Supercapacitors and catalyst layers based on conducting polymers

Keywords: Supercapacitors, catalyst layers, conducting polymers, fuel cells, oxygen reduction

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According to our original research plan we have continued the research on the composite and hydrid systems as follows: phthalocyanine, Fe-phthalocyanine, Pd-phthalocyanine, poly (copper phthalocyanine) with multi-walled carbon nanotubes, electronically conducting polymers and proton conducting Nafion.

The layer deposition and the ion exchange processes of these systems have been investigated by electrochemical quartz crystal nanobalance (EQCN), their electrocatalytic activity in respect of the oxygen reduction was studied by rotating ring-disc electrode at different conditions. Successful experiments have been carried out on the electropolymerization of indole and several amino derivatives of indole. The conditions of the electropolymerization have been optimized, and the resulting polymers have been characterized by EQCN, UV-Vis spectroelectrochemistry, impedance spectroscopy (EIS), dynamic EIS, SEM and FTIR. A novel technique, the combined EQCN-spectroelectrochemistry by using ITO covered quartz crystals has been developed. We have been cooperating with a research group of the Research Institute of Science of HAS on polyaniline interpenetrated amphiphilic conetworks which are also intented to test as supercapacitors. We have tried a bioelectrocatalytic system based on a yeast-modified platinum electrode, and it was tested with $NADP^+$ redox transformations. The results of these fundamental studies have been published in scientific journals and presented at international conferences by the PI and his students, respectively.

Publications in journals:

1. A. Kriston, B.B. Berkes, P. Simon, G. Inzelt, K. Dobos, A. Nemes: Unusual surface mass changes in the course of the oxygen reduction reaction on platinum and their explanation by using a kinetic model. J. Solid State Electrochemistry 16 (4): 1723-1732 (2012). IF: 2,279

2. B.B. Berkes, G. Inzelt, W. Schuhmann, A.S. Bondarenko: Influence of Cs^+ and Na^+ on Specific Adsorption of *OH, *O and *H at Platinum in Acidic Sulfuric Media. J. Physical Chemistry C 116 (20): 10995-11003 (2012). IF: 4,814

3. Balázs B. Berkes, György Inzelt, Elemér Vass: Electrochemical nanogravimetric study of the adsorption of 4-aminoindole and the surface layer formed by electrooxidation in aqueous acid media. Electrochimica Acta 96: 51-60 (2013). IF: 4.086

4. Balázs B. Berkes, Ákos Nemes, Colin E. Moore, Franciska Szabó, György Inzelt: Electrochemical nanogravimetric study of the electropolymerization of 6-aminoindole and the redox transformations of the polymer formed in aqueous media. J. Solid State Electrochemistry 17 (12): 3067–3074 (2013). IF: 2.234

5. Ákos Nemes, Colin E. Moore, György Inzelt: Electrochemical and nanogravimetric studies of palladium phthalocyanine microcrystals. J. Serbian Chemical Soc. 78 (12) 2017-2037 (2013) IF: 0,912

6. Balázs B. Berkes, György Inzelt: Generation and electrochemical nanogravimetric response of the third anodic hydrogen peak on a platinum electrode in sulfuric acid media. J. Solid State Electrochemistry 18 (5): 1239-1249 (2014). IF: 2,234

7. Balázs B. Berkes, György Inzelt: Electrochemical nanogravimetric studies on the electropolymerization of indole and on polyindole. Electrochimica Acta 122 (SI): 11-15 (2014). IF: 4,086

8. Balázs B. Berkes, Soma Vesztergom, György Inzelt: Combination of nanogravimetry and visible spectroscopy: A tool for the better understanding of electrochemical processes. J. Electroanalytical Chemistry 719: 41–46 (2014). IF: 2,871

9. G. Inzelt, A. Róka: Cyclic voltammetric and nanogravimetric studies of $NADP^+$ redox transformations on a yeast-modified platinum electrode. Electrochemistry Communications, 45: 9-12 (2014). IF: 4.287

10. Balázs Broda, György Inzelt: Preparation and characterization of poly(5-aminoindole) by using electrochemical quartz crystal nanobalance technique. Acta Chimica Slovenia 61 (2): 357-365 (2014). IF: 0,81

11. Ákos Nemes, György Inzelt: Electrochemical and nanogravimetric studies of iron phthalocyanine microparticles immobilized on gold in acidic and neutral media. J. Solid State Electrochemistry 18 (12): 3327-3337 (2014). IF: 2,234

