



# CONTRIBUTION OF THE PRESSURE VARIATION OF THE POROSITY TO THE ACTIVATION VOLUME EVALUATION FROM IONIC CONDUCTIVITY MEASUREMENTS UNDER PRESSURE

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**Abstract**—In the present paper the pressure variation of the porosity is expressed in terms of the elastic properties of the porous solid which consists of a one-phase solid framework and the pore space that is assumed to be empty. The equation which describes the pressure variation of the conductance of a porous ionic material is modified to include the porosity modification upon pressure. The change of the porosity induced by the pressure contributes to the value of the activation volume which is inferred from conductance under pressure experiments. Additionally, we predict that the porosity change significantly accounts for the second order pressure derivative of the conductance and consequently contributes to the estimation of the compressibility of the activation volume.  
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## 1. INTRODUCTION

The measurement of the ionic conductivity at various pressure values is a powerful tool for evaluating the volume point defect parameters in ionic crystals, such as the formation, migration and activation volume. The defect volume is respectively defined as the isothermal pressure derivative of the Gibbs energy for the formation, migration or activation process. During the last three decades, significant and pioneering pressure work on different types of ionic crystals has been carried out [1–21]. Recently, emphasis has also been given to transport experiments under pressure in polymers [22–28]. Natural ionic compounds with more complex crystal structures than those studied to date, usually exist in polycrystalline aggregates, while some ionic crystals may not even develop to dimensions necessary for electrical measurements, urging us to prepare pressurized pellets from the material's powder [8].

The changes in the electrical properties of rocks under pressure have attracted the interest of many research groups [29–40]. The potential difference between the work carried out for ionic crystals and polymers and the rock type solids is that the latter are fully or partially saturated with water or electrolyte solution. The pore space in the rock accommodates the solution and subsequently the system under consideration consists of the matrix material and the pore framework filled with conductive fluid. The conductivity of the fluid is some orders of magnitude higher than that of the matrix [30]. Thus, the effect of the conductivity on the confined pressure actually records the changes of the pore and

crack space and topology induced by the pressure variation. To the best of our knowledge there is a lack of information about the influence of pressure on the properties of the framework itself.

In the present work: (i) we develop a simple model which estimates the pressure variation of the porosity of an homogeneous porous solid in terms of easily measurable elastic constants; (ii) we derive a complete equation for the pressure variation of the conductance of a polycrystalline ionic material. It should be stressed that we do not deal with polycrystalline materials filled with conductive fluid, as mentioned in the previous paragraph. On the contrary, in our model, the pores are considered to be empty and completely insulating, while the transport processes operate through the bulk host ionic matrix. The latter visualization is related to the more realistic problem of studying either pressurized pellets [8] or naturally developed polycrystalline aggregates.

## 2. SIMPLIFIED ESTIMATION OF THE POROSITY CHANGE EFFECT UPON PRESSURE

A porous material consists of a matrix framework with a void space. In this paper we consider a homogeneous porous solid: The solid phase consists of a unique type of material (a one-phase solid). The pore space is empty, free of solution and non-conductive. If  $V_{\text{TOT}}$ ,  $V_{\text{MAT}}$  and  $V_{\text{POR}}$  denote the total volume of the specimen, the matrix grains' volume and the volume of the pore space, respectively, then [41]:

$$V_{\text{TOT}}(P) = V_{\text{MAT}}(P) + V_{\text{POR}}(P) \quad (1)$$

The porosity  $\Phi(P)$  is defined as the ratio of the pore space to the total volume:

$$\Phi(P) = V_{\text{POR}}(P)/V_{\text{TOT}}(P) \quad (2)$$

The isothermal compressibilities  $\kappa_i$  are defined as the percentage variation of the volume with respect to pressure, for a given pressure value:

$$\kappa_i(P) = \frac{1}{B_i(P)} = - \left( \frac{\partial \ln V_i(P)}{\partial P} \right)_T \quad (3)$$

where  $i = \text{TOT, MAT or POR}$  and  $B_i$  denotes the isothermal bulk modulus.

Differentiation of eqn (2) with the help of eqn (1) and eqn (3), gives:

$$\left( \frac{\partial \ln[1 - \Phi(P)]}{\partial P} \right)_T = \kappa_{\text{TOT}}(P) - \kappa_{\text{MAT}}(P) \quad (4)$$

The measurement of the compressibilities  $\kappa_{\text{MAT}}$  and  $\kappa_{\text{TOT}}$  of the single crystal and a polycrystalline material, respectively, can readily be done at the desired pressure value. Unfortunately it is often impossible to grow single crystals. To overcome this obstacle, we propose a method which has appeared in the literature [42]: The bulk modulus  $B$  vs pressure  $P$  diagram of a polycrystalline solid consists of two distinct parts: the low pressure rapid increase and the slow linear increase at high pressure. The first region corresponds to the drastic pore closure, while the latter is dominated by the elastic properties of the matrix material. The linear extrapolation from the high pressure data, leads to the zero pressure value of the matrix bulk modulus  $B_{\text{MAT}}(0)$ . Thus, a  $B(P)$  diagram provides both the total and the matrix bulk modulus values. Eqn (4) connects the pressure variation of the porosity with the elastic properties of the material, overcoming the problem of knowing the microstructural features of the solid.

