

Characterization of the Capacitance of a Rotating Ring–Disk Electrode

Noémi Kovács¹, Mária Ujvári¹, Győző G. Láng¹, Peter Broekmann²
and Soma Vesztergom^{1,2,*}

¹ Department of Physical Chemistry, Eötvös Loránd University

Pázmány Péter sétány 1/A, H-1117 Budapest, Hungary

² Department of Chemistry and Biochemistry, University of Bern

Freistraße 3, CH-3012 Bern, Switzerland

» The use of rotating ring–disk electrodes as generator–collector systems has so far been limited to the detection of faradaic currents at the ring. As opposed to other generator–collector configurations, non-faradaic detection has not yet been carried out with rotating ring–disk electrodes. In this study, ac-perturbation based detection (measurement of the ring impedance) is introduced. By taking a conducting polymer-modified disk electrode in combination with a bare gold ring as a model system, it is shown that the measured ring capacitance correlates with the polarization of the polymer film, most probably due to the effect of counter-ion exchange. The method of calculating the ring capacitance based on a small-signal sinusoid perturbation is described in the text, and the most important instrumental limitations are identified.

Keywords generator–collector systems, capacitance measurements, sine-wave correlation, poly(3,4-ethylenedioxythiophene)

INTRODUCTION

Four-electrode configurations containing two working, a single reference and a single counter electrode in the same electrochemical cell have been routinely used in electrochemistry over the past 50 years. A typical example is the rotating ring–disk electrode introduced by Frumkin *et al.* in 1959 [1]. The rotating ring–disk electrode was historically the first generator–collector system [2] used for studying the intermediates or products formed in electrode processes. The operating principle (Figure 1) of rotating ring–disk electrodes is the following: when on the generator (disk) electrode some electroactive species are formed as a result of an electrode reaction, these products can be involved in another reaction at the collector (ring), and can thus be detected [3]. When using a rotating ring–disk electrode, the transfer of species from one electrode to another occurs by convection due to the rotation of the tip.

* Address correspondence to Soma Vesztergom. Permanent address: Department of Physical Chemistry, Eötvös Loránd University, H-1117 Budapest Pázmány Péter sétány 1/A, Hungary.
E-mail: vesztergom@chem.elte.hu. Phone: +36204612429.

Although most rotating ring–disk electrode experiments are based on the measurement of steady-state currents, there is a growing interest in the application of transient techniques as well. For instance, impedance measurements on rotating ring–disk electrodes have been reported in the literature [34,35]. In these studies a sinusoid potential perturbation was applied to the generator (disk) electrode at a number of discrete frequencies. It was also shown (see e.g. [4–9]) that the simultaneous potentiodynamic perturbation of the generator and collector electrodes can result in a considerable enhancement of the detection sensitivity.

The application of transient techniques might also be expedient in the case of other generator-collector systems, such as scanning electrochemical microscopy, especially when accurate temporal resolution is to be achieved [10–13]. The simultaneous application of potentiodynamic perturbation to the generator and collector electrodes in such systems can, however, not only yield an increased detection sensitivity (when a charge transfer reaction takes place on both working electrodes), but may also broaden the application range of generator-collector systems [4–9]. Let us consider, for example, the case when an electrochemical reaction taking place on the generator yields only products which are neither reducible nor oxidable on the collector in a reasonable potential range. Such products, under steady-state conditions, should not be detectable as they cannot be involved in any charge transfer reaction. This does not mean, however, that the species may not interact with the collector electrode at all: the species can, for example, modify the structure of the electrical double-layer, which can occur by means of specific adsorption, by changing the concentrations in the diffuse double layer, etc. Such effects are, in principle, detectable by measuring the *ac* capacitance of the collector electrode. Capacitance measurements are traditionally carried out by a small-amplitude sinusoid potential perturbation of the electrode under study, and techniques based on the same *modus operandi* have often been applied in scanning electrochemical microscopy (see [14] and the references cited therein).

