

Metal Chelation with Carboxylic Acids and its structure in solution as strategy to accelerate the electrodeposition of metals in nanocavities

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Introduction.

The diffusion limited mass transport within nanoporous media can be overcome by tuning the physicochemical properties of the ions in solution (i.e. size, charge, structure, solvability, etc.) and of the pore-wall in the porous matrix (i.e. hydrophobicity, etc.). Under certain conditions, the mass transport through nano cavities is drastically accelerated. This transport regime is called surface induced phase transition (SIFT) and occurs in mesoporous and microporous systems with a strong hydrophobic interaction between solutes and walls of the confined cavity. Upon the SIFT, the attractive interaction accommodates a high enrichment of hydrophobic solutes in the confined cavity, resulting in a drastic acceleration of the mass transport. Among other systems, we have studied the zinc deposition from zinc complexes with carboxylates and searched for evidences of the occurrence of the SIFT.

Experimental.

Microporous silicon electrodes (PSi) with a pore diameter of 2 nm were prepared starting from an n-Si (100), 10-20 Ωcm as a substrate. Anodization of the silicon wafer in an electrolyte solution (22 wt% HF solution) with a current density of 2.0 mA cm^{-2} and Zinc deposition with a current density of -10 mA cm^{-2} using different zinc complexes. XAFS measurements were performed at BL01 in Spring-8 (Hyogo, Japan) and at BM25-SpLine in ESRF.

Results and Discussion.

Zn complexation to form chelates with different size and charge depends on the pH of deposition bath. Preliminary, we have investigated the solvation structure of Zn with different carboxylic acids at different pHs. Upon the complexation of Zn with carboxylates, firstly, we have observed an unambiguously different behavior when Zn is deposited on a flat Si substrate, where Zn is mainly metallic for all the pH conditions. In the case of porous substrates there exists a clear correlation between the bath pH and the Zn phase composition of the deposits. The deposition rate is clearly accelerated and the ZnO proportion decreases to be negligible at pHs above the pK_a of the carboxylic acid.

Conclusions.

XAFS has revealed the structure of Zn carboxylate complexes employed in the accelerated deposition of Zn in nano porous matrices. This controlled mechanism can be key to develop effective, rechargeable, and non-hysteretic Zn-air batteries based on nano porous electrodes. However, these ideas can be employed to achieve the homogeneous deposition of different materials within the nano cavities of porous matrices.

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