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Electrochemical Synthesis of ZnO Nanopowder Involving Choline Chloride Based Ionic Liquids

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The paper presents some preliminary experimental results regarding the electrochemical synthesis of ZnO nanopowders through anodic dissolution of Zn metal in choline chloride based ionic liquids. Electrolytes consisting in 10 mM $Zn(CH_3COO)_2x2H_2O$ dissolved in choline chloride-ethylene glycol or choline chloride-urea eutectic mixtures have been involved, with additions of 1-2 mL/L H_2O_2 30%. Current densities between 15 and 50 mA cm^{-2} were applied at electrolyte temperatures of 20-30 ^oC for durations between 3 and 5 h. XRD investigations showed the hexagonal wurtzite structure of ZnO, in agreement with other literature data. Crystallites average sizes of 12-18 nm have been determined for the anodically synthesized ZnO nanopowders. The addition of either TBAB or PVP determined a slight increase of crystallites sizes, from around 12-13 nm towards about 18 nm. According to SEM micrographs, the nanoparticles are approaching spherical shape with a slight agglomeration state, due to their small size.

The influence of the addition of different additives, such as tetrabutylammonium bromide or polyvinylpyrrolidone on the electro-synthesized ZnO nanopowder characteristics is also discussed.

1. Introduction

It is known (Moezzi et al., 2012) that zinc oxide powder has enjoyed a variety of uses in rubber and other large scale industries together with the use in chemical synthesis, cosmetics, medicine, zinc fertilizers and high technology applications as electronic ceramics, spintronics, solar cells, sensors and actuators. There are a wide variety of methods for ZnO preparation at low temperature (Gusatti et al., 2009), among them the electrodeposition in nonaqueous solvents (Swiatowska-Mrowiecka and Banàs, 2005) having special advantages as compared to aqueous solutions. However, ionic liquids have not been extensively used in the preparation of nanostructured metal oxide materials.

Azaceta et al. (2012, 2013) selected 1-butyl-1-methylpyrrolidinium bis(trifluuoromethanesulfonyl) imide ionic liquid as reaction media at 100-150^{0}C for the electrodeposition of ZnO based hybrid films; zinc bis(trifluoromethane-sulfonyl) imide and either bubbled oxygen or N-butyl-N-methyl pyrrolidinium nitrate were used as precursors.

Harati et al. (2012) has reported the electrochemical preparation of ZnO thin films in a deep eutectic ionic liquid based on choline chloride – urea (1:2) mixture containing zinc perchlorate as one of the precursors and Mo/glass substrate as substrate. Differential pulse voltammetry (DPV) were carried out in the above electrolyte at 90^{0}C, in the absence and presence of oxygen. Transparent and uniform ZnO film was cathodically deposited on Mo at -1.500 V (vs. ferrocene reference) and this process was explained by reaction of zinc cations with the generated superoxide ions from reduction of dissolved oxygen; zinc oxide film can be formed through a peroxide route. The influence of the electrodeposition duration up to 120 min on the film morphology properties was investigated. UV-vis absorption spectra, EDX, XPS, Raman, and XRD results confirmed the possible of these ZnO films for applications in thin film solar cells.

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In this paper we report a new route to obtain ZnO nanocrystalline powder from the eutectic ionic liquid based on choline chloride (1:2 molar mixtures with – ethylene glycol or urea) in which dihydrated zinc acetate and hydrogen peroxide were added. The ZnO powder was prepared at room temperature (20-25 ^{0}C) involving zinc sacrificial anode as working electrode. It is known that eutectic ionic liquids containing choline chloride are good solvents for many metal oxides, such as CuO, NiO, and especially ZnO (Abbott et al., 2006; Tian and Hua, 2010). However, the solvent property of the ChCl-EG toward ZnO will be lost when the electrolyte contains water as is our case, showing no solvation ability toward ZnO. This would result in the nucleation and growth of ZnO to lead to the formation of ZnO nanostructures (Dong et al., 2010).

