

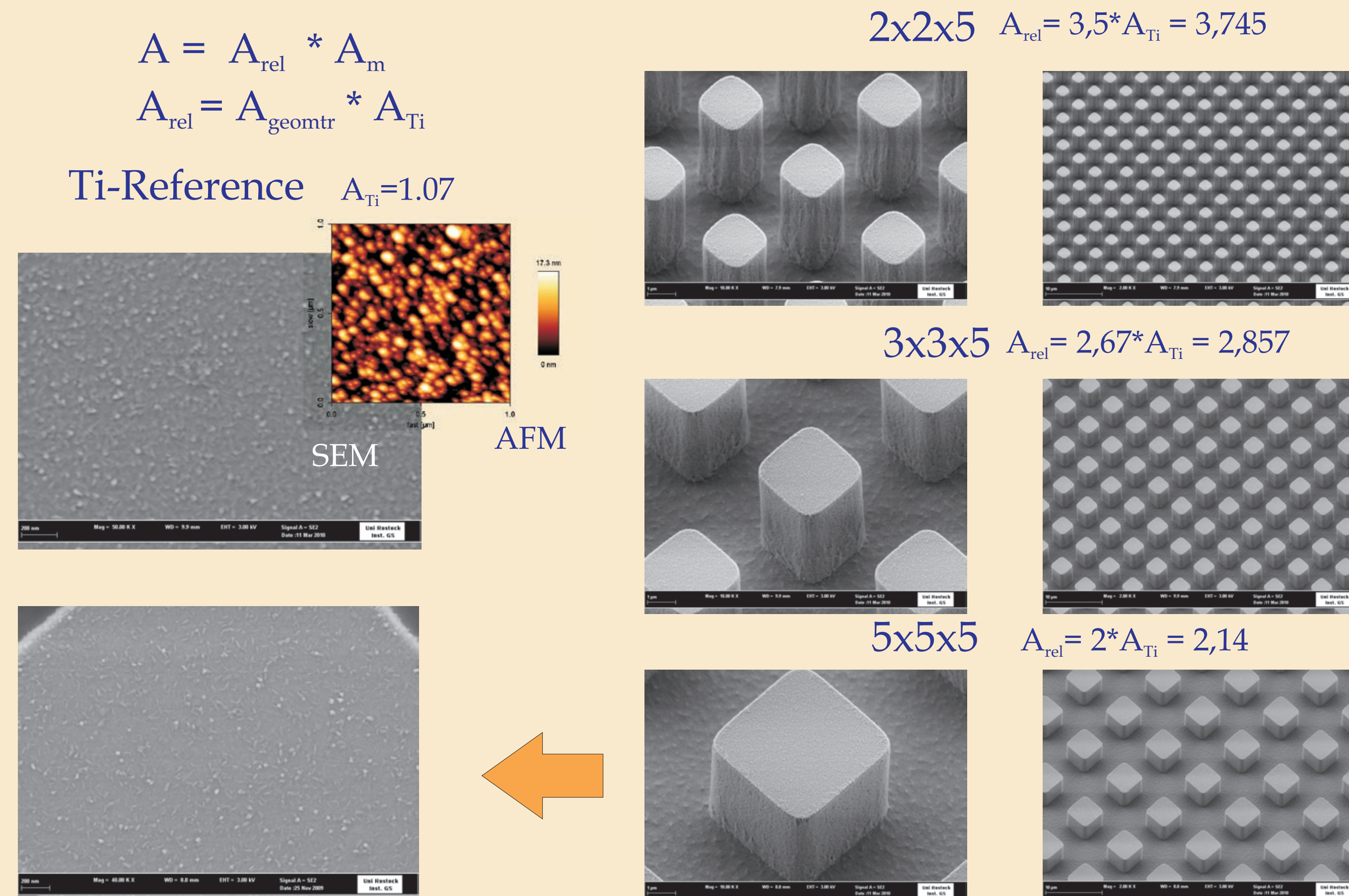
Introduction

Electrochemical methods are a good choice for the characterization of implant materials because conditions in the human body can well simulated by using a physiological liquid as electrolyte. Among others the electrochemical impedance spectroscopy (EIS) is a common used method for the determination of the real surface area of rough or otherwise structured surfaces [1]. By this method the increasing of the real surface area can be determined by measuring the capacity of the electrochemical double layer (EDL) that is covering the material surface in the electrolyte. In real measurement the capacitance of the EDL shows a no ideal behavior, i.e. a frequency dependency of the capacitance is observed. This frequency dispersion is considered by replacing the ideal capacity in the equivalent circuit by a Constant Phase Element (CPE). But in this case the difficulty is the conversion of the CPE capacitance parameter into the real capacitance. Although this problem is known a long time there are only few publications dealing with this problem and its application in practice [2, 3]. In our special case we tried to compare the real surface area of structured titanium surfaces with regular geometry. Two methods are introduced and their results are compared.

