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RELIABILITY TESTING OF PEDOT:PSS CAPACITORS INTEGRATED INTO TEXTILE FABRICS

BADANIE NIEZAWODNOŚCI KONDENSATORÓW PEDOT: PSS WBUDOWANYCH W TKANINY

Textile-based capacitors have been made from polyethylene dioxythiophene, polystyrene sulphonate (PEDOT:PSS) as the electrolyte and pure stainless steel filament yarns as the electrodes. The capacitor is well integrated into the textile structure, small in size and of light weight. Although they experience a self-discharge, the reliability of the PEDOT:PSS capacitors has been investigated by repeating up to 14 cycles of charging and discharging. Initially, the voltage output turns out to be higher with increasing number of cycles. However, after the fifth cycle, degradation of the cell starts occurring and a decreasing behaviour in the voltage output is observed. One can roughly say that these capacitors could be used up to 10–15 cycles.

Keywords: *capacitors, conductive yarns, PEDOT:PSS, voltage discharge, cycling.*

Kondensatory tekstylne wytwarza się z mieszaniny poli(3,4-dioksyetylenotiofenu) z polistyrenem sulfonowanym (PEDOT: PSS), pełniącej rolę elektrolitu oraz włókien ciągłych z czystej stali nierdzewnej, pełniących funkcję elektrod. Kondensatory tego typu są dobrze zintegrowane ze strukturą tkaniny, są lekkie i mają niewielkie rozmiary. Chociaż kondensatory PEDOT:PSS ulegają samorozładowaniu, przeprowadzono badania ich niezawodności powtarzając 14 cykli ładowania i rozładowywania Początkowo napięcie wyjściowe zwiększało się wraz ze wzrostem liczby cykli. Jednakże po piątym cyklu, dochodziło do degradacji ogniwa i obserwowano zmniejszanie się napięcia wyjściowego. Można orientacyjnie powiedzieć, że omawiane kondensatory nadają się do użytku przez maksymalnie 10–15 cykli.

Słowa kluczowe: *przędze przewodzące, PEDOT: PSS, rozładowanie napięcia, próba cykliczna.*

1. Introduction

In recent years a lot of effort is put into integrating electronic components into textiles, a new discipline called smart textile design. The applications of smart textile systems can be found in many fields: protective clothing, medical applications and sports clothing. An overview can be found in literature [2, 27, 29, 30].

Flexibility of the electronic components is desirable with these recent developments and can be achieved from organic and inorganic materials in smaller forms like microstructures or nanostructures [23].

If electronics have to be integrated into a textile garment, one is dealing with all possible electronic components like conductors, resistors, capacitors, transistors and displays. Electric conductors can be made by inserting electrically conducting yarns into a fabric [9], or by suitable coating of conductive compounds on a non-conducting yarn [6, 21, 24, 25, 26]. These conductive yarns can be made from materials like stainless steel yarns or hybrids of conducting and non-conducting yarns. Screen printing has also been successfully used to deposit conducting layers on a fabric [11]. However, textile being a flexible and porous material, one must pay special attention to the mechanical properties and their influence on the electric characteristics [22, 26]. Besides electric conductors and resistors, other components like transistors, capacitors or displays have been integrated into a textile material [3, 15, 17, 28].

It must be clearly pointed out that full integration into a fabric means that the electrical component is only made out of textile material and/or polymers embedded into the textile during the production process and not added as detachable in the final assembly of the garment. As a consequence, these components cannot be removed. Other applications involve electronic components which are attached to a fabric. Garments equipped with LED lights are a typical example of these. Maintenance and reliability of these devices is very important in their proper functioning and life span. In this respect, various experiments on reliability are conducted on the developed capacitor to determine these aspects. Care and washability are also essential if at all the device is fully compatible with the textile. Influence of several washing cycles on the electrical performance of electronic textiles like sensors and antennas have been performed by a number of researchers.

A flexible and lightweight energy storage device which is either a capacitor or a battery is described in the papers [4, 5, 7, 8, 12, 16, 18, 19]. All of them involve a textile or a textile material in either fibrous form, or in the textile structure.

