Local properties of organic coatings sampled with the AFM-based approach

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Presentation outline

- A need for local characteristics of coatings
- Atomic force microscopy based approach
- Experimental
- Distinguishing the mode of degradation
- Local impedance spectra & temperature studies
- Conclusions
A need for local characteristics of coatings

- degradation always starts from local defect(s)
- macroscopic, global approaches conceal local properties due to their averaging character:
  - little information on degradation mechanism,
  - no possibility of identification of the spots of defect onset
- crucial in such fields as:
  - special purpose coatings,
  - self-healing films or
  - thin conformal coatings in electronic industry
Atomic force microscopy based approach

• originally proposed by Kalinin’s group for investigation of transport behaviour of individual grains and grain boundaries in polycrystalline ZnO

• also utilized by O’Hayre in the field of solid polymer electrolytes, polycrystalline ZnO varistors and microscale test patterns of different electrical behaviour

• has not been adopted to organic coating investigation before
Atomic force microscopy based approach

- atomic force microscopy in contact mode
- scanning in continuous or quasi-continuous way
- single frequency voltage perturbation signal applied between tip and coated substrate
- registration of response current
- acquisition of local impedance spectrum – impedance spectroscopy
- mapping of changes of current response (impedance) over the scanned surface – impedance imaging
Atomic force microscopy based approach

\[ Z(j\omega) = \frac{R_c}{1 + j\omega C c R_c} \]

\[ \lim_{\omega \to \infty} Z(j\omega) = \frac{1}{j\omega C c} \quad \lim_{\omega \to 0} Z(j\omega) = R_c \]

- at high frequencies:
  \[ \Delta I = j\omega C c \Delta E \]
- at low frequencies:
  \[ \Delta I = \frac{1}{R_C} \Delta E \]

where:
\( \Delta I \) is the measured current amplitude,
\( \omega \) is the frequency of the perturbation signal,
\( \Delta E \) is the amplitude of the perturbation signal,
\( C \) is the capacitance of material,
\( R \) is the resistance of material.

*Rs* – solution resistance
*Rc* – coating resistance
*Cc* – coating capacitance
Experimental

• **topography and localized impedance measurements:**
  - NTEGRA Aura microscope by NT-MDT
  - contact mode AFM measurements using conductive tip covered with platinum (ca. 25nm)
  - maximum scan size: 100µm x 100µm
  - scanning frequency: 1Hz
  - perturbation frequency: 4kHz
  - amplitude of perturbation signal: 2V
  - contact force 6µN

• **spreading resistance measurements:**
  - dc bias voltage applied between tip and coated substrate: 2-10v
Experimental

- *macroscopic impedance measurements:*
  - two-electrode system
    - working electrode – metal substrate
    - counter electrode – platinum mesh
  - upon immersion in 3% NaCl solution
  - area examined 0.8mm²
  - Schlumberger 1255 FRA coupled with high-input impedance buffer ATLAS 9181
  - frequency range 1MHz – 1mHz
  - amplitude of perturbation signal 60mV
Experimental

- **investigated material:**
  - organic coating on circular carbon steel substrate 1mm in diameter
  - film thickness ca. 15µm
Distinguishing the mode of degradation

**INTACT COATING**

*topography image*

*global classical impedance spectrum*

*AC response current amplitude*
Distinguishing the mode of degradation

EXPOSURE

250h in 3%NaCl

topography image

AC response current amplitude

600h in UV
Distinguishing the mode of degradation

EXPOSURE

400h in 3%NaCl

900h in UV
Distinguishing the mode of degradation

EXPOSURE

400h in 3%NaCl

900h in UV

topography image
global classical impedance spectra
Local impedance spectra & temperature studies

*topography images*

25 °C  

100 °C  

150 °C  

*DC current maps*
Local impedance spectra & temperature studies

- **Topography Image**
- **Global Classical Impedance Spectrum**
  - Frequency: 10 kHz
- **25 °C**
- **DC Current Map**
- **Local Impedance Spectra**
Conclusions

- proposed novel AFM-based approach allows obtaining **local morphological and electrical characteristics of coatings**
- allows **identification and spatial localization** of the spots of degradation onset, also at the early stage of exposure
- makes it possible to **distinguish between different modes of degradation** of the same coating exposed to various environments
- offers **various measurement modes**: impedance imaging, local impedance spectroscopy, DC mapping
- **overcomes the averaging shortage** of global-type techniques (including classical EIS) and thus can be a supplementary approach providing **information inaccessible** by them
Atomic force microscopy based approach

The relation between frequency resolution ($\Delta f$) and time selection ($\Delta t$) is described by the uncertainty principle:

$$\Delta t \Delta f \geq \frac{1}{4\pi}$$

For the scan rate $v$ this equation takes the form:

$$\Delta x \geq \frac{v}{4\pi K f}$$

where: $K = \frac{\Delta f}{f}$ is the relative frequency resolution and $\Delta x = v \Delta t$ is the spatial resolution.