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# Time-dependent water uptake in a polymer model coating visualized by FTIR microscopy using a focal plane array detector

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**Abstract:** progress of the delamination front during cathodic delamination was imaged by FTIR microscopy. Delamination experiments were carried out using H<sub>2</sub>O and D<sub>2</sub>O-based electrolytes. Inhomogeneous propagation of the delamination front was observed.

**OCIS codes:** (300.6340) Spectroscopy, infrared; (110.3080) Infrared imaging; (240.0240) Optics at surfaces

## 1. Introduction

Polymer coatings on metals are frequently applied to determine the optical appearance of a product, and to protect the underlying metallic structural material against corrosion. Delamination of the coatings occurs when the coating is damaged and corrosive processes at the underlying metal begin. Cathodic delamination is by far the fastest - and hence the most critical - delamination mechanism. It occurs on iron, steel and galvanized steel in atmospheres with high humidity. The electrochemistry of the process has been studied extensively by scanning Kelvin probe experiments. Likewise, the corrosion products have been investigated by post-mortem analysis [1]. However, the role of water and ion transport during delamination is still largely unexplored. The vibrational spectrum of water offers a sensitive probe to the environment the water is in. In particular, the processes in the vicinity of the delamination front remain to be elucidated at a molecular level [2](Figure 1).

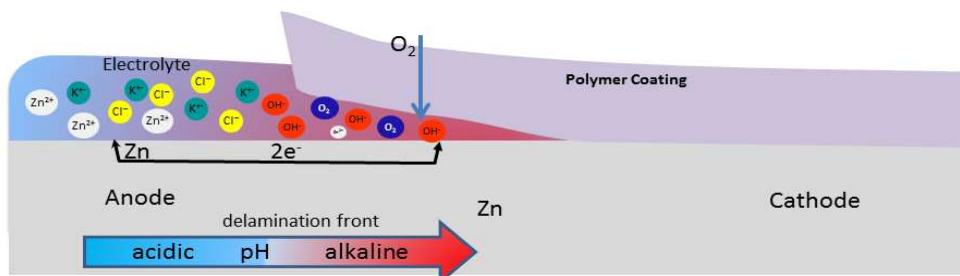


Fig. 1: Scheme representation of cathodic delamination on a polymer-coated zinc substrate.

This work uses IR imaging spectroscopy in an IR microscope equipped with a focal plane array (FPA) detector to image the temporal evolution of the spatial distribution of the water bending and stretching modes during the delamination of a model coating from metallic zinc. The model coating is poly(vinyl butyral) [PVB], which itself represents a weak coating. The spatial distribution of water is investigated by integrating the bending and stretching modes of water, both in H<sub>2</sub>O and D<sub>2</sub>O-based electrolytes.

## 2. Experimental

The PVB-coated zinc samples were placed on a zinc sheet, and with an adhesive, a reservoir was created for the electrolyte. To start the delamination process, the reservoir was filled with 0.1M KCl solution.

This sample was then placed inside a custom designed chamber under the FTIR microscopy. The chamber is flushed with air at >90% relative humidity. A CaF<sub>2</sub> window was used to illuminate the sample and to collect spectra in reflection geometry. For kinetic measurements, a macro program was used that performed repeated measurements at the same location over time. Each measurement takes around 10 min.

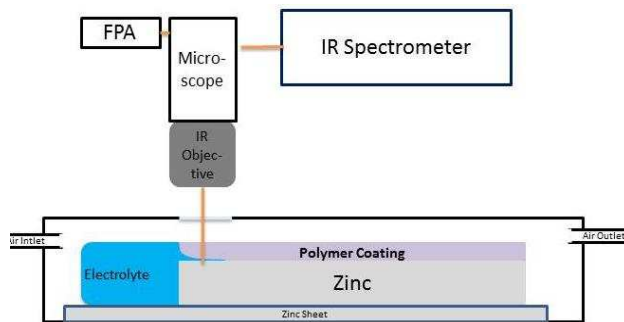


Fig. 2: Schematic view of the setup used for the experiments.

