Doctoral (Ph.D.) theses

Synthesis, characterization and potential applications of conducting polymer-based photocatalytic composite electrodes

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1. Introduction

Polymers are inorganic or organic macromolecules, building up from one or more, regularly repeated units. The two major classes of organic polymers are natural macromolecular compounds (polysaccharides, nucleic acids, caoutchouc) and synthetic macromolecular compounds (polystyrene, polyethylene terephthalate, poly(methyl methacrylate). The conducting polymers are one class of these synthetic materials, the electrical conductivity of which - in contrast to the other insulating polymers - can be changed by orders of magnitude. Their two main groups are the aliphatic (polyacetylene) and poly-aromatic or heteroaromatic (polyaniline, polypyrrole, polythiophene) polymers, all possessing extended conjugated π-electron system.

The conducting polymers themselves are important for their adjustable conductance and attractive optical properties. Their semiconductor character and absorption in the visible light brings on the possibility of their use in photocatalysis.

In the last decades, combination of conducting polymers with materials of different properties came gradually to the front. In this case, usually inorganic particles are incorporated into the organic conducting polymer matrix, but the inverse method is also applicable, when the organic conducting polymer is polymerized into an inorganic material.

Owing to the several favorable properties application of the organic conducting polymer-based modified electrodes as sensors are in the focus of interest in both the scientific and industrial life. Their simple synthesis, processability, low price and relatively long life necessitate further research and development in the field.

2. Objectives

Based on literature review and previous experiences gained in our research group we envisaged producing new, never or scarcely investigated polymer-based composite electrodes.

On the one hand our goal was the preparation of poly(3-octylthiophene) and polypyrrole based iron oxalate composites through a post-treatment by hydrogen peroxide.

In addition, the electrochemical synthesis of the conducting polymer/iron oxalate composite materials were also planned. Our concept was that we deposit a conducting polymer (pyrrole, 3,4-ethylenedioxythiophene) from an aqueous monomer solution in the presence of the very poorly water-soluble iron oxalate only, without other conducting salt.

Furthermore, the electrochemical characterization of composite materials and extensive study on their properties has been also intended.

Recent studies in our group revealed that the current related to the presence of hydrogen peroxide, measured by amperometric method on a magnetite containing polypyrrole electrode at very low peroxide contents, is directly proportional to the concentration. Thus, we wanted to study also this electrocatalytic property in more detail.

On the grounds of all these premises, we decided to focus especially on the investigation of photocatalytic properties, on the detailed study of the photo-electrochemical behaviour and on the exploration of the eventual analytical application of the various iron compounds and their hybrids with conducting polymers.

3. Experimental methods

The electrochemical data were obtained were performed on PGSTAT 10 potentiostat-galvanostat (AUTOLAB) under computer control, capable of carrying out dynamic and steady-state measurements. During the investigations a classical three electrode electrochemical cell was used, where the general working electrode was a Pt electrode, while an Au electrode during rotating disk electrode tests, and an ITO-coated glass electrode during the spectro-electrochemical measurements. In all cases a Ag/AgCl/3M NaCl reference electrode was used with a potential of 0.200 V *vs.* SHE. The counter electrode was either a Pt wire or a Pt plate. The electrochemical quartz crystal microbalance measurements were carried out by QCA917, EG&G Seiko device with Au-coated quartz crystal working electrode.

X-ray examination of the samples was performed on a Philips PW-1830 type X-ray diffractometer (2Θ = 2-80^{o}), with the radiation at the line of CuK_{α} (λ = 0.1542 nm), at 40 kV and 30 mA. During the evaluation the reflectance values of the measured diffractograms were compared with the data of JCPDS cards.

^{57}Fe Mössbauer spectra of the electrochemically prepared PPy/iron oxalate composite were acquired with a 10^{9} Bq ^{57}Co (Rh) source in transmission geometry in the Laboratory of Nuclear Chemistry at the Faculty of Science of the Eötvös Lóránd University.

Our scanning electron microscopy measurements were performed by a Hitachi S-4700 scanning electron microscope, coupled with Röntec QX2 type energy X-ray analyzer. During the visual examination of the surface local element analytical study was carried out at the same time.

