Giant ‘Dry’ Actuation of PEDOT:PSS Thin Films

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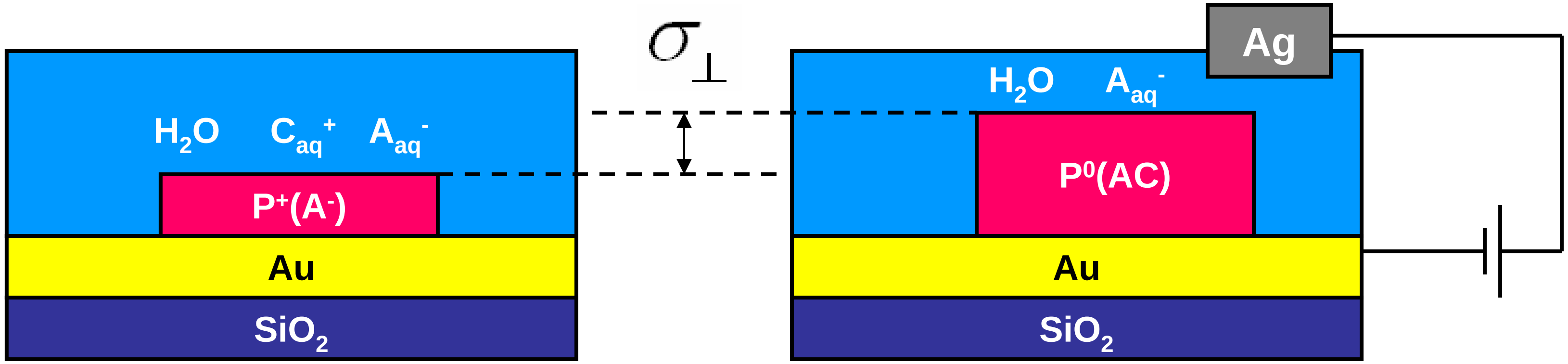
Conjugated Polymer Actuators

Two compartments: film + electrolyte

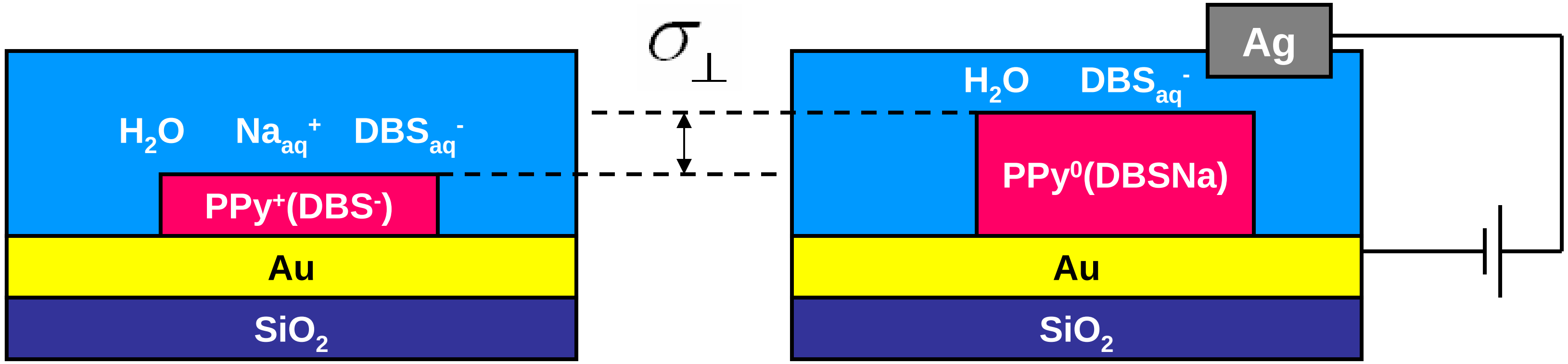


P^+	Conjugated Polymer
A^-	Anion
C^+	Cation
Electrolyte	Ions reservoir
$\sigma_\perp$ first cycle	Relative actuations
$\sigma_\perp$ normal cycle	

