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Characterization of frequency dispersion in the impedance response of a distributed model from the mathematical properties of the distribution function of relaxation times

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ABSTRACT

Heterogeneity and disorder univocally leads to distortion phenomena in the immittance response of a system. The analysis of this response in terms of a distribution of relaxation times (DRT) has become an important topic of basic and applied research. In this work we theoretically and numerically study the impact of the mathematical properties of a distribution function of relaxation times (DFRT) on the frequency dispersion displayed by the immittance response of a distributed model for an ideal dielectric system such as an ideally-polarized electrode, paying special attention to constant-phase-element (CPE) behavior. The analysis of the problem encompasses both explicit and implicit results reported in the literature, and a number of new findings. It is shown, for instance, that CPE exponent is upper bounded by 1, as found in experiments. Conditions to be fulfilled by the DFRT in order to give frequency dispersion are revealed, and CPE behavior is related to scale invariance. The extent of this capacitance dispersion on the frequency spectrum of the response is also addressed for both infinite and finite systems.

1. Introduction

Frequency dispersion observed in the immittance response of conductive and dielectric systems has been attributed to a number of phenomena, depending on the nature of the system being investigated, without a definitive choice usually being possible [1,2]. However, it is widely accepted that it results from the non-homogeneous distribution of some physical properties of the system or from system disorder.

Relationship between frequency dispersion and heterogeneity has been addressed for decades from different perspectives. One of the approaches to the problem has considered that system heterogeneity can be modeled by a distribution of time constants associated with activation or relaxation processes. Two methodologically opposite strategies, but complementary, have been followed, say, the *forward* and the *backward* approach. The backward approach consists in extracting the DFRT from immittance spectra [3–14]. Immittance is assumed to have the form of a kernel function of frequency and of the relaxation time (mostly the Debye relaxation kernel) which is distributed according to the unknown DFRT, giving a Fredholm integral equation of the first kind [3]. Although being an ill-posed inverse problem, different methods have been proposed to de-convolute impedance data: from the approximation by a Voigt series [4] to more elaborated procedures such as Fourier transform methods [5,6], maximum entropy methods [7], adaptive genetic evolution algorithm methods [8–10] or (Tikhonov) regularization methods [11–14]. Although these methods must still face several challenges [5], they have been revealed as an alternative or complementary way of analyzing electrochemical impedance spectroscopy (EIS) data, which has mostly relied on equivalent circuit interpretation.

Forward approach, to which this work belongs, is perhaps less directly applicable to experiments and more oriented to a fundamental comprehension of the problem. There, a DRT results explicitly or implicitly from the hypotheses of the model and immittance response is then calculated or simulated from the addition of the different contributions. The aim of this type of modeling is to understand how heterogeneity or disorder is reflected in the immittance response. It is worth noting that both backward and forward approaches may appear combined, as in backward DRT models that make use of a library of pre-defined DFRTs to minimize the functional form of the underlying DFRT (see e.g. [8–10]).

Among the different anomalous behaviors recognized in the literature, the CPE response [1,2], which takes the mathematical form of a fractional power-law (FPL) frequency dependence over

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limited-frequency ranges, has been likely the most addressed one because of its ubiquity. Nowadays this empirical response is widely used as a single distributed electric element [15] to model the impact of heterogeneity or disorder on EIS response. CPE impedance has the usual form [16]:

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

with the CPE parameter Q (μF cm^{-2}s$^{\alpha-1}$) and the CPE exponent $\alpha_{\mathrm{CPE}} < 1$. However, the physical information that we can extract from CPE parameters about underlying real processes, when it is used as a single circuit element, is still unclear [17,18]. For that reason it is more appropriate to fit data with a single overall model with physically-relevant parameters that hopefully can represent all physical phenomena present in the system, rather than isolating a single element, such as the CPE. That is the case, for example, of ordinary Poisson-Nernst-Planck (PNP) and anomalous (PNPA) models for charge-particle diffusion response, which include the possibility of both positive and negative mobile charge carriers, with them reacting or not reacting at the electrodes, as well as individual estimates of charge concentrations and diffusion coefficients [19,20].

Earlier works that follow the direct approach discussed above applied the concept of distribution at different levels (for a survey of the early literature see Ref. [21]): by directly considering a DFRT in their equations; by considering a distribution of activations energies under the assumption that time constants were thermally activated; or by assuming that relaxation processes of interest involve, at the elementary level, thermally activated storage (capacitance) and dissipation (resistance) of energy. This latter approach was addressed by Macdonald in a series of papers [21–23] with a model that took into account upper and lower bounds for the time constants of the system. In this form immittance response behaved ideally at the extremes of the frequency spectrum, whereas for intermediate frequency values it was shown [21,22] that an exponentially-distributed activation energy can yield CPE-like behavior (note that FPL exponent values were not limited to the range (0,1]) and other related empirical responses for certain values of the exponents involved in the activation laws. That was not the case for a Gaussian distribution of activation energies [23].

