Application Note AN-SEC-004

致色材料的光化学分析

Study of the electrochemical behavior of polymeric films

聚合物由于其的性能而受到广泛注,包括的化学定性,和化定性、可的性能、催化能力、光学和机械特性等。聚合物用于多用:感器、抗静、光二管、晶体管、柔性,以及致色中的活性材料,例如透光量的"智能"窗口。聚(3,4-乙基二吩),也称PEDOT,是市上最具价的聚合物之一。是由于其高性、化学定性、催化性能、在几乎所有常溶中的高不溶性以及有趣的致色性能(在状下透明,在中性状下着色)。在用告主要明如何使用光化学技PEDOT薄膜行估。

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)

INSTRUMENTATION AND SOFTWARE

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.

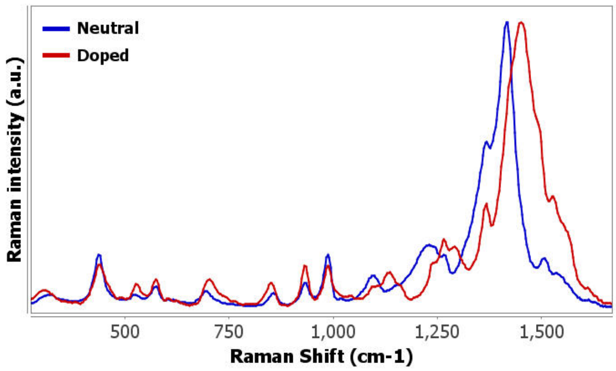

Figure 2. Raman spectra of neutral (blue line) and p-doped (red line) PEDOT.

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**).

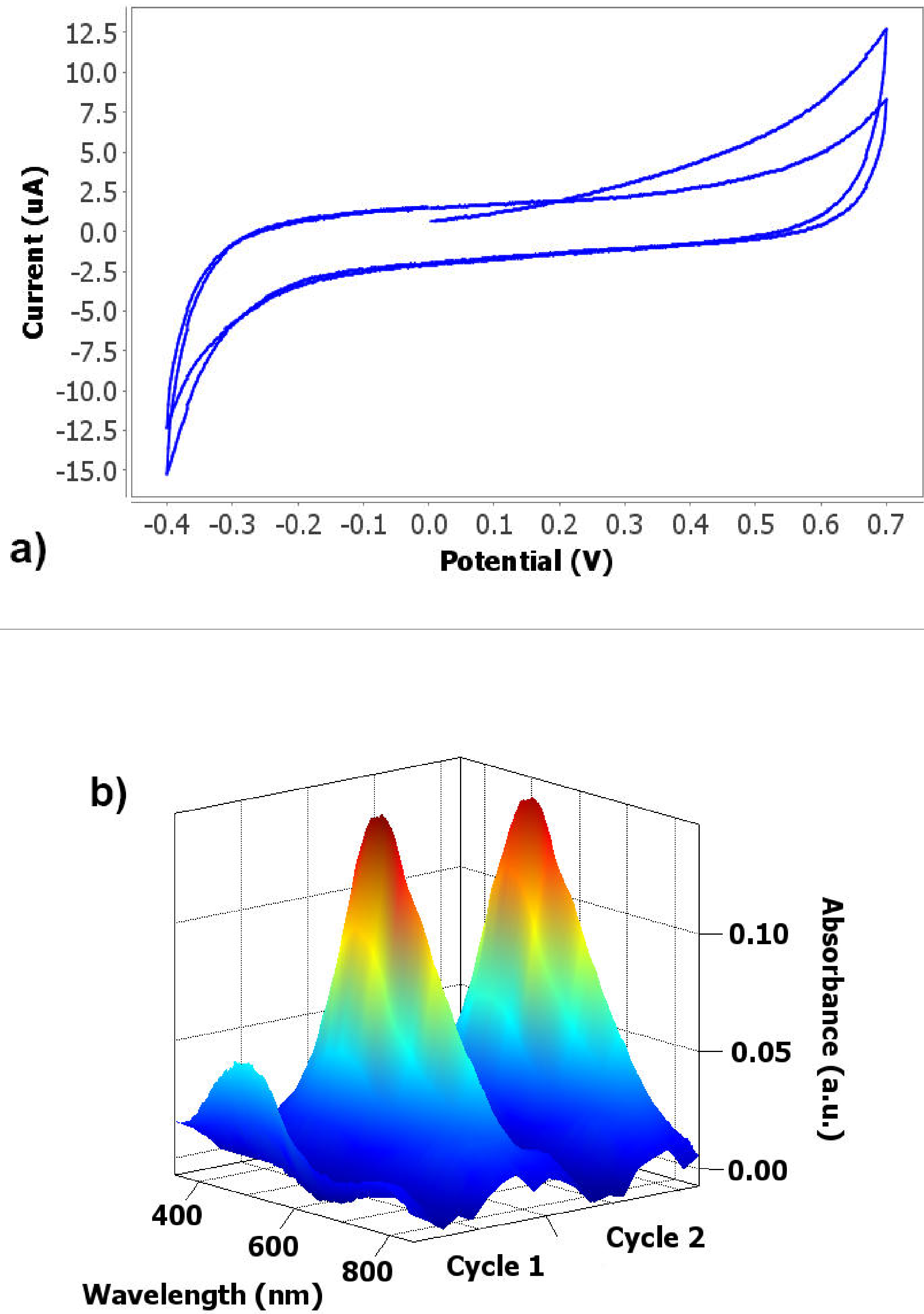

Figure 3. (a) Cyclic voltammogram and (b) 3D plot of the UV-Vis spectra obtained from PEDOT deposited on the 220AT SPE in 0.1 mol/L lithium perchlorate by scanning the potential from 0.00 V to +0.70 V and back to -0.40 V at 0.05 V/s for two cycles.

