



INTEGRATING THE THERMOELECTRIC AND SENSING PROPERTIES OF PEDOT-BASED COMPOUNDS INTO SELF-POWERED DEVICES

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Engineering and Physical Sciences
Research Council



European Thermodynamics Limited
Intelligent Thermal Management



INTRODUCTION

ORGANIC THERMOELECTRICS

Review

Thermoelectric Materials: A Brief Historical Survey from Metal Junctions and Inorganic Semiconductors to Organic Polymers

Prospero J. Taroni, Itziar Hoces, Natalie Stingelin, Martin Heeney ✉, Emiliano Bilotti ✉

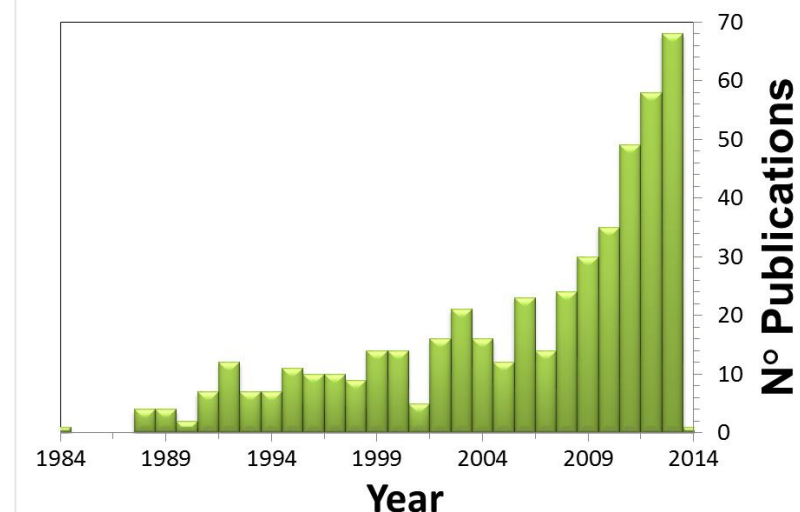
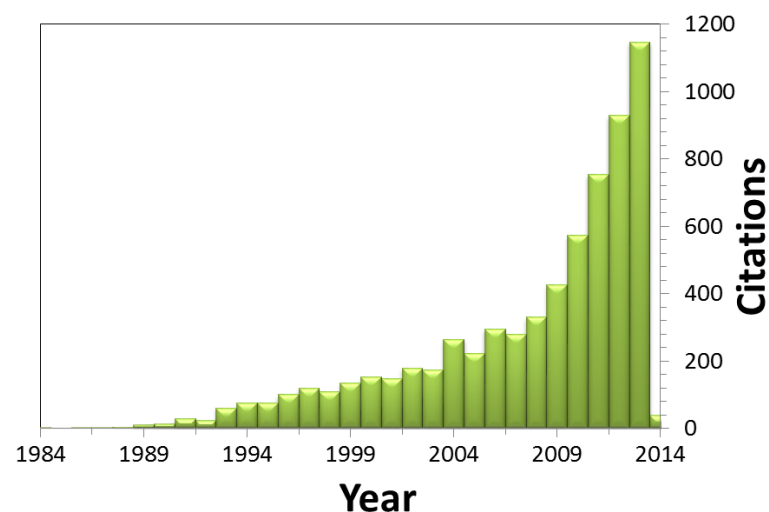
First published: 6 June 2014 [Full publication history](#)

The first *European Conference on Thermoelectrics* in 1988 had **no mention on organic materials** in their proceedings.

According to the **Thomas Reuter Web of Science** citation report for the term '**organic thermoelectric***' (last three decades) the interest has grown exponentially.

The potential advantages :

- lower cost
- relative abundance
- possibility for large area deposition.
- **However, their use is limited to lower-temperature applications.**



SIGNIFICANT PROGRESS FOR *P*-TYPE ORGANIC THERMOELECTRIC MATERIALS

nature
materials

2011

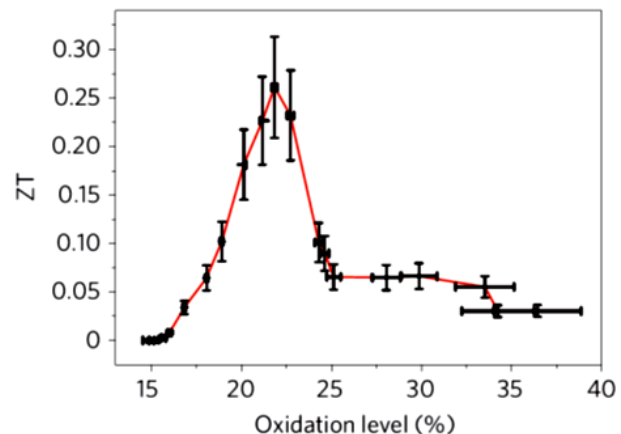
LETTERS

PUBLISHED ONLINE: 1 MAY 2011 | DOI: 10.1038/NMAT3012

Optimization of the thermoelectric figure of merit in the conducting polymer poly(3,4-ethylenedioxythiophene)

Olga Bubnova¹, Zia Ullah Khan¹, Abdellah Malti¹, Slawomir Braun², Mats Fahlman², Magnus Berggren¹ and Xavier Crispin^{1*}

The accurate control of the oxidation level in poly(3,4-ethylenedioxythiophene) (PEDOT) combined with its low intrinsic thermal conductivity ($\lambda = 0.37 \text{ W m}^{-1} \text{ K}^{-1}$) yields a **ZT = 0.25** at room temperature that approaches the values required for efficient devices.



nature
materials

2013

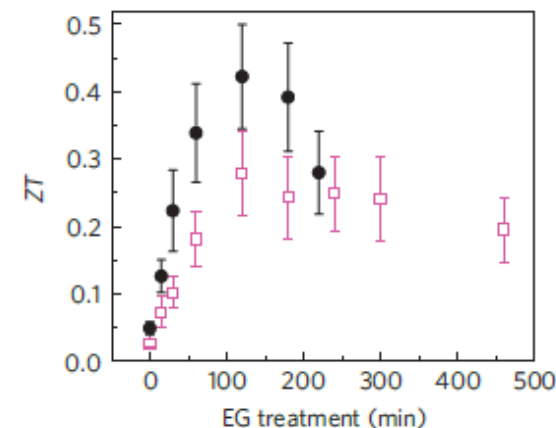
LETTERS

PUBLISHED ONLINE: 5 MAY 2013 | DOI: 10.1038/NMAT3635

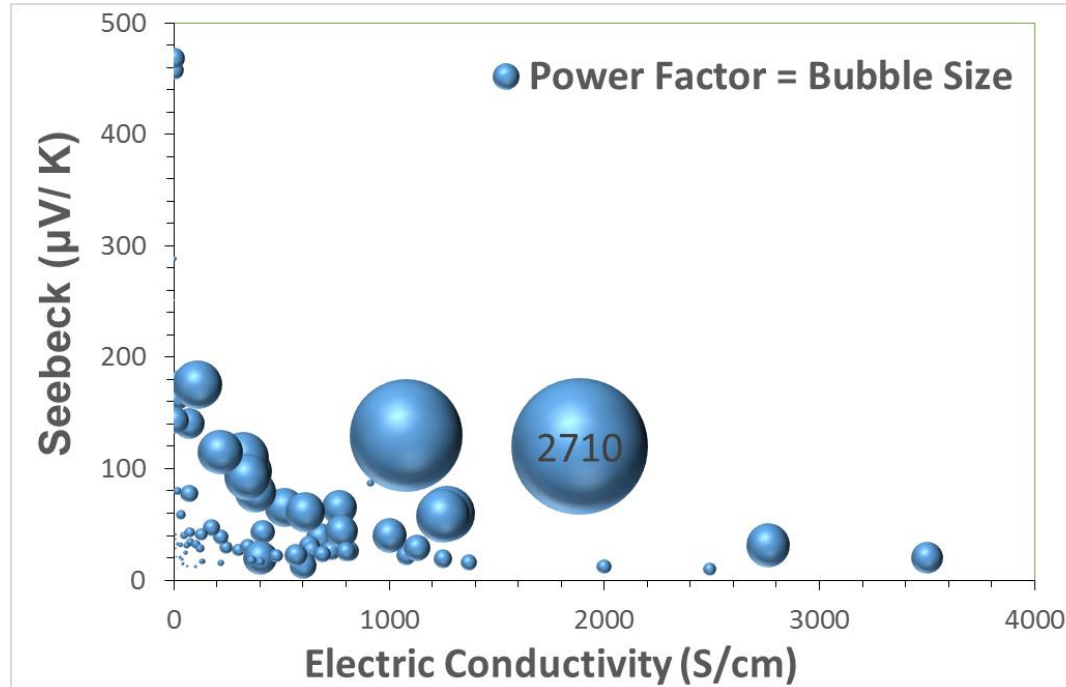
Engineered doping of organic semiconductors for enhanced thermoelectric efficiency

G-H. Kim¹, L. Shao¹, K. Zhang¹ and K. P. Pipe^{1,2*}

Reducing dopant volume is found to be as important as optimizing carrier concentration when maximizing ZT in OSCs. Implementing this strategy with the dopant poly(styrenesulphonate) in poly(3,4-ethylenedioxythiophene), we achieve **ZT = 0.42** at room temperature.



LITERATURE REVIEW: 'ORGANIC THERMOELECTRIC COMPOSITES*'



Best Power Factor for p-type composite:

LbL

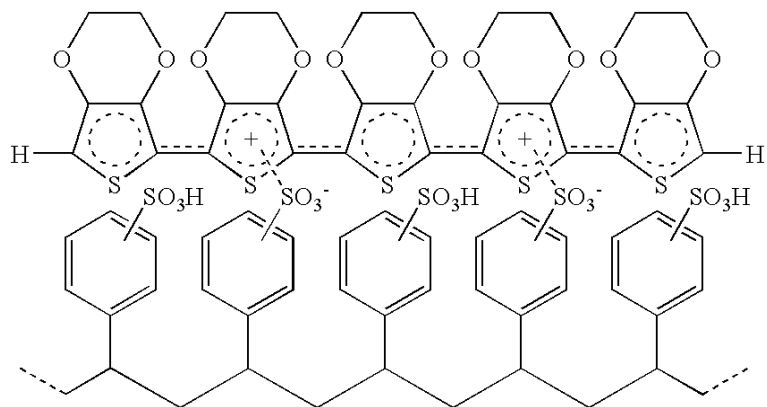
Polyaniline/
Graphene-PEDOT:PSS/
Polyaniline/
DWCNT-PEDOT:PSS

Cho, C. et al., Adv. Energy Mater. 6, (2016)

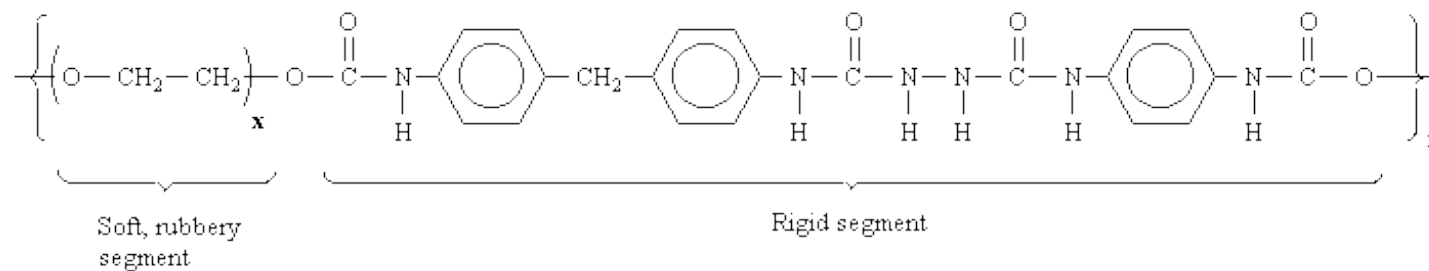
- **Highest Seebeck coefficient** for p-type materials were reported between **400 and 500 uV/ K**, but they did not generate the highest PF.
- **Highest electrical conductivity** were between **2500 and 3500 S/ cm**, but they did not generate the highest PF.
- **Best power factor** was generated by moderately high electric conductivities and Seebeck coefficients between **1000 – 2000 S/ cm** and **100 – 200 uV/ K**, respectively.

