Supplementary information:

Macroscopic modeling of water uptake behavior of PEDOT:PSS films

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Validity of the Fickian diffusion model

Moisture absorption in polymers has been extensively described by different models, among which the Fickian model, which is considered to be the simplest one. Fick's second law for a thin unidirectional sample exposed to a constant temperature and relative humidity can be written as:[1]

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial w}{\partial x} \right) \tag{1}$$

where x is the spatial coordinate, t the time, w ($mol\ m^{-3}$) the concentration of diffusing molecules, and D ($m^2\ s^{-1}$) the diffusion coefficient of molecules diffusing into the polymer network. This equation is derived from mass conservation, neglecting volume variation, and Fick's first law. 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.[1] For

1

the unidirectional case:

$$j = -D\frac{\partial w}{\partial x} \tag{2}$$

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

For a domain Ω, at every point $\underline{M}$, Eq. 1 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:

$$w = 0 \quad \forall \underline{M} \in \Omega \quad at \quad t = 0 \tag{3}$$

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

$$w = w_H \quad \forall \underline{M} \in \partial\Omega \quad \forall t \tag{4}$$

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

$$w_H = Sa^e p_{sat} \tag{5}$$

S $(mol\ m^{-3}\ Pa^{-1})$ is the solubility of water. a^e is the water activity in the environment which is related to the relative humidity as

$$a^e = \frac{\%RH}{100} \tag{6}$$

p_{sat} is the saturation vapor pressure given by Rankin's law:

$$p_{sat} = 1.01325x10^5 \cdot e^{13.7 - \frac{5120}{T}} \tag{7}$$
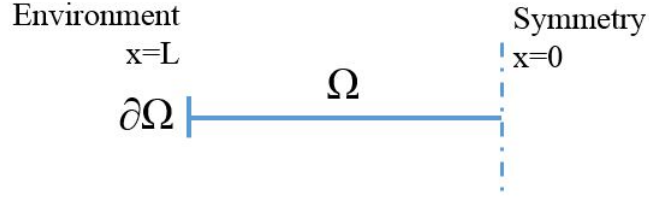
where T is in Kelvin.

Figure S1: The unidirectional geometry used in numerical simulation

Numerical implementation

The Fickian model was solved using a COMSOL Multiphysics 5.2 Software. Acknowledging that the thickness of the polymer film is much less than its in-plane dimensions, the simulation was conducted assuming a unidirectional continuum (see Figure S1). Considering the symmetry, half of the thickness (L) was analyzed. The 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 w. Afterwards, using the average of w in the whole domain Ω, the mass was derived as follows:

$$m_{sim} = \frac{\Delta m}{m_0} = \frac{M_{H_2O} \int_{\Omega} w}{\rho_0 V_0} \tag{8}$$

where M_{H_2O}=0.018 kg/mol is the molar mass of water, ρ_0=1350 $kg\ m^{-3}$ is the initial density and V_0 is the initial volume of the sample.

The mass uptake found in Eq. 8 was compared with the experimental mass uptake to identify the Fickian model parameters: diffusion coefficient, D, and solubility value, S. A MATLAB's Optimization Toolbox was used to find optimal values through nonlinear least-squares solver "lsqnonlin".

Results

Figure S2 shows a comparison between experimental results (solid line) of the moisture uptake for 50 μm film at 60 %RH (a) 26°C and (b) 50°C and the corresponding simulations using the Fickian model (dashed line). It can be seen that simulations results match with the experimental data for the absorption part, but fails to describe the desorption part. Results from all other configurations (thickness, %RH, temperature) were consistent with this finding. The Fickian model is the common model for the absorption of diffusing molecules that do not interact with the polymer network.[2] Therefore, the absorption kinetics should be identical to desorption kinetics in case of Fickian diffusion. However, after approximately 10 minutes of the drying process (enough for a full saturation of the film during the absorption), PEDOT:PSS films still retained some water: 50μm film at 60 %RH had a) 11% at 26°C and b) 7% at 50°C of water content. An explanation might be that some water molecules were strongly bounded to sulfonate groups. Our comparison proves the inability of the Fickian model to describe both absorption and desorption mechanisms of a hydrophilic PEDOT:PSS film with a unique set of parameters.
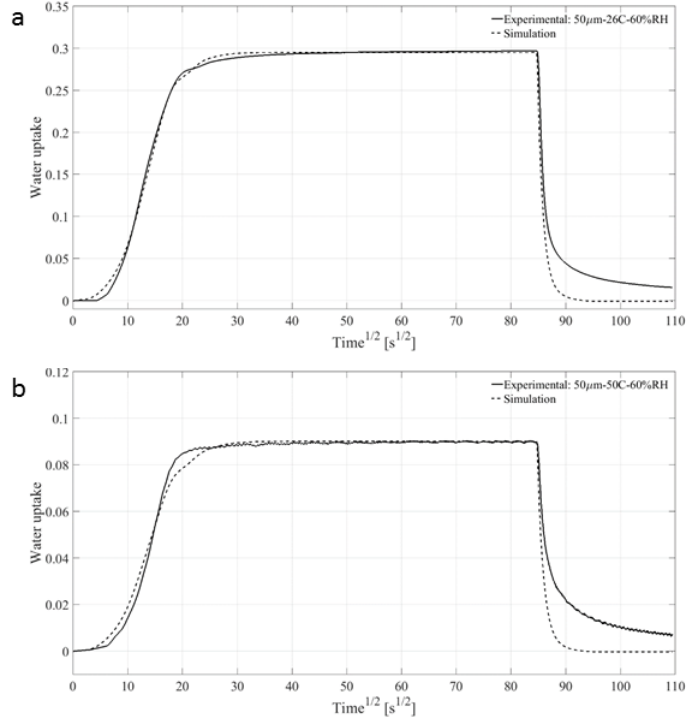
Figure S2: Comparison between simulated results using the Fickian model and experimental results: a) 50μm-26°C-60 %RH and b) 50μm-50°C-60 %RH

Diffusion-Reaction model

In addition to classical diffusion, we take into account the fact that the water can react with the substrate, which results in a global diffusion-reaction mechanism.[3] This approach can reproduce both sorption and desorption behaviors of polymer films, for different configurations (thickness, %RH, temperature). Free water molecules in the polymer network, w, form a complex Y with the reactive site of the polymer, R:

$$R + w \Leftrightarrow Y \tag{9}$$
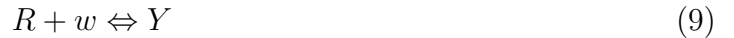
Figure S3 gives a schematic illustration of the water sorption mechanism for the diffusion-reaction model, where w, R and Y coexist in the domain Ω.

