

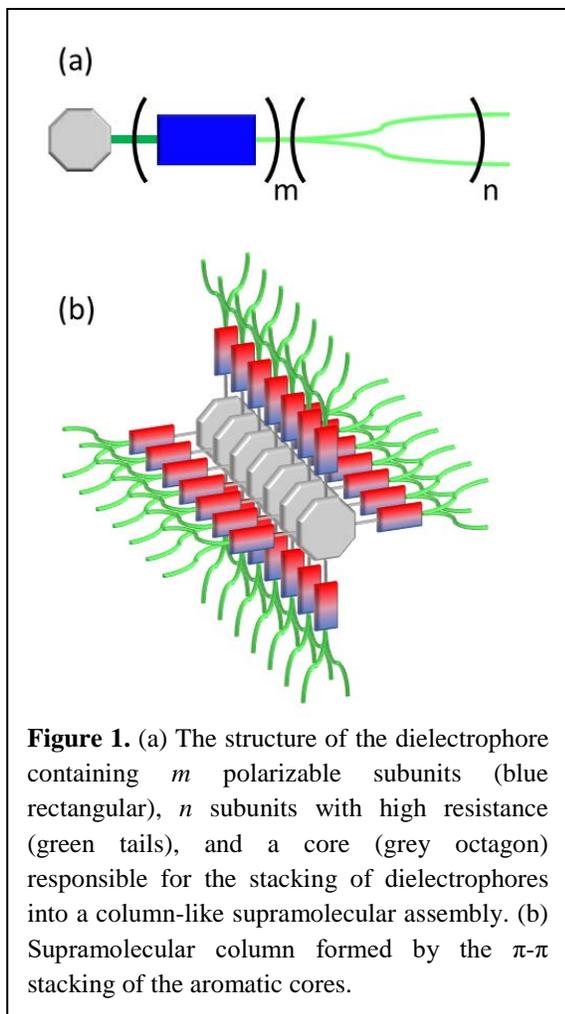
Experimental Testing of Non-Linear Dielectric Materials

INTRODUCTION

Efficient energy storage is the key component in the development of various modern technologies. In the present time, the all-electric cars start to enter the vehicle market but they are still more expensive and less trustworthy than the usual ones. Electronic devices, which are omnipresent in modern society, are also heavily dependent on reliable energy storage modules. Moreover, renewable energy sources such as solar cells and wind turbines are sustainable and environmentally friendly, but their energy production is intermittent and the effective storage would make the energy available on demand.

In the present time, the main storage devices are the *batteries*. The energy is stored electrochemically, i. e. carriers released in chemical reactions can enter electrical circuits. The energy density of batteries is relatively high and they are relatively inexpensive. During the

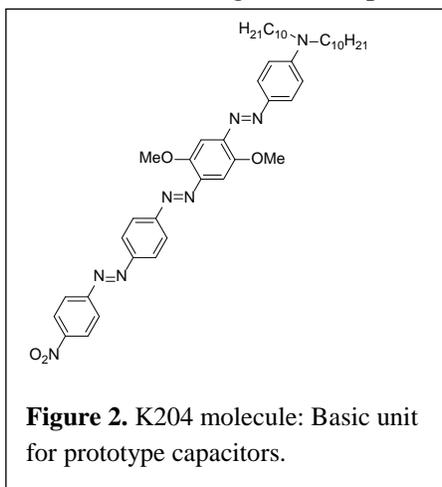
charging process, the carriers (such as lithium ions) are returned to the source. This process is slow and, moreover, it degrades the battery material. Thus, the power density of the batteries is low and their lifetime is short due to the material degradation. Furthermore, the batteries become less reliable at elevated temperatures. The alternative storage devices are *capacitors*, where the energy is stored electrostatically. The charging process is fast, leading to the high power density and the longtime reliability. The main shortcoming for capacitors is their low energy density. *Energy storage devices having both high energy density and high power density are crucial for further progress of technology. As the limitations of the electrochemical batteries are impossible to overcome, the right answer should arrive from the capacitor side.*



