Towards macroscopic modeling of electro-thermo-mechanical couplings in PEDOT/PSSS: Modeling of moisture absorption kinetics

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ABSTRACT

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Lyazzat Zhanshayeva

Organic conducting polymer, poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT: PSS), is widely recognized for its electro-actuation mechanism and is used in flexible electronics. Its high potential as actuator is based on a strong coupling between chemical, mechanical and electrical properties which directly depends on external stimuli. There is no model today to describe the interplay between moisture absorption, mechanical expansion and electrical stimulus. Elucidating the role of each component in the effective actuation properties is needed to further optimize and tailor such materials. The objective of this thesis is to develop a macroscopic model to describe water sorption kinetics of the PEDOT:PSS film. We used gravimetric analysis of pure PEDOT:PSS film of three different thicknesses to investigate absorption kinetics over a broad range of temperatures and relative humidities. Our results revealed that the moisture uptake of PEDOT:PSS film does not follow Fickian diffusion law due to the retained amount of water after desorption process. We used an existing diffusion-reaction model to describe this behavior, and COMSOL Multiphysics and MATLAB softwares to implement it. We observed that the generic model we used in our work could predict polymer behavior with 95% accuracy. However, our model was not able to properly represent the data at very high relative humidity at low temperature, which was attributed to the excessive swelling of the film. Also, we examined a relation between the moisture content of PEDOT:PSS and its mechanical strain and electrical conductivity. The results presented here are
the first step towards a general multiphysics electro-thermo-mechanical description of PEDOT:PSS based actuators.
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Chapter 1

Introduction

1.1 Motivation and Objectives

Due to their lightweight, flexibility, and ease of processability, organic conductive polymers found its wide application in electronic devices [6]. The most successful polymer among them is poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonic acid) (PEDOT:PSS). Its tunable electrical properties (conductivity can reach 4000 S/cm) by using proper treatment [7], low-voltage driven actuation mechanism [8] and its recently revealed self-healing effect [9], make PEDOT:PSS a good candidate for transparent electrodes, organic solar cells, organic light-emitting diodes, wearable textiles, artificial muscles, sensors, and actuators [6, 8, 10, 11].

PEDOT: PSS has a strong coupling between chemical, mechanical and electrical behavior which directly depends on environmental conditions. Due to the hygroscopic nature of the PSS phase, a PEDOT:PSS polymer network can absorb and desorp wa-ter molecules, when exposed to an external stimuli. Therefore, polymer film can experience dimensional and microstructural changes which leads to the actuation mechanism and affects mechanical and electrical properties. Today the phenomenological aspects of the PEDOT:PSS actuation are well known, however a generic model to describe its multiphysics response is missing. The development of such a model needs to make explicit coupling between electrical /mechanical /diffusing and thermal behavior.

Previous studies have focused on finding the physical properties of PEDOT:PSS
affected by different external stimuli. A decrease in Youngs modulus and an increase in electrical resistivity as a function of moisture uptake and a change of both stress/strain distribution were observed \[12, 13\]. However, little attention has been dedicated to water sorption properties and to develop a model to describe the underlying mechanism behind. There has been no work done in literature to describe the absorption-desorption behavior of PEDOT:PSS and hence, there is no existing computational algorithm to predict it. Such a complete multiphysics coupling will induce many parameters that have been neglected in previous works.

The objective of this thesis is to focus on the water sorption kinetics of the PEDOT:PSS and its relationship to the electrical properties. We want to find key properties of PEDOT:PSS using the experiments and to provide systematic data on key parameters involved in modeling approach through numerical simulations on COMSOL and MATLAB softwares.

1.2 Literature review

1.2.1 Conducting polymers

Conducting polymer is an organic material that conducts electricity. It has a conjugated polymer chain: an alternating single and double bonds. The general electronic configuration of six carbon atoms is \(1s^22s^22p^2\), 2 electrons in first orbital

Figure 1.1: a) Carbon atom structure, b) Electrons in a ground state and c) in an excited state
and other 4 electrons in the second (Figure 1.1a) [14]. In a ground state, it is \(1s^22s^22p_x^22p_y^12p_z^0\) (Figure 1.1b). In an excited state, one electron from \(2s\) fills \(2p_z\), which results in \(sp^2\) hybridization (Figure 1.1c). "Mixed" \(s\) and two \(p\) orbitals give three \(sp^2\) orbitals and one unhybridized \(p\) orbital. Each of them contains one electron. Two of the \(sp^2\) orbitals form a covalent \(\sigma\)-bond between two adjacent carbon atoms \((sp^2-sp^2)\) and the remaining one bonds with hydrogen or the other group, forming a covalent bond as well [15]. With one carbon atom \(2p_z^1\) orbital overlaps with another unhybridized \(p_z\) orbital of neighbor carbon. It forms one \(\pi\)-bond, whose electrons can be easily delocalized [15]. These electrons are known as conduction electrons and can easily move in the polymer chain since they do not belong to a single atom but to a group of atoms. According to Peierls instability [16], the energy gap between the filled valence band and the unoccupied valence band in the \(\sigma\)-bond is large, which explains the insulating property, while in the \(\pi\)-bond it is small, leading to semiconducting behavior.

It is possible to enhance the electrical conductivity of conducting polymers with proper chemical doping, but it is beyond the scope of this thesis. Only pristine PEDOT:PSS polymer films were used in this work.

1.2.2 Why PEDOT:PSS?

The first discovered conducting polymer in 1980s, doped polyacetylene, was not successful as a use could not be found for it because of its instability and difficult processability [17]. Later on, polythiophene derivative, poly(3,4-ethylenedioxythiophene) (PEDOT), was found to be stable in an environment with unchanged electrical properties [4]. It had advantages over other organic polymers such as high electrical conductivity and optical transparency in thin films. However, there was a main limitation of ethylenedioxythiophene (EDOT) monomers: insolubility in common solvents [18]. This problem was solved by using poly(styrene sulfonic acid) (PSS) as a counter
ion to balance the charges during the polymerization process \[18\]. It resulted in the aqueous dispersion of PEDOT:PSS producible in an industrial scale, with good film forming properties, relatively good stability and high conductivity. Dispersion of PEDOT:PSS can be used in different deposition techniques and depending on the technique, additivities nature, doping level and size of PEDOT and PSS segregated phases (varies from 3-10 nm), films with different characteristics can be formed.

