

## LEAKAGE CURRENT DEGRADATION DUE TO ION DRIFT AND DIFFUSION IN TANTALUM AND NIOBIUM OXIDE CAPACITORS

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### Abstract

High temperature and high electric field applications in tantalum and niobium capacitors are limited by the mechanism of ion migration and field crystallization in a tantalum or niobium pentoxide insulating layer. The study of *leakage current* (DCL) variation in time as a result of increasing temperature and electric field might provide information about the physical mechanism of degradation. The experiments were performed on tantalum and niobium oxide capacitors at temperatures of about 125°C and applied voltages ranging up to rated voltages of 35 V and 16 V for tantalum and niobium oxide capacitors, respectively. Homogeneous distribution of oxygen vacancies acting as positive ions within the pentoxide layer was assumed before the experiments. DCL vs. time characteristics at a fixed temperature have several phases. At the beginning of ageing the DCL increases exponentially with time. In this period ions in the insulating layer are being moved in the electric field by drift only. Due to that the concentration of ions near the cathode increases producing a positively charged region near the cathode. The electric field near the cathode increases and the potential barrier between the cathode and insulating layer decreases which results in increasing DCL. However, redistribution of positive ions in the insulator layer leads to creation of an ion concentration gradient which results in a gradual increase of the ion diffusion current in the direction opposite to the ion drift current component. The equilibrium between the two for a given temperature and electric field results in saturation of the leakage current value. DCL vs. time characteristics are described by the exponential stretched law. We found that during the initial part of ageing an exponent  $n = 1$  applies. That corresponds to the ion drift motion only. After long-time application of the electric field at a high temperature the DCL vs. time characteristics are described by the exponential stretched law with an exponent  $n = 0.5$ . Here, the equilibrium between the ion drift and diffusion is achieved. The process of leakage current degradation is therefore partially reversible. When the external electric field is lowered, or the samples are shortened, the leakage current for a given voltage decreases with time and the DCL vs. time characteristics are described by the exponential stretched law with an exponent  $n = 0.5$ , thus the ion redistribution by diffusion becomes dominant.

Keywords: niobium oxide capacitors, tantalum capacitors, leakage current, ion diffusion, ion drift.

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### 1. Introduction

Quality and life time of capacitor and supercapacitor devices have been studied for the last decades by many scientists [1–11]. The degradation of *tantalum* (Ta) and *niobium oxide* (NbO) capacitors in steady-state conditions at elevated temperatures was studied in [6–11]. The capacitor *leakage current* (DCL) is a parameter most sensitive to defects and irreversible processes in the insulating pentoxide layer. Changes of DCL in time at increased temperature and applied electric field might provide information on the physical mechanism of degradation. High temperature and high electric field applications are considered to be limited by field crystallization mechanisms and by migration of positively charged oxygen vacancies (ions) in pentoxide film [6–9]. The field crystallization model assumes that tantalum or niobium oxide crystals grow with time of operation under the amorphous anodic oxide and eventually disrupt

the dielectric layer, causing a breakdown. Until the moment of disruption no changes in leakage currents are observed. It is assumed that the rate of crystallization increases with increasing thickness of the anodic pentoxide [7] and then high-voltage capacitors should be more vulnerable to this type of failure.

The model of redistribution of positive ions in pentoxide film [7] assumes that ions move from the capacitor anode to its cathode in electric field by diffusion only and create an internal electric field in the vicinity of insulating layer-cathode interface which affects the potential barrier on this interface according to a modified Schottky conduction mechanism and consequently changes DCL.

Leakage current variations are partially reversible [10–12]. Increasing temperature results in a gradual decrease of leakage currents either without applying an external electric field or with applying a very low voltage. In some cases initial values of DCL were restored altogether. When the leakage current changes are reversible and the field crystallization is not involved, the source of DCL change must only be the ion redistribution.

Both Ta and NbO capacitors pass through high temperature technological steps which should ensure homogeneous distribution of oxygen vacancies in the dielectric layer. Therefore, we assume that the concentration of positive ions – oxygen vacancies in the pentoxide volume is constant if the experiments are performed on as-prepared samples (not subjected to an external electric field prior to the experiment). In this case the ion diffusion cannot be involved in the charge redistribution in the pentoxide volume, because no concentration gradient exists within the pentoxide layer at the beginning of ageing. Drift of charges in the external electric field must be observed first, whereas diffusion of charges occurs only after the concentration gradient is formed within the structure.