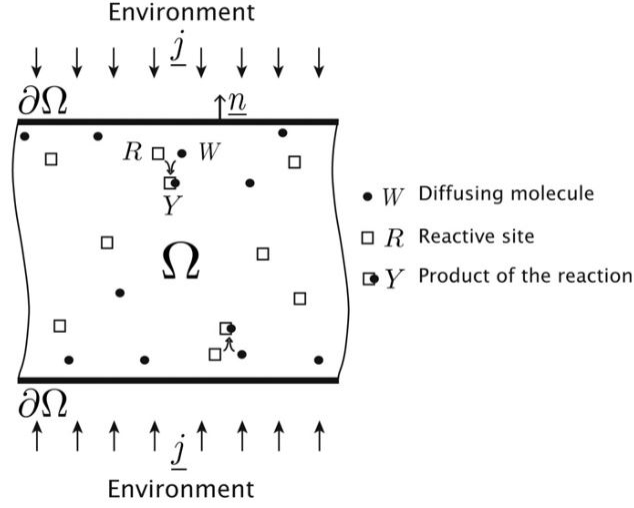For this model, the mass conservation Eq.1 is modified by adding a global reactive term

Figure S3: Schematic of water sorption mechanism for Diffusion-Reaction model[3]

r_w, which leads to:

$$\frac{\partial w}{\partial t} = -\frac{\partial j}{\partial x} + r_w \tag{10}$$

The Fickian law (presented in the previous section) assumes constant diffusion and solubility parameters. However, during the diffusion and reaction processes, the polymer undergoes local microstructural changes, resulting in non-spatially uniform diffusion and solubility parameters. At a macroscopic level, this dependance of the diffusion coefficient to the microstructure can be modeled by assuming D is a function of the local product of reaction Y. If we assume an Arrhenius-type law for the change with temperature of the diffusion coefficient, we have:

$$D(T, Y) = \widetilde{D}(Y) \cdot e^{\widetilde{E}(Y)/RT} \tag{11}$$

where $\widetilde{D}$ is the pre-exponential coefficient, $\widetilde{E}$ is the activation energy, R is the gas constant, and T is the absolute temperature. The most simple assumption is to consider that $\widetilde{D}$ and

$\widetilde{E}$ depend linearly on the product of reaction, Y:

$$\widetilde{D}(Y) = \widehat{D_0} + \widehat{D_1} \cdot Y \quad ; \quad \widetilde{E}(Y) = \widehat{E_0} + \widehat{E_1} \cdot Y \tag{12}$$

Therefore, Eq.11 becomes

$$D(T,Y) = (\widehat{D_0} + \widehat{D_1} \cdot Y)e^{\widehat{E_0}/RT}e^{\widehat{E_1}Y/RT}$$

Assuming that the perturbation is small, we can write:

$$D(T,Y) = (\widehat{D_0} \cdot e^{\widehat{E_0}/RT} + \widehat{D_1} \cdot Y \cdot e^{\widehat{E_0}/RT})(1 + \frac{\widehat{E_1}}{RT}Y)$$

By rearranging and neglecting higher orders of Y, we obtain:

$$D(T,Y) = \widehat{D_0} \cdot e^{\widehat{E_0}/RT} + (\widehat{D_1} \cdot e^{\widehat{E_0}/RT} + \frac{\widehat{D_0}\widehat{E_1}}{RT} \cdot e^{\widehat{E_0}/RT})Y \tag{13}$$

So, for a specific temperature T, D can be written:

$$D(Y) = D_0 + D_1 \cdot Y \tag{14}$$

Solubility dependence on temperature is represented by van't Hoff's law:[3]

$$S(T) = S_0 \cdot e^{\Delta H_s(Y)/RT} \tag{15}$$

where S_0 is a pre-exponential parameter, and ΔH_s is the heat of sorption. Similar to the diffusion coefficient, we assume a linear relation between the solubility and the concentration of the products of reaction:

$$S(Y) = S_0 + S_1 \cdot Y \tag{16}$$

Figure S3 shows that water molecules can exist in two forms: free water, w, or as a product of reaction with sulfonate groups, Y. Assuming that the reaction is reversible (Eq. 9) and in a constant volume, the global reactive term r_w can be written in the form of the rate law (first-order reaction):

$$r_w = -k_h(T)wR + k_r(T)Y \tag{17}$$

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, that globalizes the whole reaction mechanism.

In summary, the diffusion-reaction model includes the following governing equations:

Conservation equations:

$$\frac{\partial w}{\partial t} = -\frac{\partial j}{\partial x} + r_w \tag{18}$$

$$\frac{\partial Y}{\partial t} = r_Y \tag{19}$$

$$\frac{\partial R}{\partial t} = r_R \tag{20}$$

Constitutive equations:

$$j = -D(Y)(\nabla w - \frac{w}{w_s(Y)}\nabla w_s(Y)) \tag{21}$$

$$D(Y) = D_0 + D_1 \cdot Y \tag{22}$$

$$w_s(Y) = (S_0 + S_1 \cdot Y)a^e p_{sat} \tag{23}$$

$$r_w = -k_h(T)wR + k_r(T)Y \tag{24}$$

$$r_R = -k_h(T)wR + k_r(T)Y \tag{25}$$

$$r_Y = k_h(T)wR - k_r(T)Y \tag{26}$$

Initial conditions:

$$[w, Y] = 0 \quad \forall \underline{M} \in \Omega \quad t = 0$$

$$R = R_0 \quad \forall \underline{M} \in \Omega \quad t = 0 \tag{27}$$

Boundary condition:

$$w = (S_0 + S_1 \cdot Y)a^e p_{sat} \quad \forall \underline{M} \in \partial\Omega \quad \forall t \tag{28}$$

R_0 in Eq. 27 is the accessible amount of sulfonate groups in the polymer film that are available for reaction. The molecular weight of the PSS monomer is 184; therefore an approximate theoretical value of R_0 is 3000 $mol\ m^{-3}$.

