Application Note AN-SEC-004

Spectroelectrochemical analysis of electrochromic materials

Study of the electrochemical behavior of polymeric films

Intrinsically conducting polymers (ICPs) have received significant attention due to their exceptional properties. These include excellent chemical, thermal, and oxidative stability, tunable electrical properties, catalytic abilities, optical and mechanical features, and more. ICPs are used in myriad applications: in sensors, antistatic coatings, light-emitting diodes, transistors, flexible devices, and as the active material in electrochromic devices e.g., «smart» windows which regulate the amount of light that passes through.

Poly(3,4-ethylenedioxythiophene), otherwise known as PEDOT, is one of the most promising ICPs on the market. This is due to its high conductivity, electrochemical stability, catalytic properties, high insolubility in almost all common solvents, and interesting electrochromic properties (i.e., transparent in the doped state and colored in the neutral state). In this Application Note, PEDOT film is evaluated by spectroelectrochemical techniques.

INSTRUMENTATION AND SOFTWARE

This Raman characterization study was carried out using a SPELEC RAMAN (785 nm laser) instrument (Figure 1a), a Raman probe corresponding to the laser wavelength, and a Raman spectroelectrochemical cell for screen-printed electrodes (SPEs).

UV-Vis spectroelectrochemical measurements were performed using a SPELEC instrument (Figure 1b), a reflection probe for this spectral range, and a reflection cell for SPEs.

a)

b)

Figure 1. (a) SPELEC RAMAN and (b) SPELEC instruments used in the study of PEDOT film.

Gold SPEs (220AT) modified with a PEDOT film were used in this study. This setup allows users to obtain clear and detailed yet concise information about the behavior of PEDOT located on the electrode surface.

The SPELEC and SPELEC RAMAN instruments were controlled with DropView SPELEC software. DropView SPELEC is a dedicated software that provides spectroelectrochemical information and includes tools to perform adequate treatment and analysis of the collected data. All hardware and software used for this study is compiled in Table 1.

Table 1. Hardware and software equipment overview.

Equipment	Article number
Raman Instrument	SPELECRAMAN
Raman probe	RAMANPROBE
Raman spectroelectrochemical cell for SPEs	RAMANCELL
UV-Vis Instrument	SPELEC
Reflection probe	RPROBE-VIS-UV
Reflection spectroelectrochemical cell for SPEs	REFLECELL
Gold SPE	220AT
Connection cable for SPEs	CAST
Software	DropView SPELEC

APPLICATION: CHARACTERIZATION OF PEDOT

Raman spectroelectrochemistry was employed for the fingerprint characterization of the different oxidation states, neutral and doped, of PEDOT deposited on the Au SPE. The spectrum of the neutral state was obtained at -0.40 V (Figure 2, blue line) and p-doped PEDOT at +0.50 V (Figure 2, red line) in a 0.1 mol/L lithium perchlorate ($LiClO_4$) aqueous solution.

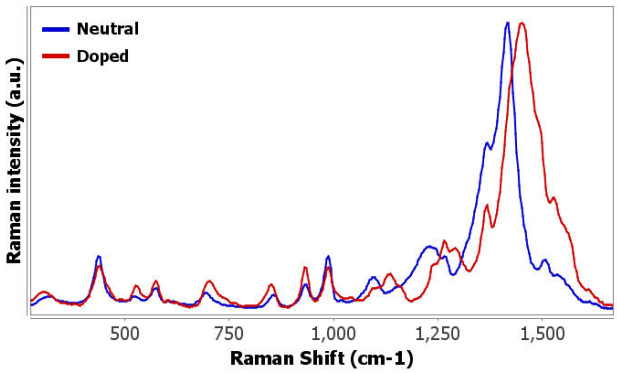


Figure 2. Raman spectra of neutral (blue line) and p-doped (red line) PEDOT.

