Impedance Spectra of Polypyrrole Coated Platinum Electrodes

Niina Onnela, Virpi Savolainen, Maiju Hiltunen, Minna Kellomäki, and Jari Hyttinen

Abstract— **Polypyrrole (PPy) coated electrodes may provide new solutions to increase the charge injection capacity and biocompatibility of metal electrodes in e.g., neural stimulus applications. In this study, electrical impedance spectra of PPy coated platinum (Pt) electrodes having three different coating thicknesses were measured and modeled. A suitable equivalent electrical circuit providing the material characteristics was chosen and the impedance data was analyzed using the model and data fitting. The modeled parameter values of different coating thicknesses were compared and our results demonstrated the changes in charge transfer properties and mechanisms of thin and thick PPy film coatings.**

I. INTRODUCTION

Good electric connection and biocompatibility between electronics and cells are essential e.g. in neurological prosthesis. The ultimate goal of our research is to develop electrodes that are usable in various implants for example by coating electrodes with electroconductive biomaterial that has good electrical properties and biocompatibility. Polypyrrole (PPy) coating provides a way to increase the biocompatibility of metal electrodes. The use of metal electrodes in neural applications might cause problems due to corrosion effects during electrical stimulation and possible long-term toxic effects on the tissue [1]. Furthermore, good electrical charge transfer capacity of materials is well warranted. PPy is shown to have good biocompatibility [e.g., 2] and thus, PPy coating may enhance the possibility of close cell-to-electrode contact. Thus PPy coating may increase the signal-to-noise ratio of measured electrophysiological signals and lower down the needed current or voltage thresholds of stimulation.

PPy is a porous coating and thus, obeys the impedance behavior typical to porous films. However, electrical features of polymer coatings vary depending on synthesis conditions that affect e.g. porosity, density, the nature of counter- and co-ions and their concentrations [3]. Due to that there is a variety of impedance models that can be applied in impedance analysis depending on the conditions of the studied polymer coating. Conducting polymers, such as PPy, have two separate ways to transfer charge in their structure. Charge carriers, such as electrons and holes, are able to move in solid phase along and between the polymer chains (impedance χ_1 in Fig. 1). Simultaneously the charge is transferred in liquid phase: In porous materials electrolyte

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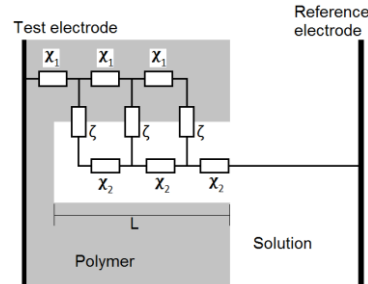
Figure 1.   Electrical modeling of a generic porous electrode.

penetrates the material via the voids, and ionic species of the electrolyte work as charge carriers (impedance χ_2 in Fig. 1). The transport of charge carriers in both phases makes the analysis of the measured impedance of porous materials more complicated than normal metal electrodes.

Bisquert et al. [4] have presented a classical impedance model for porous electrode materials:

$$Z = \frac{\chi_1 \chi_2}{\chi_1 + \chi_2}\left(L + \frac{2\lambda}{\sinh\left(\frac{L}{\lambda}\right)}\right) + \lambda\frac{\chi_1^2 + \chi_2^2}{\chi_1 + \chi_2}\coth\left(\frac{L}{\lambda}\right) \tag{1}$$

where

$$\lambda = \left(\frac{\zeta}{\chi_1 + \chi_2}\right)^{1/2}. \tag{2}$$

Elements χ_1 (polymer channel) and χ_2 (ionic channel) are impedances per unit length corresponding to the whole electrode area (Fig. 1). The element ζ is an impedance length and describes the electrical charge transfer at the distributed interface (parallel to outer interface). L stands for the thickness of the mixed phases in the electroactive layer. Impedances χ_1, χ_2, and ζ can be defined variously depending on how the charge transfer in the polymer, between the solution and polymer, and ion diffusion in the solution is believed to affect the processes.