Possible structures for modern capacitors should have two main properties which seem impossible to occur simultaneously. First, they should be highly polarizable to store electrostatic energy and, second, they should be highly resistive to prevent current leakage. The possible solution can come from

hybrid molecular structures where electrons can readily move inside the molecules to achieve the high polarization but the transfer between the molecules is strongly suppressed. We call this molecular structural unit a “dielectrophore” and its general structure is shown in Figure 1(a). With an applied electric field in horizontal direction, the electric dipole will be formed within the polarizable subunit, while the insulative tails will prevent charge transport to adjacent dielectrophores. The core subunit allows the supramolecular stacking which occurs in the direction perpendicular to the plane of the image. An example of proposed design is shown in Figure 1(b). The aromatic core allows for π - π stacking and formation of the supramolecular column. The insulating tails prevent charge transfer to adjacent supramolecular columns eliminating current leakage (dielectric loss) and dielectric breakdown. These supramolecular columns would form in the plane perpendicular to the capacitor electrodes and would remain isolated from each other in a flexible quasiperiodic order.

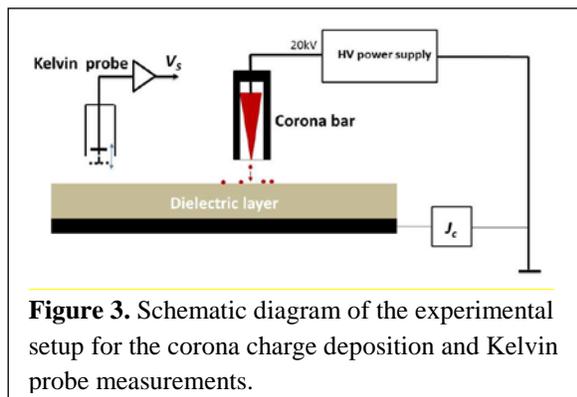
Oil-derivative organic compounds are the most suitable basis for film capacitor designs for the



following reasons. First, organic molecules allow the flexibility of design of the elementary units. Second, these molecules can form structured kinetic units required for self-assembly. Third, the π - π stacking of aromatic molecules makes it possible to form highly dense self-assembled supramolecular columns. Fourth, the obtained supramolecules would be flexible enough not to be damaged by high operating pressure. And finally, the synthesized organic materials are relatively inexpensive and can be produced in the volumes necessary to satisfy the global demand for energy storage. We have performed extensive quantum chemistry calculations to determine specific molecules optimally suited for our

purposes and in the present time one of the most promising molecular units is so-called K204 structure shown in Figure 2. The polarizable core includes four benzene rings coupled by the azo connectors, while two $C_{10}H_{21}$ tails separate the cores.

Synthesized powder of K204 is dissolved in organic solvent in preparation for solvent solution coating. Films are prepared using wire-wound wet film applicator rods on a Gardco II Automatic



Drawdown Machine. The films are several micrometers thick and prepared on either indium-tin-oxide (ITO) or aluminum-coated glass. Results for the testing of such films under electric field are shown in subsequent sections.

EXPERIMENTAL TESTING: CORONA CHARGE DEPOSITION

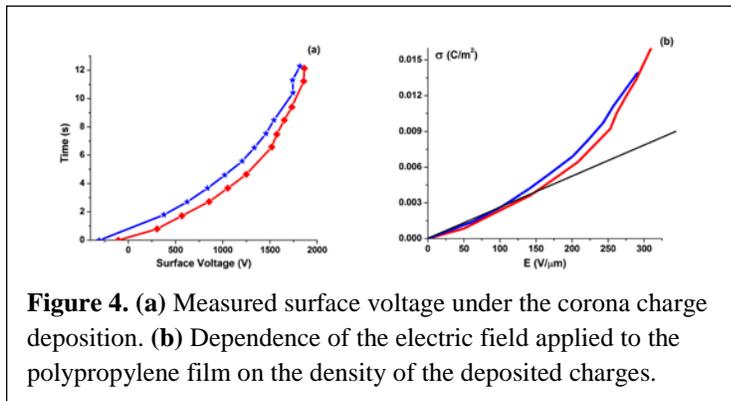
The setup of the corona charge deposition