Numerical implementation

Equations 18-28 were solved using a COMSOL Software in the same way as that described for the Fickian model. The mass derivation was modified due to the reaction product Y, which has a direct influence on mass change.

$$m_{sim} = \frac{\Delta m}{m_0} = \frac{M_{H_2O} \int_\Omega (w + Y)dV}{\rho_0 V_0} \tag{29}$$

Seven parameters have to be identified. The diffusion of water molecules into the polymer network is defined by four parameters D_0, D_1, S_0 and S_1. The reaction kinetics is described by three parameters: k_h, k_r and the concentration of accessible sulfonate groups R_0.

Parameters were identified through the MATLAB Optimization Toolbox using input data from COMSOL. The identification process was split into three main steps to identify unknown parameters in an iterative manner. For the initial guess, all parameters, except D_0 and S_0, were set to be equal to 0. Then, we proceed as described below:

1) D_0, S_0 were optimized over the time frame $[0, t_1]$ while keeping the other five parameters

constant. t_1 is the time when the concentration reaches a plateau. At the end of this step, we optimized values for D_0, S_0.

2) S_1, k_h, R_0 were optimized over the time frame $[0, t_2]$ while keeping the other four parameters constant. t_2 is the time before the desorption starts. 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 optimized over the time frame $[0, t_3]$ while keeping the other five parameters constant . t_3 is the time for the whole experiment including both sorption and desorption processes. At the end of this step, optimized values for D_1, k_r were found.

This process was repeated until a satisfactory agreement between the simulated results and the experimental observations was reached. Simulated and experimental curves were compared using the "lsqnonlin" function of MATLAB, which solves the non-linear least-squares data fitting problems. It minimizes the sum of squares of the vector-valued function, which is the difference between experimental and simulation data. Initial values, lower and upper bounds were specified individually for each parameter. Each curve was optimized separately, and parameters found for the first simulation curve were used as initial values for the next curves.

Results

The values of optimized parameters are shown in Tables S1-S3. The variation of values can be explained by a $\pm 10\%$ variation of thickness, due to the drop casting method we used to form the films.

Table S1: Parameters of the model at different temperatures for a pure film

Param.	Unit	Optimized Values			
		26^oC	37^oC	50^oC	80^oC
D_0	$10^{-12}\ m^2\ s^{-1}$	1.60 ± 0.39	1.72 ± 0.42	1.87 ± 0.16	2.21 ± 0.39
S_0	$mol\ m^{-3}\ Pa^{-1}$	11.1 ± 0.89	4.38 ± 0.34	1.16 ± 0.13	0.46 ± 0.04
D_1	$10^{-16}\ m^5\ mol^{-1}\ s^{-1}$	-2.42 ± 1.24	-2.67 ± 1.05	-4.18 ± 1.90	-10.1 ± 1.60
S_1	$10^{-4}\ Pa^{-1}$	-5 ± 0.05	-4.42 ± 0.2	-2 ± 0.01	-1 ± 0.01
R_0	$mol\ m^{-3}$	2730 ± 21	2460 ± 149	1500 ± 94	1000 ± 13
k_h	$10^{-7}\ m^3\ mol^{-1}\ s^{-1}$	3.83 ± 0.37	5.8 ± 0.75	7.74 ± 0.38	13.90 ± 0.77
k_r	$10^{-4}\ s^{-1}$	2.60 ± 0.66	3.02 ± 0.29	3.38 ± 0.73	5.04 ± 2.2

Table S2: Parameters of the model at different temperatures for a pre-treated film

Param.	Unit	Optimized Values			
		26^oC	37^oC	50^oC	80^oC
D_0	$10^{-12}\ m^2\ s^{-1}$	1.03 ± 0.06	1.15 ± 0.07	1.25 ± 0.15	1.92 ± 0.18
S_0	$mol\ m^{-3}\ Pa^{-1}$	10 ± 0.91	2.92 ± 0.25	0.81 ± 0.08	0.04 ± 0.006
D_1	$10^{-16}\ m^5\ mol^{-1}\ s^{-1}$	-1.13 ± 0.48	-3.37 ± 0.21	-4.33 ± 0.55	-5.7 ± 0.01
S_1	$10^{-4}\ Pa^{-1}$	-5.42 ± 0.44	-3.92 ± 0.11	-1.73 ± 0.07	-0.2 ± 0.001
R_0	$mol\ m^{-3}$	2690 ± 18	1910 ± 178	1220 ± 37	700
k_h	$10^{-7}\ m^3\ mol^{-1}\ s^{-1}$	0.53 ± 0.06	1.38 ± 0.02	3.9 ± 0.14	32.6
k_r	$10^{-4}\ s^{-1}$	1.68 ± 0.14	2.20	3 ± 0.11	5.52 ± 0.07

Table S3: Parameters of the model at different temperatures for a post-treated film

Param.	Unit	Optimized Values			
		26^oC	37^oC	50^oC	80^oC
D_0	$10^{-12}\ m^2\ s^{-1}$	1.76 ± 0.05	1.80 ± 0.13	1.88 ± 0.10	2.5
S_0	$mol\ m^{-3}\ Pa^{-1}$	8.39 ± 1.09	2.31 ± 0.21	0.60 ± 0.06	0.048 ± 0.009
D_1	$10^{-16}\ m^5\ mol^{-1}\ s^{-1}$	-7.30 ± 0.24	-8.64 ± 0.69	-9.5 ± 1.70	-7
S_1	$10^{-4}\ Pa^{-1}$	-2 ± 0.01	-0.84 ± 0.05	-4.17 ± 0.37	-0.1
R_0	$mol\ m^{-3}$	1540 ± 49	1390 ± 64	908 ± 45	500
k_h	$10^{-7}\ m^3\ mol^{-1}\ s^{-1}$	2.4 ± 0.49	5.64 ± 0.07	16	130
k_r	$10^{-4}\ s^{-1}$	1.56 ± 0.05	2.10 ± 0.11	2.62 ± 0.12	4.25 ± 0.10

