

The Dielectric Properties of Barrier Coatings - a Superposition of Coating Material and Pores

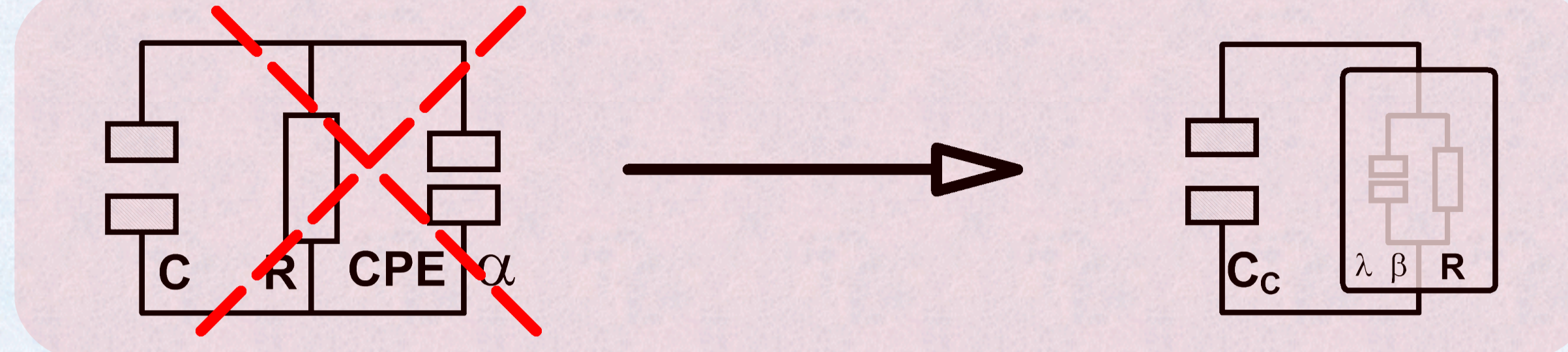


W. Strunz¹, C. A. Schiller¹, J. Vogelsang²
¹ Zahner elektrik, Kronach, Germany ² SIKA Technology AG, Switzerland



The electrochemical behavior of barrier coatings during water uptake can be separated into 2 components:

1. the impedance of the coating material
2. the impedance of free sites/pores.



Since the physical parameters characterizing the impedance of the pores depend on each other, they have to be combined to a single pore impedance

Water Uptake of Barrier Coatings

Electrochemical Impedance Spectroscopy (EIS) is a well known technique to determine the corrosion protection performance of barrier coatings, for instance by performing series measurements to monitor the change of barrier properties during water uptake [1-4]. Two examples [5] are depicted in FIG 1.

