

## Electronic Supplementary Information

### Results

#### XPS for pristine sample

The XPS wide scan of the pristine film is presented in Figure S1. We observe that a Cl peak appears while there seems to be no Fe contribution, confirming the exchange of tosylate during polymer preparation with Cl, after rinsing the polymer with HCl.

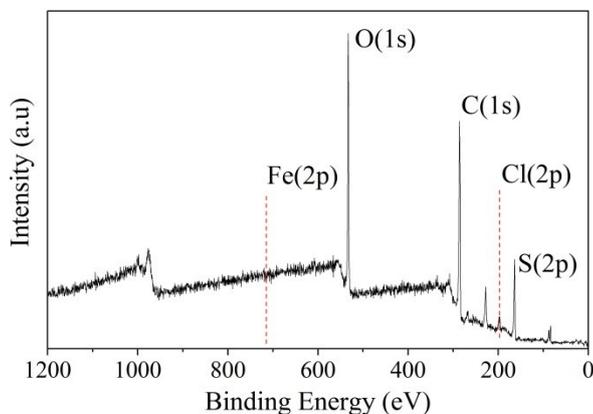


Figure S1. XPS spectrum for the pristine film.

#### Electrochemical setup for chronoamperometric and *in situ* resistometry measurements

In Figure S2a and b, we present the electrochemical cells for the chronoamperometric and *in situ* resistometry measurements on PEDOT:Cl films. The film thickness in the chronoamperometric measurements is ca. 100nm, while the film used in the *in situ* resistometry measurement has an average thickness of 185nm.

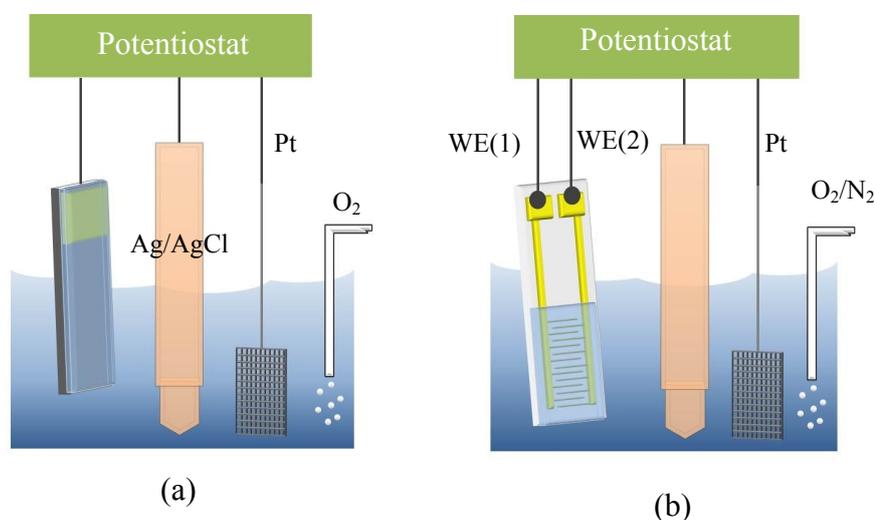
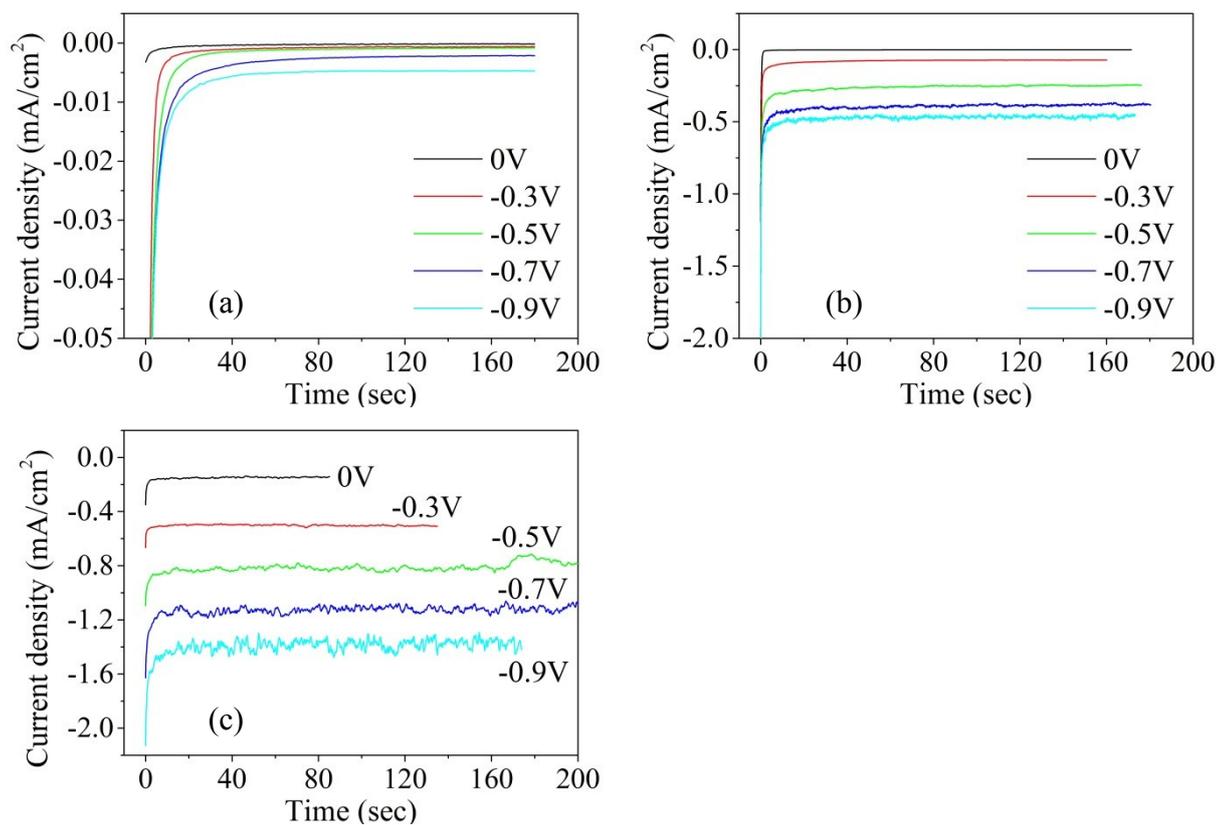