Recent studies revealed PEDOT:PSS’s self-healing property \[9\], which makes it the most promising conductive polymer today. There are two companies which provide aqueous dispersion of PEDOT:PSS: Haraeus (formerly Baytron, Germany) and Agva Gevaert (Belgium). Figure 1.3 illustrates applications of commercially available PEDOT:PSS from Haraeus: which is used in transparent electrodes, OLED displays, organic solar cells to replace ITO, wearable electronics and bioelectronics.

In this work, Haraeus Clevios PEDOT:PSS of grade PH1000 was used.

1.2.3 Actuation mechanism

PEDOT:PSS have attracted considerable research interest as an electro-mechanical actuator. It is able to transform thermal, chemical and electrical energy into me-
Figure 1.3: Microstructure of PEDOT:PSS. a) Synthesis of PEDOT oligomers on PSS chain, b) Development of gel particles, c) Film with PEDOT:PSS-rich (blue) and PSS-rich (grey) regions, d) Formed crystallites [2], e) Room temperature state and f) High temperature state [3]

Mechanical motion controlled by external stimuli such as temperature, humidity and electrical voltage.

To understand the actuation mechanism, it is essential to elucidate the microstructure of PEDOT:PSS. PEDOT oligomers synthesis on a PSS template (Figure 1.3a) forming gel particles which resemble elongated pancakes (Figure 1.3b). The resulting PEDOT:PSS film is illustrated in Figure 1.3c, where blue is PEDOT:PSS-rich and grey is PSS-rich region [2]. Simply speaking, PEDOT:PSS grain is made from short PEDOT oligomers attached to the long PSS chain. The outstanding electrical and optical properties come from positively charged PEDOT, while the role of PSS is to disperse and stabilize PEDOT in solvents. Therefore, the more structured and closer the spacing of PEDOT oligomers to each other on polymer chain, the better its electrical charge transport.

The molecular formula of PEDOT:PSS is assumed to be \((C_6H_6O_2S)_m(C_8H_8O_3S)_n\) (Figure 1.4) [3]. Molecular weights of monomers are 142 and 184, respectively.

The mechanism of actuation comes from the hygroscopic nature of PSS and the ability of PEDOT:PSS to operate under low voltages (0-10 V) [3]. PSS is able to absorb moisture from the surrounding environment. The chemical reaction of pro-
Figure 1.4: Chemical structure of PEDOT:PSS

\[ H_2O + PSS(HSO_3) + H_2O \rightarrow H_3O^+ + PSS(SO_3)^- \] (1.1)

Absorbed water molecules increase the distance between PEDOT:PSS grains, causing a volume increase. When an electric current is applied, a Joule effect results in in-the-volume heat generation and consequently temperature changes. It results in the release of previously absorbed water molecules in micro scale, which translates into geometrical shrinking at the macroscale. Therefore, water sorption can be controlled with an electric field. It should be noted that PEDOT:PSS operates in air without any electrolyte solution unlike polymers driven by electrochemical doping.

Okuzaki et al. studied actuation of PEDOT:PSS at room temperature and in humidity by applying 10 V [20]. Figure 1.5 illustrates that the film undergoes a 1.2mm contraction, which corresponds to 2.4% strain, and comes back to its initial state once the electric field is turned off, showing the reversible electro-mechanical response. Surface temperature of the film was increased due to the Joule effect and decreased to its initial value. It led to moisture desorption and subsequent uptake afterwards.

The change in the dimension of PEDOT:PSS is directly related to its water con-
Figure 1.5: Time profiles of strain, electric current, temperature and relative humidity of free standing PEDOT:PSS film under 10V

Figure 1.6: Stress-strain diagram at different %RH
tent, which in turn affects mechanical stability and electrical properties. Lang et al. investigated the dependence of mechanical properties on the moisture content of the environment [12]. Figure 1.6 illustrates the behavior of free-standing PEDOT:PSS film, which is changing from brittle at RH=23% (E=0.9GPa) to ductile at RH=55% (2.8GPa). Kus et al. reported a linear increase in electrical resistance up to RH=80% and an abrupt decrease after that value, due to swelling of the polymer at high relative humidity levels [13].

These results show that it is important to understand the water uptake mechanism to be able to control electro-actuation of PEDOT:PSS and to employ it for applications such as soft actuators.

1.3 Work frame

The behavior of actuating conductive polymers can be explained through the multiple physical models mentioned before. The main physics to consider are (i) water absorption of polymer defined by concentration, (ii) mechanics defined by strain, dis-
placement and stress, (iii) the electrical part defined by voltage, electrical flux and current, (iv) the thermal part defined by temperature. All state variables are functions of $x$ and $t$, where $x$ is a point on the domain and $t$ is a time. This coupled system would be able to fully define the state at each point of domain, by that to predict the electro-actuation of polymer.

In this work, I elucidate mainly the water diffusion part, provide with a generic model and show how it affects to other physics. Including other physics in the model is not part of this thesis, but of the big picture which will be a continuation of this work.

This thesis is organized as follows. Chapter 2 describes methodology used for the experimental part of this work, with a detailed explanation of PEDOT:PSS film preparation and the measurement technologies used. Gravimetric analysis can be used to understand the absorption-desorption mechanism by monitoring the moisture uptake of the film from a macroscopic point of view. The resulting curves can reveal the classical sorption behavior (Fickian) of the diffusion of water molecules or non-classical complex mechanism. In Chapter 3, we provide systematic data from gravimetric analysis on key parameters involved in the modeling approach, introduce water sorption models formulation, numerical implementation in COMSOL Multiphysics and MATLAB and results from the computational simulation. In addition, observed swelling behavior during both experiments and simulation will be explained. Chapter 4 is about an effect of moisture uptake of conducting polymers on electrical response. After understanding the diffusion and reaction process happening in the polymer chain with water absorption-desorption, it is possible to correlate water content and changes in electrical conductivity. A summary of the work done, along with future research directions are given in Chapter 5.
Chapter 2