$$P^+(A^-) + C^+ + e^- \leftrightarrow P(AC)$$

Conjugated Polymer Actuators

Two compartments: film + electrolyte



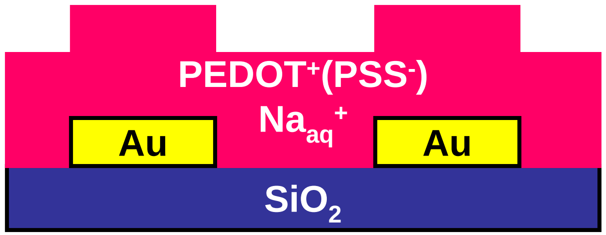
P^+	PPy^+ (polypyrrole)
A^-	DBS^- (dodecylbenzenesulfonate)
C^+	Na^+
Electrolyte	H_2O
$\sigma_\perp$ first cycle	125%
$\sigma_\perp$ normal cycle	40%

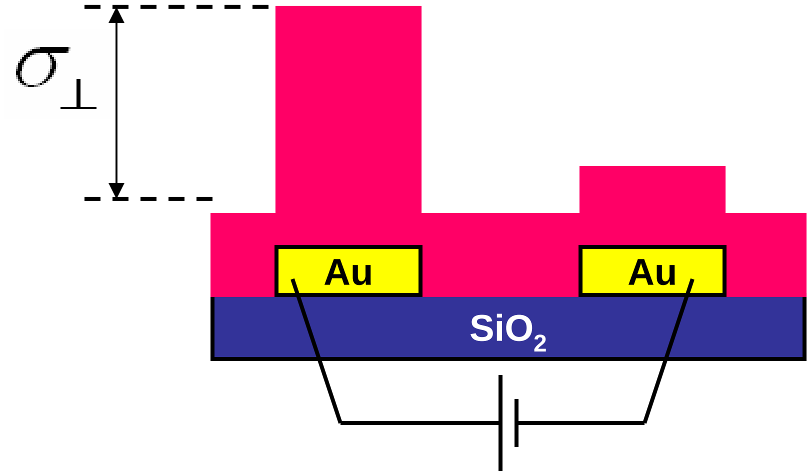
$$PPy^+(DBS^-) + Na^+ + e^- \leftrightarrow PPy(DBS\ Na)$$

E. Smela and N. Gadegaard, Adv. Mater. **1999**, *11*, 953

Here: PEDOT:PSS thin films

One compartment: thin film !