Experimental results

Sorption-desorption curves for all configurations are illustrated on Figures 4-7 for pure films, on Figure 8-11 for pre-treated and post-treated films. Only 50μm thick films were used for the EG treatment.
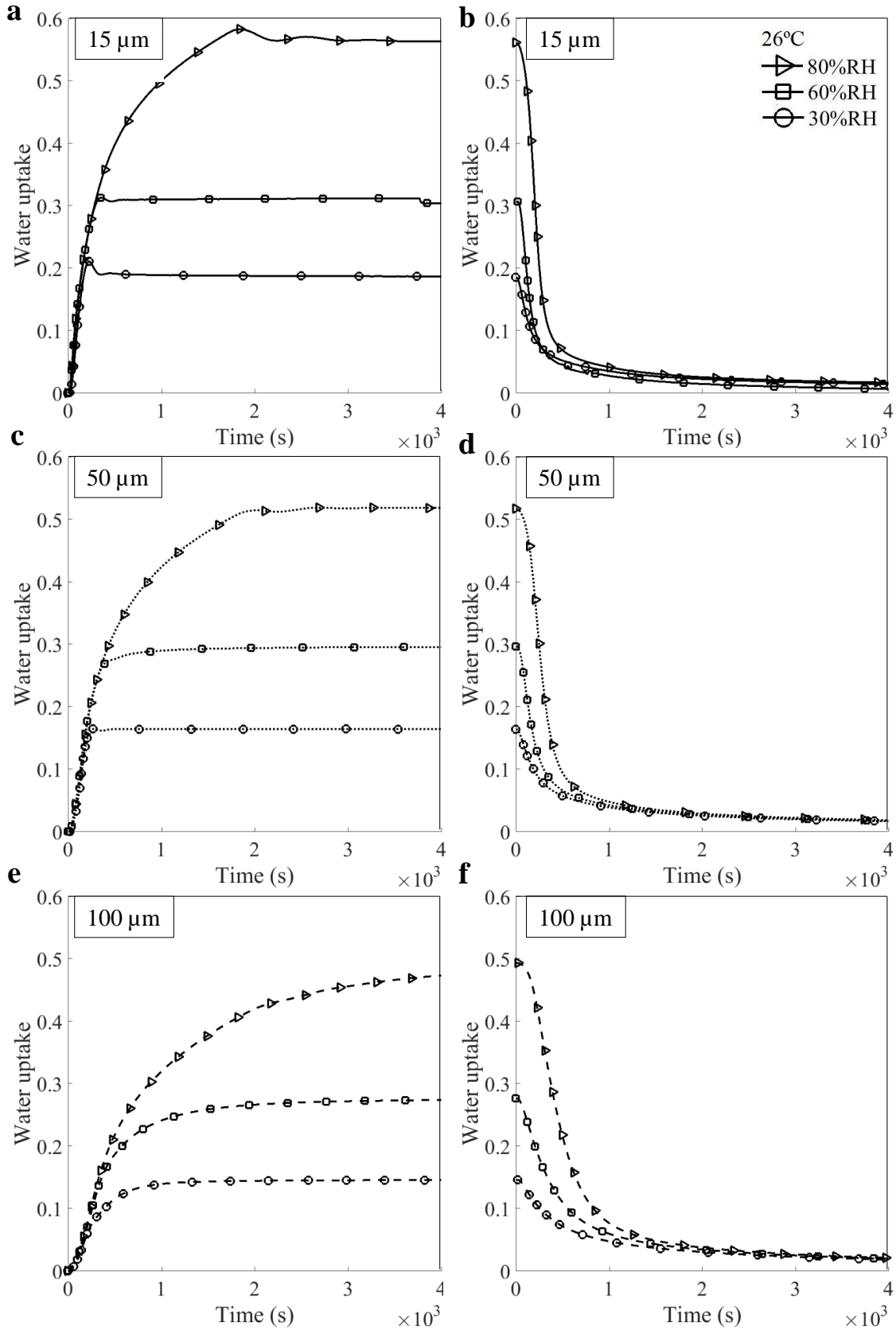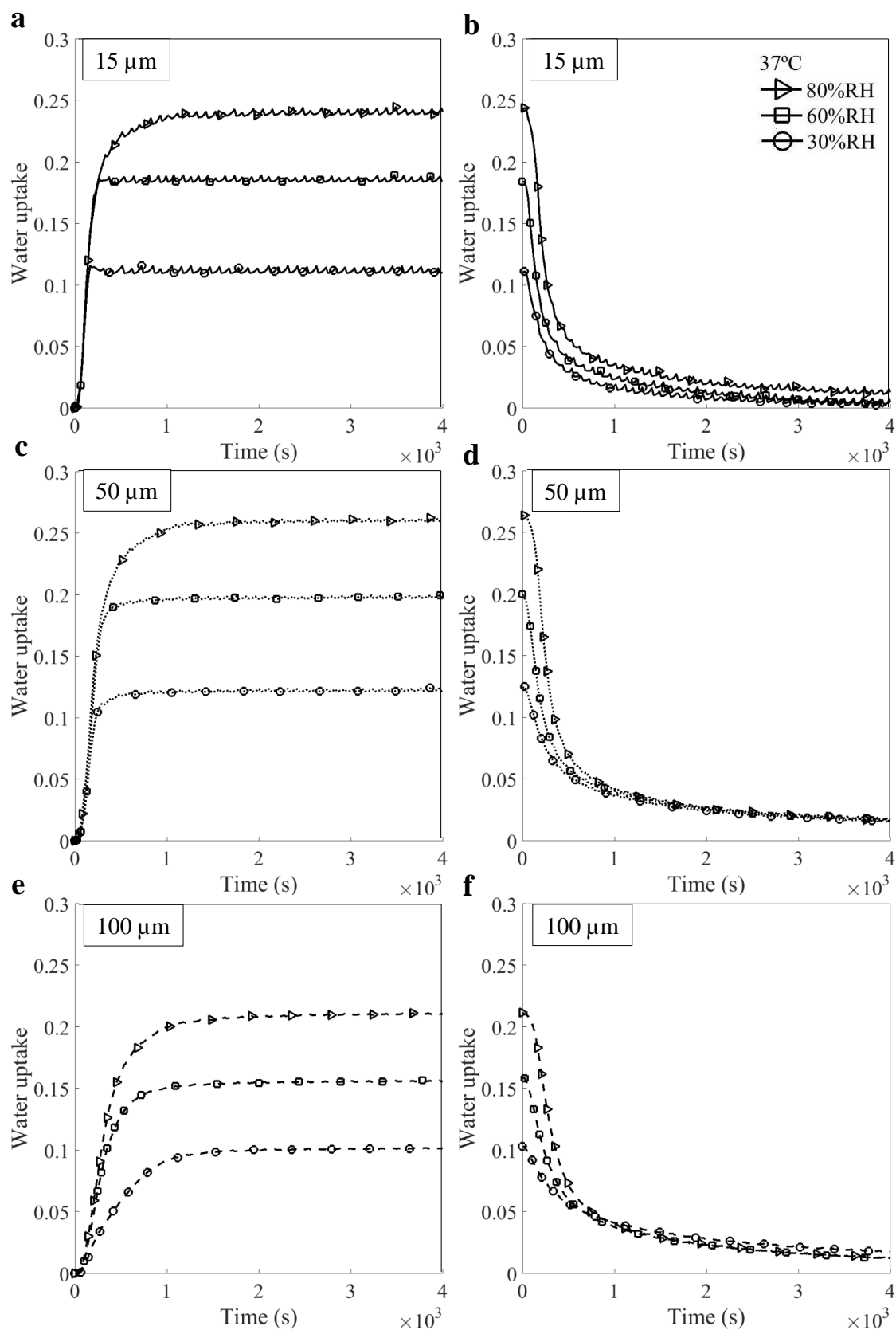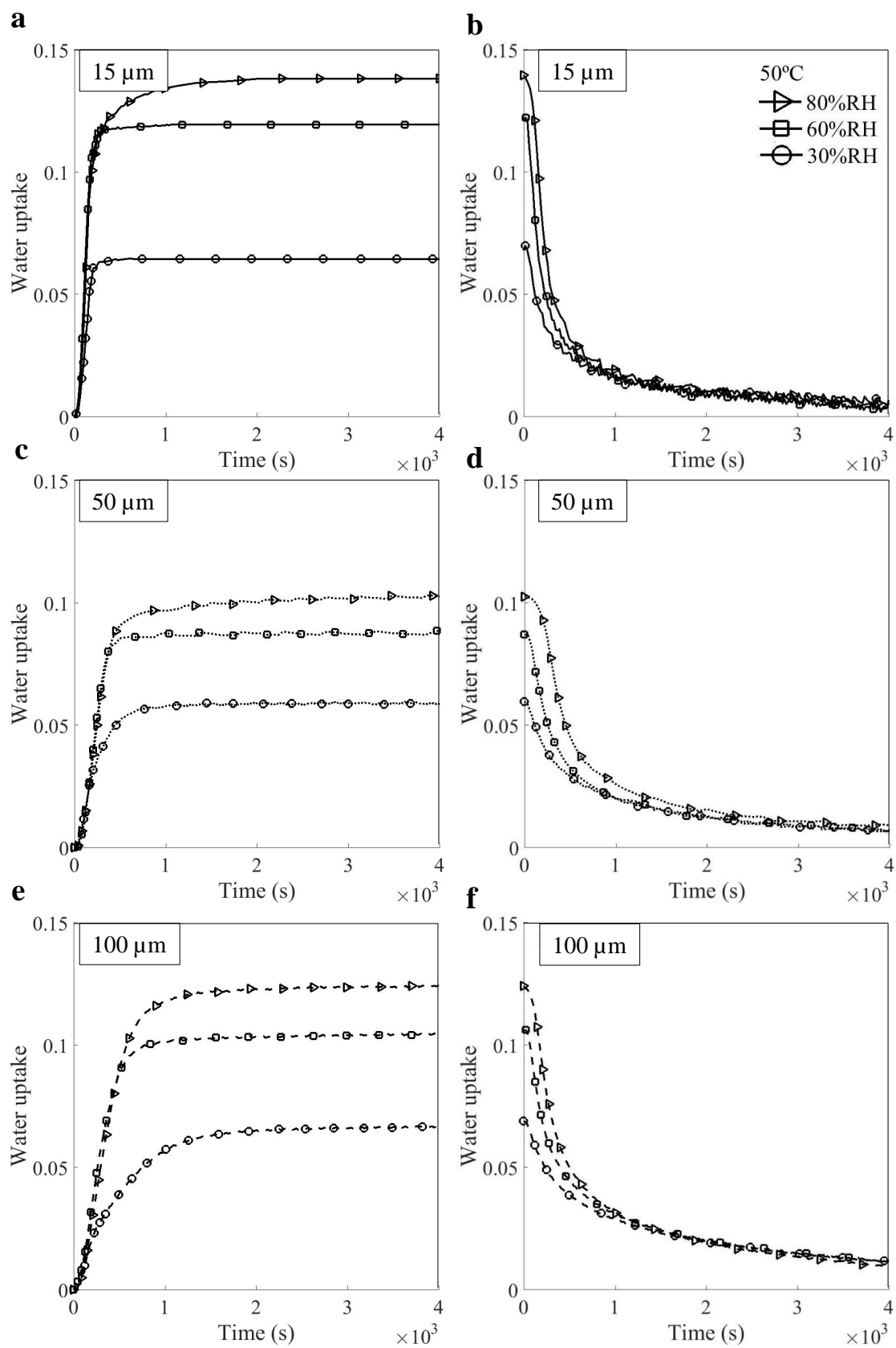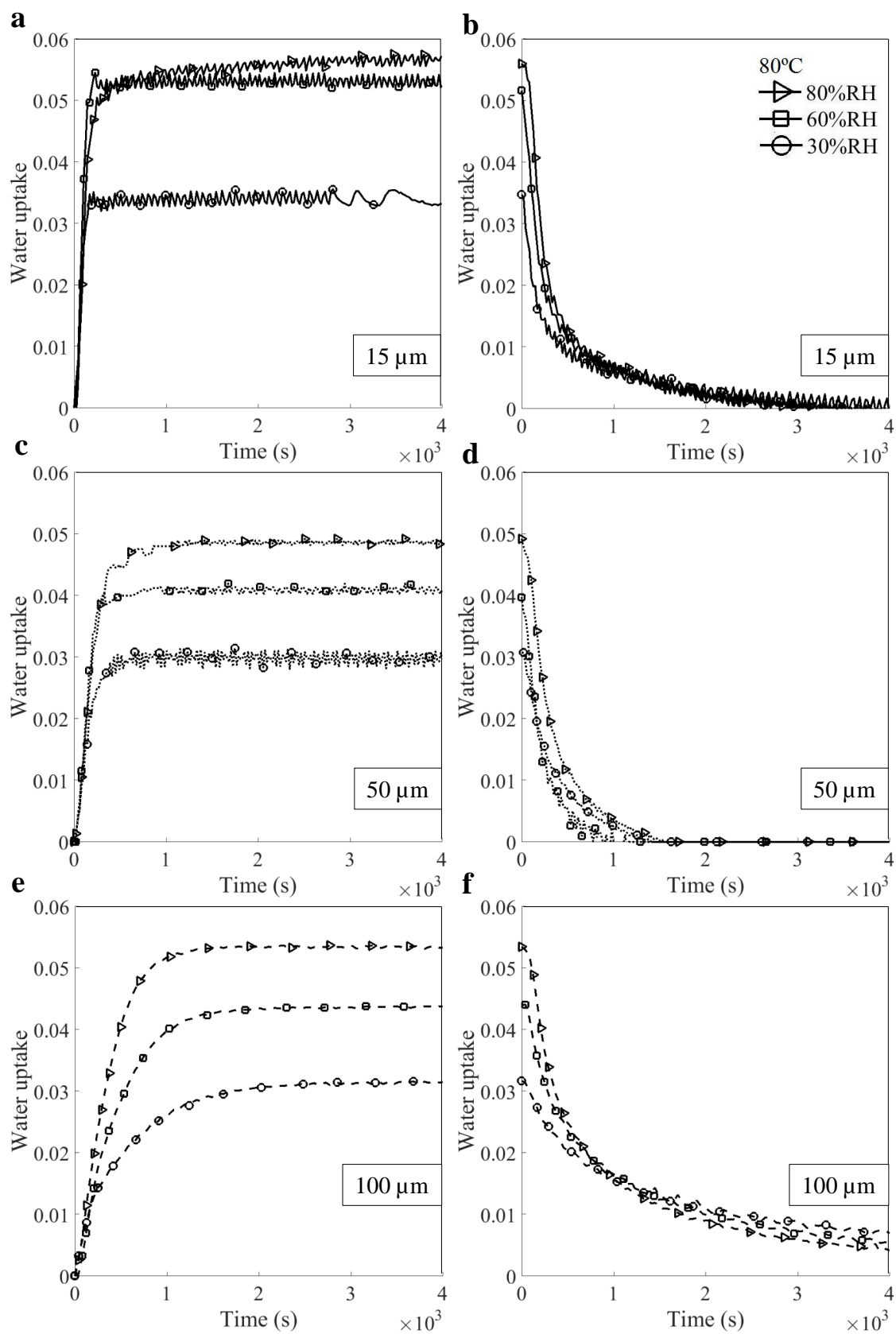
Figure S4: Sorption-desorption curves for (a-b) 15 μm, (c-d) 50 μm and (e-f) 100 μm-thick pure PEDOT:PSS