method is shown in Figure 3. Our measurement device consists of the corona bar which induces the electric breakdown of surrounding gas and directs the positive or negative ions toward the thin film surface; the amperemeter measures the current from (to) the ground to (from) the bottom electrode associated with its charging opposite to the deposited ions; and the Kelvin probe apparatus measures the surface potential with the respect to the ground. The tested area, A , is initially placed under the corona bar and charged for period of time Δt_1 . The bottom electrode current, J_c , is simultaneously measured. Then, the tested area is placed under the Kelvin probe to measure the surface potential V_S . Thereafter, the sample is placed back under the corona bar and charged again for the period of time Δt_2 , the surface potential is measured again and the procedure is repeated N times. Correspondingly, the density of the deposited charge in the n^{th} step is $\sigma_n = J_c \Delta t_n / A$, where $n = 1, 2, \dots, N$, and the total charge density at the top surface of this film is given by

$$\sigma = J_c t / A, \quad (1)$$

where t is the total time under the corona charge deposition.

To calibrate our apparatus and to compare our samples with a well-known material, we perform



the corona deposition of positive charges and Kelvin probe measurements for a thin polypropylene film. The current from the bottom electrode to the ground is kept at $J_c = 10^{-5}$ A. The results are shown in Figure 4 for two different films. Figure 4(a) shows the surface voltage measured as time elapsed with both films initially negatively charged. In both cases, after approximately 10

seconds of the charge deposition, the electric breakdown occurs, and the polypropylene films are damaged.

To verify the results of our measurements, we recalculate the surface voltage to the electric field across the 6 μm thick film and adjust our data to the initial condition of zero charge. Using Eq. (1), we express the time of Figure 4(a) in terms of the density of the deposited charges for our sample of the size $11.5 \times 6 \text{ cm}^2$. The resulting relation between the charge density and the electric field is shown in Figure 4(b). The straight line representing the linear fit of the low-field data for both films can be used for the determination of the dielectric constant. According to Gauss' Law, the electric displacement is equal to the surface charge density, and the dielectric constant is given by

$$\varepsilon = \sigma / \varepsilon_0 E \approx 2.9. \quad (2)$$

The obtained result is in a good agreement with the tabulated value for the polypropylene films, so we have verified the reliability of our approach.

The results for the K204 film are shown in Figure 5(a). It is evident from this figure that the initial

