

## Determination of the correct value of $C_{dl}$ from the impedance results fitted by the commercially available software

### Introduction

With the introduction of a constant phase element (*CPE*) as a replacement for the capacity in EIS measurements, most of the experimentally obtained results could be fitted by commercially available software ([Gamry](#), Scribner, Solartron, etc.). Much better fit results were obtained with *CPE* in comparison with the fit results obtained by using pure capacity, represented by parallel plate condenser. Taking into account that the *CPE* defines inhomogeneity of the surface in the electrochemical EIS experiments and inhomogeneity of the charge distribution in solid state EIS measurements, it is reasonable to expect that better fit for real systems is obtained by using *CPE*. The main problem in the use of commercially available software with *CPE* is the fact that the capacity, obtained by fitting procedure, does not have the dimension of capacity, i.e.,  $F\text{ cm}^{-2}$ , or  $\Omega^{-1}\text{ cm}^{-2}\text{ s}$ , but its dimension is given in  $\Omega^{-1}\text{ cm}^{-2}\text{ s}^{\alpha}$ , where  $\alpha$  is the exponent in the equation for the *CPE* [1] ( $Z_{CPE} = Z_{dl}(j\omega)^{-\alpha}$ ).

This problem has been discussed in few papers [2-4] and recently Hsu and Mansfeld [5] developed the equation for correction of capacity to its real value, in the case of parallel connection of *CPE* and  $R$ , by using equation (1).

$$C_{dl} = A_{dl}(\omega''_{\max})^{\alpha-1} \quad (1)$$

where  $\omega''_{\max}$  represents the frequency of the maximum on the  $-Z''$  vs.  $\omega$  dependence, which is independent of the exponent  $\alpha$ , while  $A_{dl}$  represents the result of fitting.

While discussing different procedures for the treatment of the distribution of time constants, M.

Orazem, *et. al.* [6] pointed out that the impedance of an equivalent circuit for parallel connection of *CPE* and  $R$  can be expressed by either equation (2) or equation (3)

$$Z(\omega) = \frac{R}{1 + (j\omega CR)^{\alpha}} \quad (2)$$

$$Z(\omega) = \frac{R}{1 + (j\omega)^{\alpha} CR} \quad (3)$$

It is important to note that equation (3) is used in all commercially available software for fitting impedance spectra.

Most recently it was shown for Ag(111) in 0.01 M NaCl [7] and Cu single crystals in 0.1 M NaOH [8] that even single crystal surfaces cannot be treated as being homogeneous and that, instead of  $C_{dl}$ , *CPE* should be introduced in the analysis of  $C_{diff}$  versus  $f$  curves for the adsorption of investigated anions. Equation (4) is obtained [7] by replacing  $C_{dl}$  by a *CPE*, and using the commercial software definition of a *CPE*.

$$C_{diff} = \frac{Y''}{\omega} = A_{dl} \omega^{\alpha-1} \sin\left(\frac{\alpha\pi}{2}\right) + \frac{C_{ad}}{1 + \omega^2 C_{ad}^2 R_{ad}^2} \quad (4)$$

Since in this equation  $A_{dl}$  does not have the dimensions of capacity, it was necessary to correct the value of  $A_{dl}$  obtained by fitting experimental  $C_{diff}$  versus  $f$  curves. According to G. J. Brug, *et. al.* [9], for a series connection of the *CPE* and  $R_s$  (solution

resistance), the value of  $C_{dl}$  should be defined by equation (5) [7].

$$C_{dl} = \left[ A_{dl} R_s^{-(\alpha-1)} \right]^{1/\alpha} \quad (5)$$

In this work the analysis of the differential capacity and the impedance of the electrochemical process corresponding to the parallel connection of  $CPE$  and  $R$  is performed in order to define the relation between the real value of the capacity and the value obtained by fitting EIS results using commercially available software.

## Results and discussion

Considering equations (2) and (3), it can be concluded that the former one, equation (2), seems to be more correct, since in this equation the frequency dispersion of the capacity, as a consequence of the surface inhomogeneity, is closely related to the charge transfer distribution over the same surface and these two factors are mutually dependent. The differential capacity derived from equation (2) is:

$$C_{diff} = (C_{dl})^\alpha (\omega R)^{\alpha-1} \sin\left(\frac{\alpha\pi}{2}\right) \quad (6)$$

The differential capacity derived from equation (3) is:

$$C_{diff} = A_{dl} \omega^{\alpha-1} \sin\left(\frac{\alpha\pi}{2}\right) \quad (7)$$

Hence, equation (6) is dimensionally correct, while equation (7) is dimensionally incorrect, *i.e.*, additional correction is necessary.

Simultaneously the real ( $Z'$ ) and the imaginary ( $Z''$ ) component of the impedance are defined by equations (8) and (9) respectively.