### 3. CORRECTION OF THE POROSITY CHANGE USING THE PRESSURE VARIATION OF THE IONIC CONDUCTANCE

Let us assume that two electrodes are attached to the two parallel surfaces (surface area  $S_{\text{TOT}}(P)$ ) of the rectangular sample of thickness  $L_{\text{TOT}}(P)$ . If the pore space is vacant, i.e., the porosity network is completely insulating, then the conduction develops through the matrix material. Consider a random cross section parallel to the sample surfaces which are in contact with the electrodes. Then, the total area of the section  $S_{\text{TOT}}(P)$  is the sum of the matrix area  $S_{\text{MAT}}(P)$  and the pore space  $S_{\text{POR}}(P)$ :

$$S_{\text{TOT}}(P) = S_{\text{MAT}}(P) + S_{\text{POR}}(P) \quad (5)$$

In any (two dimensional) cross section, the pore surface area  $S_{\text{POR}}(P)$  to the total section area  $S_{\text{TOT}}(P)$  is

approximately equal to the porosity  $\Phi(P)$  [43]:

$$\Phi(P) \cong \frac{S_{\text{POR}}(P)}{S_{\text{TOT}}(P)} \quad (6)$$

Although the last approximation is well known in the literature, it is important to clarify the limits of its validity: The equation that defines the porosity (eqn (2)) can be rewritten as an integral over the sample's length, for a constant pressure value:

$$\Phi(P) = \frac{1}{S_{\text{TOT}}(P)L_{\text{TOT}}(P)} \int_0^{L_{\text{TOT}}} \sum_i S_{\text{POR},i}(P, z) dz \quad (7)$$

where  $z$  is the axis along the sample's thickness (i.e., perpendicular to the electrodes) and  $S_{\text{POR},i}(P, z)$  is the surface area of the  $i$ -th void measured by sectioning the sample vertical to the  $z$  axis, ( $0 \leq z \leq L_{\text{TOT}}$ ). Assuming that the voids are homogeneously distributed all over the solid and that the surface of the section is larger than the grain size (and fortunately the latter does occur), we can write:

$$\sum_i S_{\text{POR},i}(P, z) \cong S_{\text{POR}}(P) \quad (8)$$

for any value of the variable  $z$ . Eqn (7) from eqn (8) becomes:

$$\Phi(P) \cong \frac{1}{S_{\text{TOT}}(P)L_{\text{TOT}}(P)} \int_0^{L_{\text{TOT}}} S_{\text{POR}}(P) dz = \frac{S_{\text{POR}}(P)}{S_{\text{TOT}}(P)} \quad (9)$$

The latter actually demonstrates that the approximation defined by eqn (6) is correct.

From eqn (6) and through eqn (5) we get:

$$S_{\text{MAT}}(P) = [1 - \Phi(P)]S_{\text{TOT}}(P) \quad (10)$$

Recalling that the cross section is parallel to the electrodes, multiplying by  $L_{\text{TOT}}(P)$ , taking the logarithm and differentiating with respect to pressure, we obtain:

$$\begin{aligned} & \left( \frac{\partial \ln S_{\text{MAT}}(P)}{\partial P} \right)_T + \left( \frac{\partial \ln L_{\text{TOT}}(P)}{\partial P} \right)_T \\ & = \left( \frac{\partial \ln[1 - \phi(P)]}{\partial P} \right)_T + \left( \frac{\partial \ln V_{\text{TOT}}(P)}{\partial P} \right)_T \end{aligned} \quad (11)$$

The last equation, due to eqn (4) can be rewritten in the following form:

$$\left( \frac{\partial \ln S_{\text{MAT}}(P)}{\partial P} \right)_T = -\kappa_{\text{MAT}}(P) - \left( \frac{\partial \ln L_{\text{TOT}}(P)}{\partial P} \right)_T \quad (12)$$

We proceed with the calculation of the last term: Taking the logarithm of the basic relation  $V_{\text{TOT}}(P) = S_{\text{TOT}}(P)L_{\text{TOT}}(P)$  and differentiating with respect to pressure, we get:

$$\left( \frac{\partial \ln L_{\text{TOT}}(P)}{\partial P} \right)_T = -\kappa_{\text{TOT}}(P) - \left( \frac{\partial \ln S_{\text{TOT}}(P)}{\partial P} \right)_T \quad (13)$$

