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Fractal-polarization correction in time domain dielectric spectroscopy

Yuri Feldman,[1,*] Raul Nigmatullin,[2] Evgeny Polygalov,[3] and John Texter[4,†]
[1]*Department of Applied Physics, Hebrew University of Jerusalem, Jerusalem 91904, Israel*
[2]*Department of Theoretical Physics, Kazan State University, Kazan 420008, Russia*
[3]*Kazan Institute of Biology of the Russian Academy of Sciences, p/b 30, Kazan 420503, Russia*
[4]*Imaging Research and Advanced Development, Eastman Kodak Company, Rochester, New York 14650-2109*

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Electrode polarization appears self-similar in time and occurs even when the geometrical electrode structure is not fractal. Problems associated with electrode polarization in time domain dielectric spectroscopy of conductive liquids persist to much higher frequencies than generally appreciated. An explicit consideration of the fractal nature of such polarization, irrespective of the fractal (geometrical) structure of the electrode, leads to a concise correction for such polarization effects. This correction is illustrated for an aqueous electrolyte. [S1063-651X(98)04912-5]

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I. INTRODUCTION

The accumulation of charge in dielectric spectroscopy (DS) on electrode surfaces results in electrode polarization that leads to the formation of electrical double layers [1–4]. The associated capacitance and complex impedance due to this polarization is so large that the correction for it is one of the major requisites in obtaining meaningful measurements on conductive samples, especially in aqueous biological and colloidal systems [3–9]. Various approaches have been used to correct for electrode polarization, including electrode separation variation [6,7,10], four-electrode methods [1,11–13], high surface area electrodes [14], and high current density [6]. The details of electrode polarization depend microscopically upon the electrode surface topography and surface area as well as the surface chemistry (reactive surface groups or atoms) and the interaction of this chemistry with the dielectric material or sample being examined. In the case of conductive liquids, the principal motivation of this work, surface ionization and ion exchange processes in the electrical double layer can depend critically upon the chemical nature of the sample being investigated as well as the chemical and physical nature of the electrodes used. Because these many effects can be so diverse, no simple correction technique has been widely accepted. We present a particular approach to correcting for electrode polarization in (two-electrode) time domain dielectric spectroscopy (TDDS) that rests upon a control experiment using a liquid control sample that mimics the ionic nature of the continuous phase of the sample investigated.

Several equivalent circuits have been proposed to describe the essential elements of a sample cell containing an electrolyte solution [3,7] and the most generally accepted approach is shown in Fig. 1(a). Under the assumption that the electrodes are blocking with respect to Faradaic electron transfer, the polarization impedance of the electrodes may be expressed as

$$Z_p = R_p + \frac{1}{j\omega C_p}, \tag{1}$$

where $j=\sqrt{-1}$. This polarization is in series with the sample admittance

$$Y = \frac{1}{R} + j\omega C. \tag{2}$$

Both C_p and R_p vary with frequency and Z_p is often considered negligible at sufficiently high frequencies. This high-frequency limit for electrode polarization has been estimated differently, depending on the particular type of electrode assembly and DS experiment, but has generally fallen in the interval 100–500 kHz. Because of the diverse nature of processes that can contribute to electrode polarization, such as the sample-dependent chemical processes alluded to above, it is difficult to estimate an upper bound for this frequency limit.

Time domain dielectric spectroscopy measurements of aqueous solutions of proteins and cell suspensions up to 5

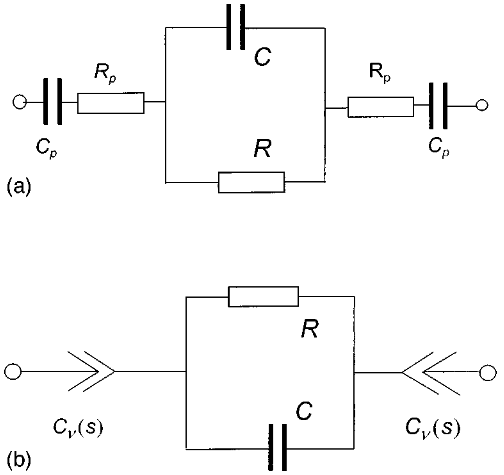

FIG. 1. Equivalent circuits for a conductive dielectric sample with electrode polarization impedance described by (a) C_p and R_p and (b) recap $C_\nu(s)$.