Yet we are unaware of any similar attempts in a rotating ring–disk electrode context, and with the present paper we aim to fill this gap. As we mentioned above, capacitance (i.e., impedance) measurements on rotating ring–disk electrodes have already been described in the literature, and in these studies the electrode made subject to the sinusoid potential perturbation was the generator (disk) electrode. As opposed to this concept, the technique we introduce here is based on a sine-wave perturbation of the collector (ring) electrode, which can be considered a novel approach to the use of rotating ring–disk systems.

The System under Study: The Electrochemical Charging/Discharging and Oxidative Degradation of Poly(3,4-ethylenedioxythiophene)

Poly(3,4-ethylenedioxythiophene) is a conducting polymer characterized by outstanding chemical stability [17]. Previous studies [18–20] have shown that poly(3,4-ethylenedioxythiophene) is electroactive in aqueous solutions, it is highly insoluble in almost any solvent, exhibits high conductivity (ca. 300 S cm^{-1}), changes its colour depending on the applied potential, and is transparent in the oxidized state.

The recent years have witnessed a great progress of research on electronic and electrochemical devices based on this polymer and its derivatives. Nowadays light emitting diodes, organic thin film transistors, solar cells, memory devices, ion-selective electrodes, microelectrode arrays, fuel cells, actuators, etc. often rely on conductive polymers [21–23]. Monitoring the degradation of polymer layers is therefore of great importance, *e.g.*, for life-time indications on these devices.

The electrochemical and mechanical properties of thin poly(3,4-ethylenedioxythiophene) films deposited on gold have already been investigated in aqueous sulfuric acid solutions [24–27]. It was shown that a sufficiently positive electrode potential ($E > 800 \text{ mV}$ vs. saturate calomel electrode) may lead to the overoxidation of the polymer. The structural changes that accompany this process result in a distorted electrochemical and mechanical behaviour, as observed by surface stress measurements, cyclic voltammetry, electrochemical impedance spectroscopy, and by scanning electron microscopy [24–27]. Apart from the morphological changes, overoxidation can also affect the charge structure of the polymer film. Poly(3,4-ethylenedioxythiophene) is a redox conductive polymer that incorporates counter-ions from the surrounding electrolyte solution in order to maintain electroneutrality, thus its charging processes may involve a detectable counter-ion flux leaving the film [28–29].

For this reason, the Au | poly(3,4-ethylenedioxythiophene) | 0.5 M H_2SO_4 electrode seems to be a promising target for studying the counter-ion flux accompanying the charging and discharging, as well as the degradation of the polymer film. Similar studies have already been carried out by the use of rotating ring–disk electrodes [30–32], but these were confined to target systems where electrochemically oxidable (usually halide) counter-ions were involved in the flux, providing means for faradaic detection. Sulphate, the most predominant counter-ion in the system studied here, is not detectable by such means; yet it may be specifically adsorbed on a bare gold ring [33] at well-chosen potentials, causing measurable changes of the interfacial capacitance (Figure 2).

EXPERIMENTAL

The measurements were carried out with a gold disk / gold ring rotating ring–disk electrode (PINE AFE7R8AuAu), the disk of which was covered with poly(3,4-ethylenedioxythiophene) under galvanostatic conditions. All the glass parts of the cell were thoroughly cleaned by Caro's acid (a 3:1 mixture of concentrated sulphuric acid and 30% hydrogen peroxide solution), a subsequent rinsing with MilliQ water and by vapour steam cleaning.

Prior to the polymer deposition, the rotating ring–disk electrode was mirror-polished first by the use of SiC paper, then with a diamond suspension (finest grain size: 0.1 μm). After polishing, the electrode surfaces were rinsed with MilliQ water and cleaned by ultrasonication.

