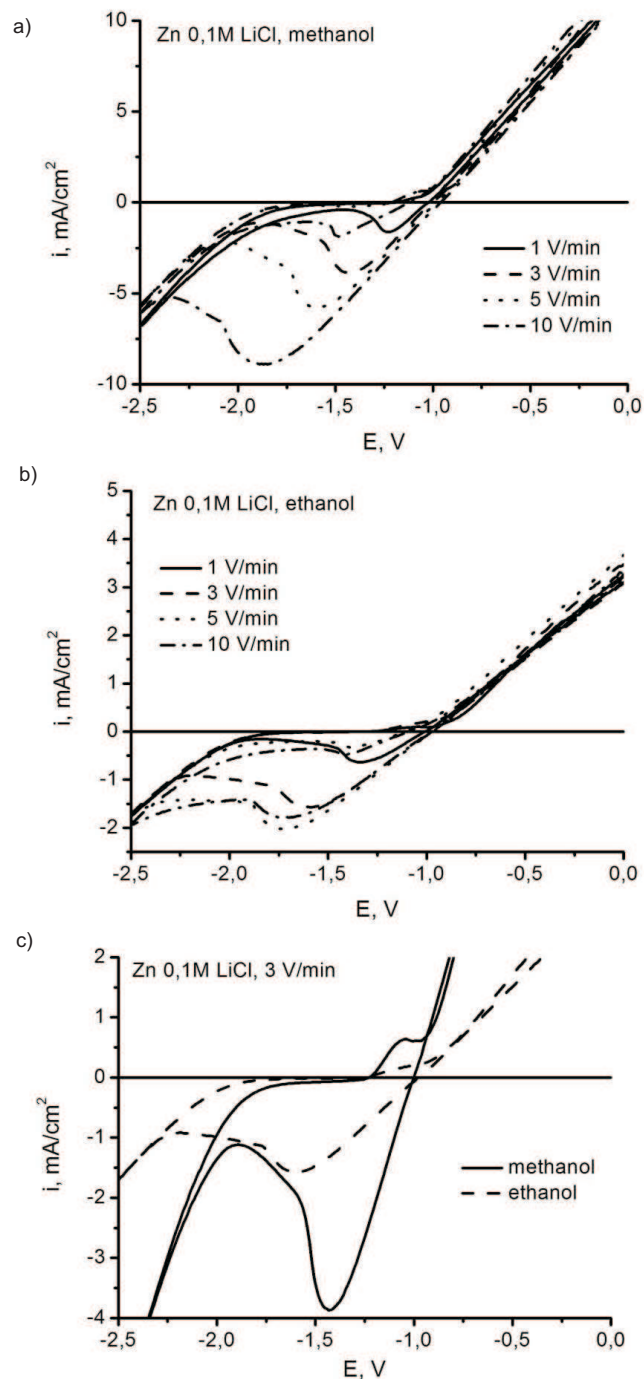
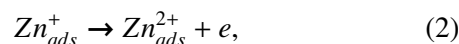
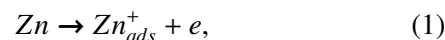


Fig. 1. Voltammetric curves (LSV) for zinc in alcohol solutions of lithium chloride, a) in methanol, b) in ethanol, c) compared

3. Results and discussion

Dissolution of zinc in anhydrous electrolytes with organic solvents, as well as in aqueous environments, proceed through a two-step, consecutive mechanism:



where the intermediate products Zn_{ads}^+ and Zn_{ads}^{2+} adsorb on the metal surface and inhibit its oxidation [18-21]. Little is known about the structure of the adsorbate.

Figures 1a, 1b and 1c show LSV polarization curves (Linear Sweep Voltammetry) of zinc in alcohol (methanol, ethanol) solutions of lithium chloride (0.1M).

The effect of kind of anion in both methanol and ethanol solutions is shown in Figures 2a and 2b.