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[*] Author to whom correspondence should be addressed. Electronic address: yurif@vms.huji.ac.il

[†] Present address: Strider Research Corporation, Rochester, NY 14610-2246.

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GHz [9] have shown that electrode polarization may not be negligible at such high frequencies. Schwan noted the porous nature of electrode polarization phenomena [6]. We now often attribute such porosity to fractality and characterize porous tortuosity in terms of fractal dimension. Schwan also mentioned the increasing magnitude of this effect with increasing frequency. While the fractal nature of electrode *surfaces* is now well appreciated [15–19], no applications for making polarization corrections, capitalizing upon the fractal nature of electrode *polarization*, appear to have been developed previously. In this paper we focus upon the fractal nature of the polarization, not upon the geometrical fractality (surface roughness or porosity) of the electrode structure.

II. THEORY

A general form for depicting the fractal nature of an electrode double-layer impedance is given by $Z(j\omega)$ [15–17],

$$Z_\nu(j\omega)=A(\nu)(j\omega)^{-\nu}, \tag{3}$$

where $0<\nu<1$, $A(\nu)$ is a parameter, and the frequency ω is located in a certain range $\omega_{\min}\leqslant\omega\leqslant\omega_{\max}$ due to the self-similar electrode polarization properties of the electrode surface [15–17]. At sufficiently high and low frequencies the self-similarity of the electrode polarization disappears. The estimation of $\omega_{\min}$ and $\omega_{\max}$ is discussed below. The exponent ν has often been connected with the fractal dimension of the electrode surface, but this connection is not necessary. Pajkossy [17(a)] has shown, however, that specific adsorption effects in the double layer do appear necessary for such dispersion. We connect the exponent to the fractality of the dynamical polarization and show that the polarization is self-similar in time, in contrast to a self-similar geometrical structure.

The frequency limits $\omega_{\min}$ and $\omega_{\max}$ may be estimated from self-similar networks, such as Coauer's branching circuit described by a heterogeneous transmission line discussed elsewhere [17(b),18,19]. The essential relation is the ordering described by the equation

$$\left(\frac{R_N C_N}{R_p C_p}\right)^{\nu}\leqslant\omega R_p C_p\leqslant 1, \tag{4}$$

where R_N and C_N are the resistance and capacitance of the Nth cell of the equivalent circuit described by scaling factors b and ξ $(0<b<1,\ 0<\xi<1)$, where

$$R_N=R_p b^N, \tag{5}$$

$$C_N=C_p\xi^N, \tag{6}$$

and R_p and C_p are the resistance and capacitance of the zeroth cell. Substitution of Eqs. (5) and (6) into Eq. (4) and rearrangement of terms gives

$$\frac{(b\xi)^{N\nu}}{R_p C_p}\leqslant\omega\leqslant\frac{1}{R_p C_p}. \tag{7}$$

We see from Eq. (7), therefore, that $\omega_{\max}$ is inversely proportional to the time constant R_pC_p and $\omega_{\min}$ is bounded from below by the scaling factor term $(b\xi)^{N\nu}/R_pC_p$. Since b and ξ are less than unity and N may be large, $\omega_{\min}$ will generally be quite small.

This specific dependence in Eq. (4) on frequency is known as the *constant phase angle* dependence [18,19]. This impedance behavior occurs for a wide class of electrodes [16,20] and suggests the introduction of a new equivalent circuit element with impedance characteristics similar to Eq. (3). We call this element a *recap* element (derived from resistance and capacitance). The electrical and fractal properties for this recap complex impedance $C_\nu(s)$ are given by

$$C_\nu(s)=R(RC)^{-\nu}s^{-\nu},\quad 0<\nu<1. \tag{8}$$

This circuit element occupies an intermediate position between R_p $(\nu=0)$ and C_p $(\nu=1)$ and expresses its impedance in the finite range of frequencies mentioned above. Using the definition of Eq. (8), we can rearrange the equivalent circuit of the measuring sample cell with electrolyte solution, as shown in Fig. 1(b). The impedance of the sample cell (electrodes) containing electrolyte solution can then be derived using one of these recap elements for the impedance at each electrode. Since electrodes generally are not perfectly identical, each can be defined according to Eq. (8) to give

$$C_{\nu_i}(s)\equiv C_{\nu_i}s^{-\nu_i}=R_i(R_iC_i)^{-\nu_i}s^{-\nu_i}, \tag{9}$$

with $i=1$ and 2. In this fractal representation the measuring cell is defined in terms of this fractal impedance of the electrode polarization.