Deposition took place in a standard three-electrode cell at room temperature under an inert gas (Ar) blanket. The depositing solution contained 0.01 mol dm⁻³ of the monomer (3,4-ethylenedioxythiophene), analytical grade, Aldrich) and 0.1 mol dm⁻³ of Na₂SO₄ (analytical grade, Fluka). Only the disk served as a substrate for the deposition, the ring electrode was covered by a tight Teflon cap, preventing it from any contact with the monomer solution. A Pt wire was used as a counter electrode, and a KCl saturated calomel electrode was used as a reference. The galvanostatic deposition lasted 30 minutes at a current density of 200 $\mu\text{A cm}^{-2}$. A commercial potentiostat (AutoLab PGSTAT 20) was used for this purpose. Before the actual measurements had taken place, the electrode tip was held in MilliQ water for a few days in order to remove any residuals of the monomer.

The measurements presented in the paper were carried out in a 0.1 mol dm⁻³ H₂SO₄ solution (analytical grade, Merck). The solution was purged by Ar and the measurements took place in an Ar atmosphere. A gold sheet with large surface area was used as a counter electrode, and an NaCl-saturated calomel electrode was applied as a reference. The reference electrode compartment was separated from the rest of the cell by a Luggin probe.

For the measurements described here, a home-made measuring system [4] was used. This system relies on the state-of-the-art data acquisition devices of National Instruments (PCI-4461 and PCI-6014 boards), and it can be used in combination with several bi-potentiostat models. The measuring system is controlled by a software written in the National Instruments LabVIEW development environment [4], providing simple means for signal acquisition and on-line data processing.

From a hardware point of view, the most important features of the measuring system are the high data acquisition and sample generation rates (at least 80 kHz and 200 kHz, respectively) and the high resolution (24 bit @ ± 10 V) of the waveform generating channels [15–16]. These parameters are crucial for the purpose of accurate double-layer investigations. For the capacitance studies, the measuring system was equipped with a PINE Model "AFCBP1" bi-potentiostat.

METHODS

The operating principle of the applied measurement method is that while the disk electrode potential is arbitrarily controlled, a small-signal sinusoid voltage perturbation is applied to the ring. Determining the capacitance of the ring electrode (C_{ring}) is in this case possible by a synchronized sampling of the ring current and potential. Both of these are sinusoid signals, and by determining the ratio of their amplitudes and the phase shift between them, the impedance (and, subsequently, the capacitance) of the electrode can be calculated. Probably the most straightforward way of carrying out these calculations is the application of sine-wave correlation [36].

Let us consider the function $y(t)$ as an example. Let $y(t)$ be a sinusoid with y_0 amplitude, φ phase and ω angular frequency: then $y(t)$ may be represented as a complex number (denoted here as \tilde{y}). The real and imaginary parts of this number can be calculated by correlating $y(t)$ with a sine and a cosine function (respectively) of the same frequency:

$$\text{Re } \tilde{y} = \int_0^T y(t) \sin(\omega t) dt = \frac{y_0 \cos \varphi}{2} \quad (1)$$

and

$$\text{Im } \tilde{y} = \int_0^T y(t) \cos(\omega t) dt = \frac{y_0 \sin \varphi}{2}, \quad (2)$$

where $T = 2\pi / \omega$ is the period (reciprocal frequency) of the $y(t)$ sinusoid. Since in practice only sampled values of the $y(t)$ function are known, the above integrals are to be replaced by summation. If the applied sampling rate (f_s) is high enough, this is possible using the formulæ

$$\text{Re } \tilde{y} = \frac{1}{n} \sum_{k=1}^n y_k \sin \frac{k\omega}{f_s} \quad (3)$$

and

$$\text{Im } \tilde{y} = \frac{1}{n} \sum_{k=1}^n y_k \cos \frac{k\omega}{f_s}, \quad (4)$$

provided that the upper limit of the summation (n) is chosen so that n / f_s is an integer multiple of the period T . In practice, the more periods we make subject to the correlation, the more accurate results we get — our possibilities are however limited by the loss of time-resolution.

