



# In-situ odd random phase electrochemical impedance spectroscopy study on the electropolymerization of pyrrole on iron in the presence of sodium salicylate – The influence of the monomer concentration

Karolina Cysewska <sup>a, b, \*</sup>, Lucía Fernández Macía <sup>b</sup>, Piotr Jasiński <sup>a</sup>, Annick Hubin <sup>b</sup>

<sup>a</sup> Faculty of Electronics, Telecommunications and Informatics, Gdansk University of Technology, ul. Narutowicza 11/12, 80-233 Gdansk, Poland

<sup>b</sup> Research Group Electrochemical and Surface Engineering, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussels, Belgium

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## ABSTRACT

In this work, the potentiostatic electropolymerization of polypyrrole (PPy) on iron in aqueous solution of sodium salicylate and pyrrole is studied in situ by odd random phase electrochemical impedance spectroscopy (ORP-EIS). The influence of the pyrrole concentration on the electrosynthesis process is investigated. The ORP-EIS technique ensures a reliable analysis of the PPy electrosynthesis on iron by means of an advanced data analysis of the non-linear and non-stationary behaviour and the signal-to-noise ratio of the system. Additionally, the structure and the chemical nature of the PPy film on iron are studied by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and glow discharge optical emission spectroscopy (GDOES). The results of the characterization confirm the presence of the passivation layer at the PPy/iron interface formed prior to the polymer deposition. The modelling of the impedance evolution over time provides the quantitative analysis of the electropolymerization of PPy on iron. The results show that the electrosynthesis of pyrrole on oxidizable iron in the presence of sodium salicylate is a complex process, which includes not only the pyrrole oxidation reactions but also reactions such as the oxidation/reduction of the iron surface and/or reactions between the iron, formed interlayer and polypyrrole.

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## 1. Introduction

Current cardiovascular stent technology is mostly based on the use of permanent stents made from corrosion-resistant metals [1,2]. These are mainly stainless steel 316L, but tantalum, nitinol, cobalt alloy and platinum iridium are commercially used as well [3]. Recent studies have shown that the presence of such materials in the human body for long time can cause re-overgrowing of the tissue within the treated portion of the vessel, which leads to the re-blockage of the circulatory system and many other clinical complications [2,3]. Thus, research on biodegradable metallic stents is conducted at present [1–3]. The materials for this purpose are active/oxidizable metals and their degradation is based on their progressive corrosion. One interesting metal for this application is

iron [3,4]. However, in order to use iron in clinical applications, its degradation rate and biological performance need to be optimized [3–5]. A favourable solution is to modify the metallic surface with conducting polymer films [6–9].

Recently, research on conducting polymers has become very important in different technological areas [10–12]. The major property of these polymers is their metallic-like conductivity resulting from the conjugated double bond in their backbone [10]. Polypyrrole (PPy) is one of the promising conducting polymers that exhibits very good environmental stability [11], excellent mechanical and thermal properties [11] and high biocompatibility [13]. Due to its unique properties, polypyrrole has been used as advanced coating material in many applications such as anti-corrosive coatings [9,14,15], biosensors [16,17] organic electronics [18] or biomaterials [9,19].

It is well known that conducting polymer films can be synthesized by chemical or electrochemical route [10]. The latter option is more favourable due to its simplicity, low cost and high reproducibility [20]. Besides, it allows controlling different properties of the polymeric material [21]. The electropolymerization process

\* Corresponding author. Faculty of Electronics, Telecommunications and Informatics, Gdansk University of Technology, ul. Narutowicza 11/12, 80-233 Gdansk, Poland.

E-mail addresses: [Karolina.Cysewska@vub.be](mailto:Karolina.Cysewska@vub.be), [kar.cysewska@gmail.com](mailto:kar.cysewska@gmail.com) (K. Cysewska).

leads to the formation of a positively charged polymer with counter-anions incorporated into its structure [22].

Both the properties of the polymeric layer and the mechanism of its synthesis are directly influenced by the experimental conditions of the electropolymerization. Thus, the choice of parameters, such as type of electrolyte/solvent, applied current density or potential, will strongly affect the synthesis process [21,23,24]. Another important element that influences the electropolymerization process is the type of substrate [25,26]. The morphology, structure, conductivity and other physicochemical properties of the polymer films change depending on the substrate [26]. The electrodeposition of conducting polymers proceeds easily on inert substrates such as platinum, gold or glassy carbon [27,28]. However, the synthesis of these polymers on oxidizable metals is a complex process, which involves different stages of the synthesis. The choice of the wrong synthesis parameters leads to a high dissolution of the metal, which hinders the polymer deposition. This is related to the fact that the oxidation potential of an active metal is much lower than the oxidation potential of the monomer [9]. One way to solve this problem is the proper selection of the type of anions in the supporting electrolyte, which can promote the passivation of the metal surface when it comes in contact with the electrolyte. This inhibits the metal dissolution and allows for a stable polymer deposition [26]. Thus, the electrodeposition of conducting polymers on oxidizable metals is a more challenging and complicated process than on inert substrates.