MOTIVATION:

To combine the electrical properties of PEDOT:PSS with the mechanical properties of Spandex



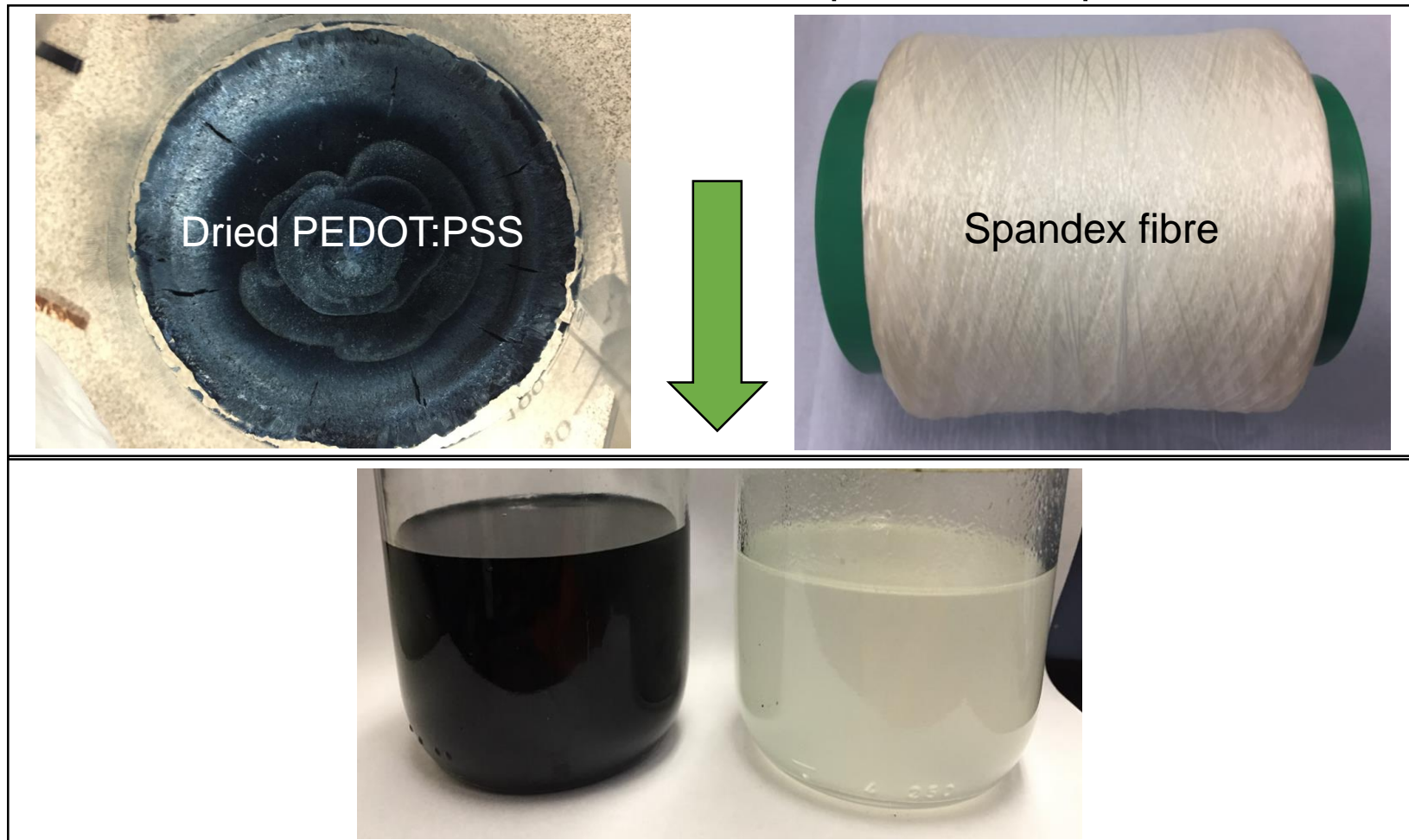
PEDOT:PSS
Clevios PH1000



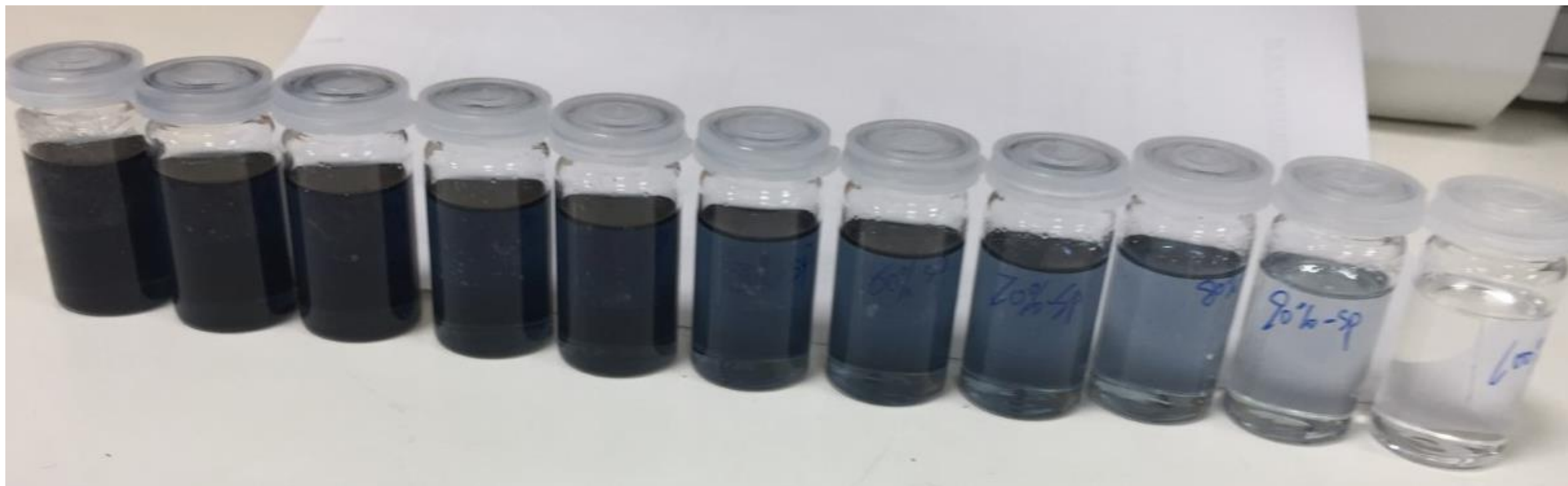
SPANDEX
Lycra® Invista

METHOD:

Fabrication of PEDOT:PSS/ Spandex composite.