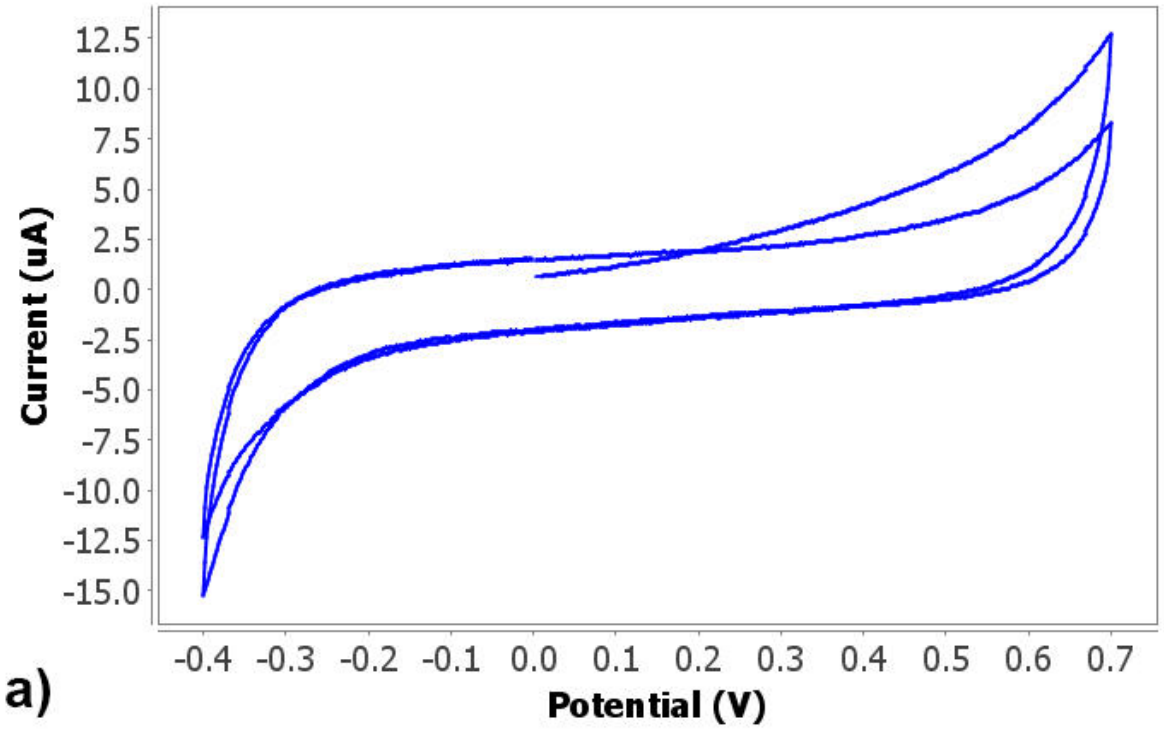
Assignments of the vibrational modes for each Raman band are listed in Table 2. The characteristic vibrational modes depend on the polymer oxidation state, particularly those located in the Raman shift region (1100–1600 cm^{-1}). Several Raman bands of PEDOT are up-shifted in the doped state. Note that although the C_{α}-$C_{\alpha'}$ inter-ring stretching vibrational mode is not detected in neutral PEDOT, it is observed at 1293 cm^{-1} in the doped state.

Table 2. Vibrational assignment of neutral and doped PEDOT [1–3].

PEDOT Raman bands (cm^{-1})		Assignment
Neutral	Doped	
445	445	Oxyethylene ring deformation
580	580	Oxyethylene ring deformation
700	710	Symmetric C_{α}-S-$C_{\alpha'}$ ring deformation
861	855	O-C-C deformation
992	992	Oxyethylene ring deformation
1101	1138	C-O-C deformation
1230	1234	C_{α}-$C_{\alpha'}$ inter-ring stretching + C_{β}-H bending
1266	1266	CH_2 twisting
-	1293	C_{α}-$C_{\alpha'}$ inter-ring stretching
1372	1372	C_{β}-$C_{\beta'}$ stretching
1422	1455	Symmetric C_{α}=C_{β}(-O) stretching
1510	1530	Asymmetric C_{α}=C_{β} stretching
1540	1560	Quinoid structure

Valuable qualitative information provided by UV-Vis spectroelectrochemistry allows the complete characterization of the PEDOT film previously deposited on the gold working electrode. Spectroelectrochemical experiments were performed in a 0.1 mol/L $LiClO_4$ aqueous solution, scanning the potential from 0.00 V to +0.70 V and back to -0.40 V at 0.05 V/s for two cycles. UV-Vis spectra were recorded in reflection configuration (300 ms integration time), resulting in almost 300 spectra collected during the electrochemical experiment. Synchronization of the electrochemical and spectroscopic responses is completely assured by the SPELEC instrument.

Cyclic voltammetry (Figure 3a) does not show any remarkable electrochemical peaks associated with the change of the oxidation state of PEDOT. However, a UV-Vis band centered at 525 nm is clearly observed in the simultaneously recorded spectra (Figure 3b).



