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AC Impedance of poled glass during de-poling

Robert Oven

School of Engineering

The University of Kent

Canterbury

Kent, CT2 7NT, UK

Abstract

It has been observed in the literature that when the DC poling voltage is removed at the end of the poling process in glass in a so called de-poling experiment, the small signal AC impedance as measured by impedance spectroscopy increases immediately. It is shown that this effect can be explained if the DC voltage causes nonlinear ionic conduction to occur in the poled layer. The DC field changes the barrier height over which ions have to jump from one site to another and this also effects the AC resistance; by removing the DC field the original barrier height is restored thus increasing the AC resistance. Analysis of experimental data using poled soda-lime glass supports this interpretation.

Email address: R.Oven@kent.ac.uk

Keywords: Electro-thermal poling, soda-lime glass, impedance spectroscopy

1. Introduction

A number of recent studies have used impedance spectroscopy as a tool to investigate the poling of glass [1-5]. The glasses used in these studies are quite diverse, ranging from sodium-calcium-phosphosilicate bio-active glass to alkali-silicate glasses. The impedance spectra have been taken during the poling processes and have enabled features of the poled layer to be observed as it develops. For example, the poled layer resistance has been observed to increase as mobile cations are removed and the layer increases in depth. Further, the poled layer capacitance is observed to decrease with time as the poled layer depth increases [5]. Another observation made is that once the DC poling voltage is removed at the end of the poling process in a so called de-poling experiment, the small signal AC impedance of the poled layer increases immediately by many times [4,5]. Then as time progresses, the impedance slowly reduces as ions back diffuse into the poled glass region. It has been suggested that this immediate increase when the field is removed is due to a change in the electronic conductivity within the poled layer for a bio-active glass [4]. For the alkali-silicate glass the immediate increase in impedance was attributed to a rapid reduction in the number of charged carriers in the depletion region [5]. We have also observed this effect in samples of electrically poled soda-lime glass and offer evidence to show that this effect in our samples is ionic in nature. But rather than reducing the DC poling voltage to zero immediately, we slowly reduce it in steps and analyse the DC and AC impedance at each step. Using this method we show that the low frequency AC resistance of the poled glass layer is dependent on the DC field. This is a result of the DC field changing the energy barriers for hopping motion of ions within the poled layer. When the DC field is reduced at the start of de-poling the energy barriers are no longer changed and the AC resistance increases.

In section 2, using the simple hopping model of ion conduction, we derive an expression for the low frequency AC resistance in terms of the applied DC voltage. In section 3 the experimental procedure and impedance measurements are described. Finally in section 4 the low frequency poled layer resistance is obtained from the impedance measurements are compared with the model.

2. Model

We assume that the current through the sample is limited by the hopping conduction of ions through the poled layer. The ions under consideration will depend on the type of anode used which are classified in the extremes as blocking and non-blocking although electrodes intermediate between these are possible [6,7]. For a blocking electrode it is well known that the removal of

mobile cations from the poled layer results in a large negative space-charge depletion region associated with the non-bridging oxygen ions (O^-). If the field is large enough then this can cause the non-bridging oxygen ions to move towards the anode [6,7]. An alternative mechanism for the neutralization of the space-charge is the motion of electrons towards the anode. It has been proposed that this may occur if the field in the poled region reaches $E_{crit} \sim 1 \text{GVm}^{-1}$, the breakdown field for silica [4]. At the other extreme, non-blocking anodes allow the injection of hydrogen H^+ , or hydronium H_3O^+ ions from the atmosphere to neutralize the space-charge in a process similar to a field assisted ion exchange [8,9]. We use the normal hopping model for the ionic current, which assumes that ions move from one site to a neighbouring one by jumping over an energy barrier. The energy barrier is lowered in one direction and increased in the counter direction due to the electric field E by an amount $\pm qaE/2$ where a is a hopping distance [9]. The current I can be written as