12. Colin E. Moore, György Inzelt: Electrochemical nanogravimetric study on the sorption processes occurring in multiwalled carbon nanotube layers immobilized on a gold surface. J. Solid State Electrochemistry 19 (1): 45–56 (2015). IF: 2,234

13. Katalin Borsos, György Inzelt: Electrochemical and nanogravimetric studies of poly(copper phthalocyanine) microparticles immobilized on gold in aqueous solutions. J. Solid State Electrochemistry 19 (9): 2565–2577 (2015). IF: 2,234

14. Balázs B. Berkes, Aliaksandr S. Bandarenka, György Inzelt: Electropolymerization: Further Insight into the Formation of Conducting Polyindole Thin Films. J Phys. Chem. C – Nanomaterials and Interfaces 119 (4): 1996-2003 (2015). IF: 4.814

15. György Inzelt, Katalin Borsos: Replacement of the glass electrode by graphite at acid-base potentiometric titrations. Studia UBB Chemia LX (3): 23-30 (2015).

16. Katalin Borsos, György Inzelt: A new electrode for acid-base titration based on poly(copper phthalocyanine). J. of Solid State Electrochemistry 20 (4): 1215–1222 (2016). IF: 2,23

Presentations at different conferences

K1. G. Inzelt: Recent advances in the development of efficient polymer electrolyte fuel cells. 3rd Regional Symposium on Electrochemistry South-East Europe (RSE-SEE) Bucharest, Romania, 2012. Key-note lecture.

K2. György Inzelt, Zoran Mandić, Marijana Kraljić Roković, Suzana Sopčić: Study on RuO_2 and RuO_2/polyaniline composite electrodes. 7th WEEM - International Workshop on the Electrochemistry of Electroactive Materials, 2012. Szeged – Hódmezővásárhely, Hungary.

K3. Balázs B. Berkes, György Inzelt: Study of Formation and Redox Behaviour of Polyindoles by Electrochemical Quartz Crystal Microbalance. 7th WEEM - International Workshop on the Electrochemistry of Electroactive Materials, 2012. Szeged – Hódmezővásárhely, Hungary.

K4. György Inzelt, Balázs B. Berkes: Nanogravimetric Study on the Adsorption and Electropolymerization of Indole and Indole Derivatives and on the Redox Behavior of Polyindoles. 63rd Annual Meeting of ISE, Prague, Czech Republic, 2012.

K5. Ákos Nemes, Ákos Kriston, György Inzelt: Analysis of the porosity, agglomerates' size and exchange current density of a PEMFC by using a two-dimensional model. 63rd Annual Meeting of ISE, Prague, Czech Republic, 2012.

K6. B.B. Berkes, G. Inzelt: Adsorption and electropolymerization of indole and indole derivatives. 3rd Regional Symposium on Electrochemistry South-East Europe (RSE-SEE), Bucharest, Romania, 2012.

K7. Gábor Érsek, Ákos Szabó, György Inzelt, Béla Iván: Synthesis and Characterisation of Polyaniline Interpenetrating in Amphiphilic Conetworks. IV. Career in Polymers, Prague, Czech Republic, 2012.

K8. G. Inzelt, B.B. Berkes: Generation and Electrochemical Nanogravimetric Response of the Third Anodic Hydrogen Peak on a Platinum Electrode in Sulfuric Acid Media. Fourth Regional Symposium on Electrochemistry, South-East Europe, Ljubljana, Slovenia, 2013.

K8. B.B. Berkes, S. Vesztergom, G. Inzelt: Combination of Nanogravimetry and Visible Spectroscopy: a Tool for the Better Understanding of Electrochemical Processes. Fourth Regional Symposium on Electrochemistry, South-East Europe, Ljubljana, Slovenia, 2013.

K9. G. Inzelt, B.B. Berkes: Preparation and characterization of poly(aminoindoles) by using electrochemical quartz crystal nanobalance. 65rd Annual Meeting of ISE, Lausanne, Switzerland, 2014.

K10. G. Inzelt, K. Borsos: Electrochemical and nanogravimetric studies of poly(copper phthalocyanine) microparticles immobilized on gold in aqueous solutions. The 8th WEEM-International Workshop on the Electrochemistry of Electroactive Materials, Bad Herrenalb, Germany, 2015.