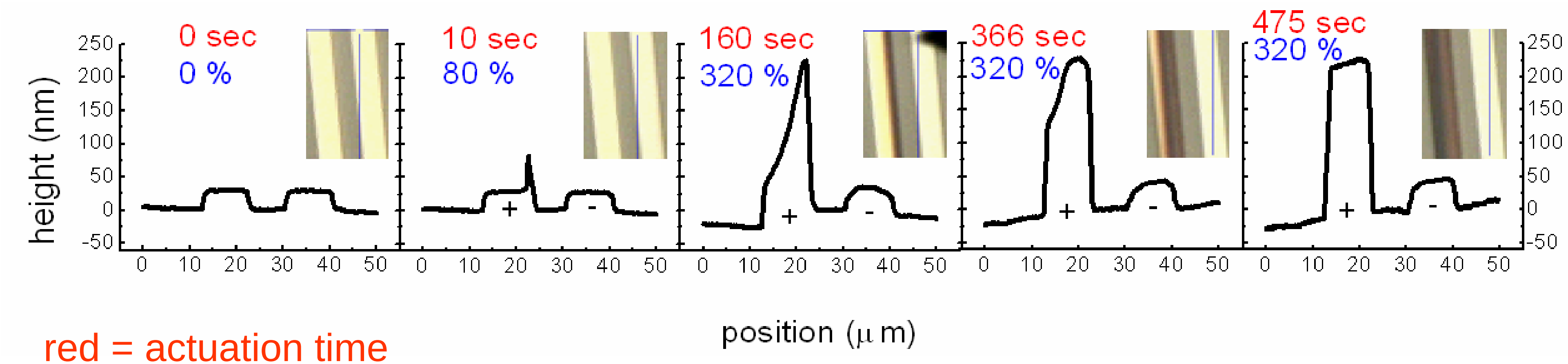




P^+	$PEDOT^+$
A^-	PSS^-
C^+	**Na^+ (ppm's)**
Electrolyte	**None**

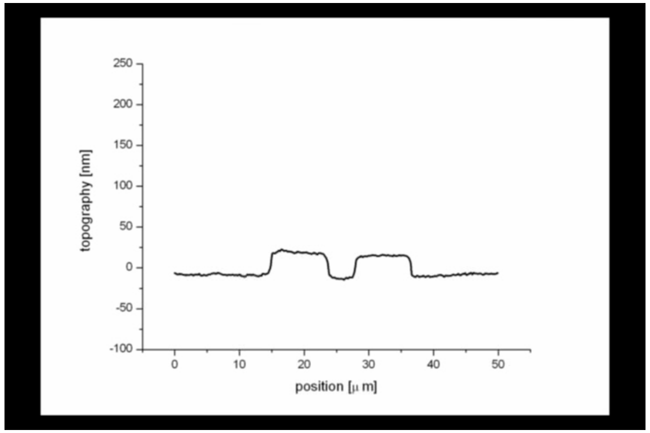
Topography + Color Changes versus time

35% water in air

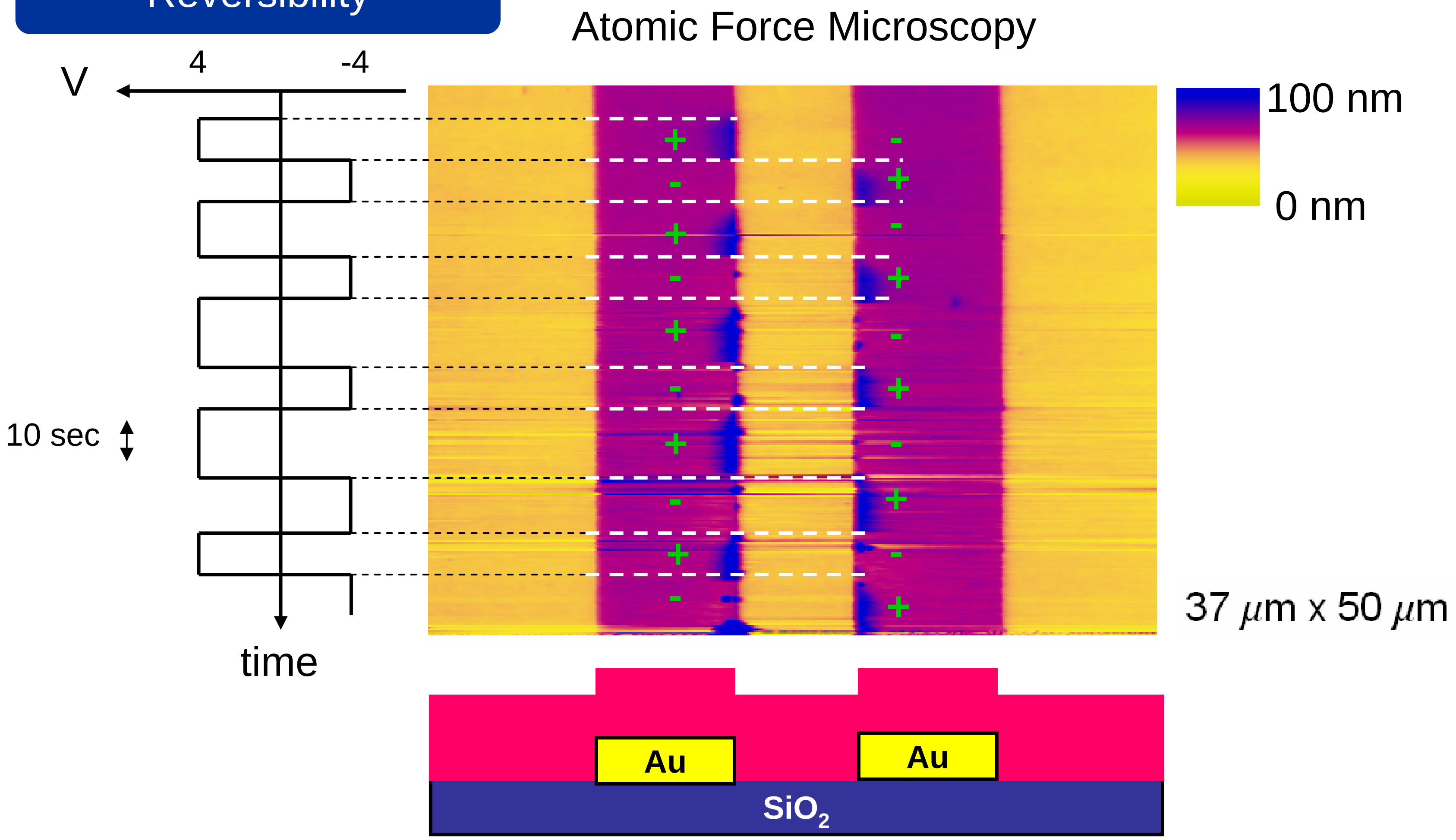


red = actuation time
blue = actuation rate

Color changing -> saturation



Reversibility



actuation time (cycles)	10 sec (10)	160 sec (10)	366 sec (4)	475 sec (2)
