Dependence of the electrical conductivity and the low-frequency dielectric constant upon pressure in porous media containing a small quantity of humidity

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Abstract

The interaction between the matrix of a porous material and a small quantity of a liquid located in its porous space induces intense polarisation phenomena and enhances the charge transport. The temperature dependence of the corresponding relaxation time was reported recently by employing the high-resolution thermally stimulated depolarisation current spectroscopy. The present work includes d.c. conductivity and a.c. capacitance measurements under pressure up to 0.3 GPa in two porous silicate materials: sandstone with 0.26 wt.% and pelite with 0.07 wt.%. The water was adsorbed from the atmospheric humidity. Electrical impedance measurements are used to monitor the effects of confining pressure on the matrix–liquid interaction. Positive activation volumes are computed from the observed variations in the d.c. conductivity of the samples with pressure. The pressure derivatives of the dielectric constant at 10^4 Hz were also obtained. The effect of pressure on the effective relaxation time that determines the humidity-related polarisation processes was estimated.

Keywords: Electrical conductivity; High-pressure; Porous materials

1. Introduction

Different researchers have recently studied the dielectric and electrical properties of porous media containing liquids [1–8]. The scope was to investigate the intense polarisation phenomena and the enhanced electrical conductivity that are related with the electrochemical interaction between the solid–liquid interface [4,6,9]. The theoretical models for the electrical properties of a multi-component system as a superposition of the conductivities and permitivities of the non-interacting individual phases require extension so as to incorporate the strong solid–liquid interaction. The investigation of the effect of pressure on the transport and polarisation effects of porous media containing humidity provides the experimental background to formulate a revised theory for the electrical properties of multi-phase media. Research on wet rocks under

pressure simulates the conditions of the earth's crust, where pressure is a function of depth, and provides experimental information that helps understand the electric signal transmission in earth's crust. These studies support the large-scale electromagnetic (magneto-telluric) explorations (that emphasise on the conductivity and permittivity of rocks to various depth or pressure) for water or oil deposits in deep earth.

Natural and artificial sandstone (which is a solid that actually consists of quartz aggregates) containing humidity [1–6] and polymers filled with liquid [7] were studied through a.c. impedance spectroscopy in order to understand the polarisation due to the solid–liquid interaction. Fruitful and significant information about the polarisation and long-range transport phenomena was gained recently by employing the powerful high-resolution thermally stimulated depolarisation current (TSDC) spectroscopy [10–12] in porous silicate geomaterials. Distinct multiple polarisation processes and long distance charge transport, which are related to the attachment of humidity at different hydrophilic sites in

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the internal pore surface, were traced. These experiments allowed the determination of the temperature dependence of the relaxation time $\tau(T)$. The scope of the present work is to learn about the polarisation and the conductivity are affect by an increase of hydrostatic pressure. The sign and the value of the migration volume for charge transport and the pressure derivative of the effective relaxation time $\tau(P)$ are obtained experimentally in the present work for the first time. Previously, complex impedance measurements under pressure have been performed on sandstone and granite samples *fully* saturated with 0.01 M KCl [13]. Such experiments were also carried out in hydrogels by varying their water content [14]. In both cases, the solid–liquid interaction was disregarded. The variation of the polarisation of the solid–liquid interface upon pressure variation has not been reported for such materials yet.