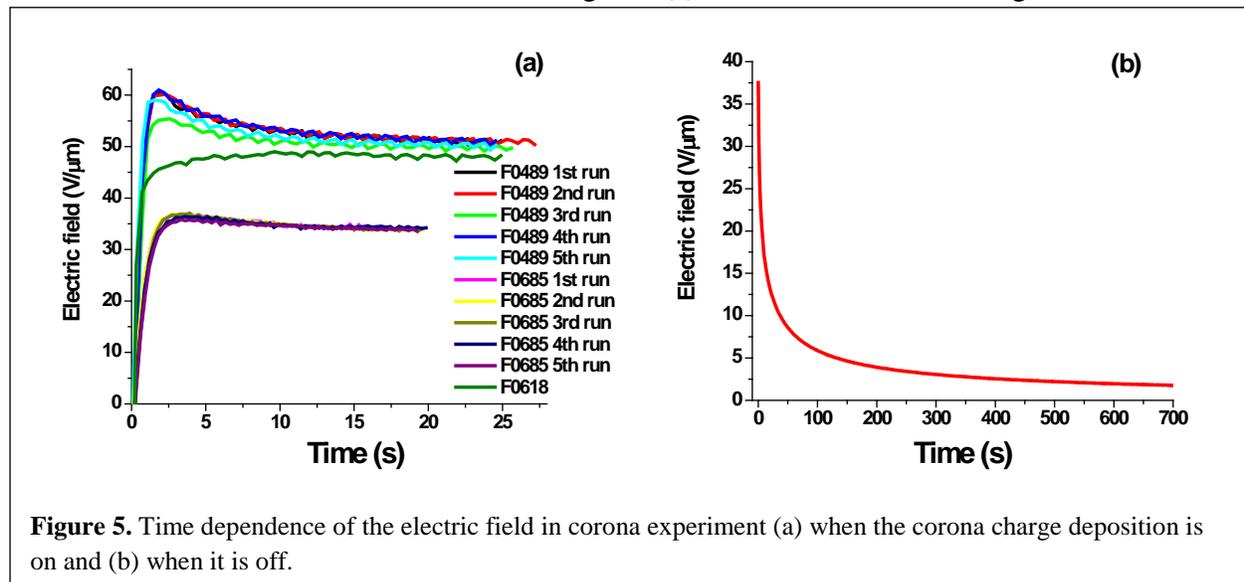


Figure 5. Time dependence of the electric field in corona experiment (a) when the corona charge deposition is on and (b) when it is off.

almost linear increase of the electric field is followed by a strongly nonlinear regime when the charge deposition does not lead to the increase of the field. Moreover, the field even initially decreases. Such regime can last up to 10 hours before the electric breakdown occurs and the sample is damaged. **We believe that this behavior can be explained by the fact that the polarization of the film under the field is delayed, with certain time needed for the crystal structure to adjust.** According to the definition of the electric displacement,

$$\sigma = \epsilon_0 E + P, \quad (3)$$

where P is the polarization, which in turn is proportional to the field. Correspondingly, when the polarization is not yet established, all the increasing charge density leads to the increase of the field. Because of the delay, polarization does not follow the field immediately, but after a delay, the increasing charge density leads to the increase of the polarization only. **The dynamic model describing this effect is currently under the development.**

The hypothesis of the delayed polarization is supported by the experimental results showed in Figure 5(b). After the corona charge deposition stops, the measured surface potential decays which according to Eq. (3) can be caused only by the increase of the polarization at given fixed charge density. One can see that the time scale of the polarization development is of the order of 10 seconds.

Corona experiments show that a large amount of charge can be deposited onto dielectrophores thin films. Correspondingly, the energy density stored in such dielectric is superior to existing electrostatic capacitors. Our estimations show that the dielectrophores thin films can store more energy than the polypropylene analogs by several orders of magnitude.

EXPERIMENTAL TESTING: COIN TWO-PLATE CAPACITORS

While the results of the corona experiments look promising, actual conclusions can be made only

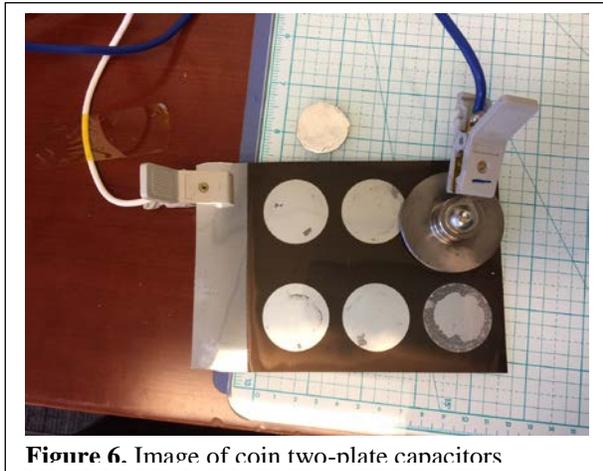


Figure 6. Image of coin two-plate capacitors

after experiments with two-plate capacitor prototypes. We prepared such devices by depositing metallic top electrodes as shown in Figure 6. They are the circles of 31 mm diameter. We performed a standard charging-soak-discharging test when initially the positive current is driven to charge the capacitor, then the established voltage is kept constant to measure the leakage current and corresponding resistance, and finally the capacitor is discharged by the constant negative current. Typical results are shown in Figure

7(a). The calculated resistivity is shown in Figure 7(b) for various capacitor voltages. It is evident from this figure that the resistivity fluctuates with the voltage but always exceeds 10^{15} Ohm-cm. It should be noted that the capacitor charging was performed with a significant current and the results are different from the corona experiment. It can be understood from the delayed polarization model that when the charging is fast, the structure does not have time to adjust and the polarization is not established.