$$I = I_0 \sinh \left\{ \frac{qaE}{2k_B T} \right\} \quad (1)$$

where the current I_0 is proportional to a Boltzmann factor involving the energy barrier height with no applied field. Assume that at the end of the poling process most of the applied voltage V is dropped across the poled layer of thickness d rather than the glass bulk and that we can use an average for E then we write $E=V/d$ within the poled region. Writing the applied voltage V in terms of its DC and AC components we have $V=V_{DC} + V_{AC} e^{j\omega t}$ where V_{DC} is the applied DC voltage and V_{AC} is the amplitude of the AC voltage of angular frequency ω . Assuming V_{AC} is small such that $\frac{qaV_{AC}}{2dk_B T} < 1$, then using $\sinh(\alpha + \beta) = \sinh(\alpha)\cosh(\beta) + \cosh(\alpha)\sinh(\beta)$, $\sinh(\beta) \cong \beta$ and $\cosh(\beta) \cong 1$ for $\beta < 1$ then eqn. (1) can be approximated by

$$I = I_0 \left[\sinh \left\{ \frac{qaV_{DC}}{2dk_B T} \right\} + \cosh \left\{ \frac{qaV_{DC}}{2dk_B T} \right\} \frac{qaV_{AC}}{2dk_B T} e^{j\omega t} \right] \quad (2)$$

The first term in eqn. (2) is the DC current I_{DC} which we write

$$I_{DC} = I_0 \sinh \left\{ \frac{V_{DC}}{V_0} \right\} \quad (3)$$

where

$$V_0 = \frac{2dk_B T}{qa} \quad (4)$$

The second term in eqn. 2, which is proportional to the derivative of the I_{DC} - V_{DC} characteristic, is an AC current of amplitude

$$I_{AC} = I_0 \cosh\left\{\frac{V_{DC}}{V_0}\right\} \frac{V_{AC}}{V_0} \quad (5)$$

So from eqn. 5 the AC resistance is

$$R_{AC} = \frac{r_{DC}}{\cosh\left\{\frac{V_{DC}}{V_0}\right\}} \quad (6)$$

where

$$r_{DC} = \frac{V_0}{I_0} \quad (7)$$

is the DC resistance of the poled glass layer at low fields. It can be seen from eqn. 6 that R_{AC} increases as the DC voltage decreases as observed initially in a de-poling experiment.

3. Experimental

In order to test the above model samples of soda-lime glass (Menzel-Glaser microscope glass typical composition (Wt %)- SiO₂ 72.2, Na₂O 14.3, K₂O 1.2, CaO 6.4, MgO 4.3, Al₂O₃ 1.2, Fe₂O₃ 0.03, SO₃ 0.3)[10] were coated with a graphite anode and cathode and poled in air at 261°C in a tubular furnace for up to 3 hours. These electrodes are thought to be at least partially of the non-blocking type allowing some hydrogen injection from the air. They also result in a poled glass that has a good surface finish to allow for optical assessment [11]. Figure 1 shows the electrical arrangements used for the experiment. The DC field was applied by a 1kV power supply and 10MΩ series resistor, which limited the maximum DC current to 100 μA (=27 μA/cm²) at the start of the poling process. The sample voltage and current were measured every 30s with a data logger during the process. The AC impedance was measured with a network analyser, the signal of which was coupled to the sample