If the coating is thin (< 100 nm), the voids of porous film are short or there are no voids, and then the electrical charge transfer in the direction transversal to electrode macroscopic surface is dominating. In that case, a model that assumes the electroactive film to be homogeneous canbe used, e.g. [5]. If the polymer coating is thicker, the porous structure enables the charge diffusion also along the parallel direction (ζ in Fig. 1) between the solid and liquid phase. Then, a model that considers the charge transfer in both phases and also the diffusion in parallel direction has to be chosen, e.g. [3,6]. [6]
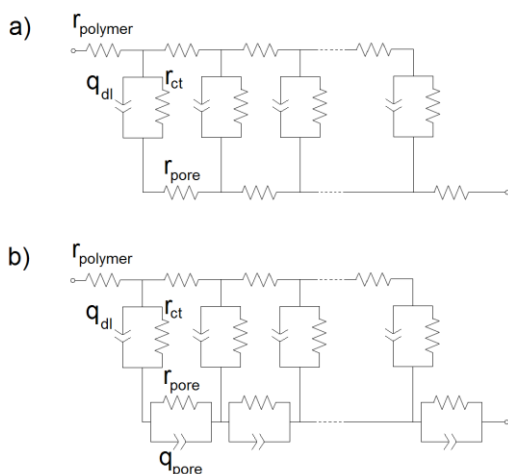
Figure 2. Electrical modeling of a generic porous electrode.

	Thin ± SD	Medium ± SD	Thick ± SD
R_s (Ω)	77.3 ± 5.4	73.8 ± 2.9	73.9 ± 3.0
$r_{polymer}$ (Ω/cm)	9.63 ± 0.75	7.83 ± 1.2	1.95 ± 0.4
r_{pore} (Ω/cm)	5×10^{19}	11.6 ± 17	0.525 ± 0.09
q_{pore} ($10^{-4}Fs^{n-1}cm$)	0.15 ± 0.16	2.18 ± 1.3	42.1 ± 1.2
n_{pore}	0.26 ± 0.02	0.50 ± 0.12	0.63 ± 0.05
r_{ct} (Ωcm)	0.47 ± 0.05	7.36 ± 1.6	126 ± 20
q_{dl} ($10^{-2}Fs^{n-1}/cm$)	365 ± 65	17.1 ± 7.3	0.52 ± 0.0
n_{dl}	0.77 ± 0.02	0.80 ± 0.01	0.79 ± 0.01
Chi-square	0.0059	0.0048	0.0046
Sum of squares	0.318	0.259	0.249

Transmission line model (1-2) has been further defined to better describe the electrochemistry of PPy [6]. Marchesi et al. [6] studied a degradation process of PPy coating on platinum (Pt) substrate and defined models that could describe the process (Fig. 2). Anomalous ion diffusion in the pores is described with r_{pore} and q_{pore}, $r_{polymer}$ represents the polymer resistance, and the interface between the solution and polymer is represented by a double-layer capacitance (q_{dl}) in parallel with the charge-transfer resistance (r_{ct}).

In this study, the equivalent circuit models of PPy type electrodes presented in [6] were fitted to actual measured electrical impedance spectroscopy (EIS) data to study the electrochemical behaviour of PPy coated Pt electrodes. Three different coating thicknesses were electrochemically polymerized and characterized using atomic force microscopy (AFM). The equivalent models were fit to the measured impedance data, and the parameter values that the impedance model gives for the samples were compared.

II.   MATERIALS AND METHODS

A. Electrode Fabrication

Electrochemical polymerization of polypyrrole-dodecylbentzenesulphonate (PPy/DBS) coating on platinum electrodes (Labor-Platina Kft, Hungary) was performed at room temperature in aqueous solution containing pyrrole (Py) 0.2 M (Sigma-Aldrich, USA) and DBS 0.05 M (Acros Organics, USA). Py was vacuum distilled prior to use, other chemicals were used as received. All solutions were prepared in deionized Milli-Q water. The coating was grown potentiostatically at 1.0 V (VerstaSTAT 3 Potentiostat/Galvanostat: Princeton Applied Research, USA) until the total charge passed was 10 C/cm^2 (thin film), 90 C/cm^2 (medium film) and 170 C/cm^2 (thick film).

B. Characterization of the Coating Thickness

The coating thickness of the samples was characterized using AFM (XE-100, Park Systems, USA). AFM image scans of 5 μm were conducted in air in non-contact mode using ACTA cantilever tips (Applied Nano Structures Inc., USA) with resonance frequency of 300 kHz and spring constant of 40 N/m.