Experimental Methodology

2.1 Material preparation

An aqueous PEDOT:PSS dispersion \( (Clevios^{TM} \) PH1000) was purchased from HC Starck, Inc. PH1000 was chosen due to its high conductivity in comparison to other commercially available grades. It has a 1:2.5 w/w ratio of PEDOT to PSS. A drop casting technique was used to prepare pristine PEDOT:PSS film. A square petri dish with a size of 8.5 cm x 8.5 cm, covered with Teflon paper, was plasma treated to remove impurities and to maximize its contact with the fluid. An expanded Plasma Cleaner PDC-001 from Harrick Plasma was used at high power and 400 mTorr pressure for five minutes. Then, an adequate amount of the dispersion was poured into the dish and was cured in a fume hood for 48 hours at room temperature. Three sample thicknesses were considered: \( 2L = 15 \, \mu m \), \( 2L = 50 \, \mu m \) and \( 2L = 100 \, \mu m \). Thickness of the film was measured using a Digital Micrometer with 1\( \mu m \) accuracy. The drop casting method is known for ease of film preparation, but it is difficult to control thickness and film uniformity. Therefore, there was a 10\% variation of thickness in polymer film samples.

For gravimetric measurements, dried polymer films were cut into 7 mm by 7 mm squares with a \( CO_2 \) Universal Laser System PLS 6.75 to fit into equipment specifications and to ensure precise dimensions of each sample. Laser settings as follows are used: Speed 5.0\%, PPI 750, Z-Axis 4.00 mm, and Power 0.5\%, 1.5\% and 2\% depending on the thickness of the film.
For conductivity measurement tests, the film was cut into 10 mm by 20 mm rectangular specimens. To measure the strain of the film, samples of the size 2 mm by 2 mm were used.

### 2.2 Gravimetric test

An IGAsorp Dynamic Vapor Sorption (DVS) analyzer (Hiden Isochema) was used for the gravimetric measurements. Temperature and relative humidity of the isolated chamber were controlled while monitoring the mass uptake of the specimen with embedded 10 µg resolution microbalance. Polymer samples were placed on suspended stainless steel mesh inside the chamber, so both sides of the film were exposed to the same conditions. The tests were conducted at a constant temperature (26°C, 37°C, 50°C and 80°C) and relative humidity (30%, 60%, 80%). We performed a systematic conditioning of the film: the moisture content of the film is removed prior to humidity exposure by drying the sample inside the equipment till mass equilibrium is reached. Hence, tests were done on dry polymer films.

![Figure 2.1: Time profile of %RH to illustrate dynamics of DVS chamber at 26°C](image-url)
This instrument allows measuring mass uptake, $m(t)$, every 20 seconds, which is a relatively high rate. However, it is important to mention that a relative humidity (RH) increase in chamber is not a step increase and decrease as you can see in Figure 2.1. There is an initial overshoot followed by stabilization for 30% RH and 60% RH. For 80% RH, it takes a longer time to stabilize. These points are important to note as we will show later, that the dynamics of the chamber might in some situations be slow compared to the dynamics of water absorption by the film.

Test for each configuration (thickness, temperature, %RH) was repeated 3 times.

### 2.3 Electrical resistance measurement

An Agilent 4980A LCR meter, 20Hz to 2MHz, is used to measure the resistance of the film with a 4-probe method at 200 mV (DC). Connectors were fixed at $l_p=1\text{cm}$ distance in parallel for all resistance measurements and placed inside a Tenney Environmental Test Chamber, model T2RC, through its access port (Figure 2.2a). The clamped samples were fully exposed to the environment, as both temperature and %RH were prescribed to the steady state target values described in the previous section. However, the dynamics of the Tenney chamber is different from the dynamics

![Figure 2.2: a) Photo and b) schematic of the experimental setup used to measure resistance of PEDOT:PSS](image-url)
of the equipment used for gravimetric analysis. Therefore, the transient phase cannot be compared between films tested in both equipment. So, we decided to analyse the electrical properties only for fully stabilized films for which the transient phase is over.

Each sample (20 mm long by 10 mm wide) was initially dried for two hours inside and then at constant temperature was subjected to increasing %RH for one hour to reach full saturation, which was followed by drying. This time frame was enough for film saturation as it was found from gravimetric tests. Resistance (R) was measured over a frequency range from the 20Hz to 2MHz domain for full spectroscopy analysis.

The electrical resistivity of the sample was calculated using the equation:

$$\rho = \frac{Rwt}{l_p} \quad (2.1)$$

where R is the measured resistance, w is the width of the sample, t is the thickness of the sample and $l_p$ is the distance between the probes (Figure 2.1b). Conductivity can be found by:

$$\sigma = \frac{1}{\rho} \quad (2.2)$$

### 2.4 Swelling measurement

A change in thickness of PEDOT:PSS at 26°C, with relative humidity increase, was captured using a high resolution QImaging QICam CCD digital camera and Leica Achromatic Lens 5X inside the environmental chamber. The sample is placed on a stand with a notch to make moisture absorption uniform from both sides of the film. At a constant temperature, the %RH of the chamber was set to 30% RH, 60% RH and 80% RH, successively, giving for each humidity level enough time for saturating the film. The time frame was found from gravimetric tests. Strain was measured
using the equation:

\[ \varepsilon = \frac{L_f - L_0}{L_0} \]  

(2.3)

where \( L_0 \) is the initial thickness and \( L_f \) is the thickness after saturation.

Figure 2.3: Schematic of the experimental setup used to measure change in thickness of PEDOT:PSS
Chapter 3

Moisture sorption-desorption behavior

3.1 Experimental results

The results from gravimetric tests were plotted as a ratio of the mass of absorbed water by PEDOT:PSS film, $\Delta m$, to the mass of the sample in the dry state, $m_0$, defined as normalized water uptake:

$$m_{\text{exp}} = \frac{\Delta m}{m_0}$$  \hspace{1cm} (3.1)

where

$$\Delta m = m - m_0$$  \hspace{1cm} (3.2)

Figures 3.1 and 3.2 show the evolution of mass uptake of PEDOT:PSS as a function of $\sqrt{t}$ for all experimental configurations (thickness, %RH) at the constant temperature of $26^\circ$C. The gravimetric experiments were found to be very reproducible for all configurations. Hence, one test for each case is presented. Stabilization of mass was reached for all experimental configurations during the three hours of the absorption test. The first hour of water absorption and desorption are plotted.

