Electrodeposition of metal oxides for electrochemical systems in ionic liquids

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Ionic Liquids, thanks to their high electrochemical and thermal stability, stand as an alternative promising medium to water in the field of electrochemistry[1]. Such attractive characteristics have so far been widely exploited for the electrodeposition of metals and semiconductors[1] and very recently for binary compounds like CuS[2]. The electrodeposition is an especially attractive method for the synthesis of electrode active materials, especially for microbatteries, thanks to the conformal deposition providing very good electric contact between current collector and active material.

Reduction of Oxygen and formation of stable superoxide/peroxide ions in ionic liquid enabled the synthesis of metal oxides such as NiO[3], ZnO[4] and CeO$_2$[5]. We have used this opportunity to electrodeposit oxide-based materials for electrochemical systems. Fundamental studies have been performed on the simple system Zn^{2+}/O$_2$ to check the behavior of oxygen reduction in the presence of metallic cations as well as the influence of different parameters on deposition (nature of Ionic Liquid, substrate, deposition potential, time and temperature as well as concentration of electroactive species and water content). Electrochemical Quartz Crystal Microbalance measurements[6] were performed to probe the type of reactions taking place at the electrode in real time.

Different morphologies and crystal orientation of the ZnO deposits have been obtained depending on the chosen electrodeposition conditions. Smooth thin layers, well crystallized and <hk0> oriented, have been synthesized at 100 °C, while by electrodeposition from other solutions (water or DMSO) either orientation <00l> or lack of any orientation is observed[7].

The EQCM measurements helped incredibly in solving the electrochemical mechanism of O$_2$ reduction in the presence of Zn^{2+}. When the electrodeposition is done at low potential, such measurements have shown competing processes associated to the reduction of zinc cations and molecular oxygen (Figure 1).

Based on the fundamental studies on ZnO, the acquired knowledge was implemented in other oxide systems capable of possessing multiple oxidation states (for example, Co^{2+}/O$_2$, Cu^{2+}/O$_2$ or Mn^{2+}/O$_2$). In this talk the main results on Zn^{2+}/O$_2$ system and comparison with other systems will be presented.
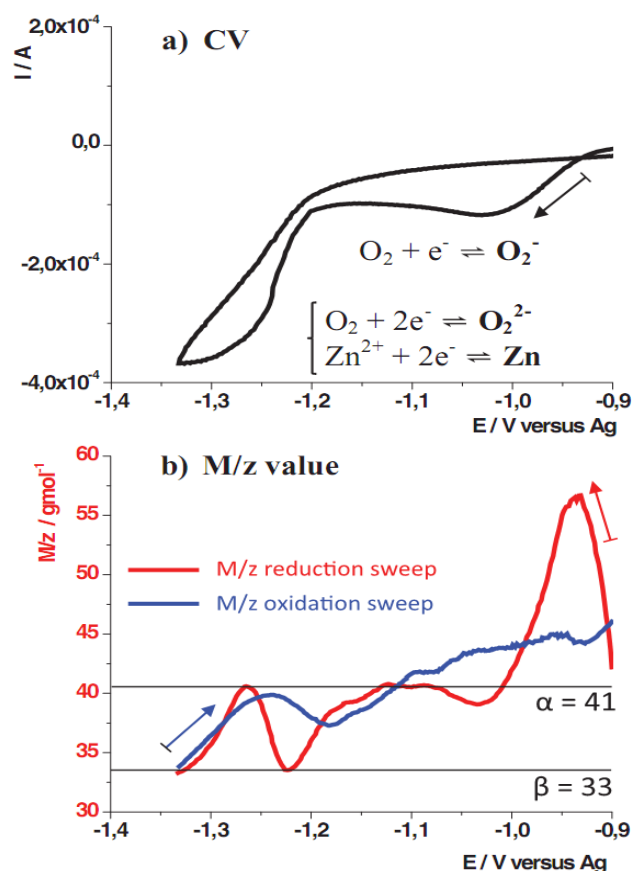

Figure 1: EQCM measurements: a) I versus E curve, b) M/z function versus potential, red (reduction sweep) and blue (oxidation sweep) curves. 0.12M Zn(TFSI)$_2$ solution under O$_2$ atmosphere. α corresponds to ZnO deposition, β corresponds to Zn deposition. T = 100 °C, WE – Pt on quartz, CE –Pt, RE-Ag, scan rate 2 mV·s^{-1}.

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