4. Summary of new scientific results

1. Chemical synthesis and characterization of the polypyrrole/iron-oxalate and the poly(3,4-ethylenedioxythiopene)/iron-oxalate composites

In the case of the posterior incorporation of the iron-containing component into polypyrrole, its presence was proved by the appearance of two identified reflections obtained during the X-ray diffraction measurements. The X-ray diffraction results obtained with the polythiophene derivative confirmed the layered structure of the polymer substrate. From the decrease in the intensity of the reflections and their shifts, the weakening of short- and long-distance interactions between octylthiophene chains, caused by the built-in inorganic component could be concluded, hence its presence influenced both the radical cation – radical cation interactions and the interactions between side-chains, resulting a comb-like, lamellar structure.

2. Electrochemical synthesis and characterization of polypyrrole/iron-oxalate films

The results obtained in the second part of the synthetic work showed that polypyrrole film was successfully prepared in the presence of iron (II) oxalate, dispersed in water, without the addition of any other conducting salt. The layer formation was studied also by the electrochemical quartz crystal microbalance (EQCM) technique. These results indicated that the positive charges of the polymer formed on the surface in the oxidized state are compensated not only by the most probable oxalate containing complex anions, but in a significant extent also by oxalate complex ions, containing irons in mixed oxidation state. This hypothesis was supported by Mössbauer spectroscopy studies: from the ratio of iron(II) and iron(III) it was concluded that the film contains both $[Fe(II)Fe(III)(ox)_3]^-$ and $[Fe(III)(ox)_3]^{3-}$ anions. The data calculated from the iron(II)/iron(III) ratio showed a good agreement with the experimental results obtained from the quartz crystal microbalance measurements.

3. Electrochemical synthesis and characterization of poly(3,4-ethylenedioxythiopene)/ iron-oxalate layers

3.1. The results showed that the electrochemical polymerization of EDOT is feasible in the presence of iron (II) oxalate in such a way that the solution does not contain any other electrolyte. The layer was stable, performed a sustained redox activity, it did not show signs of decay or overoxidation. If the solution contained dissolved oxygen, the redox

transformation of the film became asymmetric and exhibited a high cathodic charge surplus. The excess of this cathodic charge originated from the reduction of dissolved oxygen.

3.2. The PEDOT/iron oxalate layer - as a p-type semiconductor - exhibited photo-electrocatalytic effect which was connected to excitation of the neutral form of the film. The negative photocurrent depended on the amount of oxygen, this dependence gave a linear correlation between the cathodic photocurrent and the concentration of the dissolved gas. Thus, the PEDOT/iron oxalate composite electrode as a photo-electrochemical sensor can be used for measuring the concentration of oxygen in aqueous solutions. The detection limit of our electrode is below 1 ppm, and the dynamic range extends up to 20 ppm concentration.

4. Synthesis and characterization of polypyrrole layers with magnetic properties

4.1. The formation of the PPy/magnetite hybrid electrode prepared in the presence of a special conducting salt (PTO) could be proved by comparing its significantly increased activity with the electrochemical behaviour of the polymer electrode, produced without magnetite under otherwise identical conditions. Based on these results it was concluded that the PPy/PTO/magnetite hybrid electrode is particularly suitable for measuring the hydrogen peroxide content of aqueous solutions especially in the range of low concentrations. This conclusion was supported by transient and steady-state amperometric measurements in the 0 – 400 μM hydrogen peroxide concentration range. The increased activity of the electrode could be easily traced when comparing it with the behaviour of the pure polymer. This comparison revealed that the significant current increasing effect of PPy/PTO/magnetite hybrid electrode registered in the electrochemical reduction of hydrogen peroxide can be really associated with the well-known catalytic behaviour of magnetite nanoparticles, preserved also in the in-built form.

4.2. Currents detected by the amperometric technique at the PPy/PTO/magnetite electrode in the presence of both the dissolved oxygen and hydrogen peroxide originated from their concurrent reductions. It has been proved, however, that the disturbing effect of oxygen can be eliminated by applying a properly chosen potential value. It has been demonstrated that the slopes of the calibration curves, obtained either with the exclusion or in the presence of oxygen from the currents of hydrogen peroxide reduction at an optimized potential of -0.3 V, are identical. It has been shown that the three significantly different oxygen concentrations (de-oxygenated, saturated from air and from pure oxygen) affect only the intercept of the calibration curves – owing to their parallel shift. This fact is important if we take into consideration that the electrode can be used to determine the concentration of peroxide in the

presence of oxygen – after its calibration in the oxygen reduction. To the best of my knowledge, it is unique in the literature.