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.

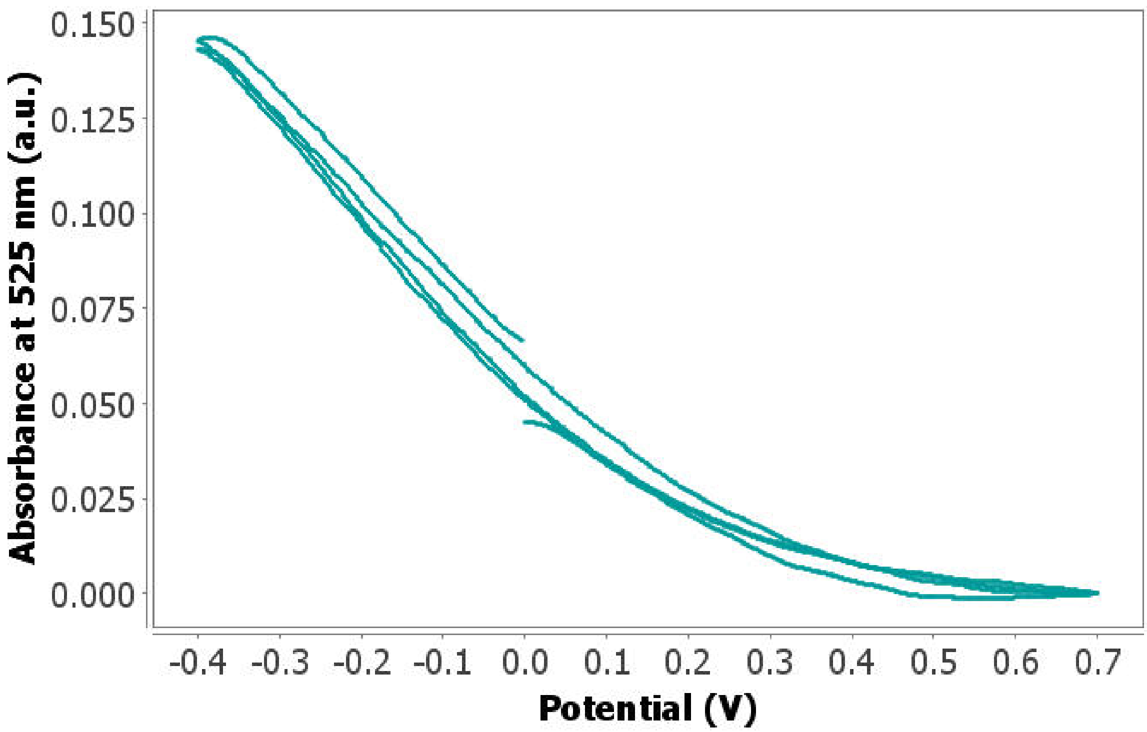

Figure 4. Evolution of the UV-Vis band at 525 nm with varying potential.

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.

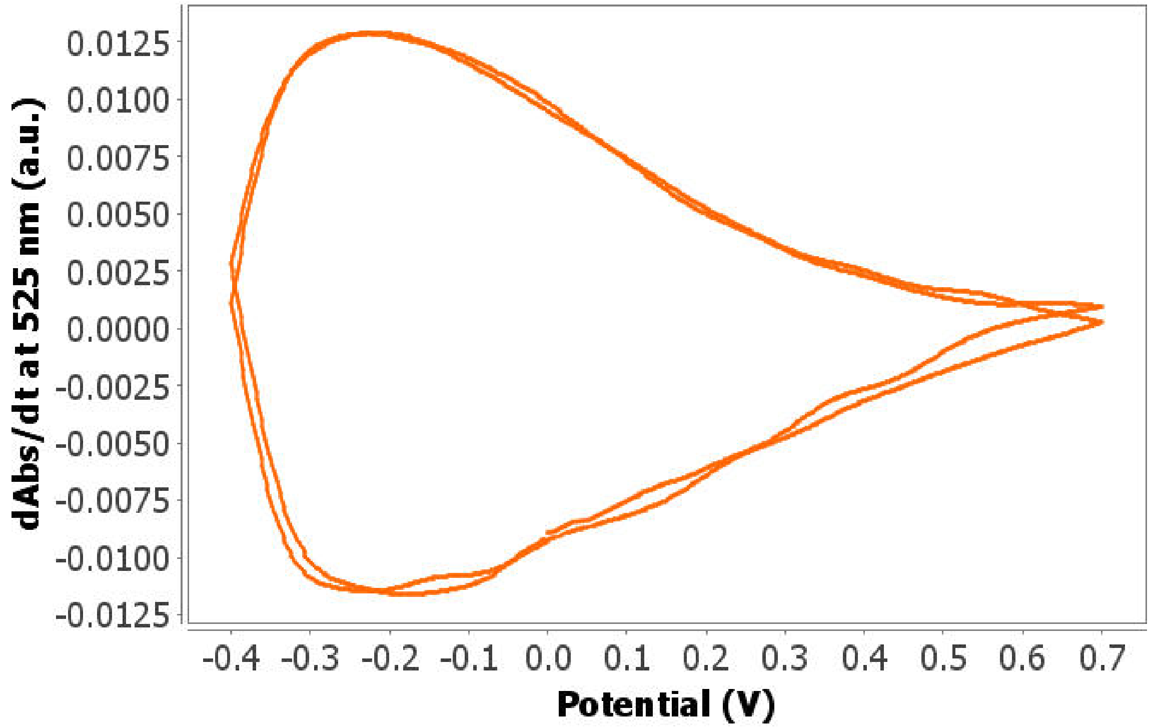

Figure 5. Derivative voltabsorptogram at 525 nm.

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

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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.

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