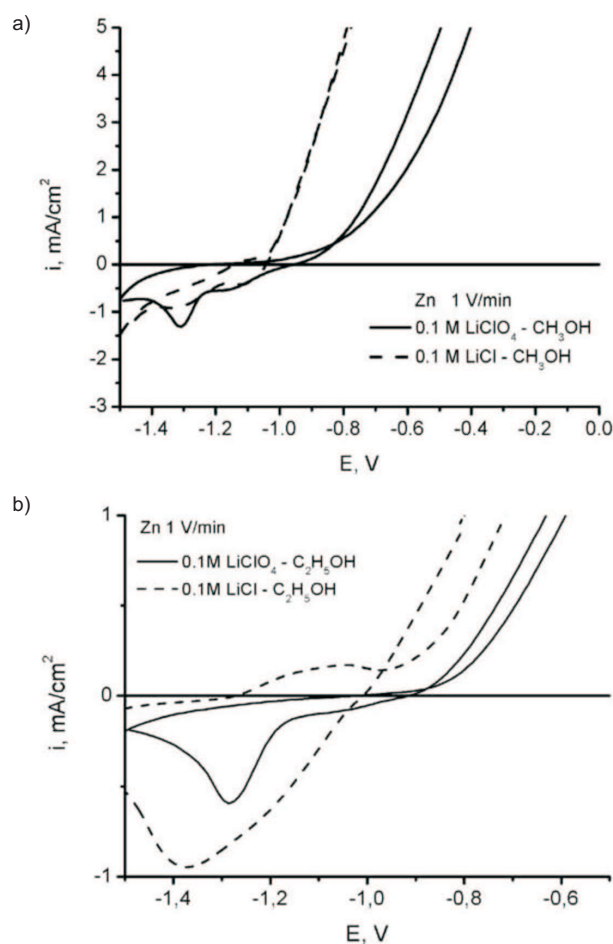


Fig. 2. Effect of the kind of anion on LSV curves, a) in methanol, b) in ethanol

Figures 3a and 3b present the effect of electrolyte concentration on course of the curves. On anodic branch-

es of the curves in methanol environments, similarly to ethanol media two different sections are observed [16]. At low anodic overvoltage polarization curve is relatively flat and at definite potential the anodic current rapidly increases. It correlates with two-step dissolution process.

Flat sections of the curves in the low potential areas, below the activation potential, are associated with solvent and the anion chemisorption, and the formation of poorly soluble, relatively stable, intermediate products of oxidation Zn (I). The product is adsorbing on the surface of metal, according to the summary reaction:



Participation of both the solvent (ROH) and the anion (A^-) in anodic oxidation of zinc, confirms the relationship between anodic current density and kind of alcohol (Fig. 1) and anion concentration (Fig. 3).

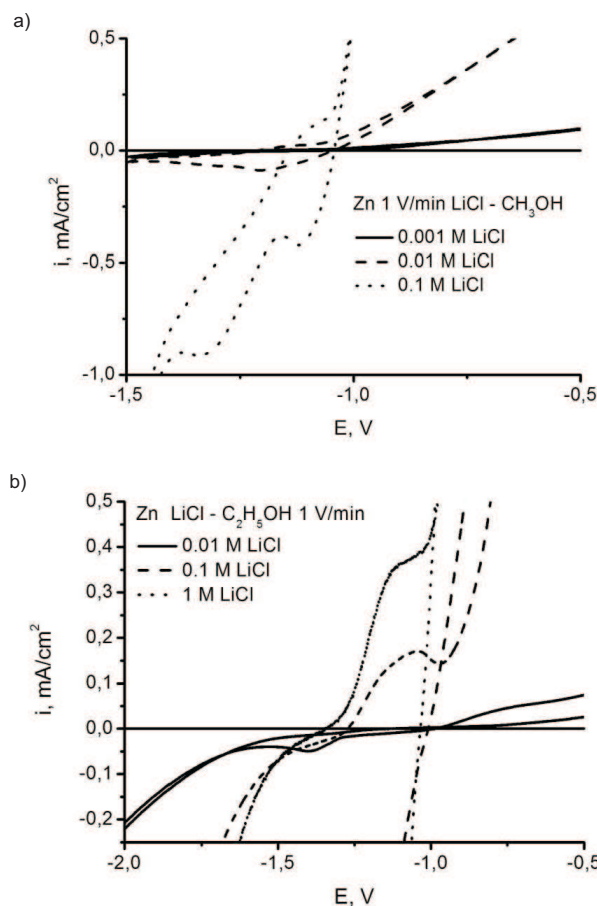
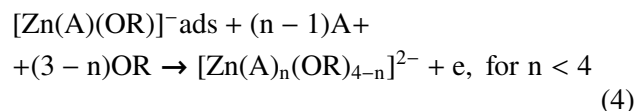


Fig. 3. Influence of the concentration of anion on LSV curves, in methanol, b) in ethanol

The intermediate products in methanol media show a much less stability than in ethanol electrolytes. It is confirmed by the shorter range of the flat section and higher anodic current density on the anodic curves in methanol environments (Fig. 1c).

