Pseudo-ferroelectric properties by space charge polarization

VIEWPOINT

Pseudo-ferroelectric properties by space charge polarization

H Kliem and B Martin

Institute of Electrical Engineering Physics, Saarland University, Campus,
66123 Saarbruecken, Germany

E-mail: b.martin@mx.uni-saarland.de

Abstract
We show that the determination of ferroelectric properties by the measurement of polarization
charge hysteresis curves can be misleading. Measurements using polyethylene oxide and
simulations with a three-dimensional hopping model, developed for the characterization of the
space charge polarization in solid electrolytes, yield hysteresis curves which for properly
chosen parameters cannot be distinguished from real ferroelectric polarization hysteresis.
Furthermore, a butterfly curve of the capacitance with varying applied bias voltage, which is
often assumed to be typical for ferroelectrics, is observed in electrolytes experimentally. Thus,
further investigations, e.g. sample thickness effects, have to be performed to confirm that the
material under test is a ferroelectric and that space charge polarization does not prevail.

1. Introduction

In a recent article Scott pointed out that not each material
which shows a closed loop in the measured charge Q versus
the applied field E is a ferroelectric as claimed in several
other publications [1]. In measurements of hysteresis curves
phenomena such as charge injection or internal space charge
polarization have to be taken into account. Measurements
normally are carried out by applying a triangular electrical field
to the specimen. Then the resulting charge Q is detected either
directly with the Sawyer–Tower method or by the measurement
of the current density j and integration over time. No matter
what method is used the sample has always to be contacted
with electrodes. So Q can consist not only of the switched
charge from the ferroelectric phase but also of terms due to
charge injection and space charge polarization [1–5]. This was
recently demonstrated by Loidl *et al* using *Musa acuminata
Colla* (bananas) [6]. In the following the influence of the
internal space charge polarization on the $Q(E)$-hysteresis will
be investigated. Charge injection will not be considered here.

2. Space charge polarization in polyethylene oxide

As a model system for a space charge polarization the ion
conducting polymer polyethylene oxide (PEO) is used. Films

of PEO with thicknesses ranging from 0.5 up to 50 μm are
spin coated onto a glass or silicon substrate covered with
aluminum. Then aluminum spots are evaporated on the top
of the sample through a shadow mask. Thus, a plane parallel
capacitance structure is produced. The native Al_2O_3 layers
between the electrodes and the polymer serve as blocking
layers preventing charge injection at moderate electrical fields.
These films show a pronounced relaxational behavior of
the dielectric permittivity in the frequency domain [7]. A
thickness dependent permittivity in the low frequency range
and a thickness independent permittivity in the high frequency
range are found. Also, the relaxation frequency is shifted
towards lower frequencies for thicker samples. Therefore, it
is concluded that an internal space charge polarization prevails
and causes the dielectric relaxation.

With this internal space charge polarization, mobile ions
are shifted by an applied electrical field towards the electrodes.
Due to image forces with the charges in the metal these ions
at the interface become partly immobilized. Some ions can
be trapped for longer times at the interfaces, others move
backwards when the field is reversed [5]. The application
of a triangular voltage with simultaneous measurement of the
charge as usually done for polarization measurements results
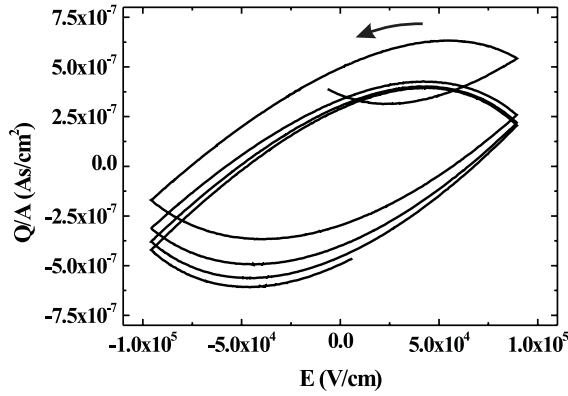in a hysteresis curve as shown in figure 1.