optical	*no color changing*	*color reversible*	*color reversible*	*color reversible*
topography	*fully reversible*	*partially reversible*	*hardly reversible*	*hardly reversible*

Summary

Several questions remain:

a) Moving or Swelling of materials?

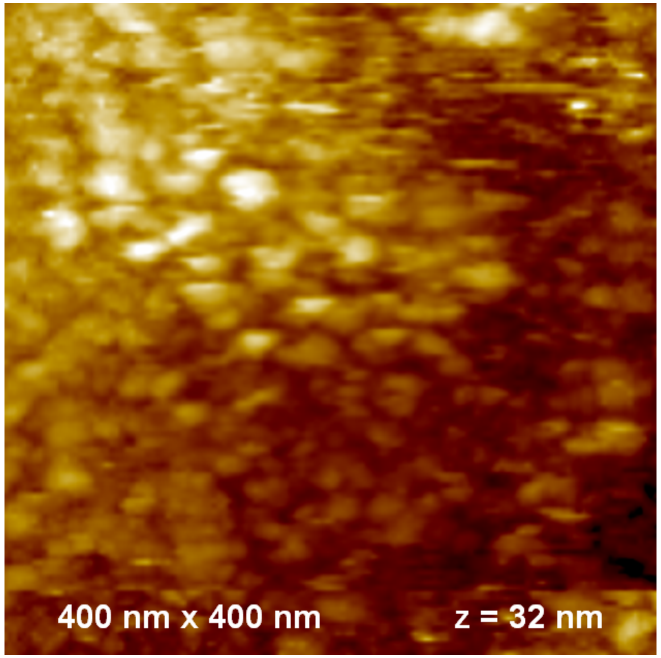
b) Electrochemical reactions and role of H_2O?

c) Influence of other parameters?