The second section corresponds to oxidation of Zn (I) to Zn (II) and strong dissolution of metal [16,17,21]. The process occurs by the formation of soluble complexes coordinated by the anion and/or alcoholates groups according to generally reaction:



The increase of carbon chain length in alcohols causes decrease of anodic current and shifts the activation potential towards higher values (Fig. 1c).

Differences in anodic current density are also associated with the rate of the change of the ligand in complexes compounds and their various solubility.

The change of reaction order versus the anion with potential values (1,6 at -1,0V and 0,53 at -0,4V) supports the replacement of ligands in coordination sphere during anodic oxidation and dissolution processes.

It is known that an important factor changing the rate of metal anodic dissolution, in organic solvents with water content [16,17,22,23]. Generally the water addition, 1-5% vol. stimulate dissolution of zinc in both alcohols at low overvoltage. It is confirmed by LSV curves, shown in Figure 4a and b.

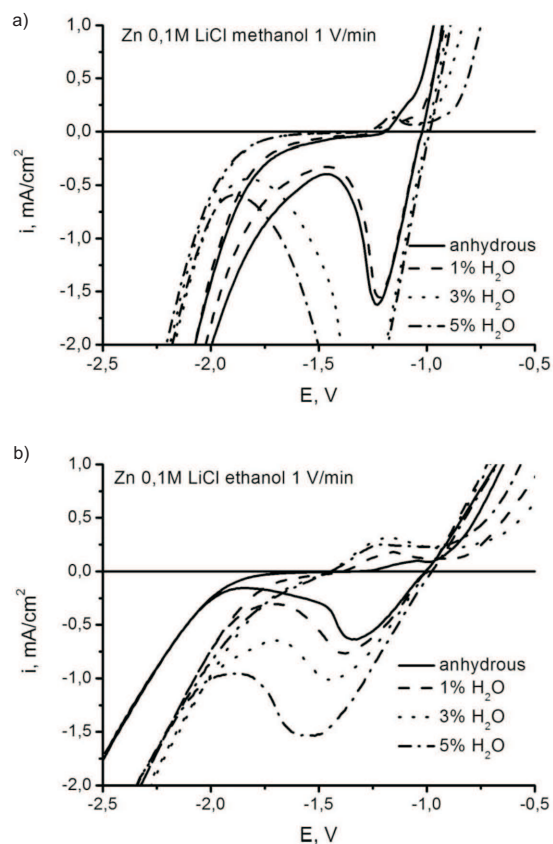
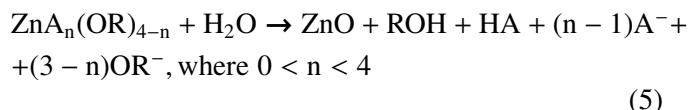


Fig. 4. Influence of water content on the polarization of zinc in ethanolic solutions of lithium chloride, a) in methanol, b) in ethanol

However, the water causes the drop of anodic current density in the second sections of anodic curves. Moreover, the presence of water strongly affects the nature of the final product. The molecules of water cause the change of ligands in the coordination sphere around the atom of zinc and finally lead to hydrolysis, according to the general reaction:



It is demonstrated by the white colloidal suspension (ZnO) formed in the both alcohol electrolytes, during polarization of zinc electrode. The formation of zinc oxide nanoparticles in both alcohol solutions of lithium chloride containing 5% vol. water, was confirmed by SEM/EDS, UV-vis, XPS and XRD analysis of products of anodic process (Figures 5-8 and Table 1-2).

However in alcohol electrolyte of LiClO_4 colloidal solutions of salts are forming, which is confirmed by XPS analysis results (Table 2).