Recalling that the polycrystalline material was assumed to be isotropic, we may write:

$$\left(\frac{\partial \ln S_{\text{TOT}}(P)}{\partial P}\right)_T = 2 \left(\frac{\partial \ln L_{\text{TOT}}(P)}{\partial P}\right)_T \quad (14)$$

The combination of eqn (13) eqn (14) yields:

$$\left(\frac{\partial \ln L_{\text{TOT}}(P)}{\partial P}\right)_T = -\frac{1}{3} \kappa_{\text{TOT}}(P) \quad (15)$$

With the help of the last relation, eqn (12) can be rewritten as:

$$\left(\frac{\partial \ln S_{\text{MAT}}(P)}{\partial P}\right)_T = -\kappa_{\text{MAT}}(P) + \frac{1}{3} \kappa_{\text{TOT}}(P) \quad (16)$$

Eqn (16) transformed the effective surface variation to volume change. Let us denote  $\sigma(P)$  using the conductivity of the matrix and  $G(P)$  the conductance of the porous sample. Assuming that the contribution of the grain boundary diffusion is low, we may write:

$$G(P) = \sigma(P) \frac{S_{\text{MAT}}(P)}{L_{\text{TOT}}(P)} \quad (17)$$

Differentiating the logarithm of the last relation, it lead to

$$\begin{aligned} \left(\frac{\partial \ln G(P)}{\partial P}\right)_T &= \left(\frac{\partial \ln \sigma(P)}{\partial P}\right)_T + \left(\frac{\partial \ln S_{\text{MAT}}(P)}{\partial P}\right)_T \\ &\quad - \left(\frac{\partial \ln L_{\text{TOT}}(P)}{\partial P}\right)_T \end{aligned} \quad (18)$$

The first term of the right hand side is equal to  $-(v^{\text{act}}/kT) + (\gamma + 1/3)\kappa_{\text{MAT}}(P)$  [17], where  $v^{\text{act}}$  is the activation volume,  $k$  is Boltzmann's constant and  $\gamma$  is the Grüneisen parameter of the matrix material. The second and third terms are given by eqns (16) and eqn (15), respectively. So, eqn (18) is rewritten in the following form:

$$\left(\frac{\partial \ln G(P)}{\partial P}\right)_T = -\frac{v^{\text{act}}}{kT} + \left(\gamma - \frac{2}{3}\right)\kappa_{\text{MAT}}(P) + \frac{2}{3}\kappa_{\text{TOT}}(P) \quad (19)$$

The pressure derivative of the conductance is governed by two competitive constituents: The quantity  $-v^{\text{act}}/kT$  characterizes the transport mechanism, while the latter  $(\gamma - 2/3)\kappa_{\text{MAT}}(P) + 2/3\kappa_{\text{TOT}}(P)$  involves the effects of lattice dynamics change (expressed through  $\gamma$ ) and

volume elastic changes on the pressure (expressed by the compressibilities). The question that arises is whether the conductance measurements upon pressure in porous materials leads to reliable values of the activation volume.

In a recent paper [21], we studied the pressure variation of the conductivity in polycrystalline dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ). In Table 1, the zero (ambient) pressure derivative  $(\partial \ln G(0)/\partial P)_T$  is depicted in comparison to the compressibility terms participating in eqn (19). Both terms contribute at about 0.7% to the value of the pressure variation of the conductivity. The percentage contribution is significantly smaller (approximately one order of magnitude) than the error in the  $v^{\text{act}}$  estimation from the slope of the  $\ln G(P)$  diagram, thus we can definitely assert that  $(\partial \ln G(0)/\partial P)_T$  leads to the reliable evaluation of the activation volume.

Supposing that a unique non electronic conduction mechanism operates, the deviation of the  $\ln G(P)$  plots from linearity can be attributed to the pressure dependence of the activation volume [44]. The compressibility  $\kappa^{\text{act}}$  of the activation volume is defined as:

$$\kappa^{\text{act}} = -\frac{1}{v^{\text{act}}} \left(\frac{\partial v^{\text{act}}}{\partial P}\right)_T \quad (20)$$

describes the pressure variation of  $v^{\text{act}}$ . Using eqn (20), the second order derivative of the conductance with pressure is:

$$\begin{aligned} \left(\frac{\partial^2 \ln G(P)}{\partial P^2}\right)_T &= \frac{v^{\text{act}}(P)\kappa^{\text{act}}}{kT} + \left(\gamma - \frac{2}{3}\right) \left(\frac{\partial \kappa_{\text{MAT}}(P)}{\partial P}\right)_T \\ &\quad + \frac{2}{3} \left(\frac{\partial \kappa_{\text{TOT}}(P)}{\partial P}\right)_T \end{aligned} \quad (21)$$