0% - 100% MIXTURES OF SPANDEX WITH PEDOT:PSS



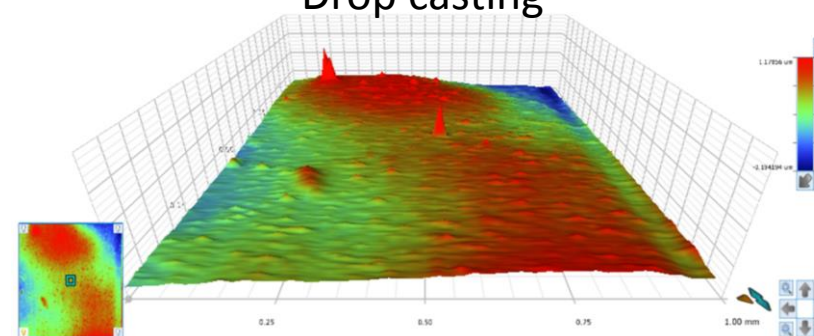
DROP-CASTED FILMS

Better electric conductivity compared to spray coating

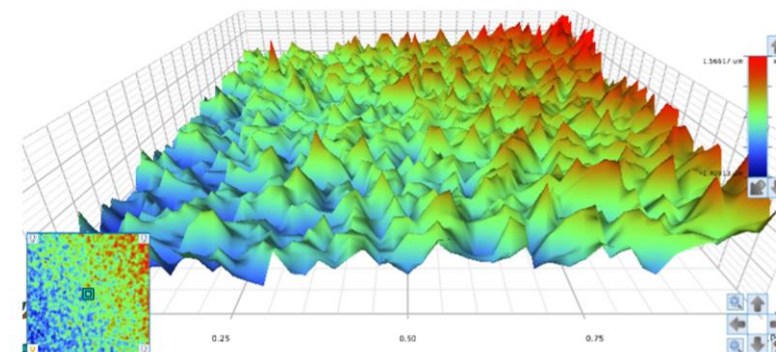


3D images - 1 x 1 cm

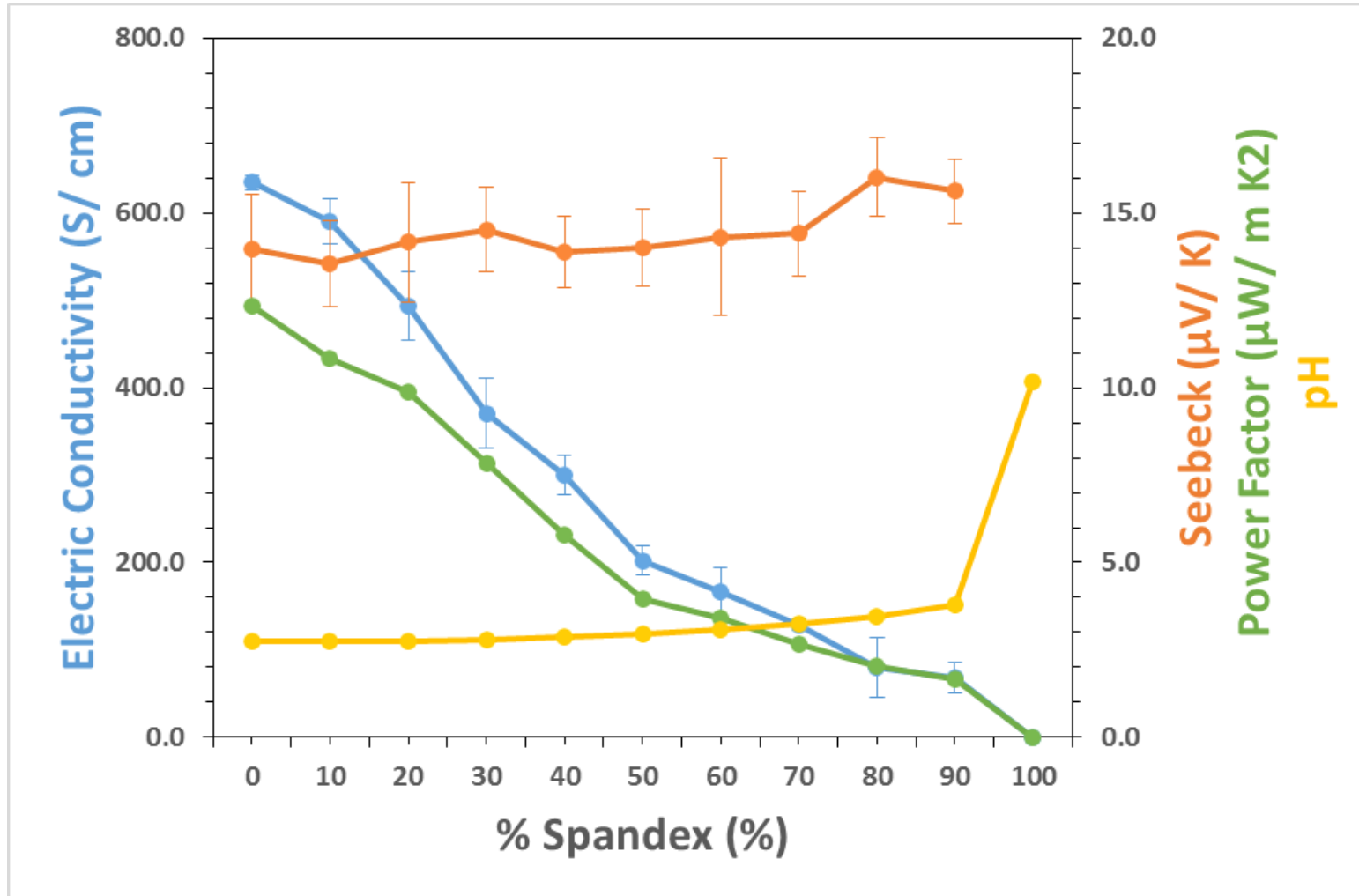
Drop casting



Spray coating

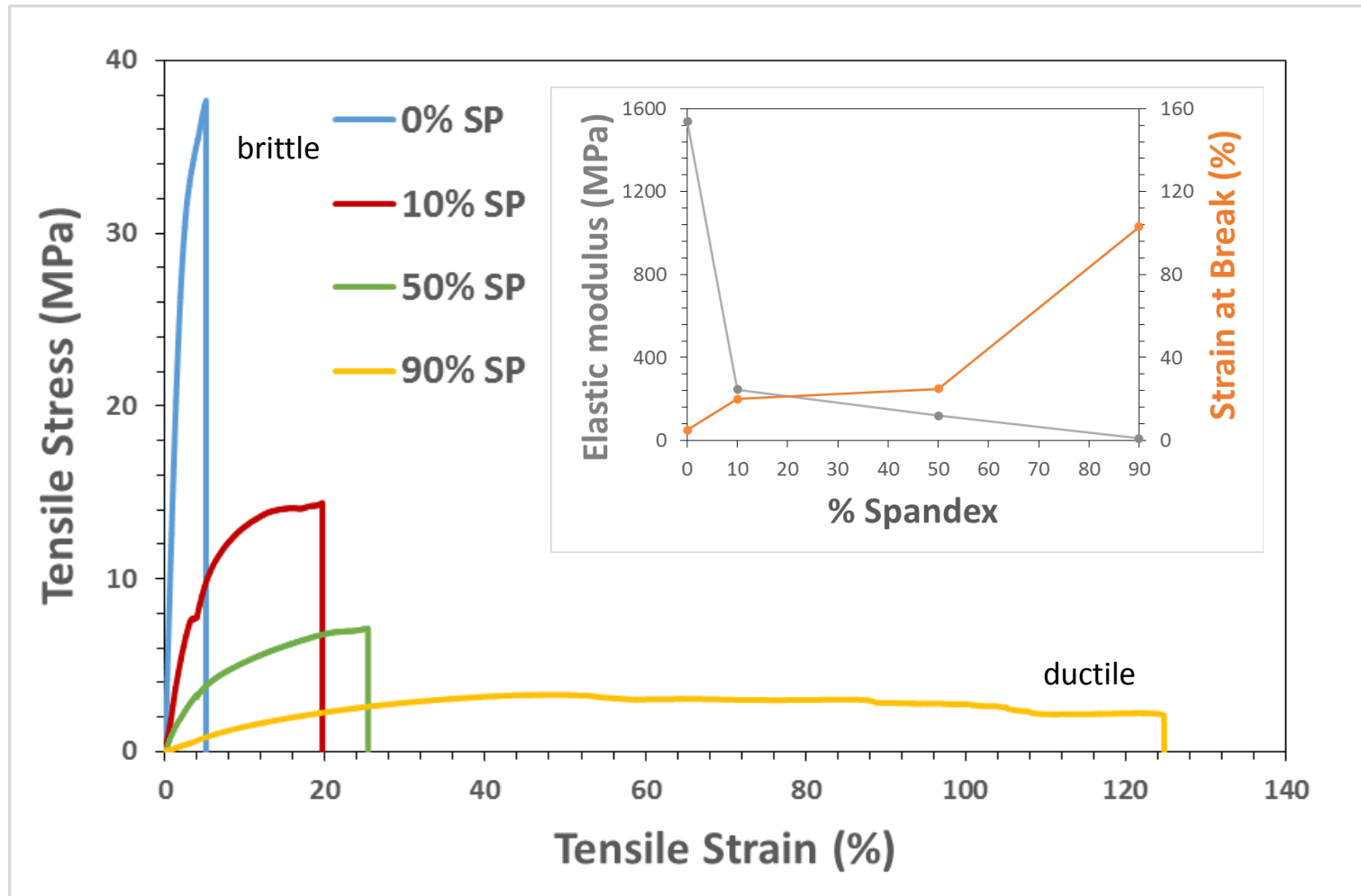


THERMOELECTRIC CHARACTERISATION OF PEDOT:PSS/ SPANDEX COMPOSITES



- The electric conductivity decreases with increased concentration of Spandex, but remains relatively high due to solvent treatment.
- The Seebeck coefficient is not significantly affected by increased concentration of Spandex.

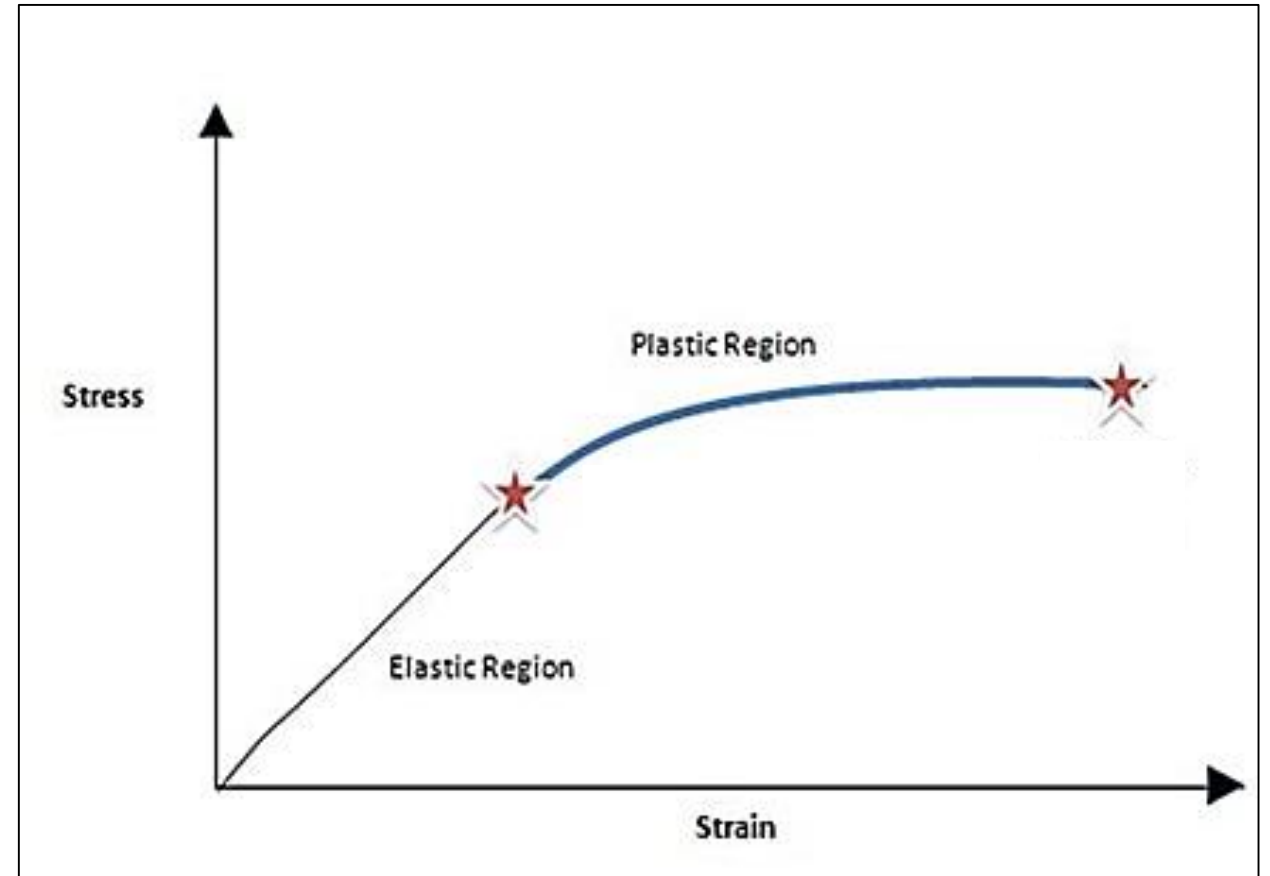
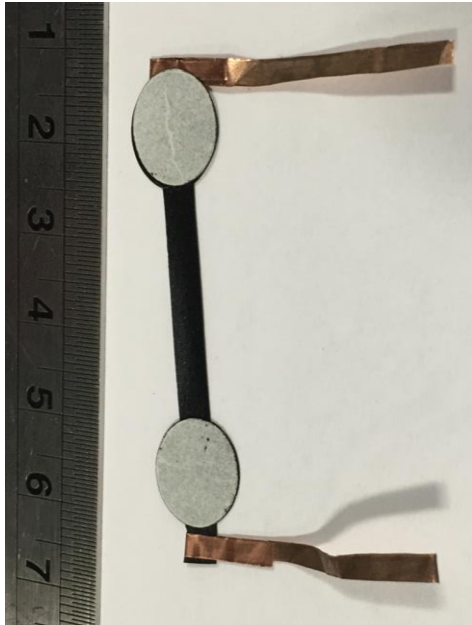
TENSILE PROPERTIES OF COMPOSITES



- The strain at break (%) increases with increased concentration of Spandex.
- The elastic modulus decrease with increased concentration of Spandex.

