

Combined Electrochemical Raman Spectroscopy for Process Characterization

Dominik Moosbauer, Dr. rer. nat., Gamry Instruments, [Dawn Yang](#), B&W Tek, Inc.

Introduction

Raman spectroscopy has proven to be an effective technology to characterize conductive polymers in combination with conventional electrochemical experiments. The mechanism of polymer conductivity is directly related to changes in the organic molecular structure caused by induced delocalization of electrons. Raman spectroscopy coupled with electrochemical techniques allows *in-situ* characterization of these molecular structure changes during the course of electrochemical reactions.

Organic electronic cells such as OLEDs (Organic Light Emitting Devices) offer a new material platform to build electronic devices which are transparent and flexible. A great part in this field of research has been focusing on improving the material structure of OLEDs by enhancing the electrical conductivity, device efficiency, and light-emitting stability over time. One promising conductive polymer for OLEDs is poly (3,4-ethylenedioxythiophene)-poly (styrenesulfonate), also referred to as PEDOT:PSS. It is widely used as charge hole injector in organic optoelectronic devices because of its high conductivity and high chemical stability.

So far, the majority of Raman experiments with conductive polymers are performed using confocal microscopic Raman spectroscopy. The analysis reveals detailed information about changes in the molecular structure at different potentials.

In this application note, a chronoamperometric Raman study on PEDOT:PSS in an OLED structure is discussed using a portable Raman spectrometer. The application is developed by Gamry Instruments and utilizes an i-Raman spectrometer from B&W Tek.

Experimental

Figure 1 shows a diagram of the setup for an electrochemical Raman measurement. It consists of a Raman spectrometer, measurement cell, potentiostat, and a computer. The [i-Raman](#) spectrometer has two different options for excitation laser wavelength: 785 nm or 532 nm. The appropriate laser wavelength should be chosen based on the materials to be characterized. In this application note, a 532 nm laser is used for PEDOT:PSS. The Raman spectrometer is connected to a computer via USB.

The target sample (PEDOT:PSS) is applied as a thin film on a metal surface which serves as a working electrode. An aqueous solution of sodium sulfate is used as an electrolyte. The electrolyte was nitrogen-purged before measuring. A graphite rod is used as a counter electrode and an Ag/AgCl electrode is used as a reference electrode.

All electrodes are connected to a Gamry potentiostat which is also connected to the computer via USB.

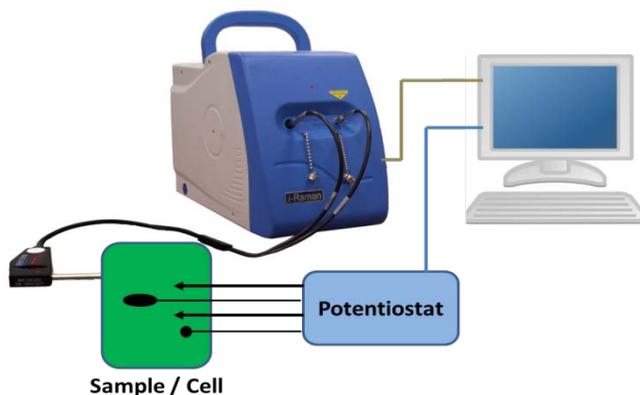


Figure 1: Illustration of the experimental setup for electrochemical Raman experiments.

Gamry's Framework software enables adjustments to various parameters for the [Raman spectrometer](#) as well as to the potentiostat. The user interface for the chronoamperometric experiment is shown in Figure 2. After starting the experiment, both the electrochemical and the Raman experiments run simultaneously.