C. Electrode Electric Impedance

The electrode EIS were measured at 37°C in phosphate buffer solution (pH 7.5) using the Solartron Model 1260A Frequency Response Analyzer and 1294A Impedance Interface (Solartron Analytical, Hampshire, UK). Measurements were conducted using a 5-mV effective sine-wave alternating voltage between 1 Hz and 1 MHz.

D. Model Based Analysis of PPy Electrode Characteristics

The ZView modeling program (Scribner Associates inc., Southern Pines, NC) was used to fit the models presented in [6] (Fig. 2) into our measured EIS data to analyze the characteristics of the PPy coating. Impedance models (Fig. 2) were fitted in series with the serial resistance R_s describing the solution resistance and bulk electrode under the coating. The model that was better fitting the data was selected for parameter analysis.

The ZView program uses complex nonlinear least squares fitting based on the Levenberg-Marquardt algorithm [7]. The aim of the fitting is to find a set of parameters which minimizes the weighted sum of squares. The chi-square value that estimates the quality of the fit is the weighted sum of squares divided by the number of degrees of freedom.

III.   RESULTS

A. Coating Thicknesses

The AFM topography images of all coating thicknesses are shown in Fig 3. Thicknesses of coatings were measured by AFM and the results were: thin 70 nm, medium 0.5 μm, and thick film 8 μm. Roughness values (R_a, n=5) were 7.0, 7.7, and 8.7 nm, respectively.
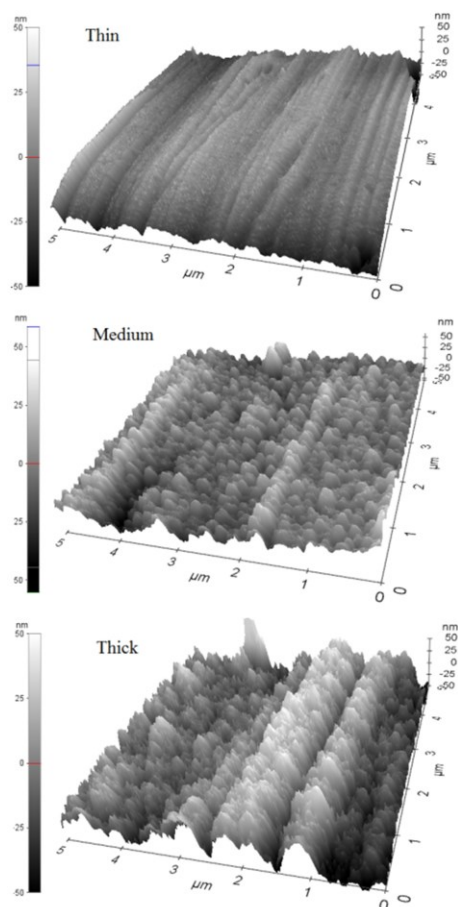
Figure 3. AFM images of thin, medium, and thick PPy films.

B. Model Fitting

First model (Fig. 2 a) gave parameter values that changed widely in a random fashion even between the samples having the same coating thickness. In addition, fitting of the second model (Fig. 2 b) resulted in better chi-square values. Thus, the fitting results obtained with the second model [6] were selected for further evaluation. Representative impedance curves with the fitting are shown in Fig. 4. Parameter values obtained from the data fitting using the model (Fig. 2 b) are shown in Table I.

As expected, series resistance, R_s, is stabile for all coating thicknesses. The amount and composition of medium, the used Pt electrodes and measurement wires are similar for all measurements and sample electrodes. Thus, the R_s representing the solution resistance and bulk electrode should not change with varying coating thickness.

