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STUDY ON CAPACITIVE BEHAVIOUR OF PEDOT:PSS BASED ENERGY STORAGE DEVICE BY MODELING THE CHARGE-DISCHARGE PROFILE

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ABSTRACT

We have fabricated a functional facile textile energy storage device made of a pair of stainless steel conductive yarns coated with poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) film. The devices having *d* 1, 2, and 3 mm with different sources of polymer were put to a series of charge-discharge measurements to determine each capacitive behaviour. The charge-discharge profiles showed disagreement with theoretical calculation for a capacitor made of two parallel wires. Capacitance was found to decrease with distance between yarn electrodes. PEDOT:PSS from two different sources showed different behaviour, indicating the role of the polymer in the energy storage mechanism.

Key Words: PEDOT:PSS; textile energy storage device; capacitance; two-parallel yarn supercapacitor

1. INTRODUCTION

With the emergence of smart textiles, the need for energy storage devices has considerably grown, because many of the proposed textile systems require energy to operate. A simple, lightweight, flexible, and low-cost textile energy storage device has been developed in our laboratory [1]. The device was based on Bhattacharya *et al*. research [2] and assembled by coating two parallel stainless steel conductive yarns attached directly to a polyester-cotton fabric with poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) film. An extensive charge-discharge experiments have been done in our previous works to test and characterize the performance of the developed cell [1, 3, 4]. It was found that storage of charge depends on the applied voltage and charging time. Charging with higher voltage gave result to higher level of residual charge in the device and lower decaying rate when discharged. It was also found that the charge decayed faster with lower output voltage when connected with lower load resistor. The longer the charging time the slower the voltage decay and the higher the output voltage in the device.

From the beginning of our work, it was already suggested that dielectric polarization of PEDOT:PSS stimulated by the electric field applied through the charging process was the reason for charge storage capability of our developed device [1, 3]. On the other hand, however, Bhattachraya *et al*. [2] had indicated that their developed device worked according to the principle of a battery in which chemical interaction occurred at the Ag/PEDOT:PSS interface. As the stainless steel electrode yarn we have been using is not chemically inert and covered by very thin layer of chrome oxide (Cr_2O_3) [1, 4], it is plausible that similar chemical interaction occurred at the interface of the polymer and electrode. This and results from our previous works [4, 5] suggest the possibility of having a pseudo-capacitor in which both double layer capacitance and surface redox reaction exist in the operation of the device.

So far, we have come up with different strategies and designs of cell in order to improve its performance and also to understand its behavior [4]. The original design of the device consisted of three conductive yarns that were stitched in parallel at a distance of 1 mm to each other. In search for a better understanding of the cell behavior and ultimately its mechanisms we modified the device by removing one conductive yarn making it resembled two-wire supercapacitor with electroactive polymer PEDOT:PSS surrounding and in between the electrodes (Figure 1). In their investigation on the effect of yarn diameter to the discharge characteristics of the developed device, Odhiambo *et al*. [1] used a similar two-dimensional geometry of two-wire capacitor as an approach to obtain the analytical solution for potential distribution and electric field surrounding the electrodes. However, they did not go with further analysis for its capacitance. The new approach provides a different perspective for our study of the device and better understanding on the effect of geometry of device design to its performance.

2. MATERIALS AND METHOD

2.1 Materials

Six types of device were prepared differing in their distance between electrodes (1, 2, and 3 mm), each having two different types of PEDOT:PSS. Basic configuration of the device is shown in Figure 1 below.

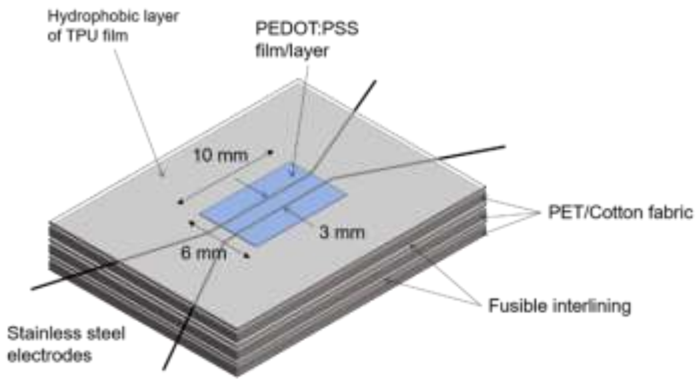

Figure 1. Design of the textile based energy storage device with conducting polymer PEDOT:PSS.