Material and methods

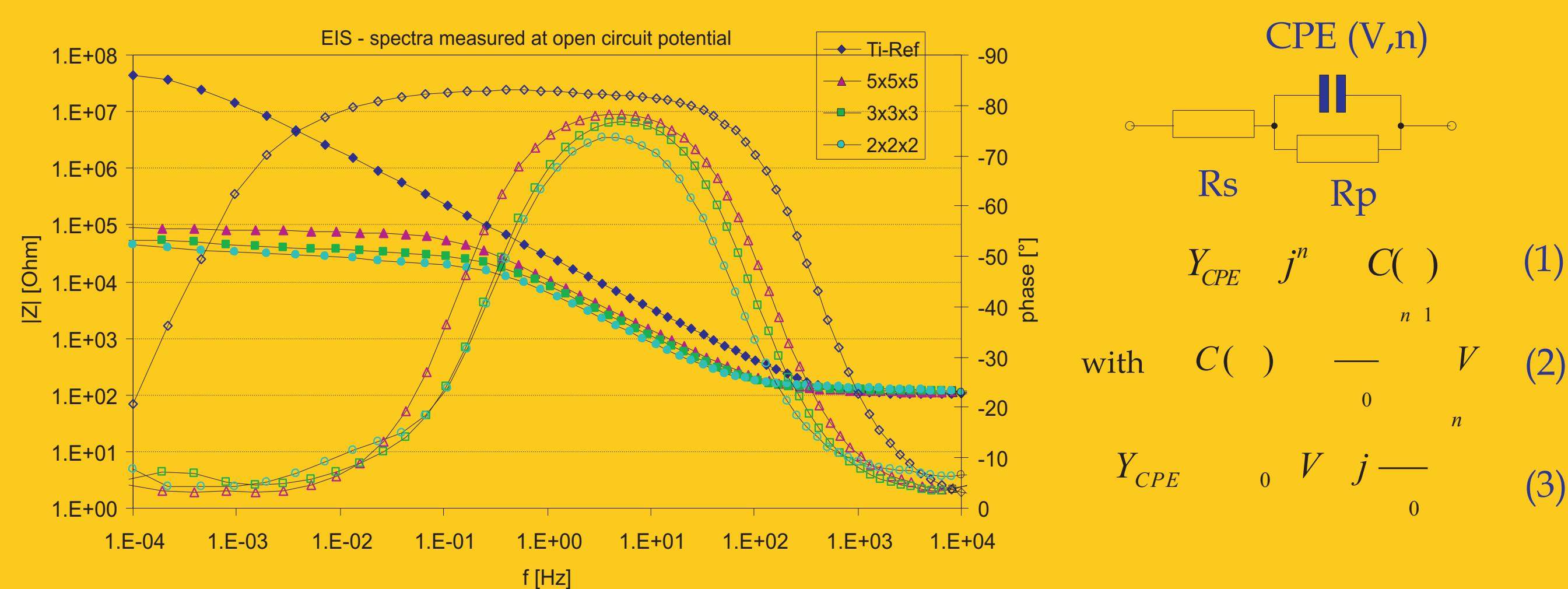
Titanium surfaces with regular geometry were produced by structuring silicon substrates with common used methods (Deep Reactive Ion Etching, DRIE) and then sputter coated with 100 nm Titanium (ZfM Chemnitz, Germany) [4]. We used pillar arrays in different lateral dimensions and the same depth of 5 μm. The pillars were quadratic with the dimensions of 2 μm (2x2x5), 3 μm (3x3x5) and 5 μm (5x5x5). The distance between the pillars was always the same as their width. For the flat reference sample Silicon was polished and also sputter coated with 100 nm Titanium. The samples were characterized by Scanning Electron Microscopy (FE-SEM Supra 25, Zeiss, Germany) and EIS (IM6e, Zahner Elektrik, Germany). The measuring area in the electrochemical experiment was the same for all samples (A_m = 19,6 mm²). The theoretical relative surface increasing of the samples (A_{rel}) was obtained by calculating A_{geomtr} from geometry and multiplying it with the surface increasing of the sputtered titanium film (A_{Ti}) measured by atomic force microscopy (JPK Berlin, Germany). SEM pictures in high magnification (see aside) show that the fine structure of the Titanium is the same on the flat reference (above) and structured (below) samples.

