

Supplementary Information

Structural electrochemistry of Poly (3, 4-ethylenedioxythiophene) and its applicability as simultaneous sensor of environmental surroundings: self-sensing electrical, thermal, and chemical working conditions

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1. Electrical conductivity

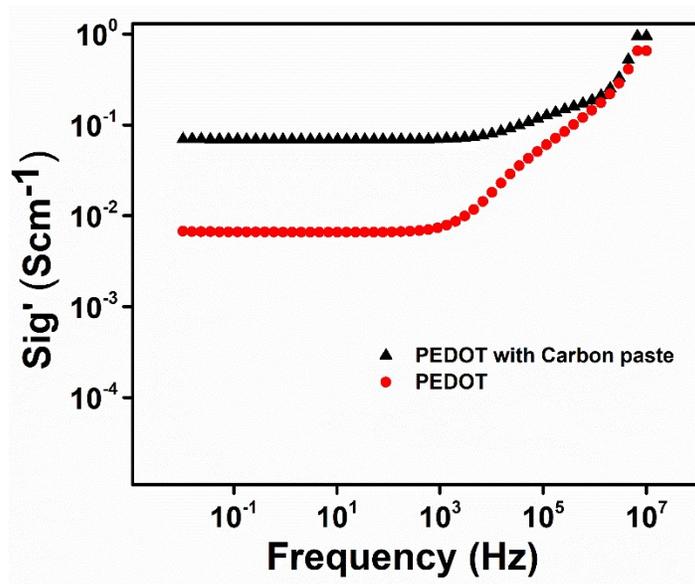


Figure S1. Log–log plot of the frequency dependence of the AC conductivity data of the PEDOT and PEDOT/Carbon paste

The pelletized samples were sandwiched between a couple of parallel gold-plated electrodes in a Broadband dielectric spectrometer (Novo Control Technologies, Germany) to measure electrical conductivity in the frequency range of 10⁻² to 10⁷ Hz at room temperature and ambient pressure. It is found that PEDOT and PEDOT/Carbon paste have electrical conductivities of 6X10⁻³ Scm⁻¹

and $7 \times 10^{-2} \text{ Scm}^{-1}$, respectively. By extrapolating the conductivity at lower frequencies, the conductivity values were determined.

2. Raman spectrum

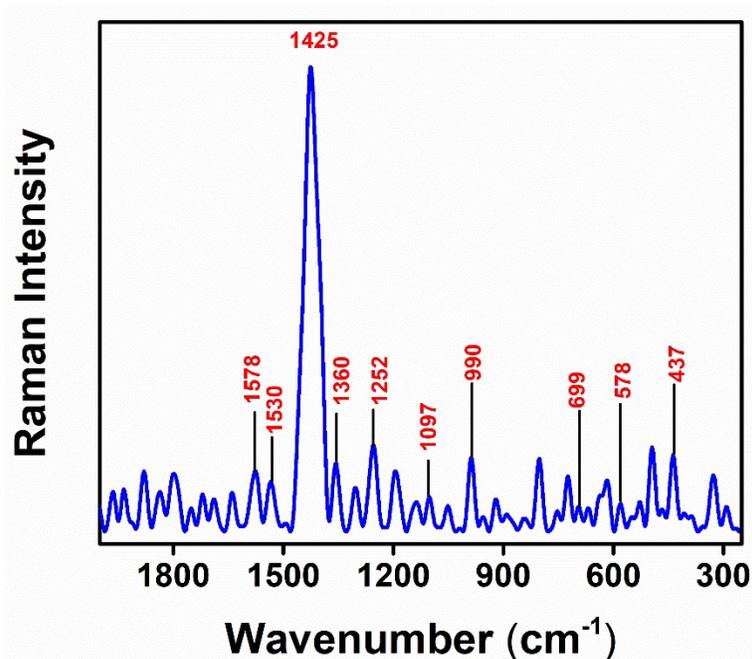


Figure S2. Raman spectrum of PEDOT

Figure S2 displays the Raman spectrum of PEDOT obtained with a BRUKER RFS 27 MultiRAM FT Raman Spectrometer excited by a Nd-YAG laser at 1064 nm. It is evident from the figure that characteristic PEDOT peaks are obtained. PEDOT's spectra show two weak bands, with peaks corresponding to the quinoid structure at 1572 cm^{-1} and the asymmetric $C_{\alpha}=C_{\beta}$ stretching at 1535 cm^{-1} . $C_{\alpha}-C_{\alpha}'$ (interring) stretching is detected by a single sharp band at 1252 cm^{-1} , which is due to the result of the overlap of two nearby bands seen in the stimulated Raman spectra at 1064 nm. The C-O-C and C-S-C deformations, respectively, are the cause of the bands at 1097 cm^{-1} and 699 cm^{-1} . The bands at 990 cm^{-1} and 578 cm^{-1} is due Oxyethylene ring deformation. The doped PEDOT is represented by the strong, sharp band at 1425 cm^{-1} . The oxidized PEDOT chain is what causes the doping of HSO_4^- .