2. Experimental details

The experiments were performed on two silicate materials, which have been studied previously through TSDC spectroscopy recently [10–12]: sandstone and fine-grain pelite of porosity 11 and 8%, respectively. The composition of sandstone is: 40 wt.% quartz, 10 wt.% amphbolite and pyroxene, 7 wt.% glimmer mica, 16 wt.% feldspars and 27 wt.% calcite. The composition of pelite is: 2 wt.% albite, 73 wt.% quartz, 2 wt.% calcite, 3 wt.% ferroan clinochlore and 2 wt.% muscovite. The exact composition was reported [10–12]. The specimens contain an inherent quantity of humidity, which is in equilibrium with the environmental humidity [10–12]. The water content was estimated through the reduction of the mass of the sample after drying under a dynamic vacuum of about 10^{-2} Pa at 373 K for 24 h: 0.26 wt.% for sandstone and 0.07 wt.% for pelite. Assuming a quartz matrix, 5.5% of the pore space of sandstone and 2% of the porosity of pelite, respectively are occupied by water adsorbed from the atmospheric humidity. The experiments were performed in a piston-type pressure vessel operating from the ambient pressure to 0.3 GPa. The electrical impedance measurements were performed at the single frequency of 10 kHz by using a two electrode impedance measurement system. A Boonton 75c bridge was employed. The d.c. conductivity measurements were carried out by using a Keithley 617 digital electrometer. Electrical contacts with the specimen were achieved with the aid of silver paste [15,16].

3. Results and discussion

The variation of the electrical conductivity with pressure is described by the activation volume v^{act}.

The activation volume is defined thermodynamically as the pressure derivative of the Gibbs free energy g^{act} for the charge transfer from one equilibrium site to a neighbouring one [17]:

$$v^{act} = \left(\frac{\partial g^{act}}{\partial P}\right)_T \tag{1}$$

The latter definition is general and describes the effect of pressure on diffusion-controlled processes. Charge transport can occur either through the bulk of the (solid) matrix or along the grain boundaries of solid aggregates. Recalling that g^{act} is related to the potential barrier separating two adjacent equilibrium sites, v^{act} indicates (to a first approximation) the change of the potential barrier on pressure. Alternatively, the activation volume v^{act} equals the difference between the volume V_S of the material when the transferring charge is in its 'activated' state and the volume of the solid V_A when the charge is in its 'normal' state [14]:

$$v^{act} = V_S - V_A \tag{2}$$

An ion diffuses in an ionic crystal by passing over a potential barrier (saddle point site; activated state) that separates two neighbouring equilibrium sites when migrating from a normal (equilibrium site) state to a neighbouring one. V_S and V_A are the volume of the crystal when *one* migrating ion crosses over the saddle point and when the charge is located at its equilibrium site, respectively. Fontanella et al. [14] extended the validity of Eq. (2) for proton-conductivity in water and aqueous solutions: proton motion is interpreted as a transition from a hydronium ion H_3O^- to a water molecule. The 'normal' state consists of a hydronium ion and a water molecule. The 'activated' state consists of a pair of water molecules sharing a proton.

Volume defect parameters have been obtained for ionic crystals [15,18–25] and polymers [14,26–32] through conductivity measurements under pressure. For the specific case of *porous media*, the activation volume value v^{act} is extracted from the variation of the d.c. conductance upon pressure and the elastic properties of the porous system [33,34]. By considering the change of the volume of the grains of a polycrystalline solid under pressure [16], the following relation was derived:

$$v^{act} = -kT\left\{\left(\frac{\partial \ln G(P)}{\partial P}\right)_T - \left(\gamma - \frac{3}{2}\right)\kappa_m(P)\right.$$
$$\left. - \frac{3}{2}\kappa(P)\right\} \tag{3}$$

where G denotes the electrical conductance, P is the hydrostatic pressure, κ_m and κ are the isothermal compressibility's of the solid phase and the porous system, respectively, and γ is the Grüneisen constant.

A similar expression results by regarding the solid as a binary system that consists of a conductive phase and an insulating one [34]:

$$v^{\text{act}} = -kT\left\{ \left(\frac{\partial \ln G(P)}{\partial P}\right)_T - \left(\gamma - \frac{2}{3}\right)\kappa_{\text{m}}(P) \right.$$
$$\left. - \frac{2}{3}\,\kappa(P)\right\} \tag{4}$$

The percentage variation of the real part of the dielectric constant ε on pressure is determined from capacitance measurements under pressure:

$$\left(\frac{\partial \ln \varepsilon}{\partial P}\right)_T = \left(\frac{\partial \ln C}{\partial P}\right)_T + \frac{1}{3}\,\kappa(P) \tag{5}$$

where C denotes the capacitance.