The ageing process in Ta and NbO capacitors can be divided into two separate phases. During the initial stage of ageing the drift process is dominant due to the application of external electric field at an elevated temperature. The second stage of ageing is affected by both the external electric field and the ion concentration gradient created in the vicinity of Ta<sub>2</sub>O<sub>5</sub> or Nb<sub>2</sub>O<sub>5</sub> – cathode interface. In this case both drift and diffusion of ions are pronounced.

In this paper we show a method of the qualitative evaluation of ion drift and diffusion processes during the ageing of Ta and NbO capacitors. Time dependencies of the leakage current are measured and evaluated and mechanisms responsible for the DCL increase are determined. The reversibility of DCL changes and their source are verified.

## 2. Experiment

The experiments were performed on tantalum capacitors with capacitance 33  $\mu$ F and nominal voltage 35 V and niobium oxide capacitors with capacitance 2.2  $\mu$ F and nominal voltage 16 V. All capacitors contain an MnO<sub>2</sub> cathode and are placed in an SMD type D case with dimensions 7.3  $\times$  4.3  $\times$  2.9 millimetres (length  $\times$  width  $\times$  height). The working temperature is in a range of  $-55$  to  $+125^\circ\text{C}$ . The dielectric thickness is about 190 nm for Ta capacitors and 170 nm for NbO capacitors. We have evaluated two sets of Ta capacitors denoted further as Ta1 and LT8, and a set of NbO capacitors denoted as NbO2. 20 samples were evaluated within each set.

We measured the leakage current evolution in time for samples powered at a nominal voltage and placed in a climatic chamber at temperature  $120^\circ\text{C}$  for NbO capacitors and  $125^\circ\text{C}$  for Ta capacitors.

The leakage currents were monitored using a PC-based data acquisition system (see Fig. 1). Here, the samples under test were soldered on an FR4 board with printed connectors, which enables simultaneous charging of up to 20 samples. PCBs with soldered samples were placed in a climatic chamber, where an appropriate value of temperature can be maintained within

a range from 30 to 300°C. The samples were connected to load resistors using multiple cables with temperature-proof PTFE insulation. The 10 kΩ load resistors were placed outside the climatic chamber. The samples were powered using a DC digital power source Agilent 6614C. To measure the voltage on the load resistors an Agilent 34970A meter with 3 pcs of a 20-channel multiplexer card 34901A was used. The climatic chamber, multi-meter and power source were interconnected via an IEEE 488 (GPIB) bus which was connected to the computer via a GPIB/USB interface Agilent 82357A.

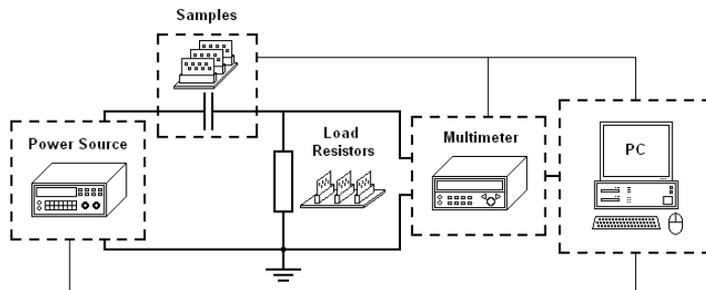


Fig. 1. A measurement system.

For measurement of the leakage current time dependence at an elevated temperature a required voltage of the power source was fixed. A voltage on the load resistor was measured periodically every 10 seconds. The leakage current value was calculated from the voltage measured on the load resistor and the load resistor value. The values of load resistors should meet the condition that the voltage on the load resistor during the experiment does not exceed 5% of the power source output voltage. Then the voltage on the measured capacitor was assumed to be constant during the experiment. The total duration of ageing experiment was near 400 hours.

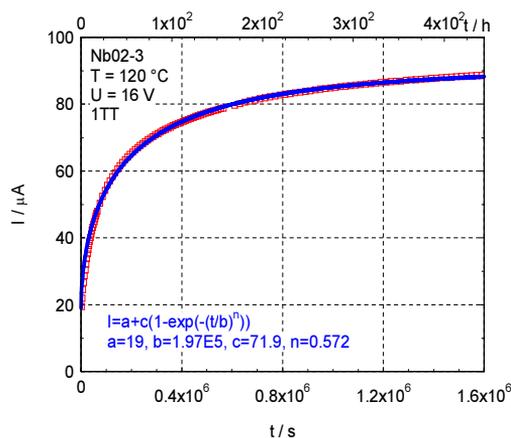


Fig. 2. A DCL vs. time characteristic for the niobium oxide capacitor NbO<sub>2</sub>-3 ageing at a nominal voltage  $V = 16$  V and temperature  $T = 120^\circ\text{C}$ .

