Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

SUPPORTING INFORMATION

Ionic-to-Electronic Coupling Efficiency in PEDOT:PSS Films Operated in Aqueous Electrolytes

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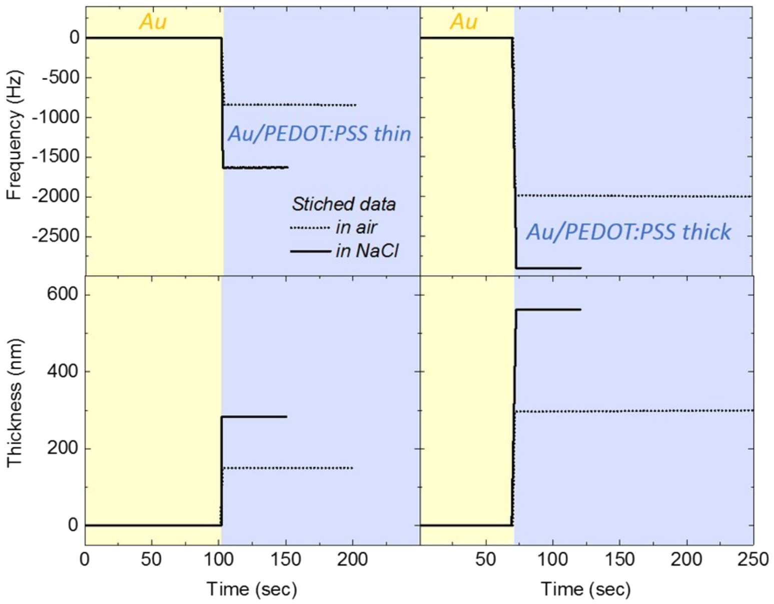
a)



b)