Figure S2. (a) Electrochemical cell for the chronoamperometric measurements and (b) electrochemical setup for *in situ* resistometry measurement. A bias of 50mV was applied and maintained between the two working electrodes (WE(1) and WE(2)), while sweeping the potential relative to the counter electrode from 0.6V to -0.9V at a scan rate of 5mV/s. The electrolyte in both setups was aqueous 0.1M KCl.

#### Chronoamperometric measurements

In Figure S3 we present the chronoamperometric measurements for PEDOT in  $N_2$  and  $O_2$ , while comparing them with the ORR performance of Pt in  $O_2$ . We use chronoamperometry in order to avoid the capacitive currents that appear in cyclic voltammetry. We record the current

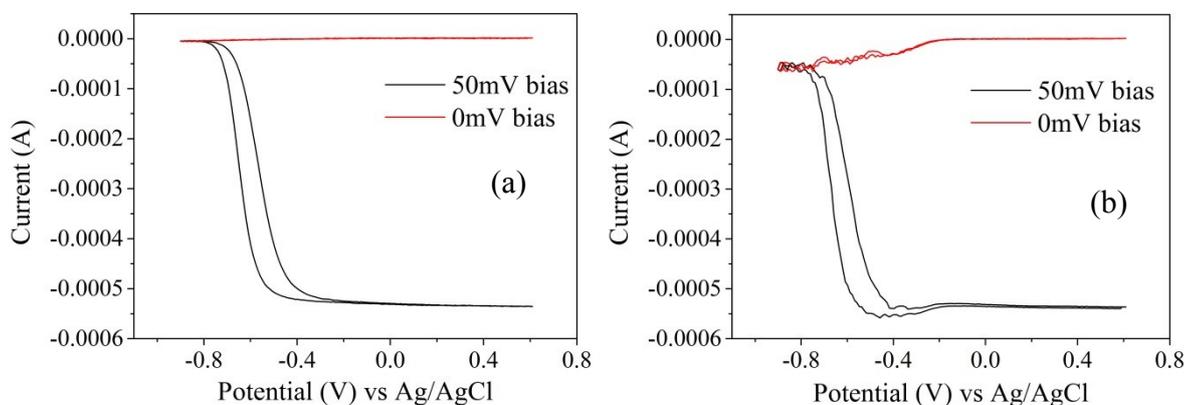
when a constant potential is applied for ca. 180sec. We observe higher current densities in the lower negative applied potentials, due to oxygen reduction reaction which dopes PEDOT and keeps it conducting.



**Figure S3.** Chronoamperometric measurements in 0.1M KCl for (a) PEDOT in  $N_2$ , (b) PEDOT in  $O_2$  and (c) Pt in  $O_2$ .

#### Raw data of *in situ* resistometry measurements

In Figure S4 we see the raw data of one device for the *in situ* resistometry measurements. The black curves present the sweeping of the potential when applying a bias of 50mV between the two working electrodes, while the red curves present the potential sweeping when the bias is 0mV. By applying 0mV bias, we short circuit the two working electrodes. Then, in order to avoid the side contributions coming from each of the gold electrode and the electrolyte, we subtract the currents of the 0mV bias curve from those of the 50mV bias curve. Finally, we calculate resistance by dividing the potential bias (50mV) with the calculated current.



**Figure S4.** Amperometric measurement when sweeping the potential (vs Ag/AgCl (3M KCl)) at a scan rate of 5mV/s and while simultaneously applying a bias of 50mV or 0mV between the two interdigitated working electrodes (WE(1) and WE(2)) of Figure S1b in  $N_2$  (a) and  $O_2$  (b).