A typical dependence measured during the experiment is shown in Fig. 2. Here, the time dependence of leakage current is shown for the niobium oxide capacitor NbO<sub>2</sub>-3 for applied nominal voltage  $V = 16$  V at temperature  $T = 120^\circ\text{C}$ . The monitored leakage current value increases from 19 μA up to 88 μA within a time interval of 400 hours (see Fig. 2).

After this the leakage current recovery was studied. The voltage was lowered down to 5 V for Ta capacitors and to 2 V for NbO capacitors. The leakage current was then monitored in about 40 to 170 hours.

Figure 3 shows DCL recovery for the niobium oxide capacitor NbO<sub>2</sub>-3. After long-time application of a nominal voltage at 120°C (see Fig. 2) the voltage was lowered to 2 V and the sample was left at 120°C. The monitored leakage current value decreased from 1.8 μA to 0.2 μA within a time interval of about 40 hours. A drop of current from 88 μA to 1.8 μA is caused by a decrease of the applied voltage from 16 V to 2 V.

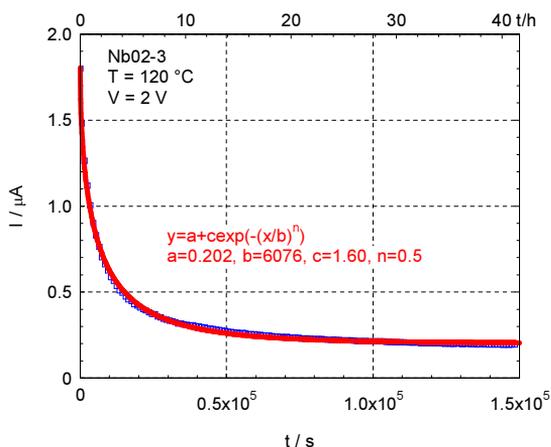


Fig. 3. A DCL vs. time characteristic for the niobium oxide capacitor NbO<sub>2</sub>-3 during leakage current recovery for applied voltage  $V = 2$  V at temperature  $T = 120^\circ\text{C}$ .

### 3. Results and discussion

The effect of electric field and high temperature on the ion drift and diffusion in tantalum and niobium oxide capacitors will be discussed. We suppose that oxygen vacancies in a tantalum or niobium pentoxide layer act as positive ions. The samples are, as produced, stored at a room temperature without application of voltage before this experiment. Therefore, we suppose that oxygen vacancies in the insulating layer are homogeneously distributed according to the thermodynamic equilibrium. This ion distribution is altered by applying an electric field. The concentration of positive ions near cathode increases due to the ion drift in the electric field. The increase of concentration of positive ions in the vicinity of insulator/cathode interface results in an exponential increase of the leakage current.

Redistribution of positive ions in the insulator volume leads to the creation of an ion concentration gradient which results in a gradual increase of the ion diffusion current in the direction opposite to that of the ion drift current component. The equilibrium between the ion drift in the electric field (from anode to cathode) and the ion diffusion due to the formed concentration gradient (in the direction from cathode to anode) for a given temperature and electric field results in saturation of the leakage current value.

The leakage current time dependence during ageing of a capacitor is described by an exponential function:

$$I(t) = I_0 + I_1(1 - \exp(-(t/\tau)^n)), \quad (1)$$

where:  $I_0$  is a DCL value at the beginning of ageing;  $I_1$  is a change of DCL due to the ageing,  $\tau$  is a time constant of the ageing process. The value of exponent  $n = 1$  when the potential barrier

on the insulating layer/cathode interface linearly decreases due to the ion drift in the electric field [13]. The value of exponent  $n = 0.5$  is only for the ion diffusion [6, 7].

### 3.1. Effect of ion drift on leakage current at beginning of ageing

DCL vs. time characteristics for initial 1 to 10 hours of ageing of tantalum capacitors at a rated voltage 35 V and temperature 125°C and niobium oxide capacitors at a rated voltage 16 V and temperature 120°C are shown in Figs. 4 and 5, respectively.