The above-described calculations may simply be implemented in LabVIEW. By applying this algorithm to the measured arrays of ring potentials and currents, the complex quantities \tilde{E}_{ring} and \tilde{I}_{ring} may be determined, and the impedance of the ring electrode can be calculated as

$$\tilde{Z}_{\text{ring}} = \frac{\tilde{E}_{\text{ring}}}{\tilde{I}_{\text{ring}}}. \quad (5)$$

If we assume that the “ring electrode” can be modelled by an equivalent circuit analogue consisting of a resistor and a capacitor connected in series, its capacitance can be defined as

$$C_{\text{ring}} = -\frac{1}{\omega \text{Im} \tilde{Z}_{\text{ring}}}. \quad (6)$$

Based on the amplitude and phase values, which can be obtained from Equations (1)–(2), it is also possible to “restore” the measured current and voltage signals — this can provide a visual feed-back on the quality of the measurements (Figure 3).

RESULTS AND DISCUSSION

Instrumental Limitations

Figure 3 presents sampled and (by the use of the above-described algorithm) restored potential and current signals measured at the ring of the rotating ring–disk electrode. The amplitude of the potential perturbation was 5 mV. The following comments are due with respect to these results:

- i.) *Increased noise level of the potential signals.* If we compare the measured potentials (upper row) with the sampled current (bottom row) in Figure 3, it is apparent that the former ones exhibit a lower signal-to-noise ratio. The explanation of this is that the PINE Model “AFCBP1” bi-potentiostat used for these measurements is equipped with a constant gain instrumental amplifier measuring the ring potential [37]. This means that the potential signal, having a peak-to-peak amplitude of ~10 mV is measured without amplification (unity gain). On the contrary, the current-to-voltage converters have a settable (and for the measurements appropriately optimized) gain, making the entire voltage swing (± 5 V) available for output. In order to overcome this problem, designing an instrumentation amplifier with settable range for the measurement of the electrode potentials is in progress.
- ii.) *Mains noise.* Especially in the case of lower frequencies it is visible in Figure 3 that the measured current and potential signals are significantly distorted by the presence

of a ~ 50 Hz noise (the mains frequency). The disturbing effect of the mains hum, that is present even if a Faraday cage is used, can be digitally eliminated by a careful selection of the correlation window size (which in this case should be an integer multiple of both the perturbation *and* the mains period, ~ 20 ms).

iii.) *Bandwidth limitations.* The bandwidth of the power amplifier of the PINE Model “AFCBP1” bi-potentiostat is hardware-limited (in order to eliminate mains-originated oscillations). This is shown by the damped electrode potential signals measured at higher frequencies (200 Hz and 533 Hz in Figure 3): in these cases, the potentiostat failed to regulate a 10 mV peak-to-peak sinusoid voltage.

It is obvious from the above considerations that many instrumental limitations have to be dealt with in order to make successful capacitance measurements on the ring of a rotating ring–disk electrode. With the potentiostats available to us, the accessible frequency range is in the low sound-frequency region, < 50 Hz. In this limited range it is still possible, however, to determine ring capacitance changes. As a demonstration, we combine the ring capacitance measurements with two disk polarization programs below.

Square-Wave Perturbation of the Disk

The graphs of Figure 4–6 show the results of an experiment where the ring capacitance was measured in parallel with a symmetric square-wave perturbation of the disk potential, at a rotation rate of 500 min^{-1} .

Prior to these measurements, the ring was “electrochemically polished” by cyclic voltammetry: that is, several consecutive triangular potential waves were applied (between -600 and 1400 mV vs. the NaCl-saturated calomel reference electrode, at a rate of 100 mV s^{-1}) in order to clean the surface from pre-adsorbed contaminants. During this process the disk was held at a constant potential, 600 mV.

For the capacitance measurements, the ring potential was set to 800 mV and a sine-wave perturbation (with 20 Hz frequency and 5 mV amplitude) was applied. In the meantime, a square-wave potential perturbation (between -200 and 600 mV vs. the NaCl-saturated calomel reference electrode, with a period of 40 s and a duty cycle of 50%) was applied to the disk, as shown in Figure 4. The currents measured at the disk in this case could be considered purely charging currents, as shown by Figure 5.