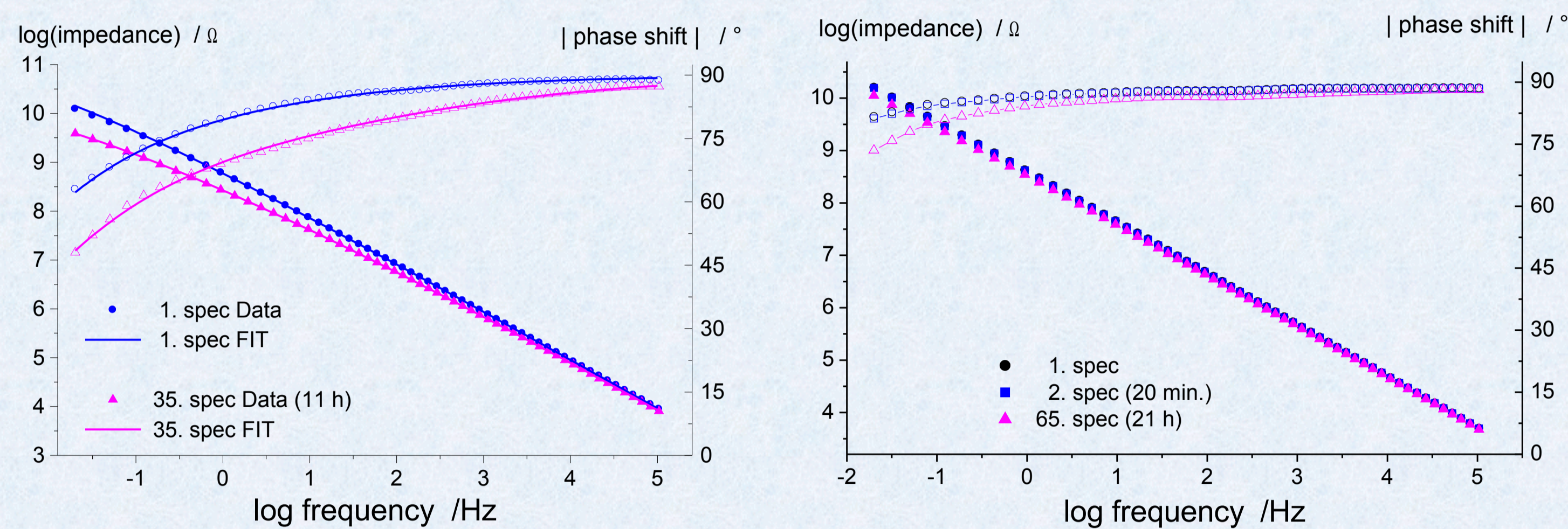
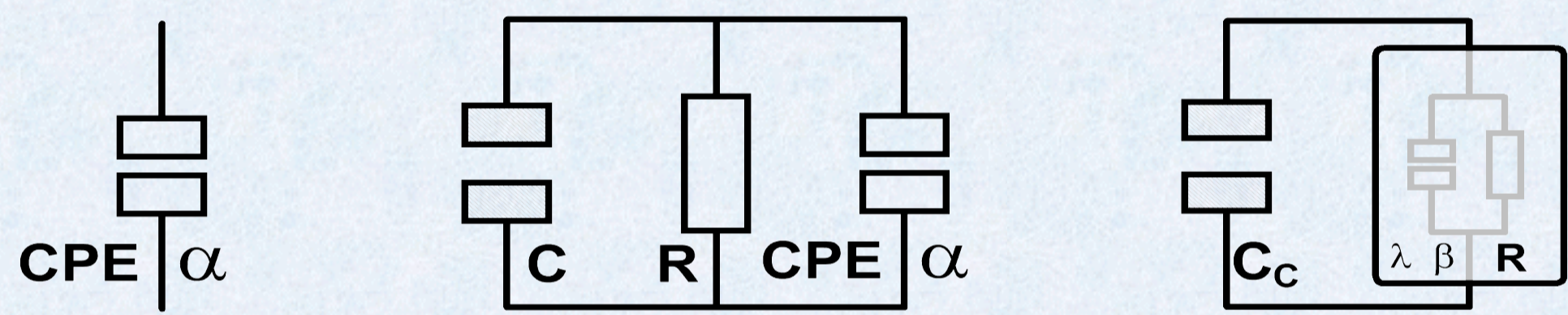


FIG 1: Evolution (data and fit) of impedance spectra during water uptake for two different coating systems [5].

In a common procedure for water uptake measurements using EIS the high frequency part of an impedance spectrum is monitored and the changes as a function of immersion time are interpreted as the change of the dielectric of the coating material using a constant phase element (CPE – Scheme 1a.).



Scheme 1: Models for the interpretation of water uptake; a.) simple CPE (left hand side); b.) capacity in parallel to a combination of a CPE and a pore resistance R (middle) and c.) coating capacity in parallel to a dielectric relaxation process (right hand side) representing the pore impedance [5].

In a recent paper [5] we reported that the water uptake can be well modeled by the superposition of two processes using a quite simple equivalent circuit, consisting of an ideal dielectric, i.e. the coating capacity C_c and an element in parallel, representing a dielectric relaxation process, for instance a two-step continuous time random walk (CTRW-2). The latter element stands for the electrical response of free sites or pores within the coating material and consists mathematically of a time constant λ_{Pore} , a fractional exponent β and requires at least a scaling factor (R_{Pore}). In the time domain, the equation for the CTRW-2 process reads:

$$U(t) = I_{\text{Exc}} \cdot R_{\text{Pore}} \cdot \left[\frac{4^\beta}{4^\beta - 1} \cdot \exp[-(\lambda_{\text{Pore}} \cdot t)^\beta] - \frac{1}{4^\beta - 1} \cdot \exp[-(4 \cdot \lambda_{\text{Pore}} \cdot t)^\beta] \right]$$

where $U(t)$ denotes the potential decay after the removal of an electrical field and I_{Exc} is the current before the removal of the field. The expression can be transformed by means of Laplace transform to yield the frequency representation of this pore impedance [6].