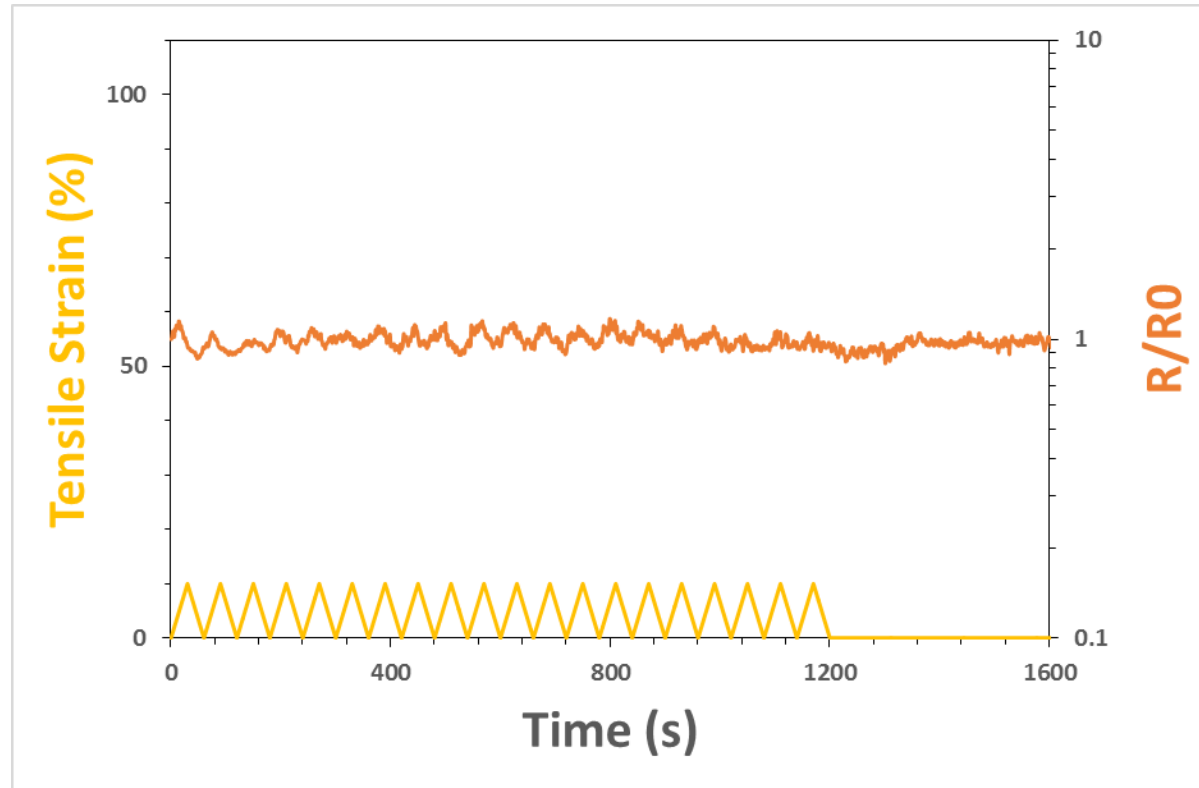
CYCLIC TEST: STRAIN SENSING WITH APPLIED VOLTAGE AND MEASURED CURRENT.

$$R = \frac{V}{I}$$

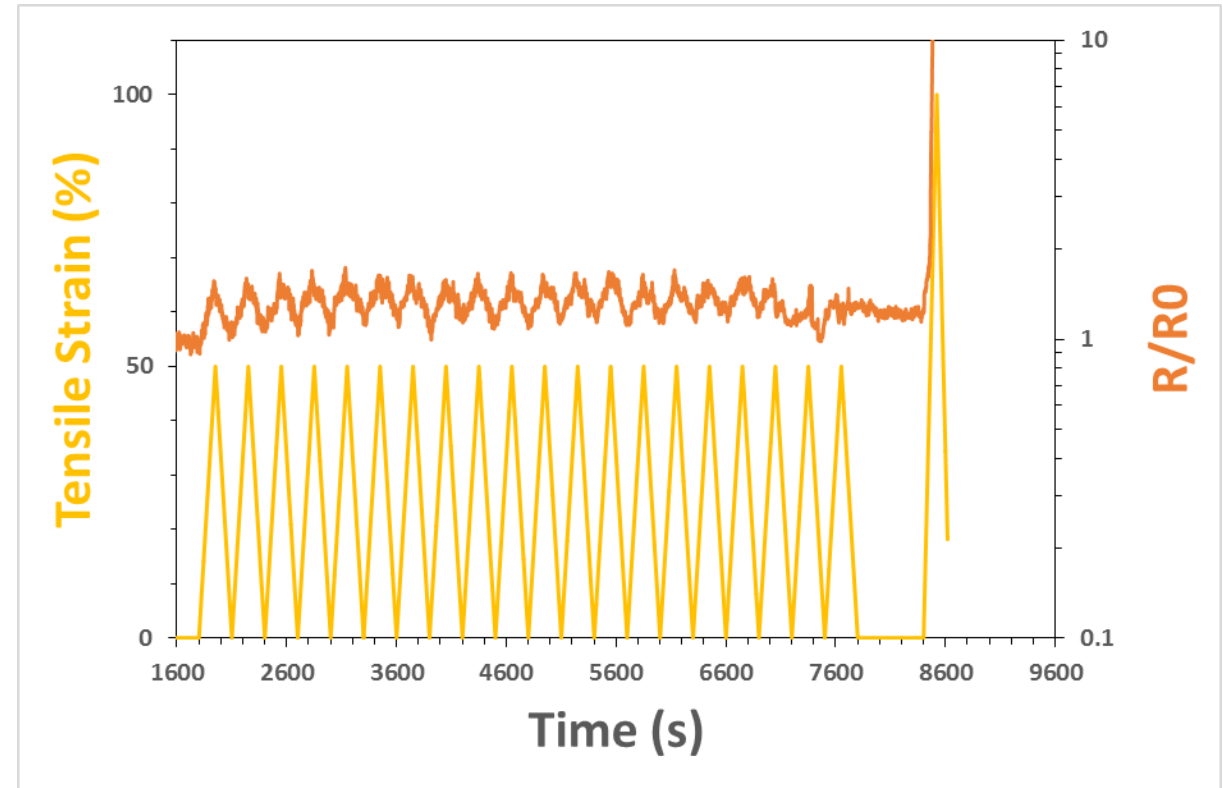


CYCLIC TEST, 90% SPANDEX AFTER EG BATH

CYCLE 1 – 10% STRAIN



CYCLE 2 – 50% STRAIN



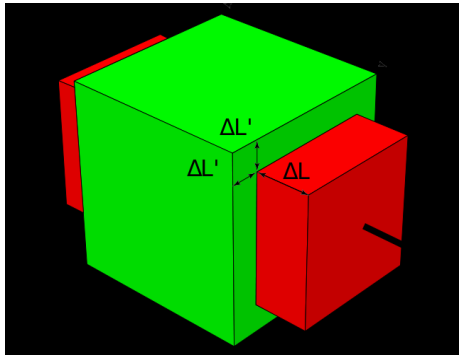
THE EFFECT OF GEOMETRIC FACTORS ON RESISTANCE (50% STRAIN)

DERIVED FROM POISSON'S RATIO

[PDF] Stress-Strain Behavior of Thermoplastic Polyurethane - Massachuset...
web.mit.edu/cortiz/www/Jerry/TPU_final.pdf
 by HJ Qi - Cited by 267 - Related articles
 The stress-strain behavior of TPUs demonstrates strong hysteresis, time ... It is hence reasonable to assume the Poisson's ratio ν ranges from 0.48 to 0.50.

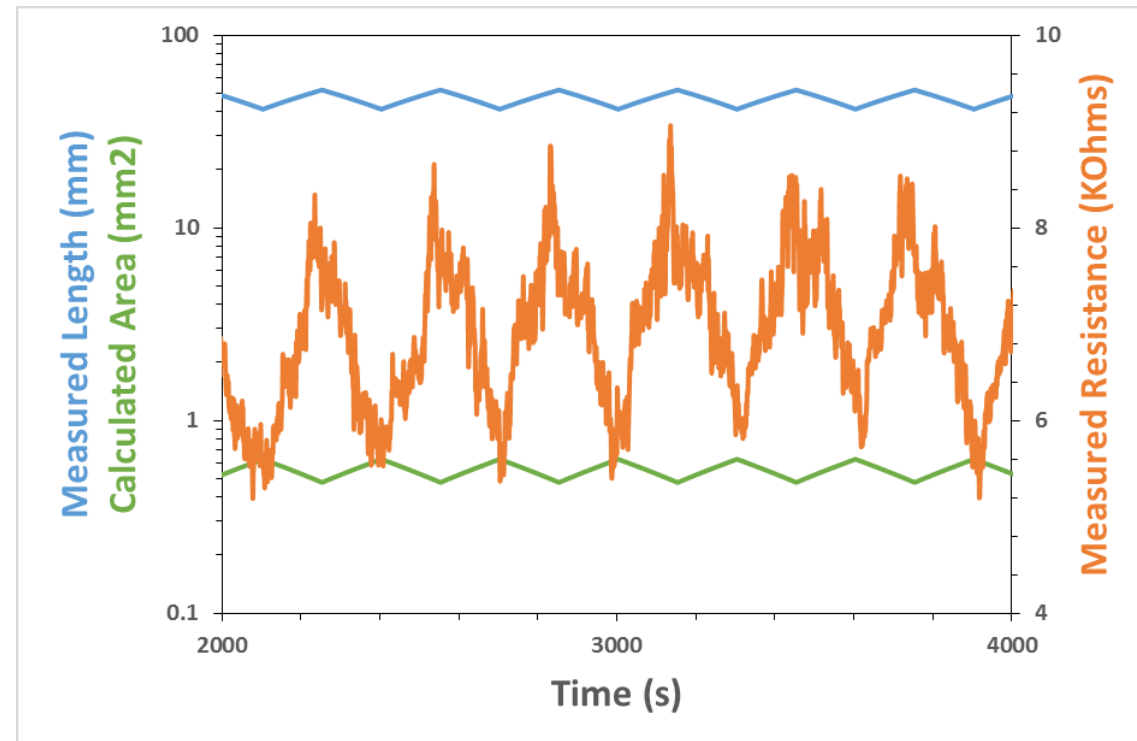
$$W = W_0 \left(1 - \left(0.5 \times \frac{\text{Extension}}{L_0} \right) \right)$$

$$T = T_0 \left(1 - \left(0.5 \times \frac{\text{Extension}}{L_0} \right) \right)$$



