33rd Annual International Conference of the IEEE EMBS
Boston, Massachusetts USA, August 30 - September 3, 2011

Printed Organic Conductive Polymers Thermocouples in Textile and Smart Clothing Applications

Trine M. Seeberg, Arne Røyset, Susannah Jahren and Frode Strisland

***Abstract*— This work reports on an experimental investigation of the potential of using selected commercially available organic conductive polymers as active ingredients in thermocouples printed on textiles. Poly(3,4-ethylenedioxythiophene):poly(4styrenesulfonate) (PEDOT:PSS) and polyaniline (PANI) were screen printed onto woven cotton textile. The influence of multiple thermocycles between 235 K (-38°C) and 350 K (+77°C) on resistivity and thermoelectric properties was examined. The Seebeck coefficients of PEDOT:PSS and PANI were found to be about +18 µV/K and +15 µV/K, respectively, when "metal-polymer" thermocouples were realized by combining the polymer with copper. When "polymer-polymer" thermocouples were formed by combining PEDOT:PSS and PANI, a thermoelectric voltage of about +10 µV/K was observed. A challenge recognized in the experiments is that the generated voltage exhibited drift and fluctuations.**

I. Introduction

THE interest for integrating electronic sensing devices in clothing is increasing, and potential applications can be found for example within healthcare, work wear, sport and leisure. Sensors that can interface the body and constantly measure, evaluate and communicate various physiological parameters can allow wireless monitoring of for example a patient at home or a worker carrying out operations in a safety critical environment [1].

Integrated human body temperature sensing in clothing is attractive. From an enhanced safety perspective, temperature monitoring can for example provide alarms for babies and people with reduced or no limb or lower body sensitivity, and it can provide health risk indications for cold environment workers. In addition, from temperature measurements in different layers of clothing, it is possible to estimate insulation properties and heat flux values. Although temperature is an obvious parameter to measure, few attempts have been reported in the literature on implementing distributed and integrated temperature measurements rather than employing regular thermistor sensors. Ziegler et al. have demonstrated the possibility of temperature measurements using textile thermocouples, but the thermocouples had small accuracy and low sensitivity compared to classic metallic wire thermocouples. The thermocouples were also highly influenced by humidity [2]. Apart from this and a few other examples, temperature measurements in clothing is today carried out almost exclusively using conventional temperature sensor technologies, in particular by employing thermistors and metal thermocouples.

Conductive polymers, such as PEDOT:PSS or polyaniline (PANI), can be expected to have interesting properties if integrated as electronics or sensors in clothing. Polymers have the advantage of being flexible, wearable, and potentially washable, and are more resistant to fatigue than the metallic equivalents [3]. Screen printing of conductor lines on textile is attractive from a manufacturing point of view, as it is a cost effective process and provides a high flexibility in the layout of wires and sensors. Duby et al. have previously reported investigations where polymers with metal particles were applied to form thermocouple test structures on textiles [4]. The resulting thermocouples gave thermoelectric sensitivities of +22 µV/K, which is comparable to current, standard metal-based thermocouples. The present work reports on an investigation on the potential of using selected inorganic conductive polymers as active ingredients in thermocouples printed on textiles. It was motivated by the expectation that organic conductive polymers can display relatively substantial thermoelectric effects [5-8], and thus have the potential for becoming an ingredient in a sensitive temperature sensor.

II. Experimental

A. Materials

Commercial solutions of polyaniline and PEDOT:PSS were chosen because of their reported relatively high conductivity and ease of application. Two different conducting polymers were used in these experiments; PANI: Panstat W from Panipol (Finland) and PEDOT:PSS: Orgacon EL-P 3041 from Agfa (Germany).

PANI is an aqueous polyaniline and binder based conductive polymer ink. An additional 5 % thickening agent DSX 3256 from Cognis was used in order to make it printable. PEDOT:PSS is a water based dispersion of Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) developed for printing. The substrate used was a cotton textile, with a thread count of 33 per cm and a thread

Manuscript received April 1, 2011. This work was supported by the Research Council of Norway and the partners of the Coldwear project (http://www.sintef.no/Coldwear).

T. M. Seeberg (corresponding author: Tel.: +47-22067803, Fax: +47 – 22062350, E-mail address: trine.seeberg@sintef.no) and Frode Strisland (e-mail: frode.strisland@sintef.no) are with SINTEF Informatics and Communication Technology, NO-0314 Oslo, Norway.