The charge transfer in the lengthwise direction of PPy chain is mainly characterized by the oxidized state of the conjugated PPy chain structure. Thus, it is expected that the polymer resistance, r_{pol} (Ω/cm), is quite stabile parameter value for all coating thicknesses. Indeed, the differences between the values of the r_{pol} of varying coating thicknesses are minimal. When the coating thickness is considered and the total resistance of the polymer chain is calculated
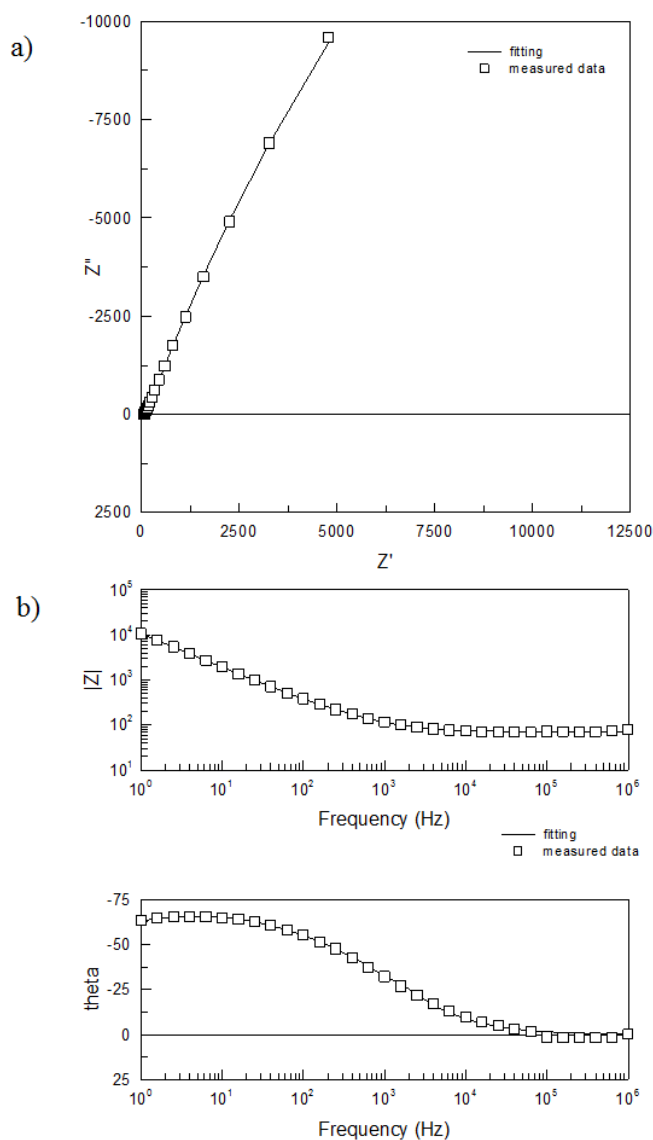

Figure 4. Impedance data ($\square$) and fitting (—) for one electrode with the PPy coating thickness of 0.5 µm (medium). a) Nyquist plot, b) Bode plot.

($R_{pol}=r_{pol}L$), then the resistance is increasing with the increased coating thickness.

In the pores the charge transfer becomes more efficient due to increased coating thickness: pore resistance, r_{pore}, decreases and capacitance, q_{pore}, increases indicating that the total impedance decreases. For thicker PPy coatings the likelihood of branching and other possible imperfections of polymer chains are greater than for thinner coatings. The imperfections of polymer chains may result in greater pore sizes in thicker coatings and thus, greater amount of liquid in the film structure. That may explain the easier ion transfer of thicker coatings. For the thinnest coating the pore resistance is huge. That may indicate that the coating is actually so thin that there are no pores and thus, no charge transfer in the pores.

Charge transfer resistance, r_{ct}, increases and double-layer capacitance, q_{dl}, decreases due to increased coating thickness. This means that the charge transfer between the polymer and pores is hindered due to increased coating thickness. That was actually unexpected behaviour. However, because the impedance measurements were carried out immediately after immersing the samples into the solution it may be that the polymer coating of thicker samples did not yet have saturated. Due to the large size of DBS counter anions used in this study, they are assumed to be entrapped in the polymer structure. Thus, the charge transfer between the PPy and the solution (in the pores) occurs through cation change. Without solution in the pores there are no cations available and thus, no charge transfer between the PPy and pores. Partly dry polymer coating does not have optimum performance for charge transfer.

IV. DISCUSSION

All coating thicknesses, especially medium and thick coatings, showed nodular surface structure that increases the effective surface area of the PPy coated electrodes. Such a structure may later also improve the cell attachment on the surfaces. The parameter values obtained from the impedance modelling were consistent with the theory of charge transfer properties of the PPy coating. The results showed that thicker coating improves the electrical charge transfer properties of the electrode. However, our results indicated that thicker polymer coatings may need more time for wetting to achieve the highest possible charge transfer properties.