In this paper, we focus on the reliability and stability of an electric energy storage device – capacitor intended to supply power to the integrated electronic components and circuits. The type I capacitor (both the anode and the cathode are made of the same material) we are investigating in this contribution uses the PEDOT:PSS polymer as the “dielectric” or “electrolyte” material between the two electrodes, which are made from pure stainless steel filament yarns sewn on a textile substrate. A first report of such a device was published by Bhattacharya [1]. Their device used silver coated polybenzoxazole (PBO) yarns as the electrodes. However, the performance of the stainless steel filament yarns is shown to be better than the silver coated yarn electrodes, as described in our article [20].

2. Sample preparation

A three layered laminate of textile substrate (woven cotton/polyester) with the same specifications as used in our paper [20] was adopted. The electrodes were pure stainless steel filament yarns from Bekinox® Bekaert. The electrodes were sewn at a close distance to each other into the fabric substrate. Therefore, there is no relative movement between the parts of the capacitor i.e the solid electrolyte and the electrodes, which may interfere with functionality. The upper surface of the fabric (except for a left out region of 10 mm by 6 mm including part of the electrodes) was made hydrophobic by using a thermoplastic polyurethane (TPU) layer from SunChemical. The TPU prevented the PEDOT:PSS from spreading too much in the fabric. Water based PEDOT:PSS from Ossila (of PEDOT:PSS ratio of 1:6, approximately) was coated in layers on the left out region. The definition of this ratio of PEDOT:PSS is important, because the product exists in different component ratios from different companies with different conductivities. The performances of the PEDOT:PSS brands as electrolyte for our capacitor are different from each other, based on the aspect ratio and may be from any other additives within the polymer solution.

A schematic view of the capacitor design is shown in Figure 1.

The PEDOT:PSS was applied on the foreseen area with a syringe while the fabric was in the oven. Each layer of PEDOT:PSS was left to dry and cure in the oven for 15 minutes at temperatures of 90-100^{0}C, before applying the next layer.

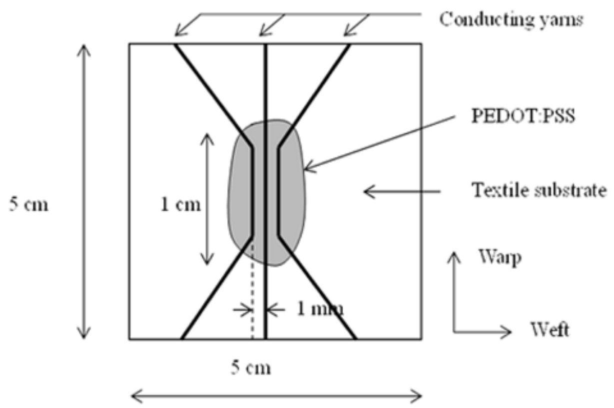

Fig. 1. Cross section view of the device

3. Material investigation

PEDOT:PSS is a conjugate polymer, namely polyethylene dioxythiophene (PEDOT) and a polystyrene sulphonate (PSS). The formulae for both polymers and how they interact are shown in Figure 2. The PEDOT molecule can lose one or more electrons whereas the PSS receives those electrons. The PEDOT has several S^+ (positive) ions whereas the PSS molecule will have then several $SO_3{}^-$ (negative) ions as shown in Figure 2. The material behaves then like a solid electrolyte. Under influence of an externally applied electrical field the charged PEDOT and PSS polymer chains will move in opposite directions so that the material will be electrically polarised and the capacitor becomes charged. After removal of the applied electrical field the ions will move back to their original position so that the material loses its polarisation.