A. Røyset (e-mail: arne.roiseth@sintef.no) and S. Jahren(e-mail: susie.jahren@sintef.no) are with SINTEF Materials and Chemistry, NO-7465 Trondheim, Norway.

diameter of approximately 200 μm. Before coating with PEDOT:PSS, the cotton was pre-treated with an acrylic coating of TA-GP from Huntsman to reduce wicking. All samples were cured for 10 minutes at 393 K before start of the measurements.

B. Manufacturing of samples by screen printing

The samples for electrical resistance measurements were made by screen printing single lines with dimensions 1 cm x 14 cm on the textile substrate. Three combinations of materials were made for the thermoelectrical measurements, Copper(Cu)/PANI, Cu/PEDOT:PSS and PEDOT:PSS/PANI. The samples were produced in two steps. The "metal-polymer" thermocouples, containing a polymer part and a copper part, were produced by first screen printing the polymer part and afterwards add the copper strip. An insulated clip was used to connect the copper part to the polymer part. The "polymer-polymer" thermocouples were produced by first printing PANI and then printing PEDOT:PSS. The dimension of the samples was 1 cm x 24 cm x 4 cm (L-form).

Screen printing was carried out using a DEK 248 Printer from DEK, UK. The screen used was a nylon screen with 33 counts per cm. The printing speed was controlled at 10 mm/s. Scanning electron microscopy (SEM) was carried out on cross sections of samples using a JEOL JSM-5900LV SEM equipped with an OXFORD Isis spectrometer with germanium detector.

C. Method for electrical measurements

An Agilent 34970A data logger with 34901A multiplexer module and Data Logger software (BenchLink Data Logger) was used to measure and log temperature, electrical resistance and voltage. Standard J-type twisted cable thermocouples attached with heat conductive paste and Kapton tape were used to measure reference temperatures. A Weiss Technik 13599 temperature chamber was used to control the temperature during the measurements.

1) Electrical resistance

The electrical properties of the single line printed conductive polymers were characterized using a four point measurement method in order to eliminate the large contact resistance between the measurement tool and the printed surface. The electrical connection between the samples and the instrument was realized by using crocodile clips (Hirschmann AFG 20 Test Clamp) and standard copper wires. The measurement length was 10 cm. Electrical resistance was measured as a function of multiple temperature cycling and time.

2) Thermoelectric voltage

The generated thermoelectric voltage was measured for all combinations of materials during multiple sequential temperature cycles. Figure 1 displays the sample combinations and polarization of the thermocouples.

One end of the thermocouples was held inside the temperature chamber and the other end was outside. The small change in the reference temperature over time was measured and compensated for in the results. T_{Diff} given in the figures in section III.C is the temperature difference between the temperature inside the chamber ($T_{Cycling}$) and the constant reference temperature outside (T_{Ref}), see Figure 1. The Seebeck coefficients were found from the temperature dependence of the thermoelectric voltage as $S(T) = -dV/dT$.

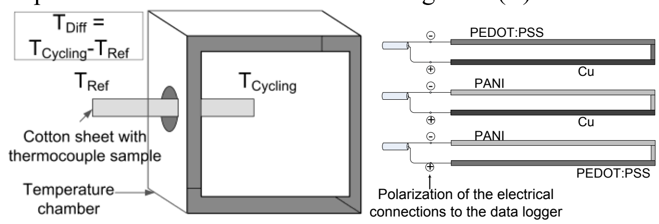

Figure 1 Setup for the thermoelectrical measurements (left), and polarization of the samples (right).

III. RESULTS AND DISCUSSION

A. Screen print of conducting polymers

Figure 2 shows SEM images of screen printed samples. The images demonstrate that both PANI and PEDOT:PSS successfully impregnated the top layer of the cotton fibers creating a well adhered coating layer. The thickness of the conducting layer was estimated from the SEM images and was 25-50 μm for PANI and 15-20 μm for PEDOT:PSS.

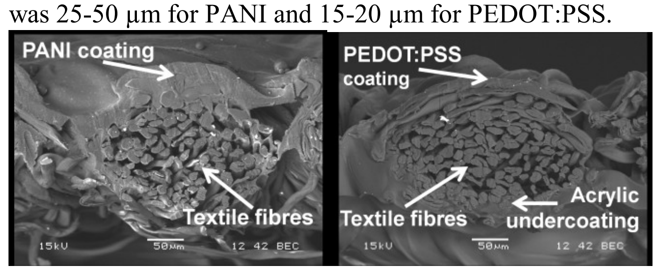

Figure 2 Cross-section of cotton textile coated with PANI (left) and PEDOT:PSS (right). The PEDOT:PSS image also shows the acrylic pre treatment on the underside of the textile.