K11. G. Inzelt: Electronanogravimetric studies of poly(copper phthalocyanine). 65rd Annual Meeting of ISE, Hague, The Netherlands, 2016.

B. Broda won the 1st prize of the student competition in chemistry (TDK) of the Eötvös L. University and 3rd Prize at the OTDK conference. In the period in question F. Szabó, B. Broda (BSc), C. E. Moore (from U.S.A.), K. Borsos (MSc) and Á. Nemes (PhD) worked in the project. PhD students, who were involved in the first phase of this research, B.B. Berkes (PhD 2013) now is a researcher of the University of Karlsruhe, and Ákos Kriston (PhD 2012) works in the Netherlands at an EU Research Institute for electrochemical power sources. In the supercapacitor project we co-operated with the research group led by Zoran Mandic at the Univ. of Zagreb, Croatia. We have also collaborated with Vladimir Mirsky at the Brandenburg Technical University within the framework of the POLYCON project of Danube States R&D network; Á. Nemes carried out conductivity measurements on phthalocyanine surface layers in Senftenberg. Dynamic impedance measurements were carried out at University of Bochum with co-operation of A. Bandarenka.

The utilization of the metal-phthalocyanine composites are in progress concerning oxygen reduction reaction in hydrogen-oxygen fuel cells. It has become evident that expensive platinum can be replaced by these cheap systems. It has been proven that the composites based on conducting polymers and carbon nanotubes can be used as effective and stable systems in supercapacitors.

Selected illustrations of the results

Polyindoles [3, 7, 10, 14, K3, K4, K6, K9]

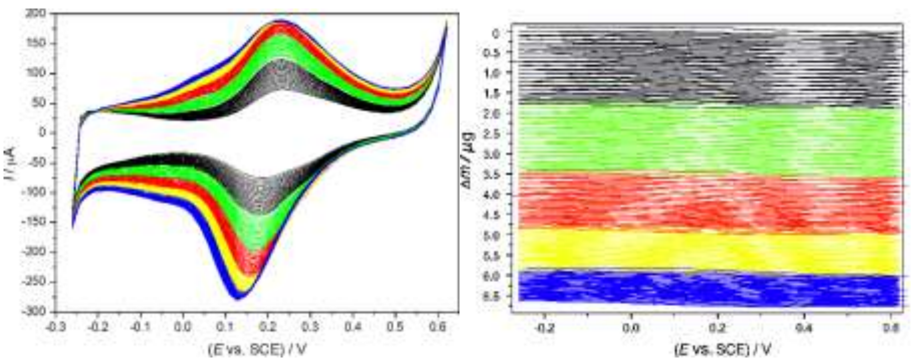

Fig. 1. The cyclic voltammetric curves and the corresponding frequency changes obtained during the electropolymerization of 5-aminoindole at Pt in contact with a solution containing 0.5 mol dm^{-3} H_2SO_4 solution and 5 mmol dm^{-3} 5-aminoindole. v = 50 mV·s^{-1}. Five consecutive runs involving 20 cycles each were applied [10].

The construction of the cell and instrumentation for combined EQCN-spectroelectrochemistry measurements by using ITO covered quartz crystals [8, K8]

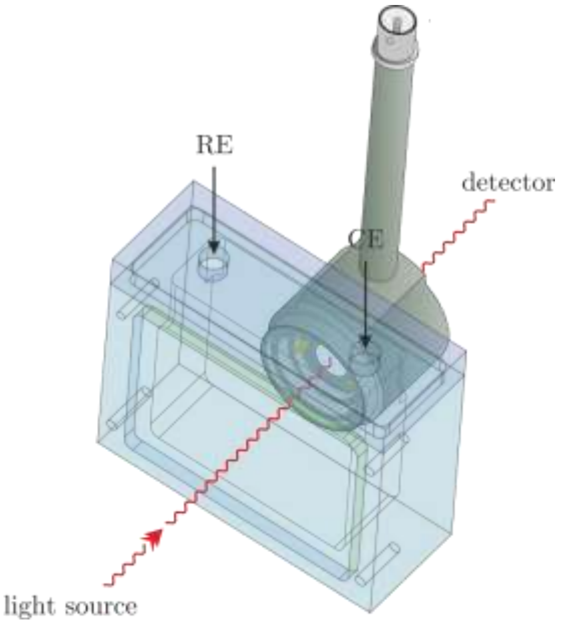

Fig. 2. The measuring cell with the crystal holder firmly attached to its rear. The transparent ITO covered quartz crystal serves as working electrode in the setup [8, K8].