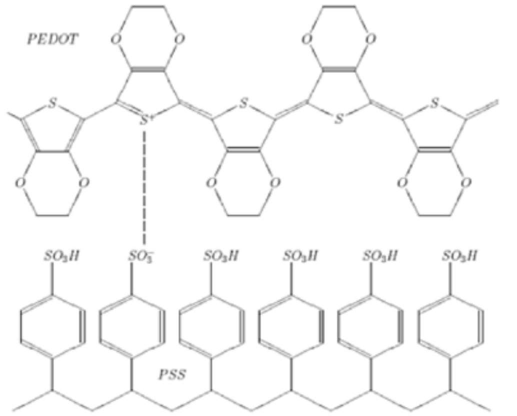

Fig. 2. Schematic of the chemical structure of PEDOT:PSS showing the ion sites

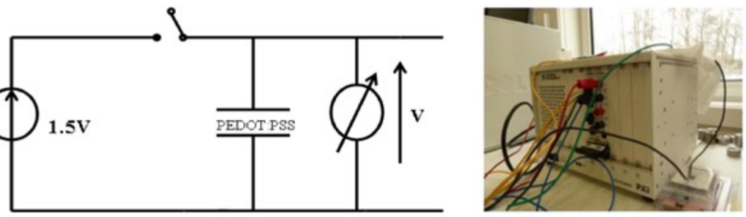

Fig. 3. Charge-discharge circuit and the NI PXI

4. Experimental electrical measurements & discussion

First of all the fabricated PEDOT:PSS textile capacitor was charged with a constant voltage of 1.5 V for 2 hours with the circuit shown schematically in Figure 3. After opening the switch the self-discharge of the PEDOT:PSS capacitor was recorded with a voltage meter having a high input resistance of 10MΩ. Since each measurement lasts for several hours, the apparatus NI PXI from National Instruments was used to carry out the operations automatically. The NI PXI 1033 is a chassis equipped with several voltage generators, a digital voltage meter and a computer interface. For the switch, a relay was used, which was controlled by one of the voltage generators. A special software package running on LabVIEW was written to carry out all the measurements automatically, including the transfer of data to an external computer.

After the charging time of 2 hours, the switch was opened and the first observed discharge characteristic was measured. The PEDOT:PSS capacitor was not connected to any voltage for at least 10 hours before the next cycle was started. A day later, the second charging cycle of 2 hours was applied followed by measuring the second discharge char-

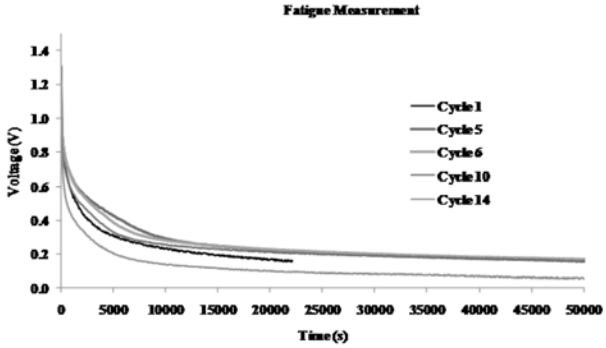

Fig. 4. Fatigue test measurements

acteristic. This procedure was repeated up to 14 times. The results are shown in Figure 4.

The output voltages have been drawn as functions of time up to 50,000 s (about 14 hours). One remarks that during the first 5 to 6 cycles the output voltage is increasing, which means that the device is improving per each subsequent cycle. This could be due to the residual charge in the device from a subsequent previous charging. But when more cycles are applied, the device seems to get worse. This could also be attributed to the onset of the degradation of the electrolyte since the experiments are conducted in the ambient environment of normal humidity and temperature, this is known to have an influence on PEDOT:PSS activity and degradation.

A closer look at the characteristic of one single graph in Figure 5 reveals the following: an immediate observation is that the voltage drops rapidly in the beginning. But after some time (100 s) the voltage tends to be more stable around a value of 0.4 V for a rather long time (up to several hours).

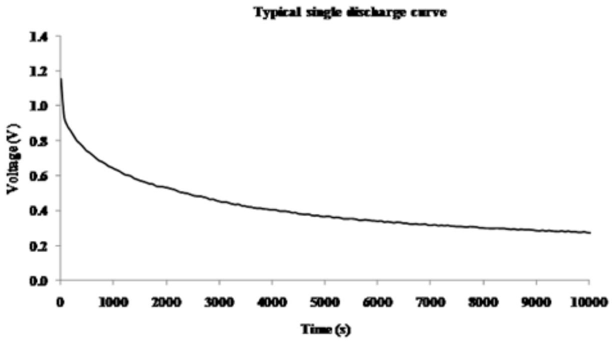

Fig. 5. Discharge characteristic of single cycle

If one takes into account that a voltage of 0.4 V is rather small as compared to the initial charging voltage of 1.5 V, then the efficiency of our fabricated device is rather low. Also the number of charging/discharging cycles is rather limited. But on the other hand, we are dealing with a device which is fully integrated into a textile fabric. This is the price one has to pay to have a completely integrated component.

