LETTER TO THE EDITOR

On the polarization mechanisms related to the liquid–solid interaction in porous media containing humidity

A N Papathanassiou

University of Athens, Department of Physics, Section of Solid State Physics, Panepistimiopolis, GR 157 84 Zografos, Athens, Greece

Abstract
The temperature dependence of the relaxation time which governs the intense polarization mechanisms produced by the electrochemical interaction between the matrix and the humidity in the pore space of siliceous sedimentary rocks was obtained recently by employing high-resolution thermally stimulated depolarization current spectroscopy. The transformation of the results from the time to the frequency domain provides an informative picture of the low-frequency responses. Our results are compared with those obtained from complex-impedance measurements.

The dielectric properties of water-containing porous materials have been investigated theoretically and experimentally for a long time. In addition to the contribution of the individual phases, the electrochemical interaction between the liquid and the solid results in significant polarization phenomena [1–5]. Thus, a small amount of humidity within the pore space of a rock enhances the dielectric constant of the system. This phenomenon has been studied experimentally through impedance spectroscopy in the last decade. It was found that the large values of the dielectric constant observed in the low-frequency region do not stem from the polarization of the electrodes, but are related to a bulk phenomenon [5, 7]. This low-frequency dispersion is attributed to the polarization of the thin layer of liquid which covers the solid grains [6]. The experiments were performed in the frequency domain within the formalism of the real and imaginary parts of the (complex) dielectric constant (ε' and ε'', respectively), while the description based on the (complex) electric modulus (M^*) was used recently [7] to study the effect of hydration in rocks on the low-frequency response.

The research was rather limited in merely proving that the low-frequency dispersion observed is actually a bulk phenomenon rather than an electrode polarization one [5, 7]. The relaxation frequency f_0 (the frequency where a dielectric loss mechanism exhibits a maximum in a $\log \varepsilon''$ ($\log f$) representation) is

$$f_0 = \frac{D}{\pi \alpha^2} \tag{1}$$

where D is the diffusion constant and α is the radius of the particles [3, 6]. However, neither a clear and definite detection of the water-matrix polarization (which is likely to operate through multiple modes of relaxation rather than one unique one), nor a quantitative study of the dynamics of the phenomenon and its temperature dependence was carried out, probably due to the low resolution of the impedance measurements, especially at low frequencies. From another viewpoint, the resolving power of the thermally stimulated depolarization current (TSDC) spectroscopy and its ability to sample any desired relaxation component were recently employed in order to decompose the dielectric spectrum into its constituents, definitive characterize the individual polarization processes and yield an accurate evaluation of the distribution of their relaxation parameters [8, 9].

Natural sandstone and pelite, which are sedimentary porous silicate rocks, were studied via the TSDC spectroscopy in two states: with an inherent quantity of humidity (i.e., in equilibrium with the ambient humidity) and after drying at elevated temperature under a dynamic vacuum [8, 9]. In each of the systems, in addition to the water dipole rotation mechanisms, a set of three distinct intense dispersions (S1, S2, S3 and P1, P2, P3) which were extremely sensitive to the pore network were identified. Standard dielectric characterization (i.e., independence of the signals of the electrode material and adequate reproducibility) proved that they are bulk mechanisms and are related to the localized motion of electric charge carriers and their subsequent trapping in internal (bulk) obstacles (traps). Another couple of humidity-enhanced relaxations (S4 and S5, for sandstone, and P4, P5, for pelite) were recorded. Except for P4, which shares the characteristics of a bulk polarization mechanism, the latter dispersions are produced by the long-distance charge motion along the thickness of the sample and the subsequent formation of space charge close to the sample–electrode interfaces.

A relaxation process is characterized by the relaxation time τ, which is temperature dependent and governed by the Arrhenius law:

$$\tau(T) = \tau_0 \exp(E/kT) \tag{2}$$
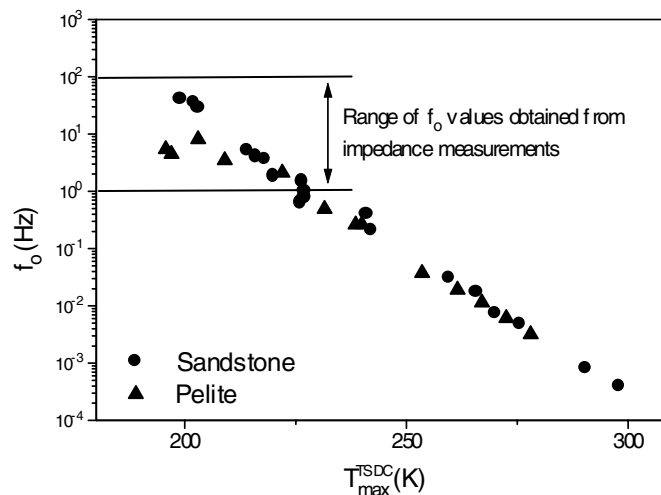
Figure 1. The frequency f_0 where a dielectric relaxation mechanism exhibits a maximum in the frequency domain at $T = 295$ K against the temperature T_{max}^{TSDC} where a TSDC response has its maximum in the TSDC spectrum. The data points were determined from the analysis of the TSDC results. The frequency values f_0 which were obtained from the analysis of the impedance measurements of reference [3] are distributed within the zone between the two parallel lines.