eqn (21) predicts that the curvature observed in a single mechanism  $\ln G(P)$  plot is not only due to the probable pressure variation of  $v^{\text{act}}$  (alternatively, to the fact that  $\kappa^{\text{act}}$  is not null) but to the pressure modification of the porosity of the sample. In the limiting case that the activation volume is constant ( $\kappa^{\text{act}} = 0$ ) (and therefore the  $\ln G(P)$  plot of a unique mechanism would decrease linearly), the  $\ln G(P)$  plot for a porous solid is expected to be curved because of the compressibility terms appearing in eqn (21). In Table 2 we present the values of the zero pressure terms participating in eqn (21) for polycrystalline dolomite. We note that the term  $(\gamma - 2/3) (\partial \kappa_{\text{MAT}}(P)/\partial P)_T$  is

Table 1. Room temperature and zero pressure data of polycrystalline dolomite. The first column corresponds to the pressure variation of the electrical conductivity, previously reported by us [21]. The second and third terms contribute to the first value according to eqn (19).  $\gamma$  is assumed to take the value 1.7 which is typical of ionic solids [44]. Due to the absence of isothermal compressibility data, we used the adiabatic ones [45] which, for the majority of geomaterials, differ from 0.5 to 1.3% at room temperature

$\left(\frac{\partial \ln G(0)}{\partial P}\right)_T$	$\left(\gamma - \frac{2}{3}\right)\kappa_{\text{MAT}}(0)$	$\frac{2}{3}\kappa_{\text{TOT}}(0)$
(GPa <sup>-1</sup> )	(GPa <sup>-1</sup> )	(GPa <sup>-1</sup> )
- 7.755	0.021	0.030

Table 2. The second order pressure derivative of the conductance obtained by second order polynomial fit to the  $\ln G(P)$  data [21]. The second and third terms are those appearing in eqn (21).  $\gamma$  was assumed to be equal to 1.7 [44]. The compressibility data come are from Ref. [45]

$\left(\frac{\partial \ln G(0)}{\partial P^2}\right)_T$	$\left(\gamma - \frac{2}{3}\right)\left(\frac{\partial \kappa_{MAT}(0)}{\partial P}\right)_T$	$\frac{2}{3}\left(\frac{\partial \kappa_{TOT}(0)}{\partial P}\right)_T$
(GPa <sup>-2</sup> )	(GPa <sup>-2</sup> )	(GPa <sup>-2</sup> )
14.88	$\approx -10^{-4}$	-2.36

practically insignificant in comparison to the second order derivative of the conductance, while  $2/3(\partial \kappa_{TOT}(P)/\partial P)_T$  contributes at approximately 16% to the left hand side of eqn (21). The experimental conductance data for dolomite showed that the  $\ln G(P)$  data are best fitted to a second order polynomial curve and consequently, the second order pressure derivative of the conductance holds a constant value throughout the pressure range where the experiments were performed. As stated above, the compressibility terms of eqn (21) account to approximately 16% for  $(\partial^2 \ln G(P)/\partial P^2)_T$ , indicating that the curvature is caused by a probable pressure dependence of  $v^{act}$ . Concerning the qualitative analysis,  $\kappa^{act}$  has to be evaluated using the compressibility correction, which proves to be higher than the error induced by the conductance measurement. We emphasized the zero pressure values for two reasons: (i) the zero pressure limit is not sensitive to the probable phenomenon of overlapping conduction mechanisms; (ii) the material becomes considerably less compressible as the pressure augments and therefore the zero pressure limit represents the extreme of the porosity contribution.

#### 4. CONCLUSIONS

In the present work we considered a porous material consisting of a one-phase solid matrix and the framework of the porous space. The latter is assumed to be empty and free of conductive fluids, thus the electrical phenomena operate through the bulk solid. An estimate of the pressure variation of the porosity was obtained. Further, we presume that the decrease in porosity is not accompanied by the formation of new conductive bonds between the grains: the system is approximated by a continuous solid containing empty spheroid voids. The evaluation of the activation volume which characterizes the transport mechanism and the compressibility of the activation volume, which are extracted by performing conductivity measurements under pressure, can be made by deriving equations that accommodate the correction resulting from the variation of the porosity with the pressure.

Our results are useful for predicting the behaviour of naturally or artificially developed polycrystalline

aggregates. The basic advantage of our model is that the phenomenon is viewed through the easily measurable material's elastic constants. The first and second order derivatives of the conductance with pressure are explicitly presented providing the background for quantitative analyses of the data coming from experiments in porous materials.

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