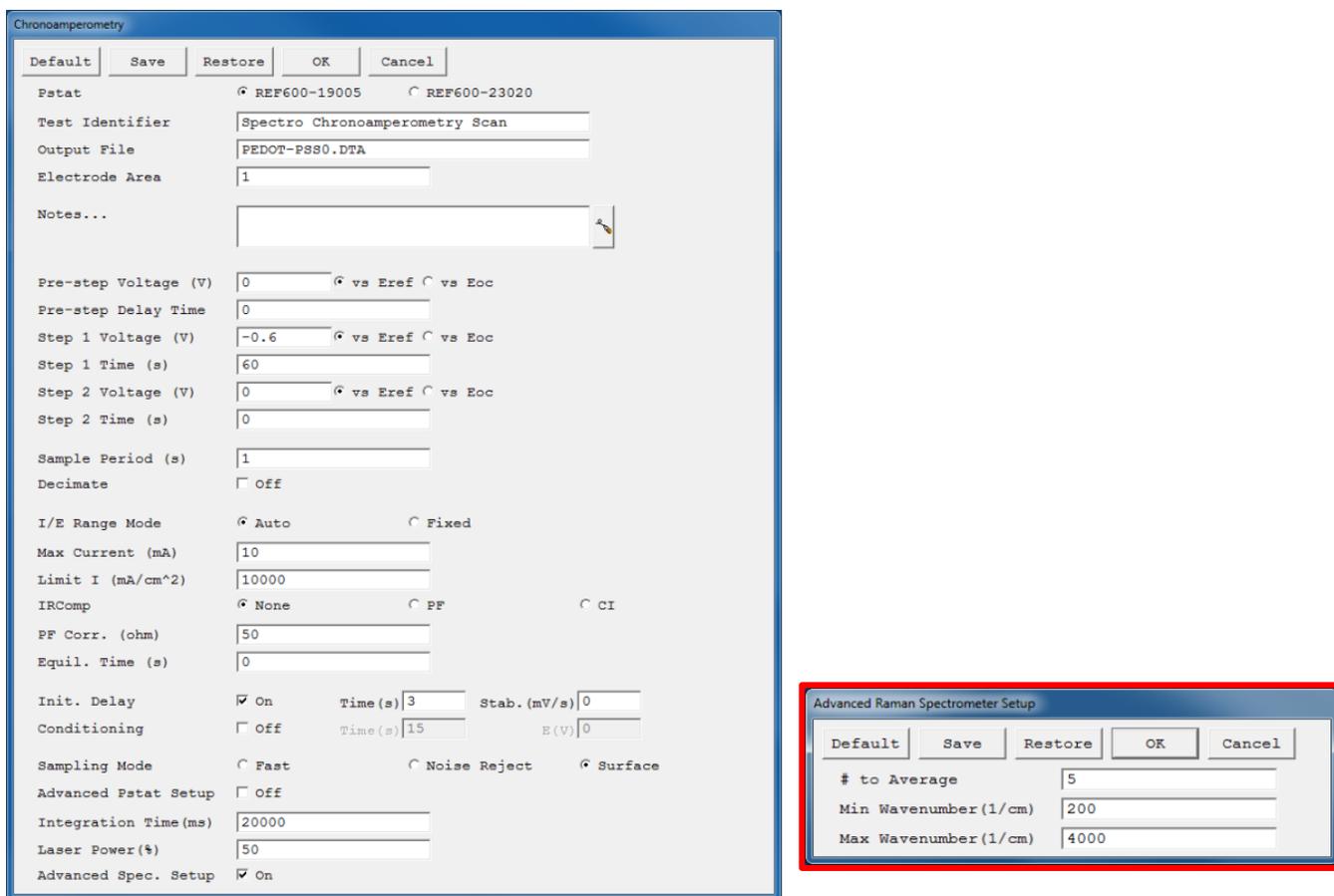


Figure 2. User interface for a chronoamperometric Raman experiment. The advanced spectrometer setup is highlighted in red.

The first part of the user interface allows for adjustments in the parameters of the chronoamperometric experiment. This part is similar to all of Gamry's standard electrochemical experiments. Three additional lines at the end contain the parameters for adjusting the Raman measurement.

The integration time (in milliseconds) indicates how long a single Raman spectrum is acquired. Longer integration times result in higher Raman intensity. However, the electrode is also under longer exposure to the laser which can alter it due to heat generation. Further, the detector can be saturated when using longer integration times. The laser power is given as a percentage of the full power. The signal intensity increases with increases in power level. Again, higher laser power can alter or destroy the sample. Finding the right level of laser intensity and integration time is important in order to achieve optimal signal-to-noise ratio without altering or destroying the sample.

