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DIELECTRIC ABSORPTION IN PEDOT:PSS CAPACITORS WITH STAINLESS STEEL YARN ELECTRODES IN TEXTILE SUBSTRATES

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Abstract. *Capacitors have been made on textile substrates. Stainless steel yarns were used as electrodes. The dielectric material was a mixture of PEDOT and PSS. Stainless steel yarns were used as the electrodes. These capacitors are developed to be inserted in wearable textiles, a research field called smart textiles. After charging, a spontaneous discharge was observed lasting for several hours. By connecting a small resistance or even a short circuit for a certain time, it was observed that the voltage starts to rise afterwards when the load resistor or the short circuit was removed. This phenomenon is known as dielectric absorption. It was observed for the PEDOT:PSS cells that the voltage recovery is relatively high as compared to other materials.*

Key words: *dielectric absorption, capacitor, PEDOT:PSS, textile.*

1. INTRODUCTION

Dielectric absorption, also called dielectric relaxation or battery action, is a phenomenon that a capacitor still contains an amount of electric charge even when the electrodes have been short circuited or connected to a resistor for a certain period of time. After removal of the short circuit, the voltage across the capacitor starts to increase. With an ideal capacitor such behaviour is not possible. It turns out that the dielectric layer is able to absorb electrostatic energy and to store it during a limited period of short circuiting. Dielectric absorption has been observed in several dielectric materials such as polymers and insulating oxides. A physical explanation is that the dielectric contains polar molecules which will be oriented along the externally applied electric field according to a Debye relaxation mechanism [1].

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Consequently, these dielectrics are lossy, i.e. that the equivalent electric network models always include both perfect capacitors and resistors [2][3][4].

For most materials the relaxation of the voltage after a short circuit is rather small, typically 0.1 % for a dielectric material like SiO_2 [2]. Generally, the relaxation is in the range 0.01 % - 10 %. Dielectric absorption is a serious problem for electronic circuit design. One has to take into account that some types of capacitors are able to produce an unexpected voltage which may inhibit the normal behaviour of the circuit [3][4].

Our research fits into the field of smart textiles, which includes the integration of electronic components into wearable textiles for different applications like medical surveillance or safety [5]. Conductors and resistors have been integrated in textiles for interconnection, heating elements and electrodes [6][7][8][9][10]. Our research is focused towards capacitors and batteries in textile structures [11][12][13][14]. The purpose is to make a device to store a small amount of electric energy which can also be fully integrated into a textile fabric so that the device is fully wearable. More specifically, a water solution of PEDOT:PSS has been deposited on a textile fabric made from cotton or polyester (PET). More details about the fabrication have been published elsewhere [15]. A photograph of a device is shown in Fig.1

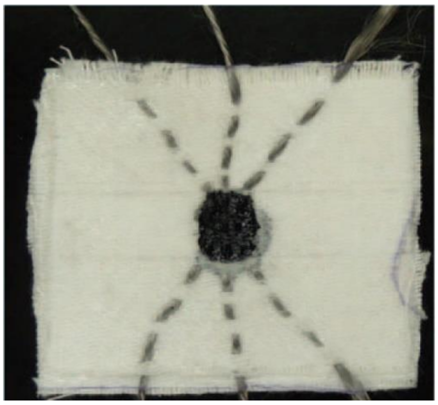

Fig. 1 Photograph of a sample. Dimensions are about 5×5 cm^2. The black area is the deposited PEDOT:PSS. Three stainless steel electrodes are sewed into the substrate.

Electric conducting yarns made from stainless steel fibers were used as electrodes as shown in fig.1 [15]. Three electrodes were inserted. During the measurements either the first and second either the second and third electrode was used. It was observed that these electrodes gave much better results in comparison with Ag electrodes used by other authors [16]. PEDOT:PSS is a mixture of two polymers: PEDOT (3,4ethylenedioxythiophene) and PSS (polystyrenesulphonate). An electron can jump from a PEDOT to a PSS molecule so that ionization occurs: $PEDOT^+$ and PSS^-. These ions give rise to electric conduction in the solid. A discussion about the energy storage possibilities of these devices can be found in [17]. Several experiments have also been carried out in order to understand the physical basics of the conducting mechanism [18][19][20][21].

An intensive search on the web of science using the topics "PEDOT" and "dielectric-absorption" or "dielectric relaxation" did not reveal any papers. Hence, to the best of our knowledge no article could be found related to dielectric absorption in PEDOT:PSS layers.

2. Experimental Measurements

For the experimental measurements the circuit shown in Fig. 2 has been used.