B. Electrical resistance

Four samples of screen printed single lines were measured ten times each at room temperature to estimate the measurement repeatability of the electrical connection method, and to evaluate the reproducibility of the samples. In these tests, the electrical connections were removed and re-attached between each measurement. The electrical resistance was found to be in the range of 20 kΩ/m for PEDOT:PSS and 8 MΩ/m for PANI. The standard deviation for repeated measurements on individual samples was small and below 3 % for PANI and 1 % for PEDOT:PSS. However, the sample-to-sample variation in electrical resistance was large as expected for systems with high thickness sensitivity: 43 % for PEDOT:PSS and 26 % PANI. This is expected to be improved in a full scale production line with an industrial screen print setup. However, whereas thermocouple measurements are not extremely sensitive to resistance values, this result also shows that other sensor principles requiring strict resistance tolerances could be difficult to realize.

1) Electrical resistance as a function of temperature

The electrical resistance of two PEDOT:PPS and two PANI samples was measured as a function of temperature. The temperature was varied between 235 K and 350 K applying the following temperature cycle: starting at room temperature, then heating to 350 K, cooling to 235 K before heating again. Five full cycles were measured, se Figure 3.

The electrical resistance for both materials changed as a function of temperature. The relative resistance change from low (235 K) to high (350 K) temperature was much higher for PANI (160-190 %) than for PEDOT:PSS (about 10 %). The measured conductive polymer samples had a negative temperature coefficient of resistance, TCR = (dR/dT)/R. This is in accordance with other observations on conducting polymers made by Kwon [10], and consistent with the conduction models based on thermal activation or by variable-range hopping [5] [11]. The PANI TCR is ~ -0.8 %/K, which is comparable to Au / Pt and what is observed for PEDOT:PSS in [10]. Our PEDOT:PSS sample showed a smaller temperature dependence, TCR ~ -0.05 %/K.

Both samples displayed some fluctuations in the electric resistance. The fluctuations for PEDOT:PSS corresponded to about 3 % (60 Ω) at high temperatures and about 1.5 % (30 Ω) at low temperatures. The corresponding numbers for PANI were 0.4 % (2 kΩ) for high temperatures and 0.4 % (6 kΩ) for low temperatures.

There was also a small drift in resistance as a function of cycle number. The drift in resistance from cycle 1 to cycle 5 was 3-5 % for PANI and 3-4 % for PEDOT:PSS. This may be attributed to the effect of initial aging, drying or moisture evaporation. In a practical application the thermocouple would benefit from being encapsulated in a moisture and oxygen impermeable coating.

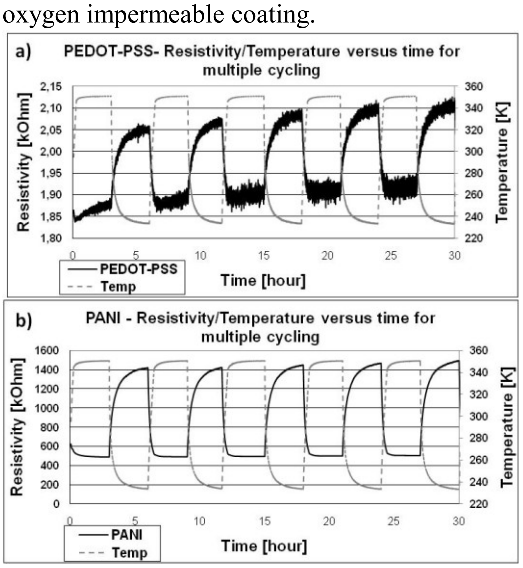

Figure 3 Electrical resistance (left axis) and temperature (right axis) as a function of time for multiple cycling of a) PEDOT: PSS and b) PANI.

C. Thermoelectric voltage measurements

The generated thermoelectric voltages were measured on two samples of each kind of thermocouple configuration (Cu/PEDOT:PSS, Cu/PANI , PEDOT:PSS/PANI). The two samples of the same kind gave similar results. The measurements were done during five temperature cycles while the chamber temperature, $T_{Cycling}$, was varied between 235 K and 350 K. T_{Ref} was about 294 K and the change in T_{Ref} was measured and compensated for in the results. Each cycle lasted 6 hours. Temperature difference (left y-axis) and thermoelectric voltage (right y-axis) versus time for the three different thermocouples combinations are showed in Figure 4. Figure 5 shows the thermoelectric voltage as a function of temperature difference during the first cycle for Cu/PEDOT:PSS and Cu/PANI. These curves were filtered and used to estimate the Seebeck coefficients.