For convenience and comparison purposes, one can evaluate a 'pore capacity C_{Pore} ' from the time constant λ_{Pore} and the pore resistance R_{Pore} according to:

$$C_{\text{Pore}} = \frac{1}{\lambda_{\text{Pore}} \cdot R_{\text{Pore}}}$$

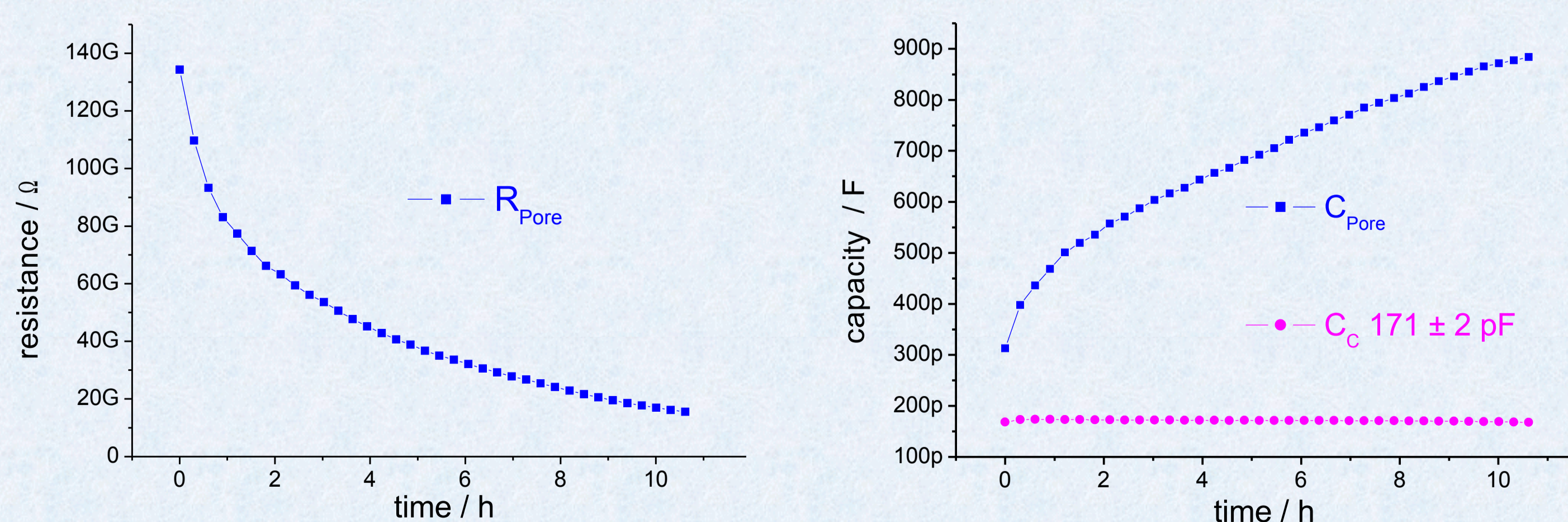
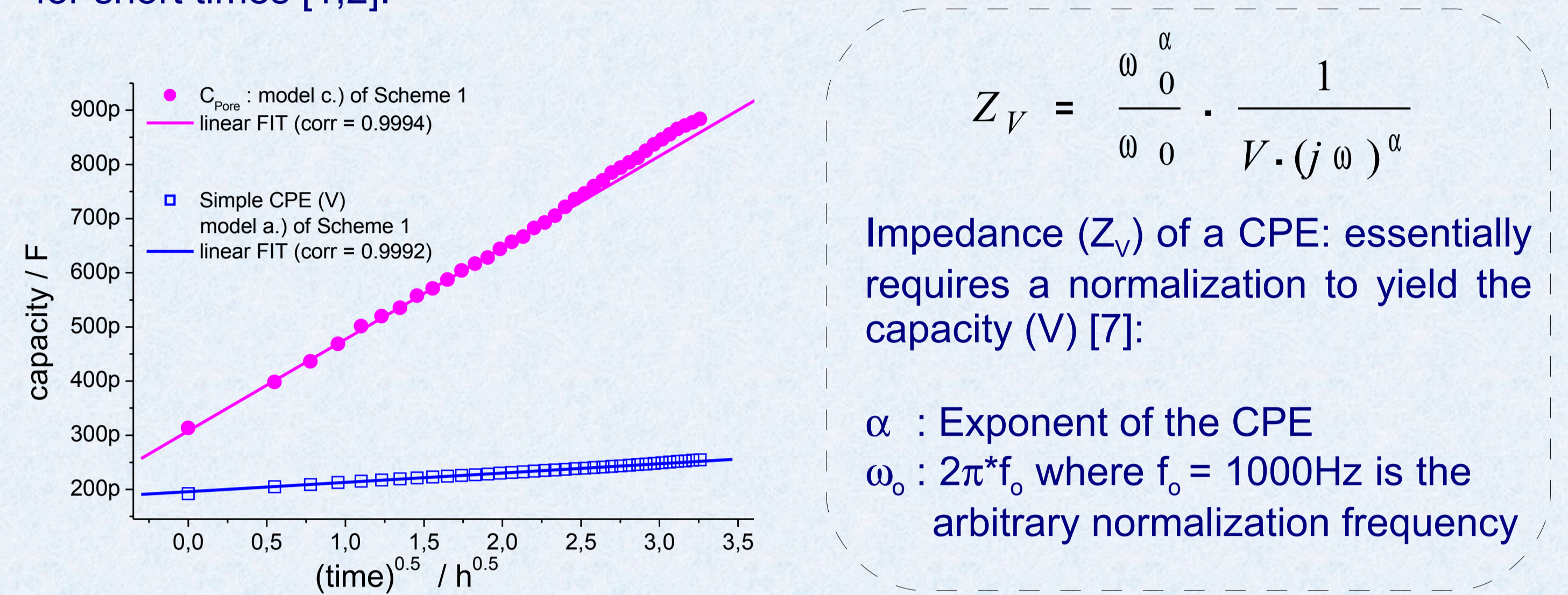