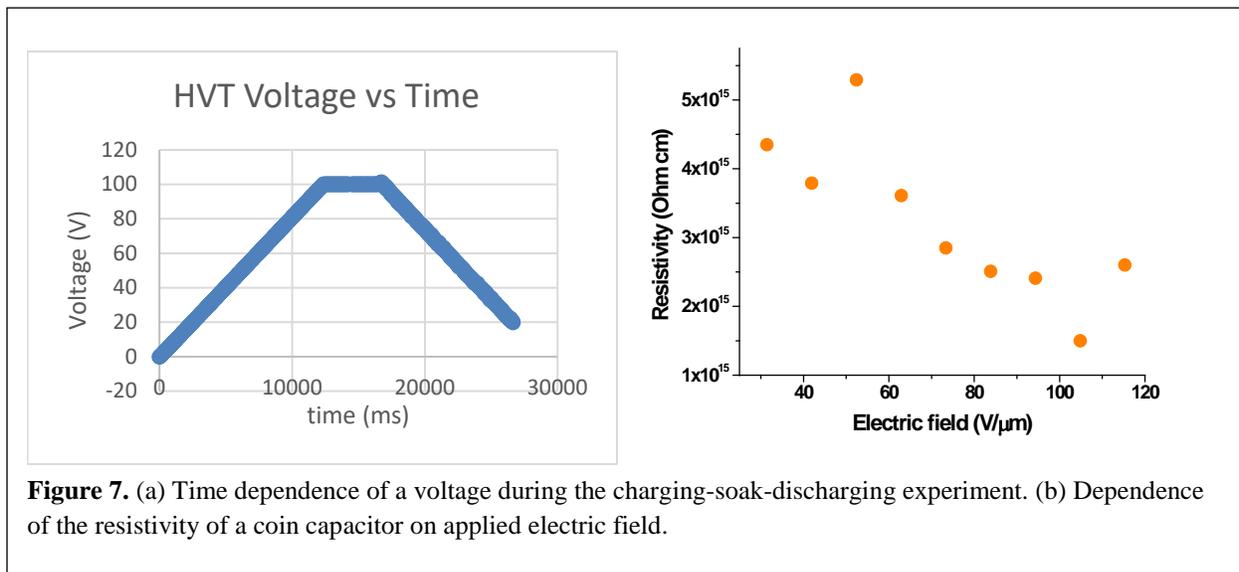


Figure 7. (a) Time dependence of a voltage during the charging-soak-discharging experiment. (b) Dependence of the resistivity of a coin capacitor on applied electric field.

To mimic the corona experiment and reveal the nonlinear properties, we perform the charging of the capacitor at smaller current of 10^{-8} A. The results are shown in Figure 8(a) for several coins. Similar to the corona results, after sharp initial increase, the voltage slightly decreases and remains almost unchanged for a long time. It should be noted that the decrease is more pronounced in the second run. This can be explained within the delayed polarization model, because the material is

already partially polarized after the first run and its alignment occurs faster.

