Doctoral (*Ph. D.*) theses

Effect of structural parameters on the thermoelectric properties of conducting polymers

BALÁZS ENDRŐDI

SUPERVISORS:

Dr. Csaba Visy

Professor emeritus

Dr. Csaba Janáky

Assistant professor

Chemistry Doctoral School

University of Szeged

Faculty of Science and Informatics

Department of Physical Chemistry and Materials Science

Szeged, 2015

I. Introduction and objectives

Possibility of harnessing the thermoelectric effects in everyday practice emerged shortly after their discovery. Since that, Peltier coolers are frequently used in the field microelectronic temperature regulation, while devices working on principle of the Seebeck effect are generally applied in radioisotope thermoelectric generators of space probes (e.g., during the former Apollo and by the Mars rover). Their widespread application – e.g., for the direct conversion of waste heat to electrical energy – however, is still limited by many factors, most importantly by the low efficiency and high price of the currently used thermoelectric materials. Therefore, beyond the investigation of the generally employed Pb, Bi, Te, Sn, Si, Se containing inorganic semiconductors, search for new possible thermoelectric materials is more and more attractive. Among other promising applicants, significant scientific interest is dedicated to intrinsically conducting organic polymers, as promising alternatives for low temperature thermoelectric applications.

Conducting polymers (CPs) show several beneficial features compared to their inorganic counterparts, such as low cost of their synthesis, low thermal conductivity, and remarkably high Seebeck coefficient. The attributes further supported by the ease of their processing (even in solution phase), induced significant scientific efforts in this area. A major drawback of CPs in thermoelectrics is their usually low electrical conductivity in their neutral form. This issue can be circumvented by doping the polymer (increasing charge carrier concentration). Note however, that the effects of increased charge carrier density is complex, because it affects thermal conductivity and the Seebeck coefficient as well (in an undesired manner). Therefore, other strategies are widely applied to increase the thermoelectric figure of merit. Composite formation is a very attractive strategy. Incorporation of highly conductive (nano)particles into the polymer matrix may allow the increase of the electrical conductivity without influencing the Seebeck coefficient and thermal conductivity unfavourably. Moreover, it was recently discovered that supramolecular and morphological features of CPs are also of importance in optimizing the thermoelectric performance.

Our research group has been active in the field of conjugated polymer based hybrid materials for 10 years. During my doctoral work I have joined one of such projects, to investigate the thermoelectric properties of CPs and their composites. During my doctoral work I have studied two fundamentally different methods to overcome the low electrical conductivity of CPs in their neutral form. Both of these aim the formation of 1 dimensional nanostructures, in which the electrical conductivity is enhanced without having a severe influence on the thermal conductivity and the Seebeck coefficient.

As a model system, poly(3-alkylthiophene)s (P3ATs) with different alkyl side chain length (varying from polythiophene itself to poly(3-dodecylthiophene)) were prepared and recrystallized to a nanofibrillar structure by exploiting their self-assembling behaviour. By comparing the thermoelectric properties of this recrystallized form and the bulk polymer we aimed to identify the effect of the supramolecular structure. Furthermore, we aimed to investigate the thermoelectric and charge storage properties of macroscopic sized multi-walled carbon nanotube array (MWCNTA) – conducting polymer composites. By infiltrating P3HT into MWCNTAs we aimed the preparation of composites in which the large Seebeck coefficient of the reduced polymer is combined with the high electrical conductivity of the carbon derivative. As another promising application, we also proposed the investigation of the charge storage properties of such hybrids.

II. Experimental methods

All chemicals were of analytical grade. The water content of the used organic solvents (nitrobenzene, chloroform, anisole, acetonitrile) was determined by coulometric Karl-Fischer titration, and it was kept below 50 ppm. Aqueous solutions were prepared by using deionized water (having a resistivity of 18.2 MΩ cm), made in a MilliQ Millipore Direct Q3 instrument. Aniline monomer was freshly distilled before use. The macroscopic, 1-2 mm high multi-walled carbon nanotube arrays (MWCN-TA) were grown by water-assisted chemical vapour deposition (CVD) method by Dóra Fejes, in the laboratory of Prof. László Forró (École Polytechnique Fédérale de Lausanne, Switzerland).

