

Adsorption of Carboxylic Acid Corrosion Inhibitors on Active and Passive Iron studied with EQCM, EIS and XPS

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Introduction

Due to stringent environmental regulations, inorganic corrosion inhibitors such as chromates, nitrites or oxides in coatings for mild steel are replaced by organic compounds, e.g. aromatic carboxylic acid based molecules. In previous studies it was shown that the effectiveness of these inhibitors is closely related to their adsorption properties [1]. In adsorption from the liquid phase, solute and solvent compete for the adsorption sites. Recently, using a rotating Electrochemical Quartz Crystal Microbalance (rEQCM) electrode [2,3], it was found that adsorption of carboxylic acid corrosion inhibitors on Fe and Au leads to a mass loss at the electrode because the mass of replaced water molecules exceeds that of the adsorbed inhibitor [3]. This is a direct experimental evidence that adsorption is a replacement reaction, giving insight in the protection mechanism of corrosion inhibitors.

In this paper, rEQCM results on iron in the active and passive state are compared to Electrochemical Impedance Spectroscopy (EIS) and ex-situ X-ray Photoelectron Spectroscopy (XPS). The inhibitor adsorption properties, modeled from rEQCM adsorption data, are discussed in terms of inhibition performance of the studied molecules in linear sweep experiments.

Experimental

The rEQCM electrode with its 10 MHz AT cut quartz crystals is described in detail elsewhere [2,3]. Fe films of 400 nm thickness were electrodeposited on the sputter deposited Au electrode on the quartz. For adsorption in the active region, Fe quartz electrodes were immersed in 1 M H₂SO₄ and then transferred into 0.1 M NaClO₄ for pre-polarization before adsorption experiments. For adsorption in passive region, passivation was achieved in boric buffer. The inhibitors chosen belong to the family of ω -benzoyl alcanoic acids. The inhibitor BAA in Fig. 1 is compared to the Br labeled molecule BAA-Br, which allows also for XPS quantification. The acid group was neutralized with NaOH in order to dissolve the inhibitor in aqueous solutions. 0.1 M perchlorate served as inert supporting electrolyte. Potentiostatic adsorption experiments with the rEQCM at 25.0 °C were performed using a sequential inhibitor addition routine [4] at potentials slightly cathodic to the corrosion potential of Fe. After each addition step, the impedance was measured from 10³ to 10⁻¹ Hz. The data was fitted using an electric circuit model. XPS Spectra were recorded with a Kratos Axis Ultra system. The presence of the oxide film was accounted for in the data evaluation, as described in [5].

Results and Discussion

As shown in Fig. 2, addition of inhibitor resulted in a frequency increase, corresponding to a mass decrease, arising from the replacement reaction between inhibitor and water molecules. BAA-Br replaced more water than BAA, in accordance with its higher hydrophobicity. Adsorption of BAA on iron oxide led to a higher mass loss than on metallic iron. This was interpreted in terms of the nanoscale roughness of the oxidized surface. A maximum

in the frequency curve was found at a concentration of 2.25×10^{-2} M, interpreted as monolayer formation at the electrode. Concentration dependent EIS measurements with BAA-Br confirmed this interpretation by a plateau found in the double layer capacitance at the same concentration. XPS data in Fig. 3 indicate that the surface concentration reaches a limit in this concentration range. The rEQCM adsorption data fitted best the Langmuir-Freundlich isotherm. Compared to BAA, BAA-Br exhibited a higher adsorption energy and replaced more water. Consistent with these observations, linear sweep experiments showed it to be more effective in suppressing the anodic dissolution in the active region. Comparison of adsorption of BAA in the active and passive region indicated a higher adsorption energy on active iron, which is in agreement with earlier XPS observations with BAA-Br [5]. The presented results confirm the usefulness of the EQCM for the characterization of competitive adsorption of corrosion inhibitors and solvent at the electrode surface.

References

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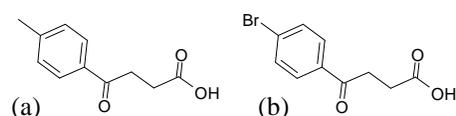


Fig. 1 The corrosion inhibitors BAA (a) and BAA-Br (b).

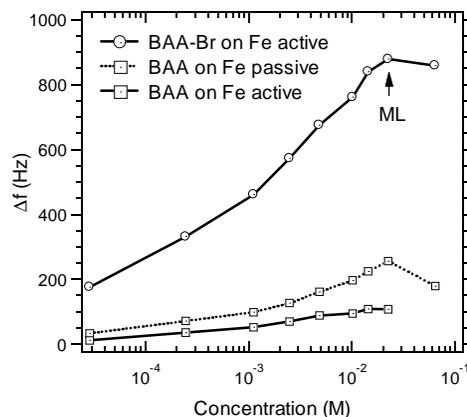


Fig. 2 rEQCM frequency response upon inhibitor addition.

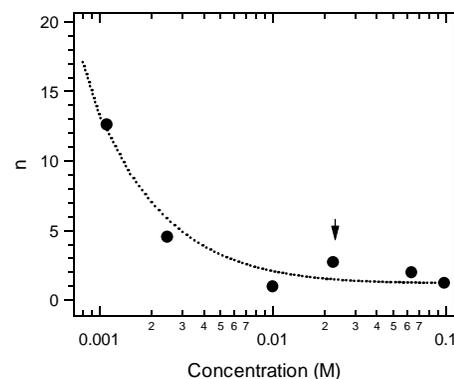


Fig. 3 Ratio of Fe atoms to BAA-Br molecules at the Fe quartz electrode, as found by XPS.