In order to derive the current-voltage relationship obtained for the equivalent circuit of Fig. 1(b), it is convenient to note the identity [21]

$$s^{-\nu}I(s)=\frac{1}{\Gamma(\nu)}\int_0^t(t-t')^{\nu-1}i(t')dt', \tag{10}$$

where $i(t)$ is a time-dependent current, $\Gamma(\nu)$ is the gamma function, s is the complex frequency, and $I(s)$ is the Laplace transform of $i(t)$. The resulting current-voltage relationship

$$\begin{aligned}V(t)=&\frac{C_{\nu_1}}{\Gamma(\nu_1)}\int_0^t(t-t')^{\nu_1-1}i(t')dt'\\&+\frac{C_{\nu_2}}{\Gamma(\nu_2)}\int_0^t(t-t')^{\nu_2-1}i(t')dt'\\&+\frac{1}{C}\int_0^t\exp[-(t-t')/\tau_c]i(t')dt'\end{aligned} \tag{11}$$

has two terms describing the polarization of the respective electrodes and a third term describing the contribution of the bulk sample, where $\tau_c=RC$. Equation (11) shows how $V(t)$ and $i(t)$ are related for different kinds of measuring cells (i.e., different C_{ν_i},ν_i) containing conductive solutions that polarize electrodes in conformity with the equivalent circuit illustrated in Fig. 1(b).

Let us consider the case where $i(t)$ is constant, as obtains at long times after all transients associated with sample relaxations have died out. For this case Eq. (11) reduces to

$$V(t) \propto \frac{C_{\nu_1}}{\nu_1 \Gamma(\nu_1)} t^{\nu_1} + \frac{C_{\nu_2}}{\nu_2 \Gamma(\nu_2)} t^{\nu_2} + R[1 - \exp(-t/\tau_c)], \tag{12}$$

where τ_c defines the time scale wherein the recap elements (the electrode polarization) affect the $V(t)$ measured for the sample cell containing a conductive solution. If we make the simplifying assumptions that (i) both electrodes of the sample cell have the same (or equivalent) fractal polarization ($\nu_1 = \nu_2$ and $C_{\nu_1} = C_{\nu_2}$) and (ii) there is no dispersion of the conductive solution (sample) in the time window defined by τ_c ($> t_{\min} = 1/\omega_{\max}$), Eq. (12) can be rewritten as

$$V(t) = Bt^{\nu} + Rt/\tau_c \quad \text{for} \quad t/\tau_c \ll 1 \tag{13}$$

and

$$V(t) = Bt^{\nu} + R \quad \text{for} \quad t/\tau_c \gg 1. \tag{14}$$

Equations (13) and (14) are particularly useful in illustrating how the contribution of electrode polarization Bt^{ν} should be subtracted from $V(t)$.

The voltage $V(t)$ observed at the sample cell (plate or cylindrical capacitor [22]) at the end of a coaxial line can be written as [9,22]

$$V(t) = V_0(t) + V_r(t), \tag{15}$$

where $V_0(t)$ and $V_r(t)$ are the incident and the reflected signals (pulses), respectively. The current flow through the sample is

$$i(t) = \frac{1}{Z_0} [V_0(t) - V_r(t)], \tag{16}$$

where Z_0 is the characteristic impedance of the coaxial line.

In the case of conductive solutions, Eqs. (15) and (16) show that both the voltage and the current flow are influenced by electrode polarization. The observed voltage $V(t)$ monotonically increases in the TDDS time window of observation and the current $i(t)$ monotonically decays. The electrode polarization *correction* is then obtained by subtracting the function Bt^{ν} from $V(t)$. The incident pulse $V_0(t)$ generally is an approximation to a step function with zero long-time slope and the monotonically increasing behavior of $V(t)$, associated with the correction Bt^{ν}, is a component of the reflected pulse $V_r(t)$. Since this component is subtracted in Eq. (15) from $V_r(t)$, it needs to be added ($+Bt^{\nu}/Z_0$) to $i(t)$ in Eq. (16).