All electrochemical measurements were performed on a Metrohm PGSTAT302 potentiostat-galvanostat instrument, in a classical three electrode electrochemical cell. Ag/AgCl/3M NaCl (E=200 mV vs. SHE) reference electrode was used during the measurements in aqueous solutions, while an AgCl coated silver wire quasi-reference was used in organic solvents. A Pt sheet was applied as counter electrode in both cases.

UV–visible spectra were recorded by an Agilent 8453 UV–visible diode array spectrophotometer in the range of 190–1100 nm, using a quartz cuvette with 1 cm path length. Structure of the polymers and the composites was studied by both infra-red and Raman spectroscopy. Fourier transform infrared spectroscopic (FT-IR) studies were performed using a Bio-Rad Digilab Division FTS-65A/896 Fourier transform infrared spectrometer equipped with a Harrick's Meridian® SplitPea single reflection diamond attenuated total reflectance (ATR) accessory. All infrared spectra were recorded between 400 and 4000 cm^{-1}, at 4 cm^{-1} optical resolution, averaging 256 interferograms. Raman spectroscopic studies were performed on a Thermo Scientific™ DXR Raman Microscope using a red laser (λ=780 nm), operating at 1 mW laser power.

Supramolecular structure of the poly(3-alkythiophene) thin layers was studied by X-ray diffraction. XRD spectra were recorded by a Rigaku Miniflex II instrument, operating with a Cu $K_{\alpha,1}$ radiation source (λ= 0.1541 nm).

For transmission electron microscopic (TEM) investigations, a FEI Tecnai G^2 20 X-Twin type instrument, operating at an acceleration voltage of 200 kV was used. The samples were studied on copper mesh TEM grids covered by carbon film. Scanning electron microscopic (SEM) images were recorded by a Hitachi S-4700 field emission scanning electron microscope, operating at an acceleration voltage of 10 kV. Elemental composition of the samples was analysed by energy dispersive x-ray spectroscopy (EDX), using a Röntec EDX detector, coupled with the SEM instrument.

Gradual oxidation of the poly(3-alkythiophene) thin layers was followed by simultaneous in situ spectral and conductance measurements in a custom designed electrochemical cell, using an Agilent 8453 UV–visible diode array spectrophotometer and a SR830 type lock-in amplifier. AC conductance change of the thin layers was monitored applying an exciting signal with 130 Hz frequency and 10 mV RMS amplitude.

Measurement of the Seebeck coefficient was carried out using custom designed setups (for bulk materials and thin layers, separately), built in collaboration with Prof. Zoltán Gingl and his co-workers at the Noise Research Group of the University of Szeged. Thermovoltage was recorded using a FES24 type data acquisition unit, operated by a NI LabVIEW software.

Electrical and thermal conductivity of the multi-walled carbon nanotube array/conducting polymer composites was studied by Péter Matus and Andrea Pisoni in the research group of Prof. László Forró (École Polytechnique Fédérale de Lausanne, Switzerland). The anisotropic electrical resistivity of MWCNTA/P3HT samples was determined adopting the Montgomery method, while thermal conductivity was determined by a quasi-stationary method, formerly validated in the same research group.

III. Summary of new scientific results

T1. Oxidation of poly(3-alkylthiophene) nanofibers with $AgClO_4$

1.1. Polythiophene and P3ATs with different side-chain length were prepared by oxidative chemical polymerization, and subsequently recrystallized in an anisole/chloroform mixture. Polymers having butyl or longer alkyl side chains were successfully recrystallized to a nanofibrillar structure, as confirmed by both spectroscopic (UV-Vis spectroscopy) and electronmicroscopic (TEM) measurements. By drop-casting the polymer solutions on solid substrates, formation of a self-assembled networks of P3AT nanofibers was experienced.

1.2. The polymer layers were oxidized with $AgClO_4$, dissolved in nitrobenzene solvent. In this redox reaction P3ATs gets oxidized, followed by the deposition of silver particles. Increasing oxidant concentration leads to a rise in both the reaction rate and the doping level (and hence the electrical conductivity) of the polymer.