The amount of absorbed water varies from minimum 15% (100 $\mu$m, 30% RH) to 56% (15 $\mu$m, 80% RH). The thinner the film and lower the %RH, the faster it reaches the saturation point and stability during the absorption process. For 30% RH and 60% RH, time to reach saturation was in the same range, while for 80% RH, it took twice as long for all the film thicknesses, which is a first sign of a different
phenomenology or an additional mechanism. Also, mass uptake is two times larger for 80% RH in comparison to 60% RH. Overshoots in mass for 15 μm can be explained by the fast response of the film to the dynamics of the chamber, following %RH change (Figure 2.1).

During the desorption process, polymer film releases water molecules relatively fast at the beginning and then slows down. Even after a one-hour desorption process, it should be noted that the PEDOT:PSS films still contain some residual mass uptake that might be the sign of asymmetry in the water absorption/desorption process. It should be noted that desorption is slower than the water absorption process for PEDOT:PSS. At 26°C after two hours of drying, the amount of remaining water was around 1%. It was observed that a higher humidity level slightly increases the amount of residual water in the network.

Figure 3.3 illustrates sorption-desorption curves for 50 μm exposed to 60%RH at four different temperatures. The amount of diffused water decreases with the temperature increase, while stability for full saturation point is reached faster (Figure 3.3a). For the desorption part on Figure 3.3b, there is no residual water at 80°C after 10 minutes, while lower temperatures still have water remaining in the polymer network. It means that higher temperatures accelerate the water release process.

Results obtained through gravimetric tests showed that diffusion of moisture into PEDOT:PSS film is mainly a reversible process, despite probably strongly asymmetric, as the release of water molecules from the polymer network goes at a slower rate (residual water). This demonstrates the importance of taking into account the desorption part of moisture mechanics to fully understand the chemical reaction that polymer is undergoing, its reversibility and diffusion kinetics at different T and %RH configurations.

The physics behind the diffusion mechanism is complicated. In the literature, the diffusivity is sometimes calculated by using only the initial linear slope of the mass
Figure 3.1: Sorption-desorption curves for 15 μm, 50 μm and 100 μm thick PEDOT:PSS films exposed to (a-b) 30 %RH, (c-d) 60 %RH and (e-f) 80 %RH at 26°C.
Figure 3.2: Sorption-desorption curves for (a-b) 15 μm, (c-d) 50 μm and (e-f) 100 μm thick PEDOT:PSS films exposed to 30 %RH, 60 %RH and 80 %RH at 26°C
uptake ($\frac{m(t)}{m_{inf}} < 0.6$). However, the error, in this case can be very high, due to the choice of the first and last data points. Most important, this way of evaluating the diffusivity assumes that the diffusion is a Fickian mechanism that needs to be verified beforehand. In fact, diffusion is strongly associated with the chemical structure of the polymer and its properties, including the properties of diffusing solute. The interaction between polar groups of the polymer chain and diffusing molecules has a major effect on this mechanism. The simple Fickian diffusion model describes the random motion of molecules without contact to the polymer, considering it as a non-polar system. However, in this work, there is a strong interaction between PEDOT:PSS and water molecules due to hydrophilic nature of the sulfonate groups. Besides, PEDOT:PSS is highly sensitive to changes in the environment (T, %RH).

The first part of this chapter shows that Fickian law fails to model water diffusion in PEDOT:PSS and a modified diffusion model is needed to describe the absorption-desorption process accurately. The second part introduces Diffusion-Reaction model formulation, numerical implementation, results and further analysis.
3.2 Fickian diffusion model

The moisture absorption in polymers has been studied extensively and described by different models. The simplest one is the Fickian model, which describes the penetration of water molecules into the polymer film. In 1D, Fick’s second law for a thin isotropic sample exposed to constant temperature and relative humidity can be written as [21]:

\[
\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right)
\]  

(3.3)

where \( t \) is time, \( x \) is the direction parallel to the thickness, \( c \) is the concentration of diffusing molecules in \( \text{mol} \, m^{-3} \) and \( D \) is the diffusion coefficient of diffusing molecules into the polymer network in \( m^2 \, s^{-1} \). This equation is derived from mass conservation, neglecting volume variation, and Fick’s first law, assuming a steady state. Fick’s first law claims that the water molecules will move from the region of high concentration to the region of low concentration across a concentration gradient [21]. In 1D:

\[
j = -D \frac{\partial c}{\partial x}
\]  

(3.4)

where \( j \) is the mass flux in \( \text{mol} \, m^{-2} \, s^{-1} \), which measures the number of water molecules passing through a unit area per second.

For the domain \( \Omega \) at every point \( M \) Eq. 3.3 can be solved with the given initial condition, assuming that there is no diffusing solute for the whole domain at the beginning of the absorption process:

\[
c = 0 \quad \forall M \in \Omega \quad \text{at} \quad t = 0
\]  

(3.5)

The surface \( \partial \Omega \) of the domain is exposed to relative humidity and the boundary
condition can be written as:

\[ c = c_H \quad \forall M \in \partial \Omega \quad \forall t \]  

(3.6)

The concentration at the boundary is prescribed (Dirichlet-type boundary condition) using Henry’s law::

\[ c_H = S a^\epsilon p_{sat} \]  

(3.7)

where \( S \) is the solubility of water in \( \text{mol m}^{-3} \text{ Pa}^{-1} \), \( a^\epsilon \) is the water activity in the environment which is equal to

\[ a^\epsilon = \frac{\%RH}{100} \]  

(3.8)

for vapor and temperature at equilibrium. \( p_{sat} \) is the saturation vapor pressure given by Rankin’s law:

\[ p_{sat} = 1.01325 \times 10^5 \cdot e^{\frac{13.77 - \frac{3180}{T}}{T}} \]  

(3.9)

where \( T \) is in Kelvin.

### 3.2.1 Numerical implementation

The Fickian model introduced in the section 3.2, was solved using COMSOL Multiphysics 5.2 Software. Equation 3.3 was written in the form of Partial Differential equations with initial and boundary conditions described in Eq. 3.5 and 3.6 (Figure 3.4). Assuming the thr thickness of the polymer film is much less than the width.
and length, 1D simulation was conducted. Considering the symmetry, half of the thickness (L) was analyzed for 15 \( \mu m \), 50 \( \mu m \), and 100 \( \mu m \) thick films. Due to the dynamics of the chamber, discussed in Section 2.2, values for the activity of water were taken directly from the results file of the DVS chamber for all configurations.