The device was fabricated on a three-layered of 5x5 cm^2 woven polyester-cotton fabrics, glued to each other with a piece of hot melt interlining adhesive. Two strands of pure stainless steel (Bekintex) conductive yarn were initially stitched to the upper layer of the textile fabric with particular distance between electrodes as mentioned above. The cell area of 6 x 10 mm^2 was created by masking the non-cell area with thermoplastic polyurethane (Epurex Film Company). Two different commercial brands of PEDOT: PSS polymer, i.e. M121 PEDOT: PSS A1 4083 (Ossila) and Orgacon ICP 1050 (Aldrich Chemistry) were used as an electro-active conducting polymer. The polymer was drop-coated seven times with drying at 90 ^{o}C between each drop to create a successive layers of polymer film which covered the two conductive yarns.

2.1 Method

Measurement and data acquisition of charge-discharge was performed by using a microcontroller "Arduino Uno" programmed specifically for this particular purpose. The set up and the program was developed in the Laboratory of Mechatronics at Politeknik STTT Bandung. Prior to the measurement of the device, the resulting instrument was tested and validated by measuring regular capacitor of known capacitance. Figure 2 shows the circuitry of charging-discharging measurement. The charging of the device (switch was at position A) was done by supplying a DC voltage (*Vs*) at 5 V with an external resistance (*R1*) of 33 kΩ. Discharging was achieved by switching to position C and the same external resistance of 33 kΩ (*R2*). During the process, the output voltage was recorded automatically by the program. The charging process was stopped after 1500 second when the voltage number reached its maximum value and remained stable at that level.

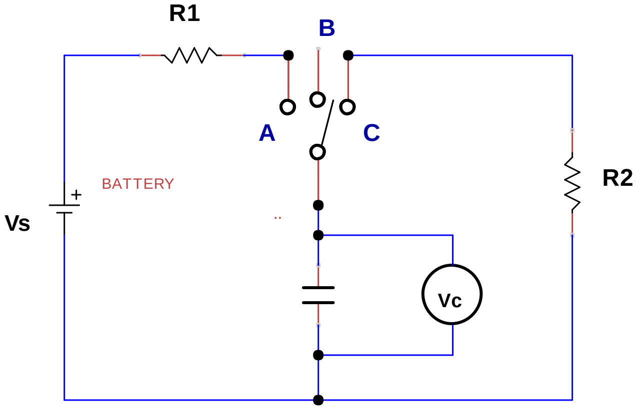

Figure 2. Schematic diagram of charge-discharge measurements set up

The resulting data was evaluated and compared with the model developed based on the approximation of the capacitance and charge-discharge behaviour of the capacitor.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 3 presents the profile of voltage accumulation and decay of devices having "Ossila" PEDOT : PSS with varying distances (1, 2, and 3 mm) during the charge-discharge experiments. From the graph, it can be seen that all devices could not reach the level of the given input charging voltage (5 V). The output voltage that can be attained was only up to about 2.2–2.7 V, around half of the input voltage. This is not surprising as we have the same observation from our previous works [4]. As expected from our understanding on the basic working principles of capacitor in general, the distance between electrodes has an effect to the behavior of the device. The further the distance, the higher the value of output voltage and thus more charge that was stored in the device. However, this is followed by faster decay and lower voltage. In other words, the gap between maximum and minimum value of charge stored is higher with device having electrode distance *d* 3 mm. On the other hand, device with shorter distance attained a lower voltage upon charging, but retained a higher voltage value when discharged. It indicates that the three devices have different capacity in storing energy. Device with larger electrode distance (e.g. *d* = 3 mm) presumably must have lower energy density compared with that of shorter electrode distance.

Results from devices with "Orgacon" polymer is not presented in this paper because from the measurement those devices could hardly store charge during the charging as shown by the voltage value close to zero. These results confirmed the previous finding by Odhiambo [6] who compared discharge profiles between three different brands of commercial PEDOT:PSS which included Ossila and Orgacon.