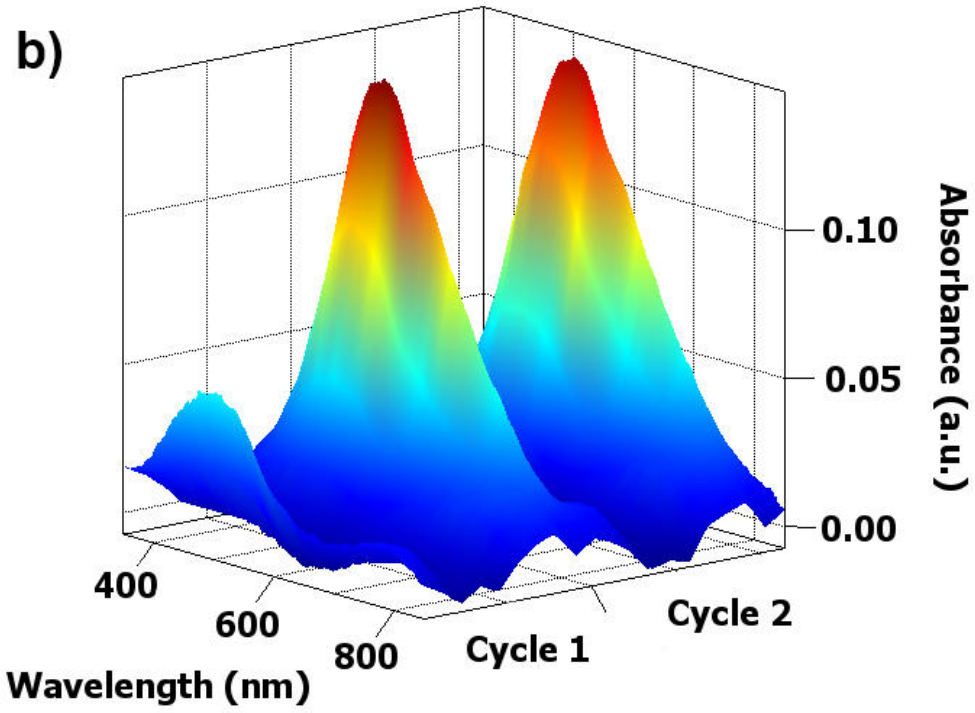


Figure 3. (a) Cyclic voltammogram and (b) 3D plot of the UV-Vis spectra obtained from PEDOT deposited on the 220AT SPE in 0.1 mol/L lithium perchlorate by scanning the potential from 0.00 V to +0.70 V and back to -0.40 V at 0.05 V/s for two cycles.

Evolution of the absorption band at 525 nm with changing potential is shown in Figure 4. Initially, absorbance decreases from 0.00 V to +0.70 V. In the backward scan, absorbance increases up to -0.40 V and decreases until 0.00 V, where it reaches a similar value as was at the beginning of the experiment. In the second scan, the spectroscopic signal shows the same spectroelectrochemical behavior. Absorbance at 525 nm at -0.40 V achieves the same value in both cycles, demonstrating the stability of this film for at least two cycles.