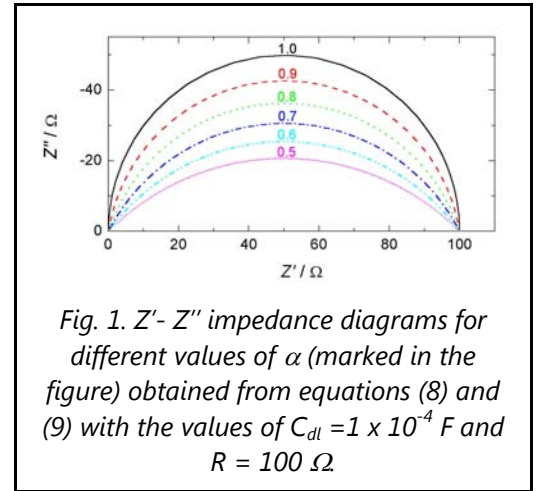
$$Z' = \frac{R \left[ 1 + (\omega CR)^\alpha \cos\left(\frac{\alpha\pi}{2}\right) \right]}{1 + 2(\omega CR)^\alpha \cos\left(\frac{\alpha\pi}{2}\right) + (\omega CR)^{2\alpha}} \quad (8)$$

$$Z'' = -\frac{R(\omega CR)^\alpha \sin\left(\frac{\alpha\pi}{2}\right)}{1 + 2(\omega CR)^\alpha \cos\left(\frac{\alpha\pi}{2}\right) + (\omega CR)^{2\alpha}} \quad (9)$$

In the case that  $CPE$  is considered as independent parameter, as in commercially available software (equation (3)), equation for the differential capacity is given by equation (7), while  $Z'$  and  $Z''$  are defined by equations (10) and (11) respectively and are dimensionally incorrect.

$$Z' = \frac{R \left[ 1 + \omega^\alpha CR \cos\left(\frac{\alpha\pi}{2}\right) \right]}{1 + 2\omega^\alpha CR \cos\left(\frac{\alpha\pi}{2}\right) + (\omega^\alpha CR)^2} \quad (10)$$

$$Z'' = -\frac{R\omega^\alpha CR^2 \sin\left(\frac{\alpha\pi}{2}\right)}{1 + 2\omega^\alpha CR \cos\left(\frac{\alpha\pi}{2}\right) + (\omega^\alpha CR)^2} \quad (11)$$



Using equations (8) and (9) it can be shown that  $Z'$ - $Z''$  diagrams (Fig. 1) are identical to the ones obtained by using equations (10) and (11), but there is significant difference in the shape of  $-Z''$  vs.  $\log f$  for these two cases. As it is mentioned in the paper of Hsu and Mansfeld [5], when impedance equations (8) and (9) are used the maximum on the  $-Z''$  vs.  $\log f$  is independent of frequency (Fig. 2). After fitting experimental results by commercially available software, the correct value of the double layer capacity can be obtained by using equation (1).

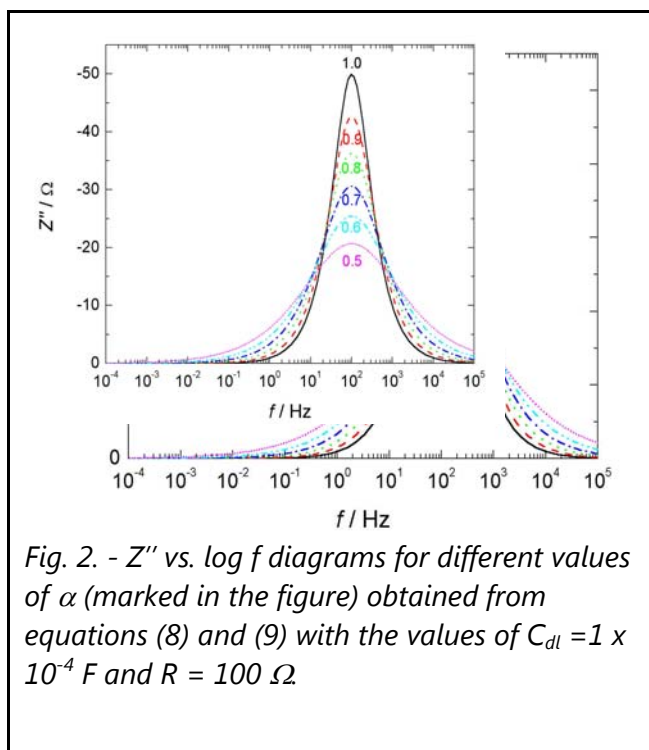


Fig. 2. -  $Z''$  vs.  $\log f$  diagrams for different values of  $\alpha$  (marked in the figure) obtained from equations (8) and (9) with the values of  $C_{dl} = 1 \times 10^{-4} \text{ F}$  and  $R = 100 \Omega$ .

The difference between the correct and fitted value of the capacity could be significant and this difference depends on the values of  $R$  and  $\alpha$ , as shown in Fig. 3.

## Conclusion

From the results and discussion it could be concluded that only in the case of parallel connection of  $CPE$  and  $R$  correction for the real value of the double layer capacity by using equation (1) is valid.

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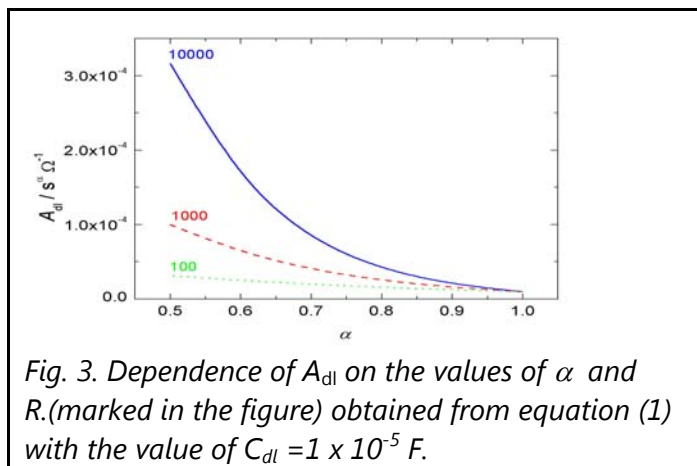


Fig. 3. Dependence of  $A_{dl}$  on the values of  $\alpha$  and  $R$  (marked in the figure) obtained from equation (1) with the value of  $C_{dl} = 1 \times 10^{-5} \text{ F}$ .

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