Figure 1. Measured hysteresis curve in PEO for $f = 0.001$ Hz. A space charge polarization prevails in the systems.
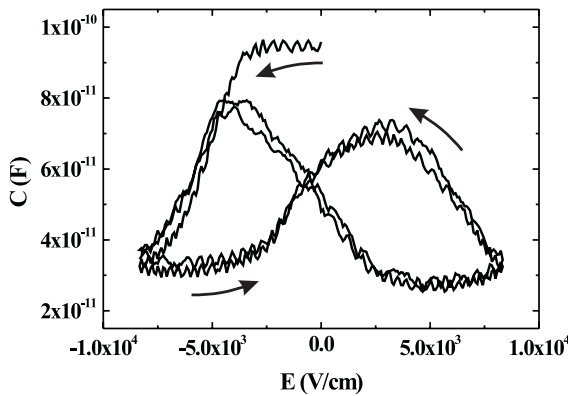

Figure 2. Measured butterfly curve at a PEO sample. Frequency of the triangular bias: 0.001 Hz, frequency of the capacitance measurement: 20 Hz.

Additionally, butterfly curves for the capacitance, which are usually looked at as typical for ferroelectrics, can be measured (figure 2) [8, 9]. Here, the capacitance of the samples at a single frequency is determined for different bias voltages. As explained before, the applied field shifts the ions from the volume of the sample towards the electrodes, where they are immobilized. Thus, the measured capacitance decreases with increasing bias voltage. When the voltage is reduced the ions are partly released to the volume of the sample and the capacitance is increased again. Because the moving ions cannot follow the bias field instantaneously, a butterfly curve appears also in systems in which a space charge polarization dominates.

3. Three-dimensional hopping model

To simulate the dielectric properties of these systems a three-dimensional hopping model is introduced [5, 10]. Here mobile negative ions can fluctuate thermally activated over barriers in a multiwell energy structure. The ions are distributed on cubic lattice cells. The cells are separated by the barrier heights $W_{\rm eff}$, which have to be surmounted by the mobile charges. For charge neutrality a constant positive background charge is introduced. The effective barrier height $W_{\rm eff}$
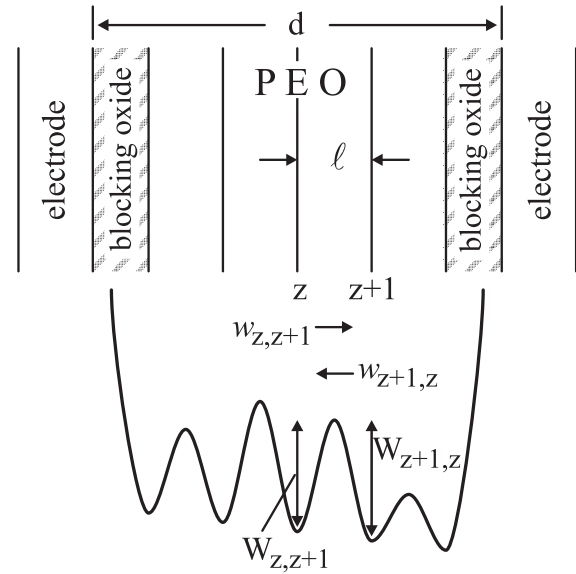

Figure 3. One-dimensional representation of the three-dimensional hopping model.

consists of an intrinsic barrier height W_0, an interaction term ΔW, and a term resulting from the applied field $\delta W = E_a q \ell$, where $\ell = 1$ nm is the hopping distance and q the elementary charge. The interaction term includes all interactions between the ions among themselves, between the ions and the background charge, and between the ions and the charges in the electrodes. This last term is calculated by the method of images. The interactions with the electrodes can predominantly be responsible for the dielectric behavior of the system when thin blocking layers are considered [5].

A one-dimensional representation of the three-dimensional model is given in figure 3. The polymer is divided into $z_{\rm m}$ layers which represent the minima in the energy structure. Blocking layers with thickness $d_{\rm bl}$, which are impermeable to the mobile ions, are placed between the polymer and the electrodes. The rate for a jump of an ion from one well to another can be calculated as

$$w_{i,k} = \nu_0 \exp\left\{-\frac{W_{\rm eff}}{kT}\right\}$$
$$= \nu_0 \exp\left\{-\frac{W_0}{kT} \pm \frac{\Delta W}{2kT} \pm \frac{\delta W}{2kT}\right\} \qquad (1)$$

for each ion i and each direction k in a deterministic way. The phonon frequency ν_0 is set to 10^{12} Hz and the intrinsic barrier height to $W_0 = 0.71$ eV. This yields for $\Delta W = \delta W = 0$ a jump rate of $w = 1$ s^{-1}. From the rates calculated with equation (1) the probabilistic hopping times