4.3. The effect of the illumination on the above described electroactivity of the PPy/PTO/magnetite electrode has been examined. The stationary photocurrents obtained at potential value of -0.3 V at increasing amounts of hydrogen peroxide and at an equilibrium concentration of oxygen followed also a linear dependence. By comparing the fitting parameters of the calibration curves obtained under illumination and in the dark, a one and a half times larger slope was obtained in the former case. This increase in the sensitivity of a photo-electrochemical hydrogen peroxide sensor, based on the future development of this electrode, can be exploited.

5. Scientific publications

Publications related to the scientific topic of the dissertation

1. C. Visy, **G. Bencsik**, Z. Németh, A. Vértes:
   Synthesis and characterization of chemically and electrochemically prepared conducting polymer/iron oxalate composites
   Electrochimica Acta, 53 (2008) *3942-3947*
   IF=3.078

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

3. **G. Bencsik**, Z. Lukács, C. Visy:
   Photo-electrochemical sensor for dissolved oxygen, based on a poly(3,4-ethylene-dioxythiophene)/iron oxalate hybrid electrode
   Analyst, 135 (2010) *375-380*
   IF=3.913

4. **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, (2011) doi:10.1016/j.electacta.2011.10.100
   IF_{2010}=3.642

Other publications

5. E. Kriván, **G. Bencsik**, C. Janáky, P. S. Tóth, B. Roósz, G. Sós, C. Visy:
   Study on the electrodeposition of organic and inorganic thermoelectric materials for composite preparation
   Reaction Kinetics and Catalysis Letters, 96 (2009) *429-436*
   IF=0.557

6. C. Janáky, **G. Bencsik**, Á. Rácz, C. Visy, N. R. Tacconi, W. Chanmanee, K. Rajeshwar:
   Electrochemical Grafting of Poly(3,4-ethylenedioxythiophene) into a Titanium Dioxide Nanotube Host Network
   Langmuir, 26 (2010) *13697-13702*
   IF=4.268

7. T. Szabó, **G. Bencsik**, G. Kozák, C. Visy, Z. Gingl, K. Hernádi, K. Nagy, G. Váró, L. Nagy:
   Interaction between photosynthetic reaction centers and ITO
   European Biophysics Journal with Biophysics Letters, 40 (2011) *S179*
   IF_{2010}=2.387

8. K. Hajdu, T. Szabó, M. Magyar, **G. Bencsik**, Z. Németh, K. Nagy, A. Magrez, L. Forró, G. Váró, K. Hernádi, L. Nagy:
   Photosynthetic reaction center protein in nanostructures
   Phys. Status Solidi B, 248 (2011) *2700-2703*
   IF_{2010}=1.349

Σ_{IF}=19.751 **Number of independent citations: 21**

Conference lectures and posters

1. C. Visy, E. Pintér, P. Makra, Z. A. Fekete, C. Janáky, **G. Bencsik**, Á. Patzkó:
   Conducting Polymer Based Transition Metal Containing Composites
   International Workshop on the Electrochemistry of Electroactive Materials (WEEM),
   Saint-Petersburg, 2006 *Oral presentation*

2. C. Visy, I. Csízi, C. Janáky, Z. Fekete, **G. Bencsik**, Á. Patzkó, E. Pintér:
   Nanoscale composites of conducting polymers: characterization and possible applications
   The International Conference on Science and Technology of Synthetic Metals (ICSM),
   Dublin, 2006 *Oral presentation*

3. C. Visy, C. Janáky, **G. Bencsik**:
   Conducting polymer based nanocomposites: characterization and possible applications
   Nanotech Northern Europe,
   Helsinki, 2007 *Poster*

4. E. Kriván**,** C. Janáky, **G. Bencsik**, C. Visy:
   Characterization and application possibilities of conducting polymer composites
   211th ECS Meeting,
   Chicago, Illinois, 2007 *Oral presentation*

5. **G. Bencsik**, C. Visy:
   Conducting polymer/iron-oxalate composites: Synthesis and characterization
   European Summer School, Magnetic nanoparticles, composite materials and optical applications,
   St. Étienne, 2007 *Poster*

6. C. Visy, E. Kriván, C. Janáky, **G. Bencsik**:
   Synthesis and characterization of iron group element compound containing conducting polymer composites
   58th ISE Meeting,
   Banff, 2007 *Oral presentation*

7. **G. Bencsik**, C. Visy:
   Vezető polimer/vas-oxalát kompozitok kémiai és elektrokémiai előállítása, jellemzése
   XXX. Kémiai Előadói Napok,
   Szeged, 2007 *Oral presentation*