films exposed to 30 %RH, 60 %RH and 80 %RH at 26ºC
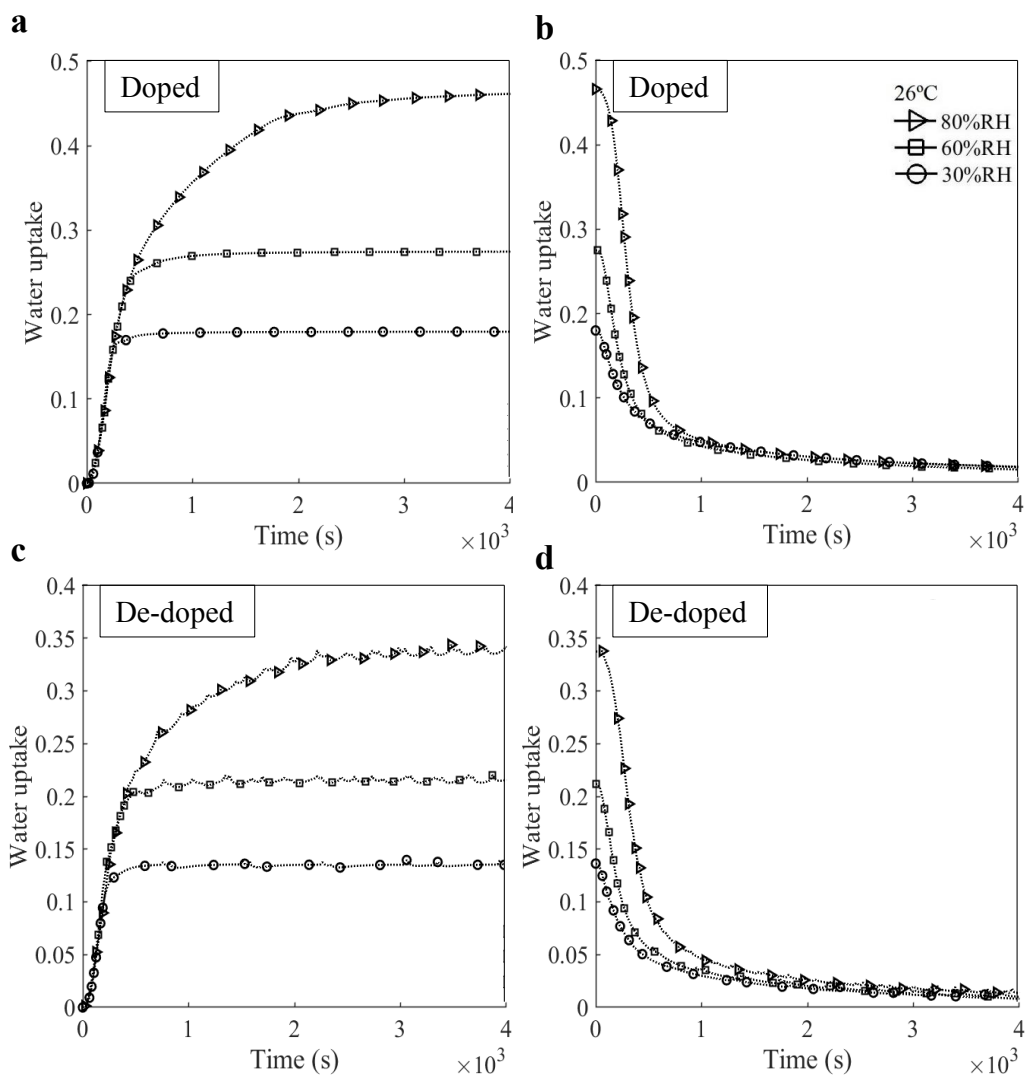
Figure S5: Sorption-desorption curves for (a-b) 15 μm, (c-d) 50 μm and (e-f) 100 μm-thick pure PEDOT:PSS films exposed to 30 %RH, 60 %RH and 80 %RH at 37°C