In total, 36 configurations (three thicknesses, three %RH, and four temperatures) were simulated to calculate the concentration field \( c \). Afterwards, using the average of \( c \) in the whole domain \( \Omega \), the mass was derived as follows:

\[
m_{\text{sim}} = \frac{\Delta m}{m_0} = \frac{M_{H_2O} \int_{\Omega} c}{\rho_0 V_0}
\]  

(3.10)

where \( M_{H_2O} = 0.018 \text{ kg/mol} \) is the molar mass of water, \( \rho_0 = 1350 \text{ kg m}^{-3} \) is the initial density and \( V_0 \) is the initial volume of the sample.

Mass uptake found in Eq. 3.10 was compared with the experimental mass uptake to identify the Fickian model parameters: diffusion coefficient, \( D \), and solubility value, \( S \). MATLAB’s Optimization Toolbox was used to find optimal values through nonlinear least-squares solver ”lsqnonlin”.

### 3.2.2 Results

Figure 3.5 shows comparison between experimental results (solid line) of the moisture uptake for 50 \( \mu m \) film at 60\% RH (a) 26\(^\circ\)C and (b) 50\(^\circ\)C and simulation of the Fickian model at the same temperature and humidity (dashed line). It can be seen that theoretical curves correlate with the experimental data only for the absorption part but fails to describe the desorption part. This is mainly due to the non linear optimization, which starts to fit the curve from the beginning \( t = 0s \). If the optimization would start from the desorption part, it will be able to describe the desorption part but not absorption. Results from all other configurations (thickness, %RH, temperature) were consistent with this finding. As it was mentioned before, the Fickian
model is the common model to describe the clustering of diffusing molecules which do not interact with polymer network [22]. Therefore, absorption kinetics should be identical to desorption kinetics in case of Fickian diffusion. Simply speaking, if it takes 20 minutes to reach full saturation of the film, 20 minutes should be enough to remove all water molecules through desorption. However, after around 10 minutes of the drying process (enough for full saturation of the film during the absorption), PEDOT:PSS films still retained some amount of water: 50μm film at 60% RH had a) 11% at 26°C and b) 7% at 50°C of water content. It may mean that some water molecules were bounded more strongly to sulfonate groups than others, which proves the inability of the Fickian model to describe both absorption and desorption mechanisms of hydrophilic PEDOT:PSS film with a unique set of parameters.
Figure 3.5: Comparison between Fickian model and experimental results: a) 50\,\mu m-26^\circ C-60\%\,RH and b) 50\,\mu m-50^\circ C-60\%\,RH

3.3 Diffusion-Reaction model

The moisture absorption mechanism of PEDOT:PSS should be explained by a more complex model than the Fickian diffusion law. The existing general approach by Yagoubi et al., on top of classical diffusion, takes into account that the water can react with the substrate resulting then in a global diffusion-reaction mechanism [3]. In this work, I used the diffusion-reaction model proposed by Yagoubi as a base, which can reproduce both sorption and desorption behavior of polymer film at different
configurations (thickness, %RH, temperature). The model was modified to fit for PEDOT:PSS film and boundary conditions.

Free water molecules in the polymer network, \( c \), and reactive site of the polymer, \( R \), form a complex \( Y \):

\[
R + c \leftrightarrow Y
\]  

(3.11)

Figure 3.6 illustrates the schematic of the water sorption mechanism for the diffusion-reaction model, where \( c \), \( R \) and \( Y \) coexist in the domain \( \Omega \).

For this model, mass conservation Eq.3.3 is modified by adding global reactive term \( r_w \), which leads to:

\[
\frac{\partial c}{\partial t} = - \frac{\partial}{\partial x}(j) + r_w
\]  

(3.12)

The Fickian law, presented in the previous section, models water uptake through constant diffusion and solubility parameters. However, during the diffusion and reaction processes the polymer undergoes microstructural changes explained in Section 1.2.3. It directly affects the diffusion rate, which cannot be uniform. Yagoubi models
diffusion kinetics from a macroscopic point of view through an Arrhenius-type law, where the diffusion coefficient is temperature dependent:

\[ D(T, Y) = \tilde{D} \cdot e^{\tilde{E}(Y)/RT} \]

where \( D_0 \) is a constant, \( E \) is the activation energy, \( R \) is the gas constant, and \( T \) is the absolute temperature. By simple linearization, we assume that \( \tilde{D} \) and \( \tilde{E} \) depend on the product of reaction between water molecules and PSS, \( Y \):

\[
\begin{align*}
\tilde{D}(Y) &= \tilde{D}_0 + \tilde{D}_1 \cdot Y \\
\tilde{E}(Y) &= \tilde{E}_0 + \tilde{E}_1 \cdot Y
\end{align*}
\]

(3.13)

Therefore, Eq.3.13 becomes

\[ D(T, Y) = (\tilde{D}_0 + \tilde{D}_1 \cdot Y)e^{\tilde{E}_0/RT}e^{\tilde{E}_1Y/RT} \]

And knowing that \( Y \approx 0 \):

\[ D(T, Y) = (\tilde{D}_0 \cdot e^{E_0/RT} + \tilde{D}_1 \cdot Y \cdot e^{E_0/RT})(1 + \frac{\tilde{E}_1}{RT}Y) \]

By rearranging and neglecting higher orders of \( Y \):

\[ D(T, Y) = \tilde{D}_0 \cdot e^{E_0/RT} + (\tilde{D}_1 \cdot e^{E_0/RT} + \frac{\tilde{D}_0 \tilde{E}_1}{RT} \cdot e^{E_0/RT})Y \]

\[ D(T, Y) = D_0 + D_1 \cdot Y \]

(3.14)

Solubility dependence on temperature is represented by van ’t Hoff’s law [5]:

\[ S(T) = S_0 \cdot e^{\Delta H_s(Y)/RT} \]

(3.15)
where $S_0$ is a constant and $\Delta H_s$ is the heat of sorption. Similar to diffusion coefficient, for an initial approximation, solubility can be simplified through the following linear relation:

$$S(Y) = S_0 + S_1 \cdot Y$$  \hspace{1cm} (3.16)

Figure 3.5 shows that water molecules can exist in two forms: free water, $c$, or as a product of reaction with sulfonate groups, $Y$. Assuming that the reaction is reversible (Eq. 3.10) and in a constant volume, global reactive term $r_w$ can be written in the form of the rate law (first-order reaction):

$$r_w = -k_h(T)wR + k_r(T)Y$$  \hspace{1cm} (3.17)

where $k_h$ and $k_r$ are rate constants as a function of temperature. It should be noted that this relationship is a simplified approximation, which generalizes the whole reaction mechanism.