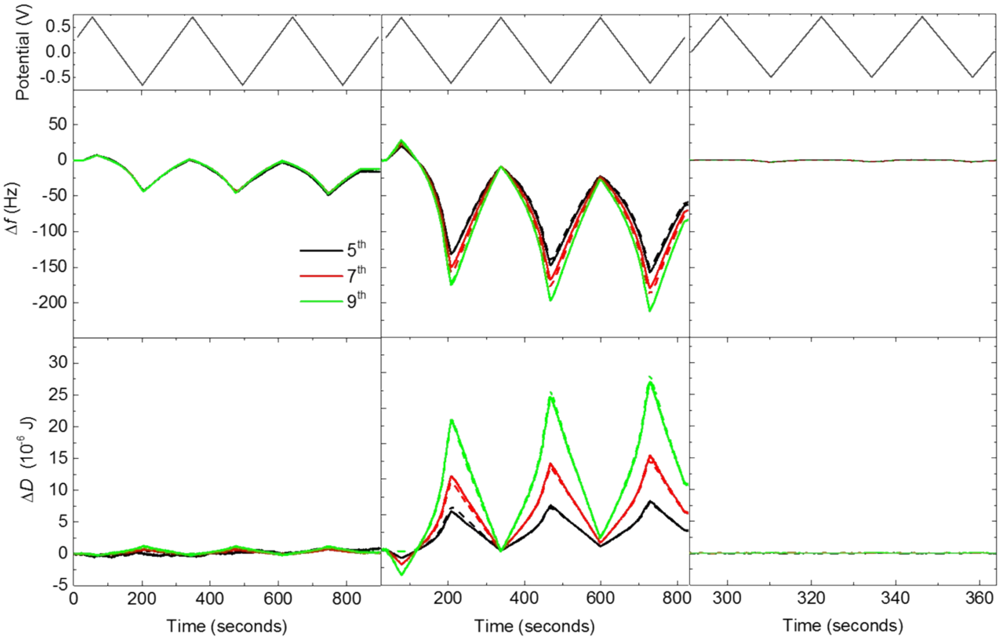


Figure S1. a) The absolute change in the oscillation frequency (Δf) versus time (5th overtone) of the bare Au sensors and Au/PEDOT:PSS coated sensors in air and in aqueous NaCl solution for the thin (left column) and thick PEDOT:PSS film (right column). The corresponding thicknesses in air (dotted lines) and in the electrolyte (solid lines) calculated by the Sauerbrey equation are shown at the bottom row. **b)** The change in EQCM-D frequency (Δf, middle row) and dissipation (ΔD, bottom row) signals recorded during three consecutive CV measurements of PEDOT:PSS films (thin film; left column, thick film; middle column) in an aqueous electrolyte solution (NaCl, 0.1 M). The overtones chosen for the analysis are the 5th, 7th and 9th; black, red and green lines, respectively. The voltage is applied vs. Ag/AgCl reference electrode at a speed of $0.01 Vs^{-1}$ starting at the open circuit potential (V_{oc}=0.29V) towards doping potentials and back towards de-doping potentials. The response of the bare Au sensor to CV is shown at the right column. The dashed lines represent the fits, with the same color code for the overtones as indicated above.

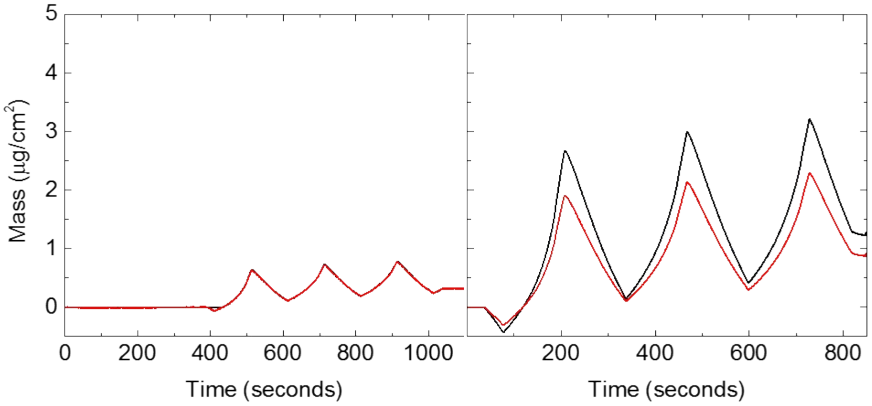


Figure S2. The evolution of the mass on PEDOT:PSS films over time during the CV measurements. The mass is calculated either using the VSE model (black line) or the Sauerbrey equation (red line) for the thin (left) and the thick (right) film.

Table S1. The mass on the PEDOT:PSS film as well as the corresponding current at the end of each CV cycle at V_{oc}.

	PEDOT:PSS thin Mass (μg/cm^2)	PEDOT:PSS thin Current (mA/cm^2)	PEDOT:PSS thick Mass (μg/cm^2)	PEDOT:PSS thick Current (mA/cm^2)
At V_{oc} before CV	0	0	0	0
1st CV cycle	0.08	5.56	0.67	6.29
2nd CV cycle	0.13	5.56	0.97	5.31
3rd CV cycle	0.14	5.36	1.08	5.40

Table S2. Volumetric site density calculated for three different scenarios of Na^+ transfer, including 0, 2 and 4 H_2O molecules coupled to each Na^+ ion. The number of cations is calculated from the mass accumulated on the film when it is de-doped at -0.85V vs. V_{oc}.

	PEDOT:PSS - thin 10^{20} sites/cm^3	PEDOT:PSS - thick 10^{20} sites/cm^3
Na^+	4.90	8.29
Na^+:$2H_2O$	1.91	3.08
Na^+:$4H_2O$	1.18	1.92

