



Electrochemical characterization of sub-micro-gram amounts of organic semiconductors using scanning droplet cell microscopy

Jacek Gasiorowski^a, Andrei I. Mardare^b, Niyazi S. Sariciftci^a, Achim Walter Hassel^{b,*}

^a Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University, Linz, Austria

^b Institute for Chemical Technology of Inorganic Materials, Johannes Kepler University, Linz, Austria

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ABSTRACT

Scanning droplet cell microscopy (SDCM) uses a very small electrolyte droplet at the tip of a capillary which comes in contact with the working electrode. This method is particularly interesting for studies on organic semiconductors since it provides localized electrochemical investigations with high reproducibility. One clear advantage of applying SDCM is represented by the very small amounts of material necessary (less than 1 mg). Organic materials can be investigated quickly and inexpensively in electrochemical studies with a high throughput. In the present study, thin layers of poly(3-hexylthiophene) (P3HT), which is one of the most often used material for organic solar cells, were deposited on ITO/glass as working electrodes in SDCM studies. The redox reactions in 0.1 M tetra(n-butyl)ammonium hexafluorophosphate (TBAPF₆) dissolved in propylene carbonate were studied by cyclic voltammetry and by electrochemical impedance spectroscopy. Two reversible, distinct oxidation steps of the P3HT were detected and their kinetics were studied in detail. The doping of P3HT increased due to the electrochemical oxidation and had resulted in a decrease of the film resistance by a few orders of magnitude. Due to localization on the sample various parameter combinations can be studied quantitatively and reproducibly.

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1. Introduction

Organic semiconductors combine the properties of semiconductors with the processability of organic molecules. Recently a lot of effort has been put in the optimization of their physical and chemical properties for organic electronics applications [1]. Big effort was put to understand and improve electrical conductivity which is one of the key points in the construction of organic electronic devices. One of the ways to increase the charge conductivity in an organic semiconductor is via doping [1,2]. There are many ways of doping organic materials:

- (1) Chemical oxidation (reduction) for p- (n) doping.
- (2) Electrochemical oxidation (reduction) for p- (n) doping.
- (3) Field induced doping in organic field effect transistors (OFETs).
- (4) Photoinduced doping.

Here electrochemical oxidation and/or reduction are of high interest since it provides easy and flexible variation of redox parameters (doping levels). The variety of physical and chemical

parameters, which can be characterized during electrochemical studies, led to the development of different *in situ* techniques [3–8]. Different spectroscopic methods used during cyclic voltammetry measurement allow studying optical, vibrational and electrical changes during oxidation–reduction processes in organic semiconductors. However, all of them are important for understanding doping effects and thus the need for different sample structures and overall big quantities of a material is one of the main obstacles. In an attempt to speed up screening of new materials a new approach leads in a strong miniaturization that allows for drastically reducing the required amount of chemicals. This can be realized by employing scanning droplet cell microscopy (SDCM) with respect to its general applicability for all electrochemical methods even including some combined techniques [9–13].

In this paper an adapted scanning droplet cell microscope and its performance for electrochemical characterization of organic semiconductors is presented. Scanning droplet cell microscopy was applied to measure cyclic voltammetry and electrochemical impedance spectroscopy. The measurement area was up to 3.2 mm² allowing multiple characterization on a 15 × 15 mm² substrate. The necessary amount of the organic material required for the study was less than 1 mg, and less than 1 ml of electrolyte solution was used. This low consumption of the materials together with large amount of reproducible information obtained makes this setup a very promising technique for screening new organic

* Corresponding author. Tel.: +43 732 2468 8700.

E-mail address: achimwalter.hassel@jku.at (A.W. Hassel).

materials. This paper describes in detail the electrochemical redox processes to characterize regioregular poly(3-hexylthiophene), a standard material for organic solar cells. Two clearly separated and fully reversible oxidation peaks were identified and characterized.

2. Experimental

2.1. Reagents and materials

For this study, a soluble derivative of polythiophenes, the regioregular poly(3-hexylthiophene) (98%, Rieke Metals) was used without further purification. The polymer was dissolved in chlorobenzene (99%, Acros Organics) with a concentration of 10 g L^{-1} and at a later stage it was deposited by spin coating on a single $15 \times 15 \text{ mm}^2$ glass/ITO ($15 \Omega/\square$, Kintec Co.) substrate. Before coating, the glass substrate was cleaned by sequential sonication in acetone, isopropanol and de-ionized water. The thickness of the P3HT layer was approximately 100 nm. For all electrochemical studies, 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAPF₆, $\geq 99\%$, Fluka Analytical), prepared by dissolving in propylene carbonate (PC, 99.7%, Sigma Aldrich), was used.