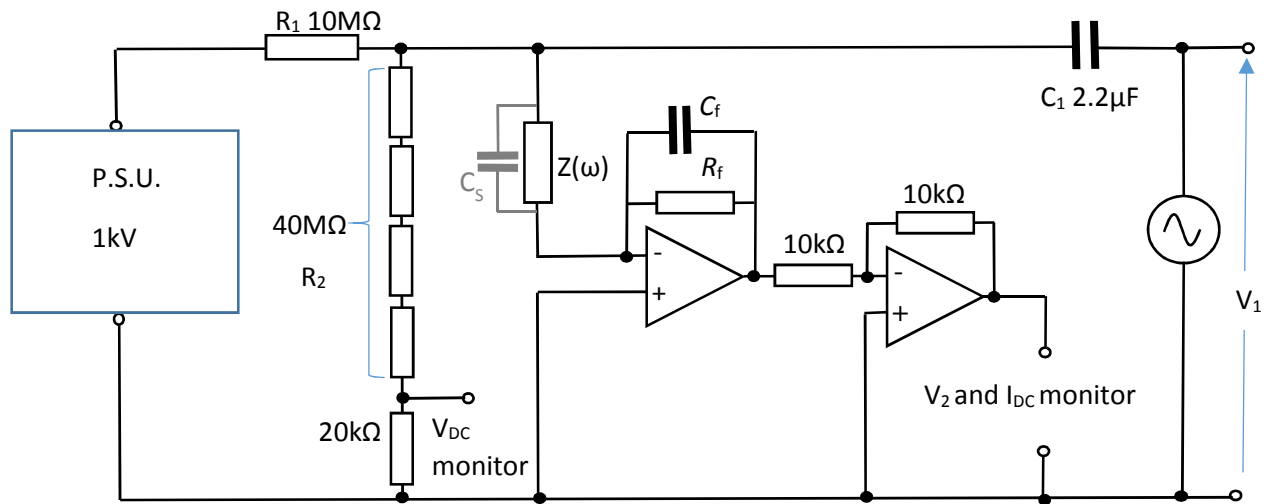


Figure 1.

Experimental arrangement for DC and AC measurements. (colour on-line)

with a coupling capacitor C_1 . With the signal source, C_1 and resistors R_1 and R_2 represented by a Thèvenin equivalent circuit, then the measured impedance $Z_m(\omega)$ can be calculated from the measured AC voltages V_1 and V_2 by

$$Z_m(\omega) = \left(j\omega C Z_f \frac{V_1}{V_2} - 1 \right) Z_{TH} \quad (8)$$

where Z_f is the impedance of the feedback network of the current-voltage converter in Fig. 1 and Z_{TH} is the Thèvenin impedance of C , R_1 and R_2 . Voltage V_1 is the reference voltage so V_2 is complex. Wide bandwidth amplifiers were used in the circuit so the frequency response over the measurement frequency range was not influenced by their gain-bandwidth limitations. The measured impedance $Z_m(\omega)$ will have a parallel stray capacitance C_s associated with it, which is between to the wires connecting the circuit to the sample in the furnace, the reactance of which is removed from $Z_m(\omega)$ to obtain $Z(\omega)$ the actual sample impedance.

4. Results and Discussion

Figure 2 shows the I_{DC} - V_{DC} data during the processing. During the poling stage the data follows the DC load line with a near constant poling current. After 3 hours of poling the sample voltage had increased to 215 V and the poling current had reduced to 85 μ A. The AC impedance spectra was then measured with $V_{AC}=1$ V with the DC voltage still applied, after which the supply voltage was reduced in steps down to zero. At each step the AC impedance spectrum was again taken whilst the DC voltage was still connected. We will call this the de-poling stage although we did not extend this stage to many hours to observe back diffusion of ions into the poled glass layer. Each spectrum took approximately 3 min to take. From the charge transported during the whole of the poling and de-poling process ($=1.03$ C) and the composition and density of the above glass a poled layer depth $d = 2.3 \mu\text{m}$ was estimated. This was verified by optical measurements using the analysis of leaky modes, which gave $d = 2.26 \mu\text{m}$ [11]. The total time for the de-poling stage was 38 min. The charge transported during de-poling only represented 3.6% of the charge transported during the whole process (poling and de-poling). Charge values were calculated by integrating the sample current. We hence conclude that the change in the value of d during the de-poling process was small. It can be seen from fig. 2 that the DC characteristics during de-poling is non-linear, indicating the presence of a high field region as suggested by eqn. 1. This part of the data was fitted to eqn. 3, which yielded $I_0 = 8.7 \mu\text{A}$ and $V_0 = 73$ V. A curve using eqn. 3 with the above parameters is shown in fig. 2. A similar sample was de-poled

