Toward a better characterization of constant-phase element behavior on disk electrodes from direct impedance analysis: Methodological considerations and mass transport effects

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ABSTRACT

Complex nonlinear-least-squares fitting of impedance data to an equivalent circuit is probably the most intuitive method used to represent the whole electrode impedance from experimental electrochemical impedance spectroscopy data. However, among other questions it has the primary problem of identifying a physically significant model representing the system under examination. In that context it then becomes very suitable the study of other analysis procedures to complement this approach. With regard to constant-phase element (CPE) behavior characterization, direct impedance analysis seems to be a good choice since CPE behavior is explicitly revealed in the high frequency decay of the imaginary component of the impedance. For that reason it is becoming popular among electrochemists who can get the CPE exponent from a simple fit of the imaginary part of the impedance to a frequency power law. There are, however, important limitations to the frequency range employed in this analysis that are commonly ignored. In the case of disk electrodes, geometrical constraints related to the insulating-metal boundary induce current and potential distributions that screen the real underlying CPE behavior in the high frequency domain. On the other hand, for lower frequencies, CPE behavior can also be masked by the effects of diffusion. In this paper we present some methodological considerations taking these effects into account in order to get a more reliable characterization of the CPE behavior from direct impedance analysis. We illustrate these issues with different experimental conditions and show that in many cases deviations can be remedied thanks to a convenient theoretical treatment that allows correct values of CPE parameters to be retrieved.

1. Introduction

Frequency dispersion observed in the impedance response of many solid electrode/electrolyte interfaces is generally accepted to originate from either surface or normal-to-surface time-constant distributions caused by interface heterogeneity [1,2]. This behavior has been related, for example, to surface disorder and roughness [3–13], to electrode porosity [13–17], to specific anion adsorption [18], to electrode geometry [1,19–21] and to normal-to surface distributions of properties in oxide layers, passive films and coatings [22,23]. In the mathematical modeling of these systems double

layer capacitance is replaced by a constant-phase element (CPE) [24] with the following impedance [25]:

$$Z_{CPE} = \frac{1}{Q(i\omega)^{\alpha}}, \tag{1}$$

with CPE parameters α – also known as the CPE exponent – and Q ($F\,cm^{-2}\,s^{\alpha-1}$).

A reliable estimate of these parameters is important because of the information we can get from them about different interface aspects. CPE exponent α is by itself a very relevant quantity since it has been usually considered as an indicator of the heterogeneity degree. From a long time many authors have argued that α is inversely related to surface roughness [5,11–13,26–28], although there is no general agreement and it is still a matter of controversy [10]. The direct association between CPE behavior and roughness appears for fractal electrodes, with theoretical relationships between the CPE exponent and the fractal dimension [7,9,29–37]. More recently [4,6] it has been shown that the extent of the deviation of α from the ideal capacitive behavior ($\alpha = 1$) seems to be more

related to surface disorder, i.e. heterogeneities on the atomic scale, rather than to roughness, i.e. geometric irregularities much larger than those on the atomic scale. In the case of polycrystalline metal electrodes, capacitance dispersion is observed even for very low degrees of roughness [5] or surface disorder [4,38]. In those cases the origin of CPE behavior seemed to be more related with the random distribution of interfacial capacitance [6,39]. In a simple model in which CPE behavior is caused by a double-layer capacity distribution along the interface [38], α is found to be closely related to the variance of the time constant distribution that exactly results in a CPE behavior. The associated (non-normalizable) distribution function of relaxation times associated to a CPE was already derived much earlier [40]. Another evidence of the importance of a reliable estimate of CPE parameters comes from the estimate of the interfacial capacitance. Different mathematical formulas, being the most relevant those of Brug et al. [38] and Hsu and Mansfeld [41], have been widely used to extract effective capacitance values – and by extension active surface area values – from CPE parameters (see [2] and references therein).

CPE parameters estimate has been mainly carried out from the complex nonlinear-least-squares fitting (CNLS) of immitance data to an equivalent electric circuit (EC) [42]. In fact, it is probably the most intuitive method used to represent the electrode impedance from experimental EIS data, and it is also the procedure providing most information about interface quantities and processes. It has, however, the fundamental problem of identifying a physically significant fitting model. Many empirical models leading to good fits of experimental data are worthwhile only to represent data and do not allow identification and interpretation of the physic-chemical parameters and processes involved. This can lead to important ambiguities that may require additional information about the system for their adequate resolution (see discussion in [43]). Besides this fundamental question, there are technical factors in the fitting procedure – e.g. the form in which data is weighted – which can lead to significant deviations in the fitted parameters. In this scenario it becomes appropriate the study and development of other approaches to complement the analysis from this technique. That might be the case of direct analysis of the imaginary component of the impedance [44], which is the object of the present study. It is based on the idea that the imaginary part of the impedance asymptotically behaves in the high frequency domain, where other effects vanish, as a power law of the form: $Z_i \sim f^{-\alpha}$. That means that CPE parameters can be easily obtained from a linear regression, without further considerations, when impedance response is obtained in the proper frequency domain. For that reason this approach has gained interest in the last years [1,2,44,45].