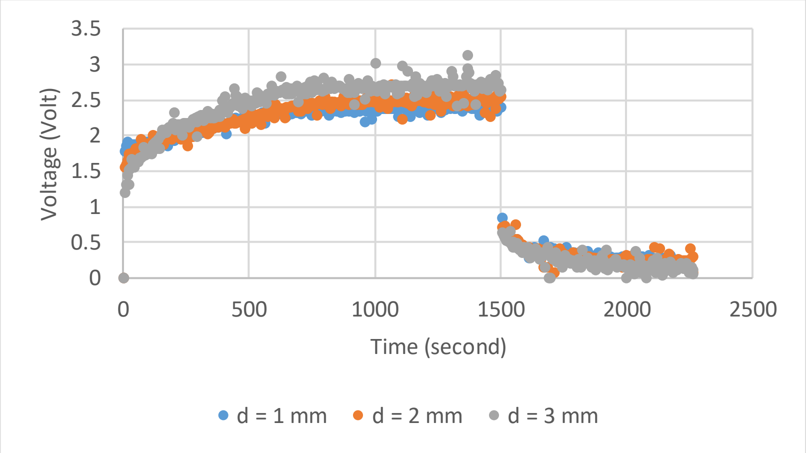

Figure 3. Voltage accummulation and decay during charge-discharge experiments with Ossila, where *d* is the varying distance between electrodes.

Theoretically, the effect of electrode distance to the energy storage ability of the device can be predicted by a mathematical model that represents the geometry of the device design and configuration. A capacitor can be in the form of parallel-plate with dielectric material in between, or cylindrical with concentric parallel-plate, and still other two parallel wires just like we have for our device. The capacitance of our device can thus be approximated based on the model of two-wire capacitor (Equation 1). According to this model, the conductive yarns in the device were assumed to be two metallic cylindrical volumes each having radius a_1 and a_2. This simplification was necessary and allowed us to make a less complicated analytical calculation because yarn is not solid but a cylindrical porous material composed of fibers. The PEDOT:PSS material, having permittivity ε, was assumed to have filled in the entire space between the two cylinders and surrounding them.

$$C = \frac{2\pi\varepsilon l}{ln\left[\frac{(d-a_1)(d-a_2)}{a_1 a_2}\right]} \quad (1)$$

For $a_1 = a_2$ and $d >> a_1, a_2$ we have

$$C = \frac{2\pi\varepsilon l}{ln\left[\frac{d^2}{a_1 a_2}\right]} = \frac{\pi\varepsilon l}{ln\left(\frac{d}{a}\right)} \quad (2)$$

where l is the length of part of the two conductive yarns which are covered with PEDOT:PSS polymer having permittivity ε, and d is the distance of separation between the yarn electrodes. From Equation (2) it can be seen that capacitance of the device is governed by the length of the yarn in the cell area of the device, the geometric mean diameter of the two conductive yarns, and the distance between them. Provided that all other information is known we can calculate the capacitance of the device. We can also predict that the capacitance decreases exponentially with distance between the two yarn electrodes just as the standard parallel plate capacitor does in linear manner.

The stainless steel conductive yarn used in this paper is the same as that used by Odhiambo [1] who had done measurement on the yarn and found an apparent diameter *a* = 762 ± 61 µm. According to the design parameter of the device, the length of yarn in the cell area which is in contact with PEDOT:PSS is *l* = 6 cm. Unfortunately, despite an extensive literature search the value of PEDOT:PSS permittivity or its dielectric constant is not known up to the writing of this paper (e.g. refs. [7–11]). Thus, for each of the devices we have the following:

$$C_{d=1} = \frac{\pi\varepsilon l}{ln\left(\frac{d}{a}\right)} = \frac{\pi(\varepsilon)(6\times10^{-2})}{ln\left(\frac{10^{-3}\times10^{6}}{762}\right)} = 0.6935\varepsilon \text{ F/m}$$

$$C_{d=2} = \frac{\pi\varepsilon l}{ln\left(\frac{d}{a}\right)} = \frac{\pi(\varepsilon)(6\times10^{-2})}{ln\left(\frac{2\times10^{-3}\times10^{6}}{762}\right)} = 0.1953\varepsilon \text{ F/m}$$

$$C_{d=3} = \frac{\pi\varepsilon l}{ln\left(\frac{d}{a}\right)} = \frac{\pi(\varepsilon)(6\times10^{-2})}{ln\left(\frac{3\times10^{-3}\times10^{6}}{762}\right)} = 0.1375\varepsilon \text{ F/m}$$

The above calculation confirms further that capacitance of the device decreases with electrode distance.