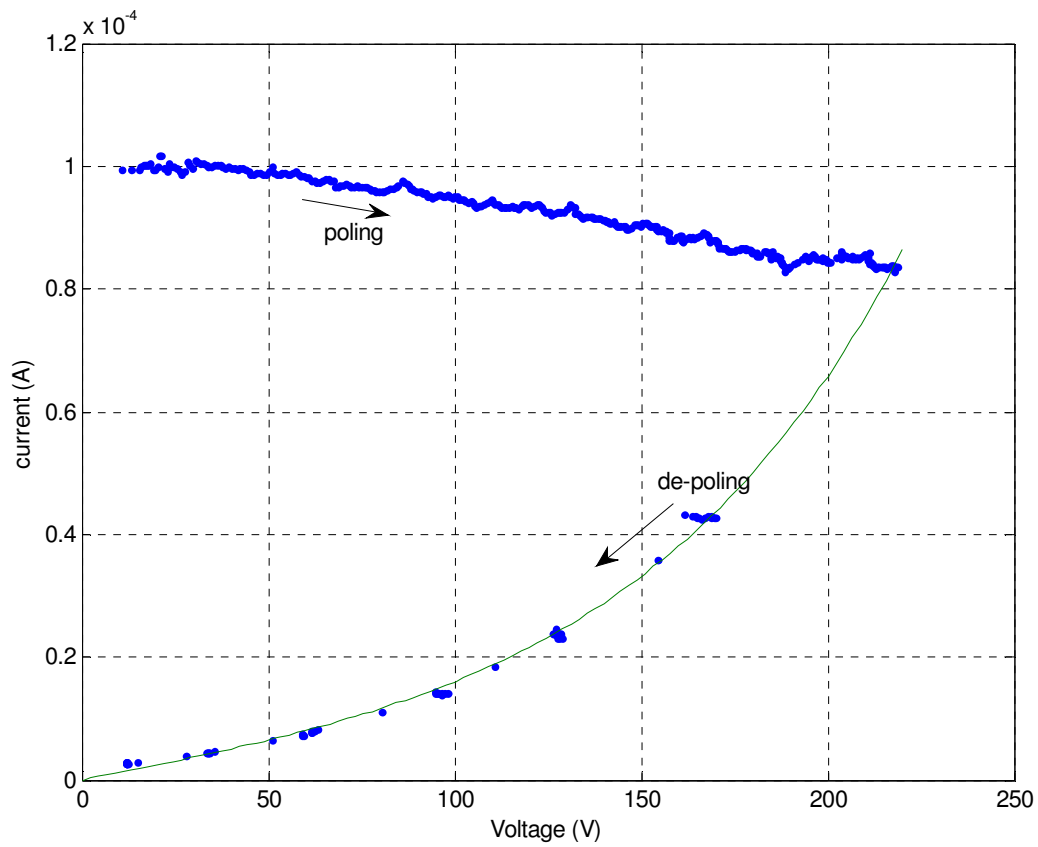


Figure 2

The DC Current - voltage characteristics during poling and de-poling of a sample. Solid curve is a fit of the de-poling data to Eqn. 3. (colour on-line)

but without the complication of delays in taking the impedance spectra and this resulted in similar values for I_0 and V_0 .

Figure 3 shows the impedance circles of the sample AC impedance $Z(\omega) = Z' - jZ''$ obtained at the end of the poling process and during de-poling process with the sample DC voltage as the parameter. This clearly shows the impedance increasing when the poling voltage is removed.

In order to analyse this data in more detail, the impedance is transformed to calculate the effective parallel resistance, R_p and the corresponding effective parallel capacitance C_p . These functions are calculated from $Z(\omega)$ by

$$R_p = \frac{[Z']^2 + [Z'']^2}{Z'} \quad (9)$$

and

$$C_p = \frac{1}{\omega} \times \frac{Z''}{[Z']^2 + [Z'']^2} \quad (10)$$

and are shown in figures 4 and 5 respectively. The low frequency value of R_p is dominated by the poled layer resistance [2, 3]. It can be seen that R_p at the end of the poling stage is $\sim 1\text{M}\Omega$ and increases as the poling voltage is decreased and reaches $\sim 9\text{M}\Omega$ at zero voltage. The low frequency plateau in C_p is equal to the poled region capacitance and it can be seen from Fig. 5 that this did not change significantly during the de-poling stage, from which we conclude that the poled glass layer thickness d was approximately maintained throughout the de-poling phase. The low frequency values of R_p are plotted in Fig. 6 as a function of V_{DC} together and compared with R_{AC} calculated from eqn. 6 using the above I_0 , V_0 parameters obtained from the DC data. It can be seen from this figure that they have the same functional form and that the greatest proportion of R_p is determined by R_{AC} i.e. is determined by the same mechanism that determines the DC data and thus explains the DC field dependency of R_p and $Z(\omega)$.