Well-developed spherical nanoparticles are forming in methanol and ethanol solvent. SEM analysis did not allow to determine the exact size of nanoparticles. In ethanol solutions the size of nanoparticles did not exceed 10 nm [16]. A comparison of the morphology of nanoparticles (Figure 5 and 6) shows that the size decreases with increasing carbon chain length. It is the consequence of changes in energy effect of the system: metal-alcohol-electrolyte – water under influence of different kind of alcohols [24].

The UV-vis adsorption spectra for methanol and ethanol anolytes show a maximum respectively at wavelengths of 360 nm and 330 nm, assigned to colloidal solutions of ZnO nanoparticles [8,9]. Position of maximum for methanol media, confirms the highest size of ZnO nanoparticles in this environment [9].

EDS analysis of ZnO nanopowders produced during anodic polarization

TABLE 1

Solution	Zn [%]	O [%]	Cl [%]	Fe [%]	Cr [%]	Si [%]
0,1 M LiCl – CH ₃ OH + 5 %H ₂ O E = -0,4V, t = 4 h, T = 298K	17,6	24,8	9,5	33,8	13,3	0,8
0,1 M LiCl – C ₂ H ₅ OH + 5 %H ₂ O E = -0,4V, t = 4 h, T = 298K	8,9	10,3	15,9	40,8	14,9	2,1

The values of the photoelectrons energy in XPS spectrum of ZnO nanopowder

TABLE 2

0.1M LiCl-C ₂ H ₅ OH + 5% H ₂ O, at E=-0,4V, t=4h, T=298K				0.1M LiClO ₄ -C ₂ H ₅ OH + 5% H ₂ O, at E=-0,4V, t=4h, T=298K				References
Band LiCl	E _B exper. [eV]	Compounds and bands (literature)	Part [%at]	Band LiClO ₄	E _B exper. [eV]	Compounds and bands (literature)	Part [%at]	
Zn 2p	1022,86	ZnO	100	Zn 2p	1023,51	ZnCl ₂	100	1022,2 [24] 1023,0 [25]
O 1s	531,72	ZnO	61,5	O 1s	531,75	ZnO	4,72	531,5 [26]
	533,32	OH, H ₂ O	38,5		533,25	-O-C=O-, H ₂ O, O (oxyanion)	95,28	533,3 [27]
Cl 2p	199,59	Cl	100	Cl 2p	196,86	Cl	18,94	199,6 [25] 197,4 [24]
					198,83	Cl	53,22	198,8 [25]
					200,22	ClO _x	27,85	200,2 [28]

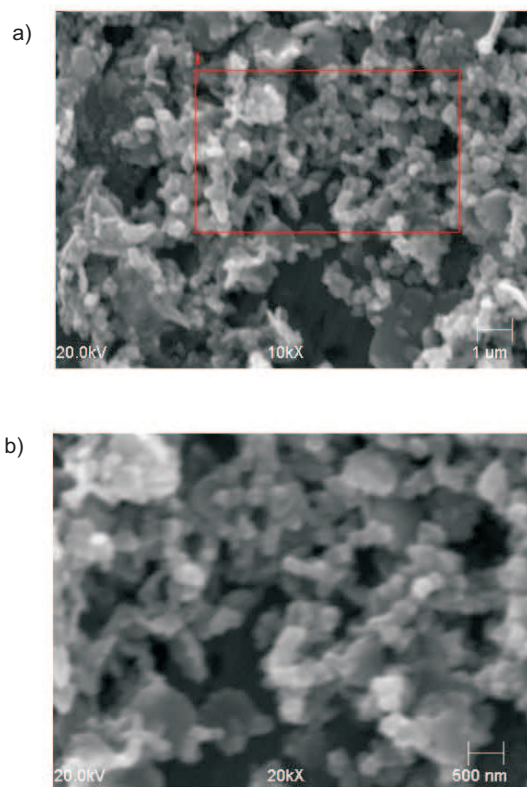


Fig. 5. SEM analysis of products of the anodic dissolution of zinc in 0.1 M LiCl-CH₃OH at E= -0,4V, t=4h, T=298K with 5% H₂O

