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Electrochemical and surface studies of the effect of naphthalene-based additives on tin electrodeposition

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Summary and outlook

Tin electrodeposition applications have rapidly evolved in the past 25 years. Usage of tin coatings has advanced from being mainly used for corrosion protection and decorative purposes, to being used in modern technology such in electronic devices, photovoltaic cells and Li – ion batteries. The new tin coating applications have also come with challenges that require the production of nanostructured deposits, multilayers coatings and composites. Furthermore, the need to reduce energy and source consumptions, and the implementation of more environment-friendly processes, require detailed and fundamental knowledge of the electrodeposition process.

The emphasis throughout this thesis is therefore to obtain detailed mechanistic information of tin electrodeposition process. The experimental and theoretical work presented in this thesis attempts to understand the mechanism of tin electrodeposition, and the effect of electrolyte anions and naphthalene-based additives, during the early and subsequent stages of the process. The experimental approach includes conventional electrochemical techniques, in-situ spectro-electrochemical and ex-situ microscopy techniques, and density functional theory studies.

Chapter 1 presents an introduction to the tin electrodeposition process, including its history and evolution. The composition of the electroplating baths is highlighted, as it is basic in the understanding of the tin electrodeposition process.

In Chapter 2, we study the tin electrodeposition mechanism on polycrystalline gold electrodes from two different electrolytes: sulfuric and methanesulfonic acid. We show the presence of at least three different tin deposition mechanisms on gold: irreversible adsorption, underpotential and overpotential deposition. Furthermore, evidences of the intricate tin underpotential deposition on gold are presented, associating it with island formation and surface alloying. We also compare the effect of sulfuric and methanesulfonic acid on the tin electrodeposition, showing that the coverage of underpotential deposited tin in the presence of methanesulfonic acid is slightly higher than in sulfuric acid. We demonstrate that kinetics of tin bulk electrodeposition in methanesulfonic acid are slower than in sulfuric acid, presumably due to Sn-MSA complex formation. Additionally, the lower tin deposition rate in methanesulfonic acid also leads to a more homogeneous coverage of the gold by tin. Moreover, our results show that Au-Sn surface alloy formation is more prominent in the presence of methanesulfonic acid, concluding that the lower deposition rate leads to a relatively more prominent surface alloying.

With the mechanism of tin electrodeposition on polycrystalline gold electrodes and the effect of sulfate and methanesulfonate anions studied, and the assignment of the peaks in the voltammetric profile done, we extended our study and focus on the effect of naphthalene-

Summary and outlook

based additives: naphthalene (NPT), naphthalenesulfonate (NPTS), hydroxynaphthalenesulfonate (HNPTS) and ethoxylated α -naphthalenesulfonic acid (ENSA, a commonly used additive in the tin electroplating industry), on the tin electrodeposition process on gold electrodes. In Chapter 3, we present the results of a detailed study using spectro-electrochemical and microscopic techniques and density functional theory calculations. We conclude the formation of condensed films of NPT, NPTS, HNPTS and ENSA, where NPT and NPTS lie flat on the gold surface and HNPTS and ENSA undergo oxidative polymerization. We demonstrate that NPTS forms a denser film due to attractive interactions via hydrogen bonding between the adsorbed molecules. Considering the density functional theory studies, we claim that naphthalene-based additive films are not very sensitive to the nature of the electrode material. NPT and NPTS bind to the gold and tin electrode surfaces mainly through Van der Waals interactions and HNPTS and ENSA undergo oxidative polymerization which is generally not very sensitive to the nature of the electrode material.