SEM and AFM



Analysis of impedance spectra with Constant Phase Elements (CPE)

The measured impedance spectra (see examples below, one for each surface modification) were fitted with a simple equivalent circuit using a Constant Phase Element (CPE) considering the observed frequency dispersion instead of a capacitance. The admittance of a CPE used for the fit by the Zahner-Software is given by equations (1-3). The frequency dependent capacity was calculated from the CPE parameters V, ω₀ and n using equation (2).

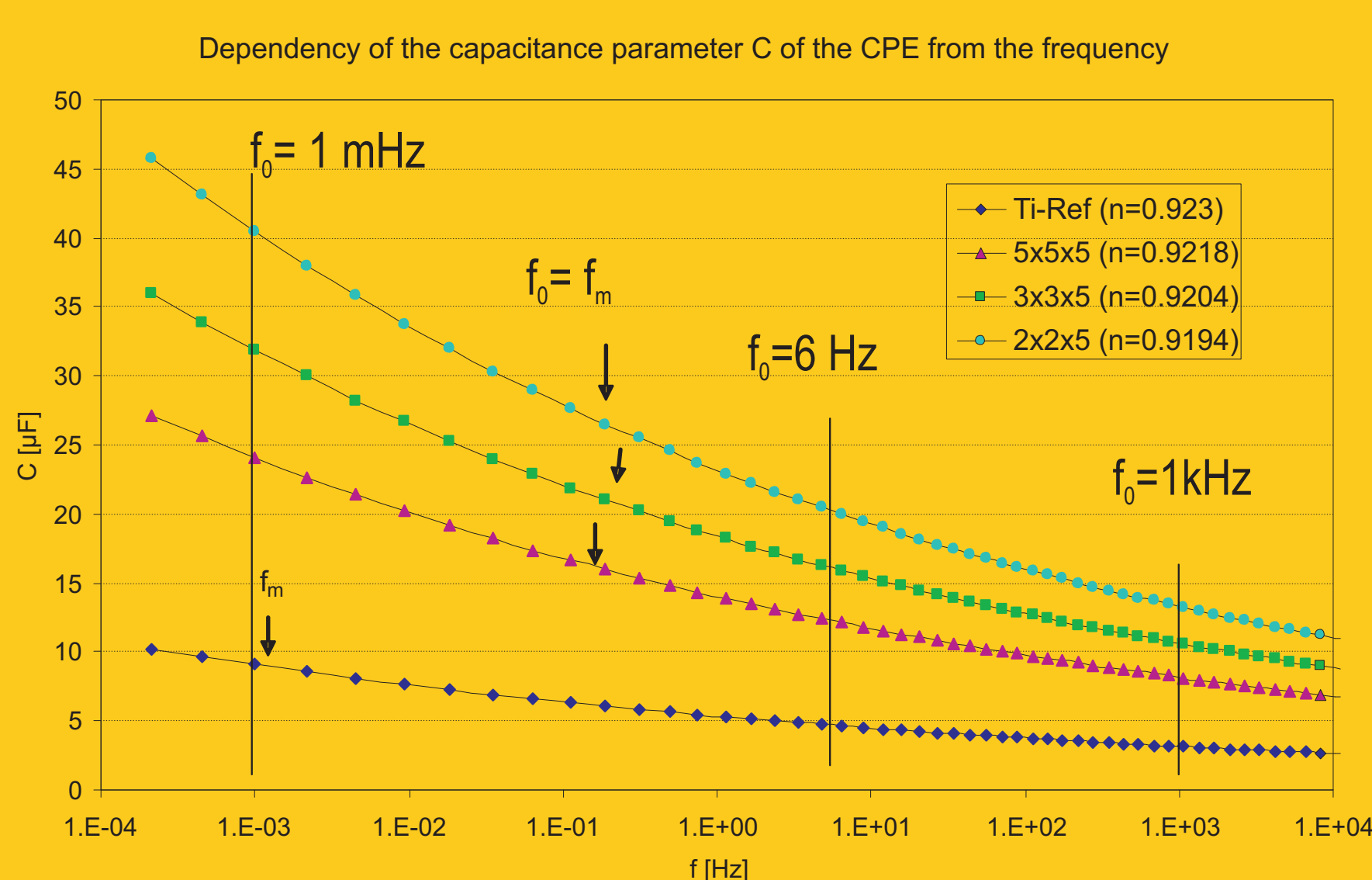


The reference frequency ω₀ is an arbitrarily selectable parameter, whose value by default is given with 6,28 kHz (f₀=1kHz) by the Zahner software but the user can change it as needed. Otherwise using equation (2) it is also possible to convert [ω₀V] to other pairs of values [C]. The results are shown in the figure below for the same examples shown in the diagram above. As you can see the frequency dependency of the capacity is higher when the exponent n stronger deflects from 1.

Now the question arises at which reference frequency ω₀ the capacity of the CPE reflects the "real capacity" of the surface and is suitable for comparison of the surface increasing of the different structured samples?

In the first way we used a fixed reference frequency to compare all samples. We did this for three several frequencies (1 mHz, 6 Hz and 1 kHz), see the picture aside.

The second way is given by literature [2]. Here it is proposed to use ω_m as reference frequency:



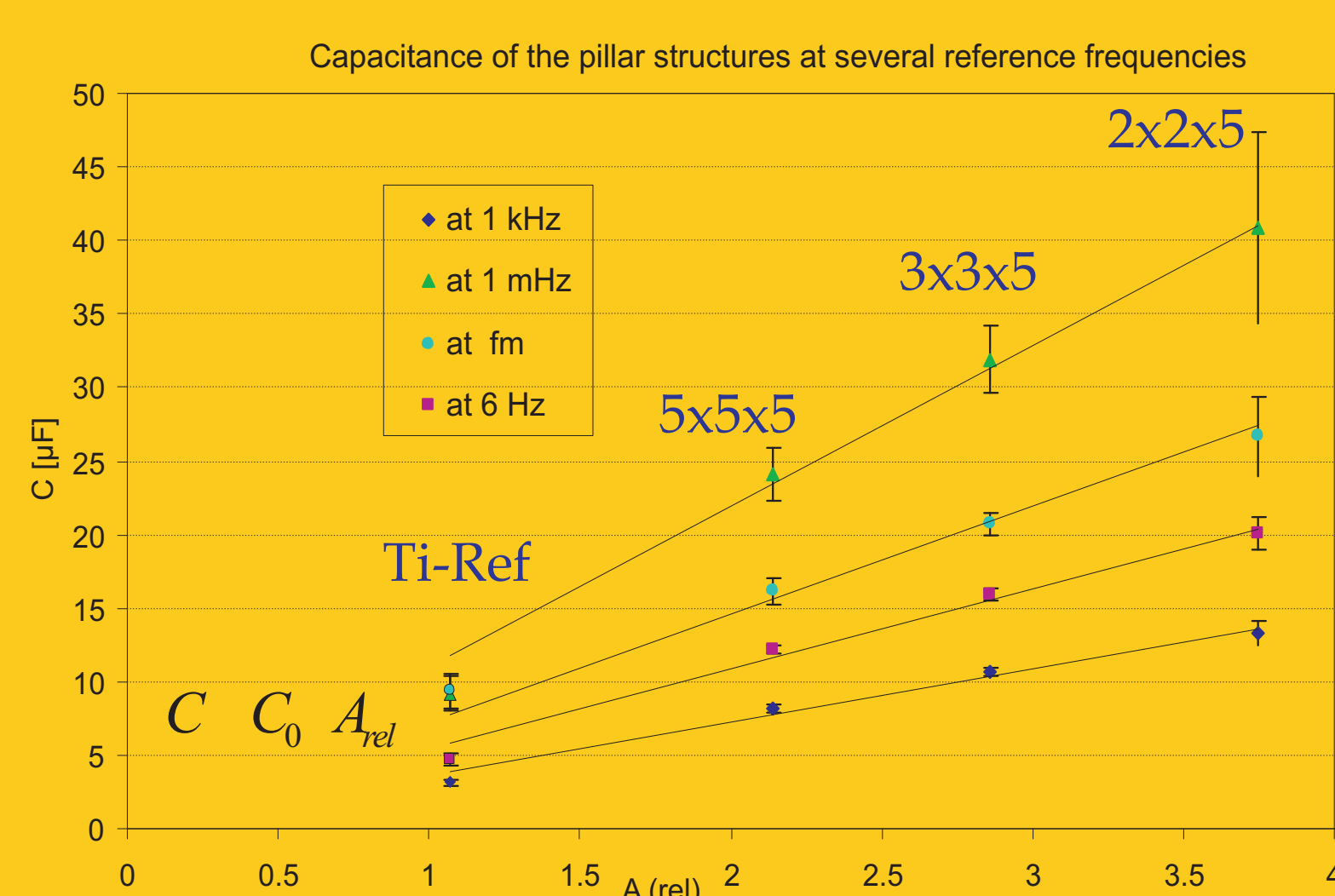
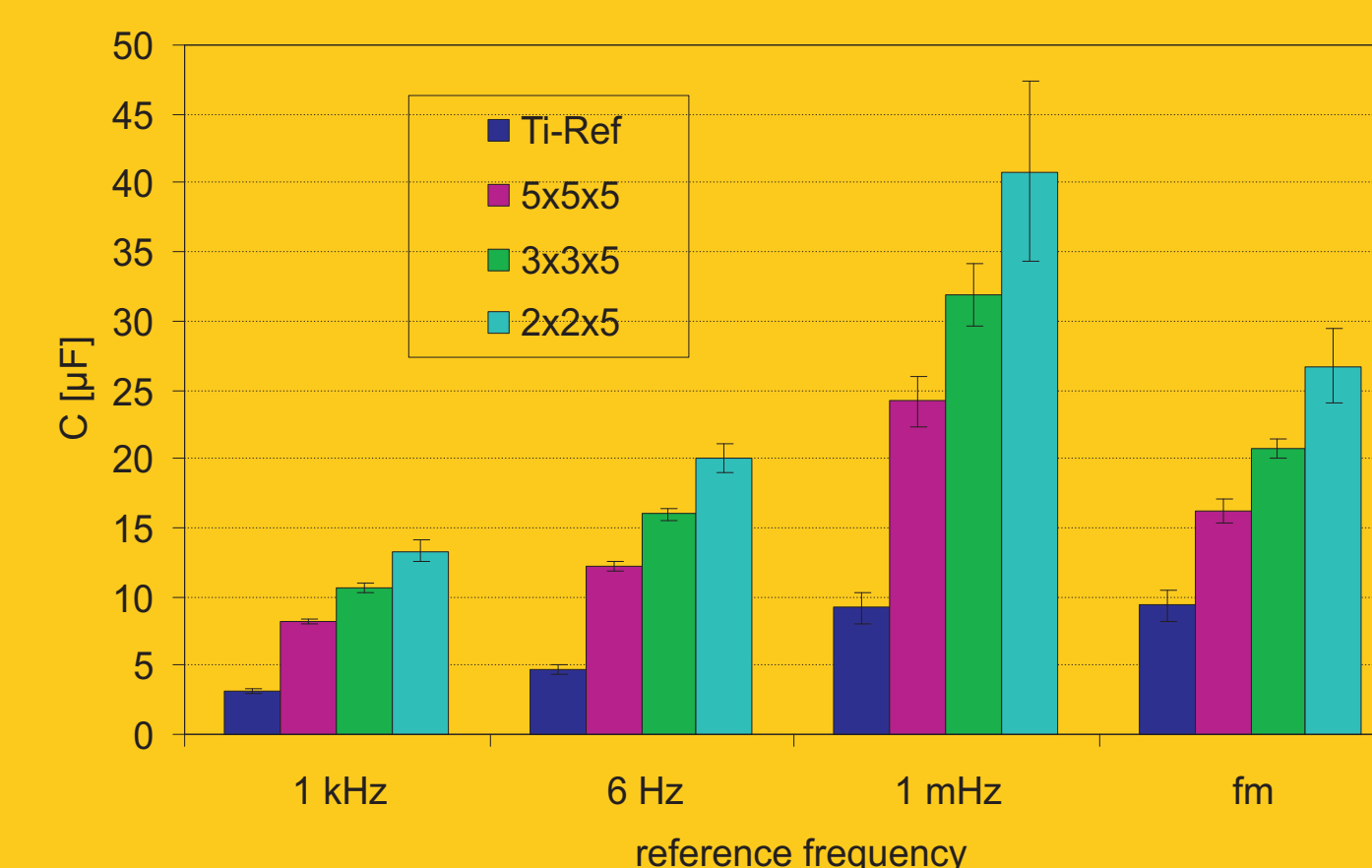
which is represented by the reciprocal of the time constant, where the modulus of the imaginary part of the impedance Z'' has a maximum.