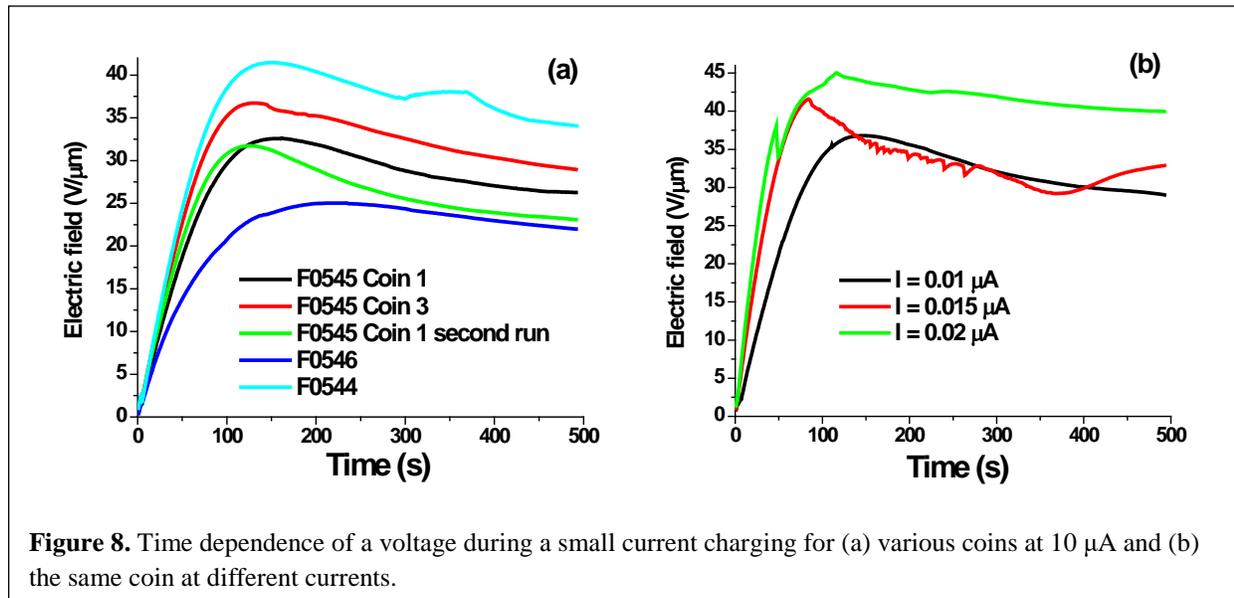


Figure 8. Time dependence of a voltage during a small current charging for (a) various coins at 10 μA and (b) the same coin at different currents.

We performed the same experiment with increased current with the results shown in Figure 8(b). At these higher current values, the curves are not that smooth and the critical voltage slightly increased, but qualitatively the results are very similar.

DISCUSSION

We would like to see if the observed phenomenology can be explained by a simple model in which

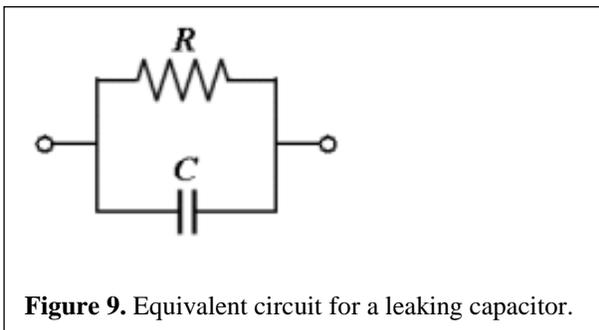


Figure 9. Equivalent circuit for a leaking capacitor.

a usual linear capacitor has a leakage. The leaking capacitor can be represented as a capacitor and resistor connected in parallel, see Figure 9. In this, the voltage drops, V , on the resistor and capacitor are the same and the total current is a sum of the displacement current through capacitor and the leakage current through the resistor as

$$I = I_D + I_L = \partial Q / \partial t + V/R, \quad (4)$$

where the first term is responsible for the charging of the capacitor. According to Gauss' Law, the surface charge density is equal to the electric displacement, which, in turn, is proportional to the electric field in the simple case of a linear capacitor with the instant polarization response,

$$\sigma = D = \epsilon E, \quad (5)$$

where ϵ is the permittivity of the material inside the capacitor. In this situation, the charging of the capacitor leads to the increasing of the electric field (and voltage) and, correspondingly, to the increasing of the leakage current, which is directly proportional to the voltage. **If the total current is kept constant, there is a possibility that at certain voltage the leaking current becomes equal to the total current, the displacement current vanishes, the charging of the capacitor stops, so the voltage becomes constant, leading to the picture similar to Figure 8(a).**