Assuming that the device being studied in this paper behaves according to the classic capacitor, capacitance can be determined empirically from charge-discharge curve by fitting the data with mathematical model for capacitor. The voltage of a capacitor as a function of time during charging and discharging can be determined by equations (3) and (4) respectively.

$$V(t) = V_C = V_0\left(1 - e^{-\frac{t}{R_1C}}\right) \tag{3}$$

$$V_C = V(t) = V_0.e^{-\frac{t}{R_2C}} \tag{4}$$

Fitting the data by using Equation (3) and (4) yields the value of *RC*. Because *R* is known we can then determine the value of capacitance *C* of the device.

Figure 4 shows the curve fitting of charge-discharge data from device with *d* = 3 mm to represent the three devices. It can be seen that the data do not fit to the usual exponential shape of capacitor according to Equation (3) and (4) as shown by the continuous line “model 1” in Figure 4. It must be noted, however, that V_0 in this particular case is not the input voltage applied to the device during charging. It is the maximum output voltage attained by the device or the initial voltage recorded by the measuring instrument at the beginning of discharge. The observation applies for the three devices with different electrode distance *d*. The dashed line “model 2” which seems to fit better was obtained by using a logistic model with the following form:

$$V(t) = \frac{a}{(1+b.e^{-ct})} \tag{5}$$

$$V(t) = \frac{a}{(1-b.e^{-ct})} \tag{6}$$

for charging and discharging respectively, where *a* and *b* are unknown constants, and *c* is presumably equivalent to *RC* in Equation (3) and (4). We do not know at this point if the model has any physical meaning that explains the working principles of our device, but it is clear from Figure 4 that the device did not follow the charge-discharge profile of a standard capacitor. Therefore, the device did not work like a standard capacitor and alternative model is required. The model shown by Equation (5) and (6) might be one of the possibilities.

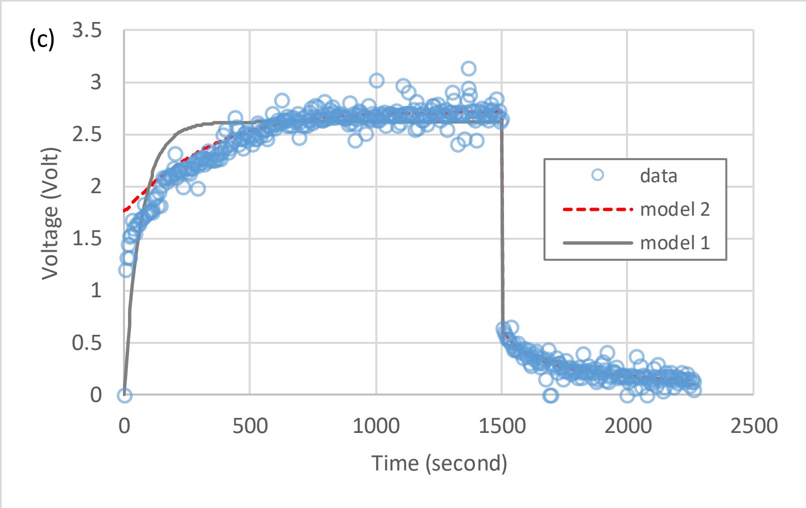

Figure 4. Curve fitting of charge-discharge data from different devices with varying electrode distance *d* = 3 mm.

4. CONCLUSION

Capacitive behaviour of textile-based energy storage devices consisting of two strands of stainless steel electrode yarns of different distance covered with electroactive polymer PEDOT:PSS of different sources has been studied. Devices with different distance between electrodes showed different capacity in storing energy. Compared with devices having *d* 1 and 2 mm, device with *d* 3 mm had higher gap between maximum and minimum value of charge accumulated. Unknowing the actual permittivity value of PEDOT:PSS with *d* 1, 2, and 3 mm, calculation of capacitance of each device was obtained to be 0.6935$\mathcal{E}$, 0.1953$\mathcal{E}$, and 0.1375$\mathcal{E}$ F/m respectively. Compared to Orgacon, Ossila was found to work more effectively for this application. According to our modeling and curve fitting, the charge-discharge profiles of all devices did not work like a standard capacitor as they do not fit its usual exponential shape. Alternative model for characteristics of this energy storage device is required for further analysis of its specific behaviour.

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