The relaxation time τ, which is a time constant for the transition of a set of charges from one state to another one, is generally defined as $\tau = \varepsilon/\sigma$, where σ denotes the conductivity [35]. The variation of τ upon pressure change is:

$$\left(\frac{\partial \ln \tau}{\partial P}\right)_T = \left(\frac{\partial \ln \varepsilon}{\partial P}\right)_T - \left(\frac{\partial \ln \sigma}{\partial P}\right)_T \tag{6}$$

The relative d.c. conductance G/G_0, where G_0 is the zero-pressure conductance, is plotted against pressure in Fig. 1 for sandstone and pelite. The conductance decreases more rapidly with pressure for sandstone than for pelite and may be explained by the difference in their micro-structural features. A straight line was fitted to the experimental data points in order to estimate the derivative $(\partial \ln G/\partial P)_T$. The activation volumes were obtained by using Eqs. (3) and (4) and the results are listed in Table 1. The Grüneisen constant was taken equal to 1.7, which is typical for ionic solids
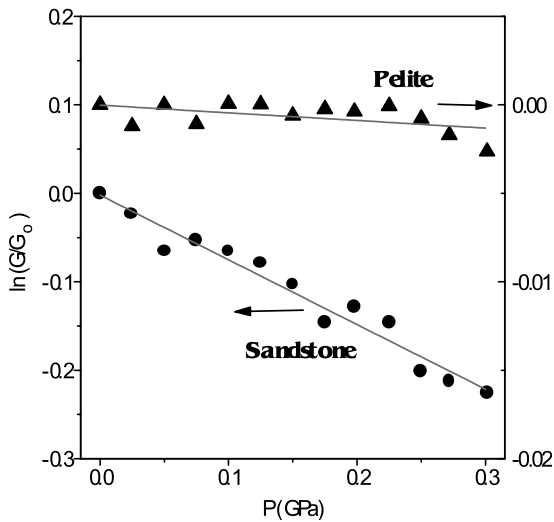

Fig. 1. The room temperature d.c. conductance of sandstone (circles) and pelite (triangles) against pressure. The straight lines were fitted to the data points.

[17]. A typical ambient pressure value $\kappa = 1.7 \times 10^{-10}$ Pa^{-1} was used. The interpolation of the high-pressure data to the ambient pressure bulk compressibility value $\kappa_{\text{m}} = 5.6 \times 10^{-11}\ \text{Pa}^{-1}$ was employed [36]. The positive sign of v^{act} indicates probably an outward dilatation of the material when the charge transport operates. This behaviour is typical for the ionic conductivity.

The relative conductance and capacitance of sandstone measured at the frequency of 10^4 Hz are shown in Fig. 2. A similar diagram for pelite is presented in Fig. 3. The a.c. conductivity plots are similar to the d.c. plots (Fig. 1) but they cannot yield reliable quantitative results since the measured a.c. conductance values consist of both the d.c. conductivity and the a.c. component of the localised motion of charges. The d.c. conductance was determined by the pulsed-voltage technique: a pulse of voltage was applied for a short time interval by the power supply of the digital electrometer, while the current flowing through the specimen was recorded at the same time. The d.c. conductance was estimated as the ratio or the current amplitude over the voltage amplitude. The procedure was repeated and a (more precise) mean value of conductance was obtained. The pulsed-voltage method is typical for preventing the space-charge formation resulting from the non-ohmic sample-electrode interface. A second-order polynomial fit to the ln $C(P)$ data yielded the ambient pressure derivative of the capacitance. By using Eq. (5), the percentage variation of the low-frequency dielectric constant was estimated (Table 1). The pressure derivative of the dielectric constant is positive, indicating that the polarisation effects are enhanced by the application of pressure.