From the sinusoid ring potentials and currents, the ring capacitance was calculated using the algorithm described above. The correlation window size was set to 200 ms (corresponding

to 4 perturbation sine-waves). With respect to the determined ring capacitance (Figure 6), we note the following:

- i.) *Peak-like features.* The peak-like features of Figure 6 are related to an electrical cross-talk between the disk and the ring that occurs due to the shared current routes of these electrodes. This *IR*-drop effect [6] distorts the baseline of the measured sinusoids, which results in ill-determined capacitance values. Thus the peak-like features in Figure 6 can be considered measurement artefacts, as their size and shape depends heavily on the correlation window size applied in the calculations. The intensity of these peaks can be suppressed by choosing smaller window sizes, but this in turn yields an increased noise load on the rest of the curve. (The 200 ms correlation window size applied here presents an optimum from this point of view).
- ii.) *General trend.* The ring capacitance shows a net decrease during the measurements. This could be attributed to the effect of organic molecules (monomers or oligomers), which after leaving the disk electrode can adsorb on the originally clean ring surface. These dielectric species can decrease the ring capacitance either by increasing the double layer thickness, or by decreasing (locally) the relative permittivity within the double layer [38,39]. The role of instrumental drift in the slow decrease of the capacitance curve can be ruled out, as checked by test measurements on a dummy cell.
- iii.) *Sub-segment trends.* The rate of the capacitance changes, although it is always negative, seems to vary in Figure 6 in correlation with the applied disk potential. At more negative disk potentials (–200 mV vs. the NaCl-saturated calomel reference electrode), the ring capacitance decreases heavily; however at more positive disk potentials the decrease becomes much slower. The interpretation of this effect is not at all straightforward, but the two most likely explanations are the following: *a.)* polarizing the disk to more negative potentials causes organic species to leave the film at a much higher extent, which increases the adsorption rate of these species at the ring electrode; and *b.)* at negative potentials, the charge-compensating sulphate ions are leaving the polymer film, get specifically adsorbed on the ring surface, and are thereby causing an increase of C_{ring} .

Both of the above explanations (and also their synergic combination) is possible, but at this stage we do not have enough information to be more specific with respect to this question. Yet we must point out that for these measurements to work, it is necessary to select a high enough set potential for the ring electrode. By choosing a lower potential set-point (e.g., –100 mV instead of 600 mV vs. the NaCl-saturated

calomel reference electrode), no disk-related capacitance changes can be detected. This, we believe, is due to the fact that at these potentials no sulphate ions can be specifically adsorbed on the ring electrode. We must further emphasize that the *rotation* of the ring–disk system also plays an important role in these measurements, as on a stagnant electrode no disk-related capacitance changes can be measured. (This observation supports that the measured effects indicate a chemical interaction, and are not due to an electrical cross-talk between the generator and collector electrodes [6].)

Triangular Perturbation of the Disk. Effects Accompanying the Overoxidation of Poly(3,4-ethylenedioxythiophene)

The graphs of Figure 7 show the results of an experiment where the ring capacitance was measured in parallel with a triangular perturbation of the disk potential. In order to have a relatively clean collector surface, the ring was again “electrochemically polished” prior to the measurements, as it was described before. The ring potential was then set to 600 mV vs. the NaCl-saturated calomel reference electrode, and a sine-wave perturbation (frequency: 20 Hz, amplitude: 5 mV) was applied to it.

In parallel with the ring capacitance determination, several cyclic voltammograms were recorded on the disk electrode. The lower vertex of these CVs was set to -200 mV vs. the NaCl-saturated calomel reference electrode, and the applied sweep-rate was 10 mV s^{-1} . After recording a few potential cycles with the same parameters, the upper vertex potential of the cycles was gradually increased (from 600 to 800, then to 1200 mV, as shown by the green curve in Figure 7). Increasing the upper vertex potential to above 800 mV has triggered strong anodic currents on the disk, indicating the overoxidation and subsequent degradation of poly(3,4-ethylenedioxythiophene). This is visualized by the CVs shown in the insets of Figure 7, as well as by the scanning electron micrographs of Figures 8 and 9 (showing the polymer film prior to and after oxidation, respectively).