Polyaniline–multiwalled carbon nanotube composite [12]

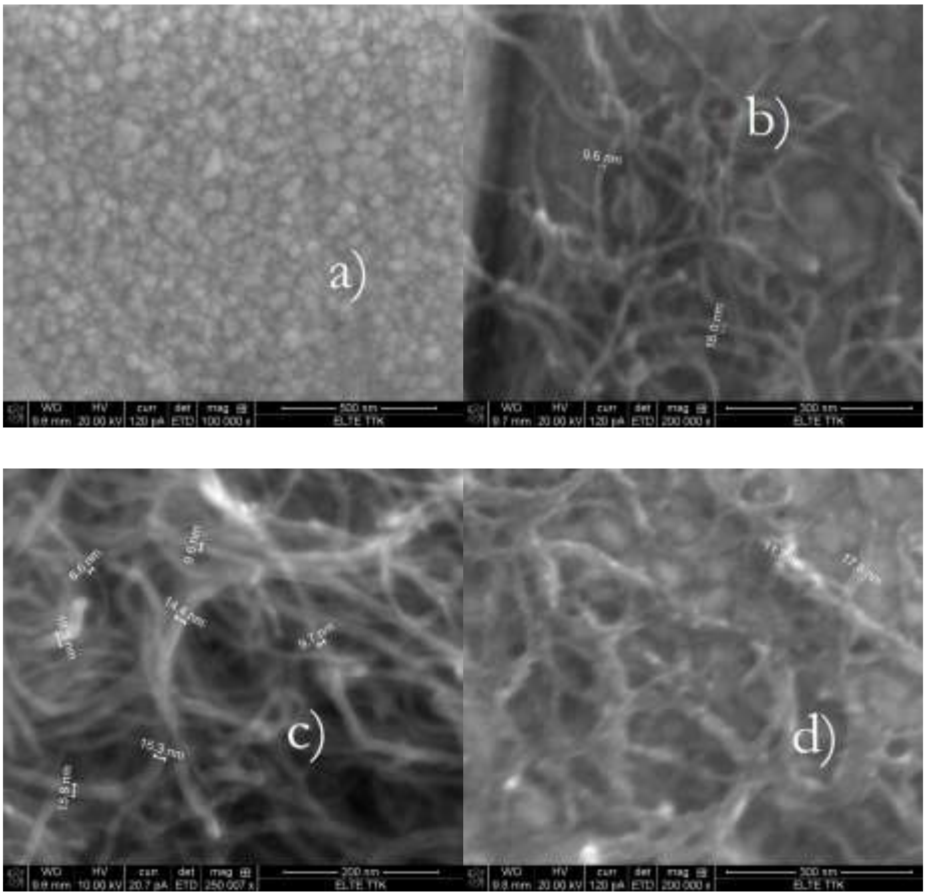

Fig. 3. SEM pictures of the EQCN gold electrode (a), the gold electrode covered with MWCNT (b), the Au-MWCNT electrode after aniline adsorption (c), Au-MWCNT-polyaniline [12].

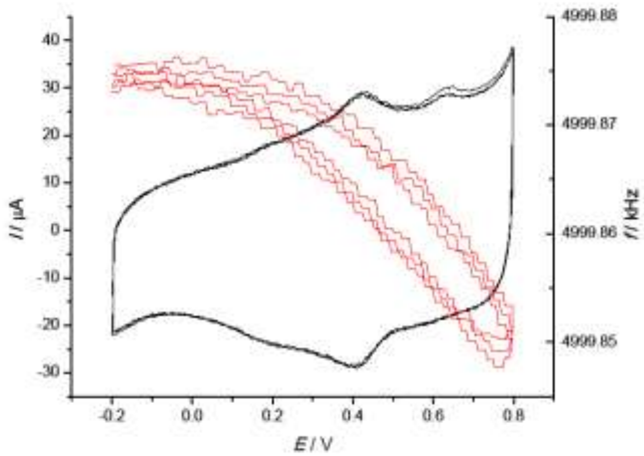

Fig. 4. The cyclic voltammograms and the simultaneously obtained EQCN frequency responses during cycling of an Au│MWCT-polyaniline electrode in in 0.5 mol dm^{-3} H_2SO_4 solution. Scan rate: 50 mV s^{-1}[12].