T2. Thermoelectric properties of P3HT nanofibers

2.1. Electrical conductivity of the P3HT increases during the oxidation (with the doping level), while the Seebeck coefficient ceases to a minimum value. Consequently, the increase of the doping level (varied by the reaction time) leads to a broad maximum in the power factor. The power factor showed a monotonous rise with the oxidant concentration, mostly dictated by the increased electrical conductivity (and the more or less constant Seebeck coefficient) of the heavily doped polymer. The best power factor measured for the nanofibrillar P3HT is about 50 times larger, than the best value reported in the literature.

2.2. Thermoelectric properties of P3HT before and after the recrystallization were examined and compared. It was found that the nanofibrillar structure has no effect on the Seebeck coefficient, but leads to an enhanced electrical conductivity, rooted in the improved charge carrier mobility compared to that of the bulk polymer. Recrystallization of P3ATs therefore results in better thermoelectric properties.

T3. Effect of the oxidant, and the alkyl side chain length of poly(3-alkylthiophene)s on the thermoelectric properties

3.1. Best thermoelectric power factors were recorded for heavily doped polymer for all the investigated P3ATs. While the Seebeck coefficient was found to be independent from the length of the alkyl side chain, shorter chains lead to more closely packed structures and enhanced electrical conductivity. The highest thermoelectric power factor, P∼10 $\mu WK^{-2}m^{-1}$ was achieved for the heavily doped P3BT nanofibers.

3.2. Effect of the dopant's nature was also investigated. No significant difference was found by comparing the thermoelectric power factor of Fe^{3+} and Ag^{+} doped P3BTs. Upon this, we conclude that the silver nanoparticles, formed in the redox reaction, has no, or just slight contribution to the enhanced electrical conductivity.

T4. Electrochemical synthesis of macroscopic MWCNTA/conducting polymer composites

4.1. The MWCNTAs show proper wetting in the solvents, used during the electrochemical synthesis of the composites (water, acetonitrile). The MWCNTAs can be directly applied as working electrodes by mechanically detaching them from the silicon substrate and placing between two conductive glass (indium tin oxide covered) sheets. The MWCNTAs show stable, capacitive electrochemical behaviour in the potential window, applied during the electropolymerizations.

4.2. Continuous growth of the polymer was experienced at the initial stage of the potentiodynamic synthesis of MWCNTA/P3HT composites. However, the growth rate of the polymer gradually ceases with the number of the polymerization cycles. The electroactivity of the composite reached its maximum value after ∼50-60 polymerization cycles. Upon Raman spectroscopic measurements this termination results in an inhomogeneous composite with a low amount of P3HT incorporated in the MWCNTA, especially in its deeper regions.

4.3. Continuous growth of the polymer was achieved by applying potentiostatic electropolymerization. Our studies on the structure of this latter composite ev-

idenced the formation of uniform P3HT coating with constant thickness on the individual carbon nanotubes from the top to the bottom of the MWCNT structure. Electron microscopic images (SEM) proved, that the composition of the hybrids can be tuned by the polymerization time, and hence by the transferred charge. By applying long enough polymerization time, a compact hybrid structure was formed.

T5. **Thermoelectric properties of macroscopic sized MWCNTA/conducting polymer composites**

5.1. Thermoelectric studies on the potentiostatically prepared MWCNTA/P3HT hybrids revealed a slight increase in the Seebeck coefficient with the gradually increasing polymer amount. Although by completely filling the carbon framework a quasi-bulk CP-phase was formed, the high Seebeck coefficient characteristic for the neutral bulk P3HT was not observed in the hybrid configuration.

5.2. Similar experiments (optimization of the polymerization method, investigation of the structure of the composite), performed with another polymer, poly(3,4-ethylenedioxythiophene), led to very similar results, namely to slight increase in the Seebeck coefficient and moderate decrease in the electrical conductivity. Upon this, we conclude, that there is no synergistic or even additive combination of the high Seebeck coefficient of the polymer and the high electrical conductivity of the MWCNTA. In such hybrids the carbon component dominates the thermoelectric properties even at high polymer loadings.

T6. Charge storage properties of macroscopic MWCNTA/polyaniline composites

6.1. Based on the significant increase in the charge capacitance of the MWCNTAs upon the polymer infiltration, MWCNTA/polyaniline composites were prepared by potentiodynamic electropolymerization. Continuous growth of the polymer coating was experienced during the polymerization. The SEM measurements evidenced the gradual filling of the gaps among the individual nanotubes in the MWCNTA structure.