The relaxation time τ may be regarded as an effective time constant for the transition of an electrically charged medium from one equilibrium state to another one. The results presented in the preceding paragraphs (i.e. the pressure derivatives of the d.c. conductance and the capacitance) yield the dependence of τ on pressure through Eq. (6). The latter relation indicates that the pressure derivative of the relaxation time is determined by two competing factors: the pressure derivative of the d.c. conductivity that corresponds to long-range charge transport and the pressure derivative of the dielectric constant (or the capacitance) that is assumed to be related with the short-range charge motion. As can be seen in Table 1, the conductivity component actually determines the pressure derivative of the relaxation time for sandstone, while the permittivity component is greater than the conductivity component of pelite. The pressure variation of τ is positive for both sandstone and pelite (Table 1), indicating that pressure acts as an advancing factor in humidity-related relaxation processes; i.e. the increase of pressure strengthens the humidity related polarisation effects.

Table 1
The pressure derivatives of the d.c. conductance G and the capacitance C at 10^4 Hz, the activation volume v^{act}, the pressure derivatives of the low-frequency dielectric constant ε and the relaxation time τ for *as-received* specimens

	$(\partial \ln G(P)/\partial P)_{T=298\ \mathrm{K}}$ $(10^{-10}\ \mathrm{Pa}^{-1})$	v^{act} (cm^3/mol) at $T=298$ K		$(\partial \ln C(P=0)/\partial P)_{T=298\ \mathrm{K}}$ $(10^{-12}\ \mathrm{Pa}^{-1})$	$(\partial \ln \varepsilon(P=0)/\partial P)_{T=298\ \mathrm{K}}$ $(10^{-11}\ \mathrm{Pa}^{-1})$	$(\partial \ln \tau/\partial P)_{T=298\ \mathrm{K}}$ $(10^{-10}\ \mathrm{Pa}^{-1})$
		Eq. (3)	Eq. (4)			
Sandstone	-7.3 ± 0.4	2.5 ± 0.1	2.2 ± 0.1	-9.4 ± 0.1	4.72 ± 0.05	7.8 ± 0.1
Pelite	-0.04 ± 0.02	0.7 ± 0.3	0.4 ± 0.2	-3.5 ± 0.1	5.32 ± 0.1	0.6 ± 0.1

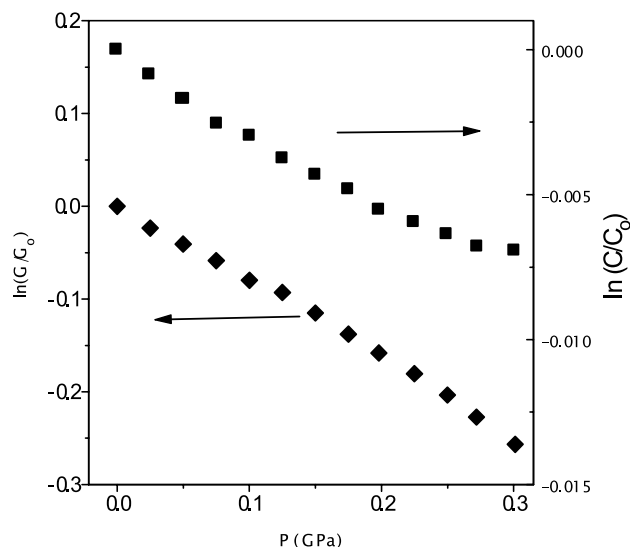Details are given in the text. The zero-pressure practically coincides with the ambient pressure.

Fig. 2. The logarithm of the relative capacitance C/C_0 (squares) and the relative conductance G/G_0 (diamonds) of sandstone vs pressure at 10^4 Hz.

The results should compare with those obtained for dry specimens (Table 2). The change of the conductance
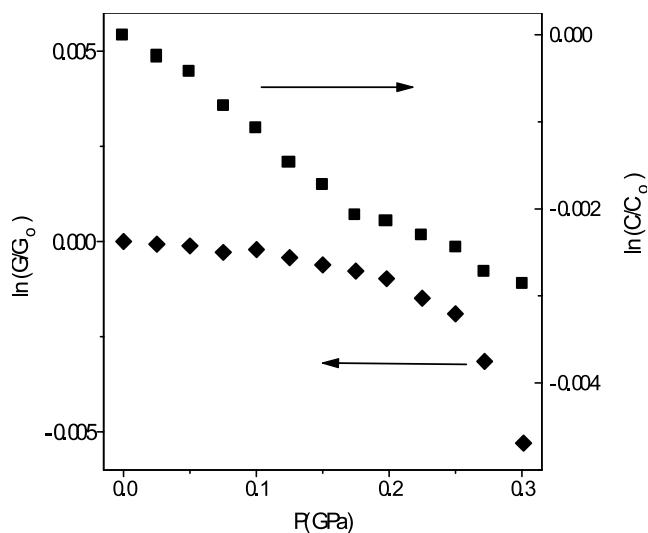