Surface changing in depletion area

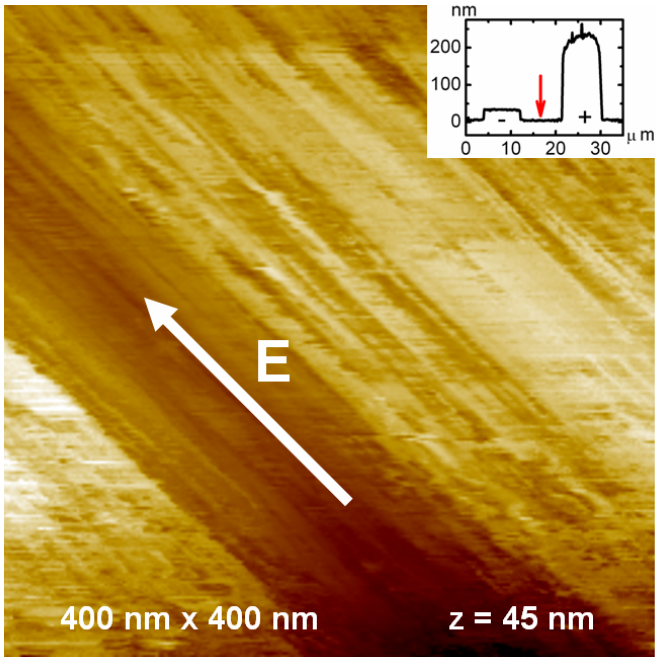
Scanning Tunneling Microscope pictures

pristine



Bias = 0.5 V
Integral gain = 0.6
Proportional gain = 5
Current setpoint = 500 fA

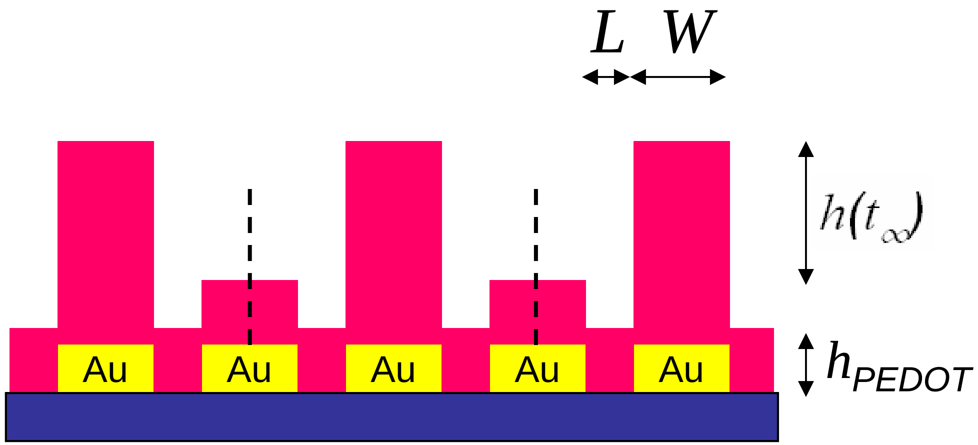
after field



Bias = 1.5 V
Integral gain = 2
Proportional gain = 4
Current setpoint = 100 fA

Moving or Swelling of materials?
Fibrous lines indicate Motion of material (transport and/or alignment of PSS chains)

Volume conservation?



$$h(t_\infty) = h(t_0) + (\frac{2L}{W} + 1)h_{PEDOT}$$

L (µm)	$h(t_\infty)$ (nm)	
	Experiments	Calculated
4	229	138-156
10	228	210-240
20	229	330-380

← swelling (row L = 4)

← does not work (row L = 20)

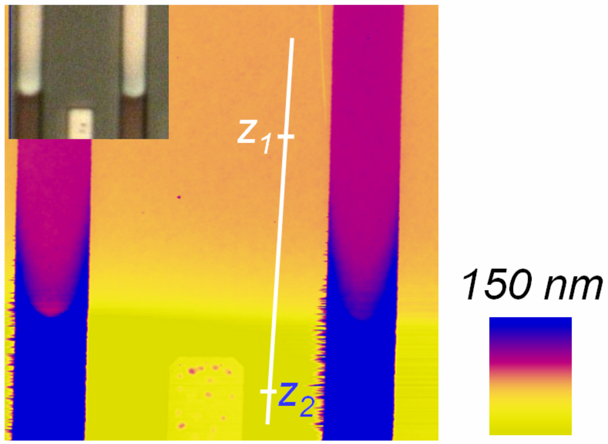
Hypothesis: PEDOT is the limiting factor

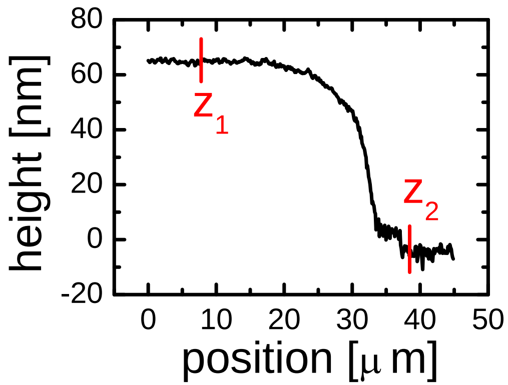
PEDOT available not only responsible of volume change -> swelling