To sum up, the diffusion-reaction model includes following governing equations:

Conservation equations:

$$\frac{\partial c}{\partial t} = -\text{div}(j) + r_w$$  \hspace{1cm} (3.18)

$$\frac{\partial Y}{\partial t} = r_Y$$  \hspace{1cm} (3.19)

$$\frac{\partial R}{\partial t} = r_R$$  \hspace{1cm} (3.20)

Constitutive equations:

$$j = -D(Y)(\nabla w - \frac{w}{c_s(Y)} \nabla c_s(Y))$$  \hspace{1cm} (3.21)

$$D(Y) = D_0 + D_1 \cdot Y$$  \hspace{1cm} (3.22)
\[ c_s(Y) = (S_0 + S_1 \cdot Y)a^{\alpha}p_{sat} \quad (3.23) \]

\[ r_w = -k_h(T)wR + k_r(T)Y \quad (3.24) \]

\[ r_R = -k_h(T)wR + k_r(T)Y \quad (3.25) \]

\[ r_Y = k_h(T)wR - k_r(T)Y \quad (3.26) \]

Initial conditions:

\[ [c, Y] = 0 \quad \forall M \in \Omega \quad t = 0 \]

\[ R = R_0 \quad \forall M \in \Omega \quad t = 0 \quad (3.27) \]

Boundary condition:

\[ c = (S_0 + S_1 \cdot Y)a^{\alpha}p_{sat} \quad \forall M \in \partial \Omega \quad \forall t \quad (3.28) \]

\[ R_0 \] in Eq.3.27 is an initial amount of sulfonate groups in polymer film. Knowing the molar weight of PSS from Section 1.2.3, approximate theoretical value of \( R_0 \) is equal to 3000 \( \text{mol m}^{-3} \).

### 3.3.1 Numerical implementation

Equation 3.16 to 3.26 were solved using COMSOL Software in the same way as it was described in Section 3.1.1. The mass derivation is modified due to the reaction product \( Y \), which has a direct influence on mass change.

\[ m_{sim} = \frac{\Delta m}{m_0} = \frac{M_{H_2O} \int_{\Omega} (c + Y)dV}{\rho_0 V_0} \quad (3.29) \]
Diffusion-reaction model is more complex than Fickian and has seven parameters to identify. The diffusion of water molecules into polymer networks is defined by four parameters $D_0, D_1, S_0$ and $S_1$ (Eq. 3.14, 3.16). The kinetics of reaction is described by three parameters: $k_h, k_r$ and concentration of sulfonate groups $R_0$.

Figure 3.7 illustrates a flowchart of how parameters were calculated through the MATLAB Optimization Toolbox using input data from COMSOL. The calculation was split into three main steps to identify unknown parameters in an iterative manner. At the starting point, all parameters, except $D_0$ and $S_0$, were set to be equal to 0. Then it is followed by the main steps:

1) $D_0, S_0$ were calculated while the other five parameters are fixed for the time frame $[0, t_1]$, selected from experimental data. $t_1$ is the time when the concentration reaches a plateau (See Figure 3.7). At the end of this step, we have optimized values for $D_0, S_0$.

2) $S_1, k_h, R_0$ were calculated while other four parameters are fixed for the time frame $[0, t_2]$ selected from experimental data. $t_2$ is the time before the desorption starts (See Figure 3.7). Here, values of $D_0$ and $S_0$ found in step 1 were used as an input. At the end of this step, optimized values for $S_1, k_h, R_0$ were found.

3) $D_1$ and $k_r$ were calculated while the other five parameters are fixed for the time frame $[0, t_3]$. $t_3$ is the time for the whole experiment including both sorption and desorption processes (See Figure 3.7). Here, values of $S_1, k_h, R_0$ found in step 2, were used as an input. At the end of this step, optimized values for $D_1, k_r$ were found.

After the steps described above, if the simulation curve fits experimental data on a satisfactory level, we finish the calculations. Otherwise, we return to step 1 taking as the input values of $S_1, k_h, R_0, D_1, k_r$ found in steps 2 and 3.

The simulation and experimental curves were compared using the "lsqnonlin" function of MATLAB, which solves the nonlinear least-squares data fitting problems. It minimizes the sum of squares of the vector-valued function, which is the difference
Figure 3.7: Flowchart explaining iteration process of the optimization problem
between experimental and simulation data. Also, initial values of the parameter and its lower and upper bounds are specified individually. Iteration terminates when the solver reaches a stopping criteria specified by the user. For this problem, the stopping criteria were the tolerance of the function value \(1 \times 10^{-8}\) and the number of maximum iterations (500). Each curve was optimized separately, and parameters found for the first simulation curve were used as initial values for the next curves.

### 3.3.2 Results

Table 3.1: Parameters of the model at different temperatures.