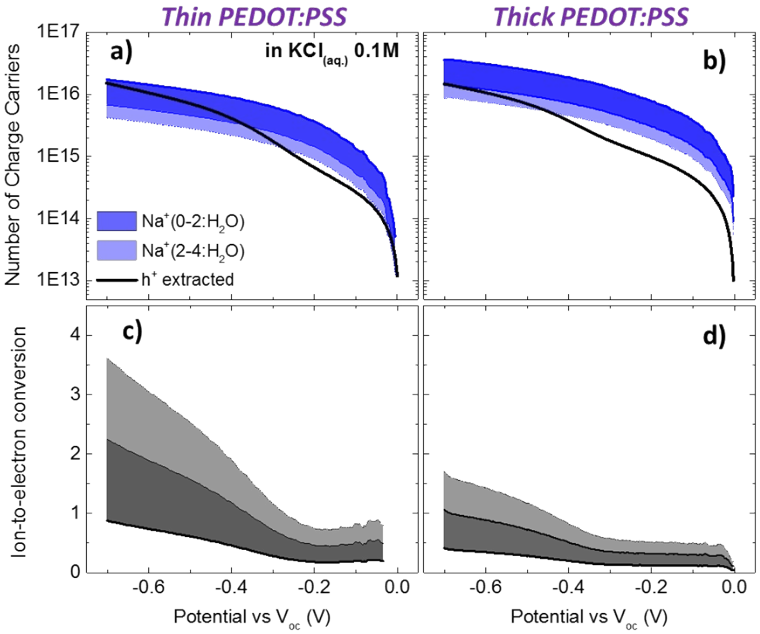


Figure S3. The evolution of the number of charge carriers, i.e. holes (h$^+$, black lines) and K$^+$ ions (blue lines), during the backward voltage scan of the CV cycle for the **a)** thin and **b)** thick film. The efficiency of ion-to-electron conversion calculated for the **c)** thin and **d)** thick film. The color code represents the case when K$^+$ injection does not involve any water molecules (darkest color, blue or grey) and when each K$^+$ ion is coupled to 2 or 4 water molecules (the color of the shaded area gets lighter with more water involved, blue or grey).

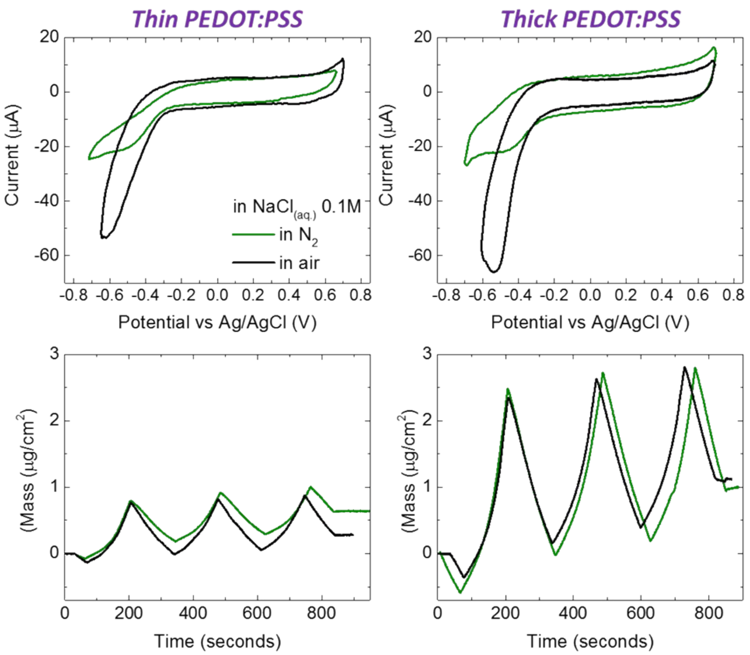


Figure S4. Top panel depicts CV curves of thin (left column) and thick (right column) PEDOT:PSS films in $NaCl_{(aq.)}$ 0.1M in air (black) and under rigorous bubbling with N_2 for ca. 2 hours (green). The potential scan starts at V=V_{oc} towards ca.+0.7V and then back towards ca. -0.7 V vs. Ag/AgCl with a rate of 0.01V·sec^{-1}. The corresponding mass which moves into or out of the films recorded for each case is presented at the bottom panel. The mass was calculated by treating the raw QCM-D data shown in the following Figure S5 with the VSE model.