FIG 2: Evolution of the coating (FIG 1, left hand side) parameters during water uptake for a representative coating system according to the pore model (Scheme 1c)).

Concerning FIG 2 one immediately recognizes that the coating capacity C_c stays constant whereas the pore parameters R_{Pore} and C_{Pore} change with immersion time.

Diffusion in Barrier Coatings

For a quantitative characterization of the water uptake in barrier coatings, the determination of diffusion type as well as the determination of the amount of incorporated electrolyte is a common task. Assuming Fickian diffusion, the plot of $C(t)$ as a function of the square root of the immersion time should result in a straight line for short times [1,2].



$$Z_V = \frac{\omega^\alpha}{\omega^\alpha} \cdot \frac{1}{V \cdot (j\omega)^\alpha}$$

Impedance (Z_V) of a CPE: essentially requires a normalization to yield the capacity (V) [7]:

α : Exponent of the CPE
 ω_0 : $2\pi \cdot f_0$ where $f_0 = 1000\text{Hz}$ is the arbitrary normalization frequency

FIG 3: Determination of diffusion type for short immersion time (coating of FIG 1, left hand side); blue squares according to model a.) and magenta discs according to model c.) of scheme 1.

For short times, the linear relationship indicates Fickian diffusion, independent of the model for the evaluation of the corresponding capacities. The numerical difference in intercept and slope derives from the normalization of the CPE (V). The accuracy however, expressed by the correlation coefficient (corr) is still the same.

Fickian Diffusion – long time

For longer immersion times, ideal Fickian diffusion can be evaluated quantitatively when plotting $\ln(C(t))$ as a function of time, where $C_{t=0}$ is the (Pore) capacity at the beginning of the experiment and C_∞ at saturation, L stands for the coating thickness and D is the diffusion coefficient [3,4].

$$\ln(C(t)) = \left[1 - \frac{8}{\pi^2} \cdot \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \cdot \exp\left[-\frac{(2n+1)^2 \cdot \pi^2}{4 \cdot L^2} \cdot D \cdot t\right] \right] \cdot \ln\left(\frac{C_\infty}{C_{t=0}}\right) - \ln(C_{t=0})$$