Let us estimate the field which corresponds to the situation when all the current through a coin two-plate capacitor is the leakage current. The leakage current is given by

$$I_L = V/R, \tag{6}$$

The resistance can be expressed in terms of the resistivity as

$$R = \rho d/S, \tag{7}$$

where d is the plate separation (film thickness of $8.7 \mu\text{m}$) and S is the plate area (circle of the diameter $a = 3.1 \text{ cm}$). Substituting Eq. (7) into Eq. (6), we obtain

$$I_L = VS/\rho d = ES/\rho, \tag{8}$$

where $E = V/d$ is the field across the capacitor. Correspondingly, the field can be calculated as

$$E = \rho I_L/S = 4\rho I_L/\pi a^2. \tag{9}$$

Even with the underestimated value of the resistivity of 10^{15} Ohm cm , we obtain approximately $132 \text{ V}/\mu\text{m}$ for the current of 10^{-8} A . This is about four times larger than the value of the constant

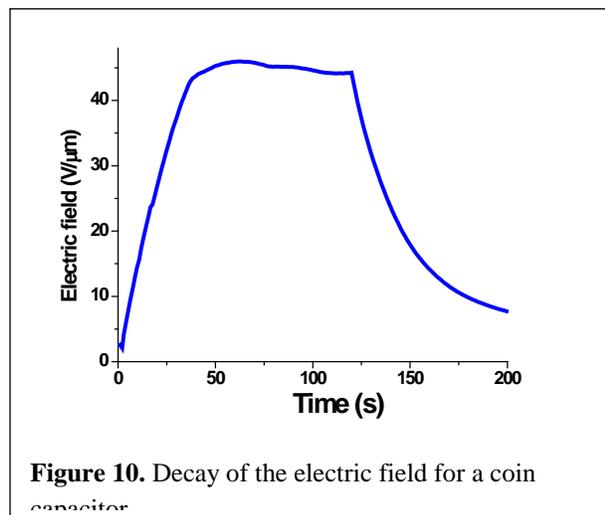


Figure 10. Decay of the electric field for a coin capacitor

field on Figure 8(a), which means that not all the current through a system is the leakage current and the charging of the capacitor continues. Moreover, if the leakage is the reason for the field saturation, with the current increasing two times, the saturation field should be increased two times as well, because the leakage current is directly proportional to the voltage. However, it is not the case, as can be seen from Figure 8(b). **Therefore, the field saturation should be explained by means of a different model.** It should be emphasized that the delay of polarization can be seen in the coin-capacitor

situation, as can be seen from the decay of the electric field when the current through the capacitor stops, see Figure 10.

CONCLUSIONS

We have performed the electric field testing of thin films of organic dielectrics to check the feasibility of their usage for the energy storage. The testing has been done using (i) corona charge deposition with a virtual top electrode and (ii) current driven in a standard two-electrode capacitor configuration. In both cases we have observed field saturation, i.e. the situation when the continuing charging does not lead to the increase of the voltage. Moreover, negative dynamic capacitance, i.e. decrease of the voltage with the amount of the stored charge increased, has been observed in both of experiments. We have ruled out the simple explanation of the observed phenomenology by the capacitor leaking because of the following reasons:

1. The estimations of the leakage current show that it is approximately four times smaller than the total current driven through the capacitor, i.e. three quarters of the current is the displacement current and the charging is continued even in the field saturation regime;
2. Two times increase of the driven current does not lead to the saturation field being increased twice, which would be the case for the leakage current having an Ohmic character;
3. The saturation fields observed in the corona and coin capacitor experiments are almost the same, while the leakage is completely different in the two-plate capacitors with direct electron injection and in the corona experiment when the *ions* are deposited on the top virtual electrode. Moreover, the corona experiments were performed at much larger current but the material had the time to adjust during the Kelvin probe measurement of the potential when there was no charge deposition.

However, the large leakage current is still a problem and should be strongly suppressed in actual devices. The model based of the delay of the polarization in this material is under the development in the present time.