

Semiconductor/conjugated polymer/electrolyte interfaces studied with infrared photospectroelectrochemistry

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Abstract

The photoinduced formation of charge carriers in polyethylenedioxythiophene (PEDOT) on a Ge electrode in contact with the electrolyte solution under applied potential are studied by in situ IR spectroscopy. Difference spectra between illumination and dark show the formation of positive charge carriers in the neutral (undoped) form, whereas no significant spectral changes occur in the oxidized (p-doped) and reduced (n-doped) forms of PEDOT.

Key words: Infrared spectroscopy, In situ electrochemical spectroscopy, Photoinduced absorption spectroscopy, Semiconductor/electrolyte interfaces, Polythiophene and derivatives, Low-bandgap conjugated polymers

1. Introduction

For electrochemical photovoltaic applications, thiophene based conjugated polymers show interesting properties in liquid [1] as well as solid [2] electrolyte systems. Information on molecular level in contact with the electrolyte solution during illumination can be obtained by in situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy [3–5]. In this paper, we present results of in situ ATR-FTIR spectroscopic studies of polyethylenedioxythiophene (PEDOT), a low band gap conjugated polymer, in a photospectroelectrochemical cell. From difference spectra between illumination and dark conditions of the polymer on a Ge reflection element, the nature of the photoinduced charge carriers can be studied.

2. Experimental

PEDOT was electropolymerized from monomer solution on a germanium reflection element. The

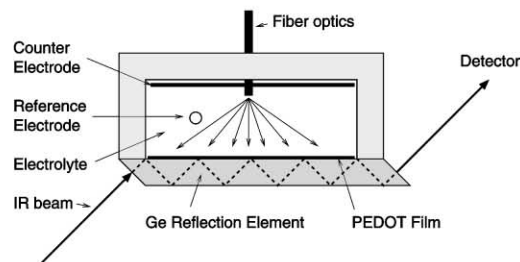


Fig. 1. Photospectroelectrochemical cell

electrolyte was 0.1 M tetrabutylammoniumperchlorate in acetonitrile. As reference electrode Ag/AgCl wire, as counter electrode platinum foil was used. The illumination was done with an Ar⁺ laser at 488 nm, 30 mW/cm². The FTIR spectrometer was a Bruker IFS66S with an MCT detector, using a 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 $-\Delta T/T$, ($\Delta T = T(\text{light on}) - T(\text{light off})$). The photospectroelectrochemical cell is shown in Fig. 1.

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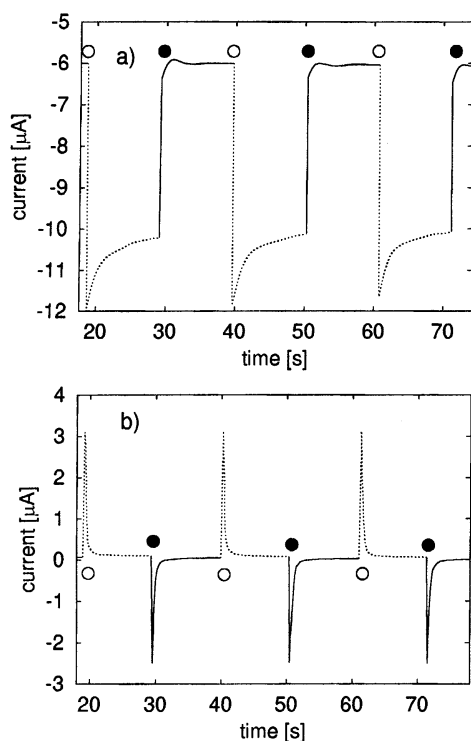


Fig. 2. Current/time curves. (a) at -900 mV, (b) at $+300$ mV. \circ Light on, \bullet light off.

3. Results and Discussion

In Fig. 2, current/time curves at -900 mV and $+300$ mV are shown. The curves follow the behaviour known from other photoelectrochemical conjugated polymer systems [1,7]. In the potential range, where the neutral form of PEDOT is stable (Fig. 2a), a reductive photocurrent is found, whereas in the potential range of p-doped PEDOT the photocurrent is oxidative (Fig. 2b). At more negative potentials, where n-doped PEDOT is stable, a large base current occurs which prevents the detection of the photocurrent (not shown here).

With neutral PEDOT (Fig. 3), the photoinduced FTIR spectrum shows the formation of charge carriers under illumination, which have the same absorption pattern as electrochemically p-doped polymer [6]. In the potential range of p-doped PEDOT, the photoinduced absorption becomes broad and unstructured with a low signal/noise ratio. In the potential range of n-doped PEDOT, no significant photoinduced spectral bands were detected. 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 formation of positive charge carriers (p-polarons) under illumination and demonstrate the capabilities of in situ

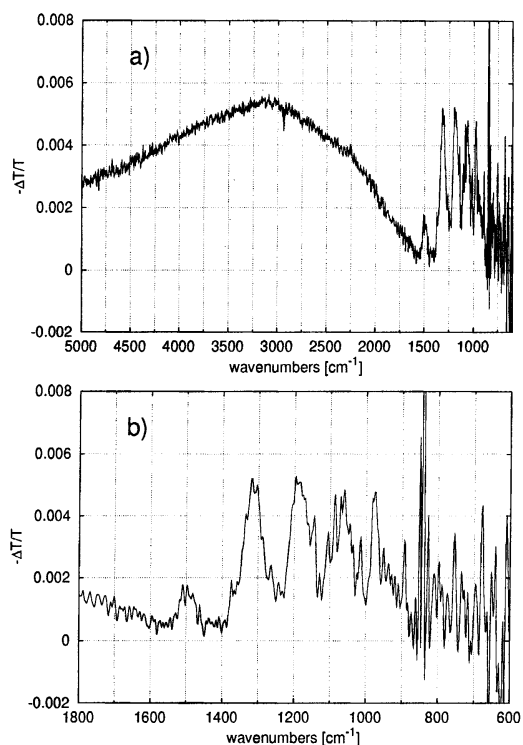


Fig. 3. Photoinduced difference spectrum at -900 mV. (a) extended spectral range, (b) vibrational spectral range.

ATR-FTIR spectroscopy for the determination and investigation of the photoinduced charge carriers in conjugated polymers used in photoelectrochemical energy conversion systems.

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