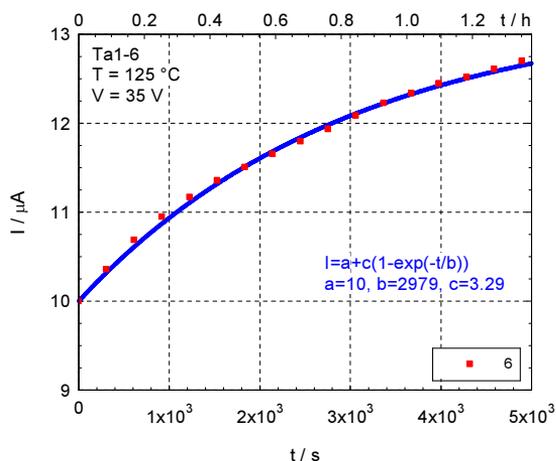


Fig. 4. DCL vs. time characteristics for a nominal voltage  $V = 35$  V at temperature  $T = 125^\circ\text{C}$  – beginning of the ageing process for the tantalum capacitor Ta1-6.

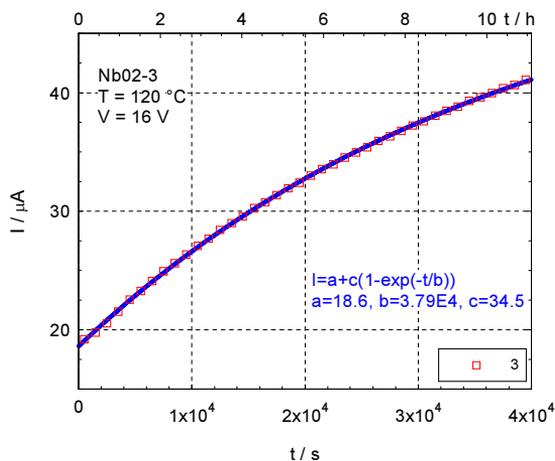


Fig. 5. DCL vs. time characteristics for a nominal voltage  $V = 16$  V at temperature  $T = 120^\circ\text{C}$  – beginning of the ageing process for the niobium oxide capacitor Nb02-3.

At the beginning of ageing the electron transport is mostly controlled by the ion drift from anode to cathode. The measured time dependencies of leakage current can be modelled by (1) using an exponent  $n = 1$  during the first 1 hour for a tantalum capacitor and during the first 10 hours for a niobium oxide capacitor. A starting value of DCL at the beginning of ageing is

$I(0) = 10 \mu\text{A}$  for sample Ta1-6 and  $I(0) = 18.9 \mu\text{A}$  for sample Nb02-3. A time constant of ageing process determined from the fit of experimental data is about 3000 s for sample Ta1-6 and about  $3.8 \times 10^4$  s for sample NbO2-3 considering the ion redistribution caused only by drift in the electric field. A time constant for niobium oxide capacitors is higher due to a lower applied electric field and a slightly lower temperature during the ageing process.

### 3.2. Effect of medium-term application of electric field on ion transport in insulating layer

A time dependence of the leakage current of tantalum sample Ta1-4 within the initial 5 hours of ageing is shown in Fig. 6. Here, the experimental data are modelled by (1) using the exponent value  $n = 0.629$ .

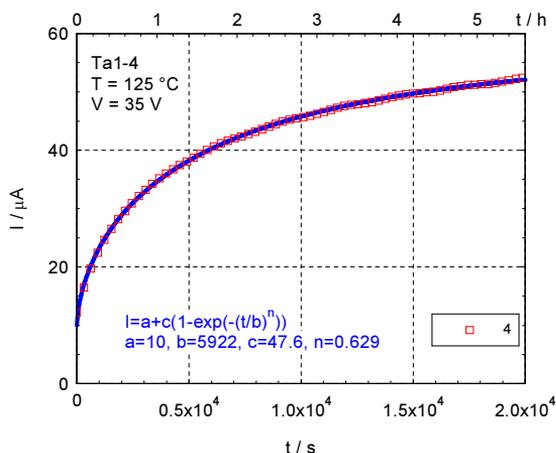


Fig. 6. DCL vs. time characteristics for the tantalum capacitor Ta1-4 for a nominal voltage  $V = 35$  V at temperature  $T = 125^\circ\text{C}$  – initial 5 hours of the ageing process. A model of experimental data includes the ion movement by both drift and diffusion.

