Doctoral (*Ph.D.*) theses

Achievement of simultaneous spectroelectrochemical and *in situ* conductance techniques and their application to the characterisation of the redox transformation of conducting polymers

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Szeged, 2012

1. Introduction and objectives

Since their discovery at the end of the 1970s, conducting polymers have received a great interest in the last three decades. The most specific character of these materials is their electronic conductance, which makes them suitable to work as "organic" electrodes. Electronically conducting polymers offer perspectives in sensor applications either as the sensitive components or as matrices for immobilisation of specific substrates.

The application of *in situ* combined electrochemical methods has lead to the more and more adequate interpretation of the insulating/conducting transition. By applying techniques such as spectroelectrochemistry in the UV-Vis-NIR and in the IR or Raman regions, the electrochemical quartz crystal microgravimetry (EQCM) or the *in situ* a. c. impedance or *in situ* conductance method, manifold independent information could be obtained from the complex phenomenon of the redox transformation, involving multiple electron transfers, combined with structural modifications, due to ionic and solvent movements. As a result, different charge carriers have been identified, called as monocations/polarons or dications/bipolarons.

Although several studies have been appeared in which the different *in situ* methods have been applied for the same polymer, in most of the cases the methods could not be applied for obvious reasons for the same sample. Later, the simultaneous combination of two *in situ* techniques has brought new advantages, by delivering information about the process from different aspects.

We applied the new combination of two *in situ* techniques. As it will be demonstrated, the simultaneous monitoring of optical changes gives a unique opportunity to distinguish whether mono- or dicationic species are primarily correlated with the development of the conductance of the given polymer.

Thus, simultaneously applied *in situ* conductance and spectroelectrochemical techniques proved to be able to distinguish between different cases, giving an answer, which charge carrier—identified by their optical behaviour—is primarily responsible for the development of the name-giving property of the given conducting polymers. On the grounds of the systematically performed experimental results we came to the conclusion that the ions, participating in the charge compensation within the polymeric layer, play the crucial role in this distinction. As extreme cases, polymers may behave as anionic or cationic exchangers, depending first of all on the immobilization of the charge compensating anions, present in the film at the end of the polymerization.

2. Experimental methods

All electrochemical measurements were performed on a PGSTAT302 (Autolab) instrument, in a classical three-electrode electrochemical cell. The reference electrode was a Ag/AgCl/3 M NaCl electrode, having a potential +0.210 V *vs*. standard hydrogen electrode (SHE).

EQCM measurements have been carried out by using a quartz crystal resonator and analyzer EQCM-Oscillator (Autolab module) and EQCM type 5510 (Institute of Physical Chemistry, Warsaw, Poland). The crystals were gold coated f_0=6 MHz and f_0=10 MHz and had an overall diameter of 1.36 cm and 1.40 cm, while the piezoelectrically active area (identical with the geometric area) of the Au working electrode was 0.352 cm^2 and 0.196cm^2. The EQCM system was calibrated by electrochemical deposition of lead and silver, using the standard procedure, and the value of −5.04 ng/Hz and -0.86 ng/Hz calibration constants were obtained.

In situ UV–Vis–NIR spectroscopic measurements were carried out by using an Agilent 8453 UV–visible diode array spectrophotometer in the range of 350–1100 nm. The data obtained from ac impedance measurements at 130 Hz were analyzed by a lock-in amplifier (SR 830). Simultaneous ac conductance and *in situ* UV-Vis-NIR spectroscopic measurements were performed at an ITO-coated glass electrode, consisting of four 10-15 μm wide and 3mm long needles, forming gaps of 10-15 μm width between neighbouring electrode parts, of which two were used as the working electrode at once. When the polymer layer is forming on the ITO needle-shaped electrode, the film can grow over the gap, forming electrical contact between the parts, so that conductance can be measured.

The spectral behaviour have been investigated by FT−IR spectroscopy, while for the elementary analysis, EDX measurements have been used. For these methods, thicker layers have been synthesized, with a deposition charge density of 300 mC/cm^2.

Cyclic voltammetric curves have been registered at different sweep rates between 10 and 100 mV/s in the both aqueous organic and solutions.

For clarity, the composition of the solutions and their notation are summarized in Table 2.1.