Fig. 3. The logarithm of the relative capacitance C/C_0 (squares) and the relative conductance G/G_0 (diamonds) of pelite vs pressure at 10^4 Hz.

and the capacitance is different for the dry material compared with the as-received one. Thus, the values presented in Table 1 for the as-received materials incorporate the contribution of the humidity-related phenomena, indeed. We observe that the pressure variation of the conductivity is larger for dried samples. The increased activation volumes can be viewed as larger volume changes resulting from the removal of the humidity coating and the reduction of conductive paths. The conductivity exhibits strongly ionic features in the dry material than in the humid one, where proton transport induces smaller volume changes. The pressure derivatives of the dielectric constant are smaller than those mentioned for the as-received specimens. These values correspond to capacitance changes of the host matrix that are induced by the increase of pressure. In Table 2, the pressure derivative of the relaxation time for the host material has been calculated by using Eq. (6) these values are larger than those estimated for the as-received samples. The absence of the conductive humidity coating reduces the dependence of the transition time of a set of charges from one state to another slower upon pressure. It seems that relaxation processes are more sensitive on pressure changes in porous media containing a small quantity of humidity.

The influence of pressure on the humidity-related polarisation and conductivity processes is an over-parameterised problem, which has not been treated yet theoretically. Charges either diffuse along the humidity coating over the size of the grains or are unable to leave the surface, or diffuse through the bulk of the specimen. In both cases, pressure reduces the mobility of the transferring entities. The influence of pressure on the strength of the polarisation is likely to be controlled by the effect of pressure on the surface charge density, on the size of the grains, on the polarisation of the fluid itself and on the variation of the so-called surface potential [37].

4. Conclusions

The charge transport in porous media with a small amount of humidity proceeds through an outward

Table 2
The pressure derivatives of the d.c. conductance G and the capacitance C at 10^4 Hz, the activation volume v^{act} and the pressure derivatives of the low-frequency dielectric constant ε and the relaxation time τ for *dry* specimens

	$(\partial \ln G(P)/\partial P)_{T=298\ K}$ $(10^{-10}\ Pa^{-1})$	v^{act} (cm³/mol) at $T=298$ K		$(\partial \ln C(P=0)/\partial P)_{T=298\ K}$ $(10^{-12}\ Pa^{-1})$	$(\partial \ln \varepsilon(P=0)/\partial P)_{T=298\ K}$ $(10^{-11}\ Pa^{-1})$	$(\partial \ln \tau/\partial P)_{T=298\ K}$ $(10^{-10}\ Pa^{-1})$
		Eq. (3)	Eq. (4)			
Sandstone	-12.4 ± 0.3	4.3 ± 0.1	3.7 ± 0.1	-31.1 ± 0.1	2.56 ± 0.05	12.6 ± 0.1
Pelite	-0.11 ± 0.05	2.7 ± 0.3	1.1 ± 0.2	-12.9 ± 0.1	6.8 ± 0.1	0.8 ± 0.1

relaxation of the material as can be inferred from the positive values of the migration volume. The variation of the conductivity with pressure is significantly larger than the change induced to the dielectric constant of sandstone. The role of pressure on the effective relaxation time that governs the intense humidity-related polarisation phenomena in sandstone is dominated by the decrease of the conductivity on pressure. On the contrary, the relaxation time of the humidity-related polarisation phenomena in pelite result mainly from the pressure dependence of its dielectric constant.

Acknowledgements

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