$$t_{i,k} = \frac{1}{w_{i,k}} \ln(x_{i,k}) \qquad (2)$$

are determined using random numbers $x_{i,k} \in \,\,]0, 1]$. Then, a dynamic Monte Carlo step is carried out, i.e. only the ion with the smallest hopping time $t_{\rm min}$ jumps in the appropriate direction. Afterward, the total system time is increased by $t_{\rm min}$ and the algorithm continues by recalculating
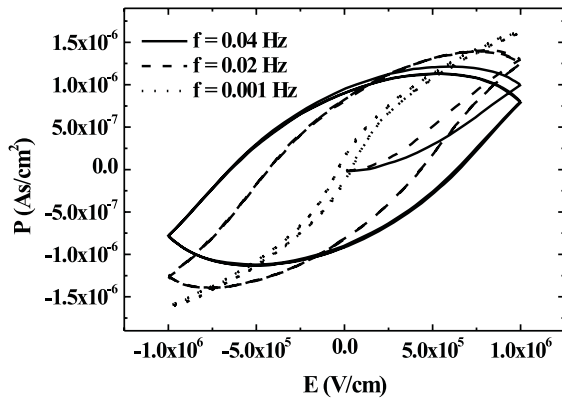
Figure 4. Simulated hysteresis curve for a blocking layer thickness $d_{bl} = 2$ nm and different frequencies of the triangular signal.
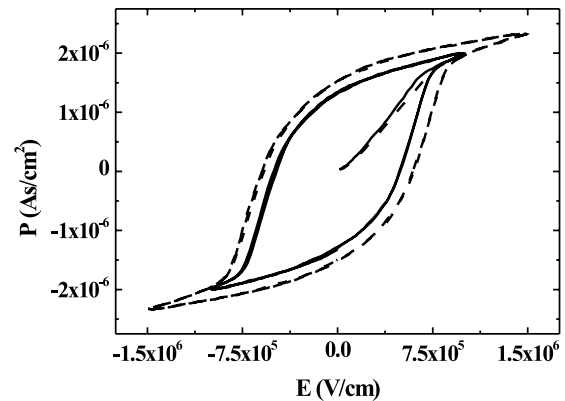

Figure 5. Simulated hysteresis curve for a blocking layer thickness $d_{bl} = 0.25$ nm and different magnitudes of the triangular signal ($f = 0.002$ Hz).

the interaction terms for the new charge distribution. In this way the time dependent behavior of the system is simulated.

4. Results

The hysteresis curve found as a result of the simulation with a relatively thick blocking layer $d_{bl} = 2$ nm for different frequencies of the applied triangular field is given in figure 4. For higher frequencies $f = 0.04$ Hz the result of the simulation can be compared to the measurement qualitatively. The shift of the charges between the electrodes yields a hysteresis of the polarization P versus the applied field E. The mobile ions can follow the applied field only with delay. At frequencies below $f \leqslant 0.02$ Hz the hysteresis vanishes more and more. For these frequencies the ions can follow the applied field nearly instantaneously. For $f = 0.001$ Hz a quasi-static state is reached. The polarization depends only on the magnitude and not on the slope of the applied field. Thus, the hysteresis shrinks and almost a single curve is found.

By reducing the blocking layer thickness to $d_{bl} = 0.25$ nm, electrode effects become more important. The mobile ions can be pinned to the electrodes due to the attractive interactions with their image charges. When ions have reached the electrode due to the applied field they get trapped and a high field in the opposite direction is necessary to shift the ions back into the volume of the sample and to reduce the polarization. This looks like the appearance of a coercive field. A simulation of the hysteresis curves for this system at a frequency $f = 0.002$ Hz is given in figure 5. A high remanent polarization P_{rem} is observed due to the influence of the electrodes. Furthermore, the polarization reaches a saturation state P_{sat} where the polarization can only be slightly increased by increasing the applied field. This graph which results only from a space charge polarization cannot be distinguished from the hysteresis found in ferroelectric materials [8, 9, 11–14]. The simulation of the butterfly curve (figure 2) is not possible at present due to expected extremely high computation times.

5. Conclusion

It has been shown that some pseudo-ferroelectric properties can be obtained in systems in which a space charge polarization prevails. A discrimination between ferroelectricity and space charge polarization, only by the measurement of the charge Q versus the applied field E, is almost not possible. Additional data have to be taken into account to confirm that the observed material is a ferroelectric. With electrical methods a discrimination can be reached by the measurement of the dielectric permittivity. In the case of a ferroelectric, its temperature dependence has to follow the well-known Curie–Weiss law. There is also no pronounced thickness dependence of the dielectric permittivity in the low frequency range for ferroelectrics while there is in ionic conductors. Furthermore, the space charge polarization has a thickness dependent saturation, while ferroelectric saturation polarization is thickness independent in as far as dead layers are not present.

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