Metal-phthalocyanines [5, 11, 13, 15, 16, K10, K11]

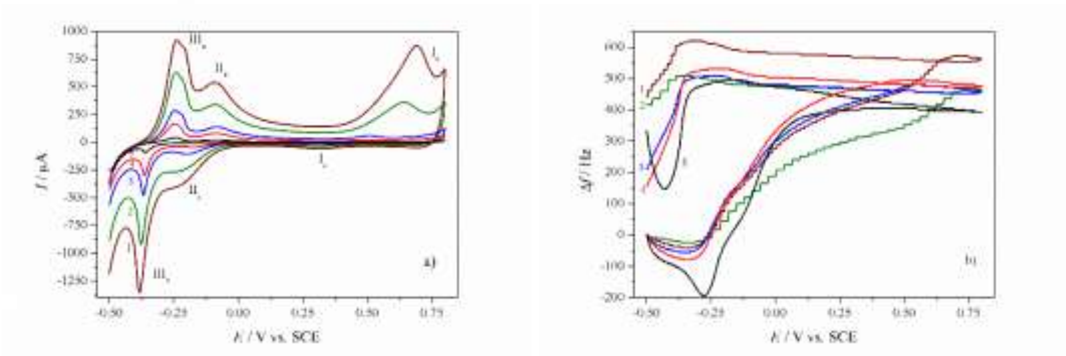

Fig. 5. Scan rate dependence of the cyclic voltammetric (a) and the simultaneously obtained EQCN frequency responses (b) for an Au│FePc electrode. Electrolyte: 0.5 mol dm^{-3} sulfuric acid. Scan rates are: 100 (1), 50 (2), 20 (3), 10 (4), and 2 mV s^{-1} (5) [11].

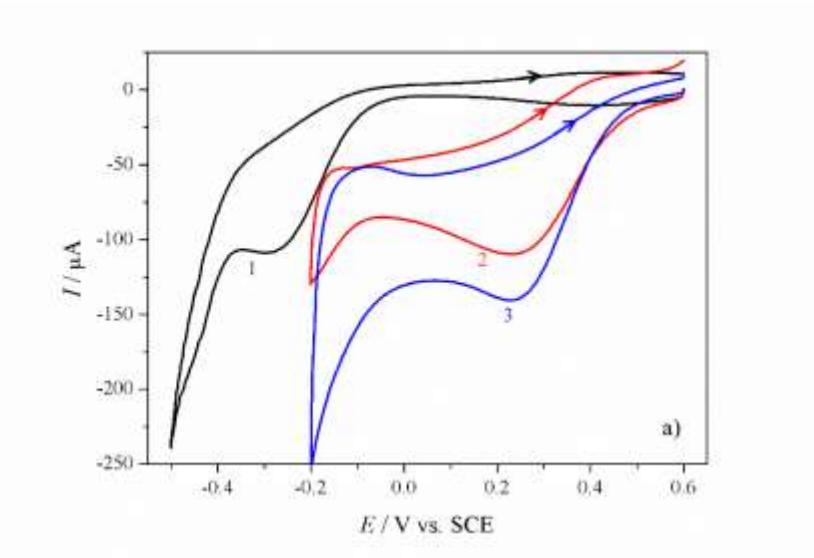

Fig. 6. Cyclic voltammetric responses for an Au (1), an Au│FePc (2) and a Pt (3) electrode in the presence of oxygen. Electrolyte: 0.5 mol dm^{-3} H_2SO_4. Scan rate: 50 mV s^{-1} [11].

