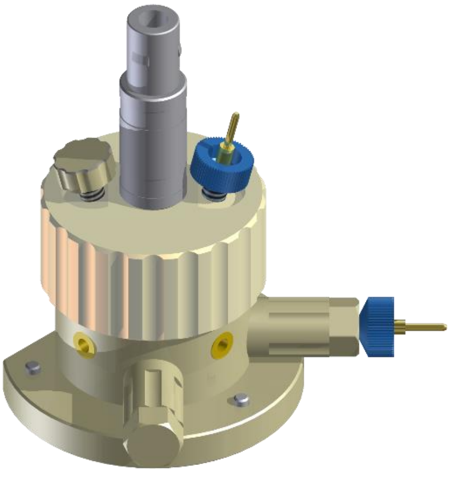
Application note

Electrochemical Characterization of a Conducting Polymer Thin Film



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rhd instruments GmbH & Co. KG

Introduction

Conducting polymer thin films are employed in many types of electrochemical devices such as solar cells, sensors, electrochromic windows, supercapacitors, etc [1, 2]. Three-electrode electrochemical characterization of such samples can be practically challenging due to the need to soak the film in electrolyte while also bringing it in electrical contact with the measurement device. The TSC Surface measurement cell (see title page figure and **Figure 1**) enables the study of electrochemical surface reactions on a flat sample mounted on the working electrode, with the possibility of including a variety of reference and counter electrodes.

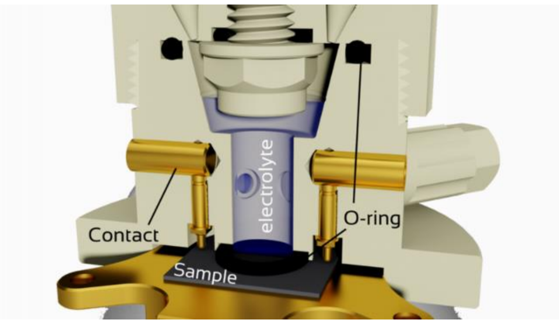

Figure 1*. The TSC Surface measurement cell. The sample is located at the bottom, the counter electrode is at the top of the cell, and a reference electrode can be inserted through one of the four ports (see title page figure).*

In this application note, the electrochemical properties of the conducting polymer poly-3,4-ethylenedioxythiophene (PEDOT) doped with polystyrene sulphonate (PSS) was characterized in a three-electrode setup using the TSC Surface measurement cell. Cyclic voltammetry was used to investigate the electrochemical doping, and the charge transfer resistance of that process was studied by electrochemical impedance spectroscopy (EIS). The areal capacitance of the PEDOT film was calculated by both methods and compared.

Experimental

A thin layer of PEDOT:PSS was drop cast onto a glassy carbon surface (1 × 1 cm^2) from a 1% aqueous solution. The solvent was slowly evaporated by placing the specimen on a hot plate (50 °C), followed by drying in a vacuum oven (50 °C) over night. The specimen was placed in a TSC Surface measurement cell (rhd instruments GmbH & Co. KG) inside a glove box. The cell was filled with tetrabutylammonium hexafluorophosphate (TBAHFP, 1.0 M in acetonitrile) electrolyte, and equipped with a Ag$^{0/+}$ reference electrode (Ag | 10 mM AgNO$_3$, 10 mM [2.2.2]Cryptand, 0.5 M TBAHFP (acetonitrile), -0.665 V vs Fc$^{0/+}$) and a glassy carbon counter electrode. The electrolyte volume in this cell is 0.5 ml, and the active area is 0.283 cm^2, defined by an O-ring (6 mm Ø) pressing against the sample. The cell was sealed inside the glove box and all electrochemical measurements were carried out outside of the glove box in a Microcell HC temperature control setup (rhd instruments GmbH & Co. KG), set at 20 °C unless otherwise stated. A Metrohm Autolab PGSTAT302N equipped with a FRA32-module was used, and controlled through the NOVA 2.1.6 software. Temperature control was automated from NOVA using a Microcell HC plugin. Cyclic voltammetry was performed with an α value of 0.3, suitable for observing capacitive processes [3]. EIS between 1 MHz and 0.1 Hz with an amplitude of 10 mV rms was performed after a 2 min holding time at the desired bias potential. The impedance data was evaluated by equivalent circuit fitting in RelaxIS 3 (rhd instruments GmbH & Co. KG). RelaxIS 3 was also used for visualization and analysis of the EIS data, while the other figures in this application note were created using the Edelweiss software (rhd instruments GmbH & Co. KG).