The poly(3,4–ethylenedioxythiophene) (pEDOT) films were prepared potentiostatically at the +1.1, +1.2, +1.3 V potentials and also poly(3-octylthiophene) (pOT), poly(3-hexylthiophene) (pHT), poly(3-metylthiophene) (pMT) were deposited at +1.7 V potential from anhydrous solution. The poly(3-thiophene-acetic-acid) (pTAA) and poly(3-

thiophene-butyric-acid) (pTBA) films were deposited potentiostatically at E_{pTAA} = +2.5V and E_{pTBA} = +2.3V potential from anhydrous nitrobenzene.

2.1. Table The composition of the polymerization solutions and their notation.

monomer	conducting salt	system notation
0.01 M EDOT	0.05 M SDS, 0.03 M $PIPESH_2$, 0.1 M $PIPESNa_2$ in water	pEDOT/SDS, PIPES/water
0.1 M OT	0.1 M Et_4NPF_6 in acetonitrile	pOT/Et_4NPF_6/AN
0.1 M TBA	0.1 M Bu_4NBF_4 in acetonitrile	pTBA/Bu_4NBF_4/AN
0.1 M TAA	0.1 M Bu_4NBF_4 in acetonitrile	pTAA/Bu_4NBF_4/AN
0.1 M OT	0.1 M Bu_4NBF_4 in acetonitrile	pOT/Bu_4NBF_4/AN
0.01 M EDOT	0.05 M Bu_4NCl in water	pEDOT/Bu_4NCl/water
0.01 M EDOT	0.1 M cetyl-Me_3NCl in water	pEDOT/cetil-Me_3NCl/water
0.01 M EDOT	0.05 M Bu_4NF in water	pEDOT/Bu_4NF/water
0.01 M EDOT	0.05 M SDS in water	pEDOT/SDS/water
0.01 M EDOT	0.025 M Bu_4NBF_4 in water	pEDOT/Bu_4NBF_4/water
0.1 M HT	0.1 M Et_4NPF_6 in acetonitrile	pHT/Et_4NPF_6/AN
0.1 M MT	0.1 M Et_4NPF_6 in acetonitrile	pMT/Et_4NPF_6/AN

3. New scientific results

T.1. The polymerisation of the conducting polymers onto the special ITO electrode

pEDOT has been synthesized successfully onto a special ITO electrode as a first step from buffered aqueous solution in the presence of solubilising sodium-dodecyl-sulfate (SDS). We have presented the absorbance changes recorded at characteristic wavelengths *vs.* the simultaneous *in situ* conductance change during the electrochemical polymerization. The selected absorbance data represent and follow the formation of neutral (560 nm) and the two oxidized species, attributed to monocationic/polaronic (770 nm) and dicationic/bipolaronic (970 nm) forms. During the electrochemical deposition the absorbance of the film increases in the whole visible wavelength range. The observed parallel accumulation of the optically different segments expresses no specific or favoured role in the development of the conductance of the film.

T.2. Application of the simultaneous combined technique during the redox process

2.1. In the first part of the work, we studied pEDOT films. The combination of the two *in situ* applied techniques evidently makes possible to visualize the parallel spectral and conductance changes in function of a common variable, the potential.

2.2. The combined technique could identify two charge carriers. By the combination of the two *in situ* methods, the correlation of the conductance and the formation/transformation of the different species can be revealed.

T.3. Relation between the development of the conducting state and the formation of the charge carriers

3.1. In order to elucidate the correlation between the conductance and the formation of the charge carriers, the derivative of the absorbance change with respect to time of the species was studied, which – based on the Lambert-Beer law – is proportional to their formation rate. By plotting the conductance *vs*. the rate of absorbance change, the difference in the behaviour of the two charge carriers has cleared.

3.2. The redox transformation of pEDOT/SDS, PIPES/water and pOT/Et_4NPF_6/AN has been studied and compared by combining simultaneous *in situ* UV–Vis–NIR spectroelectrochemical and ac conductance techniques. These experimental results clearly evidenced that the conductance increase of pEDOT is in strict correlation with the rate of the increase (dA/dt) of the species absorbing in the medium wavelength range (770 nm–

monocations). In contrast, the conductance of pOT does not increase with the fast formation of species absorbing in the medium wavelength range, but it can be perfectly correlated with the rate of the formation of species absorbing at 1050 nm. This absorbance range is assigned to dications (bipolarons), thus in pOT the development of the conducting state should be attributed to species considered as the dication form.