The impact of heterogeneity and disorder on immittance response has also been revealed in resistor-capacitor (RC) networks. In an early work Scheider [24] showed that the FPL exponent in branched ladder RC networks modeling the double-layer charging is completely determined by the branching type in the pathways of charge spreading. Random RC networks have represented appropriate models to investigate frequency dispersion observed in real disordered dielectric and conductive materials [25]. Near the percolation threshold for dc conductivity, where a kind of metal-insulation transition occurs, high-frequency response of FPL form is observed. Hamou et al. [26] related this response to the DRT approach and showed that a composite fitting model involving two separate dispersive models was required for good fitting of network data.

An important idea behind these models –of interest to the present work– is the separability of the immittance behavior into dissipative and energy-storing elemental processes. For interfacial phenomena this leads to a coupling of the local solution resistance to the interfacial capacitance, which has been widely assumed as the principal cause of CPE-like behavior (see an excellent discussion in [27]). The paradigm of the coupling between interfacial and bulk quantities is perhaps an electrode with irregular surface, and for that reason surface roughness has been, by far, the most addressed and investigated cause for CPE-like behavior [27]. Within this context, fractal or porous electrodes have represented perfect system models because their symmetry properties allowed different treatments for the immittance response and led to relationships between the CPE exponent and the fractal dimension (Liu's branched pore model in [28] is an example of it). A complete review on these models can be found in [29]. Interestingly, CPE exponent was limited by 1 (as found in experiments), which corresponded to perfect smooth electrodes, and decreased as long as fractal dimension increased. Even though the applicability of these results to real systems was a matter of controversy [27,30–32], they put on the table the idea of a possible connection between CPE behavior and scale invariance. In fact, a current density distribution along an electrode with no characteristic size, i.e., a fractal, leads to an impedance response with no characteristic frequency [33]. The same principle applies to porous electrodes for frequencies at which the penetration depth of the ac signal is smaller than the pore depth, so they behave as having no characteristic depth [34], or to random RC networks discussed above [26], with FPL response related to critical phenomena and fractal properties.

For perfectly smooth surfaces, the classical approach has consisted in considering the coupling of a homogeneous solution resistance with a distributed capacitance. In this regard, it was shown that a spatial distribution of active capacitive domains with the same specific capacitance is not enough to get a CPE response [35]. However, a non-homogeneous interfacial specific capacitance yields frequency dispersion in the form of distorted impedance diagrams when it is trivially distributed [36], or with a FPL dependence when the spatial distribution of capacitances is self-similar [37]. A more general model for an arbitrary number of distributed interfacial parameters was presented by Lukács [38] in the form of a series involving the moments of the parameter distributions. Distorted EIS diagrams, but not of CPE form, were obtained. For a lognormal distribution of parameters [39] no distortion was reported for simple elementary circuits, and a pseudo-CPE behavior was obtained under rather arbitrary assumptions. Finally, it is worth noting that current and potential distributions at the origin of CPE-like behavior may have nothing to do with distributed parameters, but result from electrode geometry effects [40].

With regard to the experimental works, Kerner and Pajkossy [32,41,42] proposed that frequency dispersion is due to heterogeneity or disorder on the nano and atomic scales rather than roughness on the micro or macroscopic scales. Surface heterogeneity may have a geometric origin (steps, terraces, kinks, grain boundaries, dislocations, etc) or be an intrinsic property of the surface as in polycrystalline electrodes. Whatever the case, it yields an energetic heterogeneity which causes a distribution of reactivity and capacitance, and although this effect can be enhanced by roughness, it is not always the case [27]. Recent experiments support this hypothesis [18]. On the other hand, it has also been argued that capacitance dispersion at medium-low frequencies is purely of kinetic rather than structural interfacial origin, and that heterogeneity is caused by slow processes within the double layer such as specific adsorption and related effects [27,32,43–46].

The aim of the present work is to formally review the relationship between interfacial heterogeneity and frequency dispersion from the analysis of a simple distributed model. The purpose is to characterize frequency dispersion from the mathematical properties of the DFRT and to provide a theoretical framework that comprises much of the phenomenology reported in the literature as well as new one. A significant difference with previous works, where frequency dispersion was roughly recognized from the inspection of the complex-plane or Bode plots of the immittance functions of the system, comes from the