6.2. Galvanostatic charge-discharge measurements were conducted to determine the specific capacitance of the hybrids with different composition. At a moderate polymer loading the specific capacitance (normalized to the mass of the deposited polymer) show a maximum (650 F g^{-1}), which is comparable to the values reported earlier in the literature. However, it is important to notice that in our case this result was gathered on macroscopic samples. This fact was quantified by calculating capacitance values, normalized by the geometrical surface area of the electrode. The obtained extraordinary high values (1-3 F cm^{-2}) are much larger compared to those usually reported for conducting polymer/nanocarbon hybrids.

IV. Scientific publications

Hungarian Scientific Bibliography (MTMT) identifier: 10030827

Publications related to the scientific topic of the dissertation

[1] **B. Endrődi**, J. Mellár, Z. Gingl, C. Visy, C. Janáky: *Reasons behind the improved thermoelectric properties of poly(3-hexylthiophene) nanofiber networks*
RSC Advances, 4:55328-55333 (2014)
IF=3.840

[2] **B. Endrődi**, J. Mellár, Z. Gingl, C. Visy, C. Janáky: *Molecular and Supramolecular Parameters Dictating the Thermoelectric Performance of Conducting Polymers: A Case Study Using Poly(3-alkylthiophene)s*
The Journal of Physical Chemistry C, 119: 8472-8479 (2015)
IF_{2014}=4.772

[3] **B. Endrődi**, G. F. Samu, D. Fejes, Z. Németh, E. Horváth, A. Pisoni, P. Matus, K. Hernádi, C. Visy, L. Forró, C. Janáky: *Challenges and Rewards of the Electrosynthesis of Macroscopic Aligned Carbon Nanotube Array / Conducting Polymer Hybrid Assemblies*
Journal of Polymer Science, Part B: Polymer Physics, *accepted for publication,* DOI: 10.1002/polb.20150173
IF_{2014}=3.830

ΣIF=12.442

Other publications

[4] G. Bencsik, C. Janáky, E. Kriván, Z. Lukács, **B. Endrődi**, C. Visy: *Conducting polymer based multifunctional composite electrodes*
Reaction Kinetics and Catalysis Letters, 96(2):421-428 (2009)
IF= 0.557

[5] C. Janáky, **B. Endrődi**, A. Hajdú, C. Visy: *Synthesis and characterization of polypyrrole–magnetite–vitamin B12 hybrid composite electrodes*
Journal of Solid State Electrochemistry, 14(2):339-346 (2010)
IF=2.234

[6] C. Janáky, **B. Endrődi**, K. Kovács, M. Timko, A. Sápi, C. Visy: *Chemical Synthesis of Poly(3-thiophene-acetic- acid) / Magnetite Nanocomposites with Tunable Magnetic Behaviour*
Synthetic Metals, 160(1–2):65–71 (2010)
IF=1.871

[7] C. Janáky, **B. Endrődi**, O. Berkesi, C. Visy: *Visible-Light-Enhanced Electrocatalytic Activity of a Polypyrrole/Magnetite Hybrid Electrode toward the Reduction of Dissolved Dioxygen*
The Journal of Physical Chemistry C, 114(45):19338–19344 (2010)
IF=4.520

[8] G. Bencsik, C. Janáky, **B. Endrődi**, C. Visy: *Electrocatalytic properties of the polypyrrole/magnetite hybrid modified electrode towards the reduction of hydrogen peroxide in the presence of dissolved oxygen*
Electrochimica Acta, 73:53–58 (2012)
IF=3.777

[9] T. Szabó, M. Magyar, Z. Németh, K. Hernádi, **B. Endrődi**, G. Bencsik, C. Visy, E. Horváth, A. Magrez, L. Forró, L. Nagy: *Charge stabilization by reaction center protein immobilized to carbon nanotubes functionalized by amine groups and poly(3-thiophene acetic acid) conducting polymer*
Physica Status Solidi B, 249(12):2386–2389 (2012)
IF=1.489