The exponent  $n$  values in a range from 0.5 to 1 correspond to the ion movement by both drift and diffusion. The drift transport from anode to cathode is a result of the external electric field. The ion diffusion in the opposite direction appears as a result of the ion concentration gradient formed in the vicinity of cathode interface. However, during medium-term application of the electric field the drift transport mechanism still remains dominant.

During long-term application of the electric field the equilibrium of the ionic drift and the diffusion transport mechanism is achieved.

### 3.3. Effect of long-term application of electric field on ion transport in insulating layer

A DCL vs. time characteristic for tantalum capacitor Ta1-4 when a voltage  $V = 35$  V at temperature  $125^\circ\text{C}$  was applied within a time interval of 80 hours is shown in Fig. 7. Fig. 2 shows the time dependence of leakage current for niobium oxide capacitor NbO2-3 for an applied nominal voltage  $V = 16$  V at temperature  $T = 120^\circ\text{C}$  in a time interval of 400 hours.

In both cases the measured time dependencies of leakage current can be modelled by (1) with an exponent  $n \approx 0.5$ . A starting value of DCL at the beginning of ageing is  $I(0) = 10 \mu\text{A}$  for sample Ta1-4 and  $I(0) = 19 \mu\text{A}$  for sample Nb02-3. A time constant of the ageing process is  $\tau = 2.10 \times 10^4$  s for sample Ta1-4 and  $\tau = 1.97 \times 10^5$  s for sample NbO2-3 considering the ion redistribution by both drift in electric field and the diffusion mechanism. A time constant for

niobium oxide capacitors is about one order of magnitude higher due to a lower applied electric field and a slightly lower temperature during ageing.

The monitored leakage current value increases from 10  $\mu\text{A}$  to 73  $\mu\text{A}$  within a time interval of 80 hours for sample Ta1-4, while the expected DCL value at saturation is 74.46  $\mu\text{A}$ . The monitored leakage current value increases from 19  $\mu\text{A}$  to 88  $\mu\text{A}$  within a time interval of 400 hours for sample NbO2-3, while the expected DCL value at saturation is 90.9  $\mu\text{A}$ .

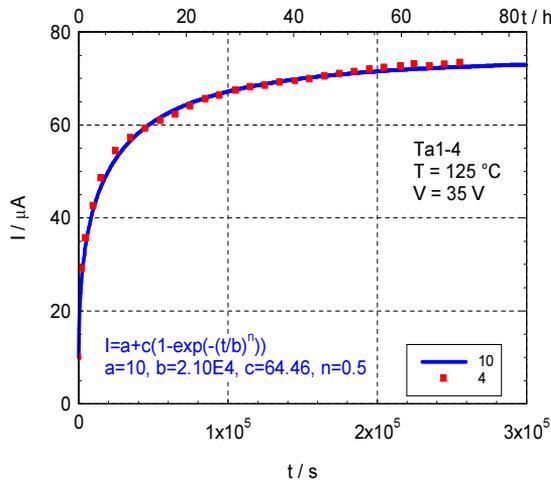


Fig. 7. DCL vs. time characteristics for the tantalum capacitor Ta1-4 for a nominal voltage  $V = 35 \text{ V}$  at temperature  $T = 125^\circ\text{C}$ .

### 3.4. Reversibility of leakage current changes

When the external electric field is lowered or switched off, the ion drift component decreases or drops down to zero. The concentration of positive ions in the vicinity of insulating layer/cathode interface is higher compared with its value in the insulating layer volume. The diffusion of ions due to the concentration gradient becomes the dominant ion transport mechanism in the tantalum or niobium pentoxide layer. The ions – oxygen vacancies – diffuse in the direction from cathode to anode to restore the homogeneous distribution of ions in the pentoxide layer volume. A decrease of the positive ion concentration, in the vicinity of insulating layer/cathode interface, results in an increase of the corresponding potential barrier and consequently in a decrease of the capacitor’s leakage current.

A leakage current vs. time dependence during the recovery process is described by:

$$I(t) = I_0 + I_1 \exp(-(t/\tau)^n), \quad (2)$$

where:  $I_0$  is an expected value of the leakage current for the time at infinity;  $I_1$  is a value of the leakage current lowering due to the ion redistribution in the pentoxide layer and  $\tau$  is a time constant of the recovery process. The exponent is  $n \approx 0.5$  for both short-time and long-time periods. It means that the ion diffusion is the dominant transport mechanism within the recovery process.