2. Experimental Part

To perform experiments, choline chloride-based ionic liquids were synthesized as shown in Table 1.
Choline chloride ($HOC_2H_4N(CH_3)_3Cl$) (ChCl) (99 %), ethylene glycol (EG) (99.5 %), urea (NH_2CONH_2) (99.5 %), hydrogen peroxide (H_2O_2) (30 wt. % in water), zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) (ZnAc) (98 %), tetrabutylammonium bromide ($C_{16}H_{36}BrN$) (TBAB) (≥ 98 %), poly (N-vinyl-pyrrolidone) with a molecular weight of 55000 (PVP), were used as received. The eutectic mixtures have been prepared by mixing and heating reagents in the stated proportions at a temperature in the range 80 ^oC -100 ^oC, with gentle stirring until a homogeneous, clear liquid was formed.

Table 1: Ionic liquids systems involved in ZnO electrochemical synthesis

Nr. crt.	System type	Electrolyte composition
1.	ILEG-H_2O_2-ZnAc	ILEG (ChCl:EG 1:2 molar ratio) + 0.01M $Zn(CH_3COO)_2 \cdot 2H_2O$ + 1.5 mL/L H_2O_2
2.	ILEG -TBAB	ILEG (ChCl:EG 1:2 molar ratio) + 0.01M $Zn(CH_3COO)_2 \cdot 2H_2O$ + 1.5 mL/L H_2O_2 + 5 mM of TBAB
3.	ILEG-PVP	ILEG (ChCl:EG 1:2 molar ratio) + 0.01M $Zn(CH_3COO)_2 \cdot 2H_2O$ + 1.5 mL/L H_2O_2 + 7 g/L PVP
4.	IL	IL (ChCl:urea 1:2 molar ratio) + 0.01M $Zn(CH_3COO)_2 \cdot 2H_2O$ + 1.5 mL/L H_2O_2

The electrochemical synthesis experiments were performed in stationary conditions and in an open system (with the electrolyte in contact with air and atmospheric humidity), using a DC power supply (0-5 A, 0-60 V) and a two electrode configuration. Pure Zn strips have been used as sacrificial anode and a Pt sieve as cathode. The ratio of anodic to cathodic area was 1:1. Current densities between 15 and 50 mA cm^{-2} were applied at electrolyte temperatures in the range of 20-30 ^oC for durations between 3 and 5 h. After Zn anode dissolution, 30-50 mL of water has been added to the electrolyte. The formed white precipitate has been washed with deionized water and ethanol and then subjected to centrifugation at 4000 rpm for 15 min. This sequence has been followed by drying at 105 ^oC for 3 h and calcination at 300 ^oC for 1 h to obtain nano-ZnO powder. Faradaic efficiency was also determined.
To obtain information on the composition and structure of the nanosized TiO_2, X-ray diffraction (XRD) was studied by a Rigaku Ultima IV diffractometer with graphite diffracted beam monochromator for CuK_α radiation (λ = 1.5406 Å), at a speed of 2 s/step (1step = 0.05^0). The nanopowder morphology was analyzed by scanning electron microscopy (SEM) associated with energy-dispersive X-ray (EDX) analysis involving a FESEM-FIB Auriga equipment (Carl Zeiss Germany) and a INKA-ENERGY 250 detection probe, respectively. The UV-VIS absorption spectra were recorded from 200 to 700 nm on dry nanopowder samples using a JASCO 570 UV-VIS spectrophotometer with an integrating sphere. Anodic behavior of Zn electrode in choline chloride based ionic liquids has been carried out invloving cyclic voltammetry and chronoamperometry, using a three electrode glass cell with a Zn rod as working electrode (ϕ 7 mm) having an exposed constant geometrical area of 0.38 cm^2, a Pt counterelectrode and a Ag wire quasi-reference electrode. The reference and counter electrodes were directly immersed in the solutions without using a separate compartment. The working electrode was polished with 0.3 µm alumina paste, rinsed and dried prior to all measurements. The cyclic voltammetry studies were performed using an Autolab PGSTAT 12 potentiostat controlled with GPES software at sweep rates between 10 and 50 mV s^{-1}. Chronoamperometric measurements (I-t curves) have been recorded for different applied voltages, involving the same three-electrode cell.