Table 1. The temperature $T_{\max}^{\text{TSDC}}$ where the maximum of the TSDC components is located and the relaxation parameters (E_0 and τ_0) of the relaxation constituents obtained by applying the thermal sampling scheme in the TSDC experiments [8, 9]. The relaxation time τ and the equivalent frequency f_0 where a dispersion maximizes in the frequency domain at $T = 295$ K are also depicted.

	$T_{\max}^{\text{TSDC}}$ (K)	E_0 (eV)	τ_0 (s)	τ (s) at $T = 295$ K	f_0 (Hz) at $T = 295$ K
			Sandstone (reference [8])		
S1	199.0	0.571	6.84×10^{-13}	0.0039	41
	202.0	0.592	3.42×10^{-13}	0.0044	36
	203.0	0.579	7.17×10^{-13}	0.0056	28
S2	214.0	0.590	2.45×10^{-12}	0.0295	5.4
	216.0	0.591	3.10×10^{-12}	0.0388	4.1
	218.0	0.610	1.65×10^{-12}	0.0436	3.6
	220.0	0.590	7.10×10^{-12}	0.0854	1.9
S3	226.0	0.603	1.23×10^{-11}	0.2466	0.65
	227.0	0.611	7.30×10^{-12}	0.2005	0.79
	227.0	0.612	5.47×10^{-12}	0.1562	1.02
	226.5	0.619	2.79×10^{-12}	0.1050	1.52
	226.5	0.610	4.09×10^{-12}	0.1080	1.48
S4	241.0	0.743	8.17×10^{-14}	0.4038	0.39
	242.0	0.742	1.60×10^{-13}	0.7602	0.210
S5	259.5	0.781	2.25×10^{-13}	4.9579	0.0321
	265.8	0.790	2.83×10^{-13}	8.8851	0.0179
	275.5	0.792	9.71×10^{-13}	32.9811	0.0048
	270.0	0.784	8.47×10^{-13}	21.0016	0.0076
	290.5	0.813	2.72×10^{-12}	211.05	0.00075
	298.0	0.815	4.80×10^{-12}	402.93	0.00040
			Pelite (reference [9])		
	$T_{\max}^{\text{TSDC}}$ (K)	E_0 (eV)	τ_0 (s)	τ (s) at $T = 295$ K	f_0 (Hz) at $T = 295$ K
P1	195.7	0.440	8.91×10^{-10}	0.0293	5.4
	197.0	0.441	1.04×10^{-9}	0.0355	4.5
P2	203.0	0.521	2.45×10^{-11}	0.0195	8.2
	209.0	0.522	5.54×10^{-11}	0.0459	3.5
P3	222.0	0.620	1.92×10^{-12}	0.0752	2.1
	231.5	0.622	7.66×10^{-12}	0.3242	0.49
P4	238.5	0.643	6.23×10^{-12}	0.6023	0.26
	239.9	0.645	5.72×10^{-12}	0.5984	0.27
P5	253.5	0.651	3.20×10^{-11}	4.2376	0.038
	261.5	0.687	1.52×10^{-11}	8.3149	0.019
	267.0	0.682	3.08×10^{-11}	13.8219	0.012
	272.5	0.695	3.48×10^{-11}	26.0264	0.0061
	278.0	0.700	5.51×10^{-11}	50.1751	0.0032

where k is Boltzmann's constant, E is the activation energy and τ_0 is the pre-exponential factor. The TSDC signals were analysed within the model of the normal distribution of the activation energy values around a central value E_0. The temperature T_{max}^{TSDC} where the TSDC component exhibits its maximum, the activation energy values and the pre-exponential factors obtained for each mechanism are shown in table 1. The relaxation time at room temperature ($T = 295$ K) is subsequently obtained from equation (2). Afterwards, by using the relation

$$2\pi f_0 \tau = 1 \tag{3}$$

the relaxation parameters obtained from the analysis of the TSDC signals are converted to the f_0-values at room temperature (table 1). The order of magnitude of f_0 varies from 10^{-4} to 10^2 Hz for sandstone and 10^{-3} to 10^1 Hz for pelite. In figure 1, f_0 is plotted against the temperature T_{max}^{TSDC} where a TSDC response has its maximum in the TSDC spectrum. We mention that the impression is that the results for sandstone and pelite superimpose, but this is actually an effect of displaying the data using a very wide range on a logarithmic scale on the ordinate axis. Our high-frequency results are compatible with those reported for artificial sandstone containing liquids of various conductivities, were f_0 ranges from 10^0 to 10^2 Hz [3]. The low-frequency relaxations ($f_0 < 1$ Hz) are determined well only by TSDC experiments. Such information could hardly be obtained by impedance spectroscopy. The activation energy values should be compared with the value 0.59 eV reported for the solid–liquid interaction in organic porous media accommodating organic fluids [5].

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