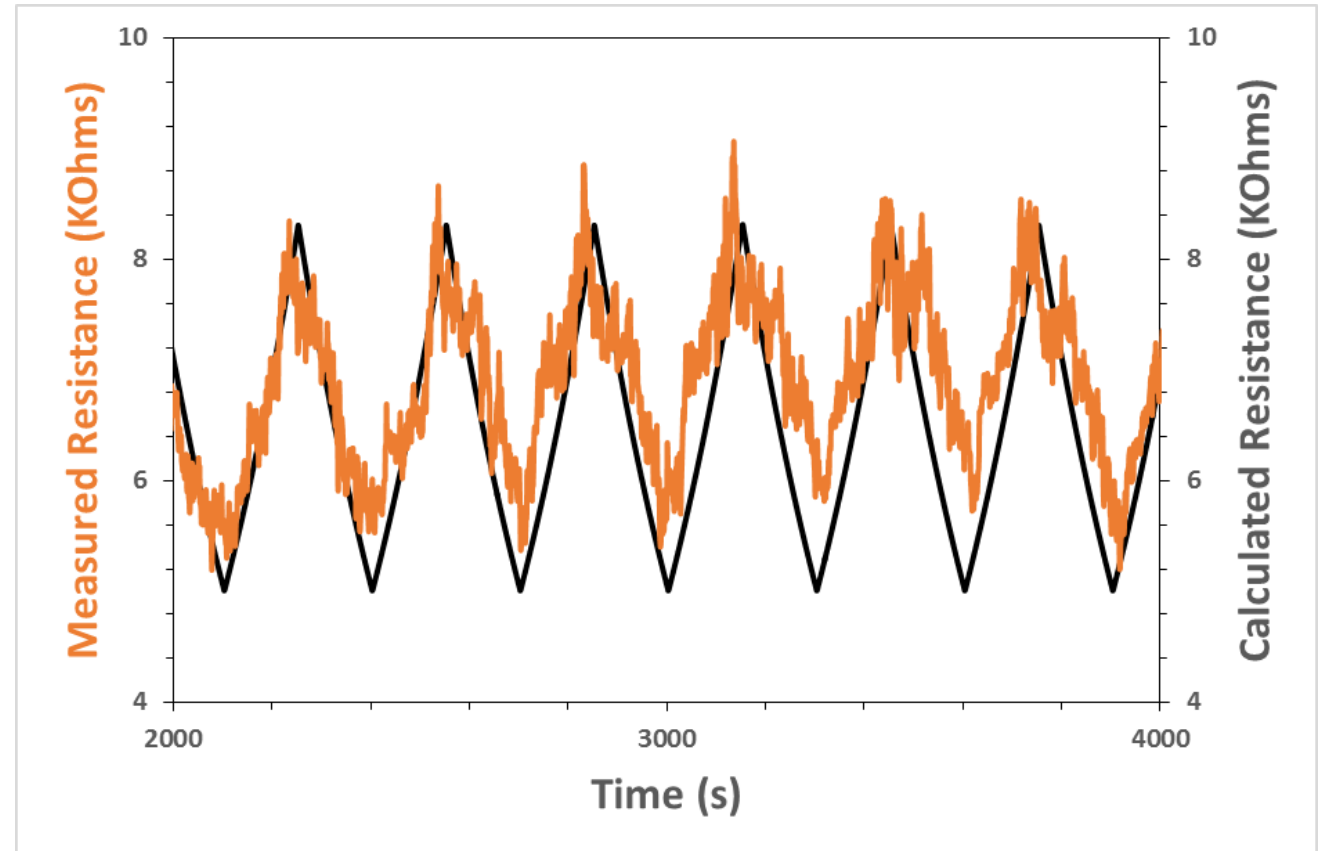
$$R = \frac{\rho L}{A}$$

ρ = resistivity
 L = length
 A = cross sectional area



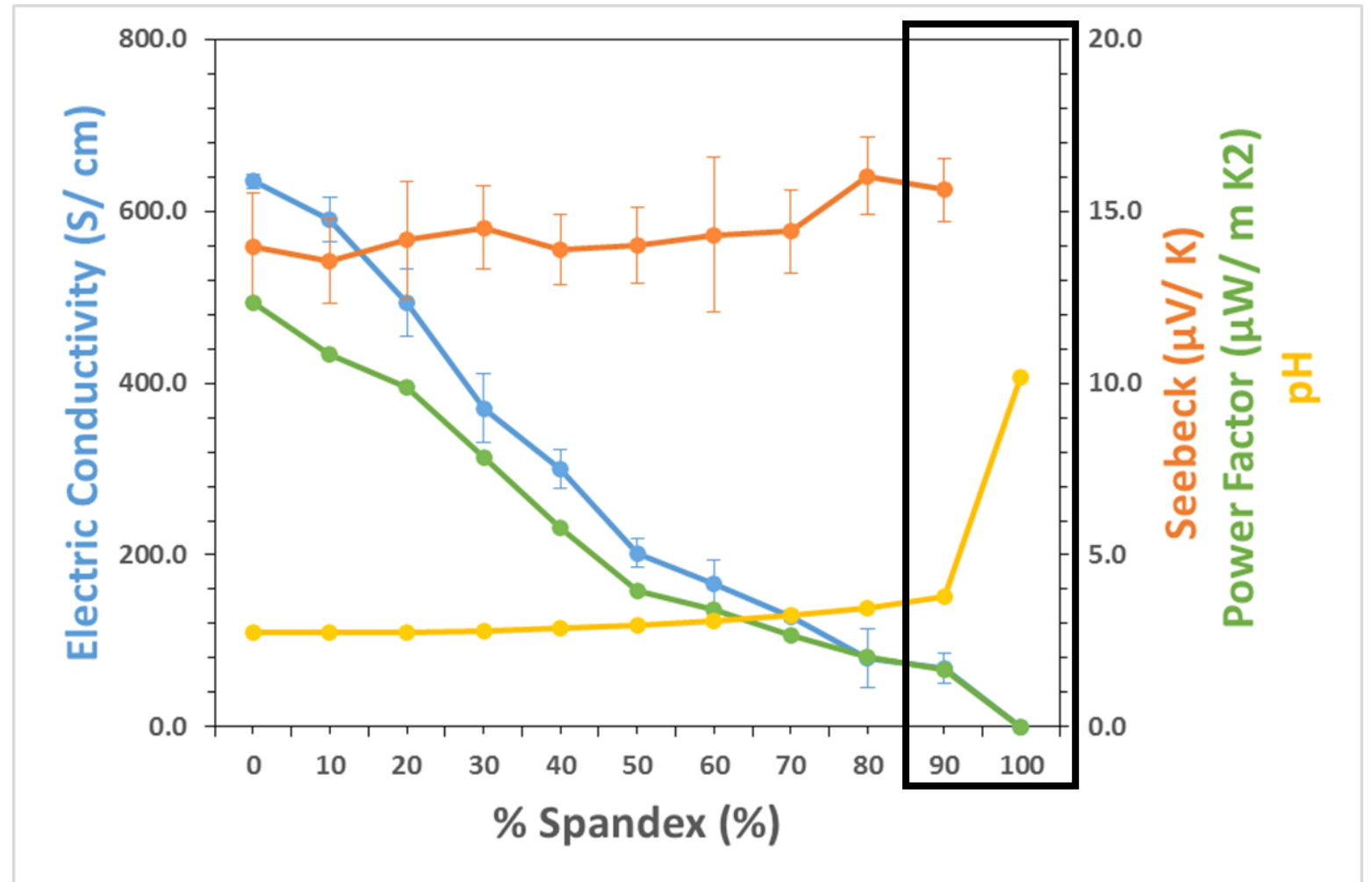
THE EFFECT OF GEOMETRIC FACTORS ON RESISTANCE (50% STRAIN)

- The sample did not recover its length very quickly, so at the minimal extension point, the measured resistance corresponds to a slightly stretched sample.
- The calculated resistance still very close to the measured resistance, so there is no indication of significant changes in the resistivity during extension.
- Variation of resistance with cycle is likely to be due to geometric factors only.



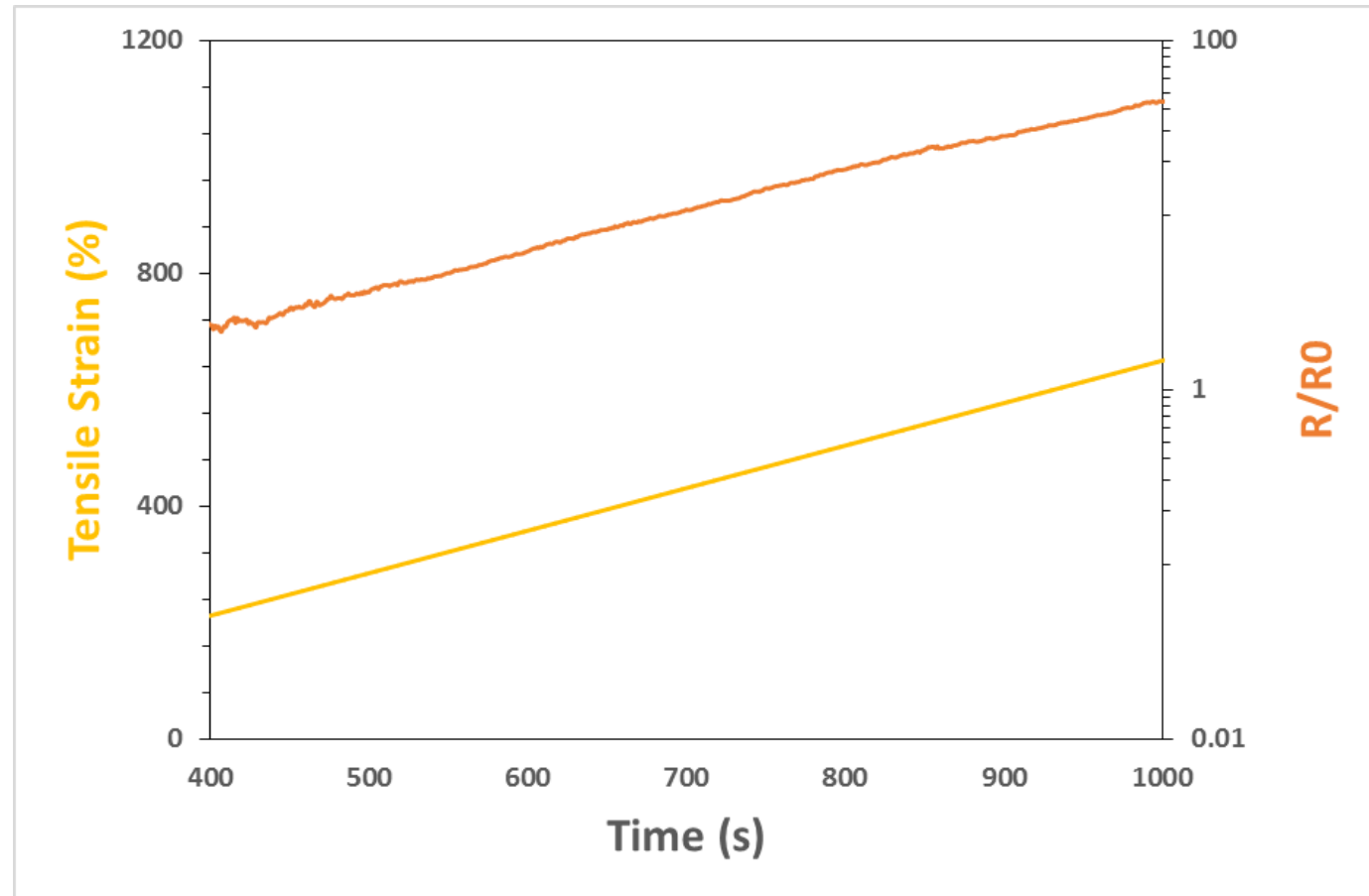
IMPROVING THE SENSITIVITY TO STRAIN

- The use of a lower concentrations of PEDOT to Spandex – **sensitivity not only affected by geometrical factors, but also to changes in resistivity due to a closer proximity to percolation.**