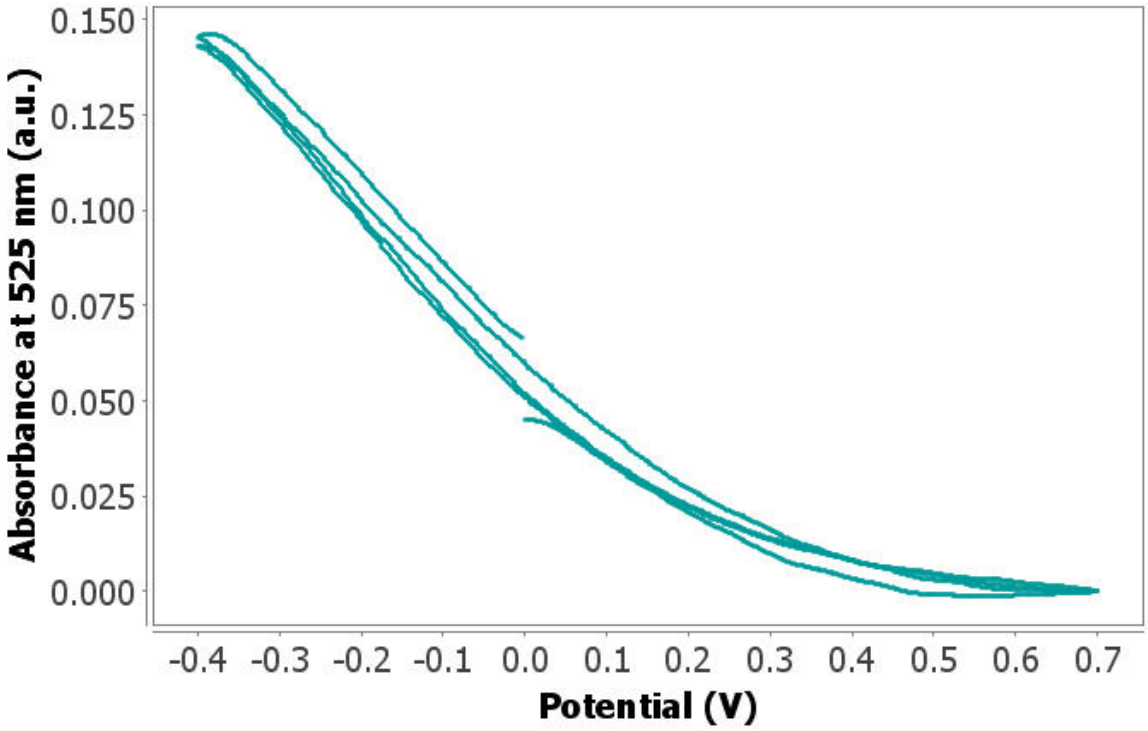


Figure 4. Evolution of the UV-Vis band at 525 nm with varying potential.

Evolution of this absorbance band with potential agrees with the electrochromic properties of PEDOT, being colorless in the doped state at positive potentials, while it is colored in the neutral state at negative potentials.

Figure 5 displays the relevant derivative voltabsorptogram (dAbs/dt vs. potential) at 525 nm. The derivative curve is only related to the faradaic component of the concomitant current flow. As can be observed in Figure 5, this derivative curve proves the polymer doping and de-doping processes through its reversible behavior.

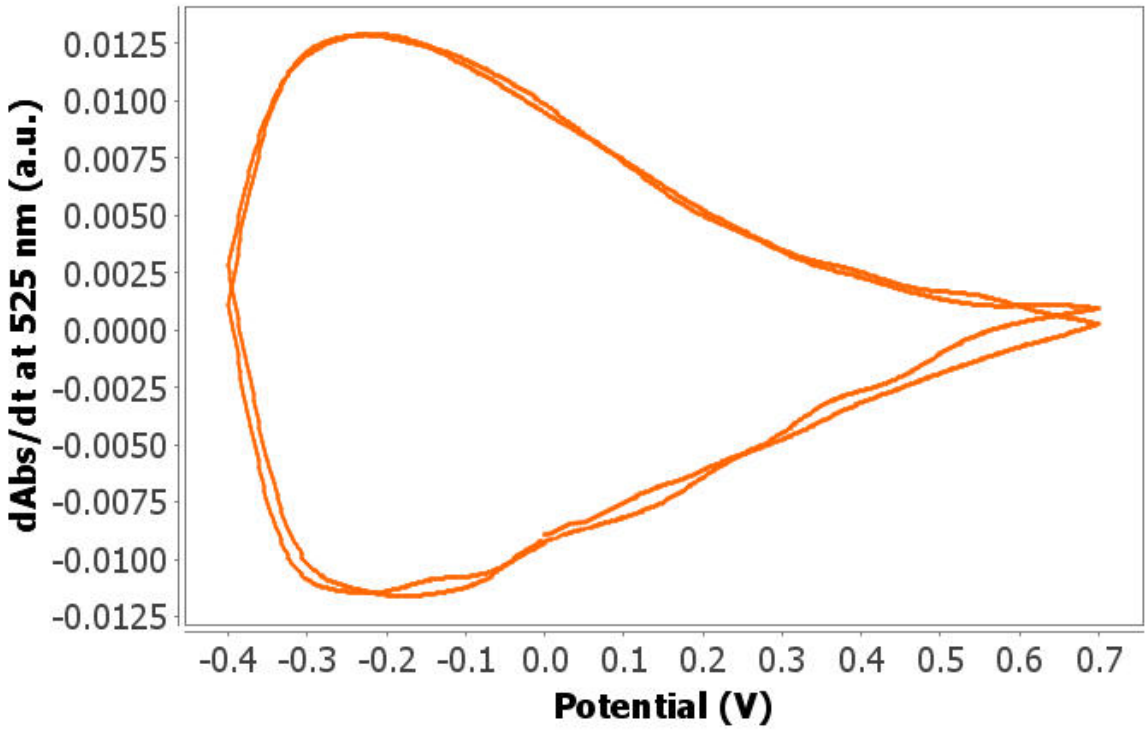


Figure 5. Derivative voltabsorptogram at 525 nm.

