

# Atomic Level Studies of Adsorption of Additives at the Electrode Surfaces during Electrodeposition of Zinc on Iron Electrodes

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A molecular level understanding of the processes taking place at the electrode/electrolyte interfaces during an electrodeposition reaction is very important in designing such a system. The earlier stage of the electrodeposition process is known to affect the mechanical properties of the finally electrodeposited products.<sup>1,2</sup> In this context, a good understanding of the underpotential deposition process itself and the roles of organic molecules on it is very important as well. In this study, we present results of our recent studies of the effects of the organic additives such as benzoic acid (BA) and polyethylene glycols (PEGs) on the initial stages of zinc electrodeposition process at the iron electrode studied by electrochemical quartz crystal microbalance (EQCM) measurements and *in-situ* scanning tunneling microscopy (STM) in an acidic zinc chloride solution. These additives are used widely in the industrial zinc plating baths.

*In situ* STM experiments were carried out in this study using an Fe(110) single crystal whose surface is very well defined on an atomic scale. Figure 1 shows an STM image (a) of the Fe(110) surface obtained in a 0.1 M KCl solution at an open circuit potential of -0.31 V vs. Ag/AgCl (in saturated KCl) electrode and an atomic model (b) explaining the observation. We believe the topology of the Fe(110) surface is determined by the oxygen atoms covering on iron surfaces upon exposure to the electrolyte. Our subsequent results on adsorption of additive molecules (not shown here) studied using STM indicate that PEGs are adsorbed strongly in a self-assembled manner, while BA molecules are adsorbed randomly on the electrode surface, affecting the electrodeposition of zinc from the earlier stages.<sup>3</sup> Thus, PEGs control the access of zinc ions, while BA molecules appear to suppress the growth of dendrites in their adsorbed states. Also, protons are shown to compete with zinc ions during the electrodeposition of zinc by various other experiments independently run, and organic additives such as BA, PEGs, or their mixtures induce a change in the movement of these ions near the substrate electrode surface.<sup>4</sup> During the zinc electro-deposition, the presence of BA does not impose an extra overpotential owing to its weak or almost no interaction with zinc ions. However, it appears to determine the surface roughness by directing the incoming zinc ions. BA is adsorbed strongly at the dendritic sites of more negative potentials of the electrode although it is randomly adsorbed on the iron surface at around the open circuit potential (not shown). Its role seems to control the deposition rate at the dendritic sites by blocking the active surface via adsorption. On the other hand, PEGs are adsorbed more or less evenly with a well-ordered structure on the iron surface. However, PEGs appear to be desorbed from the iron surface in the underpotential deposition region of zinc ions. PEGs form a stronger complex with zinc ions and, thus, require a considerably large overpotential for its deposition. In addition, they interact effectively with incoming protons at the electrode surface and inhibit the

hydrogen reduction during the initial zinc deposition step. BA and PEGs not appear to interact closely with each other and show an intermediate behavior between those of BA and PEGs when both are present.

These conclusions were reached by obtaining the STM images as well as the EQCM data. A number of STM images obtained *in situ* during the electrodeposition experiments and EQCM data supporting our conclusion will be presented along with other electrochemical data.

## REFERENCES

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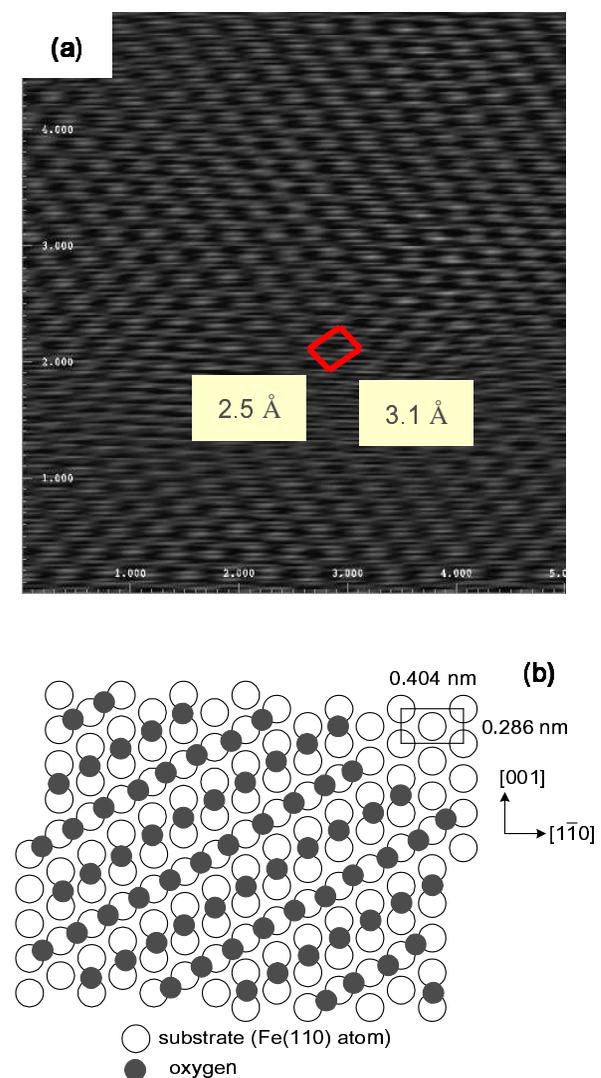


Figure 1. (a) An EC-STM image at an open circuit potential (-0.31 V) and (b) a proposed structure based on the image shown in (a). The tip bias was 25 mV with a tunneling current of 3 nA. The scanned area is  $5 \times 5$  nm. These figures were reproduced from Ref. 3.