Spectroelectrochemical techniques as modern tools for investigating charge transfer processes in conjugated polymers

Tomasz JAROSZ, Katarzyna KRUKIEWICZ, Mieczyslaw LAPKOWSKI, Wojciech DOMAGALA* – Department of Physical Chemistry and Technology of Polymers, Faculty of Chemistry, Silesian University of Technology, Gliwice, Poland.

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Electrochemistry is a rapidly developing field of chemistry, whose fruits are widely applied commercially. Electrochemical analysis techniques allow charge transfer processes, taking place in studied systems, to be followed. Information obtained through electrochemical analysis alone is sufficient to describe a simple reaction, but with increasing complexity of investigated systems, it becomes more difficult to identify electrochemical processes taking place and assign them to specific chemical species.

The first literature reports describing the use of spectroelectrochemical techniques studied electrolysis reactions of dissolved organic compounds [1–4]. In these studies, UV-Vis spectroscopy was used as a diagnostic tool to link observed current signals with changes in the concentrations of reacting species. Further development of spectroelectrochemical techniques brought on a multitude of reports, dedicated to a wide array of phenomena and materials [5, 6]. Among the latter, considerable research attention has been devoted to the design and study of organic compounds, belonging to the group of conjugated polymers. These materials are widely used in optoelectronics and are the basis for the development of organic electronics devices, such as modern photovoltaic panels, light-emitting diodes, field effect transistors, electrochromic windows and chemical sensors.

The wide range of potential applications stems from the specific properties of conjugated polymers, in particular their low work function, the ability to control their conductivity and colour, as well as their compatibility with solution-processing techniques. The physicochemical properties of these materials and their changes in the course of charge transfer processes are one of the main topics of research conducted, with the use of spectroelectrochemical techniques, at the Department of Physical Chemistry and Technology of Polymers at the Silesian University of Technology.

The standard technique for monitoring changes in the optical properties of conjugated polymers in real time, during the processes of their electrosynthesis or doping / dedoping, is the multi-channel, time-resolved UV-Vis spectroelectrochemistry. The use of this technique, for following electrochemical polymerisation, enables repeatable fabrication of polymer layers exhibiting specific properties and being of a given thickness. Electrochemical methods of control of the amount of polymer deposited on the electrode are susceptible to the influence of several phenomena. Conversely, the ability of a polymer, with a specific doping level, to absorb electromagnetic radiation is proportional to the thickness of the layer. This technique is widely used in the search for materials for use in electrochromic windows, where it is used for the simultaneous determination of colours attainable by the investigated system and the time required for switching between them (Fig. 1).

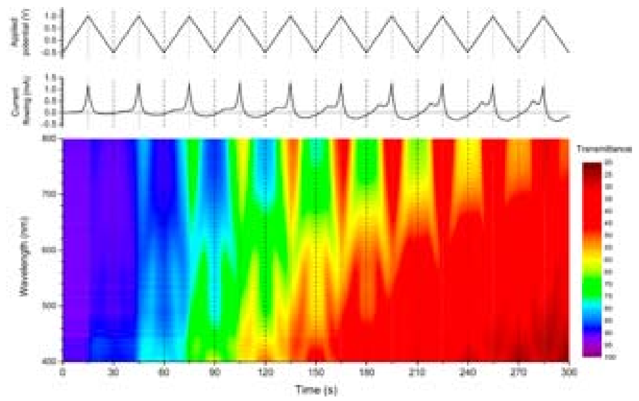

Fig. 1. Monitoring the changes of visible light absorption spectrum of poly(3-dodecylpyrrole), *in situ* **during its electrochemical synthesis using cyclic voltammetry. Accumulation of polymer film at the electrode is manifested by growing current intensities of characteristic oxidation and reduction peaks together with diminishing transmittance (growing absorbance) of the semi-transparent electrode + polymer layer system. Fine, time resolved measurements of the full absorption spectrum, permit complete evaluation of electrochromic properties of the polymer film with increasing thickness**

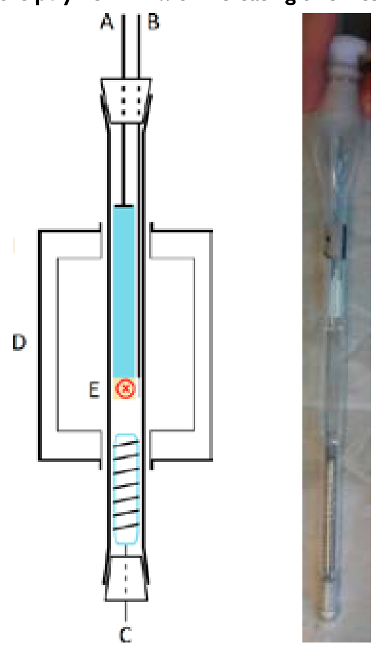

Fig. 2. Schematic diagram and photograph of the cell used for EPR-UV-Vis-NIR spectroelectrochemical measurements.
A - working electrode: glass slide coated with indium tin oxide layer (ITO); B - reference electrode: silver wire, C - counter electrode: platinum spiral supported on a glass float, D - EPR spectroemeter resonant cavity, E - polymer film at the working electrode. The red cross and circle denote the position of spot of light beam passing perpendicularly through the cell, and its size relative to the area of the polymer film.