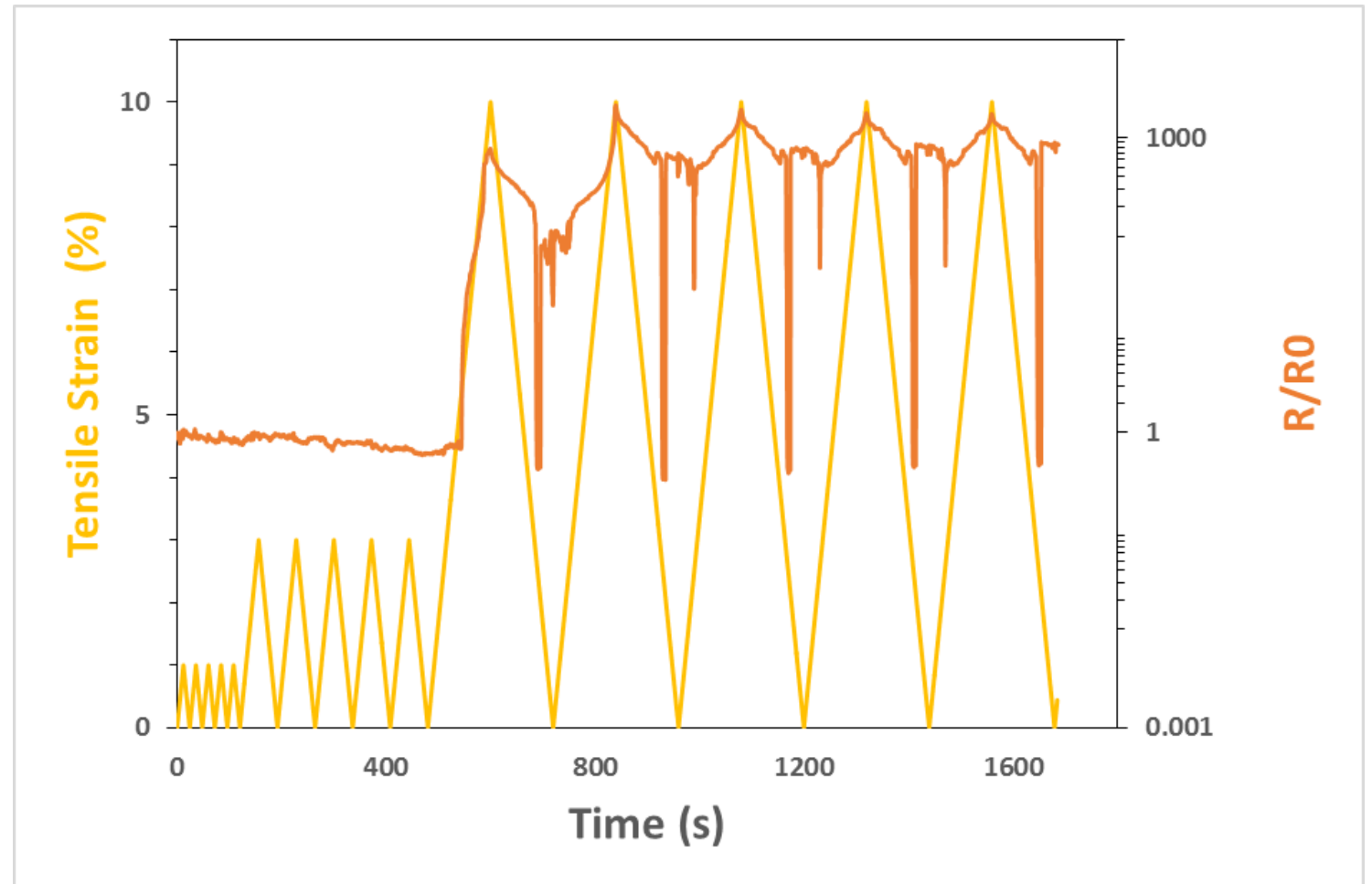
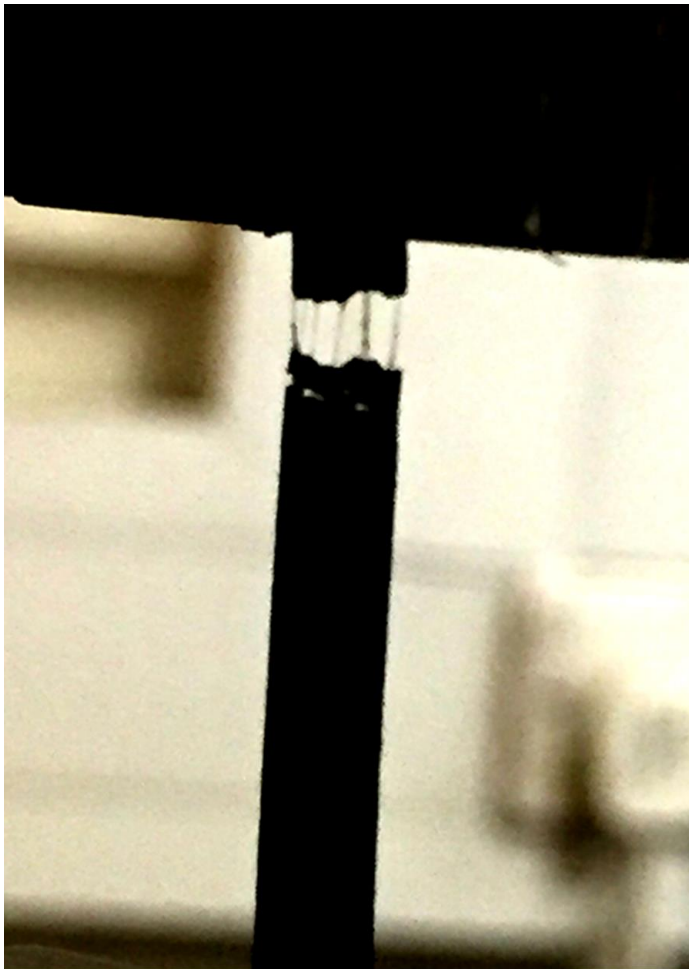


IMPROVING THE SENSITIVITY TO STRAIN

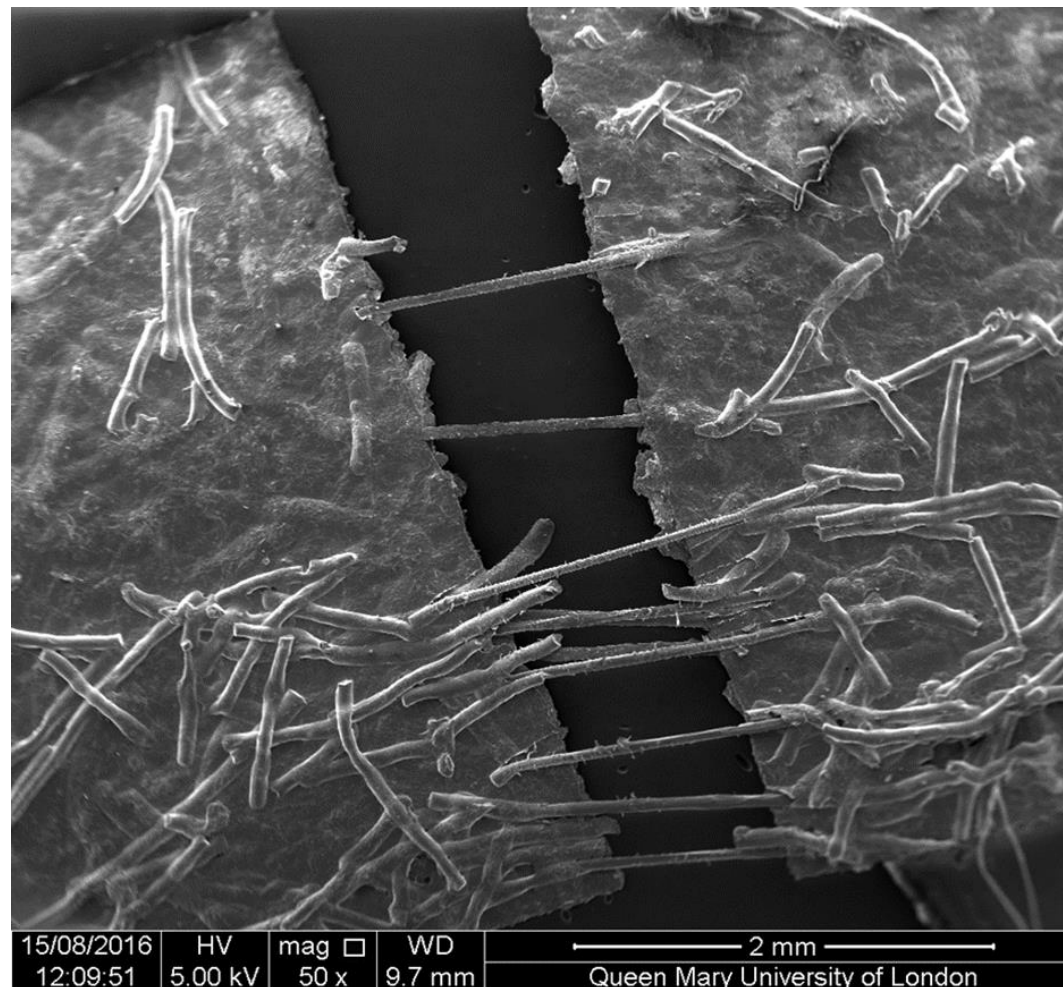
A higher strain % may also generate higher sensitivity.