<table>
<thead>
<tr>
<th>Param.</th>
<th>Unit</th>
<th>Optimal Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>26^\circ C</td>
</tr>
<tr>
<td>(D_0)</td>
<td>(10^{-12} m^2 s^{-1})</td>
<td>1.60 ± 0.39</td>
</tr>
<tr>
<td>(S_0)</td>
<td>(mol m^{-3} Pa^{-1})</td>
<td>1.10 ± 0.89</td>
</tr>
<tr>
<td>(D_1)</td>
<td>(10^{-16} m^5 mol^{-1} s^{-1})</td>
<td>-2.42 ± 1.24</td>
</tr>
<tr>
<td>(S_1)</td>
<td>(10^{-1} Pa^{-1})</td>
<td>-5 ± 0.05</td>
</tr>
<tr>
<td>(R_0)</td>
<td>(mol m^{-3})</td>
<td>2730 ± 21</td>
</tr>
<tr>
<td>(k_h)</td>
<td>(10^{-7} m^3 mol^{-1} s^{-1})</td>
<td>3.83 ± 0.37</td>
</tr>
<tr>
<td>(k_r)</td>
<td>(10^{-1} s^{-1})</td>
<td>2.60 ± 0.66</td>
</tr>
</tbody>
</table>

Table 3.1 gives optimized parameters at each temperature (results of \(26^\circ C-80\%\)RH were excluded, and the explanation will be given later). The average value for each parameter at each temperature was presented because values for each configuration (thickness, \%RH) vary in a range of \(\pm 5\%\). It can be explained by a \(\pm 10\%\) variation of thickness due to the drop casting method we used to form the films. This is a simple way to make a thin film which has a drawback because of the difficulty to control the thickness and to get a uniform film.

\(D_0\) increases with temperature. Temperature increase causes an increase in kinetic energy of diffusing molecules, and therefore it accelerates the diffusion process. \(S_0\) solubility coefficient decreases with temperature due to strengthened hydrogen bonding between PSS chain and PEDOT:PSS grains ([3]). It means that it will be more difficult for water molecules to bond with sulfonate groups. The decrease of reac-
tive substrate concentration, $R_0$, with temperature justifies the fact that less amount of sulfonate groups undergo chemical reaction with temperature increase. However, for all films prepared under the same condition, $R_0$ should be constant. Therefore, model should include another term to describe dependence of available reactive sites on temperature:

$$R = R_0(1 - f(T)) \quad (3.30)$$

where $R_0$ is the concentration of PSS, which will be constant for all configurations (thickness, temperature, %RH) and negative $f(T)$ is the term to show that less amount of reactive site will contribute into reaction with increase in temperature.

$k_r$, backward reaction rate coefficient, increases with temperature increase. According to experimental tests higher temperature results in the faster removal of remaining water which justifies the change of $k_r$.

$k_h$, forward reaction rate coefficient, increases with temperature increase because high temperature accelerates the reaction between water molecules and sulfonate groups.

The solubility and diffusivity of the polymer decrease ($S_1 < 0, D_1 < 0$) with the progression of the reaction between sulfonate groups and water molecules. To understand physical interpretation, let's consider two forms of absorbed water molecules: free and bonded. Free water molecules fill pores and voids of the polymer matrix, and with time the amount of free volume decreases causing a reduction in water concentration diffusing inside and therefore, slow down of the diffusion rate. Similarly, there is a fixed amount of sulfonate group per volume of the polymer film. It forms hydrogen bonds with water molecules and with water uptake, amount of reactive site able to react decreases. It leads to a decrease in solubility and diffusion rate.

The model was able to fit all the experimental results except at 80% RH and 26°C. The difference was between the saturation plateau of simulation and experimental curves which become negligible with the temperature increase. Therefore
Experimental results for higher temperatures were reproduced for all humidity levels by the given model. Figures 3.8 and 3.9 illustrate a comparison between experimental and simulated mass uptake of the 50um thick film at 26°C and 50°C, respectively. Figure 3.8c illustrates that the model is unable to reproduce experimental result at 80% RH at 26°C, however, can do it for 50°C (Figure 3.9c). Slight variations of simulation curves for other configurations can be a result of nonuniform sample thickness due to the drop casting method. Other than that, presented simple sorption-desorption model is following mass uptake kinetics very well.

![Figure 3.8: Comparison between simulation and experimental curves for 50 μm at 26°C: a) 30%RH, b) 60%RH and c) 80%RH](image-url)
The contribution of diffusive water molecules \( w \) and reaction product \( Y \) to water uptake of the polymer is plotted for 50\( \mu \)m at 26\(^{0}\)C and 50\(^{0}\)C at different %RH on Figure 3.10 and 3.11. According to the solution we found, mass uptake comes mainly from the diffusion of free water.

The distributions of \( w \) and \( Y \) concentrations are plotted on Figure 3.12 for (a) 26\(^{0}\)C and (b) 50\(^{0}\)C. The concentration of the product of the reaction, \( Y \), is the only function of temperature and does not change with relative humidity, while the concentration

Figure 3.9: Comparison between simulation and experimental curves for 50\( \mu \)m at 50\(^{0}\)C: a) 30\% RH, b) 60\% RH and c) 80\% RH
of water molecules in the polymer chain, \( w \), depends on both. It increases with the increase in %RH and decreases with the increase in T. \( w \) comprises 70-94% of the water content. It is clear from these results that solubility decreases with temperature and obeys van ’t Hoff’s law. It is important to note that values used to plot 80% RH on Figure 3.13a should be revised in future, due to observed swelling effect (Section 3.4) and variation of optimized parameters from the values given in table 3.1.

To sum up, 36 configurations (thickness, temperature, %RH) were studied. Table 3.2 gives the list of all configurations. All curves were reproduced by the Diffusion-Reaction model, except at 26\(^{\circ}\)C and 80%RH for all film thicknesses (highlighted with pink color).
Figure 3.11: Contribution of \( w \) and \( Y \) to mass uptake for 50 \( \mu m \) at 50\( ^0 \)C: a) 30% RH, b) 60% RH and c) 80% RH

Figure 3.12: Evolution of \( w \) and \( Y \) with %RH for 50 \( \mu m \) at a) 26\( ^0 \)C and b) 50\( ^0 \)C
Table 3.2: List of all 36 configurations

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Temperature</th>
<th>%RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>15μm</td>
<td>26°C</td>
<td>30%</td>
</tr>
<tr>
<td></td>
<td>37°C</td>
<td>30%</td>
</tr>
<tr>
<td></td>
<td>50°C</td>
<td>30%</td>
</tr>
<tr>
<td></td>
<td>80°C</td>
<td>30%</td>
</tr>
<tr>
<td>50μm</td>
<td>26°C</td>
<td>30%</td>
</tr>
<tr>
<td></td>
<td>37°C</td>
<td>30%</td>
</tr>
<tr>
<td></td>
<td>50°C</td>
<td>30%</td>
</tr>
<tr>
<td></td>
<td>80°C</td>
<td>30%</td>
</tr>
<tr>
<td>100μm</td>
<td>26°C</td>
<td>30%</td>
</tr>
<tr>
<td></td>
<td>37°C</td>
<td>30%</td>
</tr>
<tr>
<td></td>
<td>50°C</td>
<td>30%</td>
</tr>
<tr>
<td></td>
<td>80°C</td>
<td>30%</td>
</tr>
</tbody>
</table>
### 3.4 Hygroscopic swelling