Figure S6: Sorption-desorption curves for (a-b) 15 μm, (c-d) 50 μm and (e-f) 100 μm-thick pure PEDOT:PSS films exposed to 30 %RH, 60 %RH and 80 %RH at 50ºC

Figure S7: Sorption-desorption curves for (a-b) 15 μm, (c-d) 50 μm and (e-f) 100 μm-thick pure PEDOT:PSS films exposed to 30 %RH, 60 %RH and 80 %RH at 80°C

Figure S8: a) Sorption and b) desorption curves for 50 μm EG pre-treated PEDOT:PSS film exposed to 30 %RH, 60 %RH and 80 %RH at 26°C. c) Sorption and d) desorption curves for 50 μm EG post-treated PEDOT:PSS film exposed to 30 %RH, 60 %RH and 80 %RH at 26°C.
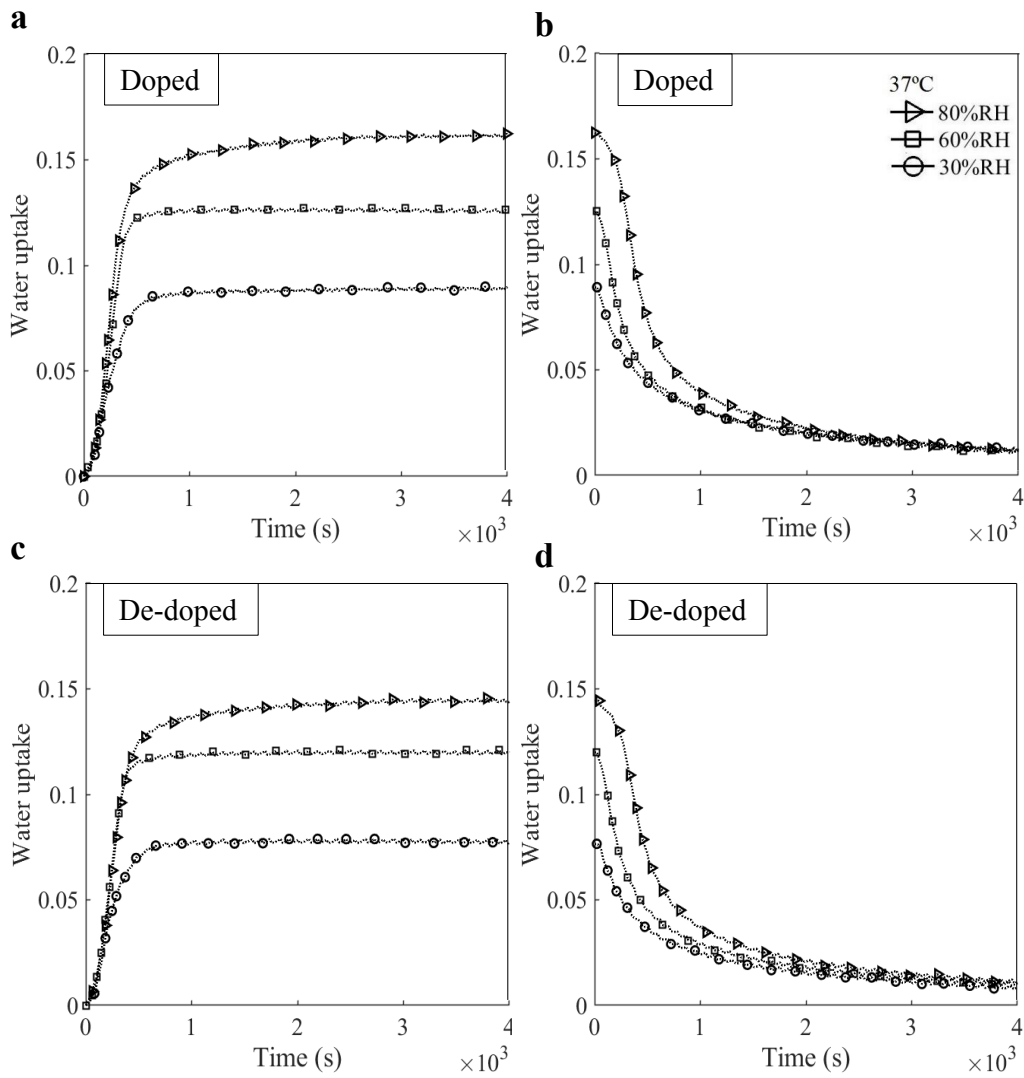
Figure S9: a) Sorption and b) desorption curves for 50 μm EG pre-treated PEDOT:PSS film exposed to 30 %RH, 60 %RH and 80 %RH at 37°C. c) Sorption and d) desorption curves for 50 μm EG post-treated PEDOT:PSS film exposed to 30 %RH, 60 %RH and 80 %RH at 37°C.
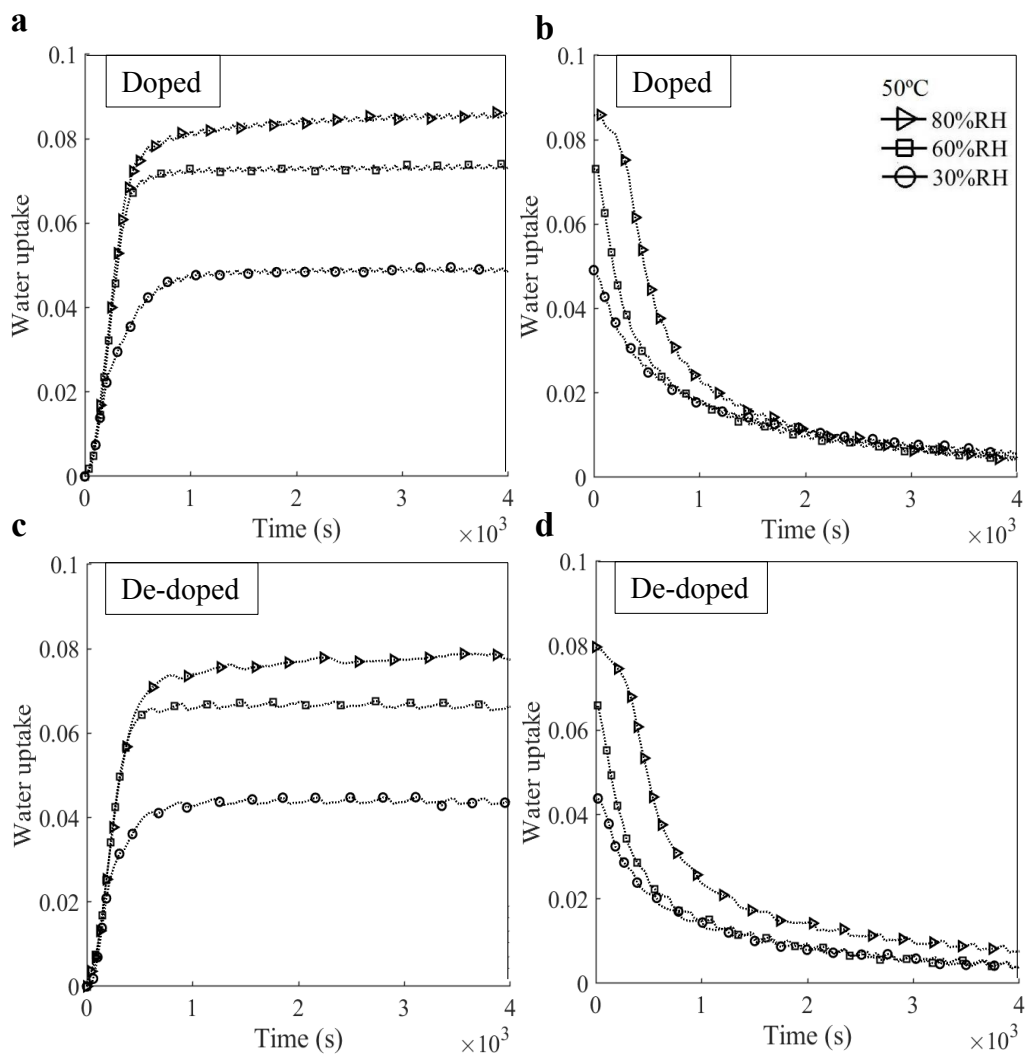