We have assumed in the model that the region over which the high field exists is equal to the poled glass thickness d . However, there is some evidence in the literature of a more complex poled layer structure involving additional layers. For a non-blocking anode, there is evidence that an additional high field region existing between the anode and the exchanged layer, which is depleted of not only single valent cations ions but also of some O^- and possibly divalent cations Ca^{2+} and that a large proportion of the applied voltage is dropped across it [9]. In order to investigate this assumption

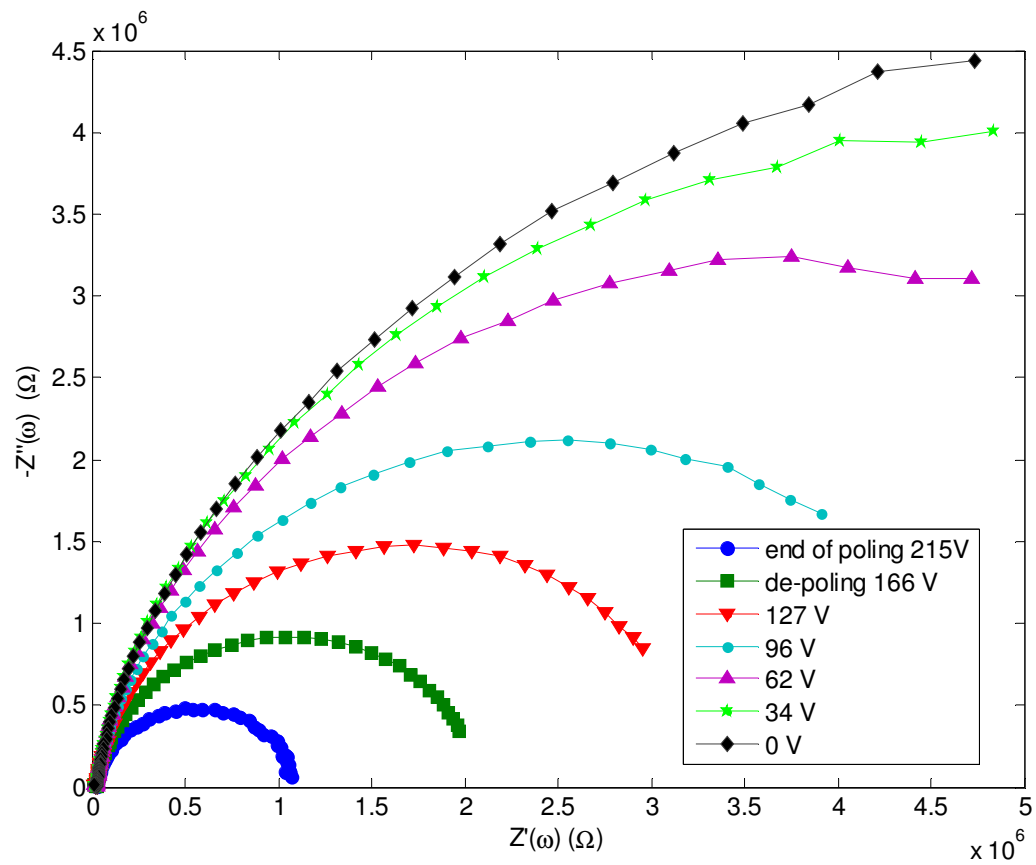


Figure 3

Impedance circles of data at end of poling and during de-poling. The voltage during de-poling is the parameter. (colour on-line)