Combination of Movement and Swelling

Depletion and thickness dependence

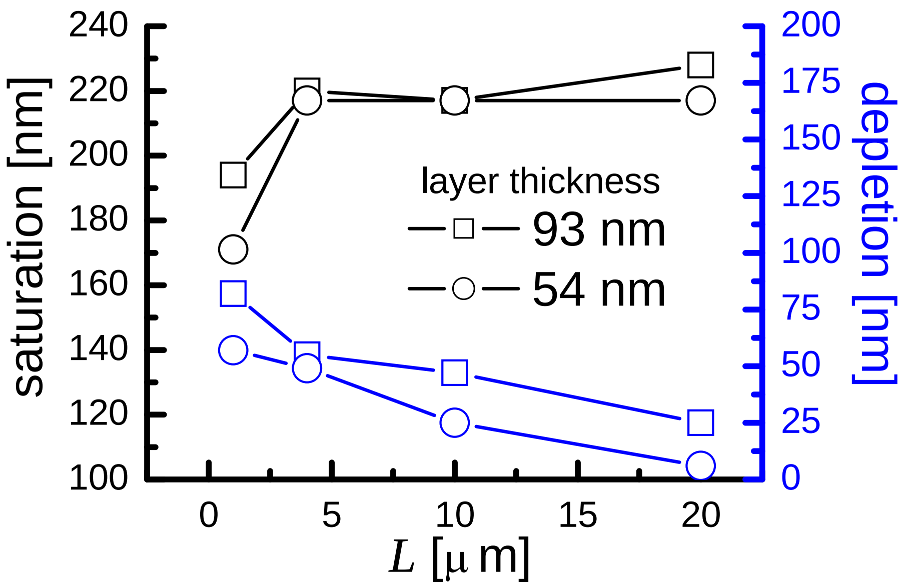
Atomic Force Microscopy





depletion = $|z_1 - z_2|$

38% water in air



For channels < 4μm, somewhat less increase in height -> Swelling present

For channels ≥ 4μm, saturation independent of initial thickness-> Swelling present

Summary

Several questions remain:

a) Moving or Swelling of materials?

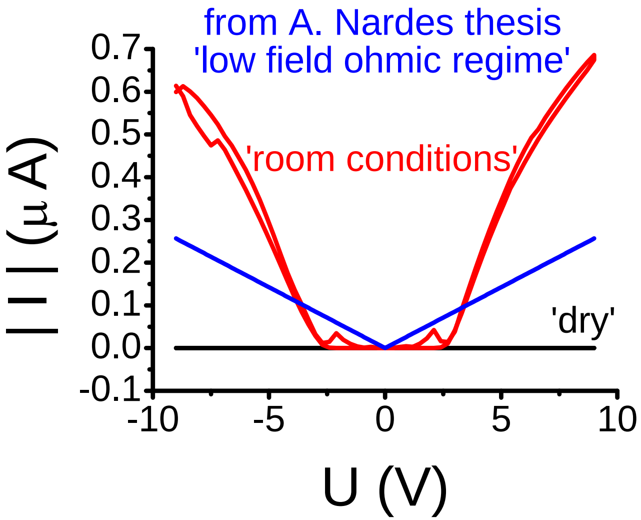
b) Electrochemical reactions and role of H_2O?

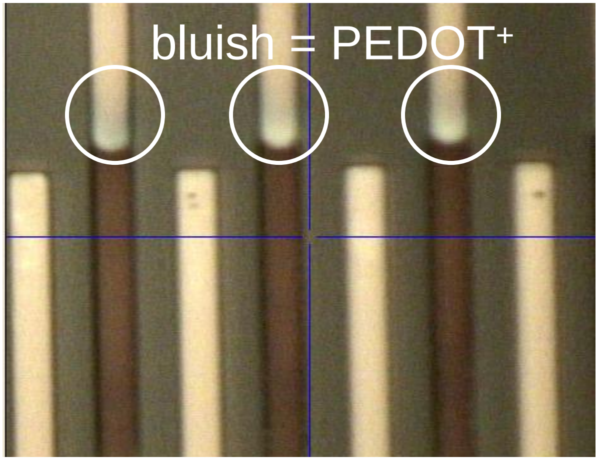
c) Influence of other parameters?

Ionic current

Clues for RedOx reactions:

- *bumps in IV curves*
- *strong effect of H_2O*
- *color changing.*





U > 3V fast increase of conductivity, ionic?
The actuation should stop when ion movement stops.

