The Determination of the Critical-Pigment-Volume Concentration Using Relaxation Voltammetry

W. Strunz, ZAHNER-elektrik
www.zahner.de
Outline

- Principle of RV
- Characterization of RV experiments
- The Pigment Volume Concentration
- Determination using EIS
- Investigated Coating systems
- Experimental Results
- Summary
The Principle of RV

- Double Potentiostatic Experiment
- Symmetric Square Wave Perturbation around OCP
- Excitation time ≈ 100 s
- Sampling rate ≈ 200 Points/s
- Current: pA-range

Diagram:

- OCP
- +U_{EXC}
- -U_{EXC}
- t0, t1, t2, t3, t4
- Time axis
Combining anodic and cathodic decay

\[ I_{\text{exc}} = 684 \pm 3 \text{ fA} \]

\[ C_C = 164 (150) \text{ pF} \]

\[ C_{DL} = 2,27 (2,2) \text{ nF} \]

\[ R_C = 9,92 (10) \text{ G}\Omega \]

\[ R_{CT} = 4,99 (5) \text{ G}\Omega \]

Residual: \( \pm 20 \mu\text{V} \)

\[ (\chi^2 = 4 \cdot 10^{-5}) \]
Subtracting DC-trend (like Coul-Count)

- Residual
- Standard Deviation (SDev)
- Current (similar evaluation)
- Potential

“Coul-Count“: http://www.ifinkor.de/Leistungen/coulcount_details.htm
Classification of Coatings (I) (Different Coatings)
- ln (Decay) vs $\sqrt{t}$

In $[U/U_{exc}]$ [a.u.]

$z : z = \sqrt{t}$
Classification of Coatings (II) (Same Coating Systems)

Change of Temperature
(Ph.D. Thesis Hartmut Ochs)

Water Uptake

\[ \ln \left( \frac{U}{U_{EXC}} \right) = z = \frac{\sqrt{t}}{s^{0.5}} \]

\[ \ln (U) = \frac{z}{\sqrt{t}} / s^{0.5} \]

5 °C
20 °C
45 °C

2 h : A
8 h : B
24 h : C
Pigment-Volume Concentration

\[ PVK = \frac{\sum V_P + \sum V_F}{\sum V_P + \sum V_F + \sum V_B} \]
• Spectra recorded 24 hours after immersion
• (from Ph. D. Thesis of Hartmut Ochs)
2 Base systems with different pigment morphology (particle size)

- System A with 57% PVC
- System B with 50% PVC
- Pigments partially substituted with Micaceous Iron Oxide (MIO)
Relaxation Voltammetry

- Complete Water Uptake measurements (~ 24h)
- $U_{\text{EXC}} = \pm 20 \text{ mV}$
- Exitation time: 120 s (+90 s meas +120 s wait)
- Single measurement requires 13 minutes
- Evaluation: time domain quantities
PVC - Experimental Results
- Potential Decay

undercritical  overcritical

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PVC - Experimental Results
- Potential Decay
\[ \ln(\text{Decay}) \text{ vs } \sqrt{t} \]
PVC - Experimental Results
- Potential Decay
\[ \ln(\text{Decay}) \text{ vs } \sqrt{t} \]

undercritical  overcritical
No significant change (neither increase nor decrease)

PVC - Experimental Results
- Standard Deviation Potential

undercritical  overcritical
Pigment-Volume Concentration
- Current before Interrupt

undercritical  overcritical

“Percolation”
Increasing Standard Deviation for Overcritical Systems

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**Decay not too different**

### Undercritical

<table>
<thead>
<tr>
<th>R [GΩ]</th>
<th>C [F]</th>
<th>Y₀ [Fα]</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>1.5n</td>
<td>550p</td>
<td>0.74</td>
</tr>
</tbody>
</table>

### Overcritical

<table>
<thead>
<tr>
<th>R [MΩ]</th>
<th>C [F]</th>
<th>Y₀ [Fα]</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>624</td>
<td>6.4n</td>
<td>3.8n</td>
<td>0.74</td>
</tr>
</tbody>
</table>
PVC - Experimental Results
- FIT after 24 h (R | | CPE)

undercritical

overcritical

Big difference (diffusion in overcritical system)

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Summary

Determination of CPVC - water uptake measurements (RV)

- Potential Decay
  - Simply transient-form of decay ("post C-type")
  - Standard deviation of potential = constant

- Evolution of Current
  - Percolation-type transition
  - Standard deviation increasing

- FIT with $R||CPE$
  - Transition from "capacitive" to diffusion
Thank you for your attention
Normalization of CPE (R || CPE !) - heuristic derivation

\[ Z_{R||C} = \frac{R}{1 + R \cdot C \cdot j \cdot \omega} \]

\[ Z_{R||CPE} = \frac{R}{1 + (\tau \cdot j \cdot \omega)^\alpha} \quad \text{with} \quad \tau = R \cdot Y_0 \]

\[ C = \frac{1 - \alpha}{R^{\alpha}} \cdot \frac{1}{Y^{\alpha}} \]

Normalized capacity is independent of the exponent \( \alpha \)

**FIGURE 1.** Frequency dependence of \( Z'' \) and \( \Phi \) for different \( n \) values: \( R_s = 1 \, \Omega, \) \( R = 1 \times 10^4 \, \Omega, \) and \( C = 1 \times 10^{-5} \, F. \)**
Critical Pigment-Volume Concentration

- Taken from Ph. D. Thesis of Hartmut Ochs
- from RV (total DC-resistance)
Anregungszeit ($t_{\text{EXC}}$): einer der wichtigsten Parameter auch für ‘Kurzzeitauswertungen’ (ISL: $I_{\text{EXC}}$ !)
Water uptake – Evolution of Spectra

![Graph showing log(impedance) vs log frequency with phase shift for different specs.]

- 1. spec
- 2. spec (20 min.)
- 84. spec (26 h)

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Water uptake – Application of Z-HIT

- Only the lowest frequencies are affected
- Only at the earliest spectra
Pigment-Volume Concentration
- Current before Interrupt

undercritical  overcritical

"Percolation"