3. Theoretical Investigation – Chrono potentiometric Results

The capability of PEDOT to perceive its operating conditions in a reactive manner is confirmed by its redox reactions³. The Nernst equation is employed to represent the potential of the electrode material under equilibrium conditions ⁵⁷.

$$E = E_0 - \frac{RT}{nF} \ln \frac{[A^-][PEDOT^*]}{[(PEDOT)^{n+}(A^-)_n(H_2O)_m]} \quad (S1)$$

The reaction elucidates the relationship between various components such as the evolved potential (E), standard electrode potential (E₀), universal gas constant (R), Faraday constant (F), anion concentration ([A⁻]), concentration of the active polymer centre ([PEDOT*]), and concentration of the oxidized polymer centre of PEDOT ([(PEDOT*)_n+(A⁻)_n(H₂O)_m]). Potentiometric sensors are based on the Le Chatelier principle, which states that a system seeks to counteract changes in chemical equilibrium caused by physical or chemical variables. However, the electrochemical redox reaction of PEDOT and other conducting polymers operates beyond equilibrium, deviating from this principle. Otero et al. have introduced a new interpretation of the Le Chatelier principle for such systems, suggesting that changes in the reaction rate prompt a shift in reaction energy to accommodate the new energetic demands. Consequently, variations in the working energetic conditions of the reaction can be detected by monitoring the material's potential. The rate of the reaction of the PEDOT can be expressed as

$$r = k[PEDOT^*]^a[A^-]^b \quad (S2)$$

The reaction rate is denoted by the variable "r" and the kinetic coefficient is represented by "k", "a" and "b" are the reaction orders related to the active polymeric centres and the anion/electrolyte concentration, respectively. When a steady current is applied to the PEDOT electrode material, a correlation between the current and the reaction rate can be established.

$$r = \frac{q}{FV} = \frac{it}{FV} \leftrightarrow i = \frac{rFV}{t} \quad (S3)$$

The quantities q (charge), i (current), t (time of current flow), F (Faraday's constant), and V (volume of the PEDOT polymer) are interconnected. The electrochemical kinetics' Butler-Volmer

equation was employed to establish the correlation between the rate constant and the potential evolution in both the anodic and cathodic redox processes

$$i_a = FV k_{\alpha} [PEDOT^*]^a [A^-]^b \quad (S4)$$

$$= FV k_{\alpha 0} [PEDOT^*]^a [A^-]^b \exp\left(\frac{(1-a)nF(E-E_0)}{RT}\right) \quad (S5)$$

In this context, the potential generated during the reaction relies on various factors, including the electrolyte concentration, applied current, and/or temperature. It is possible to derive an equation to articulate the interrelationship between these factors and the resulting evolved potential.

$$E_a = E_0 + \frac{RT}{(1-a)nF} \left(\ln\left(\frac{i_a}{FV}\right) - b \ln [A^-] - a \ln [PEDOT^*] - \ln k_{\alpha 0} \right) \quad (S6)$$

Equation (7) and (8) elucidate the sensor-like behaviour of the PEDOT electrode during the anodic process. A similar equation can be derived for the cathodic process. The material undergoes n consecutive steps during the oxidation process, allowing for the formulation of a comprehensive equation.

$$E_n(t) = E_0 + i_a Z + (n-1)\Delta E + \frac{RT}{(1-a)F} \left\{ \ln\left(\frac{i_a}{FV}\right) - b \ln [A^-] - a \ln \left([PEDOT^*]_{initial} - \frac{i_a t}{FV} \right) - \ln k_{\alpha 0} \right\} \quad (S7)$$

Equation (S7), (S8), and (S9) present mathematical relationships that elucidate the connection between the electrical energy consumed by the reaction of the electrode material as a function of the experimental factors, such as the applied current, electrolyte concentration, and temperature. When one variable alters while others remain constant, the resulting electrical energy demonstrates a direct correlation with that particular variable. In the case of the studied PEDOT in this investigation, the consumed electrical energy follows a linear pattern with the applied current under stable electrolyte concentration and working temperature. Similarly, the logarithm of the electrolyte concentration exhibits a linear relationship with the electrical energy expended during the redox reaction, maintaining constant current and working temperature. Thus, the PEDOT electrode demonstrates its potential as an electrochemical sensor, capable of detecting changes in its chemical environment during operation.