III. EXPERIMENT

Dielectric measurements were made using a TDS-2.1 (Dipole TDS Ltd., Jerusalem) time domain dielectric spectroscopy system. The general principles of time domain dielectric spectroscopy and a detailed description of this instrumentation and software algorithms have been described elsewhere [22]. The measurements were done in a time window of 5 μs. In the framework of a lumped capacitance approximation [22], we used a parallel plate capacitor as a sample cell and we highly polished the steel electrodes in order to satisfy the approximation, implicit in Eq. (14), that both electrodes are essentially identical. The capacitance of the empty cell (filled with air) was calculated as $C_0 = 0.2$ pF.

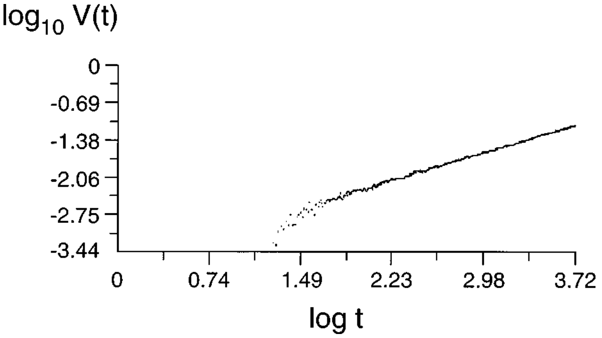

FIG. 2. Voltage $V(t)$ applied to the electrolyte solution; $\nu = 0.785$ and $B = 0.593$ (with polished stainless steel electrodes). V and t have unit of volts and seconds, respectively.

We examined a strong electrolyte solution of NaCl in water at 25 °C. This solution was $0.1M$ NaCl adjusted to pH 1.25 with $0.05M$ HCl and had a low-frequency conductivity of 1.57 S m^{-1}. The TDDS multiwindow measurements [22] allow long-time (up to 5 μs) registration of signal tails, where the signal from a dielectric with low-frequency conductivity has completely relaxed (decayed) and only the signal from the electrode polarization remains. This is true for simple electrolyte solutions where no other relaxation processes can be detected [23]. The experimental signal $V(t)$ is illustrated in Fig. 2, where it is plotted on a log-log scale. The fractality index ν was determined to be 0.785 with $B = 0.593$ by linear regression of the asymptotically linear portion. We reiterate that the value of this index is strictly dependent on the electrode material [24], the electrode polishing, and the surface chemistry attendant to the interactions of the aqueous electrolyte with the electrode surfaces.

This electrode polarization correction for TDDS measurements of conductive biological or colloidal samples can be summarized in the following way. A reference sample with equivalent continuous phase conductivity and electrolyte composition is measured and these data are used to fit the parameters ν and B (as was illustrated above for the data in Fig. 2). Then other samples having equivalent continuous phase conductivity and electrolyte composition may be measured with the same electrodes. The polarization correction embodied in the ν and B obtained earlier is applied by subtraction of Bt^{ν} from $V(t)$ [or from $V_r(t)$] and by adding this same function (scaled by Z_0) to $i(t)$. These corrected signals are then Fourier analyzed [22] to obtain the resulting dielectric spectra $\epsilon'(\omega)$ and $\epsilon''(\omega)$. In this exposition of the correction procedure we have illustrated the method focusing upon the polarization properties of a simple two-component electrolyte solution. After correction in this case we are left with the properties of the neat solvent, water.