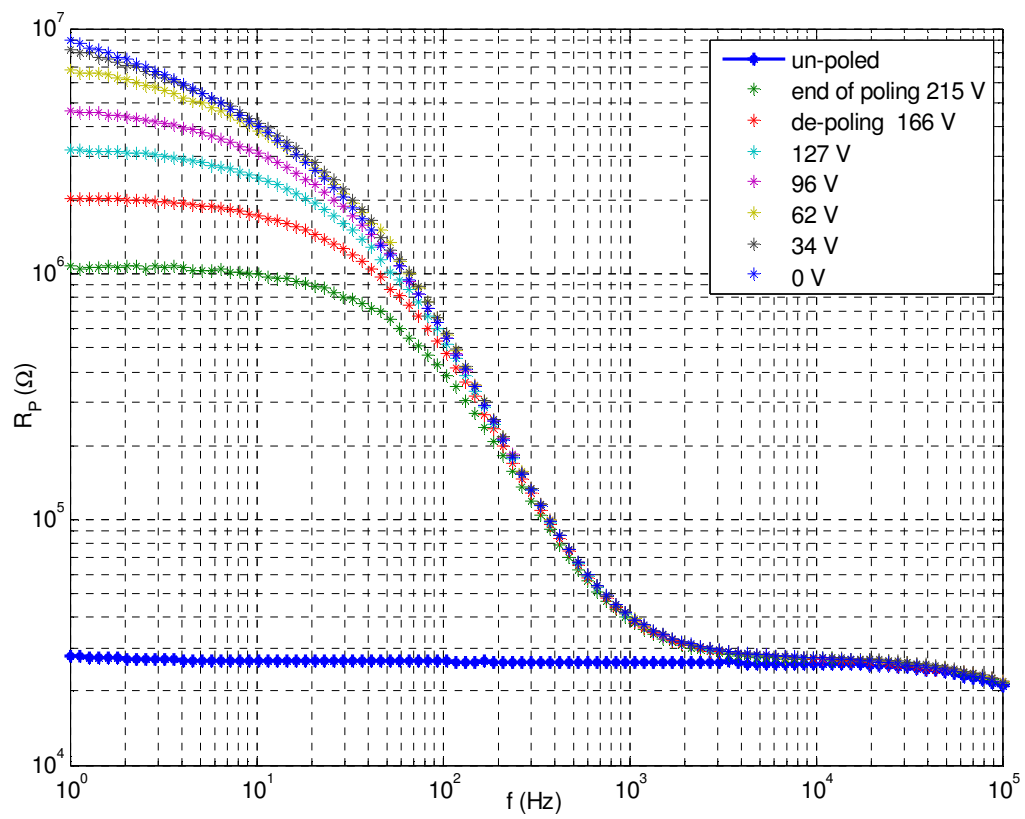


Figure 4

Effective parallel resistance R_p as a function of frequency at the end of the poling stage and during the de-poling stage. (colour on-line)

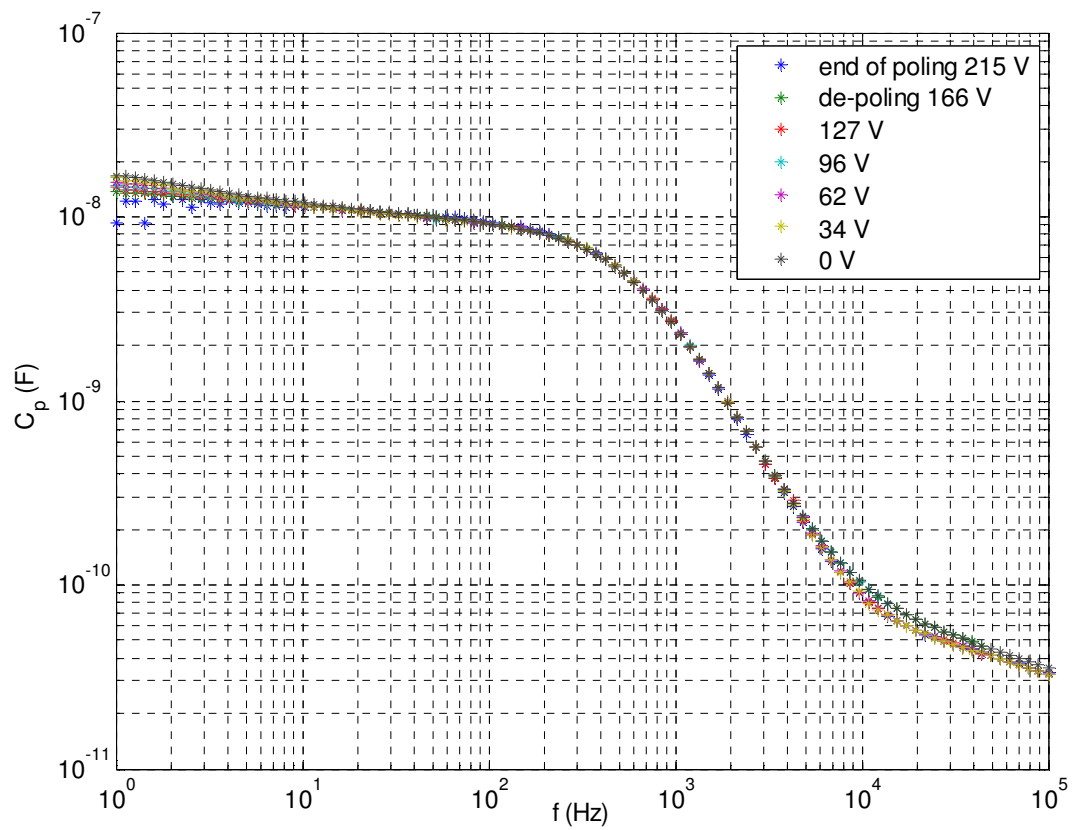


Figure 5

Effective parallel capacitance C_p as a function of frequency at the end of the poling stage and during the de-poling stage. (colour on-line)