The calculated ring capacitance changes are correlated with the applied disk potential. Similarly to the previous case (Figure 4–6, when a square-wave signal was used to control the disk potential) there is a net decrease of the measured ring capacitance. Closer inspection of this curve reveals, however, a certain periodicity: the ring capacitance curve shows local maxima when the disk electrode is negatively polarized. This effect becomes more obvious

after a slight overoxidation of the poly(3,4-ethylenedioxythiophene) film, which can be interpreted as a result of the increasing film surface area and/or the effect of free gold surfaces becoming available due to the degrading polymer film. (See also the scanning electron micrographs in Figures 8–9.)

At sufficiently positive potentials the increased porosity of the film and the free gold surfaces may provide new adsorption sites for the sulphate counter-ions in the electrolyte solution, while at more negative potentials they may release the previously adsorbed sulphate. This may account for the temporary increases of the measured ring capacitance (indicating sulphate flux), as shown in Figure 7.

SUMMARY AND OUTLOOK

The use of rotating ring–disk electrodes as generator-collector systems has so far been limited to the detection of faradaic currents. As opposed to other generator-collector configurations – such as scanning electrochemical microscopy, where *ac* detection methods are commonly applied [14] –, non-faradaic detection has not yet been carried out with rotating ring–disk electrodes. The aim of the present paper was to show that *ac*-perturbation based detection is also possible with rotating ring–disk electrodes: by using a poly(3,4-ethylenedioxythiophene)-modified disk electrode in combination with a bare gold ring, it was shown that the measured ring capacitance changes can be correlated to the polarization of the polymer film. The measured effects are in alignment with the results of previous rotating ring–disk electrode studies of polymer films [30–32], where the counter-ion flux was assessable by the standard (faradaic) method of detection, and with the electrochemical properties of poly(3,4-ethylenedioxythiophene), as studied by the use of other techniques [18–29].

To the best of our knowledge, *ac*-capacitance based detection has never been carried out with rotating ring–disk electrodes. As is the case with many new techniques, there are still many instrumental limitations which have to be dealt with in order to make the measurement of ring capacitance changes more accurate, and thus the results of this paper are by no means meant to be utterly conclusive.

As it was emphasized in the discussion section, the measured ring capacitance only shows a limited correlation with the applied disk potential. In all our experiments, a net capacitance decrease was measured (most probably due to the adsorption of disk-originated organic compounds at the ring electrode). Since this general decrease seems to be independent of the applied disk potential, we believe that it is the *change* of the ring capacitance (i.e., dC_{ring} / dt as

opposed to C_{ring} itself) which is more informative with respect to the processes occurring at the disk. However, due to the instrumental limitations addressed in the paper (low bandwidth and the inaccurate potential measurements) it is still not possible to measure this derivative at sufficiently accuracy. Solving the instrumental issues (*e.g.*, by constructing a dedicated control circuit for these measurements) will be the subject of a future study.

ACKNOWLEDGEMENTS

This research was supported by the European Union and the State of Hungary, co-financed by the European Social Fund in the framework of TÁMOP 4.2.4.A/1-11-1-2012-0001 ‘National Excellence Program’.

Financial support from the Hungarian Scientific Research Fund (grant № K-109036) and from MKB Bank Zrt. (Budapest) is gratefully acknowledged. The authors thank National Instruments Hungary Ltd. for the donation of data acquisition cards.

S. Vesztergom gratefully acknowledges the support of SciEx NMS^{ch} (project № 13.060) for making his research-stay available at the University of Bern.

