

Ionic transport in silica xerogels investigated by dynamic current-voltage characteristics

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The essence of the dynamic current-voltage characteristics (DCVCs) method is the application of linearly changing voltage to a sample with a plane-parallel electrode system. Previous theoretical considerations have shown that the method may be applied to low thermal conductivity materials, *e.g.*, SiO₂ porous xerogels, in order to investigate ionic transport therein. The low thermal conductivity of SiO₂ xerogels entails a high temperature gradient occurring when DCVCs are measured in vacuum at elevated temperatures. Therefore, it is possible to deduce the sign and mobility of ions responsible for electrical conductivity inside the materials from the characteristic shape of DCVCs.

Keywords: porous xerogels, high temperature gradient, dynamic current-voltage characteristics, ionic transport, ionic mobility.

1. Introduction

In recent years, electrical properties of porous solids, in particular those obtained by the sol-gel method [1]–[5], have been a subject of detailed studies. However, despite numerous attempts, little is known about ionic mobility in such materials [4]. Additionally, the available information concerning the type and sign of the moving ions is still somewhat questionable, because of certain difficulties that usually appear in experimental practice. As ionic mobility in the investigated solids is extremely low, *e.g.*, of 10^{-12} – 10^{-13} m²/Vs at room temperature for silica xerogels [4], measurements of the current are required to last for several hours, which may entail significant dielectric polarization. Moreover, ionic transport in porous materials usually exhibits significant dispersion. As a result, one has to deduce the time-of-flight of charge carriers from broadened pulses, strongly disturbed by the polarization current. Another experimental difficulty involves the lack of electrodes effectively injecting ions into an examined solid. Liquid ionic electrodes, sometimes used to investigate polymers ([6], [7]) cannot be applied, as measurements of porous samples must be carried out in vacuum. Additionally, strongly non-uniform temperature distribution within the sample, due to its extremely low heat conductivity, may influence the mobility of ions

and complicate the analysis of the current traces. These facts show a significant disadvantage of the conventional time-of-flight method.

In the present study, a technique based on dynamic current-voltage characteristics (DCVCs), in which the sample voltage varies continuously at a constant rate, has been applied to investigate the drift mobility of ions in silica xerogels. The method also makes use of the presence of a high temperature gradient in the sample, exceeding in our experiment the value of 10^3 K/cm. Such temperature gradient involves a considerable non-equilibrium dissociation. The dissociation of ion-generating admixtures present in the xerogel is much stronger in the near-electrode area of higher temperature. Hence, a narrow surface region of the sample of elevated ion concentration may act as a virtual ionic electrode. With a known sign of the electrode potential, mainly ions of the same sign will influence the value and pattern of current in the tested specimen. Theoretical fundamentals and model calculations for DCVCs are presented in [8]. A short comment on the results is given in the next section.

The scope of this paper is to present a comparison of theoretical presumptions with DCVCs measured in doped silica xerogels, SiO_2 , and the use of these results to determine ionic mobility in the investigated material.

2. Theoretical fundamentals

The discussed DCVCs have been determined in the set-up presented in Fig. 1.

The principle of the experiment is to measure the current $I(t)$, flowing through a specimen of thickness d in the presence of temperature gradient $\beta_T = (T_1 - T_2)/d$ (with T_1 and T_2 being the temperatures of the warm and the cold sample surfaces, respectively) at a linearly increasing field intensity, $E(t) = \beta_E t$ (with β_E the field increase rate). Neglecting the influence of space charge, carrier diffusion and the

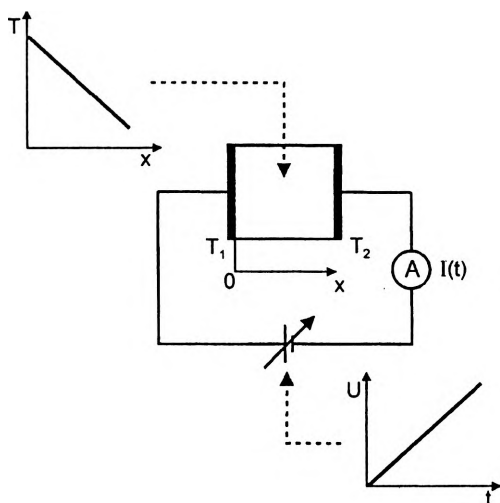


Fig. 1. Schematic diagram of an experimental configuration for DCV measurements.