Figure 3 shows DCL recovery after long-time application of a nominal voltage  $V = 16 \text{ V}$  at  $120^\circ\text{C}$ . Here, a time dependence of the leakage current is shown for niobium oxide capacitor NbO2-3 for a voltage lowered down to  $V = 2 \text{ V}$  at temperature  $T = 120^\circ\text{C}$ . The monitored leakage current value decreases from 1.8  $\mu\text{A}$  to 0.2  $\mu\text{A}$  within a time interval of about 40 hours. A time constant of the recovery process for niobium oxide sample NbO2-3 is about 6000

seconds. We can see that an equilibrium value  $I_0 = 0.20 \mu\text{A}$  is achieved within the monitored time interval.

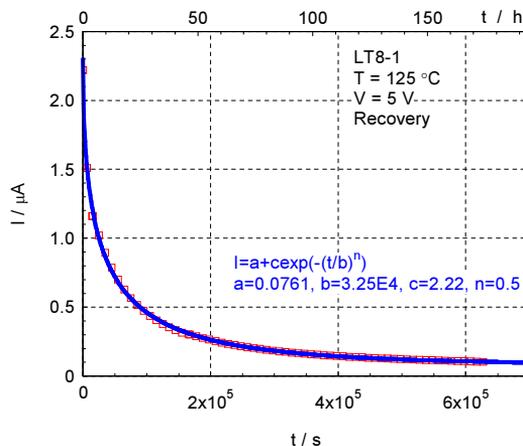


Fig. 8. DCL vs. time characteristics for the tantalum capacitor LT8-1 with an applied voltage  $V = 5 \text{ V}$  at temperature  $T = 125^\circ\text{C}$  during a leakage current recovery.

A similar experiment was performed on the tantalum capacitor LT8-1. A DCL recovery after long-time application of a nominal voltage  $V = 35 \text{ V}$  at  $125^\circ\text{C}$  is shown in Fig. 8. Here, a time dependence of the leakage current is shown for a voltage lowered down to  $V = 5 \text{ V}$  at temperature  $T = 125^\circ\text{C}$ . The monitored leakage current value decreases from  $2.3 \mu\text{A}$  to  $0.1 \mu\text{A}$  within a time interval of about 170 hours. A time constant of the recovery process for tantalum sample LT8-1 is  $3.25 \times 10^4$  seconds. We can see that an equilibrium value  $I_0 = 0.076 \mu\text{A}$  is not achieved within the monitored time interval. The higher time constant determined for the tantalum sample is probably affected by a higher external electric field acting on the sample during the recovery experiment.

#### 4. Conclusions

A method for the qualitative evaluation of ion drift and diffusion processes during ageing of Ta and NbO capacitors at an elevated temperature is presented. Time dependencies of DCL are measured for a rated voltage at temperature  $125^\circ\text{C}$  for Ta capacitors and  $120^\circ\text{C}$  for NbO capacitors. The mechanisms responsible for a DCL increase are determined using the parameters of exponential fit of the measured data.

Oxygen vacancies in a tantalum and niobium pentoxide layer act as positive ions. The homogenous distribution of ions corresponding to the thermodynamic equilibrium is supposed to have occurred before ageing. After application of an electric field the ion distribution is changed due to ability of the ions to move. The concentration of positive ions near cathode increases due to the ion drift in the electric field. An increase of the positive ion concentration in the vicinity of insulator/cathode interface results in an exponential increase of the leakage current. A time constant of the ageing process due to the ion drift decreases with increasing the electric field and an exponent  $n = 1$  for a linear decrease of the potential barrier on the insulating layer/cathode interface due to the ion drift in the electric field only.

Redistribution of positive ions in the insulator volume leads to creation of an ion concentration gradient, which results in a gradual increase of the ion diffusion current in the

direction opposite to that of the ion drift current component. The equilibrium between the two, for a given temperature and electric field, results in saturation of the leakage current value. The exponent  $n$  value decreases with an increase of value ion diffusion current from 1 to 0.5, whereas  $n = 0.5$  when the equilibrium between the ion drift and diffusion is achieved.

DCL changes are fully reversible when the source of DCL increase is only the ion redistribution by drift and diffusion. The samples left at an elevated temperature react to an external electric field drop with a progressive decrease of DCL in time. From the exponential fit of measured DCL time dependence we derived the exponent value  $n \approx 0.5$  for both short-time and long-time periods. It means that the ion diffusion is the dominant transport mechanism within the DCL recovery process. A time constant of the recovery process is directly proportional to the external electric field value.

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