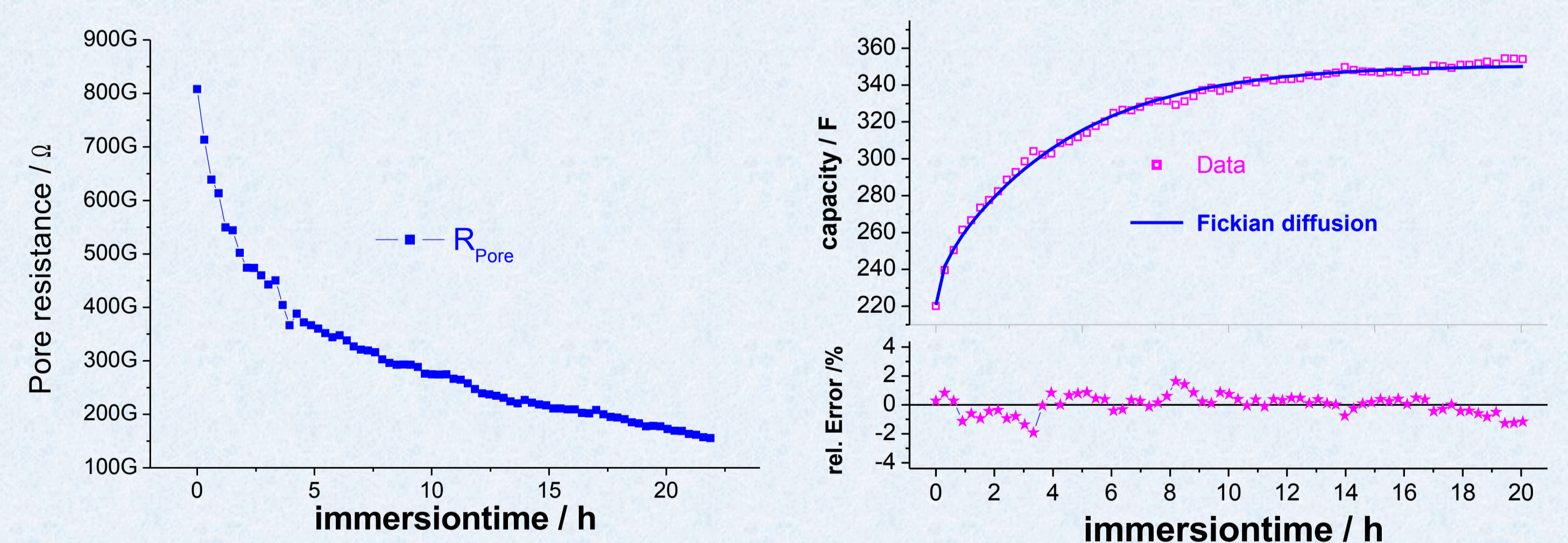


FIG 4: Evolution of R_{Pore} and C_{Pore} (coating of FIG 1, right hand side). Blue line on the right hand side: fit for Fickian diffusion. Small diagram at the bottom: relative error between data and fit \Rightarrow confirmation of Fickian diffusion

Conclusion

On summarizing the results, i.e.

- The accuracy of the determination of the diffusion type for short times of immersion using the 'pore impedance' corresponds to the traditional procedure (pure CPE)
- The evolution of R_{Pore} is obtained by fitting each impedance spectrum of the series according to the pore model which implies a strong extrapolation to lower frequencies (see FIG 1, right hand side)
- The value of the simulated pore resistance is extremely high and exceeds 500 GΩ at the early stages of water uptake
- Nevertheless, combining R_{Pore} and λ_{Pore} yields C_{Pore} which can be well fitted, assuming ideal Fickian diffusion

one has to conclude that these two parameters depend on each other. Hence, the electrochemical response of the free sites within the coating material must be modelled by a single element to take into account this physical dependency.

References

- [1] A. S. Castela, A.M. Simões; Prog. Org. Coat 46, (2003) 55
- [2] A.M. Simões, D.E. Tallman, G.P. Bierwagen; Electrochem. Solid State Letters 8 (2005) B60
- [3] E.P.M van Westing, G.M. Ferrari, J.H. de Wit; Corr. Sci 36 (1994) 957

- [4] M. M. Wind and H. J. W. Lenderink; Prog. Org. Coat 28 (1995) 239
- [5] W. Strunz, C. A. Schiller, J. Vogelsang, Materials and Corrosion 59 (2008) 159
- [6] W. Strunz, C. A. Schiller, J. Vogelsang, El. Acta 51 (2006) 1437
- [7] Zahner Software manual, Kronach Germany