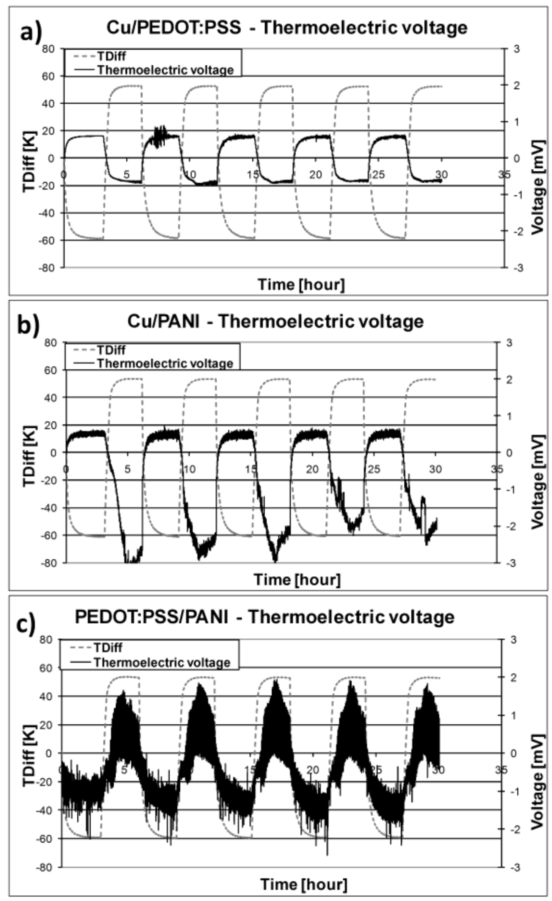

Figure 4 Thermoelectric voltage versus time for a) Cu/PEDOT:PSS , b) Cu/PANI and c) PEDOT:PSS/PANI for multiple cycling of temperature.

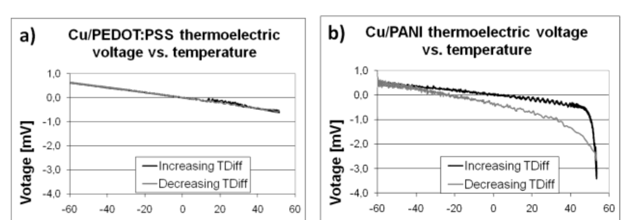

Figure 5 Thermoelectric voltage (right axis) versus temperature difference (left axis) for a) Cu/PEDOT:PSS, b) Cu/PANI. The data corresponds to the first cycle in Figure 4 a) and b).

The Cu/PEDOT:PSS thermocouples displayed fluctuations in the thermoelectric voltage within one cycle, but they were relatively stable from cycle to cycle for both high and low temperatures. The fluctuations for most cycles were about 0.1 mV, but during the 5th cycle in sample 2 and the 2th cycle in sample 1 more noise (0.6 mV) were generated. The thermoelectric voltage was estimated to be -11 μV/K for the thermocouple corresponding to a Seebeck coefficient of 18 μV/K for PEDOT:PSS alone (the Seebeck coefficient for Cu is 7 μV/K [9]). This was observed over the whole temperature range in the experiments.

For low temperatures inside the chamber, the Cu/PANI thermocouple displayed only small fluctuations in the thermoelectric voltage (0.2 mV) within each cycle, and the voltage level was stable from cycle to cycle. On the other hand, for high temperatures, the voltage level was not stable. The timescale for the observed drift was in the order of one hour, firstly the voltage was decreasing and then later increasing again. A hysteresis of about 1 mV was observed. The origin of the observed drift and hysteresis is not known but one possible cause is the geometry of the setup, with the conductors crossing an opening in the oven and the various moisture levels. Temperature induced strain may have an influence, but this is less likely as it has been demonstrated that strain has a much smaller impact on the Seebeck coefficient than on the conductivity [6]. For increasing temperature and $T_{Cycling}$ between 235 K and 335 K, a slope of -8 μV/K was estimated for the thermocouple corresponding to a Seebeck coefficient of 15 μV/K for PANI alone.

The PEDOT:PSS/PANI thermocouples showed rapid, substantial fluctuations in the thermoelectric voltage. In addition, there was a large, slow drift at high temperatures, but this pattern was repeatable from cycle to cycle. A large hysteresis of approximately 0.5 mV was observed. It was not possible to accurately estimate a thermoelectric voltage because of the large fluctuations. However, the average slope in the temperature range of T_{Cycle} from 235 K to 293 K was estimated to be about 10 μV/K (after filtering the data).

