

# **Infrared Photospectroelectrochemistry of Germanium/Pedot/Electrolyte Interfaces**

Helmut Neugebauer, Teketel Yohannes, and N. Serdar Sariciftci  
Physical Chemistry, Johannes Kepler University Linz  
Altenbergerstr. 69, A-4040 Linz, Austria

## **ABSTRACT**

Difference infrared spectra between illumination and dark of a polyethylenedioxythiophene (PEDOT) covered germanium electrode in contact with the electrolyte solution and under applied potential are shown. The spectra show a different behavior at different redox (doping) states of the polymer. The photoinduced formation of positive charge carriers was found by illumination of the neutral (undoped) form, whereas no significant spectral changes occur in the oxidized (p-doped) and reduced (n-doped) form of PEDOT.

## **INTRODUCTION**

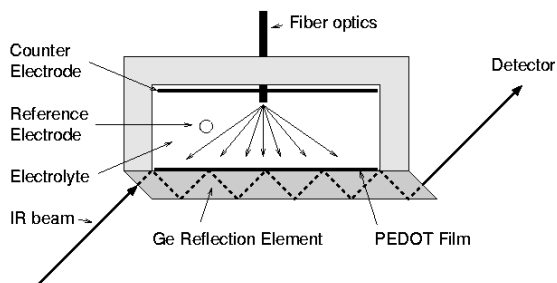
Due to the inexpensiveness and easy fabrication, the use of organic materials is very attractive for photovoltaic energy conversion. In photoelectrochemical cells, thiophene based conjugated polymers show interesting properties in liquid [1] as well as solid [2] electrolyte systems.

For a better understanding of the behavior of the photoactive semiconducting polymer, information on a molecular level of the processes in the substance in contact with the electrolyte solution during illumination is necessary. In situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy has proved to be a valuable tool for providing these information [3,4]. In this paper, we present results on in situ ATR-FTIR spectroscopic studies of polyethylenedioxythiophene (PEDOT), a low band gap conjugated polymer, in a photospectroelectrochemical cell. Difference spectra between illumination and dark conditions of the polymer on a germanium reflection element in contact with the electrolyte solution under applied potential are shown.

## **EXPERIMENTAL**

PEDOT was electropolymerized from monomer solution on a germanium reflection element. The electrolyte was 0.1 M tetrabutylammoniumperchlorate in acetonitrile. As reference electrode Ag/AgCl wire, as counter electrode Pt foil was used. The illumination was performed with an Ar<sup>+</sup> laser at 488 nm, 30 mW/cm<sup>-2</sup>. The FTIR spectrometer was a Bruker IFS66S with an MCT detector, spectral resolution 4 wavenumbers. The measurement procedure for a photoinduced spectrum was a coaddition of 30 repetitions of 10 scans (light on) and 10 scans light off. The spectra are shown as  $-\Delta T/T$ , ( $\Delta T = T(\text{light on}) - T(\text{light off})$ ). Spectroelectrochemistry was done with a potential scan rate of 5 mV/s and a simultaneous measurement of IR spectra by coadding of 32 interferograms

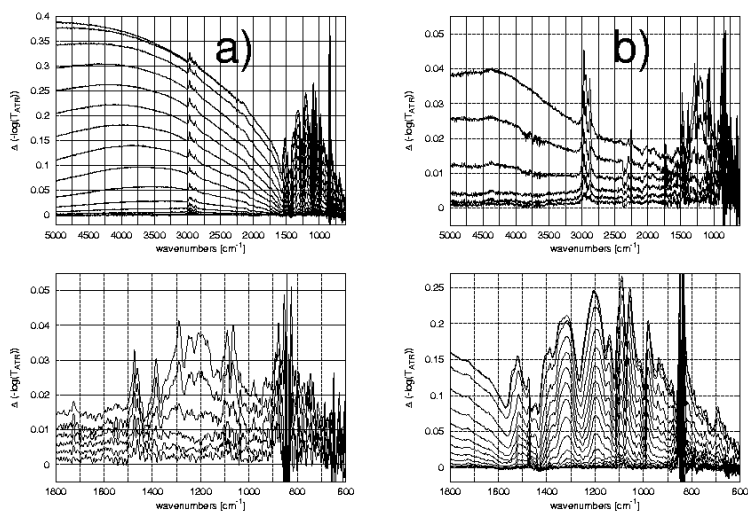
for one spectrum, covering about 85 mV in the cyclic voltammogram. Difference spectra with the spectrum of the neutral form as reference are shown. The photospectroelectrochemical cell is shown in Figure 1.