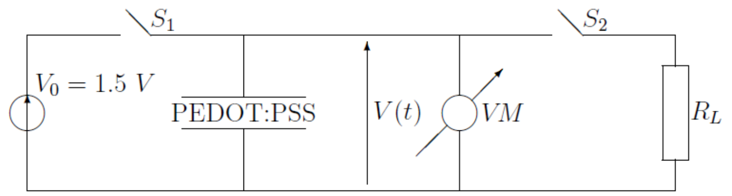

Fig. 2 Schematic layout of the measuring circuit

The PEDOT:PSS capacitor has been charged at a constant voltage V_0 = 1.5 V for a sufficiently long time, around 2 hours by closing the switch S_1. The switch S_1 was opened and the voltage V(t) was recorded as a function of time with the voltage meter VM. The input resistance of VM was about 10 MΩ so that its current consumption was always below 150 nA. Fig.3a shows the decaying voltage V(t) with the label "initial". One remarks a steep decay in the beginning followed by a long period with a very slow voltage decay [15].

After several other measurements, exactly the same experiment was repeated again and plotted in fig.3a with the label "final". It turns out that this curve has a similar shape but the voltage values are higher. This result agrees with reliability experiments carried out on similar samples [22]. It was found that the PEDOT:PSS capacitors are improving during the first 5 to 7 charging/discharging cycles. If more charging/discharging cycles have been applied, the capacitances start to get less efficient [23]. The conclusion is that one cannot assign one single discharge curve to a given device.

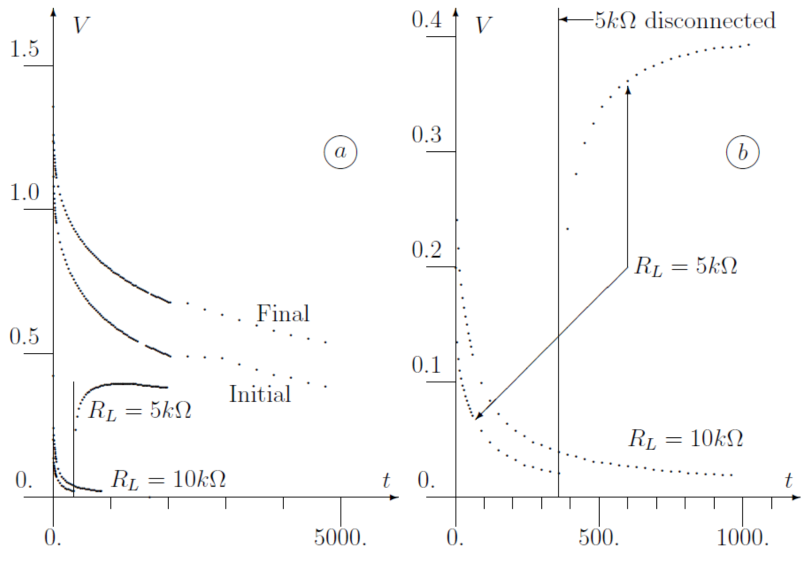

Fig. 3 Voltage decay curves of PEDOT:PSS cells, with and without resistive load. (a) general view (b) detailed view of the dielectric absorption.

A similar experiment was carried out with a R_L = 10 kΩ load resistor connected to the PEDOT:PSS capacitor. The curve is shown in fig.3a along with a more detailed view in fig.3b. As expected, the discharging voltage is much lower if one compares with the "initial" or the "final" curve. For the load R_L = 5 kΩ , the discharging curve is a little bit below the R_L = 10 kΩ curve. After 360 seconds discharging, the R_L = 5 kΩ was disconnected by opening the switch S_2. As can be seen in fig.3b, the output voltage started to increase considerably. The output voltage reached almost 80 % of the values of the "initial" curve. Remark that a load resistor of only R_L = 5 kΩ is much smaller than the internal resistance of the PEDOT:PSS cells which has been measured to be around 300 kΩ. These results are quite different from the results obtained with other dielectric materials, where the recovery is at most 15 % after a short circuiting of only 10 seconds. Our result is totally different: even after a load period of 360 seconds, the voltage recovery is almost 80 % of the voltage which would have been obtained without any load resistor.

In a second series of experiments, the PEDOT:PSS cell was short circuited (R_L = 0 Ω) for a certain period by closing the switch S_2 (fig.2). The results are shown in fig.4.