T.4. Influence of the monomers and the solvents on the development of the conducting state

Systematic studies on the redox transformation of various conducting polymers (polymerised from different monomers) and in different solvents to elucidate the background of the different behaviours suggest that the observed difference can be connected to the different polymerization circumstances. In pTBA/Bu_4NBF_4/AN, pTAA/Bu_4NBF_4/AN, pOT/Bu_4NBF_4/AN and pOT/Et_4NPF_6/AN systems the conductance increased during the redox transformation with the formation of dicationic/bipolaronic species.

T.5. The unexpected interaction between the poly(3,4–ethylenedioxythiophene) film and the dopant Cl^- ions

5.1. We found an anomalous behaviour for the chloride ion doped pEDOT, which result is about to change former perception, namely that the mobility of small spherical anions endows the films always with anion exchange property. As it is demonstrated, a strong interaction between the polymer and this anion leads to a film, which – in spite of the expectations – exhibits perfect cation exchange property. The amount of the chloride ion in the layer proved constant by the EQCM results, indicating only cationic movements during the redox transformation of the pEDOT/Bu_4NCl/aqueous film.

5.2. Semi-empirical and DFT calculations (performed at the University of Tartu) indicated that chloride ions interact with the alpha carbon atoms of the thiophene rings of EDOT oligomers, creating sp^3 hybridized perturbations in the polymer chain.

T.6. The immobilisation of the Cl^- ion into the pEDOT film

6.1. FT-IR spectra evidenced the existence of C-Cl bonds. A similar pattern was proved with a film prepared in the presence of Bu_4NF.

6.2. Elementary analysis, performed by EDX spectroscopy with 8 polymer samples of different oxidation state showed the permanent presence of constant amount of chlorine (S/Cl ~ 5.65), independently of the oxidation state of the pEDOT layer.

6.3. The formation of such bond may decrease the conjugation of the polymeric backbone, which was reflected in the smaller redox activity of the Cl-containing samples. Importantly, we proved that even without utilizing large/macromolecular anions, pEDOT can be forced to act as a cation exchanger.

6.4. Further experiments with pEDOT/Bu_4NCl in water, where the development of the conducting state is directly related to the appearance of the first charge carriers, showed that the redox transformation starts with cation removal. Thus, the increase in the amount of monocatinic/polaronic forms seems to be correlated with the conductance.

T.7. Development of the conducting state and its relation with the movement of cations and anions

7.1. Combined *in situ* spectral and conductance measurements effectively proved the correlation between the development of the conducting state and the formation of the charge carriers. This behaviour is in connection with the fact that the charge transfer causes either the movement of the cations or anions. Our EQCM results suggest alternative models for the relation of the charge carriers and the moving cations or anions.

In the case of immobilised anions, the redox process starts with the migration of the cations out of the film, leaving back the anions in their proper position they occupied in the conducting state. Thus, the conductance increases most of all with the absorbance change at the monocatinic/polaronic form.

In anion exchanging films, the charge transfer forces the flux of anions in, from the side of the film/solution interface, and the macroscopic conductance requires the proper berth of the anions. This stage can be achieved through a dense enough distribution of the charge carriers. Thus, the onset of the conductance is delayed, and it is a result of the interaction of charge carriers in a later stage of the redox transformation, after their significant charge density has been achieved. In this case the development of the conducting state is connected to the formation of the dicationic/bipolaronic species.

7.2. The *in situ* spectroelectrochemistry hyphenated with the ac conductance technique can be widely applied for studying the mechanism of the redox transformation of various transparent electroactive layers.

Beyond the extension of the general theoretical knowledge on the molecular level redox behaviour of conducting polymers, we believe that the results are important also from practical aspects, giving an orientation how to design optimally performing polymer-based devices, such as fast-switching electronic or electrochromic devices.

4. Scientific publications

Papers related to the dissertation:

1. **Combination of in situ UV-Vis-NIR spectro-electrochemical and a. c. impedance measurements: A new, effective technique for studying the redox transformation of conducting electroactive materials.**

E. Peintler-Kriván, **P. S. Tóth**, C. Visy

Electrochemistry Communications, 11, (2009) 1947-1950.