Results

A cyclic voltammogram (CV) of the PEDOT:PSS coating can be seen in **Figure 2**, showing its pseudocapacitive behaviour [2]. During the oxidative sweep, the onset of the doping process occurred at around -0.5 V vs $Ag^{0/+}$, below which the capacitance was much lower. Above 0.8 V vs $Ag^{0/+}$, irreversible oxidation currents that lead to the degradation of the PEDOT:PSS material were increasingly prevalent.

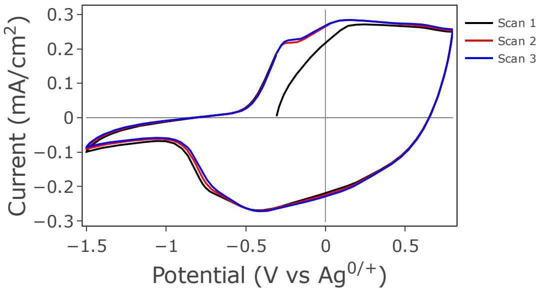

Figure 2. *PEDOT:PSS CV at 0.1 V/s, 20 °C.*

CVs limited to the doped region, and normalized by scan rate, are shown in **Figure 3**. At the lowest scan rates, some redox peaks with large peak split were observed, originating from faradaic processes, either of the PEDOT itself, or of some species dissolved in the electrolyte. At intermediate scan rates (5 – 200 mV/s), the CVs were mostly overlapping, *i.e.* the current was directly proportional to the scan rate, indicating that the doping process was kinetically limited in this region. At higher scan rates, however, the normalized current dropped as the doping became mass transport limited.

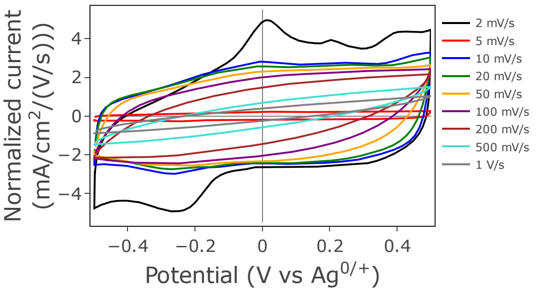

Figure 3. *PEDOT:PSS doped region CVs normalized with respect to the scan rate (2nd scan, 20 °C, α = 0.3).*

The areal capacitance (C) of the PEDOT coating was 2.6 mF/cm² [2], evaluated from cyclic voltammetry in the kinetically limited domain by

$$C = \frac{\int_{t_1}^{t_2} j(t)dt}{E_2 - E_1}$$

where $j(t)$ is the current density over time, and E_1 and E_2 are the potentials at the limits t_1 and t_2, respectively. With completely constant scan rate (ν) and uniform current sampling, this simplifies to

$$C = \frac{\bar{J}}{\nu}$$

where $\bar{J}$ is the average current density. Hence, the unit of the normalized current in **Figure 3** is also equivalent to mF/cm^2.

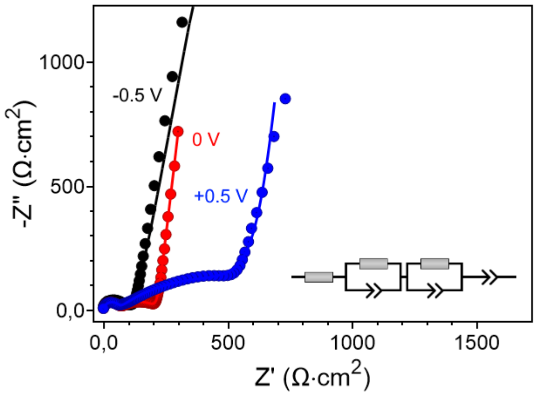

Figure 4. *EIS spectra of PEDOT:PSS at -0.5 V (black, data below 20 Hz not shown), 0 V (red), and +0.5 V (blue) vs Ag$^{0/+}$ (20 °C) and the equivalent circuit used to fit the data (fits shown as solid lines).*

EIS was performed at varying bias potentials to further characterize the PEDOT doping process. The spectra in **Figure 4** show a small semicircle at high frequencies that was largely independent of bias potential and temperature, which might be a reference electrode artefact, or correspond the charge transfer between the glassy carbon electrode and the PEDOT:PSS coating. At intermediate frequencies, a very flattened semicircle appeared, which had a strong dependence on both the bias potential and the temperature. This feature was assigned to the charge transfer resistance (R_{CT}) of the PEDOT doping process, in parallel to the interfacial double layer capacitance. At the lowest frequencies, -*Z*" increased as the thin film bulk was polarized. Based on these spectrum features, the equivalent circuit shown in **Figure 4** was fitted to the recorded data (solid lines in **Figure 4**). The bulk capacitance fitted from EIS was more or less constant above -0.2 V vs Ag$^{0/+}$, and had CPE α values close to 1, indicating a nearly ideal capacitance. When using a capacitor rather than a CPE for fitting, a bulk capacitance of 2.2 mF/cm^2 could be extracted, similar to that determined by CV.

