Accelerating the Time Scale of Coating Tests - Can the Combination of Linear Small Signal Methods with Electrochemical Stress Improve the Coating Lifetime Prediction ?

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Introduction

Electrochemical small signal methods, mainly ac-impedance spectroscopy (EIS), have proved to be outstanding testing tools for the determination of the actual corrosion state of coatings. Nevertheless, a reliable prediction from the actual electrochemical state to future corrosion behavior is still difficult.

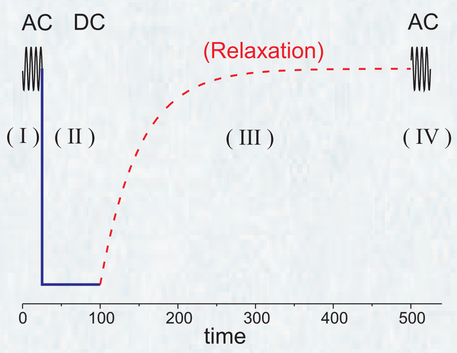
A promising strategy for the lifetime prediction of coating systems is the combination of subsequent state-determination with phases of corrosive stress. A statistical analysis of the results on several samples will increase the forecast significance additionally.

Recent research results on food packaging materials were published [1,2], which use the so called **AC-DC-AC**-method. This technique seems very attractive, because state determination as well as stress are of electrochemical nature. The complete procedure is performed in an automatic test routine without exchanging the sample between different environments.

The **AC-DC-AC**-method is based on the experience, that the deterioration progress of coatings is often accompanied by delamination processes. Coating delamination can be provoked by means of cathodic polarisation: Provided that high overpotentials are applied, very small coating defects undetectable for the linear state determination test generate conducting pathways which may enable a chemical reaction at the metallic surface site and therefore, the formation of hydrogen and an alkaline environment. **The coating adhesion is destabilized by the alkaline hydrolysis and** the hydrogen pressure in turn supports an accelerated delamination, which can be detected by the following state determination.

The AC - DC - AC - technique

- fully automated using SCRIPT



(I) EIS-measurement at OCP : determination of the actual state

(II) Cathodic polarization (time t) : 8 V for t = 120 s

(III) Relaxation phase ($t_{Rel} = 4 * t$) : return to OCP (approximately)

(IV) EIS-measurement : determination of the NEW actual state

- steps (I) - (III) are repeated n-times
- time required for a single cycle : about 20 minutes

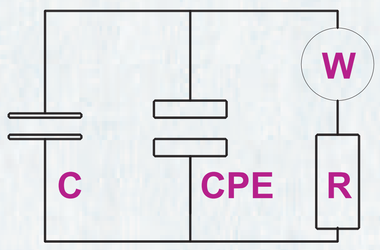
Model for the Evaluation of the Impedance Spectra

Dielectric properties represented by

C : Coating capacity : high frequency limit
CPE: Constant phase element (normalized at f = 1000 Hz)

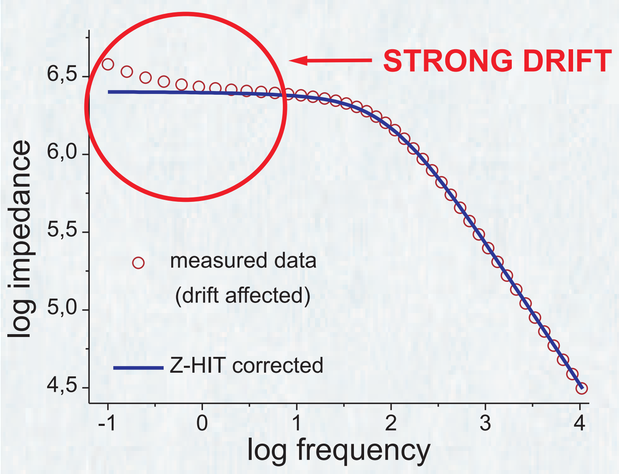
Conductive pathway represented by

R : Pore resistance
W : Warburg impedance



Evaluation of Drift Affected Data - the Z-HIT Algorithm

$$\ln|H(\omega_0)| \approx const. + \frac{2}{\pi}\int_{\omega_S}^{\omega_0}\varphi(\omega)d\ln\omega + \gamma \cdot \frac{d\varphi(\omega_O)}{d\ln\omega}$$



After cathodic stress, the system does not return to the OCP exactly and/or changes it's state due to the stress.

The following impedance spectrum is superimposed by a 'rest-relaxation'.

Mainly the impedance data at the low-frequency side are affected.

The Z-HIT enables the reconstruction of a causal impedance modulus course from the course of the phase shift within the measured frequency range and therefore eliminates the drift [3-5].

[1] J. Hollaender; *Food Additives and Contaminants* Vol. **14** No. 6-7 (1997) 617
[2] J. Hollaender; *Proceed. of 10th International Congress On Canned Foods* May 1991 (Paris) page 153
[3] W. Ehm, H. Göhr, R. Kaus, B. Röseler, C.A.Schiller; Acta Chim. Hung. 137 (2000) 145
[4] C. A. Schiller, F. Richter, E. Gülzow, N. Wagner; J. Phys. Chem. Chem. Phys. 3 (2001) 374
[5] W. Ehm, R. Kaus, C. A. Schiller, W. Strunz; submitted to J. Electrochem. Soc. (Jan. 2001)

Results

As can be seen in figures 1. - 4., the coatings are affected to a different degree by the cathodic stress. It is important to note that the effect of stress can be best seen in the middle and the low frequency part of the corresponding impedance spectra. According to the selected equivalent circuit, a degradation of the coating can be attributed to a decrease of the parametetrs which describe the conductive (ionic) branch of the equivalent circuit, i.e. R and W, whereas the dielectric properties - represented by C and CPE - remain almost constant.