displacement current on the considered course of $I(t)$, the equation of one-sign-carrier transport has been solved

$$E(t) \frac{\partial}{\partial x} [\mu(x)n(x, t)] + \frac{\partial n(x, t)}{\partial t} = 0 \quad (1)$$

where $n(x, t)$ denotes free carrier concentration. Ionic mobility $\mu(x)$ is assumed to follow the relationship

$$\mu(x) = \mu_0 \exp\left[-\frac{W_a}{kT(x)}\right]. \quad (2)$$

In Eqs. (1) and (2), μ_0 stands for the pre-exponential factor, W_a – for activation energy, k – for the Boltzmann constant, $T(x)$ – for temperature along the sample (see Fig.1). Having introduced the function

$$u(x, t) = \mu(x)n(x, t) \quad (3)$$

into Eq. (1), one obtains the following formula for the current $I(t)$, flowing in the specimen:

$$I(t) = \frac{eSE(t)}{d} \int_0^d u(x, t) dx \quad (4)$$

where e is the elementary charge, and S is the electrode surface. In order to analyze the experimental data, we shall recall the case of continuous generation of electric charge in the thin near-electrode layer of the specimen. According to Eq. (4), the current in the measuring circuit is given by

$$I(t) = g_{in} E(t) x_0(t), \quad t \leq \tau, \quad (5a)$$

$$I(t) = g_{in} E(t) d, \quad t > \tau \quad (5b)$$

where $g_{in} = e\mu(0)u(0)S/d$ is the sample conductance related to the charge generated in the near-electrode layer, and τ – the time of flight of ions. The function $x_0(t)$ describes the instantaneous position of the carrier front. It can be obtained by means of numerical calculations from the relationship

$$\int_0^{x_0(t)} \frac{dx'}{\mu(x')} = \frac{\beta_E t^2}{2}. \quad (6)$$

Figure 2 exhibits exemplary DCVCs computed from formulae (5a) and (5b) for parameters corresponding to the experimental conditions: $\beta_E = 0.34$ V/cms, $d = 0.05$ cm, $\beta_T = 1260$ K/cm, $T_2 = 350$ K, $\mu_0 = 2$ cm²/Vs and $W_a = 0.65$ eV.



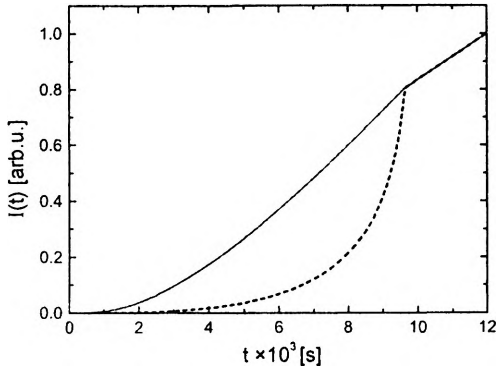


Fig. 2. Theoretical DCVCs for the case of broadening carrier packet moving towards the colder (solid line) and the warmer (dashed line) sample surfaces. The parameters are in the text.

The courses shown in Fig. 2 are related to two ion-generating regions, *i.e.*, to a layer of either higher T_1 or lower T_2 temperature (the latter case refers to ionic injection). A pronounced difference in DCVC courses for time $t < \tau$ enables us to determine at which sample surface an excess ion packet is generated. With known direction of electric field we also know the sign of ions responsible for the measured DCVCs. As can be seen from the courses, the time of flight of ions is also pronounced: this time being over, the $I(t)$ relationship proceeds from a power into a linear one. From DCVCs obtained for different temperatures T_2 one can independently determine activation energy W_a , as well as the μ_0 factor, hence also the effective ion mobility [8].

3. Experiment and results

3.1. Details of procedure

SiO_2 silica xerogels obtained by the sol-gel method have been tested. Ionogeneous 0.03 mole RbCl salt was doped into xerogel prior to starting the hydrolysis and polycondensation processes. Details of the procedure to obtain SiO_2 xerogels used in our experiment are described in [9]. Disc-shaped samples of thickness d of ca. 5×10^{-2} cm were put inside a vacuum test chamber ($p \approx 1$ Pa), allowing us to stabilize temperature with an accuracy of $\Delta T = \pm 0.5$ K and to independently measure T_1 and T_2 . Microprocessor-controlled power supply (Stanford Research Systems PS 325/2500V-25W) made it possible to set the rate of sample voltage variation. During measurements, sample voltage was increased at $\beta_v = \beta_E d = 1$ V/min. The measuring process was controlled by a computer program automatically recording time t , voltage $V(t)$, current $I(t)$ and temperatures T_1 and T_2 .

3.2. Results

Figure 3 displays a typical DCVCs course obtained in the experiment. Measuring points have been obtained for steady temperatures on both surfaces of the sample: $T_1 = 413$ K (the surface in contact with the heater) and $T_2 = 350$ K (the surface exposed



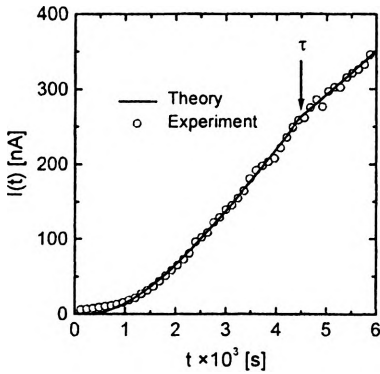


Fig. 3. Experiment – a comparison with theory. Measuring points have been obtained for $T_1 = 423$ K and $T_2 = 353.8$ K. The fitting parameters: $W_a = 0.61$ eV, $\mu_0 = 2$ cm²/Vs. The arrow marks the ions time-of-flight $\tau = 4440$ s.

