Ionic liquid based cathodic electrodeposition of metal oxides for energy field applications.

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Metal oxide nanostructured thin films are promising materials in different areas of the energy field such as photovoltaic cells [1], energy storage [2] and saving (e.g. light emitting diodes [3]). Among different deposition methods, electrochemical deposition is an attractive cost-effective method to obtain thin films materials. Various metal oxides can be deposited from the electroreduction of oxygen in aqueous electrolytes (*equation 1)* [4,5]. However, the production of hydroxides as intermediate species in this process limits the technique. Traces of OH- may remain in the metal oxide. In other cases, the metal oxide cannot be obtained due to the deposition of the metal hydroxide as stable phases [6,7].

$$O_2 + H_2O + 4e^- = 4(OH)^- \qquad (1)$$

$$M^{2+} + 2(OH)^- = M(OH)_2 = MO + H_2O \qquad (2)$$

In this work, we present an electrochemical route for the deposition of metal oxides from aprotic N-buyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide ionic liquid (PYR14TFSI) based electrolytes [8]. The new approach is based on the electrochemical reduction of O_2 in a solution containing metal bis(trifluoromethanesulfonyl) imide salt. The metal oxide is formed from the reaction of the metal cation (M^{2+}) and superoxide species (O_2^-) generated from the O_2 reduction (*equation 3)*. Since no OH- are involved in the process, the formation of metal hydroxide phase is avoided.

$$O_2 + e^- = O_2^- \qquad (3)$$

$$M^{2+} + 2O_4^- = MO_4 = MO + 3/2O_2 \qquad (4)$$

The presentation will be focused on the electrodeposition of two different metal oxides:ZnO and NiO. The mechanisms involved in both deposition processes were analyzed by cyclic voltammetry. The physico-chemical properties of the obtained thin films were analyzed by X-ray photoelectron spectroscopy (XPS), X-ray diffraction spectroscopy (XRD), optical spectroscopy and Scanning Electron Microscopy (SEM). NiO thin films were successfully electrodeposited [10] proving the potential of the present approach to deposit metal oxides, which are not possible to obtain in aqueous electrolytes [7]. On the other hand, ZnO nanocrystalline films with innovative microstructural properties in comparison to those generally obtained in aqueous media [9]. It is worth to highlight the wide range of morphologies obtained by just varying the electrodeposition parameters such temperature or zinc salt concentration, (Figure 1). In this context, the influence of the interaction between ionic liquid moieties and metal oxide surfaces on the crystal growth will be discussed.

Finally, ZnO-NiO heterostructures have been obtained by a sequential electrodeposition of zinc and nickel oxide films. Current-voltage characteristics show good rectifying behavior, suggesting the n-p heterojunction formation.

All in all, an innovative electrochemical route based on aprotic ionic liquids electrolytes to obtain nanocrystalline films of different metal oxides, avoiding metal hydroxide formation, will be presented. The peculiar properties of the obtained metal oxide films open wide possibilities for the integration of metal oxides in a new generation of optoelectronic devices and their application in the energy field.

References

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Figures

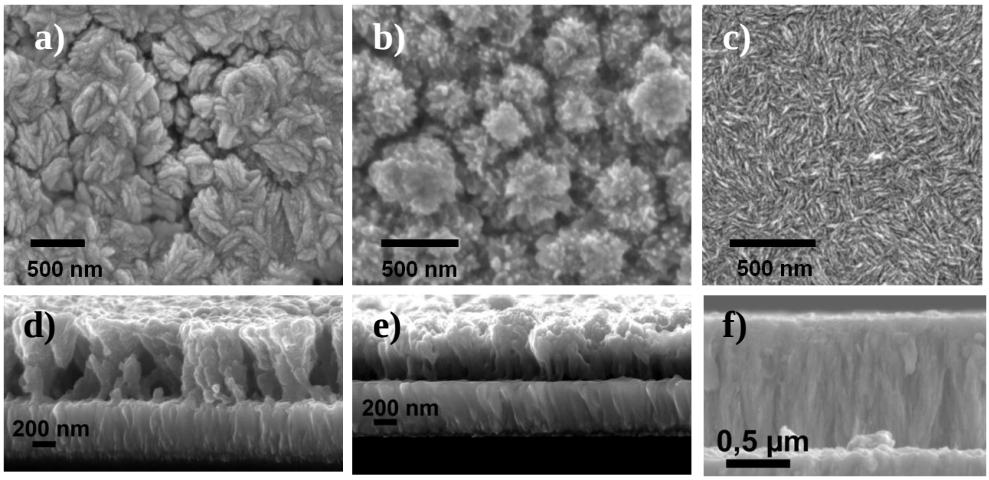

Figure 1: SEM micrographs of the top view (a, b and c) and cross sections (d, e and f) of ZnO films obtained under different electrodeposition conditions.

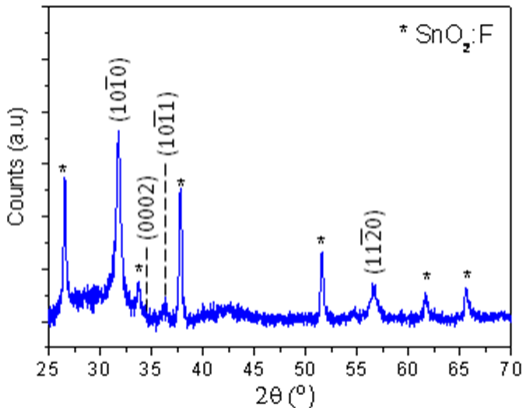

Figure 2: XRD pattern of ZnO films obtained from Pyr14TFSI based electrolytes.