[10] PS. Tóth, G. F. Samu, **B. Endrődi**, C. Visy: *Hyphenated in situ conductance and spectroelectrochemical studies of polyaniline films in strongly acidic solutions*
Electrochimica Acta, 110:446–451 (2013)
IF=4.086

[11] **B. Endrődi**, A. Bíró, I. Tóth, C. Janáky, C. Visy: *Layer by Layer Growth of Electroactive Conducting Polymer/Magnetite Hybrid Assemblies*
Synthetic Metals, 171:62-68 (2013)
IF=2.222

[12] M. Magyar, K. Hajdu, T. Szabó, **B. Endrődi**, K. Hernádi, E. Horváth, A. Magrez, L. Forró, C. Visy, L. Nagy: *Sensing hydrogen peroxide by carbon nanotube/horseradish peroxidase bio-nanocomposite*
Physica Status Solidi B, 250(12):2559:2563 (2013)
IF=1.605

[13] **B. Endrődi**, A. Kormányos, C. Janáky, O. Berkesi, C. Visy: *Fixation of laccase enzyme into polypyrrole, assisted by chemical interaction with modified magnetite nanoparticles: A facile route to synthesize stable electroactive bionanocomposite catalysts*
Electrochimica Acta, 122:282-288 (2014)
IF=4.504

[14] **B. Endrődi**, D. Hursán, L. Petrilla, G. Bencsik, C. Visy, A. Chams, N. Maslah, C. Perruchot, M. Jouini: *Incorporation of cobalt-ferrite nanoparticles into a conducting polymer in aqueous micellar medium: strategy to get photocatalytic composites*
Acta Chimica Slovenica, 61(2):376-381 (2014)
IF=0.686

[15] PS Tóth, **B. Endrődi**, C. Janáky, C. Visy*: Development of polymer - dopant interactions during electropolymerization, a key factor in determining the redox behaviour of conducting polymers*
Journal of Solid State Electrochemistry, DOI: 10.1007/s10008-015-2791-1 (2015)
IF_{2014}=2.446

Publications in national journals

[16] **Endrődi Balázs**, Kormányos Attila, Bencsik Gábor, Peintler-Kriván Emese, Janáky Csaba, Visy Csaba: *Polipirrol/magnetit kompozit vékonyrétegek szintézise és elektrokatalitikus tulajdonságaik jellemzése*
Magyar Kémiai Folyóirat 120(2-3):67-71, 2014

ΣΣIF=42.439

Conference lectures and posters

1. **B. Endrődi**, C. Janáky, G. Bencsik, C. Visy: *Electroreduction and Sensing of Dissolved O_2 and H_2O_2 on a Polypyrrole/Magnetite Hybrid Electrode*
9th Spring Meeting of the International Society of Electrochemistry,
8-11 May, 2011, Turku, Finland – poster presentation
2. **B. Endrődi**, E. Kriván, M. A. Azam, G. F. Samu, A Varga, C. Visy: *Thermoelectric and electrochemical properties of highly ordered conducting polymer/carbon nanotube structures*
7th Workshop on the Electrochemistry of Electroactive Materials
3-8 June, 2012, Hódmezővásárhely-Szeged, Hungary – oral lecture
3. **B. Endrődi**, A. Bíró, C. Janáky, C. Visy: *Layer by Layer Growth of Conducting Polymer/Magnetite Hybrid Assemblies and Their Application as Modified Electrodes*
63rd Annual Meeting of the International Society of Electrochemistry
19-24 August 2012, Prague, Czech Republic – poster presentation
4. **B. Endrődi**, A. Kormányos, C. Janáky, O. Berkesi, C. Visy: *Laccase-enzyme entrapment into a conducting polymer matrix assisted by magnetite nanoparticles: A simple route to form bionanocomposites for electrochemical oxygen reduction*
12th Topical Meeting of the International Society of Electrochemistry (Bioelectrochemistry)
17-21 March, 2013, Bochum, Germany – poster presentation
5. **B. Endrődi**, C. Janáky, C. Visy, 2014: *Silver decorated conducting polymer nanofibers: A possible route to form hybrid materials with enhanced thermoelectric properties*
International Conference on Science and Technology of Synthetic Metals
30 June – 5 July, 2014, Turku, Finland– poster presentation
Wiley Best Poster Award
6. **B. Endrődi**, J. Mellár, Z. Gingl, C. Visy, C. Janáky: *Effective control over the thermoelectric properties of poly(3-alkylthiophenes) – the role of molecular and supramolecular features*
6th Szeged International Workshop on Advances in Nanoscience (SIWAN)
15-18 October, 2014, Szeged, Hungary – oral lecture