The quality of the Seebeck coefficient measurement was highest for the Cu/PEDOT:PSS sample, with best linearity and least voltage fluctuations. The combination of PANI and Cu gave significantly different results with large drift in Seebeck voltage after the $T_{Cycling}$ was settled at 350 K. The "polymer-polymer" thermocouple gave similar fluctuations and drift as the Cu/PANI thermocouple. This observation supports that the fluctuations and drift observed in the Cu/PANI samples is mainly caused by the PANI. Further, it is an indication that the main source for drift and fluctuations in the PEDOT:PSS/PANI samples was related to PANI.

The Seebeck coefficients of PEDOT: PSS and PANI were found to be +18 and +15 μV/K, respectively. A Seebeck coefficient of about +3 μV/K for the PANI/PEDOT:PSS thermocouple was therefore expected. The observed slope was +10 μV/K, but considering the high noise level in the measurements this result was in accordance with the expectations.

We have estimated that conductive polymer based thermocouples can give a measurement accuracy of the order +/- 1 K, but problems like static electricity effects and significant stretching or bending of the thermocouples can reduce it. This accuracy will be acceptable for several kind of health monitoring applications, such as temperature exposure for harsh environments workers. However, better accuracy would be needed for instance for measurements of fever conditions.

IV. CONCLUSION

It was possible to print commercial organic conducting polymers, PEDOT: PSS and PANI, on cotton by using screen printing. The electrical resistance was found to be in the range of 20 kΩ/m for PEDOT:PSS and 8 MΩ/m for PANI at room temperature. The electrical resistance decreased as a function of temperature for both PEDOT:PSS and PANI. The main change in resistance was reversible, but there was a small drift in the resistance for multiple termocycling.

The Seebeck coefficient was found to be about 18 μV/K for PEDOT:PSS (valid in the whole measured temperature range, $T_{Cycling}$ from 235 to 350 K) and 15 μV/K for PANI (valid for increasing temperature up to $T_{Cycling}$ 335 K), when thermocouples were realized in combination with Cu. When polymer thermocouples were formed by combining PEDOT:PSS and PANI, a thermoelectric voltage of about 10 μV/K were observed.

These first experiments indicate that it is possible to use screen printed organic conducting polymers as thermocouples.

REFERENCES

[1] J. Ogando, "Fabrics get smart", Electronics Design, Design News, May 14, 2006.

[2] S.Ziegler,M. Frydrysiak, "Initial Research into the Structure and Working Conditions of Textile Thermocouples", FIBRES & TEXTILES. Vol. 17, No. 6 (77) , 84-88, 2009.

[3] S.Tang, G.Stylios, "An overview of smart technologies for clothing design and engineering", Intern J of cloth.Vol. 18, No.2,108, 2006

[4] S. Duby, B. Ramsey, D. Harrison, G. Hay, "Printed thermocouple devices", IEEE Sensors Proceedings, 2004.

[5] A. Shakouri, S. Li, "Thermoelectric Power Factor for Electrically Conductive Polymers", Proc. Int. Conf. Thermoelectrics, 1999.

[6] Y. Hiroshige, M. Ookawa, N. Toshima, "Thermoelectric figure-of-merit of iodine-doped copolymer of phenylenevinylene with dialkoxyphenylenevinylene", Synt. Met. 157, 467, 2007.

[7] S. Wakim, B. Aïch, Y. Tao, M. Leclerc, "Charge transport, photovoltaic and thermoelctric properties of Poly(2,7 Carbazole) and Poly(Indolo[3,2-b] Carbazole) derivatives", Polymers Reviews 48, 432, 2008.

[8] R. B. Aïch, N. Blouin, A. Bouchard, M. Leclerc, "Electric and thermoelectric properties of Poly(2,7-Carbazole) Derivatives", Chem. Mater. 21 pp. 751, 2009.

[9] C. Nordling, J. Õsterman. "Physics handbook for science and Engineering", Studentlitteratur. Sweden pp. 44, 2008.

[10] I.W.Kwon, H.J.Son, W.Y.Kim, Y. S. Lee, H.C. Lee, "Thermistor behavior of PEDOT:PSS thin film", Synth. Met. 159, pp.1174, 2009.

[11] S. Bhadra, D. Khastgir, N. K. Singha, J. H. Lee, "Progress in preparation, processing and applications of polyaniline". Progress in Polymer science 34, pp. 783, 2009.