3. Results and Discussion

Usually, after anodic dissolution of Zn electrode in the above mentioned electrolytes, some amounts of water were directly added to the ChCl based ionic media to facilitate the formation of the white precipitate. The obtained ZnO powders after the applied thermal treatment were white. However, when ILEG-PVP system was involved, a dark grey tone was evidenced. Faradaic efficiencies of 85-92 % were determined in ILEG based electrolytes whereas slightly higher values, in the range of 90-95 % were calculated in the case of IL one. During electrochemical process, approx. 5-7 % of the anodically dissolved Zn was deposited onto the cathode, in the case of ILEG and IL systems. The addition of TBAB or PVP significantly diminished, respectively hindered the deposition phenomenon (up to 0.1-0.2 % of the dissolved Zn in the presence of TBAB, zero percentage when PVP was added).

In order to get information on the electrochemical behavior of Zn electrode in the proposed choline chloride based ionic liquids electrolytes, cyclic voltammograms have been recorded at 25 ^{o}C in the precursors (pure ILEG, ILEG-H_2O_2, ILEG_ZnAc) and in the full electrolyte (ILEG-H_2O_2-ZnAc). For the sake of clarity Figure 1 presents the CV curves in the case of pure ILEG and the full electrolyte, ILEG-H_2O_2-ZnAc. As illustrated in Figure 1 curve 1, a large oxidation peak on the anodic branch (or a plateau) is evidenced during scanning starting from the stationary potential. This peak is centered at around -0.5 V for pure ILEG and at approximatively -0.8 V for ILEG-ZnAc system (not shown here). The peak magnitude remained almost the same, regardless the applied scan rate or the number of cycles. By extending the anodic scan up to +2 V, a continuous increase of current was recorded, reaching the same maximum current values of 34-38 mA at any scan rate. By reversing the scan in cathodic direction, the current decreased on an identical route as in the forward scan.

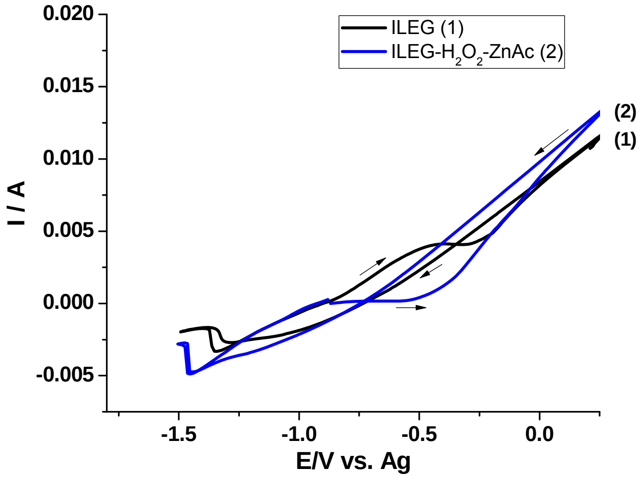

Figure 1: CV curves of Zn working electrode in different choline chloride based ionic liquids systems (scan rate: 50 mV s^{-1}, 25^{o}C) (S_{WE} = 0.38 cm^2)

According to the literature (Stypula et al., 2011; Swiatowska-Mrowiecka and Banàs, 2005), it is supposed that within the first part of potential scan, from -0.8 V to -0.3V, Zn metal electrochemical dissolution takes place producing univalent Zn^+ cations which are closely adsorbed onto the zinc anode surface, according to Eq(1):

$$Zn - e \rightarrow Zn^{+}_{ads} \quad (1)$$

In the next portion, along the linear portion of anodic branch and reversing scan, it is clear that a massive production of zinc ions occurs due to high polarization values. The processes taking place in this part of CVs may be described as both subsequent oxidation of Zn^+ intermediate cations and electrochemical dissolution of Zn atoms from metallic anode, according to Eq(2) and Eq(3):

$$Zn^{+}_{ads} - e \rightarrow Zn^{2+} \quad (2)$$

$$Zn - 2e \rightarrow Zn^{2+} \quad (3)$$

Oppositely, CV curves for ILEG + H_2O_2 and ILEG + H_2O_2 + ZnAc systems did not exhibit any anodic peak and the current increased continuously by scanning up +2 V anodic potential limit and an exact route on reversing scan is recorded. An example is illustrated in Figure 1 curve 2. This behavior suggests that the H_2O_2 addition completely inhibits the processes (1) and (2) and only massive electrochemical dissolution of zinc anode takes place (process (3)).