The comparative dielectric spectra of simple electrolyte solution with and without electrode polarization correction (pH$=1.25$) are presented in Fig. 3. The permittivity before and after electrode polarization correction is illustrated in Fig. 3(a). The uncorrected permittivity appears to exhibit an anomalously large value at low frequencies and appears to undergo some sort of dispersion process in the 100 kHz to 1 MHz region. This dispersion is highlighted as a peak in the

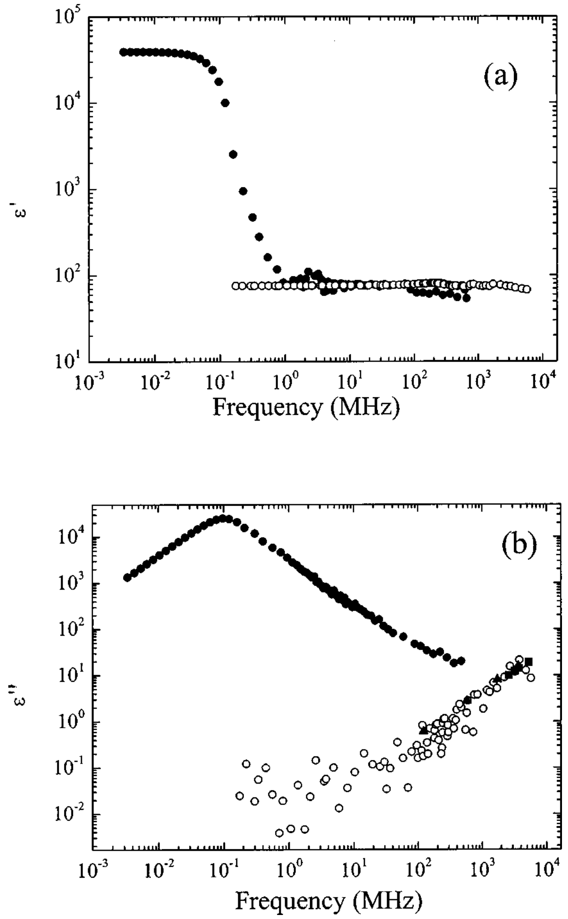

FIG. 3. Fractal electrode polarization correction for dielectric spectra (a) ε' and (b) ε'' of a simple electrolyte solution: $0.1M$ NaCl at pH 1.25; ●, uncorrected; ○, corrected; ▲, pure water at 20 °C [25]; ■, pure water at 25 °C [23].

uncorrected dielectric loss spectrum of Fig. 3(b), peaking at 100 kHz. This dispersion essentially completely vanishes after correction for electrode polarization. The corrected permittivity in Fig. 3(a) is essentially independent of frequency at about 78. The dielectric loss, after correction for electrode polarization, becomes very small, in the range 100 kHz to 100 MHz, but shows a steady increase with increasing frequency. This increase is consistent with the well-known dielectric loss maximum of water in the region 3–6 GHz and compares well with the experimental dielectric loss values for water reported at 20 °C [25] and 25 °C [23] and illustrated in Fig. 3(b) for comparison.

The practical estimation of the frequency limits for these experimental conditions may be made by transforming Eq. (4) by inversion to the inequality

$$R_pC_p \leq t \leq R_pC_p(b\xi)^{-N\nu}. \tag{17}$$

In our experiments the incident pulse has a time window of 10 μs. This corresponds to a lower-frequency limit of 100 kHz and a *de facto* upper bound of 10^{-5} s in Eq. (17). An estimation of $\omega_{\max}$ can be made more definitely. According to Schwan [1,6], typical values of electrode polarization resistance and capacitance for $0.1M$ NaCl are $R_p \cong 1\ \Omega$ and $C_p \cong 0.7\ \mu$F at 100 kHz for large platinum electrodes (2.5 cm in diameter). In our experiments the electrode diameter is 0.3 cm. Using the same value of R_p as Schwan ($\cong 1\ \Omega$) and from the ratio of electrode areas we find that $C_p \cong 0.01\ \mu$F at 100 kHz, so that $R_pC_p \cong 10^{-8}$ s. This is equivalent to an estimate for $\omega_{\max}$ of 100 MHz.

IV. CONCLUSION

The data derived here after correction for electrode polarization are in good agreement with previously published aqueous data. These data show unequivocally the need for electrode polarization correction at frequencies in excess of 100 MHz and that such a correction can be effected by explicitly considering the fractality of electrode polarization. The application of this technique is not limited to polished steel electrodes and may be extended to electrodes having a fractal surface topography. Extensions of the methods described here to other types of dielectric spectroscopy experiments are under investigation.

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