2.2. Scanning droplet cell microscopy

For all the electrochemical investigations, a scanning droplet cell microscope with a three electrode configuration was used [14]. This special feature of small area localization in SDCM can be exploited for various studies in thin film combinatorial libraries [15]. Since only a small electrolyte droplet comes in direct contact with the working electrode surface, even on small samples a high number of investigations can easily be done applying various electrochemical techniques. This increases the number of possible measurements on a single sample and decreases the overall amount of organic material (<1 mg) and electrolyte volume (<1 ml) needed. Fig. 1 shows a photograph of the SDCM during an electrochemical measurement. A plastic block is used for fixing the cell body to an XYZ translation stage which is used for moving the tip of the cell to various locations on the sample surface. The sample representing the working electrode (WE) is electrically contacted using a tungsten needle pressed on a small Indium (In) droplet placed on the ITO substrate. This ensures a good stability of the contact over time. The inset of Fig. 1 shows a schematic representation of the SDCM. The cell was built using a tapered glass capillary (Pasteur pipette) for which a tip diameter of 2 mm was

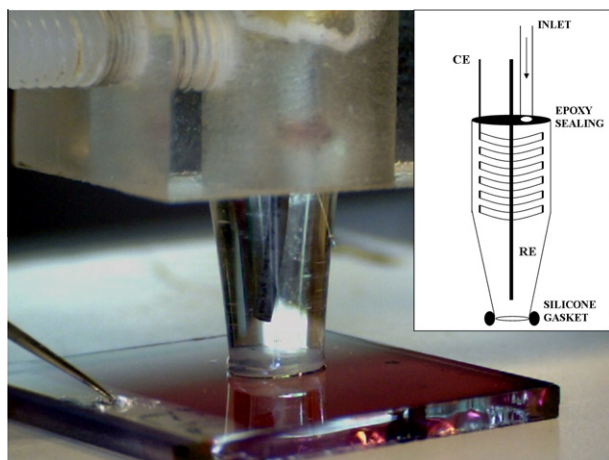


Fig. 1. Photograph and scheme (inset) of the scanning droplet cell microscope (SDCM).

achieved by appropriate grinding. At the top part, an electrolyte inlet is provided by using a 1 mm in diameter Teflon tube connected to the inner volume of the cell and isolated from the exterior by using a two component epoxy resin. An Ag/AgCl quasireference electrode (QRE) was prepared by electrodeposition of AgCl in 1 M HCl on an Ag wire 0.5 mm in diameter. The potential of the RE was found to be 0.211 V vs. standard hydrogen electrode (SHE). Further on, in the entire study all the potential values are given as referenced to the SHE. Details about the AgCl electrodeposition are provided elsewhere [16]. The QRE was also inserted into the cell body from the top, keeping a minimum distance to the WE surface (approximately 1 mm) and fixed with epoxy resin. A gold stripe (Wieland Dentaltechnik 99.999%) (2 mm wide) was used as counter electrode (CE) forming a coil at the top part of the glass capillary, where the inner diameter is still large enough for avoiding electrical contact with the RE. The CE was also embedded into the epoxy resin at the top, which in the final stage of the manufacture completely isolated the inner volume of the cell from exterior. A soft silicone gasket was formed on the rim of the SDCM tip by dipping the capillary in liquid silicone followed by drying it under N₂ flow. This procedure ensured the use of the SDCM with a highly reproducible wetted area in the contact mode, when the cell is pressed against the WE surface and the gasket seals the electrolyte inside the cell for avoiding any air contact [17]. This is an important aspect for the electrochemistry of organic materials when non-aqueous electrolytes are used due to the water contamination from the surrounding atmosphere. The reason behind is that non-aqueous electrolytes are preferred due to the large electrochemical window as compared to aqueous electrolytes.

2.3. Electrochemical characterization

All the electrochemical measurements were performed using a combination of a Solartron 1287 potentiostat and a Solartron 1260 frequency response analyzer. Cyclic voltammetry was used for basic characterization of the oxidation of P3HT. For this purpose, the maximum achievable potential was increased from 0 V vs. SHE in steps of 0.05 V up to 1.5 V. Different rates of the potential increase were used ranging between 0.001 V s^{-1} and 0.1 V s^{-1} . Potentiostatic experiments were performed at potentials ranging from 0 V to 1.5 V. Electrochemical impedance spectroscopy (EIS) was used for characterization of the P3HT, by alternating the potentiostatic experiments with impedance measurements. A peak–peak AC perturbation of 0.02 V was applied and the frequency was scanned between 100 kHz and 1 Hz. Mott–Schottky analysis was used for the characterization of the semiconducting properties during doping of P3HT.

3. Results and discussion

3.1. Cyclic voltammetry studies

Fig. 2 shows a series of cyclic voltammograms measured using TBAPF₆ electrolyte dissolved in propylene carbonate, with a rate of potential increase of 0.01 V s^{-1} . The maximum achievable potential was increased in 0.05 V steps up to 1.5 V for carefully probing the oxidation and the reduction potentials of the polymer. Two distinct and reversible oxidation potentials were found. The maximum of the first oxidation peak was measured at 0.52 V and the maximum of the second oxidation peak was found at 0.93 V. The reproducibility and stability of the oxidation potentials can be directly analyzed from the CVs shown in Fig. 2. It was found that the first oxidation potential is shifting by 0.1 V during the entire series of investigation. For the second oxidation potential, only a slight shift smaller than 0.1 V was noticed. A constant shifting

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