IF=4.243

2. **Application of simultaneous monitoring of the in situ impedance and optical changes on the redox transformation of two polythiophenes: Direct evidence for their non-identical conductance-charge carrier correlation.**

P. S. Tóth, E. Peintler-Kriván, C. Visy

Electrochemistry Communications, 12, (2010) 958-961.

IF=4.282

3. **Electrosynthesis and comparative studies on carboxyl-functionalized polythiophenes derivates.**

P. S. Tóth, C. Janáky, Z. Hiezl, C. Visy

Electrochimica Acta, 56, (2011) 3447-3453.

IF_{2010}=3.642

4. **Fast redox switching into the conducting state, related to single mono-cationic/polaronic charge carriers only in cation exchanger type conducting polymers.**

P. S. Tóth, E. Peintler-Kriván, C. Visy

Electrochemistry Communications, 18, (2012) 16-19.

IF_{2010}=4.282

5. **On the unexpected cation exchange behavior, caused by covalent bond formation between PEDOT and Cl^- ions, extending the conception for the polymer – dopant interactions.**

P. S. Tóth, C. Janáky, O. Berkesi, T. Tamm, C. Visy

Journal of Physical Chemistry B *Submitted* **(IF_{2010}=3.603)**

ΣIF=16.449

Other publications:

6. **Study on the electrodeposition of organic and inorganic thermoelectric materials for composite preparation.**

E. Kriván, G. Bencsik, C. Janáky, **P. S. Tóth**, G. Sós, C. Visy

Reaction Kinetics and Catalysis Letters, 96, (2009) 429-436.

IF=0.557

7. **Application of classical and new, direct analytical methods for the elucidation of ion movements during the redox transformation of polypyrrole.**

C. Janáky, G. Cseh, **P. S. Tóth**, C. Visy

Journal of Solid State Electrochemistry, 14, (2010) 1967-1973.

IF=2.234

ΣIF=2.791

Conference lectures and posters:

1. **Simultaneous detection of conductance and spectral changes of conducting polymers.**

P. S. Tóth, E. Kriván, C. Visy

216th ECS Meeting, Vienna, 2009. (poster)

2. **Egyidejű in situ a.c. impedancia és spektroelektrokémiai vizsgálatok vezető polimereken.**

Tóth P. S., Visy C.

XXXII. KEN, Szeged, 2009. (lecture)

3. **Simultaneous monitoring of the in situ a. c. impedance and the optical changes in nanocoatings during their redox transformation.**

P. S. Tóth, E. Peintler-Kriván, C. Visy

2nd International Conference on Functional Nanocoatings, Dresden, 2010. (lecture)

4. **Simultaneous monitoring of optical and conductance changes during the redox transformation of transparent conducting layers.**

C. Visy, **P. S. Tóth,** E. Peintler-Kriván

CIMTEC 5th forum of new materials, Montecatini Terme, 2010. (lecture)

5. **Identification of the charge carrier, primarily responsible for the development of the name-giving property of conducting polymers.**

C. Visy, **P. S. Tóth,** C. Janáky, E. Peintler-Kriván

61st ISE Meeting, Nice, 2010. (lecture)

6. **In situ spektroelektrokémiai és vezetésváltozási vizsgálatok szubsztituált politiofén vezető polimer filmeken.**

Tóth P. S., Visy C.

XXXIII. KEN, Szeged, 2010. (lecture)

7. **Electrosynthesis and simoultaneously performed in situ impedance and UV-VIS-NIR studies on poly(3-thiophene-butyric-acid).**

P. S. Tóth, C. Janáky, E. Peintler-Kriván, C. Visy

219th ECS Meeting, Montréal 2011. (lecture))

8. **Vezető polimerek kombinált, egyidejű spektroelektrokémiai és vezetésváltozási vizsgálata.**

P. S. Tóth, C. Janáky, E. Peintler-Kriván, C. Visy

MKE 1. Nemzeti konferencia, Sopron, 2011. (lecture)

9. **Tiofén típusú vezető polimerek vizes közegben történő előállítása ionos és nem ionos felületaktív anyagok alkalmazásával.**

Tóth P. S., Visy C., C. Perrouchot, M. Jouini

XXXIV. KEN, Szeged, 2011. (lecture)