



Research paper

Tailoring the electrochemical degradation of iron protected with polypyrrole films for biodegradable cardiovascular stents



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ABSTRACT

The degradation of polypyrrole (PPy) coated iron is studied in phosphate buffer saline solution at 37 °C by odd random phase multisine electrochemical impedance spectroscopy (ORP-EIS). PPy is electro-polymerized with anti-inflammatory salicylates incorporated in the film, as a drug release system. The modelling of EIS over time provides the quantitative description of the corrosion behaviour of the material. Thus, the reliable analysis of the degradation stages of PPy coated iron is attained. The outcome of the present study shows that the degradation of iron can be tailored by tuning the properties of the PPy coating for possible medical applications.

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1. Introduction

Nowadays permanent metallic cardiovascular stents are long-term implants [1,2]. The presence of such an implant for long time in human body can cause overgrowth of tissue within the treated portion of the vessel, blockage of the circulatory system and many other clinical complications, such as thrombosis, prolonged physical irritations or chronic inflammation [2,3]. Therefore, in recent years, there is an interest to create biodegradable metallic cardiovascular stents [1–3]. Iron and its alloys are promising materials for this application and have attracted the attention of many researchers [1–6]. Iron possesses very good mechanical properties, similarly to 316L stainless steel (used in permanent cardiovascular stents); it also has favourable biological properties and high biocompatibility [1,2]. However, bare iron degrades too slow on the long term, yet too fast in the initial stages in a physiological media, making it difficult to use in clinical applications [6]. In order to enhance the corrosion rate of iron, the current technology is focused on modifying the iron structure, for example by alloying [6]. Nevertheless, it is also desirable to

inhibit its degradation at the initial stages after the implantation. This inhibition will provide a good biocompatibility and an appropriate cell proliferation, which are very crucial during the first days after the implantation [1–3,6].

One promising solution is to modify the surface of the metal with conducting polymer films [7–12]. The principal property of these polymers is their metallic-like conductivity due to the conjugated double bond in their backbone [13]. One of the most interesting among the conducting polymers is polypyrrole (PPy) [14–17]. It exhibits high biocompatibility [14], very good stability in different environments [9,15], good adhesion to the substrate [16], excellent electrical, mechanical and thermal properties and high conductivity compared to other conducting polymers [15]. Because of such distinctive properties, PPy has been used in different applications including anti-corrosive coatings [7,8,18,19] and drug release systems [20]. One of the common methods of synthesis on metallic substrates is electrochemical polymerization [21]. This method allows controlling the film properties and provides stronger bonding of the polymer to the substrate compared to a chemical approach [22]. Depending on the polymerization conditions, different morphology, electrical and corrosion properties of the conducting polymer film can be obtained [23]. However, when deposited on an oxidizable metal, an inappropriate selection of the synthesis conditions leads to the dissolution of the substrate, since the potential at which the metal dissolves is much lower than the oxidation potential of the

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monomer. Thus the deposition of the polypyrrole becomes hindered [22,24]. Therefore, the choice of the electropolymerization conditions, including the type of electrolyte, is very critical to obtain stable and protective conducting polymer coatings on such kind of metals [7,25].

Polypyrrole has been electropolymerized on several types of oxidizable metals such as magnesium [26], aluminium alloy [27], copper [28], zinc [29], steel and iron [8,19,30–32]. In contrast to the noble metals, such as platinum, where direct deposition of pyrrole occurs [33], non-noble metals seem to require the formation of a stable interface prior to the polymerization. It was shown that in the presence of certain electrolytes, such as oxalic acid [22] or sodium salicylate [8,28], just before the polymer deposition, a passivation layer is formed on the surface of the active metals. This layer blocks the dissolution of the iron substrate and thus provides a stable deposition. It also enhances the adhesion of the polymeric film in the further stages of the electropolymerization [22].

In addition, PPy can be also used to load and release drugs with therapeutic activity, like salicylates [8,9,34], which can be incorporated during the electropolymerization as dopants. Sodium salicylate belongs to the family of non-steroidal, anti-inflammatory agents that reduce pain and fever. During the implant degradation, it could be released into the body, decreasing a possible inflammation caused by the implantation process [9].

The corrosion properties of PPy coatings on different metals have been intensively studied in recent years, for various applications and by utilizing several methods [22,28,34–39]. It was reported that conducting polymers synthesized under certain conditions can prevent the corrosion of certain metals. Bazzaoui et al. studied PPy coated iron in 0.1 M HCl at room temperature using potentiodynamic polarization; they observed the inhibition of the corrosion process by the polypyrrole, synthesized from a solution of saccharin and pyrrole [37]. An improved corrosion protection of steel was also achieved by polypyrrole deposited from a salicylate solution [34]. The protection, assessed by electrochemical impedance spectroscopy in sodium chloride, remained stable up to 20 days.