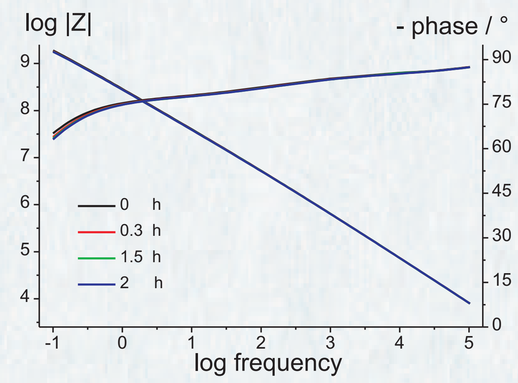
Furthermore, a comparison of fig. 3 and fig. 4 suggests that an initial high Ohmic system is not a guarantee for good coating performance.

1.) Type A : High Ohmic barrier coating

- not affected by cathodic stress

Time/ h	R / 10^9 Ω	C / pF	CPE / pF	α	W *)
0	12.1	165	86	0.782	-
0.3	10.3	165	89	0.781	-
1.5	9.8	165	89	0.780	-
2	9.4	164	90	0.781	-

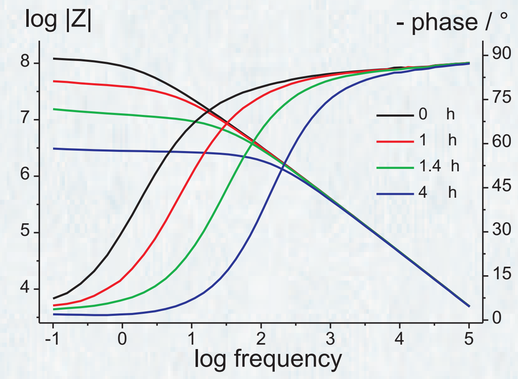
*) not significant



2.) Type B : High sensitive to cathodic stress

- decrease of R and W

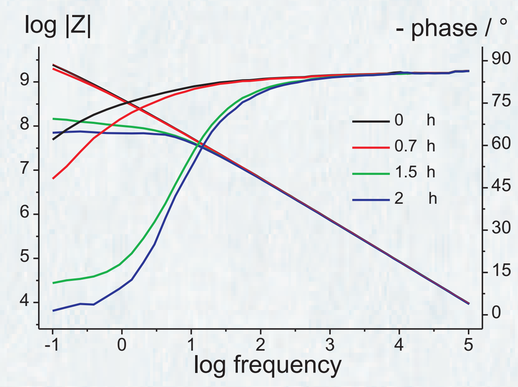
Time/ h	R / 10^6 Ω	C / pF	CPE / pF	α	W / 10^6 $s^{-1/2}$
0	121	286	114	0.749	3.65
1	41.4	292	111	0.731	2.64
1.4	12	300	102	0.685	1.04
4	2.76	286	129	0.731	0.12



3.) Type B : Sensitive to cathodic stress although exhibiting an initial high Ohmic resistance

- decrease of R and W

Time/ h	R / 10^9 Ω	C / pF	CPE / pF	α	W / 10^9 $s^{-1/2}$
0	2.16	127	83.4	0.848	3.59
0.7	1.71	132	88	0.833	1.22
1.5	0.1	136	79.5	0.825	0.028
2	0.08	122	95	0.853	0.003*)

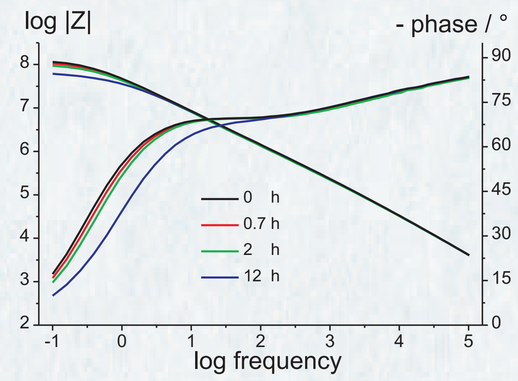


4.) Type A : Barrier coating

- almost not affected even at prolonged stress

Time/ h	R / 10^6 Ω	C / pF	CPE / pF	α	W / 10^9 $s^{-1/2}$
0	150	229	487	0.752	-
0.7	132	224	505	0.753	-
2	113	221	525	0.754	-
12	66	253	449	0.733	-

*) not significant



Outlook

The AC-DC-AC technique, which is used in the food packaging testing since several years, seems to be a promising tool for the evaluation (ranking) of the coating performance with respect to the corrosion protective behavior too.

The scope of this technique is by far not limited to the procedure presented here.

Considering coating types which are more sensitive to oxidative degradation, one can suppose that the application of anodic stress-potentials may result in a ranking of these coatings.

Besides obvious modifications like size, sign and duration of the stress-potential (as well as the duration of the entire experiment), this technique possesses the advantage that it is fully automated including a statistical analysis of several specimens of the same coating type using SCRIPT.