If "Advanced Spectrometer Setup" is checked, an additional window appears after pressing "OK" (see Figure 2). This setup allows the user to adjust additional Raman settings. The first line called "# to Average" adds an averaging function. The final Raman spectrum will be averaged based on multiple spectra. This improves the signal-to-noise ratio of the measurement but leads to longer exposure times to the laser. The other two parameters are called "Min Wavenumber" and "Max Wavenumber" and define the spectral range of the Raman Shift (cm^{-1}) display during the experiment. Regardless of the set range, the complete spectrum from 176 cm^{-1} to 4000 cm^{-1} is saved in the final measurement file.

Test Results and Discussions

Figure 3 shows a series of Raman spectra at different potentials during several chronoamperometric experiments with PEDOT:PSS. The integration time was set to 20 seconds and five spectra were averaged, resulting in an exposure time of 100 seconds for each saved spectrum. The laser power was set to 50%.

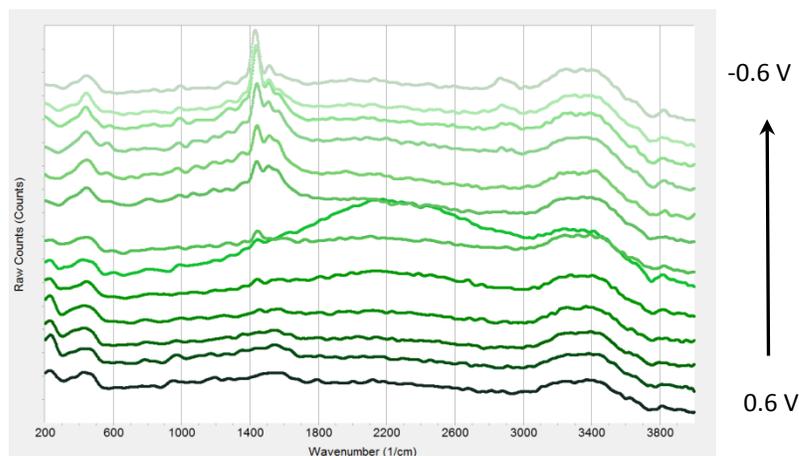


Figure 3: Raman spectra at different potentials from 0.6 V to -0.6 V from bottom to top in 0.1V steps.

An Interface 1000 potentiostat was used for the chronoamperometric experiment. The polymer was reduced in several steps from 0.6 V to -0.6 V. When decreasing the potential, a peak at 1447 cm^{-1} begins to appear which gets more intense at negative potentials. In addition, the peak shifts by -17 cm^{-1} between 0 V and -0.6 V. Three weaker bands appear at about 1520 cm^{-1} , 1570 cm^{-1} , and 2870 cm^{-1} .

Literature shows that the strong peak at 1447 cm^{-1} can be assigned to ring C-C stretching vibrations from PEDOT¹. The negative shift is the result of an increase in the conjugation length of oxidized parts to their neutral state during reduction.

Reduction of PEDOT can lead to reduced efficiency and long-term stability of LEDs. During operation of LEDs, electrons are withdrawn from PEDOT and form electron holes in the polymer layer. On the flip side, electrons are injected into the electron transporting layer near the cathode. Recombination between electrons and electron holes lead then to emission of radiation. However, recombination does not always occur. Electrons can migrate to the PEDOT-PSS layer and reduce PEDOT.

Conclusions

Electrochemical techniques and Raman spectroscopy can be used simultaneously to characterize electrochemical reactions. The combined technology allows for detailed characterization of various reaction mechanisms.

By using the portable i-Raman system in combination with a potentiostat from Gamry Instruments, structural changes of PEDOT:PSS during its electrochemical reduction were analyzed by means of chronoamperometric Raman experiments. The results provide useful information for improving OLED efficiency and lifetime.

References

1. S. Sakamoto, M. Okumura, Z. Zhao, Y. Furukawa, Chem. Phys. Lett., 412 (2005) 395-398.

Additional resources:

[i-Raman datasheet](#)

[i-Raman Plus datasheet](#)

If you have any questions about the application or would like to know how Raman would work for your application, please contact us at appnote@bwtek.com or call us at +1 (855) 297-2626 to speak with an expert.