Research efforts directed at modifying the electrochemical cells resulted in the creation of experimental setups fulfilling the requirements for carrying out spectroscopic measurements

Corresponding author:
Wojciech DOMAGALA – Ph.D., Eng., e-mail: wojciech.domagala@polsl.pl

using infrared spectroscopy (IR), Raman spectroscopy, electron paramagnetic resonance (EPR), and development of corresponding spectroelectrochemical techniques. Monitoring different aspects of the chemical transformations occurring as part of a charge transfer process, allows the electrical and optical properties of macromolecules, characterised by a certain degree of doping, to be related to specific changes in their electronic and chemical structure.

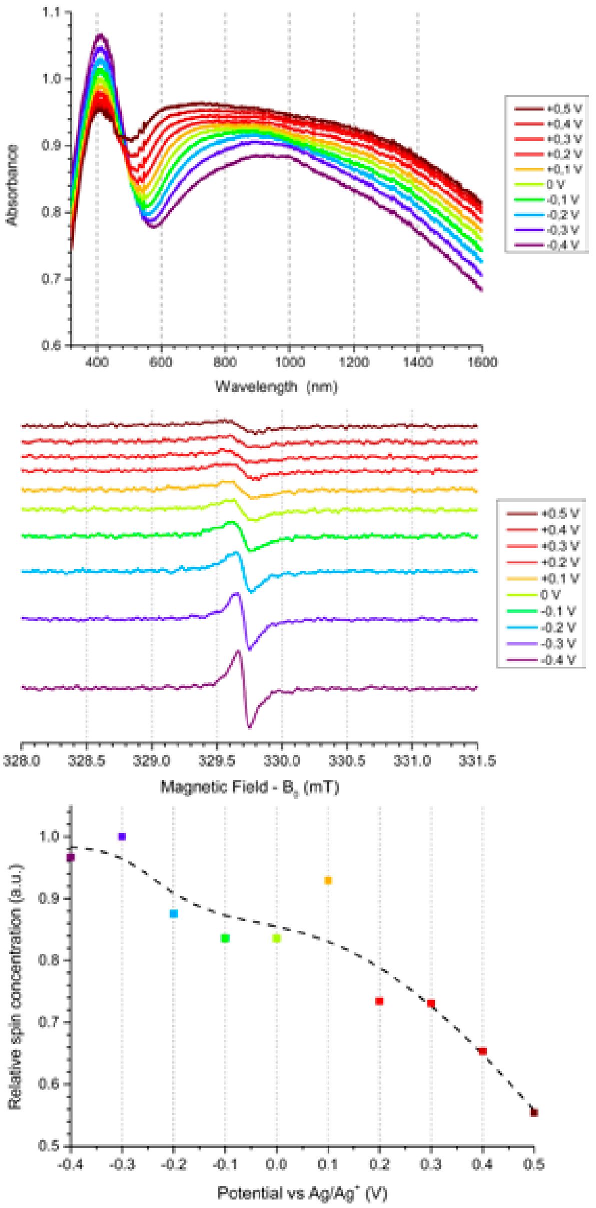

Fig. 3. Collection of absorption (a) and EPR (b) spectra, registered concomitantly *in situ* during electrochemical doping of electrosynthesised poly(N-methylpyrrole) at semi-transparent working electrode. Subfigure (c) shows the concentration of paramagnetic species computed by double integration of the EPR spectra presented in (b)

Each of the abovementioned spectroscopic techniques provides information about a certain aspect of the changes taking place in the system. The results collected by these techniques are complementary to each other; combining them, a detailed model of the investigated electroactive system can be formulated and in-depth understanding of changes occurring within it can be gained. When using standard spectroelectrochemical techniques, it is necessary to perform a series of measurements to obtain all the required information. This necessitates precise standardisation of the results and faithful reconstruction of the conditions during each measurement in the series. Using higher-order techniques, however, it is possible to circumvent this requirement through simultaneous acquisition of desired experimental data for a single sample, at set conditions. This is particularly useful for studies of conjugated polymer films which can suffer from degradation caused by long-term measurements and damage to the sample during its transfer between different experimental setups. For this reason, it is preferable to develop spectroelectrochemical techniques comprising more than one type of spectroscopic measurement, dubbed higher-order spectroelectrochemical techniques. Because of the accumulation of requirements related to the simultaneous execution of many electrochemical and spectroscopic measurements, the development of appropriate procedures is a highly complex task.

The leading technique belonging to this group is EPR-UV-Vis-NIR spectroelectrochemistry [7] (Fig. 2), allowing the changes in optical and magnetic properties of conjugated systems to be followed simultaneously under precise electrical potential polarisation conditions, as shown in Figure 3 for poly(N-methylpyrrole).

