



PEDOT:PSS is a highly conductive and industrially important polymer used in energy devices, sensors, transparent electrodes, and wearable electronics. Its performance depends strongly on synthesis conditions, making in-situ characterization critical. In this application note, the eSorptionProbe, a next-generation EQCM-D that naturally functions as the working electrode in both a beaker setup and an electrochemistry Raman cell, is used to monitor the real-time electropolymerization of PEDOT:PSS. Mass changes, viscoelastic behavior, Raman spectra, and electrochemical response, including capacitance evaluation via cyclic voltammetry and EIS (Electrochemical impedance spectroscopy), were monitored simultaneously. This integrated approach provides powerful insight into the electropolymerization and in-situ properties of PEDOT:PSS coatings and serves as a platform for the design and optimization of functional polymer layers.

Summary

PEDOT:PSS is an industrially relevant coating with a high conductivity, that has a wide range of exciting applications in diverse fields such as energy, sensing, lighting, transparent electrodes and wearable bioelectronics.¹ The properties of the coating are highly tunable, depending on factors such as the counter-ion, secondary doping and polymerization method. When it was first synthesized, it was considered something of a breakthrough material as PEDOT can be easily electropolymerized from a solution of the EDOT monomer, forming a polymer of high conductivity of up to 200 S cm^{-1} , a value previously-unseen until then. Adapting the polymerization process in the presence of PSSNa produces a polymer that is both conductive and highly stable, which appears as either transparent or dark blue depending on the thickness. Today, PEDOT:PSS is available commercially and continues to be studied in academic and industrial

laboratories for its unique properties. This application note describes the use of EQCM-D (electrochemical quartz crystal microbalance with dissipation monitoring), Raman spectroscopy, and electrochemical measurements to investigate the synthesis of the coating. Frequency and dissipation (damping) responses are recorded simultaneously across multiple harmonics and correlated in real time with electrochemical and Raman signals.

Method

The potentiostat/galvanostat used was a Metrohm Autolab AUT204 equipped with FRA32M module. The EQCM-D system was a 3T analytik, eSorptionProbe OS. With this system both the fundamental and several overtone frequencies can be measured. The software packages used were NOVA, qGraph and qGraph Viewer for associating the QCM-D and electrochemical data.

Part 1 - Electropolymerisation

In the first part of this experiment, a PEDOT coating was deposited on the EQCM probe via constant current deposition. The parameters are listed in Table 1. Under these conditions EDOT is polymerized to the PEDOT and PSS is incorporated in the form of a charge-balancing counter ion PSS⁻.

Table 1. Parameters used in part 1 of this experiment.

Component	Details
Technique	Chrono-potentiometry
Technique Parameter	80 μ A, 150 seconds
Cell	Three-Electrodes
Working Electrode	QCM Au Crystal
Counter Electrode	Pt
Reference Electrode	Ag/AgCl
Electrolyte	0.01 M EDOT, 0.1 M PSSNa*

* Molarity was calculated from the mass of the repeating unit.

In the literature, for PEDOT:PSS no large morphological differences have been found between constant current, potential or potentiodynamic deposition therefore constant current was selected for ease of use.² Indeed, in this work both were trialed and no large difference in the frequency or damping signal was seen. The frequency and damping signal were modelled in the qGraph Viewer software using the viscoelastic method.

Part 2 - Coating Assessment

In the second part of this experiment, the presence of PEDOT was confirmed via Raman spectroscopy and the capacitance of the polymer coating measured. The coating was washed in Ultrapure water and then left to dry for 24 hours. The coated probe was then transferred to the DRP-RAMANCELL-M, and the cell filled with 0.1 M KCL. Raman spectroscopy was conducted with an i-Raman Plus 532H system (B&W TEK) with 100% laser power and 20 second integration time and 3 time averaging. The capacitance of the coating was assessed by two different means - cyclic voltammetry and EIS. For these measurements, the WE was the EQCM probe, the CE was a Pt wire electrode and the reference electrode was Ag/AgCl. Cyclic voltammetry (CV) was conducted in the non-faradaic region between 0 and 0.4 V, at a variable scan rate of 0.1, 0.05, 0.02, 0.005 and 0.001 V/s. The anodic and cathodic current at 0.2 V was extracted and plotted against the scan rate according to the below equation. The resulting slope of this graph is the capacitance of the electrode.

$$i = EDLC \frac{dV}{dt}$$

Where i is the current, EDLC is the electric double layer capacitance and dV/dt is the scan rate.