The PEDOT doping R_{CT} evaluated by EIS is shown as a function on the bias potential in **Figure 5**. Below the doping onset (-0.5 V vs Ag$^{0/+}$, see **Figure** *2*), it was very large (>10 kΩ·cm^2), but quickly dropped by about two orders of magnitude as the conducting polymer was doped. Interestingly, above 0 V vs Ag$^{0/+}$ it increased again, *cf.* the red and blue spectra in **Figure 4**.

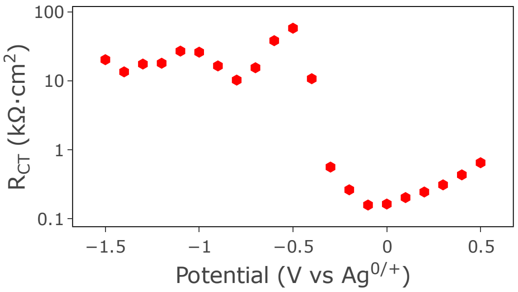

Figure 5. *Fitted PEDOT doping charge transfer resistance (logarithmic y-axis) versus the bias potential at 20 °C.*

The temperature dependence of R_{CT} at 0.5 V vs Ag$^{0/+}$ (**Figure 6**) conformed to the Arrhenius equation between 20 and 60 °C:

$$\frac{1}{R_{CT}(T)} = A \cdot e^{-\frac{E_a}{k_B T}}$$

where T is the temperature, A is a preexponential factor, E_a is the activation energy, and k_B is the Boltzmann constant. Non-linear fitting in RelaxIS yielded an activation energy for the PEDOT doping process of 0.23 eV ($r^2 = 0.997$). Note that this pertains to the charge transfer reaction, not the charge transport through the polymer [4]. In order to study the electronic conduction through the film, a different electrode geometry is required.

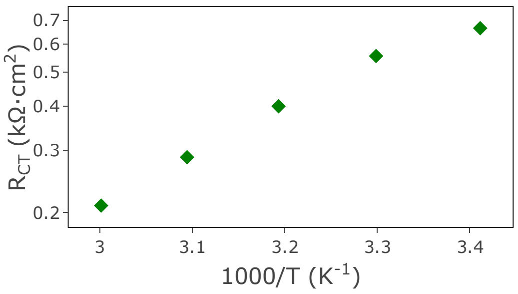

Figure 6. *Arrhenius plot of the PEDOT doping charge transfer resistance at +0.5 V vs* $Ag^{0/+}$.

Summary

A PEDOT:PSS thin film was electrochemically characterized in a three-electrode setup in the TSC Surface measurement cell. A kinetically limited pseudocapacitive doping current was observed with cyclic voltammetry at -0.5 – +0.8 V vs $Ag^{0/+}$ and 5 – 200 mV/s, corresponding to a capacitance of 2.6 mF/cm^2. EIS revealed a charge transfer resistance of the doping process with a minimum at moderate doping levels. The temperature dependence of this resistance revealed an activation energy of 0.23 eV.

Literature

[1] N. K and C. S. Rout, "Conducting polymers: a comprehensive review on recent advances in synthesis, properties and applications," *RSC Advances*, vol. 11, pp. 5659-5697, 2021.

[2] C. Karlsson, J. Nicholas, D. Evans, M. Forsyth, M. Strømme, M. Sjödin, P. C. Howlett and C. Pozo-Gonzalo, "Stable Deep Doping of Vapor-Phase Polymerized Poly (3, 4-ethylenedioxythiophene)/Ionic Liquid Supercapacitors," *ChemSusChem*, vol. 9, no. 16, pp. 2112-2121, 2016.

[3] M. Seralathan, R. A. Osteryoung och J. G. Osteryoung, ”General equivalence of linear scan and staircase voltammetry,” *Journal of Electroanalytical Chemistry*, vol. 222, pp. 69-100, 1987.

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