Joint consideration of the above information permits interpretation of the spectral transitions in the visible and near infrared regions to be carried out, by identifying the bands corresponding to different types of charge carriers, each differing in their magnetic properties (polarons, polaron pairs, bipolarons), that can be generated in a conjugated polymer. Numerical analysis of spectra yields semi-quantitative description of processes taking place, which supplemented with suitable standardisation, together with quantitative coulometric data about the amount of charge exchanged at the electrode, affords comprehensive quantitative picture of the redox processes taking place in investigated systems, greatly contributing to detailed discussion of their doping / dedoping phenomena. The Department of Physical Chemistry and Technology of Polymers at the Silesian University of Technology is one of the three leading scientific institutions worldwide, capable of conducting research using this technique. The results of studies of manifold conjugated polymer families are published in reputable international journals [8–20].

Acknowledgements

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Tomasz JAROSZ – M.Sc., graduated from the Faculty of Chemistry at Silesian University of Technology in Gliwice (2011), where he is currently a Ph.D. student.
e-mail: tomasz.jarosz@polsl.pl

Katarzyna KRUKIEWICZ – M.Sc., graduated from the Faculty of Chemistry, Silesian University of Technology, Gliwice (2011); currently being a Ph.D. student at the same university. Scientific interests: electropolymerization processes, biomedical applications of conducting polymers, surface physicochemistry.
e-mail: katarzyna.krukiewicz@polsl.pl

Mieczysław ŁAPKOWSKI – Ph.D., D.Sc., Eng., Professor, graduated from the Faculty of Engineering and Chemical Technology at Silesian University of Technology in Gliwice (1974). Defended his Ph.D. thesis in 1982, acquired habilitation in 1990, and the title of Professor in 1998. Currently, he is the head of the Department of Physical Chemistry and Technology of Polymer at the Faculty of Chemistry of Silesian University of Technology, as well as a professor in the Centre of Polymer and Carbon Materials of the Polish Academy of Sciences in Zabrze.
e-mail: mieczyslaw.lapkowski@polsl.pl

*Wojciech DOMAGAŁA – Ph.D., Eng., graduated from the Faculty of Chemistry at Silesian University of Technology in Gliwice (2000). Defended his Ph.D. thesis in 2007. Currently, he is a researcher at the Department of Physical Chemistry and Technology of Polymer at the Faculty of Chemistry of Silesian University of Technology, as well as principal investigator of research projects, funded both by Polish and European agencies.
e-mail: wojciech.domagala@polsl.pl

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NOWE INWESTYCJE

Lubelski Park Naukowo-Technologiczny – placówka w Tel Awiwie

Lubelski Park Naukowo-Technologiczny bodaj jako pierwszy w kraju, otworzy swoją placówkę w... Izraelu. Jak poinformował prezes LPNT Tomasz Małecki, ta strategiczna decyzja zapadła 6 sierpnia br. Biuro powstanie do końca I kwartału 2016 r. i będzie dawało możliwość: startupom, lokatorom i partnerom LPNT prowadzenia działalności operacyjnej oraz udziału w globalnych programach akceleracji partnerów. *(kk)*

(http://innpoland.pl, 7.08.2015)

Nowy zakład recyklingu tworzyw sztucznych

W ostatnich dniach czerwca br. firma Evoltaic Sp. z o.o. uruchomiła w Ostrowcu Świętokrzyskim nowy zakład recyklingu tworzyw sztucznych. W ramach inwestycji na działce o powierzchni 1,2 ha powstał nowoczesny obiekt składający się z dwóch hal produkcyjnych o powierzchni 3,5 tys. m^2 oraz nowoczesnego biurowca. Przedsięwzięcie zostało zrealizowane na terenie rewitalizowanej starej huty. W zakładzie produkującym wysokiej czystości regranulat znajdzie zatrudnienie 100 osób. *(kk)*

(http://www.plastech.pl/, 2.07.2015)

OCHRONA ŚRODOWISKA

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PGE oferuje panele słoneczne dla tych, którzy chcą produkować prąd na własne potrzeby. „Energia przyszłości" to najnowsza oferta pakietowa PGE Obrót, spółki z Grupy Kapitałowej PGE, która sprzedaje energię elektryczną ponad 5 mln klientów. Przygotowana została wspólnie z Bankiem Ochrony Środowiska z myślą o właścicielach nieruchomości, którzy świadomie wybierają rozwiązania przyjazne środowisku oraz obniżające koszty energii elektrycznej. W ramach oferty klienci indywidualni, którzy chcą wytwarzać energię elektryczną na własne potrzeby, mogą na bardzo korzystnych warunkach finansowych zainstalować panele fotowoltaiczne, czyli urządzenia, które pozwalają na produkowanie energii elektrycznej z promieni słonecznych. *(kk)*

(http://www.gkpge.pl, 6.08.2015)

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