The FTIR microscope used was a Bruker Hyperion 3000 equipped with a 64\*64 pixel FPA connected to a Vertex 70v spectrometer. The imaged region was 170 μm \* 170 μm.

### 3. Results and Discussion

During delamination, the passage of the delamination front was observed (Figure 3 and 4). Directly at the delamination front, the integrated absorbance of water is highest.

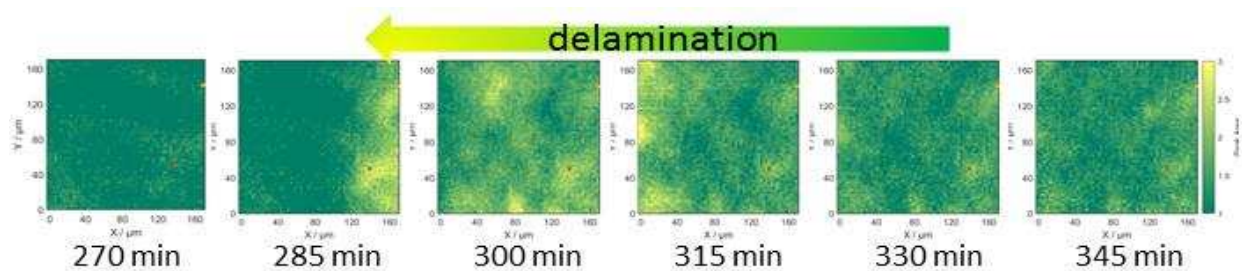


Fig. 3: In situ FTIR images after different exposure time. a) Chemical map based on the integrated intensity of the scissors vibration mode of water at ~1640 cm<sup>-1</sup>.

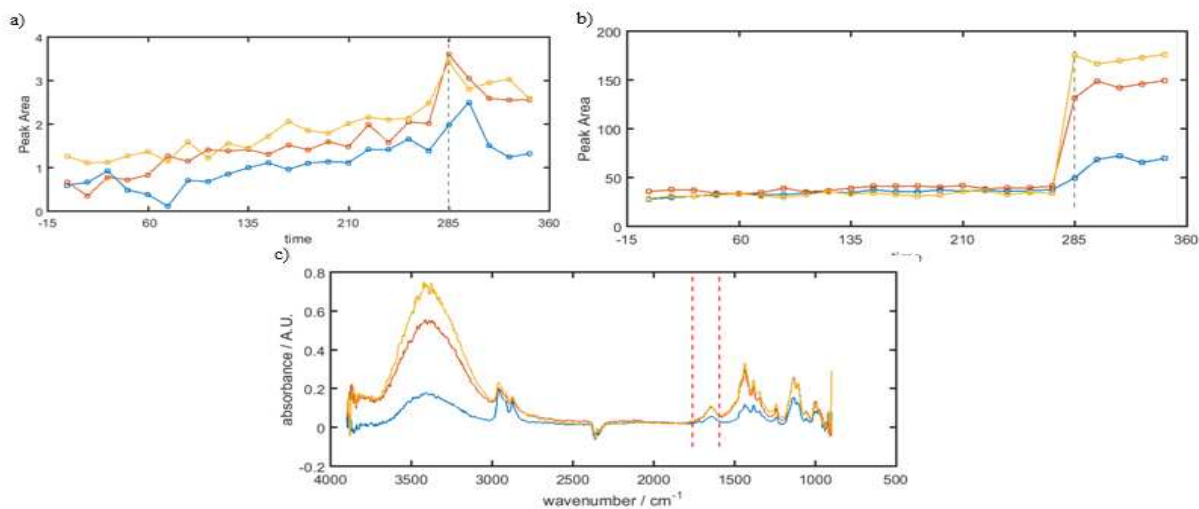


Fig. 4: Peak area of the a) water peak at ~1640 cm<sup>-1</sup> b) water peak based on the OH stretching mode ~ 3400 cm<sup>-1</sup> versus Time on 3 different positions (Measurement points are shown in Figure 3). c) Example of in situ IR spectra after 285 min on the 3 different positions.