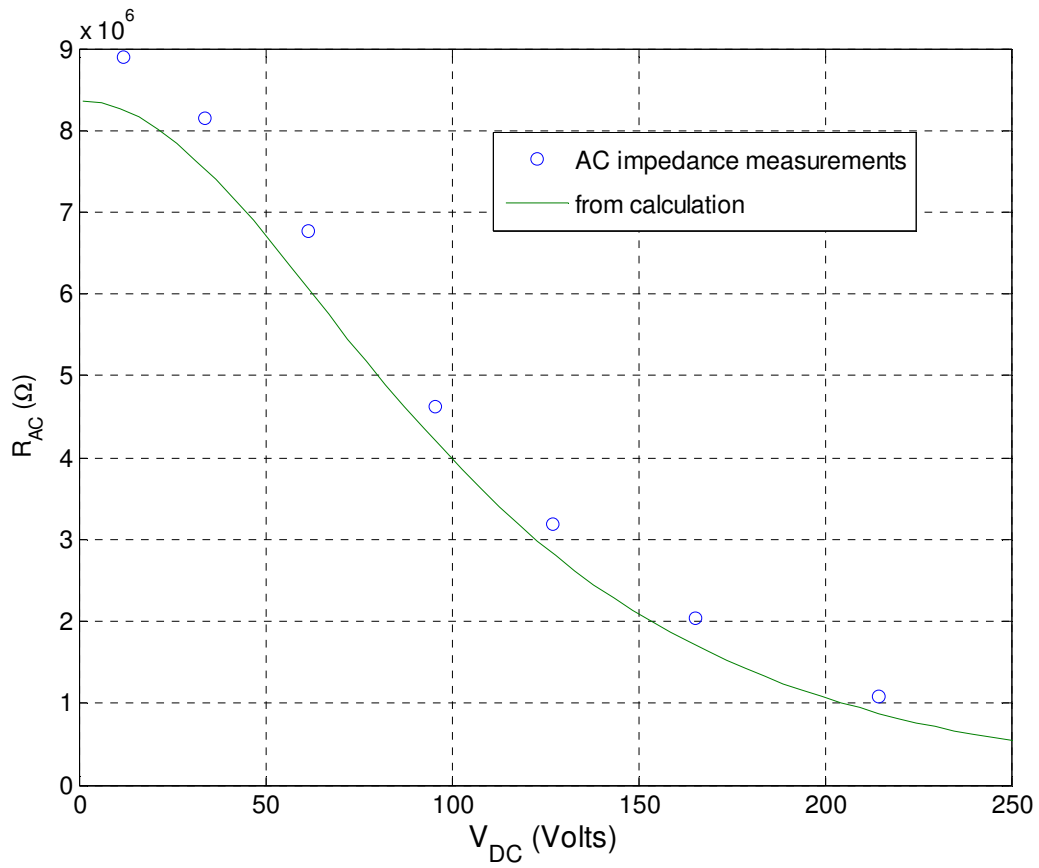


Figure 6

Low frequency AC resistance deduced from the impedance measurements R_p (o) and from eqn. 6 (line) using V_o and I_o values obtained from the DC current-voltage data during de-poling. (colour on-line)

further a sample was poled for a reduced time of 1.5 hours before the de-poling process. The total charge transported through the sample was 0.46C. The analysis of the I_{DC} - V_{DC} data obtained during de-poling gave $V_0=32V$. Thus V_0 appears to scale in proportion to d in accordance with eqn. 4 which adds some weight to the above assumption.