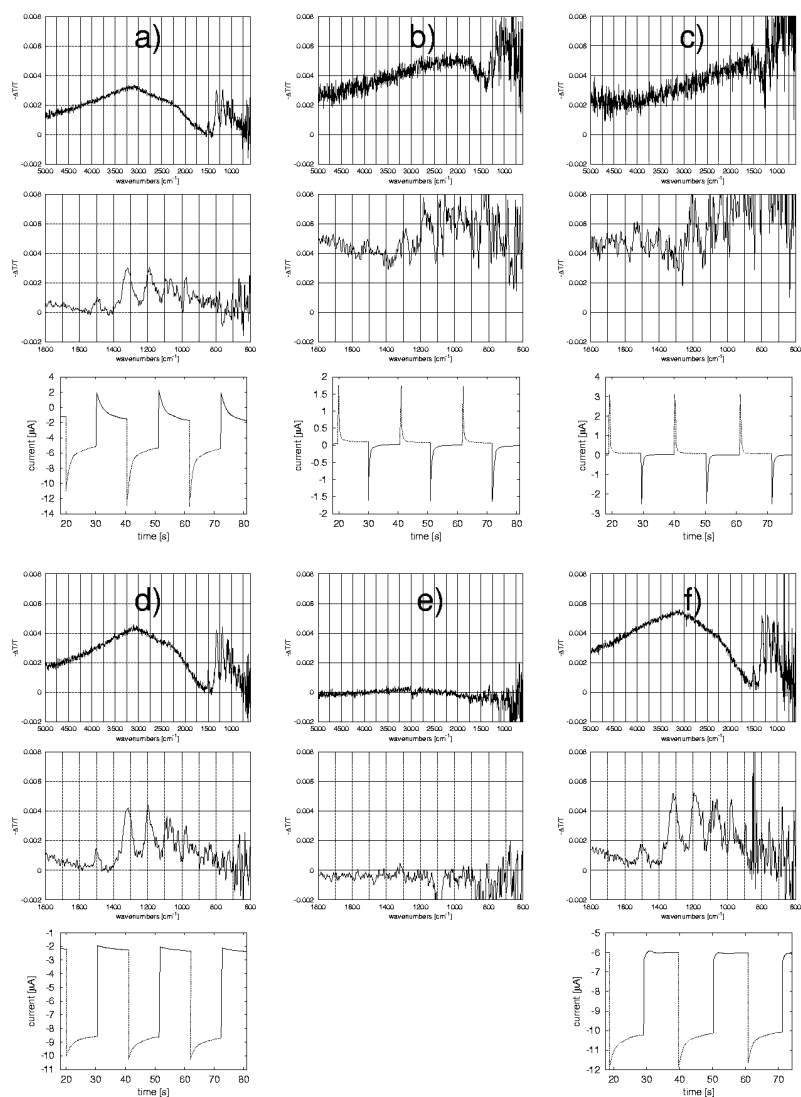
**Figure 1:** Photospectroelectrochemical cell.

## RESULTS AND DISCUSSION

Figure 2 shows difference spectra recorded during oxidation (p-doping, Figure 2a) and reduction (n-doping, Figure 2b) of PEDOT [5]. Different spectral signatures for both types of doping can be seen. The spectra are the basis for the identification of the photoinduced charge carriers during the photospectroelectrochemical experiments.



**Figure 2:** a) Difference spectra during oxidation (p-doping). Upper spectrum: full scale, lower spectrum: expanded range. b) Difference spectra during reduction (n-doping). Upper spectrum: full scale, lower spectrum: expanded range.



**Figure 3:** Photoinduced difference spectra at various potential values. In each part of the figure the full spectral range (top), the expanded spectral range (middle) and the corresponding current/time curve (bottom) is shown. a)  $-700$  mV, b)  $+100$  mV, c)  $+300$  mV, d)  $-900$  mV, e)  $-1700$  mV (no current/time curve), f) again  $-900$  mV.

The current/time curves follow the behavior known from other photoelectrochemical conjugated polymer systems [1,6]. In the potential range, where the neutral form of PEDOT is stable, a reductive photocurrent is found, whereas in the potential range of p-doped PEDOT the photocurrent is oxidative. The large base current in the potential range of the n-doped polymer prevents the detection of the photocurrent at these high negative potentials.

Spectroelectrochemical difference spectra during oxidation (p-doping) and reduction (n-doping) show, that the spectral signatures of p-doped PEDOT and n-doped PEDOT are different [5]. These spectra are used as a basis for comparison with the photoinduced difference spectra obtained at constant potential during the illumination/dark cycles. At -700 mV, where PEDOT is in the neutral form, the photoinduced FTIR spectrum clearly shows the formation of charge carriers under illumination, which have the same absorption pattern as the p-doped polymer. In the potential range of p-doped PEDOT, the photoinduced absorption becomes broad and unstructured. The signal/noise ratio decreases, since the infrared absorption of the polymer increases with doping level. In the potential range of n-doped PEDOT, the photoinduced absorption shows no significant spectral bands. The spectral behavior as well as the current/time characteristics are completely reversible. The same current/time curves and the same photoinduced infrared spectra occur after switching from oxidized or reduced states of PEDOT back to the neutral state.

The results clearly show the capabilities of in situ ATR-FTIR spectroscopy for the investigation of the photoinduced charge carriers in conjugated polymers used in photoelectrochemical energy conversion systems.

The addition of C<sub>60</sub> to the PEDOT/electrolyte interface (film formation by dropcasting from toluene solution on the surface of a PEDOT covered Ge reflection element) does not influence the spectral behavior and the current/time characteristics. Other conjugated polymers, like poly-3-methylthiophene, change their photocurrent behavior by addition of C<sub>60</sub> [7]. Further investigations on fullerene containing systems by photospectroelectrochemical techniques are in progress.

## ACKNOWLEDGMENTS

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