An alternative method to obtain the capacitance is electrochemical impedance spectroscopy (EIS). In this method the capacitance was obtained by measuring at the open circuit potential (OCP) in the frequency range of 10 kHz to 0.1 Hz, with an amplitude of 10 mV. The data above 1000 Hz was discarded due to the presence of reference electrode and inductance artifacts. The remaining was fitted to a simple equivalent circuit containing a resistor and constant phase element and the effective capacitance calculated from the below equation:

$$C_{eff}(F) = Y_0^{\frac{1}{n}} \cdot \left(\frac{1}{R_s}\right)^{\frac{n-1}{n}}$$

Results

In Figure 1, the potential, frequency Δf and damping $\Delta\Gamma$ signal as a function of time is shown. At the application of the current, the potential rises rapidly to around 0.85 V a potential that by CV is associated with the oxidation of the monomer EDOT to short-chain oligomers.³ The potential falls slightly but reaches a steady state, consistent with the behaviour seen in most constant current measurements. At the same time the frequency signal falls, signaling an increased mass at the working electrode. Across the full course of the experiment, $\Delta f = -11,000$ Hz, corresponding to a mass change per area density of around 48,000 ng/cm². Two regions of this signal response can be identified, one in the first 10-20 seconds of the deposition where the reaction is more likely to be associated with the oxidation of the monomer and its conversion to short chain oligomers.³ Here the fall in frequency and rise in damping happens more rapidly. At a certain point though the oligomers begin to polymerize and the mass thereafter increases at a stable rate, remaining consistent throughout the rest of the deposition. At the same time, the rise in damping is becoming slower over time.

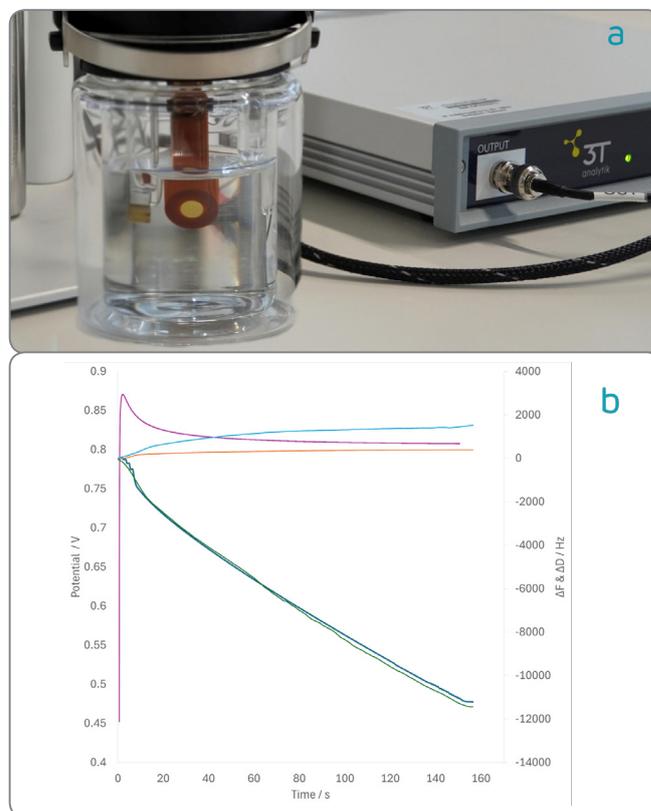


Figure 1. (a) The eSorptionProbe integrated into a standard electrochemical beaker cell is shown, operating as the working electrode. (b) Potential (purple), frequency (dark green, fundamental, light green, F3 overtone) and damping (orange, fundamental, blue, F3 overtone) signals recorded during the course of the deposition.

To investigate dynamic changes in the mechanical properties of the deposited layer, the change in damping relative to frequency ($\Delta\Gamma/\Delta f$ -ratio), was plotted as a function of time in Figure 2. The $\Delta\Gamma/\Delta f$ -ratio rapidly increases to a value about 0.25 at the onset of monomer oxidation to short chained oligomer. This indicates that the oligomer layer is viscoelastic in nature. Soon after, coinciding with oligomer polymerization, the $\Delta\Gamma/\Delta f$ -ratio rapidly drops to values below 0.1, and is continuously dropping henceforth.

Damping signals >10% of the frequency shift is a key indication that a layer has viscoelastic properties.⁴ Such layers require viscoelastic modelling tools (also provided in qGraph Viewer) for precise calculation of layer thickness.

In this case, however, the damping drops to values well below <10% of the frequency shift during PEDOT:PSS polymerization. This indicates that the final polymer layer is rigid and that the Sauerbrey equation applies:

$$\Delta\phi = -Cf \cdot \Delta f$$

Where $Cf = 4.3 \text{ ng} \cdot \text{cm}^{-2} \cdot \text{Hz}^{-1}$ is the sensitivity coefficient for this crystal, and $\Delta\phi = \Delta m / A\rho$ represents the area density. The layer thickness can then be calculated by dividing $\Delta\phi$ by the material density ρ .