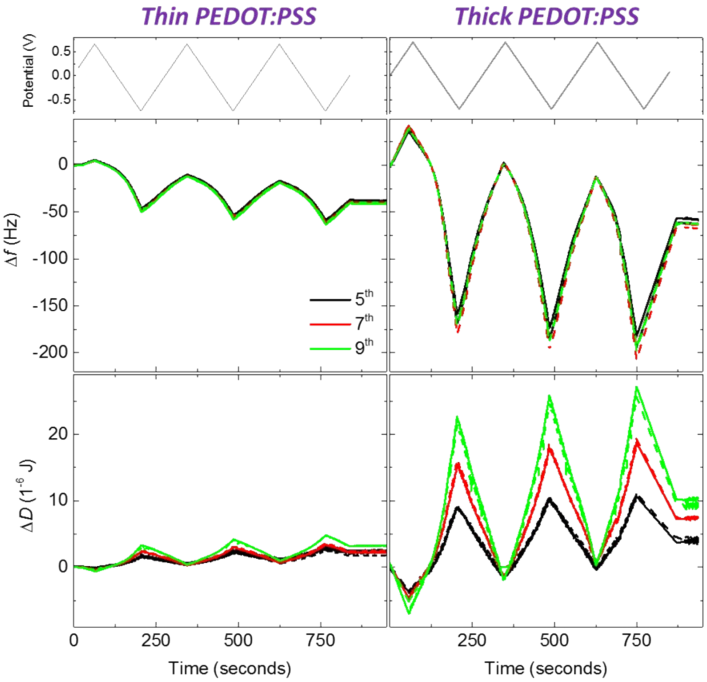


Figure S5. The change in EQCM-D frequency (Δ*f*) and dissipation (Δ*D*) signals recorded during three consecutive CV measurements (thin film; left column, thick film; right column) in a deoxygenated-$NaCl_{(aq.)}$ solution (0.1M). The overtones chosen for the analysis are the 5th, 7th and 9th; black, red and green lines, respectively. The voltage is applied vs. Ag/AgCl reference electrode at a speed of $0.01 Vs^{-1}$ starting at the V_{oc} towards doping potentials and back towards de-doping potentials. The dashed lines represent the fits, with the same color code for the overtones as indicated above.

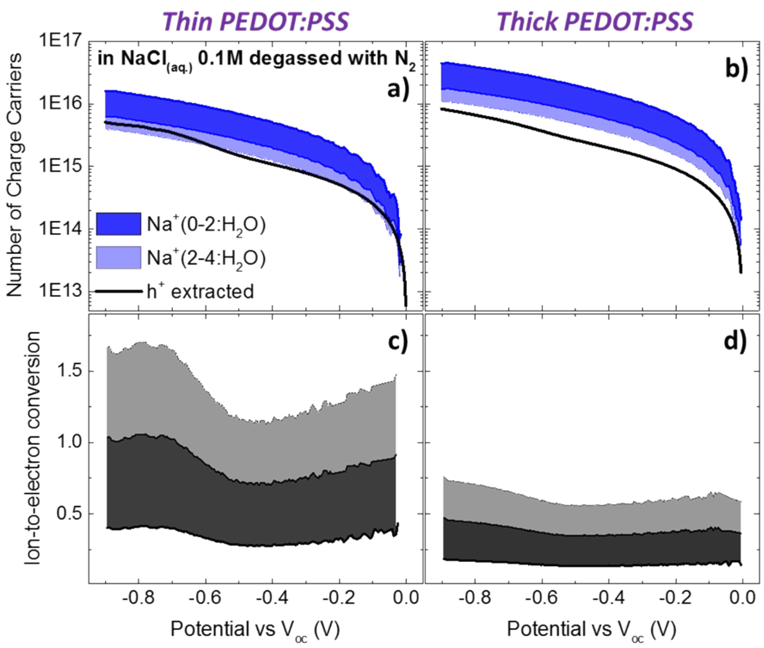


Figure S6. The evolution of the number of charge carriers, i.e. holes (h^+, black lines) and cations (blue lines) during the backward voltage scan of the 2nd CV cycle for the **a)** thin and **b)** thick film. The efficiency of ion-to-electron conversion is calculated for the **c)** thin and **d)** thick film. The color code represents the case when Na^+ injection does not involve any water molecules (darkest color, blue or grey) and when each Na^+ ion is coupled to 2 or 4 water molecules (the color of the shaded area gets lighter with more water involved, blue or grey). The NaCl solution has been deoxygenated by vigorous bubbling with N_2 for over 2 hours.