For $V_0=73V$ and $d=2.3 \mu m$ eqn. 4 gives $a = 2.9 \text{ nm}$. This is of the order of 6 times larger than a jump distance estimated from the mobile cation (Na^+ and K^+) concentration in the original glass ($a \cong C^{-1/3}$ where $C \sim 7.3 \times 10^{27} \text{ m}^{-3}$ gives $a \sim 0.52 \text{ nm}$). Larger than expected values of a are commonly found in high field conduction experiments in bulk glass samples. Values of a that are up to 20 times larger have been found at lower temperatures on bulk glass conductivity measurements using large AC fields [12]. These large values for a are attributed to the disordered nature of the energy wells that can be expected in real glass samples.

Finally we note that the motion of electrons within the poled layer at the end of our poling experiments can probably be discounted since the average field is $215V/2.3\mu m = 9 \times 10^7 \text{ Vm}^{-1}$, which is an order of magnitude less than the critical field $E_{crit} \sim 1 \text{ GVm}^{-1}$ at which electrons could be expected to be released.

5. Conclusions

In conclusion we have provided evidence that the initial increase in the impedance which is observed when the DC poling voltage is removed in a de-poling process is ionic in nature. We have shown that it is due to the low frequency AC resistance increasing, and can be explained by application of the hopping model of ionic conduction in glass. The DC field changes the barrier height over which ions jump from one site to another thereby also changing the low frequency AC resistance; by removing the DC field the original barrier height is restored. Our results show that the low frequency AC resistance follows a functional form that is consistent with this model. We are however unable to draw any conclusions as to the relative magnitudes of hydrogen or oxygen ion motion during poling from the work.

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References

- [1] R. Mariappan and B. Roling, "Investigation of bioglass-electrode interfaces after thermal poling", *Solid State Ionics* **179** 671-677 (2008)
- [2] C.R. Mariappan and B. Roling "Mechanism and Kinetics of Na⁺ ion depletion under the anode during electro-thermal poling of a bioactive glass", *J. Non-Cryst. Solids*. **356** 720-724 (2010)
- [3] J. Zakel, V. Heddinga, S.O. Steinmuller and B. Roling "Investigation of sodium ion depletion layers in electrothermally poled bioglasses by combining impedance spectroscopy and ToF-SIMS depth profiling", *Solid State Ionics* **237** 46-49 (2013)
- [4] J. Zalel, M. Balabajew and B. Roling "On the mechanism of field-induced mixed ionic-electronic transport during electro-thermal poling of a bioactive sodium-calcium phosphosilicate glass", *Solid State Ionics* **265** 1-6 (2014).
- [5] C. McLaren, M. Balabajew, M. Gellert, B. Roling and H. Jain "Depletion Layer Formation in Alkali Silicate Glasses by Electro-Thermal Poling", *J. Electro. Chem. Soc.* **163** H809-H817 (2016)
- [6] D.E. Carlson "Ion Depletion of Glass at a Blocking Anode:1, Theory and Experimental Results for Alkali Silicate Glasses", *J. Amer. Ceram. Soc.* **57** 291-294 (1974)
- [7] M. Dussauze, V. Rodriguez, A. A. Lipovskii, M. Petrov, C. Smith, K. Richardson, T. Cardinal, E. Fargin and E. I. Kamitsos, "How Does Thermal Poling Affect the Structure of Soda-Lime Glass?", *J. Phys. Chem. C* **114** 12754–12759, (2010)
- [8] M. I. Petrov, Ya. A. Lepen'kin, and A. A. Lipovskii "Polarization of glass containing fast and slow ions" *J. of Appl. Phys.* **112**, 043101 (2012)
- [9] D.E. Carlson "Anodic Proton Injection in Glasses" *J. Amer. Ceram. Soc.* **57** 461-466 (1974)
- [10] A.V. Redkov, V.G. Melehin, V.V. Statcenko and A.A. Lipovski "Nanoprofiling of alkali-silicate glass by thermal poling" *J. Non-Cryst. Solids*. **409** 166-169 (2015)
- [11] R. Oven "Measurement of the refractive index of electrically poled soda-lime glass layers using leaky modes" *Appl. Opt.* **55** (32). 9123-9130 (2016).
- [12] A. Heuer, S. Murugavel and B. Roling "Nonlinear ionic conductivity of thin solid electrolyte samples: Comparison between theory and experiment" *Phys. Rev. B* **72** 174304 (2005).