The main purpose of this research is to investigate the reliability of the PEDOT:PSS textile capacitors. Other authors reported that a similar device with silver coated PBO yarn electrodes could be charged/discharged up to 4 times [1]. Accordingly our results presented in Figure 4 show that devices equipped with stainless steel electrodes can be charged and discharged up to 14 times. At least one day elapsed between each two cycles. Also Figure 4 clearly shows the degradation of the cells after 5 to 6 cycles. Up to 5 cycles the output voltage is increasing but for more cycles the decreasing behaviour is clearly observed. After 5 charging/discharging cycles, the devices started to get lower output voltages. A clearer view of this phenomenon is shown in Figure 6, where the recorded output voltage is displayed as a function of the number of cycles N at several times after opening the switch *S* (t = 3000 s, t = 6000 s, t = 12000 s, t = 18000 s and t = 36000 s). Remark that t = 36000 s corresponds to 10 hours of discharging time.

One can roughly say that these capacitors can be used up to 10-15 charging/discharging cycles. This number is rather small and one might have the impression that these components are inapplicable in practice. However, for wearable textiles, electric components with a limited reliability have proved their applicability [10]. Besides this, the study of PEDOT:PSS capacitors integrated into fabrics started very recently, therefore this topic is still in the initial phase of fundamental research.

The voltage measurements were done with a digital instrument (National instrument) with a 3 digit accuracy. From Figure 6, one might have the wrong impression that the measurements contain large errors because the curves are far from being smooth. This phenomena is entirely due to the (still unknown) physical mechanisms inside the PEDOT:PSS material.

Taking into account that the discharge curves were recorded with a device having a 10 MΩ input impedance, the current could be easily evaluated. A numerical integration gave the total charge. The ratio of this charge with respect to the applied voltage yields a capacitance value around 18000μF. By adding resistors in parallel, the internal series resistance was measured to be 300 kΩ.

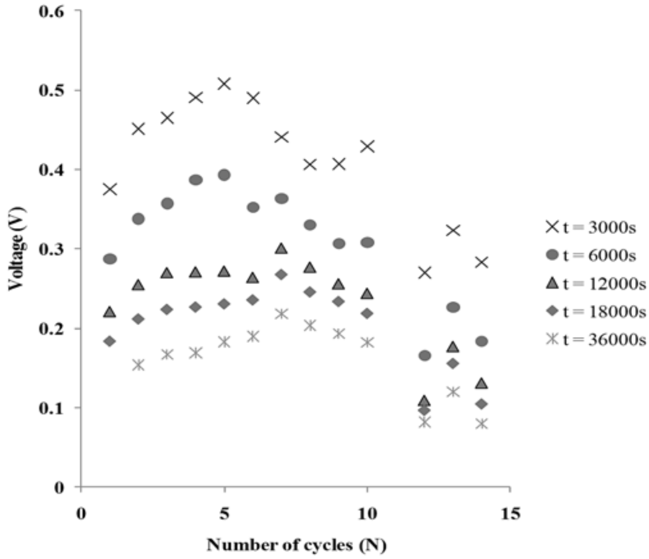

Fig. 6. Graph showing discharge behaviour of the capacitors at specific times for different number of cycles (N)

A typical problem related to PEDOT:PSS is that the electric conduction mechanism is still not well understood. As some authors claim it is still under debate [13, 20] or in other words a lot of research has to be done to fully understand the fundamental phenomena happening in this material. It was mentioned before that ions are responsible as shown in Figure 1. The charge and discharge is expected to involve cation transport [14], where migration is expected to occur. But some authors found that by using silver coated yarn electrodes electrolytic phenomena occur i.e deposition of silver ion that moves from the anode electrode to the cathode, this observation was done using SEM [1].

We observed that with silver coated yarn electrodes the output voltage was even lower (up to 50 %) than with the stainless steel contacts [20]. All these experiments have proved that other phenomena like electrolysis cannot be excluded. Hence, one can start the discussion whether we are dealing with a capacitor or a battery or a mixture of these. Obviously, when the conduction mechanism will be better understood, it will be easier to search for devices with better characteristics and performance.

5. Conclusion

A capacitor well integrated into the textile structure that is small and light weight has been made. The device shows some robustness and can withstand up to 15 cycles of each 7200 seconds charging at 1.5V. However, the efficiency of energy storage is still very low due to the self-discharge. One can roughly say that these capacitors could be used up to 10–15 cycles, with no significant difference in the output energy level for the first 10 cycles. This shows the limited level of reliability of the capacitor. Consequently, the decay of the discharge characteristic has to be taken into account during the design phase of the application if the capacitor will be used for a more efficient performance. More fundamental research will still be necessary in the future. The self-discharge of the capacitors has to be improved.

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