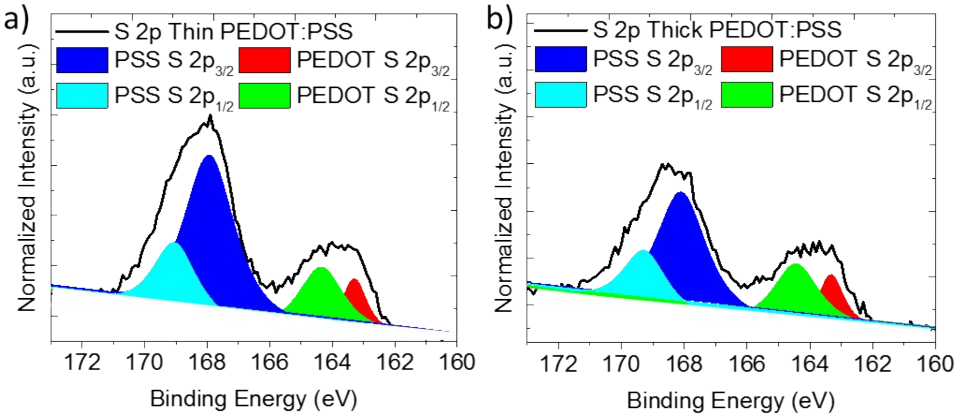


Figure S7. XPS S 2p spectra of thin **a)** and thick **b)** PEDOT:PSS films. The surface ratio of PSS to PEDOT was calculated using the ratio of integral area (black curves) from the peaks assigned to PSS (S $2p_{3/2}$ ~ 168 eV and S $2p_{1/2}$ ~ 169 eV) and to PEDOT (S $2p_{3/2}$ ~ 163 eV and S $2p_{1/2}$ ~ 164 eV). The fitted curve for PSS is composed of two types of sulfur atoms: S $2p_{1/2}$ which originates from neutral sulfur atoms (*e.g* SO_3H) and S $2p_{3/2}$ attributed to ionic sulfur atoms (*e.g.* SO_3^- $PEDOT^+$). The doublet peaks at 163.3 eV and 164.4 eV are attributed only to the sulfur atom in the PEDOT chains.

Table S3. Relative areas of convoluted peaks of S 2p spectra of PEDOT:PSS films.

Peak assigned to	FWHM (eV)	Sample	Binding Energy (eV)	Area (%)
PEDOT $2p_{3/2}$	0.961	Thin	163.295	8.50
		Thick	163.326	10.06
PEDOT $2p_{1/2}$	1.731	Thin	164.350	18.21
		Thick	164.442	21.29
PSS $2p_{3/2}$	1.958	Thin	167.936	52.57
		Thick	168.100	47.98
PSS $2p_{1/2}$	1.717	Thin	169.043	20.72
		Thick	169.276	20.67

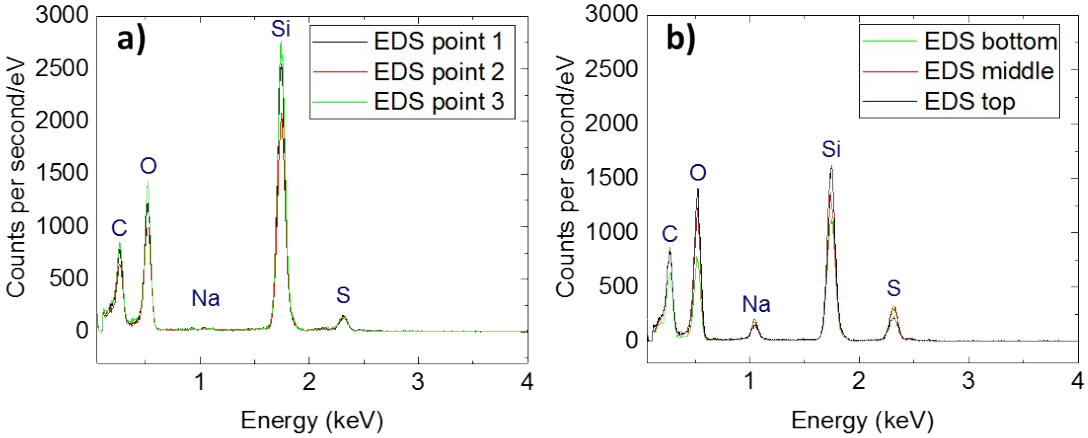


Figure S8. EDS spectra acquired from 3 different spots within the cross section of the **a)** thin and **b)** thick PEDOT:PSS film.