REFERENCES

1. Frumkin, A.N.; Nekrasov, L.N.; Levich, V.G.; Ivanov, Yu.B. Die Anwendung der rotierenden Scheibenelektrode mit einem Ringe zur Untersuchung von Zwischenprodukten elektrochemischer Reaktionen. *J. Electroanal. Chem.* **1959**, *1*, 84–90.
2. Barnes, E.O.; Lewis, G.E.M.; Dale, S.E.C.; Marken, F.; Compton, R.G. Generator-collector double electrode systems: A review. *Analyst* **2012**, *137*, 1068–1081.
3. Bard, A.J.; Faulkner, L.R. *Electrochemical methods: Fundamentals and applications*. Wiley, New York, USA, 2001.
4. Vesztergom, S.; Láng, G.G. The construction of a novel electrochemical measuring system for enhanced rotating ring–disk electrode experiments. *Instrum. Sci. Technol.* **2013**, *41*, 82–95.
5. Vesztergom, S.; Barankai, N.; Kovács, N.; Ujvári, M.; Láng, G.G.; Wandlowski, Th. Rotating ring–disk electrode with dual dynamic potential control: Theory and practice. *Acta Chim. Slovenica* **2014**, *61*, 223–232.
6. Vesztergom, S.; Ujvári, M.; Láng, G.G. Dual cyclic voltammetry with rotating ring–disk electrodes. *Electrochim. Acta* **2013**, *110*, 49–55.
7. Vesztergom, S.; Ujvári, M.; Láng, G.G. Dual dynamic voltammetry with rotating ring–disk electrodes. *in*: Y. Saito and T. Kikuchi (Eds), *Voltammetry: Theory, Types and Applications*. Nova, New York, USA, 2013.
8. Vesztergom, S.; Ujvári, M.; and Láng, G.G.; RRDE experiments with potential scans at the ring and disk electrodes. *Electrochem. Comm.* **2011**, *13*, 378–381.

9. Vesztergom, S.; Ujvári, M.; Láng, G.G. RRDE experiments with independent potential scans at the ring and disk electrodes — 3D map of intermediates and products of electrode processes. *Electrochem. Comm.* **2012**, *19*, 1–4.
10. Trinh, D.; Keddám, M.; Novoa, X.R.; Vivier, V. Alternating-current measurements in scanning electrochemical microscopy, Part 1: Principle and theory. *ChemPhysChem* **2011**, *12*, 2169–2176.
11. Trinh, D.; Keddám, M.; Novoa, X.R.; Vivier, V. Alternating-current measurements in scanning electrochemical microscopy, Part 2: Principle and theory. *ChemPhysChem* **2011**, *12*, 2177–2183.
12. Ktari, N.; Combellas, C.; Kanoufi, F. Local Oxidation of polystyrene by scanning electrochemical microscopy. *J. Phys. Chem. C* **2011**, *115* 17891–17897.
13. Wang, Q.; Rodríguez-López J.; Bard, A.J. Reaction of Br₂ with adsorbed CO on Pt, studied by the surface interrogation mode of scanning electrochemical microscopy. *J. Am. Chem. Soc.* **2009**, *131*, 17046–17047.
14. Eckhard, K.; Schuhmann, W. Alternating current techniques in scanning electrochemical microscopy (AC–SECM). *Analyst* **2008**, *133*, 1486–1497.
15. National Instruments. NI 446x specifications. 2008.
16. National Instruments. NI 6013/6014 user manual. 2008.
17. Kvarnström, C. Poly(thiophene). In: Bard, A.J.; Inzelt, Gy.; Scholz, F. (Eds.) *Electrochemical dictionary*. 2nd Ed., Springer, Heidelberg, 2012.
18. Bobacka, J.; Lewenstam, A.; Ivaska, A. Electrochemical impedance spectroscopy of oxidized poly(3,4-ethylenedioxythiophene) film electrodes in aqueous solutions. *J. Electroanal. Chem.* **2000**, *489*, 17–27.
19. Yamato, H.; Ohwa, M.; Wernet, W. Stability of polypyrrole and poly(3,4-ethylenedioxythiophene) for biosensor application. *J. Electroanal. Chem.* **1995**, *397* 163–170.
20. Sakmeche, N.; Aeiyaç, S.; Aaron, J.-J.; Jouini, M.; Lacroix, J.Ch.; Lacaze, P.-C. Improvement of the electrosynthesis and physicochemical properties of poly(3,4-ethylenedioxythiophene) using a sodium dodecyl sulfate micellar aqueous medium. *Langmuir* **1999**, *15*, 2566–2574.
21. Inzelt, Gy. *Conducting polymers: A new era in electrochemistry*. Springer, Heidelberg, 2012.
22. Lang, U.; Naujoks, N.; Dual, J. Mechanical characterization of PEDOT–PSS thin films. *Synth. Met.* **2009**, *159*, 473–479.
23. Wang, G.-F.; Tao, X.-M.; Wang, R.-X. Flexible organic light-emitting diodes with a polymeric nanocomposite anode. *Nanotechnology* **2008**, *19*, 145201.
24. Ujvári, M.; Takács, M.; Vesztergom, S.; Bazsó, F.; Ujhelyi, F.; Láng, G.G. Monitoring of the electrochemical degradation of PEDOT films on gold using the bending beam method. *J. Solid State Electrochem.* **2011**, *15*, 2341–2349.
25. Láng, G.G.; Ujvári, M.; Bazsó, F.; Vesztergom, S.; Ujhelyi, F. In-situ monitoring of the electrochemical degradation of polymer films on metals using the bending beam method and impedance spectroscopy. *Electrochim. Acta* **2012**, *73*, 59–69.
26. Láng, G.G.; Barbero, C. *Laser techniques for the study of electrode processes*. Springer, Heidelberg, 2012.
27. Ujvári, M.; Gubicza, J.; Kondratiev, V.; Szekeres, K.J.; Láng, G.G. Morphological changes in electrochemically deposited poly(3,4-ethylenedioxythiophene) films during overoxidation. *J. Solid State Electrochem.* **2015**, *19*, 1247–1252.
28. Andrieux, C.P.; Savéant, J.M. Electroneutrality coupling of electron hopping between localized sites with electroinactive counterion displacement. Part 1. — Potential-step plateau currents. *J. Phys. Chem.* **1988**, *92*, 6761–6767.