Polypyrrole has already been electrochemically polymerized on different kinds of active metals such as steel/iron [8,29,30], magnesium [31,32], nickel [27], zinc [28] or copper [33,34] and in presence of several kinds of supporting electrolytes [8,27,30,31]. It is observed that the mechanism of the polymer synthesis is directly dependent on the types of active metal and supporting electrolyte [26]. In literature, many studies reveal the passivating properties of oxalate anions during the electropolymerization of pyrrole on iron [35–37] or steel [38]. In the presence of these anions the passivation of iron/steel occurs immediately after the electrosynthesis current or potential is applied. The next stages of the electropolymerization in presence of oxalates are the decomposition of the passivated layer and the subsequent electropolymerization of pyrrole directly on the metallic surface [37,38]. A different behaviour is seen in the case of salicylate anions for iron [8,9,39], copper [34], magnesium [32] or zinc [28]. Here, the polymer is deposited directly on the passivation layer, which is formed at the beginning of the electropolymerization process. This layer inhibits the metal dissolution and allows for a stable polymer deposition. The composition of the passivation layer is still under debate. Mostly, it is described as a metal oxide/hydroxide and/or a metallic salt. Srinivasan et al. [32] determine the interlayer between magnesium and PPy as a magnesium-salicylate complex. However, El Jaouhari et al. [39] characterize the passivation layer on iron as an iron oxide and/or iron salicylate complex. Similar passivating properties are also observed in the case of malic acid with iron [40], sulfuric acid with steel [41] or dodecylbenzenesulfonic acid with copper [33]. On the contrary, the electropolymerization of pyrrole on oxidizable metals is not found to be possible in the presence of polystyrenesulfonate (PSS) [35,36] or dodecyl sulfate ( $\text{DS}^-$ ) anions [36]. Therefore, the fact that the metal passivation occurs without hindering the polymer deposition demands a careful choice of media and parameters for a successful electropolymerization of pyrrole on active metals. This particularity of the electrosynthesis process makes the direct electrodeposition of PPy possible without any chemical or electrochemical pretreatment.

Previous studies show that PPy doped with salicylate can provide corrosion resistance to iron. The level of protection depends on the synthesis conditions used during the electropolymerization

[8,14]. Polypyrrole films electrosynthesized in the presence of sodium salicylate under different conditions reveal different morphological, electrical and redox properties [8,42,43]. Our previous study show that the degradation of iron can be tailored by changing the properties of an electropolymerized salicylate-doped polypyrrole film [9]. Exposed to a human body-like electrolyte, PPy coatings synthesized under certain conditions inhibit the corrosion of iron at the beginning of the immersion and later they promote the degradation of the metal in a steady manner. This characteristic is very desirable in the case of medical applications, such as biodegradable metallic cardiovascular stents. It is also observed that the passivation interlayer formed on iron surface prior to the PPy electrodeposition has a major impact on the corrosion properties of the coated iron [9]. Therefore, a more detailed study of the synthesis of the salicylate-doped polymer film on iron is crucial to gain insight into the processes occurring during the material degradation.

Different measurement techniques are used to study the electrochemical polymerization of pyrrole on oxidizable metals. Most investigations make use of potential sweep methods [32,34,39,44,45] or under potentiostatic/galvanostatic control [34,35,40,41,46]. Other measurement techniques such as X-ray photoelectron spectroscopy (XPS) [33,41], time-of-flight secondary ions mass spectrometry (ToF-SIMS) [33], electrochemical quartz crystal microbalance (EQCM) [28] or in-situ Raman spectroscopy [37] are also used to get insight into the polymer electrosynthesis. Moreover, there are some attempts to study the electropolymerization by electrochemical impedance spectroscopy (EIS) [47,48]. Popkirov et al. [47] study the galvanostatic electrosynthesis of bithiophene on platinum substrate in an acetonitrile solution containing  $\text{NBt}_4\text{BF}_4$ . Based on the EIS measurements, it is suggested that three processes occur in the system: charge transfer of the polymerization reaction, charge transfer of the oxidation/reduction reactions of polybithiophene and diffusion of the ions through the polymer film. All are dependent on the thickness of the polymeric layer [47]. The initial stages of the potentiostatic electropolymerization process of polyaniline (PANI) on platinum from acid aqueous solution are also studied by EIS [48]. For this case, two processes are observed: the charge transfer of the polymerization at high frequencies and a diffusion contribution in the low frequency range; the latter is associated with the transport of the monomer from the bulk of the electrolyte [48].

In this work, the electrochemical polymerization of pyrrole on iron from an aqueous solution of sodium salicylate is studied in-situ by odd random phase electrochemical impedance spectroscopy (ORP-EIS). The ORP-EIS technique ensures reliable experimental data and impedance modelling based on the advanced data analysis of the non-linear and/or non-stationary behaviour and the signal-to-noise ratio of system [9,49,50]. Once the quality of the experimental data is confirmed, the impedance spectra are fitted to an electrical equivalent circuit that represents the electrochemical processes occurring during the electropolymerization. The parameters that describe the electrochemical system are estimated using a statistically founded methodology. The evolution of the parameters describing the polymerization process is evaluated. This approach provides a reliable and quantitative study of the PPy electrodeposition on iron in the presence of sodium salicylate. To the best of our knowledge, this subject has not been investigated with this approach before.

## 2. Experimental

### 2.1. Chemicals and materials

The chemicals used in this work are pyrrole monomer ( $\geq 99\%$ ,

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