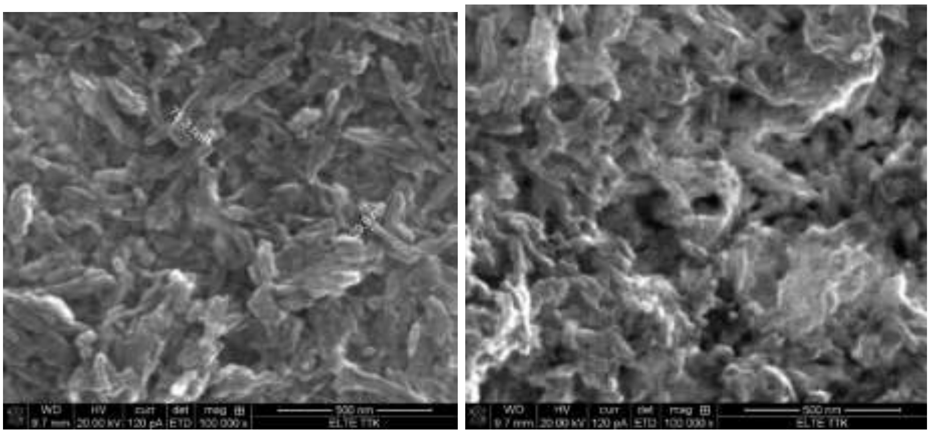

Fig. 7. SEM pictures of the EQCN gold electrode covered with Fe-phthalocyanine microparticles a) freshly prepared layer, b) after cyclic voltammetric investigations [11].

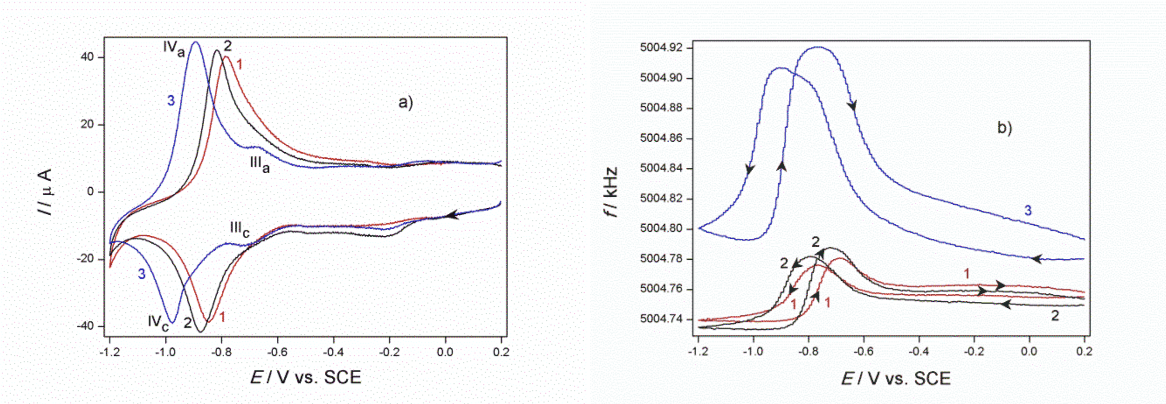

Fig. 8. Cyclic voltammetric (a) and the simultaneously obtained EQCN frequency (b) responses for an Au│poly(CuPc) electrode in contact with electrolyte solutions of 0.5 mol dm^{-3} KCl + suitable concentration of KOH for adjusting pH values. pH values are: 11.0 (1), 11.4 (2), and 12.38 (3), respectively. Scan rate: 20 mV s^{-1} [13].