A dedicated tool for this exists in qGraph Viewer. For the layer thickness calculation, a density of 1.011 g cm^{-3} was used, which is the density provided for dried coating of the commercially available PEDOT:PSS by Sigma-Aldrich. The

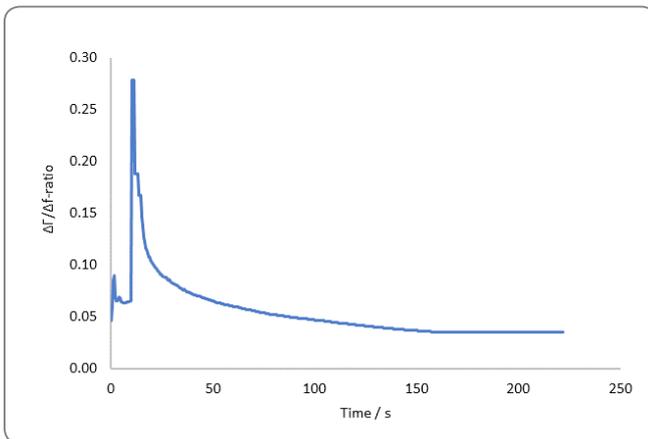


Figure 2. $\Delta\Gamma/\Delta f$ -ratio of the fundamental frequency over the course of the experiments. The initial rapid increase to ratios of 0.25 to rapid but gradual drop over time indicates that the layer stiffens as the polymerization occurs.

qGraph Viewer software estimates a total thickness of the layer at 474-486 nm, using Δf_1 and Δf_3 , respectively. In the second part of the experiment, following washing, mounting in a Raman cell and immersion of the EQCM probe in KCL, the Raman spectrum shown in Figure 3 was collected.

The Raman spectrum unambiguously confirms the presence of PEDOT at the electrode surface, with the bands beyond 1000 cm^{-1} being particularly relevant for this. The highest intensity peak, the one at $\sim 1430 \text{ cm}^{-1}$ has in the past been used to guide doping of the polymer film as the red and blue shift of this band corresponds well with changes in the electronic structure of the polymer.⁵ A full list of the Raman shift of each band and their assignments is given in Table 2 below.

Table 2. Raman band assignments and Raman shift.⁵

Assignment	Wavenumber / cm^{-1}
PSS	990
PSS	1097
PEDOT ($C_\alpha-C_\alpha$)	1255
PEDOT ($C_\beta-C_\beta$)	1369
PEDOT ($C_\alpha=C_\beta$)	1430
PEDOT ($C_\alpha=C_\beta$)	1502
PSS	1568

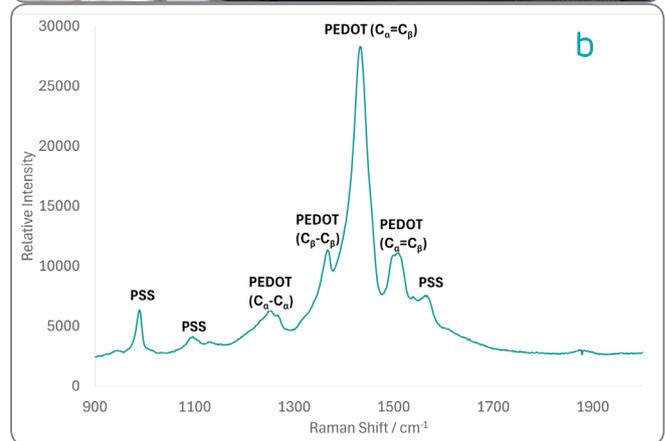
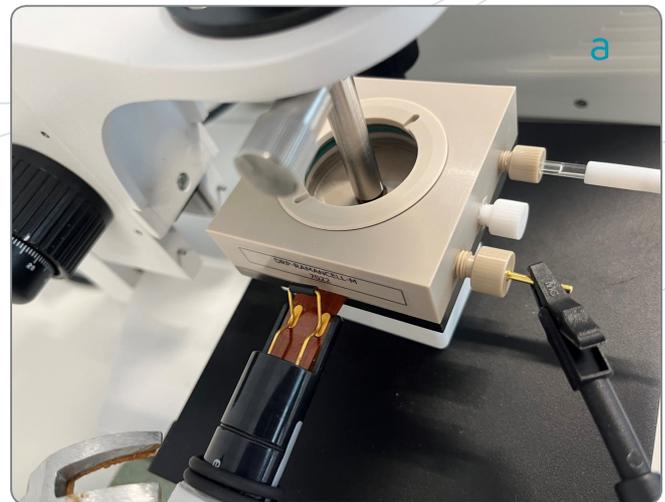


Figure 3. (a) The EC-Raman cell at the center contains the Raman probe and probe holder, with the inserted eQCM-D eSorptionProbe functioning as the WE and shown on the side. (b) Raman spectrum of the coated electrode, confirming presence of PEDOT:PSS.