29. Lovrić, M.; Scholz, F. A model for the coupled transport of ions and electrons in redox conductive microcrystals. *J. Solid State Electrochem.* **1999**, *3*, 172–175.
30. Pickup, P.G.; Osteryoung, R.A. Charging and discharging rate studies of polypyrrole films in AlCl_3 : 1-methyl-(3-ethyl)-imidazolium chloride molten salts and in CH_3CN . *J. Electroanal. Chem.* **1985**, *195*, 271–288.
31. Shinohara, H.; Kojima, J.; Aizawa, M. Electrically controlled ion transfer and pH change near a conducting polymer-coated electrode. *J. Electroanal. Chem.* **1989**, *266*, 297–308.
32. Salzer, C.A.; Elliott, C.M. Quantitative in situ measurement of ion transport in polypyrrole/poly(styrenesulfonate) films using rotating ring–disk voltammetry. *Anal. Chem.* **1999**, *71*, 3677–3683.
33. Pajkossy, T.; Wandlowski, Th.; Kolb, D.M. Impedance aspects of anion adsorption on gold single crystal electrodes. *J. Electroanal. Chem.* **1996**, *414*, 209–220.
34. Annergren, I.; Keddah, M.; Takenouti, H.; Thierry, D. Modelling of the passivation mechanism of Fe–Cr binary alloys from *ac* impedance and frequency resolved *rrde* — II. Behaviour of Fe–Cr alloys in 0.5 M H_2SO_4 with an addition of chloride. *Electrochim. Acta* **1997**, *42*, 1595–1611.
35. Pilbáth, Zs.; Sziráki, L. The electrochemical reduction of oxygen on zinc corrosion films in alkaline solutions. *Electrochim. Acta* **2008**, *53*, 3218–3230.
36. Lasia, A. *Electrochemical impedance spectroscopy and its applications*. Springer, Berlin, 2014.
37. Pine Instruments Company. AFCBP1 Bi-potentiostat manual. 1995.
38. Bockris, J.O'M.; Devanathan, M.A.V.; Muller, K. On the structure of charged interfaces. *Proc. Roy. Soc. London* **1963**, *A274*, 55–79.
39. Frumkin, A. Über die Beeinflussung der Adsorption von Neutralkmolekülen durch ein elektrisches Feld. *Z. Phys.* **1926**, *35*, 792–802.