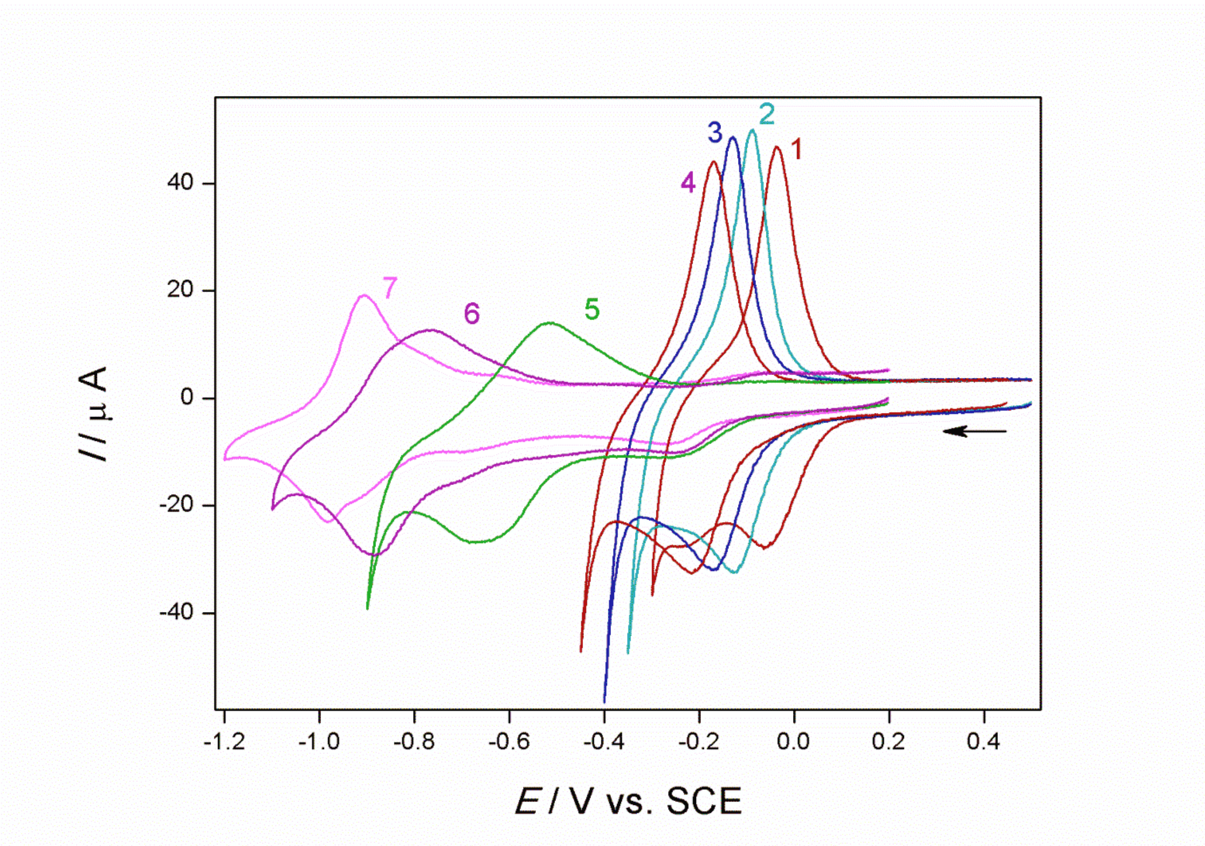

Fig. 9. Cyclic voltammetric responses of an Au│poly(CuPc) electrode in contact with sulphate electrolytes (H_2SO_4 or H_2SO_4 + Na_2SO_4 or Na_2SO_4 + NaOH) of different pH values: 0.3 (1),

1.18 (2), 2.17 (3) 2.57, (4), 7.8 (5), 11.1 (6) and 12.7 (7). Scan rate: 10 mV s^{-1}. The total concentration of the sulphate ions was kept practically constant at 0.5 mol dm^{-3} [16].

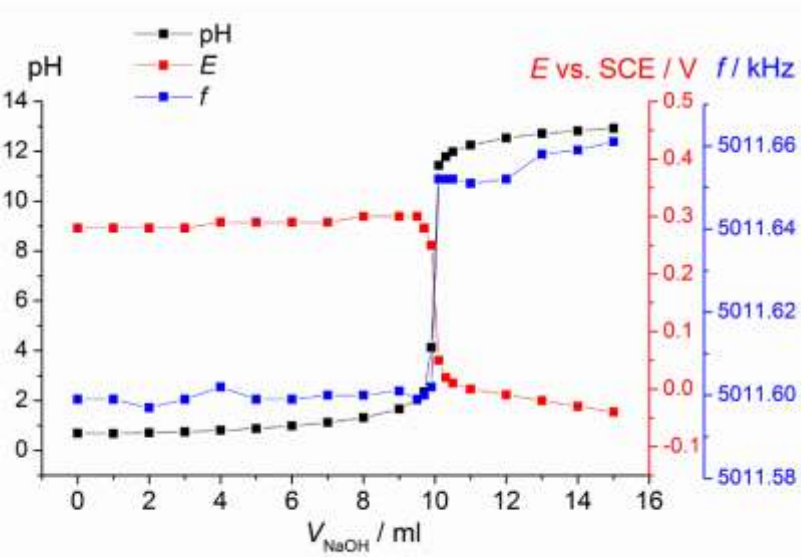

Fig. 10. Potentiometric titration curves obtained for the titration of 100 cm^3 0.1 mol dm^{-3} $HClO_4$ with 1 mol dm^{-3} NaOH at an Au–EQCN│poly(Cu-phthalocyanine) (potential curve – red and EQCN frequency curve – blue) and at a glass electrode (pH curve – black), respectively. *V* is the volume of the 1 mol dm^{-3} NaOH titrant added [16].

For the detailed description and explanation of the results please consult the papers indicated.