CYCLIC TEST - 50% SPANDEX AFTER CRACKING SHOWS HIGHEST SENSITIVITY

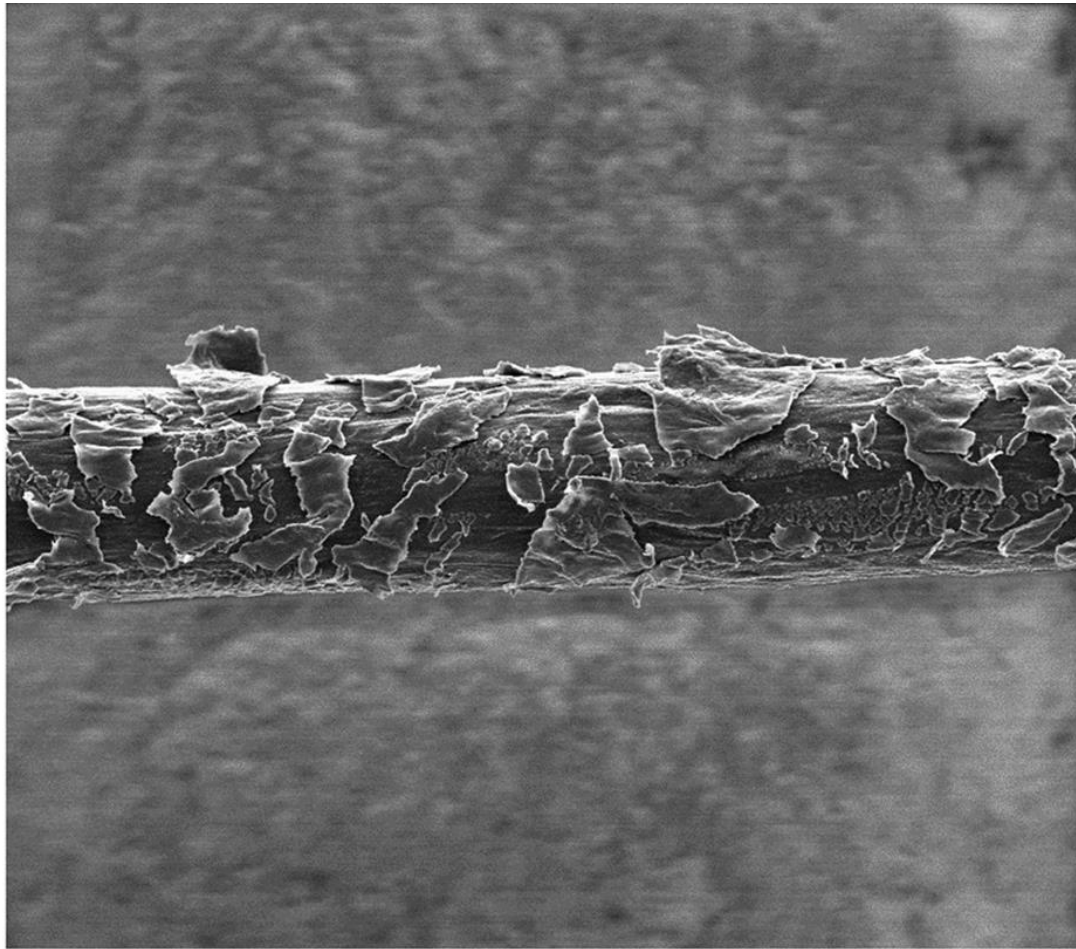


SEM of a cracked film

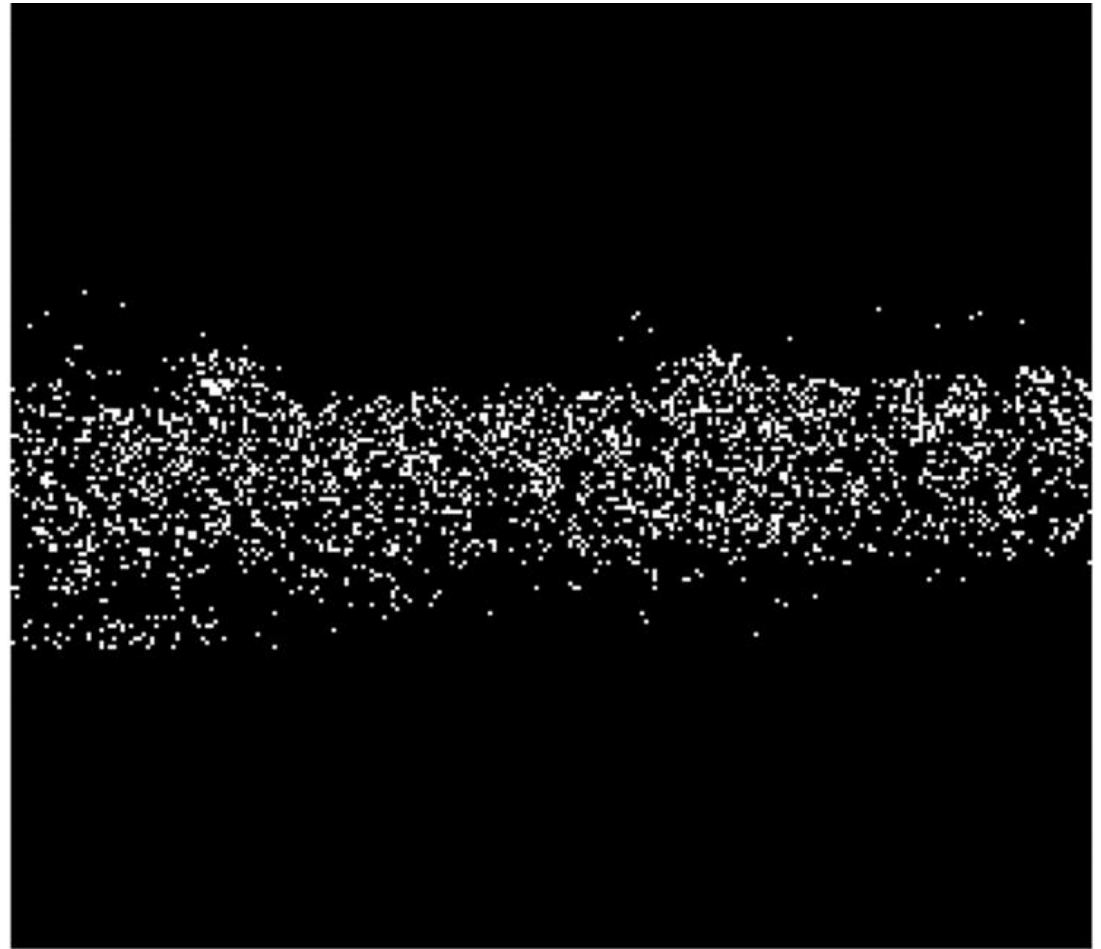


SEM

EDX – NITROGEN (FROM SPANDEX)



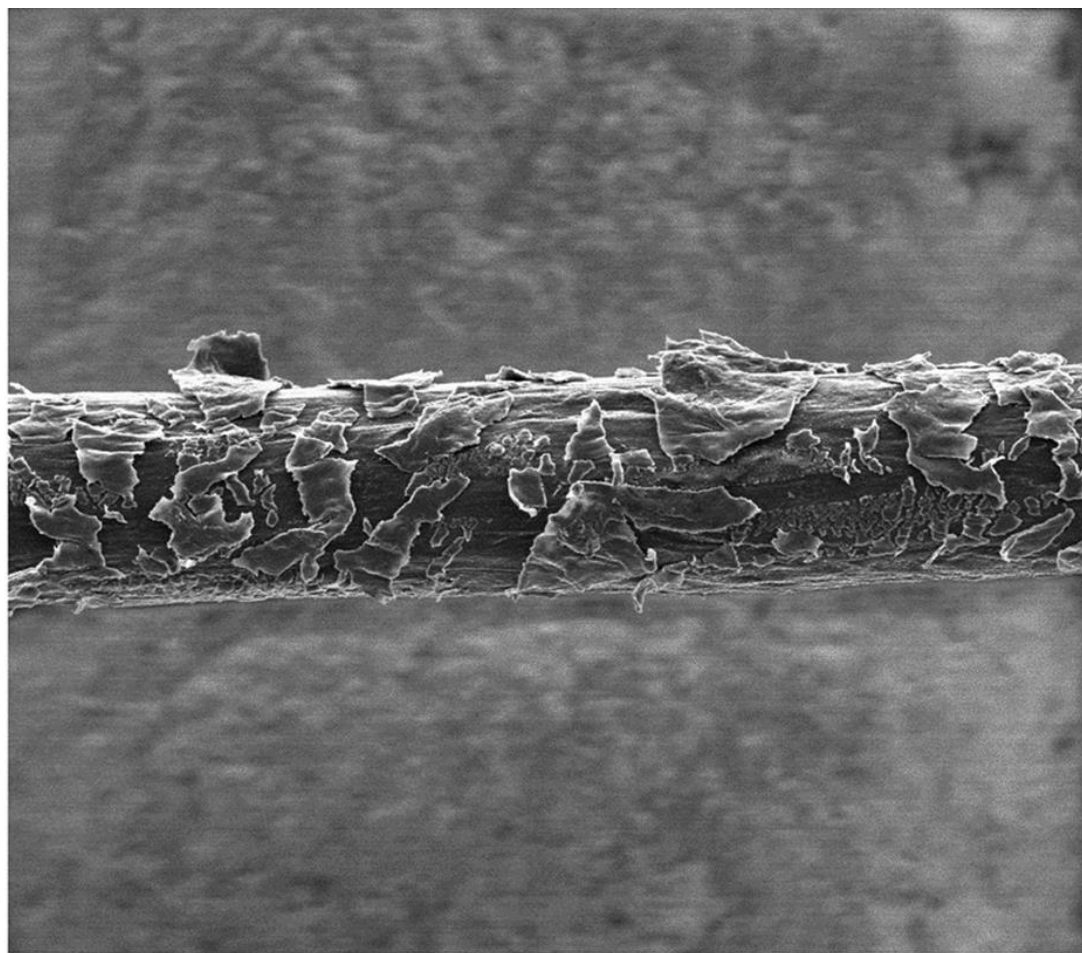
100µm Electron Image 1



100µm N Ka1_2

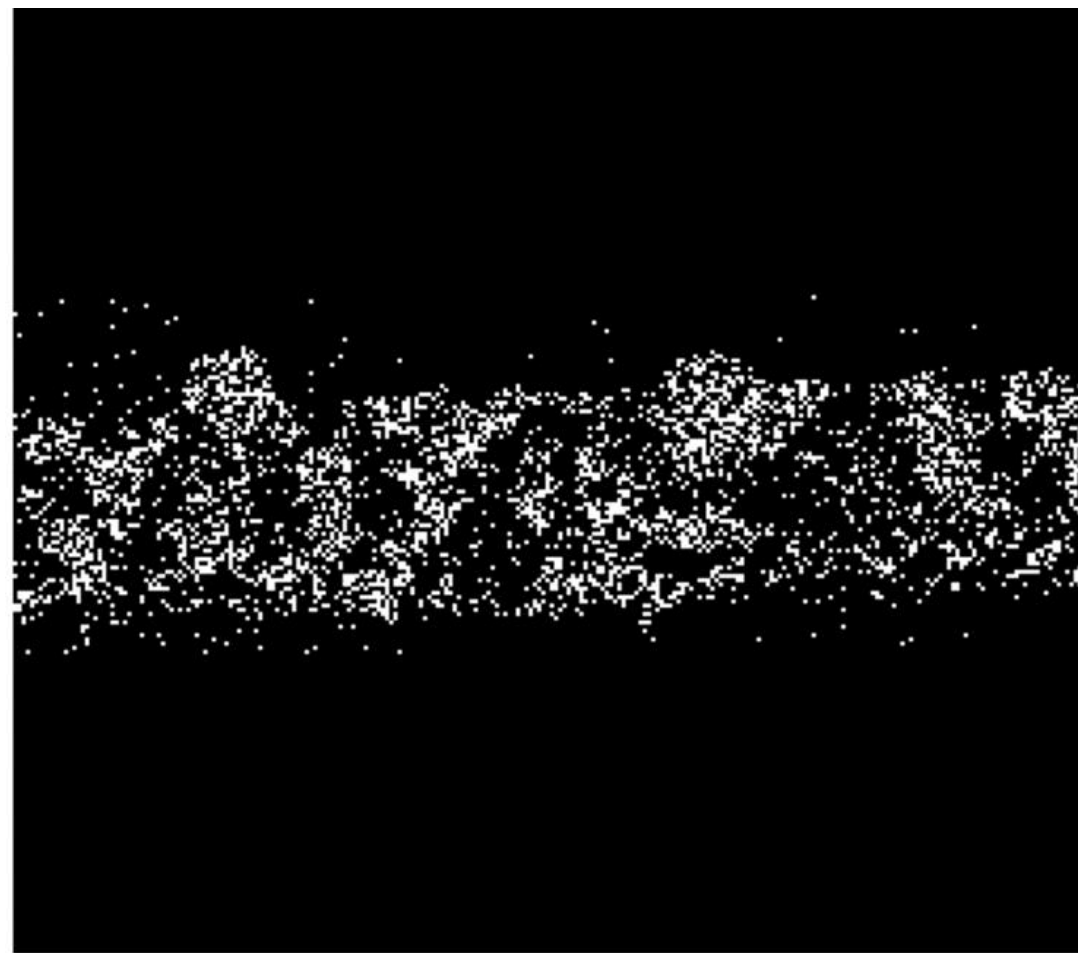
SEM

EDX – **SULPHUR** (FROM PEDOT:PSS)