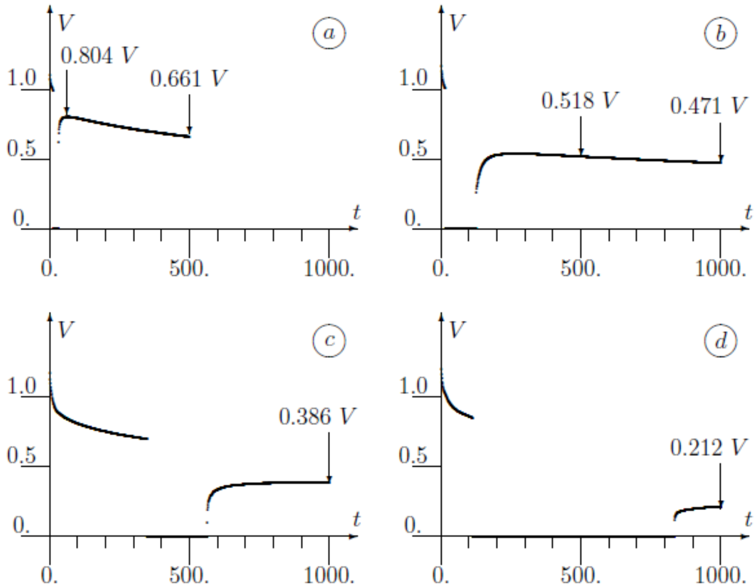

Fig. 4 Transient voltages measured with short circuit periods of (a) 19 s, (b) 111 s, (c) 215 s and (d) 721 s

Each time, the PEDOT:PSS cells were charged to 1.5 V during two hours. After a certain discharge time when only the voltage meter was connected (fig.2), the short circuit was applied intentionally. Four tests are shown in fig.4 done with the following short circuiting periods: (a) 19 s, (b) 111 s, (c) 215 s and (d) 721 s. It is remarkable to note that even a long short circuit time of 721 s, which is about 12 minutes, was not enough to completely discharge the PEDOT:PSS cell. Moreover, these long short circuit times did not have any negative influence on the cells. The cells could be recharged and discharged again without any problem.

As already mentioned, the PEDOT:PSS cells always show a voltage decay after charging, even when no load resistor was connected. Experiments carried out with a load resistor in the range of $R_L > 100\ k\Omega$ did not provide clear results. The difference between the discharging curves with $R_L > 100\ k\Omega$ and $R_L = \infty$ were hardly visible. Therefore our experiments have been done with lower values: $R_L = 10\ k\Omega$, $R_L = 5\ k\Omega$ and even $R_L = 0$.

The PEDOT:PSS cells are not perfect capacitors. The self-discharge is clearly visible from the results shown in fig.3. It is not so obvious to evaluate the voltage recovery because the output voltage even decays without any short circuiting. Hence, the initial voltage (1.5 V in our experiments) will be used as the reference one. In fig.4 some numerical values for the voltages are shown. If we consider the value of 0.2121 V obtained after a short circuiting period of 721 s (fig.4d), the voltage recovery is found to be 0.212/1.5 = 14 %. For the shorter circuit period of 19 s, one gets 0.804/1.5 = 53.6 % (fig.4a). From the literature voltage recoveries are in the range 0.1 - 10 %. With our experiments we have shown that much higher values can be obtained using PEDOT:PSS cells. As far to our knowledge, no voltage recovery values higher than 10 % have been reported in the literature.

3. Discussion

A frequently used model for dielectric relaxation is a parallel connection of several *RC* networks. When such a circuit is short circuited, all the individual capacitors can only be discharged through the resistors. This explains why still a charge will remain after a certain short circuit period. Such a network can also be represented by the following complex dielectric constant, known as the Cole-Cole model [24]:

$$\varepsilon = \varepsilon_h + \frac{\varepsilon_l - \varepsilon_h}{1 + (j\omega\tau_0)^\alpha} \tag{1}$$

which represents a lossy dielectric material, because it has a non-zero imaginary part. It should be noted that this model was used for the first time a long time ago to explain the dielectric behaviour of electrolytes [19]. Later on, this model was described in other papers and textbooks as well for several dielectric materials [25][26][27]. This might be an argument that the electric properties of the PEDOT:PSS are also due to mobile ions. The PEDOT:PSS being a mixture of two polymers, PEDOT and PSS, or if charged $PEDOT^+$ and PSS^-, it is clear that ionic conduction takes place. The fact that we are dealing with polymers, i.e. long molecules, explains the large time constants observed in the experiments.

The parameter α in (1) is related to the variance of the time constant distribution [25]. If $\alpha = 1$, only one time constant τ_0 occurs. For $0 < \alpha < 1$ a distribution of time constants centered around τ_0 will be observed. The smaller the value of α, the wider the distribution will be.

The dielectric relaxation observed in the PEDOT:PSS cells, can be explained by the fact that even a short circuiting for a relatively long period is not enough to provide enough time for all the $PEDOT^+$ and PSS^- ions to move back to their equilibrium position, which corresponds to charge neutrality and hence zero output voltage.

4. CONCLUSION

Electroconductive cells with stainless steel yarns as the electrodes and PEDOT:PSS as the dielectric material have been made on textile substrates. It was found that very high values for the voltage recovery after a short circuit could be observed. This phenomenon known as dielectric absorption, has been detected in several materials but the voltage recovery never exceeded 10 %. In the PEDOT:PSS much higher voltage recoveries have been measured.

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