It is worth to mention that at the end of cathodic branch of all voltammograms the small peak which appears within -1.35V to -1.45 V potential range (see also Figure 1) may be ascribed to the electroreduction of new formed Zn^{2+} cations, according to Eq(4):

$$Zn^{2+} + 2e \rightarrow Zn \quad (4)$$

However, the position and amplitude of these cathodic peaks do not depend substantially on scan rate or cycling, but depend on the nature of the ionic liquid system, respectively on the H_2O_2 content (1-2 mA in the absence and 4-5 mA in the presence of H_2O_2). This is another support for a favorable influence of H_2O_2 to Zn^{2+} production.

Based on the above observations, it can be supposed the mechanism for the reaction process in investigated H_2O_2 containing ionic liquids involves a simultaneous oxidation of the peroxide ion (O_2^{2-}) together with the electrodissolution of Zn metal. The new formed species, superoxide ion (O_2^-) and Zn^{2+} ion proceed to precipitate zinc oxide according to Eq(5), with zinc superoxide (ZnO_4) as intermediate species (Azaceta et al., 2009):

$$Zn^{2+} + O_2^- \rightarrow ZnO_4 \rightarrow ZnO_2 + O_2 \leftrightarrow ZnO + 3/2\ O_2 \quad (5)$$

Figure 2 presents typical current versus time curves for Zn working electrode recorded at different applied potentials using ILEG-H_2O_2-ZnAc electrolyte. The anodic current had initially a maximum value, which is attained in the first 40-50 s when the applied potential belongs to the plateau region (E = -0.66V, E=-0.2V) and in the first 5 s when it is situated on the massive Zn dissolution zone (E = 0.5V). Then it attains a quasi-constant value which depends on the applied potential.

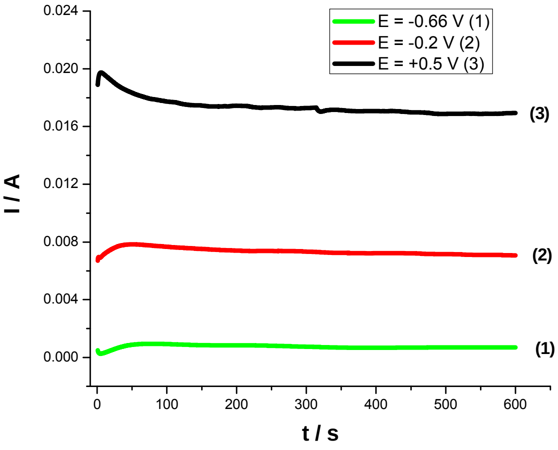

Figure 2: I-t curves for Zn working electrode in ILEG-H_2O_2-ZnAc electrolyte for different values of the applied potential ($t = 25\,^{O}C$; $S_{WE} = 0.38\ cm^2$)

Figure 3 presents the XRD patterns of ZnO powder anodically synthesized in different choline chloride based ionic liquids systems.

All observed peaks correspond to the hexagonal wurtzite structure of ZnO (according to the standard card JCPDS 00-036-1451), in agreement with other literature data (Flickyngerova et al., 2008). No other peaks related to other potential impurities compounds resulting from decomposition of ionic liquids were evidenced. All the obtained nanopowders exhibit the highest intensities of crystal growth orientation on the (101) plane, located at 36.3 °. The crystallites average sizes of 12-18 nm have been determined using the well-known Scherrer equation:

$$d = \frac{0.9\ \lambda}{\beta\ \cos\theta} \tag{6}$$

where: λ is X-ray wavelength, θ the diffraction angle and β the half width at half height for the diffraction peak. The addition of either TBAB or PVP determines a slight increase of crystallites sizes, from around 12-13 nm towards about 18 nm.