We have shown earlier [8] that when comparing thin and thick PPy coating, the thinner has greater charge capacity than the thicker one. PPy coating improves the conductivity of the platinum by decreasing impedance values at low frequencies. However, impedance spectra of PPy electrodes of different coating thicknesses do not vary remarkably. Thus, we need impedance modelling and parameter value analysis to study if the electrochemical properties of PPy coatings do change with varying coating thickness.

Generally, the impedance spectra of PPy films can be separated into two patterns: a Warburg-like response that dominates at high frequencies and some type of charging mechanism characterized by capacitive-like patterns at low frequencies [3,6]. In [3], the charging mechanism of the PPy film is explained through the charging capacity of the polymer and polymer/solution interface, and the electrical behavior of the pores is resistive. In [6] instead, the pores and interface impedance are modeled to be responsible for the anomalous transport effects of PPy coated Pt electrodes. Our impedance spectra are dominated by the high frequency behavior and the capacitive-like pattern is not very apparent. This may support the assumption that thicker coatings were still partly dry during the impedance measurements and thus, the capacitive properties of polymer/solution interface were not so dominant.

In further studies the stability of the electrodes could be followed during longer time period and the EIS measurements should be conducted after longer time of immersion of electrodes. In addition, the EIS measurement results achieved in a phosphate buffer solution in this study may be very different from those measured in the neural cellular environment. Thus, the electrodes should also be implanted and tested in a real cellular environment.

PPy coating thickness is considered in the model with the fixed parameter value, L. Swelling of PPy in aqueous solution, caused by the penetration of solvated ions into the structure, is not taken into account. That may cause slight errors to our modeling approach.

Properties of PPy can vary depending among others on the polymerization conditions and chosen counter ion and thus, the same model is not necessarily appropriate for PPy samples produced differently. To fully understand the processes such as transport of ions in the polymer, between the film and solution, and in the pores, parameter values that describe the impedance behavior of PPy electrodes are well warranted. The suitability of the model used in this study [6] will be further tested in our future studies that characterize the long-term performance of the PPy coatings.

REFERENCES

[1] D. R. Merril, M. Biksom, J. G. R. Jefferys, "Electrical stimulation of excitable tissue: design of efficacious and safe protocols" *Journal of Neuroscience Methods*, vol. 141, pp. 171-198, 2005.

[2] X. Wang, X. Gu, C. Yuan, S. Chen, P. Zhang, T. Zhang, J. Yao, F. Chen, and G. Chen, "Evaluation of biocompatibility of polypyrrole in vitro and in vivo" *Journal of Biomedical Materials Research A*, vol. 68, pp. 411-422, 2003.

[3] G. Garcia-Belmonte, J. Bisquert, "Impedance analysis of galvanostatically synthetized polypyrrole films. Correlation of ionic diffusion and capacitance parameters with the electrode morphology" *Electrochimica Acta*, vol. 47, pp. 4263-4272, 2002.

[4] J. Bisquert, G. Garcia-Belmonte, F. Fabregat-Santiago, and A. Compte, "Anomalous transport effects in the impedance of porous film electrodes" *Electrochemistry Communications,* vol. 1, pp. 429–435, 1999.

[5] A. Ramanavicius, A. Finkelsteinas, H. Cesiulis, A. Ramanaviciene, "Electrochemical impedance spectroscopy of polypyrrole based electrochemical immunosensor" *Bioelectrochemistry,* vol. 79, pp. 11-16, 2010.

[6] L. F. Q. P. Marchesi, F. R. Simões, L. A. Pocrifka, and E. C. Pereira, "Investigation of Polypyrrole Degradation Using Electrochemical Impedance Spectroscopy" *The Journal of Physical Chemistry,* vol. 115, pp. 9570-9575, 2011.

[7] D. Marquardt "An Algorithm for Least-Squares Estimation of Nonlinear Parameters" *SIAM Journal on applied Mathematics,* vol. 11, pp. 431-441, 1963.

[8] V. Savolainen, M. Hiltunen, A. Kevin, S. Nymark, M. Kellomäki, and J. Hyttinen, "Fabrication of electroconductive polypyrrole coatings on platinum electrodes", in *Proc of 8th Int. Meeting on Substrate-Integrated Microelectrode Arrays,* Reutlingen, Germany, 2012, pp. 291-292.