In the H<sub>2</sub>O spectra, total absorption was observed in the OH stretching mode region. Furthermore, spectra are affected by water present inside the coating before experiments. Therefore, a similar experiment was performed with D<sub>2</sub>O-based solution (Figure 5). In D<sub>2</sub>O, water previously present in the coating does not contribute to the spectra. A delamination front was observed in the experiments in D<sub>2</sub>O. More detailed analysis of the spatio-temporal patterns developing during the initial stages of cathodic delaminations [3] will give more detailed insight into the process initiating cathodic delamination. Such understanding is required to develop strategies for a successful slowdown of delamination.

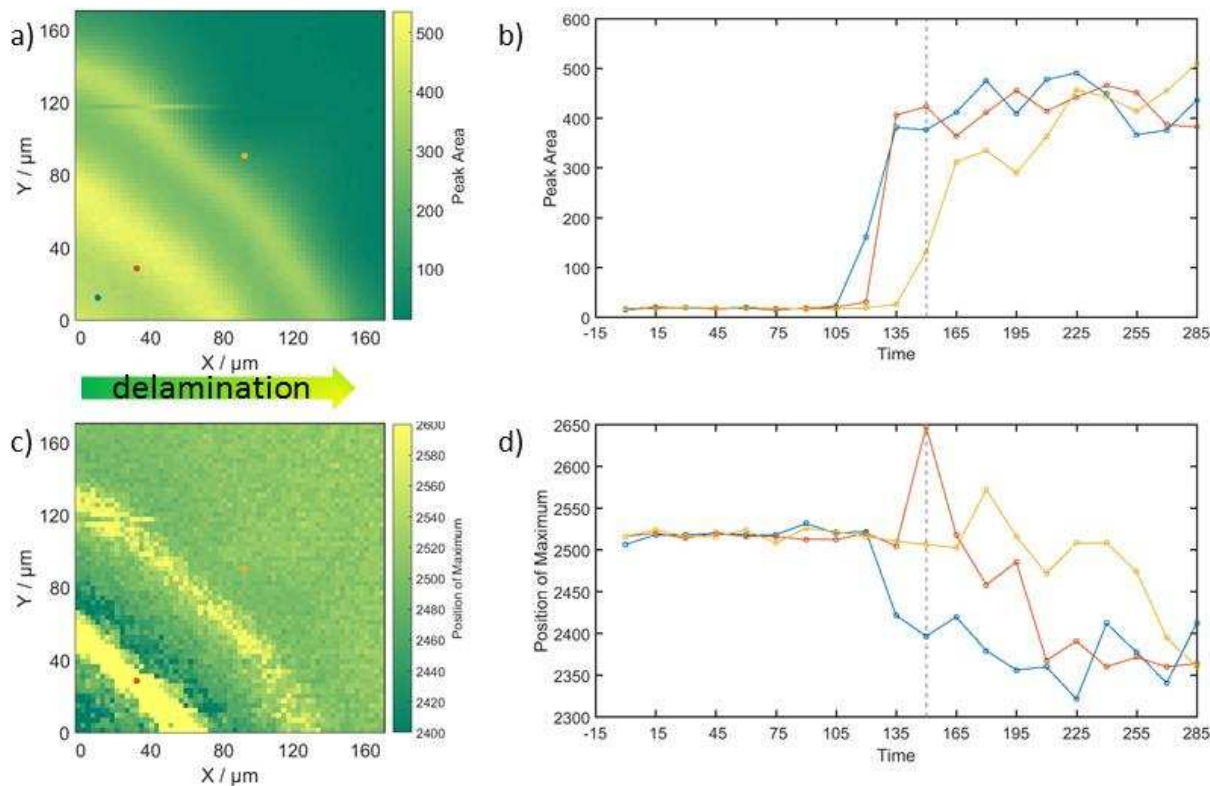


Fig. 5: Investigation of the D<sub>2</sub>O Peak at ~2500 cm<sup>-1</sup> based on DO<sup>-</sup> stretching mode on 3 different positions a) Peak area at the starting of the delamination b) Peak area versus time. c) Peak shift at the starting of the delamination d) Peak shift versus time.

#### 4. Acknowledgements

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#### 5. References

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