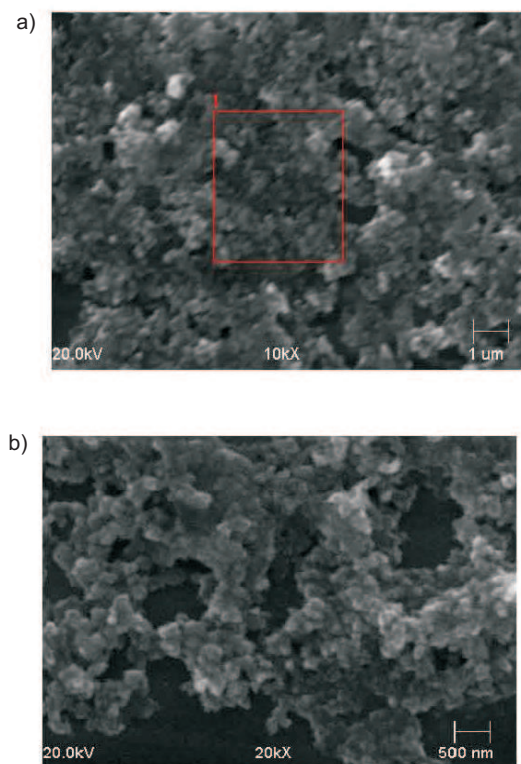


Fig. 6. SEM analysis of products of the anodic dissolution of zinc in 0.1 M LiCl-C₂H₅OH at E= -0,4V, t=4h, T=298K with 5% H₂O

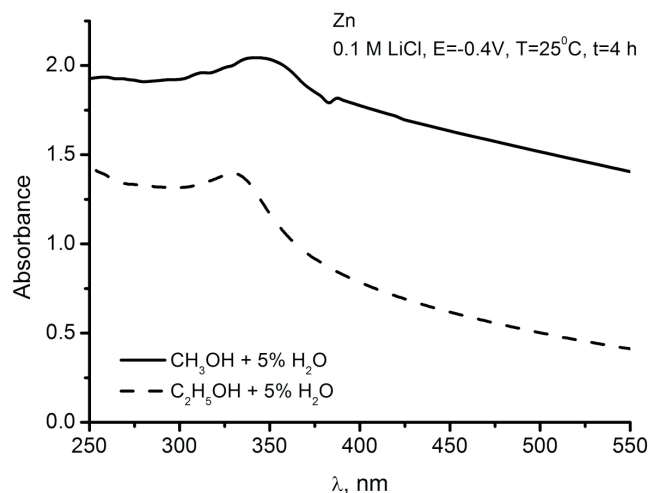


Fig. 7. UV-vis spectra of the colloidal solution of products of the anodic dissolution of zinc E= -0,4V, t=4h, T=298K w 0,1 M LiCl – in alcohols

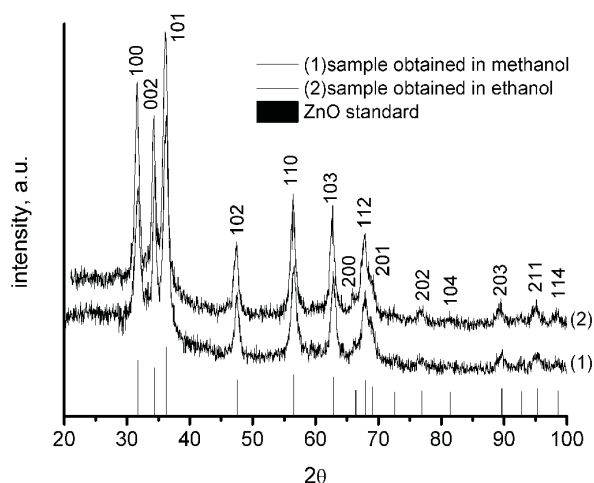


Fig. 8. XRD spectra of ZnO nanopowder

4. Summary

All analyzed parameters kind of alcohol, water and anion, significantly affect the rate of oxidation and dissolution of zinc, especially in the area of high potentials, as well as the nature of the products. The rate of anodic dissolution of Zn in methanol solvent is higher than in ethanol. As a result of anodic dissolution of zinc in both alcohol solutions of lithium chloride colloidal nanoparticles of zinc oxide were formed.

Chemical composition spectroscopic and X-ray diffraction analysis confirm the presence of ZnO nanoparticles in anolytes. Anodic dissolution of zinc in methanol and ethanol solutions of lithium chloride is a simple and easy process of synthesis of zinc oxide nanoparticles.

Acknowledgements

This work was supported by MNiSZW (the research grant Nr N N508 475538).

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