$|Z''(\omega_m)|_{max}$

Because the time constant C*Rp is different for all samples the reference frequency ω_m = ω₀/2 also had to be determined individually for all samples, see the picture above. As you can see, ω_m for the flat reference sample is very different from that of the other samples because Rp is much higher.

Results of Electrochemical Impedance Spectroscopy

In the picture aside the results for the capacity are shown for all investigated samples. The first three groups (1kHz, 6 Hz, 1 mHz) show the results obtained by the first way using a fixed reference frequency for all samples. The last group (ω_m) shows the results for the second way recommended in literature. As you can see, we got different results for the proportions of the capacity of the structured samples among each other. But because the samples have a defined geometrical structure it is possible to evaluate these experimental results by calculating the theoretical surface increasing and comparing it with them.



In this figure the capacity is shown as a function of the relative theoretical increasing of the surface area A_{rel} given by the geometry of the samples and their fine structure of the titanium film. All curves show a good linear dependency, that means that the relations between the samples in surface increasing are reflected correctly independent of the use of several reference frequencies. Merely the slope of the regression line is different depending on the use of the several reference frequencies. But what is the physical meaning of this slope? It must be the capacity C₀ of a sample with A_{rel}=1, i.e. the total capacity of a sample with a flat surface of the measuring area (A=A_m = 19,6 mm²).

In our experiment this capacity C₀ is different depending on the used reference frequency and so we have to decide which C₀ is the right value for the total capacity. The second method proposed in literature (reference frequency ω_m) seems to be plausible, using this method we obtain app. 7,31 μF for the total capacity of a flat sample with A_{rel}=1, or measuring area A=A_m of 19,6 mm², respectively. But there is no evidence for the accuracy of this result and it has to be found to evaluate the result in practice.

Conclusions and Summary

Characterizing the surface increasing of structured samples by measuring the double layer capacity with EIS is a common used method. But normally at structured surfaces a frequency dispersion appears and this has to be considered by using a CPE in curve fitting and calculating its capacitance from the CPE-parameters V and n. Especially if the exponent n of the CPE strongly deflects from 1 the error in calculated capacity can be very high. With the help of defined geometrically structured samples we tried to calculate the surface capacity considering the frequency dispersion and we used two methods for it. We got different results depending on the chosen method. Now it is necessary to find another method for verification these results and to decide which method is better suited to obtain a value for the real capacity from the CPE.

References

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Regina Lange
 University of Rostock, Department of Informatics and Electrical Engineering
 Albert-Einstein-Str. 2, D-18051 Rostock
 +49 381 498 7236 Fax +49 381 498 118 7236
 E-Mail: regina.lange@uni-rostock.de