Figure S10: a) Sorption and b) desorption curves for 50 μm EG pre-treated PEDOT:PSS film exposed to 30 %RH, 60 %RH and 80 %RH at 50°C. c) Sorption and d) desorption curves for 50 μm EG post-treated PEDOT:PSS film exposed to 30 %RH, 60 %RH and 80 %RH at 50°C
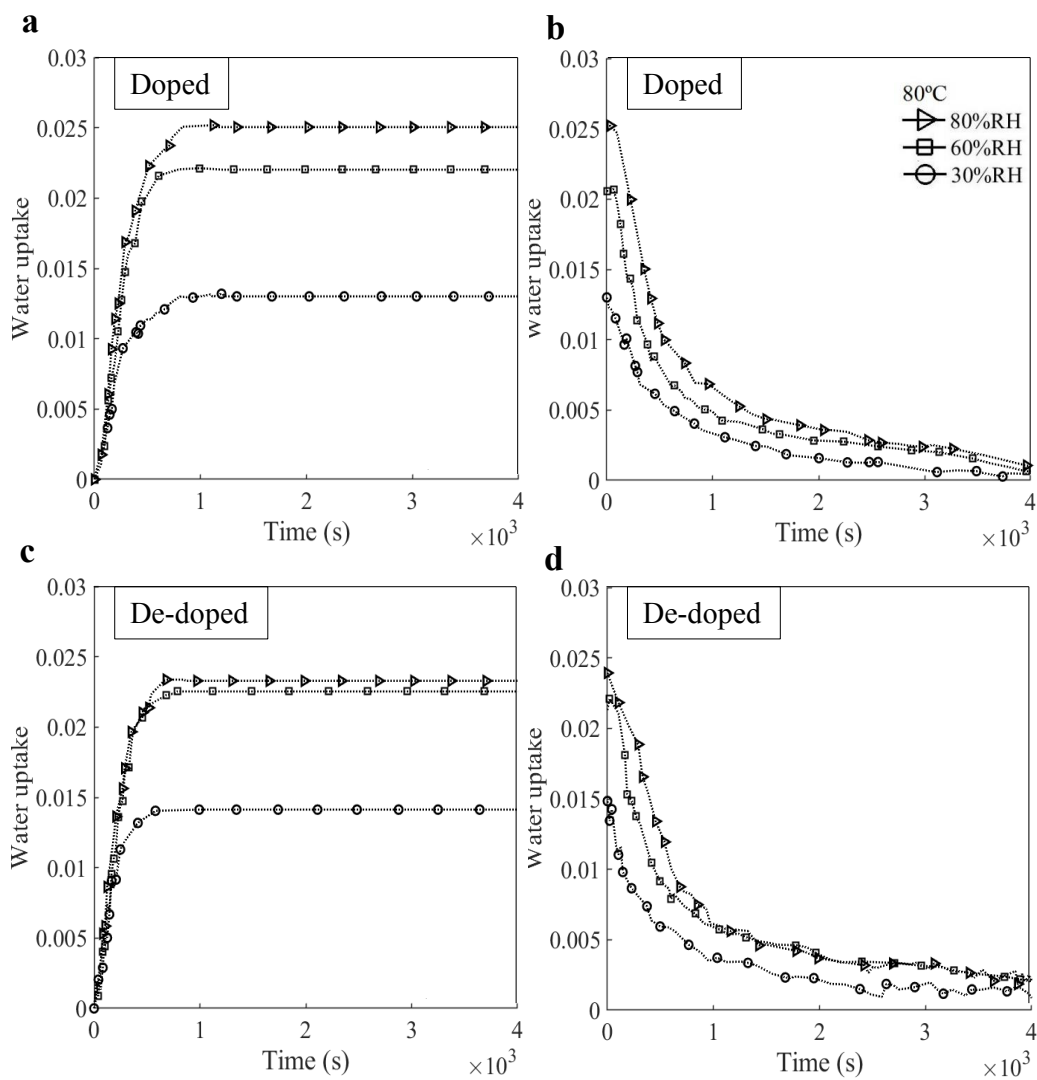
Figure S11: a) Sorption and b) desorption curves for 50 μm EG pre-treated PEDOT:PSS film exposed to 30 %RH, 60 %RH and 80 %RH at 80°C. c) Sorption and d) desorption curves for 50 μm EG post-treated PEDOT:PSS film exposed to 30 %RH, 60 %RH and 80 %RH at 80°C.

References

(1) Miller, F. P.; Vandome, A. F.; John, M. B. *Fick's Laws of Diffusion*; VDM Publishing, 2010.

(2) Shirangi, M. H.; Michel, B. *Moisture Sensitivity of Plastic Packages of IC Devices*; 2010.

(3) El Yagoubi, J.; Lubineau, G.; Roger, F.; Verdu, J. A fully coupled diffusion-reaction scheme for moisture sorption-desorption in an anhydride-cured epoxy resin. *Polymer (United Kingdom)* **2012**, *53*, 5582–5595.