The mechanism of corrosion protection of iron or steel by a conducting polymer depends on the polymer/metal electrochemical system [28]. In many cases corrosion protection involves a redox reaction (probably catalytic) that forms passivating layer at the metal/polymer interface [28,32,40–42]. In other words, conducting polymer films help to stabilize this layer as a result of galvanic coupling between the coating and the metal [34]. Such mechanism was reported in the case of PPy-salicylates deposited on steel [28], PPy-oxalates on iron [32] or polyaniline (PANI) deposited on steel [41].

In most of the studied cases it is desirable to achieve a stable polymer/metal system with a high corrosion protection of the metal [22,28,34–39]. Yet, for biodegradable metallic stents, the system needs to evolve over time. Besides, it is important to investigate the corrosion and degradation processes of such system under conditions that simulate the human body environment.

In this work, the corrosion performance of differently prepared PPy coatings on iron has been studied at 37 °C in phosphate buffer saline solution (pH 7.4) for the first time. Polypyrrole is electrochemically synthesized in the presence of sodium salicylate, which is incorporated in the coating. The degradation study is performed by odd random phase electrochemical impedance spectroscopy (ORP-EIS) [43–45]. The ORP-EIS data are fitted to the proposed electrical equivalent circuit that represents the electrochemical processes. The parameters that describe the electrochemical system are estimated using a statistically founded method. Besides, the quality of the modelled data is statistically evaluated by confronting the modelling errors against the noise levels. The evolution of the parameters describing the degradation

of the PPy/Fe system is obtained. This way, a reliable, quantitative analysis of the behaviour of PPy coated iron in a simulated human body environment is attained. To the best of our knowledge, this subject has not been investigated with this approach before.

2. Experimental

2.1. Chemicals and materials

The following chemicals are used: pyrrole monomer ($\geq 99\%$, Acros Organics), sodium salicylate ($\geq 99.5\%$, EMSURE), phosphate buffer saline pH 7.4 (PBS, PanReac AppliChem) containing 2.7 mM KCl, 140 mM NaCl and 10 mM phosphate. The electrolyte for electropolymerization consists of a solution of 0.1 M pyrrole and 0.1 M sodium salicylate. All solutions are made with Mili-Q water.

The substrate is a pure iron plate ($\geq 99.8\%$, Chempur Feinchemikalien und Forschungsbedarf GmbH).

2.2. Sample treatment

The iron plate is embedded in an epoxy resin. The iron electrode is mechanically grinded with abrasive papers 220, 500 and 1200 SiC grade (Struers), rinsed with ethanol and dried. After the polymerization experiments, the sample is rinsed with Mili-Q water and dried in an N_2 stream.

2.3. PPy film synthesis

The electropolymerization measurements are performed in a one-compartment, three-electrode cell controlled by a Bio-Logic SP-200 potentiostat. The working electrode is the iron with an exposed area of 3.39 cm². A Ag/AgCl_{sat} is used as reference electrode and a platinum grid, as counter electrode.

The polymer films are electrochemically synthesized on iron in a one step process at 1.2 V vs. Ag/AgCl_{sat} from solution of 0.1 M pyrrole and 0.1 M sodium salicylate, at room temperature. Two coatings, named here PPy₁ and PPy₂, are deposited with the electropolymerization time limited by a specific charge: 6.37 C cm⁻² for PPy₁ and 2.11 C cm⁻² for PPy₂.

A preliminary characterization of the corrosion protection of the freshly prepared polymeric films is carried out by potentiodynamic polarization in PBS solution (pH 7.4) at 37 °C from –300 mV to 1 V (vs. OCP) with a 3 mV s⁻¹ scan rate. The temperature during the measurements is controlled by a JULABO F12 thermostat.

The film thickness is measured from cross-sectional scanning electron microscope (SEM) images, using JEOL JSM-IT300LV with a tungsten filament source. The thickness of the PPy₁ and PPy₂ coatings is determined to be $\sim 20 \mu\text{m}$ and $\sim 10 \mu\text{m}$, respectively (see Supplementary contents, Figure A).

2.4. ORP-EIS measurements

The degradation measurements of PPy₁/Fe and PPy₂/Fe are performed by ORP-EIS during 2 weeks and 1 week, respectively.

The ORP-EIS technique uses an odd random phase multisine as excitation signal. Such signal consists of the sum of harmonically related sine waves with random phases. Only odd harmonics are excited and, per group of 3 consecutive harmonics, one is randomly omitted [43,44]. This allows for the determination of the non-stationarities and non-linearities of the studied system. Every ORP-EIS measurement and its noise distortions are obtained from the calculations of 4 multisine periods. Besides, due to the multisine excitation signal, the measurement time is reduced. The detailed description and explanation of the technique can be found in previous works [44,45].

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