Possible reactions

Possible redox reactions:

Anode

$PSS^- \rightarrow PSS_{dark}? + e^-$

Cathode

$PEDOT^+ + e- \rightarrow PEDOT_{blue}$
$PEDOT_{blue} + H^+ \rightarrow PEDOTH^+_{colorless}$

Possible swelling due to osmotic effect

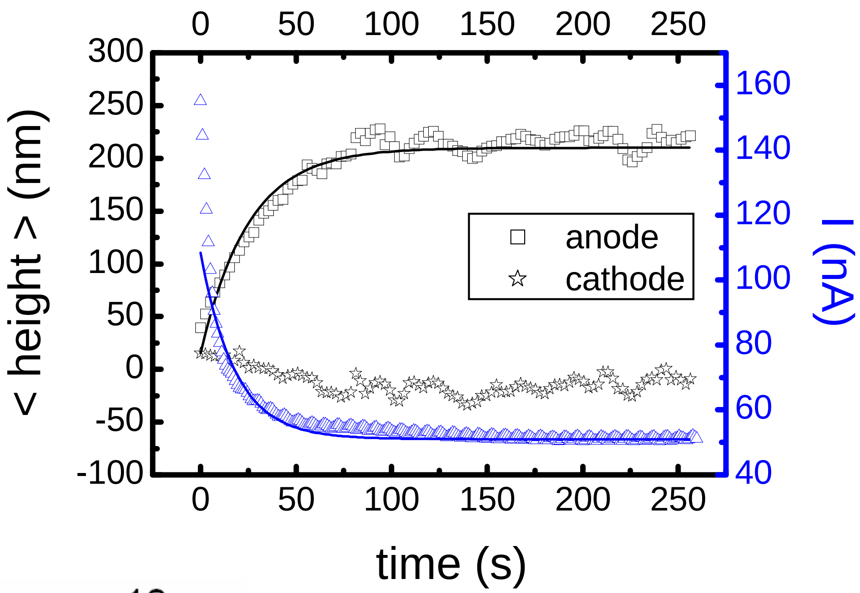
Quantitative analysis

$$I_i = I_{i0} \exp(-\frac{t}{\tau}) + I_{e^-}$$

Assume only ions contribute to V and I_i ($I_e = 0$):

$$V(t_\infty) = \frac{V_c.\tau.I_{i0}}{q} = h.W.L$$

where h is the averaged height, W and L are the width and length of the electrode.



$\tau_{current}$ = 18 sec

τ_{anode} = 25 sec

$$h(t_\infty) = \frac{V_c.\tau.I_{i0}}{q.W.L}$$

Analysis of the current to calculate the ion movement is hampered by the changing ohmic contribution to the current.

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Different PSS concentration

PEDOT :PSS
1 :x

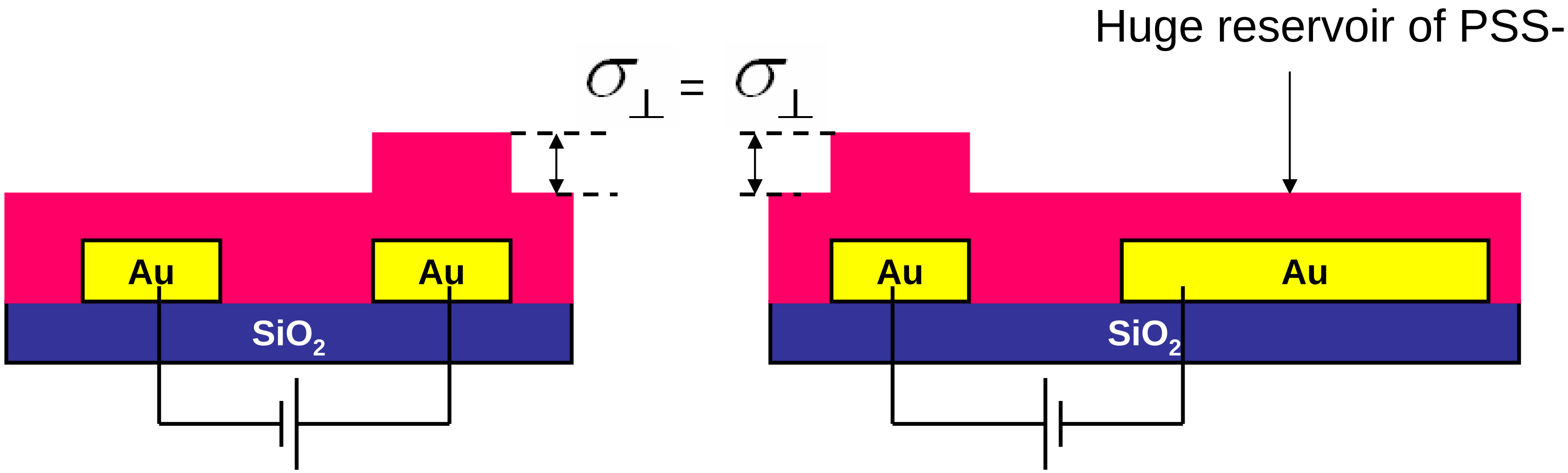
x	$\sigma_{\perp}$ first cycle
1	0 %
6	381 %
20	130 %