100µm

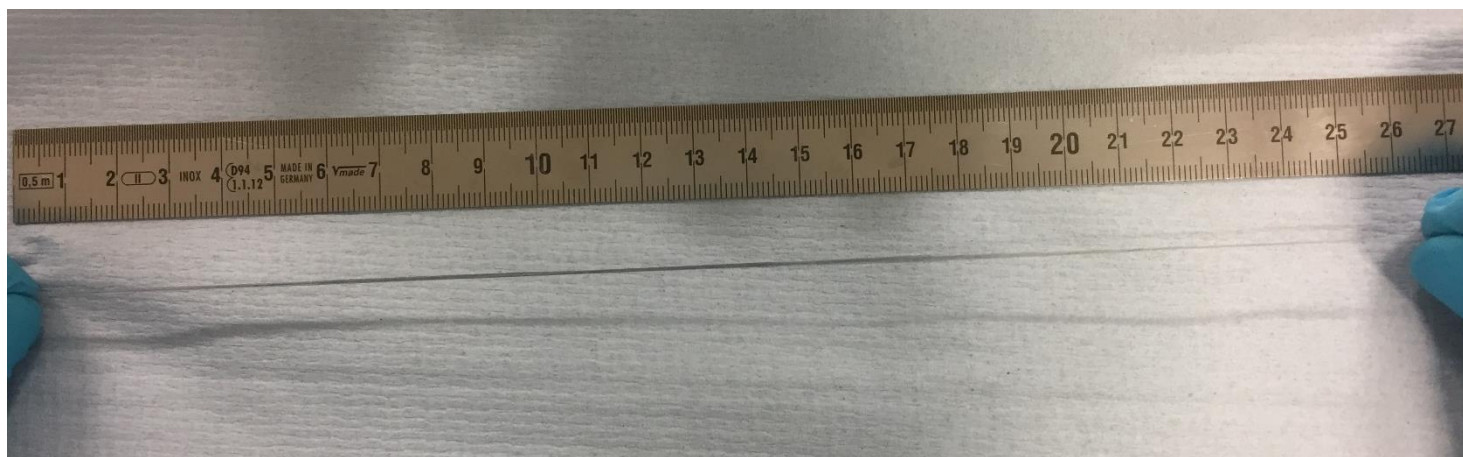
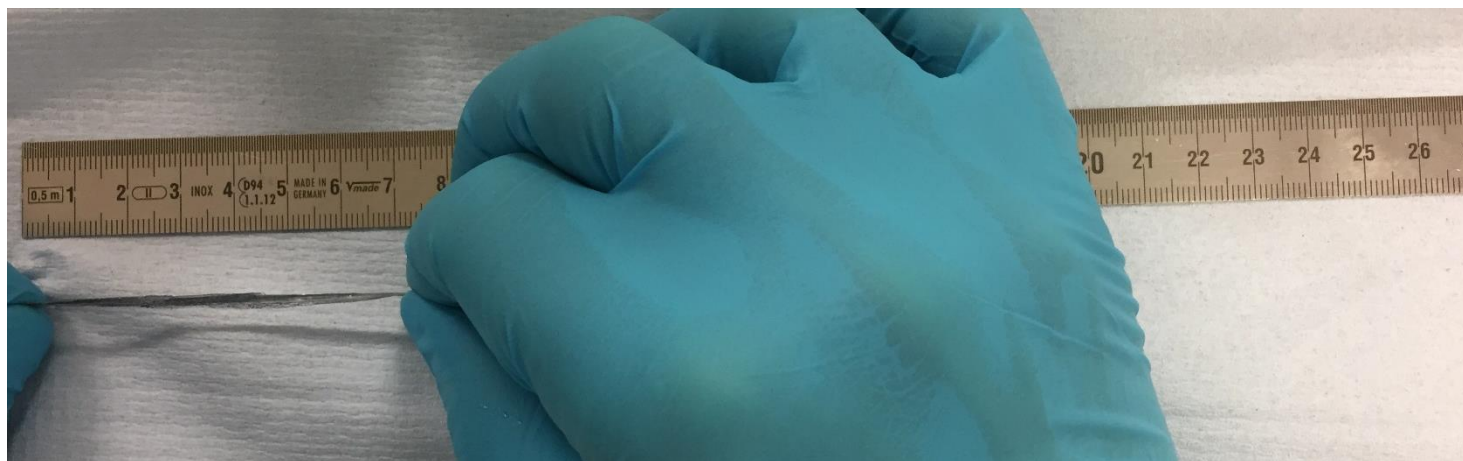
Electron Image 1



100µm

S Kα1

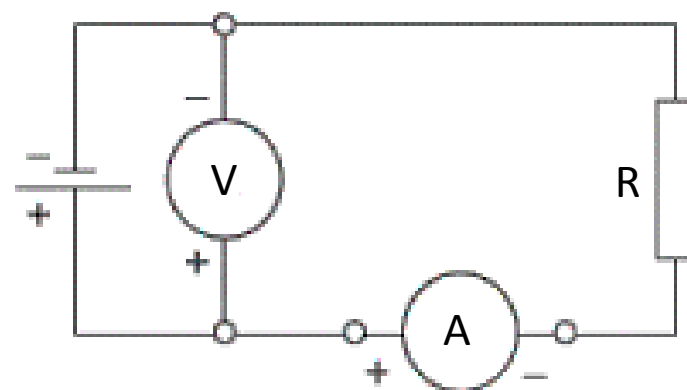
NEW DEVICE CONCEPT: SPANDEX FIBRE COATED WITH PEDOT:PSS



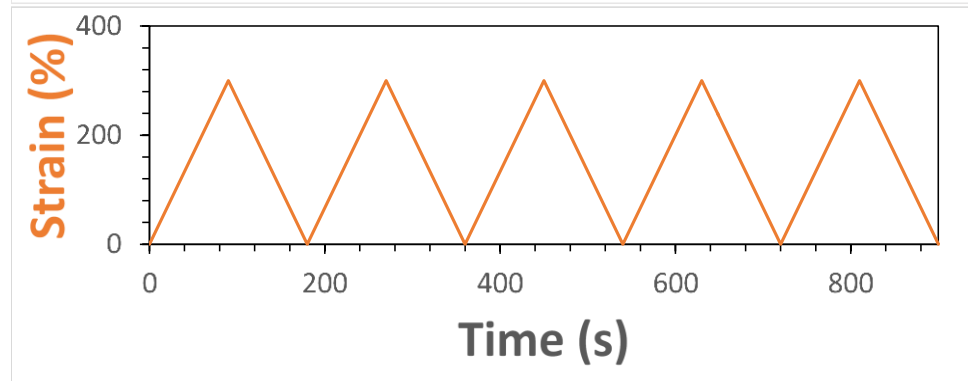
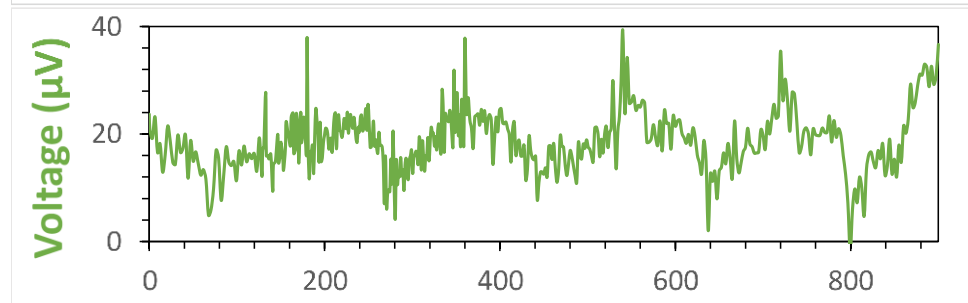
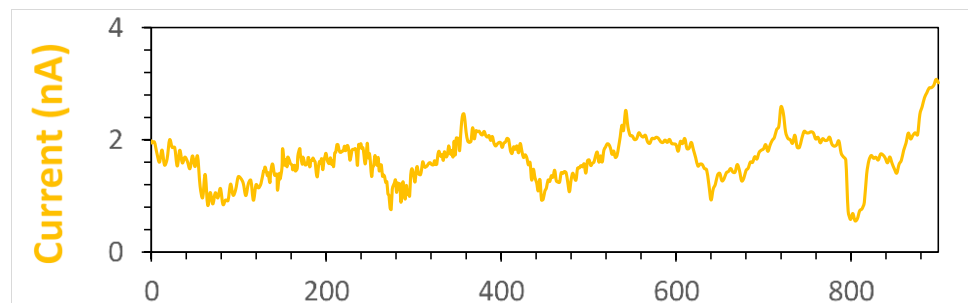
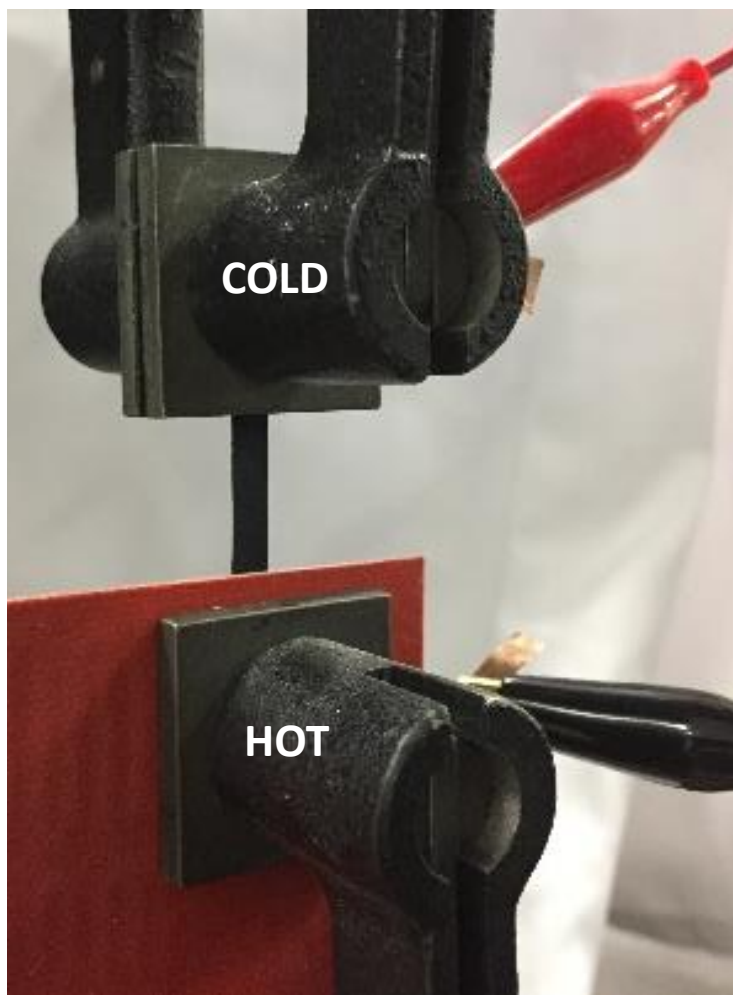
SELF-POWERED STRAIN SENSOR

PROVE OF CONCEPT

$\Delta T \sim 10^\circ\text{C}$
TEMPERATURE GRADIENT
CREATES A VOLTAGE
THAT POWERS THE DEVICE.



10 M Ω LOAD



Acknowledgments

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