to vacuum). The electric field was directed towards the surface of the higher temperature T_1 . By comparison of curves in Figs. 3 and 2, one may see that the current derives from carriers being generated in the near-electrode region of temperature T_1 . Taking into account the direction of the electric field, one may conclude that measured current is mainly due to negative ion packet drift. In Fig. 3, the arrival time τ of an ion packet front to the opposite electrode of temperature T_2 is marked. With a known time τ , a computer program searching for the best fit of the theoretical curve allows us to find an adequate approximation of the activation energy W_a and the pre-exponential factor μ_0 . With given values of W_a and μ_0 , it is possible to determine ionic mobility μ , which – due to a high temperature gradient in the sample – corresponds well to temperature T_2 . Making use of the expression $E(t) = \beta_E t$ and of Eq. (6), one may obtain

$$\tau^2 = \frac{2}{\beta_E \mu_0} \int_0^d \exp\left[\frac{W_a}{kT(x)}\right] dx. \quad (7)$$

For a high temperature gradient, the main contribution to the integral in Eq. (7) is made by the near-electrode region of temperature T_2 . Hence, the formula (7) may be approximately replaced with

$$\tau^2 \approx \frac{2kT_2^2}{\beta_E \beta_T \mu_0 W_a} \exp\left(\frac{W_a}{kT_2}\right). \quad (8)$$

Equation (8) allows us to determine the mean values of energy \bar{W}_a and factor $\bar{\mu}_0$ from the experimental relationship $\tau = f(T_2)$. The value of \bar{W}_a may be read from the slope, the value of $\bar{\mu}_0$ – from abscissa of the plotted line $\log(\tau^2 \beta_T / T_2^2) = f(10^3 / T_2)$. Using the least squares method, activation energy $\bar{W}_a = 0.65$ eV and factor $\bar{\mu}_0 = 7.16$ cm²/Vs have been determined from data shown in Fig. 4.



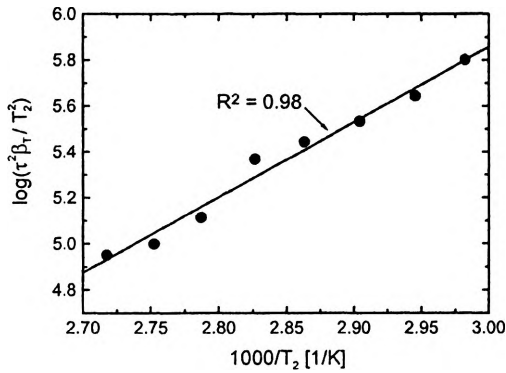


Fig. 4. Experimentally determined ions time-of-flights $\tau = f(T_2)$ (full circles) and the fitting line $\log(\tau^2\beta_T/T_2^2) = f(10^3/T_2)$. From its slope and abscissa the mean values of $\bar{W}_a = 0.65$ eV and $\bar{\mu}_0 = 7.16$ cm²/Vs have been obtained. The correlation coefficient R^2 is also indicated.

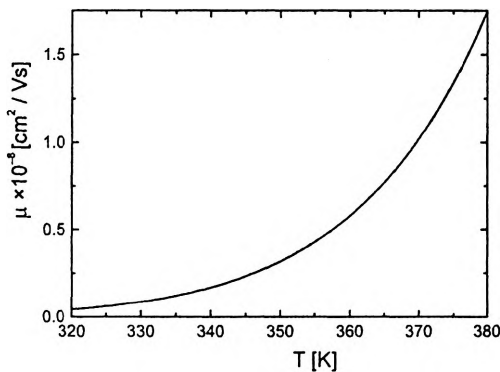


Fig. 5. Exponential temperature dependence of negative ion mobility in SiO₂ silica xerogel with 0.03 mole RbCl admixture. The curve has been obtained for parameters \bar{W}_a and $\bar{\mu}_0$ resulting from Fig. 4.

Finally, from Eq. (2) and the already determined parameters \bar{W}_a and $\bar{\mu}_0$, we may establish the temperature relationship of negative ion mobility for the examined xerogel in the test temperature range of 330–370 K. The relationship is shown in Fig. 5.

4. Conclusions

The paper deals with preliminary results of tests limited to negative ions. Their transport in SiO₂ xerogels has been investigated in a relatively narrow temperature range with a dynamic electric field. Despite these limitations, the presented results have confirmed the theoretically predicted possibility to use DCVCs courses to investigate ionic transport in porous SiO₂ xerogels. Extremely low heat conductivity of the material involves a high temperature gradient in the samples and results in the characteristic shape of DCVCs. The relationship between DCVC shape and the direction of ionic drift (in accordance with or opposite to the temperature gradient),



as well as clearly pronounced times of flight, allow us to determine the sign of ions, their mobility and activation energy. The suggested method of determining these values appears to open a way to a more accurate investigation of ionic transport mechanism in porous materials.

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