Furthermore, in chapter 3 we also show tin electrodeposition is strongly affected by the presence of the NPT, NPTS, HNPTS, and ENSA films. Our results show that tin bulk electrodeposition is inhibited in the presence of NPT and NPTS, but promoted in the presence of HNPTS. Regarding the morphology of the tin deposits, NPT and NPTS exhibit a similar morphology, but tin deposit grown in the presence of HNPTS exhibits markedly smaller features. We show that the presence of sulfonated additives during tin electrodeposition on gold leads to some form of sulfur incorporation in the AuSn alloys, with thiosulfate identified as a possible intermediate in the reaction. Furthermore, we determine that ENSA exhibits a similar behavior to NPT and NPTS during the tin deposition process: a suppression of the bulk Sn electrodeposition, but essentially no effect on the AuSn alloy formation, besides sulfur incorporation. Lastly, the lack of a strong effect of naphthalene-based additives on the AuSn alloying process is ascribed to the slow nature of Sn UPD on gold and AuSn alloying process.

Following the studies of the effect of naphthalene-based additives on tin electrodeposition on gold electrodes, Chapter 4 focuses on the effect of naphthalene-based additives on the kinetics of tin electrodeposition process. Owing to the complexity of the early stages of tin electrodeposition and its fast kinetics on gold, a change of the substrate from gold electrodes to boron doped diamond (BDD) electrodes was made.

In Chapter 4, we study the effect of naphthalene-based additives on the kinetics of tin electrodeposition on a boron doped diamond electrode. Current transients in the presence of NPT, NPTS and HNPTS were analyzed with the standard Scharifker-Hills model: the steady state nucleation rate (AN_0) and the number density of nucleation sites (N_0) were determined at different applied potentials. In the absence of additives, the nucleation and growth process is shown to transition from progressive to instantaneous with increasingly negative potential. A decrease in the nucleation kinetics of tin deposition on BDD was observed in the presence of naphthalene-based additives: NPT showed the smallest effect on the reduction of the kinetics, followed by NPTS, and the strongest effect was observed in the presence of HNPTS. Moreover, we show that Sn (II) is not complexed by the additives (NPT, NPTS, HNPTS, and

presumably neither by ENSA-6) and charge transfer kinetics is not influenced by the presence of the additives. Additives only affect the nucleation process. Furthermore, the behavior of ethoxylated α -naphthalenesulfonic acid (ENSA) exhibits an identical behavior that on gold, i.e., a strong inhibition of the tin deposition process.

Lastly, in Chapter 5 we use the gathered knowledge of the effect of naphthalene-based additives on tin electrodeposition on more stable substrates, i.e., gold and boron doped diamond electrodes, to provide insights of the interaction of the additives with iron and their effect on the overall tin deposition process on an iron electrode. We showed the effect of NPT and NPTS on tin electrodeposition remains mainly independent of the substrate. HNPTS shows a stronger decrease of tin deposition, according to what has been previously observed on tin deposition on a BDD electrode. Furthermore, we showed that transport of Sn (II) ions from the bulk to the electrode surface is not affected by NPT, NPTS and HNPTS. We verified that ENSA-6 forms a thick film on the iron surface, a behavior correlated the strongest inhibition of tin deposition on gold, BDD and iron electrodes.

Outlook

This thesis has shown that kinetics of the tin deposition is strongly affected by the presence of the different species in solution. Nonetheless, little attention has been paid to the chemistry of the complexes that exists in the bulk solution of the electroplating baths. Despite large number of studies acknowledge the importance of complexes, there are virtually no studies that identify in detail the speciation of the tin electroplating solutions. The identification of the species in solution would allow to explain differences in the kinetics, but also in the thermodynamics of the tin deposition process.

Attention should be given to understand the interaction of single and mixtures of molecules used as additives with the substrate; more in-situ spectro-electrochemical studies are required. These studies are crucial to comprehend the role of additives during the nucleation and growth of tin deposits.

Moreover, this thesis has shed light on the importance and also the complexity of understanding the mechanism of tin electrodeposition and the effect of the substrate. Future research should make use of in-situ microscopic techniques such as scanning tunneling microscopy and atomic force microscopy, in order to get information at atomic-scale of the early stages of the tin electrodeposition. The use of well-defined surfaces (single crystals) would help to interpret the data. Furthermore, considering the increase of tin coating, tin-composites and tin alloys applications, it is also very important to study the tin deposition on multiple substrates, including highly reactive surfaces such as iron and steel.