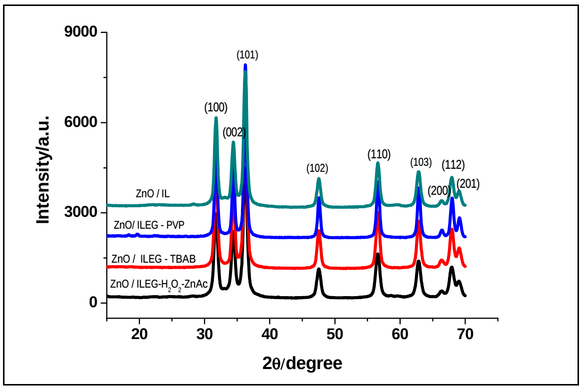

Figure 3: X-ray diffractograms for ZnO powder anodically synthesized in different choline chloride based ionic liquids systems

SEM micrographs, as exemplified in Figure 4, suggested that the nanoparticles are approaching spherical shape having crystallite sizes of about 15-31 nm, relatively similar to the calculated values from XRD patterns. It may be noticed a slight agglomeration state of the nanoparticles in the SEM images, due to their small size.

EDX spectra of the anodically obtained ZnO nanopowder (not shown here) revealed the fact that oxygen is slightly higher than zinc.

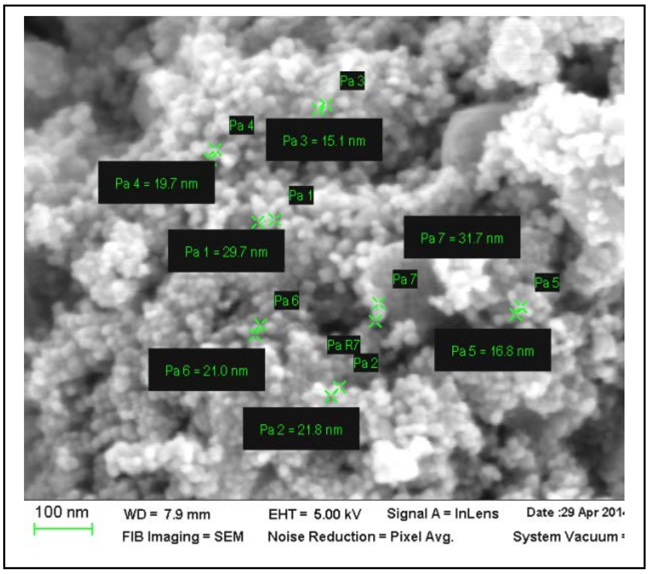

Figure 4: SEM micrograph of ZnO nanopowder anodically synthesized in ILEG electrolyte after the applied thermal treatments at 105 °C for 3 h and 300°C for 1 h

4. Conclusions

It has been reported the successful electrochemical synthesis of ZnO nanopowders involving anodic dissolution of zinc electrode in in choline chloride-ethylene glycol or choline chloride-urea eutectic mixtures with additions of hydrogen peroxide.

This is an easy and efficient procedure allowing faradaic efficiencies of minimum 85 % for applied current densities between 15 – 50 mA cm^{-2} and operating temperatures of 20-30 °C .

The cyclic voltammetry investigations showed a continuous increase of current during anodic scan, assigned to a continous dissolution of metallic Zn and simultaneous oxidation of the peroxide ion (O_2^{2-}); both formed species precipitate as ZnO. XRD investigations showed the hexagonal wurtzite structure of ZnO, in agreement with other literature data. Crystallites average sizes of 12-18 nm have been determined for the anodically synthesized ZnO nanopowders. The addition of either TBAB or PVP determined a slight increase of crystallites sizes, from around 12-13 nm towards about 18 nm. According to SEM micrographs, the nanoparticles are approaching spherical shape with a slight agglomeration state, due to their small size.

Further investigations will be performed, for a better understanding of ZnO nanopowders electrochemical formation mechanism associated with the obtained structural characteristics, as an important factor to influence their potential applications, to establish an industrially compliant technological process.

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