Parameters given in Table 3.1 are material properties, which should not change with the variation of relative humidity. After not being able to find the same values for all humidity levels at 26°C, we decided to evaluate the strain by measuring the change in thickness of the polymer films. Figure 3.14 shows strain vs. relative humidity. Change in thickness was measured at three %RH levels and only at 26°C because experimental setup cannot be exposed to higher temperatures. Strain remains approximately the same for 30 and 60% RH, while increases significantly at 80% RH. This expansion of the polymer film is explained by the swelling effect, which is already described in the literature [13]. It means that water uptake at 30% RH and 60% RH does not cause the swelling of PEDOT:PSS film. Therefore, the volume change of polymer film exposed to high humidity should be taken into account in the model to describe the moisture absorption-desorption mechanism. It can be the main reason why the model presented in the previous section did not reproduce the experimental curve for this %RH and T configuration.

There are different theories to explain the swelling effect in polymers: (i) excess of free water in the polymer network, (ii) bonded water or (iii) contribution of both states of water molecules. In the first case, free water molecules easily diffuse into the surface and interfacing area of grains, and fill free volume. Therefore, it increases the distance between the grains causing the film expansion. The second case is mainly for hydrophilic materials, which can interact with water molecules. There is a common theory that hygroscopic swelling of polymers is a result of hydrogen bonding which alter micro structure of the polymer. The third case is a contribution of both free and bonded water molecules.

To include swelling of the polymer into the model, it is essential to understand what is the main reason: free water and/or bonded water. They can have different effects on mechanical, electrical and thermal properties of PEDOT:PSS. In general,
swelling can be described as a function of both $w$ and $Y$. This is the future work and beyond the scope of this thesis.
Chapter 4

Relationship of water content to Electrical conductivity

4.1 Electrical conductivity

The response of PEDOT:PSS regarding electrical resistance over a broad spectrum of frequencies exposed to different humidity levels and temperatures were studied. Figure 4.1 shows how resistivity of PEDOT:PSS film changes with %RH at different temperatures. At 26°C there is a linear increase in resistivity with relative humidity increase, which is consistent with findings of Kus et al. [13]. Physical interpretation requires microstructural knowledge. Short PEDOT oligomers are attached to the PSS chain, which is hydrophilic. Therefore, water molecules in the polymer matrix increase the distance between PEDOT chains, which are responsible for the conductivity of the film. It is more difficult for electrons to hop at longer distances, and that is why resistivity of the film increases. In addition, it can also be explained by a dipole moment of water molecules which may increase the resistivity of PEDOT:PSS film. It is interesting to note that an increase in resistivity is not linear for higher temperatures and at 80°C the increase in resistivity from 30% RH to 60% RH is followed by a decrease at 80% RH. Kus et al. found that at room temperature after 80% RH, resistivity decreases and explains it by the formation of water meniscus layer which contributes to ionic conductivity of the film. It means that the saturation point at 26°C is after 80% RH, while for higher temperatures this value shifts and is between 60 and 80% RH according to our findings (Figure 4.1). A decrease in resistivity with a temperature increase is consistent with the results of Zhou et al [3]. They
found an increase in conductivity while PEDOT:PSS film was heated from $-150^\circ C$ to $+250^\circ C$ range. It can be explained by the removal of water molecules by heating at micro level, which results in a decrease of the distance between PEDOT oligomers. In addition, conductivity of the polymer film improves at higher temperatures due to the increase in thermal energy of the electrons which is enough to hop to neighbor sites.
To sum up, resistivity of PEDOT:PSS increases with the moisture uptake until it reaches saturation point, then it decreases. Resistivity decreases with the temperature increase. The electrical behavior of PEDOT:PSS is not included in the model presented in this thesis because this part is still in progress.
Chapter 5

Conclusion

5.1 Summary

In this work, I studied temperature-dependent moisture absorption and changes in electrical conductivity of organic conducting polymer, poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS), towards macroscopic modeling of electro-thermo-mechanical couplings. Based on this study, we found:

- Gravimetric tests are relevant to understand the sorption-desorption mechanism of PEDOT:PSS. It was found that the simple Fickian model is not able to describe the whole water transport process, but can simulate water uptake kinetics. It is mainly due to the remaining water molecules in the polymer network during the drying process in the time frame enough to reach saturation point. Therefore, the desorption process is slower than sorption process.

- The model proposed to describe moisture sorption of PEDOT:PSS was able to fit experimental curves from gravimetric tests, except for 80% RH and 26°C due to the swelling effect. At higher temperatures, the difference between experimental curves and simulation curves were negligible. The model consists of the basic water transport mechanisms: diffusion and reaction. It was found that the desorption part of water transport is slower due to the reaction. Dissociation of the reaction product, $Y$, goes at a slower rate than the diffusion of free water molecules.
• The PEDOT:PSS behavior highly depends on the environmental conditions. It was demonstrated that mechanical strain increases due to the swelling effect at higher humidity levels. Electrical resistivity of polymer linearly increases with %RH until the saturation point, after which it drops sharply, possibly due to the contribution of water ions to conduct electrical current. In addition, resistivity decreases with an increase in temperature, due to the removal of water molecules from polymer network.

5.2 Future research work

The work done in this thesis is just the beginning on macroscopic modeling of electro-thermo-mechanical couplings. Future research work to be done is:

1. The mechanical part. Introduce the mechanical part into the computational model to simulate the behavior of polymer film in terms of strain and displacement. To do that, there is a need for a full systematic data: (i) measure strain for all configurations (thickness, temperature, %RH) to understand the whole picture. (ii) relate water uptake to the strain change with time

2. The electrical part. Introduce the electrical part into the computational model to simulate the behavior of polymer film in terms of electric potential. (i) Find how electrical properties change with water uptake, and how free water and/or bonded water contribute to this change.
REFERENCES