8. C. Janáky, **G. Bencsik**, E. Peintler-Kriván, C. Visy:
   Elektromosan vezető összetett anyagok, kombinált tulajdonságok, új lehetőségek
   Ipari Kapcsolatok Napja,
   Szeged, 2007 *Poster*

9. C. Visy, E. Kriván**,** C. Janáky, **G. Bencsik**:
   Conducting polymer composites as new electrodes for clean energy technologies
   6th Spring Meeting of ISE,
   Foz do Iguaçu, 2008 *Oral presentation*

10. **G. Bencsik**, C. Visy:
Photo-electrochemical Properties of Polypyrrole/Iron Oxalate Composite
1st International Conference on Functional Nanocoatings,
Budapest, 2008 *Poster*

11. C. Visy, E. Kriván, C. Janáky, **G. Bencsik**:
Conducting Polymer Based Multifunctional Nanocoatings
1st International Conference on Functional Nanocoatings,
Budapest, 2008 *Oral presentation*

12. C. Visy, E. Kriván, C. Janáky, **G. Bencsik**:
Conducting polymer based multifunctional composites
CONPOEX EU6 Meeting,
Borovets, 2008 *Oral presentation*

13. **G. Bencsik**, C.Visy:
Photo-electrochemistry of iron oxalate containing conducting polymers
59th ISE Meeting,
Seville, 2008 *Poster*

14. C. Visy, **G. Bencsik**, C. Janáky, E. Kriván:
Conducting polymer-based composite catalysts for photo-, magneto- and bio-electrochemistry
59th ISE Meeting,
Seville, 2008 *Oral presentation*

15. **G. Bencsik**, C.Visy:
Synthesis and characterisation of photo-active conducting polymer/iron oxalate composites
Szeged International Workshop on Advances in Nanoscience (SIWAN),
Szeged, 2008 *Poster*

16. **G. Bencsik,** C. Janáky, C. Visy:
Electrochemically synthesized conducting polymer based composite thin layer electrodes with photocatalytic and magnetic behaviour
VI. International Workshop on Electrodeposited Nanostructures (EDNANO),
Berndorf, 2008 *Oral presentation*

17. C. Janáky, **G. Bencsik**, E. Kriván, Á. Patzkó, E. Pintér, C. Visy:
Conducting polymer based multifunctional nanocomposites
Zing Nanomaterials,
Playa del Carmen, 2008 *Oral presentation*

18. C. Janáky, **G. Bencsik**, E. Kriván, Á. Patzkó, E. Pintér, C. Visy:
Multifunctional nanocomposites of conducting polymers
First International Conference on Multifunctional, Hybrid and Nanomaterials,
Tours, 2009 *Poster*

19. **G. Bencsik**, Z. Lukács, C. Visy
A ppm-level oxygen sensor, based on the photo-electrochemical behaviour of iron oxalate containing conducting polymers
7th Spring Meeting of ISE,
Szczyrk, 2009 *Poster*

20. 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 (WEEM),
Szczyrk, 2009 *Oral presentation*

21. **G. Bencsik**, Z. Lukács, C. Visy:
Photo-electrochemical Oxygen Sensor Based on a Poly(3,4-Ethylenedioxythiophene)/Iron Oxalate Hybrid Electrode
216th ECS Meeting,
Vienna, 2009 *Poster*

22. **G. Bencsik**, Z. Lukács, C. Visy:
Photo-electrocatalytic reduction of oxygen at a poly(3,4-ethylenedioxitiophene)/iron oxalate thin layer electrode
2nd International Conference on Functional Nanocoatings,
Dresden, 2010 *Poster*

23. K. Hajdu, T. Szabó, M. Magyar, **G. Bencsik**, Z. Németh, K. Nagy, A. Magrez, L. Forró, G. Váró, K. Hernádi, L. Nagy:
Photosynthetic reaction center protein in nanostructures
25th International Winterschool on Electronic Properties of Novel Materials (IWEPNM),
Kirchberg, 2011 *Poster*

24. 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 ISE,
Turku, 2011 *Poster*

25. T. Szabó, **G. Bencsik**, G. Kozák, C. Visy, Z. Gingl, K. Hernádi, K. Nagy, G. Váró, L. Nagy:
Interaction between photosynthetic reaction centers and ITO
8th European Biophysics Congress,
Budapest, 2011 *Poster*