However, this asymptotic behavior may be not reached in many experimental conditions, as it is the case of disk electrodes. In a series of theoretical papers in which different scenarios were addressed, Huang et al. [19–21] explored the role of geometry-induced current and potential distributions on the global and local impedance responses of disk electrodes. They showed that these distributions affected the impedance response above a critical frequency, here denoted to as f_{max}, inducing and apparent pseudo-CPE behavior in those cases for which local capacitive behavior is ideal, or masking the underlying local CPE behavior when it is the case. This characteristic frequency takes the value $f_{max} = \kappa/2\pi C_{DL}r_0$ – being C_{DL} the interfacial capacitance, r_0 the disk radius and κ the conductivity of the electrolyte – for local capacitive behavior, whereas it is $f_{max} = (2\pi)^{-1}(\kappa/Qr_0)^{1/\alpha}$ for local CPE behavior with parameters α and Q. An important point is that this characteristic frequency can be well within the range of experimental measurements, thus representing an upper bound to the experimental frequency range to be considered in EIS data analysis when characterizing the real underlying behavior.

In a recent paper [45] we presented experimental results that were in agreement with this theory. There we showed that the crossover to the geometry-dominated regime may preclude the asymptotic underlying CPE behavior to be reached, thus leading to erroneous estimates of CPE parameters from direct analysis. In [45] we focused our analysis on the high frequency domain and we disregarded the effects of mass transport. It must be stressed however, that even for frequencies below f_{max}, convergence to the power law behavior can be very frequently affected by slower processes such as mass transport, the influence of which should also be taken into account in the analysis. In this sense, the present paper analyzes, with the help of theoretical modeling and experiments, the extent of these effects on the estimate of CPE parameters from direct analysis of the imaginary part of the impedance. The purpose is to provide some methodological insights aimed to get a reliable characterization of CPE behavior. We also discuss the optimal experimental conditions to measure CPE behavior.

2. Theory

We shall investigate CPE behavior of reactive electrodes with faradaic reactions. To set the basic ideas discussed thorough the paper we shall start by performing a simple analytical analysis with the help of the Randles circuit presented in Fig. 1(a), commonly used in EIS for interpretation of impedance spectra and which models interfacial electrochemical reactions in presence of convective diffusion. CPE impedance is given in (1) whereas the convective diffusion impedance $Z_D(f)$ has the expression of a finite stationary diffusion layer:

$$Z_D(f) = Z_D(0) \frac{\tanh\left(\sqrt{if/f_D}\right)}{\sqrt{if/f_D}},$$ (2)

where f_D is the characteristic frequency associated to the diffusion impedance.

Let us denote by f_0 the characteristic frequency associated to the relaxation of the pure CPE, i.e. without diffusion. f_0 is the frequency that maximizes the imaginary part of the impedance and has the form:

$$f_0 = \frac{1}{2\pi}(QR_{ct})^{-1/\alpha}.$$ (3)

The global impedance of interface model in Fig. 1(a) can be then expressed as function of dimensionless frequency $F = f/f_0$ as:

$$Z(F) = R_e + R_{ct}\frac{1}{(iF)^\alpha + [1 + z_D(F)]^{-1}},$$ (4)

where dimensionless convective diffusion impedance $z_D(F)$ has the form

$$z_D(F) = R\frac{\tanh\left(\sqrt{iF/\gamma}\right)}{\sqrt{iF/\gamma}},$$ (5)

with dimensionless parameters $R = Z_D(0)/R_{ct}$ and $\gamma = f_D/f_0$. In this form the influence of mass transport on high frequencies appears parameterized by both the ratio R between the dc impedance of mass transport and the charge transfer resistance, and the ratio γ of their respective characteristic frequencies.

CPE parameters estimate will be carried out from the analysis of the imaginary component of the impedance $Z_i(f)$ in the high frequency domain [44]. To estimate the CPE exponent we introduce the effective CPE exponent α_{eff} according to

$$\alpha_{eff}(f) = \left|\frac{d\log|Z_i(f)|}{d\log f}\right|,$$ (6)