7. **B. Endrődi**, C. Visy, C. Janáky: *Molecular and Supramolecular Parameters Dictating Thermoelectric Performance of Conducting Polymers: A Case Study Using Poly(3-alkylthiophenes)*
E-MRS 2015 Spring Meeting
11-15 May, 2015., Lille, France – oral lecture

8. **B. Endrődi**, C. Visy, C. Janáky: *What dictates the thermoelectric performance of conducting polymers: A case study using poly(3-alkylthiophenes)*
34th International Conference on Thermoelectrics & 13th European Conference on Thermoelectrics
June 28-July 2, 2015., Dresden, Germany – oral lecture

Co-author at international conferences

9. C. Janáky, **B. Endrődi**, C. Visy: *Chemical and electrochemical synthesis of conducting polymer based magnetic nanocomposites*
Frühjahrssymposium, 11th Young Scientists Conference on Chemistry,
11-14 March, 2009, Essen, Germany – poster presentation

10. C. Janáky, G. Bencsik, Z. Lukács, **B. Endrődi**, C. Visy: *Conducting Polymer Based Hybrids for Analytical and Biotechnological Applications*
International Workshop on the Electrochemistry of Electroactive Materials
14-19 July, 2009, Szczyrk, Poland – oral lecture

11. C. Janáky, **B. Endrődi**, E. Kriván, C. Visy: *Properties of a polypyrrole/magnetite/vitamin B12 hybrid: a conducting polymer based electrode for bioelectrocatalysis*
216th ECS Meeting,
4-9 October, 2009, Wien, Austria – oral lecture

12. C. Janáky, **B. Endrődi**, C. Visy: *Synthesis, characterization and application of conducting polymer based magnetic electrodes*
216th ECS Meeting,
4-9 October 2009, Wien, Austria – oral lecture

13. C. Janáky, **B. Endrődi**, C. Visy: *Photoelectrocatalytic Reduction and Sensing of O_2 and H_2O_2 on Conjugated Polymer Based Magnetic Electrodes*
219th ECS Meeting,
1-6 May, 2011, Montreal, Canada – poster presentation

14. D. A. Ungor, E. Kriván, **B. Endrődi**, C. Janáky, C. Visy: *Synthesis and characterization of conducting polymer nanofiber composites*
7th Workshop on the Electrochemistry of Electroactive Materials,
3-8 June, 2012, Hódmezővásárhely, Hungary – poster presentation

15. D. A. Ungor, A. Varga, E. Kriván, **B. Endrődi**, C. Janáky, C. Visy: *Synthesis, characterization and possible applications of conducting polymer fiber – noble metal nanocomposites*
Third International Conference on Multifunctional, Hybrid and Nanomaterials,
3-7 March, 2013, Sorrento, Italy – poster presentation

16. **B. Endrődi**, G. F. Samu, D. Fejes, Z. Németh, C. Janáky, K. Hernádi, L. Forró, C. Visy: *Thermoelectric and supercapacitive properties of self-standing highly-ordered conducting polymer/carbon nanotube structures*
ChemOnTubes 2014
30 March – 3 April, 2014, Riva del Garda, Italy – poster presentation

17. **B. Endrődi**, C. Janáky, C. Visy: *Conducting Polymer Based Thermoelectric Composites: Today and Possible Tomorrow*
Workshop on the Electrochemistry of Electroactive Materials 2015
31 May – 5 June, 2015, Bad Herrenalb, Germany – oral presentation

18. A. Varga, **B. Endrődi**, C. Visy, C. Janáky: *Photocatalytic deposition and characterization of CdS/P3HT nanofiber composites*
Workshop on the Electrochemistry of Electroactive Materials 2015
31 May – 5 June, 2015, Bad Herrenalb, Germany – poster presentation