The capacitance of the coated electrode was also calculated from two methods and compared to that of the bare electrode. In Figure 4, the CV in the non-faradaic region is shown. From this, the anodic and cathodic currents at 0.2 V for each scan rate was extracted and plotted vs the scan rate. The slope of these lines gives the capacitance directly and in each case was $\sim 700 \mu\text{F}$.

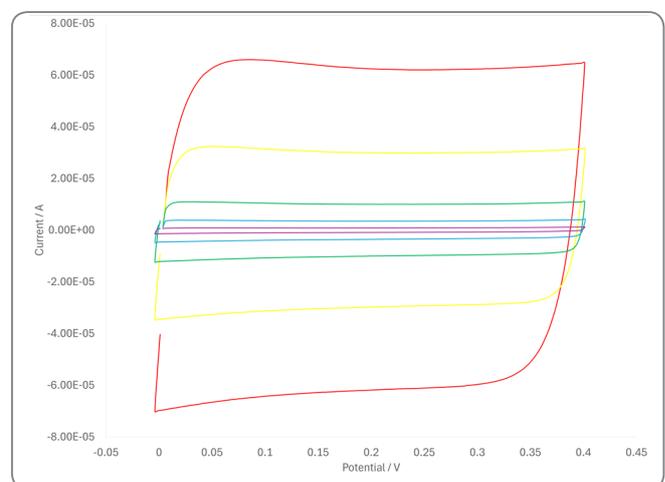


Figure 4. CV in the non-faradaic region is shown for the coated electrode, at various scan rates.

The Nyquist and Bode plot of the coated electrode is shown in Figure 5. The plots indicate R-C type behavior and are thus consistent with an intact coating. A constant phase element was actually used to model the non-ideality of the capacitance. The effective capacitance was extracted using the equation shown above and was calculated at around 710 μF . The consistency between these two values grants confidence in the two methods. The EIS method was used to obtain the capacitance of the bare electrode and was calculated at 80 μF .

The close to 8-fold increase in the capacitance upon coating the electrode is consistent with the pseudo-capacitive nature of this polymer, as well as the general increase in the effective electrochemical surface area (roughness) that comes with coating an electrode.¹

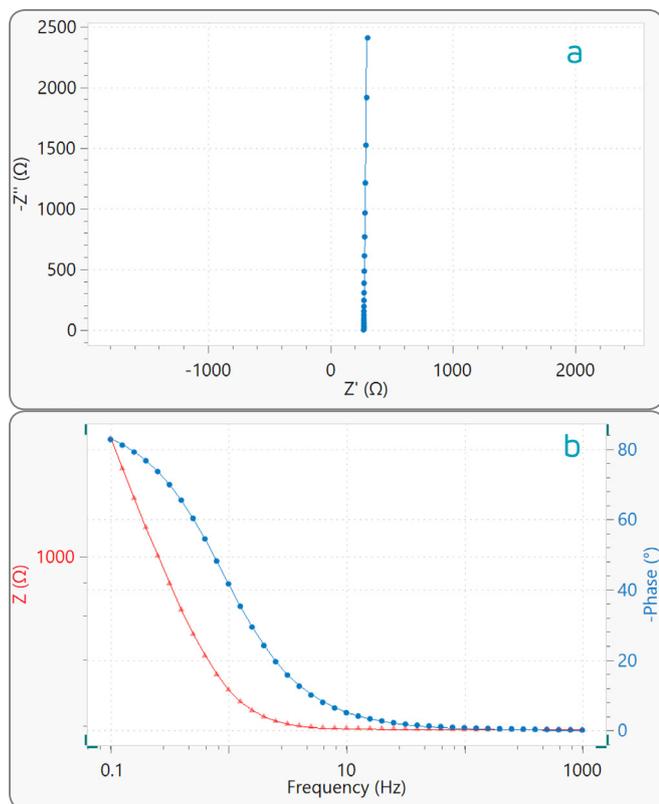


Figure 5. Nyquist (a) and Bode (b) plot of the coated electrode in the frequency range of 1000 to 0.1 Hz.

Conclusion

In this application note a novel probe-based system for EQCM-D analysis of an industrially relevant polymer coating was shown. EQCM-D has been shown to be highly effective in aiding the design and optimization of this type of coating, and this probe-based system affords the additional chance to obtain Raman spectra in situ. The system is therefore a powerful aid for researchers working in this field.

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