130 x 20 / 6 = 430 % ~ 381 %

Valid hypothesis: PEDOT is the limiting factor.

Other experiment

Elongation on Asymmetric fingers = Elongation on Symmetric fingers



The expectation of a large cathode is to increase the amount of mobile available PSS^-.
The saturation does not depend on the amount of PSS! But PEDOT.

Conclusions

We know for sure:

PEDOT:PSS thin films can be vertically actuated with 4V when moisture > 20%

Vertical actuation = 380% at first cycle

> 120% in normal cycle in a reversible way

PEDOT is the limiting factor

Actuation rate depends on PEDOT:PSS ratio

The total volume of material is not perfectly conserved -> swelling contribution

Next experiments:

Study the moisture effect in glovebox

Thanks to

nanoned

TU/e

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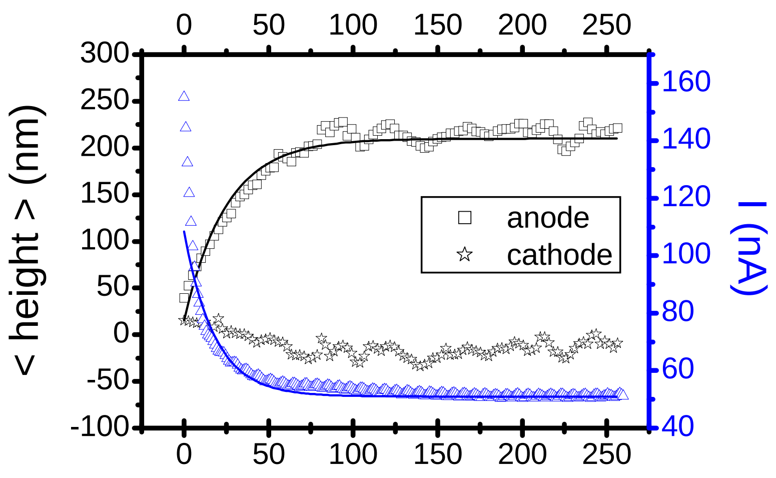
Bea Langeveld
René Janssen

PHILIPS

Margreet de Kok
Paul van Hal

Quantitative analysis

$$I_i = I_{i0}\exp(-\frac{t}{\tau}) + I_{e^-}$$



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$$h(t_\infty) = \frac{V_c.\tau.I_{i0}}{q.W.L}$$

L (μm)	$h_{experiment}(t_\infty)$ (nm)	$N_{PSS} = \frac{1}{e}\int_0^{+\infty}(\frac{dQ}{dt} - \frac{UWt\sigma_{PEDOT:PSS//}}{L})dt$	V_c volume per transported charge (Å^3)	$h_{calculated}(t_\infty)$ (nm)
4	229	$3.95.10^{15}$	171	229
10	228	$1.32.10^{16}$	171	86
20	229	$4.12.10^{15}$	171	229

same batch/device (rows above)

The volume per transported charge is smaller than one single PSS.
Therefore other contributions should be taken into account -> swelling