CONCLUSION

Spectroelectrochemistry is a multi-response technique that provides outstanding results in the characterization of electrochromic materials, e.g., PEDOT polymer.

Raman spectroelectrochemistry gives fingerprint results that allow discrimination between neutral and doped states of the sample since the position of Raman bands depends on the oxidation state. In addition, UV-Vis spectroelectrochemistry shows the presence of an absorption band in the visible region that enables the spectral monitoring of the electrochemical characterization of PEDOT. Absorbance decreases at positive potentials (doped state) while increasing at negative potentials (neutral state).

Analysis of the stability of the PEDOT coating with potential as well as achieving a complete understanding of its optical properties are crucial in the development of new applications.

REFERENCES

1. Feng, Z.-Q.; Wu, J.; Cho, W.; et al. Highly Aligned Poly(3,4-Ethylene Dioxythiophene) (PEDOT) Nano- and Microscale Fibers and Tubes. *Polymer* **2013**, *54* (2), 702–708. https://doi.org/10.1016/j.polymer.2012.10.057.
2. Garreau, S.; Louarn, G.; Froyer, G.; et al. Spectroelectrochemical Studies of the C_{14}-Alkyl Derivative of Poly(3,4-Ethylenedioxythiophene) (PEDT). *Electrochimica Acta* **2001**, *46* (8), 1207–1214. https://doi.org/10.1016/S0013-4686(00)00693-9.
3. Tran-Van, F.; Garreau, S.; Louarn, G.; et al. Fully Undoped and Soluble Oligo(3,4-Ethylenedioxythiophene)s: Spectroscopic Study and Electrochemical Characterization. *J. Mater. Chem.* **2001**, *11* (5), 1378–1382. https://doi.org/10.1039/b100033k.

RELATED APPLICATION NOTES

AN-SEC-001 Spectroelectrochemistry: an autovalidated analytical technique – Confirm results via two different routes in a single experiment.
AN-SEC-002 Gathering information from spectroelectrochemical experiments – Calculation of electrochemical parameters from data
AN-RA-004 UV-Vis spectroelectrochemical monitoring of 4-nitrophenol degradation.
AN-RA-005 Characterization of single-walled carbon nanotubes by Raman spectroelectrochemistry.

CONTACT

Metrohm Nordic AB
Box 11065
161 11 Bromma
mail@metrohm.se

CONFIGURATION

Raman Probe
Reflection probe designed to be used with a single excitation 785 nm wavelength (up to 500 mW). Suitable to work with DropSens Raman Cell for Screen-Printed Electrodes or with any conventional Raman set-up.

Raman Cell for Screen-Printed Electrodes

Black teflon reflection cell for performing Raman Spectroelectrochemistry with screen-printed electrodes in combination with ref. RAMANPROBE.

SPELEC UV-VIS Instrument (200-900 nm)

SPELEC is an instrument for performing spectroelectrochemical measurements. It combines in only one box a Lightsource, a Bipotentiostat/Galvanostat and a Spectrometer (UV-VIS wavelength range: 200-900 nm) and includes a dedicated spectroelectrochemical software that allows optical and electrochemical experiments synchronization.

Reflection Cell for Screen-Printed Electrodes

Cell in Teflon suitable to perform reflection experiments with standard format Screen-Printed Electrodes with the electrochemical cell in the middle of the strip. Closing system with powerful magnets.

Reflection probe VIS-UV

Reflection probe VIS-UV designed to perform reflection experiments suitable to work with our Reflection Cell for our Screen-printed electrodes or with any conventional cell.

Stat Cable connector for Screen-Printed Electrodes

Connects any DropSens equipment with DropSens Screen-Printed Electrodes

Screen-Printed Gold Electrode (Aux.:Au; Ref.:Ag) / Ink AT

Screen-Printed Gold Electrode (Aux.:Au; Ref.:Ag) / Ink AT. Suitable for working with microvolumes, for decentralized assays or to develop specific sensors.

Spectroelectrochemical Raman instrument (785 nm laser)

SPELECRAMAN is an instrument for performing spectroelectrochemical Raman measurements. It combines in only one box a laser class 3B (785 nm ± 0.5), a bipotentiostat/galvanostat and a spectrometer (wavelength range 787 – 1027 nm and Raman shift 35 - 3000 cm^{-1}) and includes a dedicated spectroelectrochemical software that allows optical and electrochemical experiments synchronization.