Electrochemical molecular modeling: exploring the metal/inhibitor/water electrified interface

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Innovative technological solutions are proposed daily to mitigate corrosion, but one of the most efficient, green, and cost-effective alternatives is using small organic molecules as corrosion inhibitors. A significant effort is made worldwide to propose and test new inhibitors. However, a question remains: What properties must a molecule have to be an effective inhibitor? Molecular modeling can help answer that question by exploring the several interfaces involved at the nanoscale.

Most of the theoretical results in the literature either under-explore their potential by following standard procedures or apply overly simplistic models that neglect fundamental aspects of the corrosion process. With the objective of overcoming that issue, we present a novel approach by creating an accurate model of the interface between the inhibitor, metal, and solvent, as sketched in Figure 1. The quantum character of the metallic slabs and inhibitor molecules attached to them are considered via the non-equilibrium Green's functions (NEGF) method [1,2], allowing for applying a potential to the electrodes. Yet, the corrosive medium is considered by explicitly incorporating water molecules at a molecular mechanics level using the quantum mechanics/molecular mechanics (QM/MM) method [3]. All those features are implemented in the efficient SIESTA code [4,5], a well-established materials modeling code based on density functional theory (DFT).

We showcase our approach by investigating the interaction between 2-mercaptobenzoimidazole (MBI) and Cu slabs. Our findings demonstrate that the inhibitor film physically blocks the metallic surface, displacing the water molecules from the interface. Besides that, we could access the charge redistribution at the interfaces due to the presence of the inhibitors, demonstrating that our methodology can include the effect of a voltage applied to the electrodes, thus going far beyond standard DFT simulations. In summary, this work's significance lies in introducing a method that considers all the necessary ingredients to simulate corrosion properly, significantly improving how we approach this critical problem.
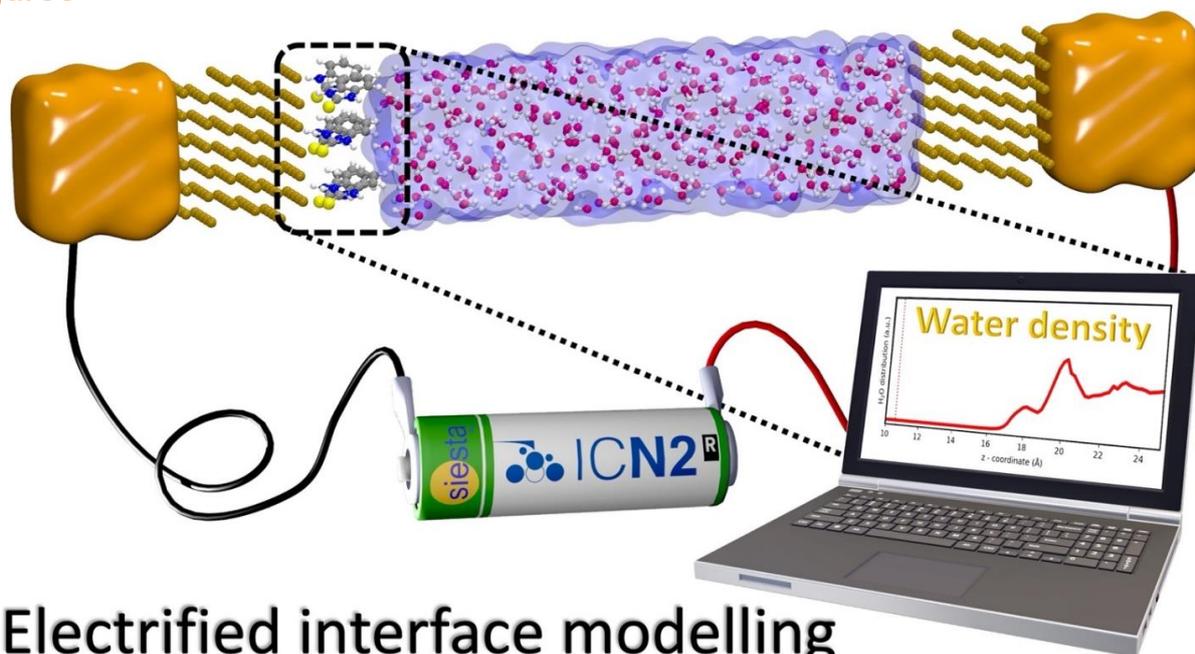
Acknowledgments

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Figures

Figure 1. Sketch for the electrified interface modelling at the nanoscale. Two electrodes are coupled to the copper metallic slab, with one side covered by corrosion inhibitor molecules. The central region contains bulk water molecules. The computer shows the water density at the interface, demonstrating that no water molecules get closer to the metal under high coverage.