Study of the electrochemical stability of polypyrrole coating on iron in sodium salicylate aqueous solution

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A B S T R A C T

In this work electrochemical stability of optimized PPy film on iron in aqueous solution of sodium salicylate is studied. The main drawback of conducting polymers is their possibility to undergo an irreversible degradation (overoxidation). The overoxidized polymers lose their properties, for example, conductivity and redox activity, what excludes them from some practical applications. This study demonstrates that lowering the concentration of salicylate in the electrolyte increases the electrode potential, at which overoxidation of PPy begins. It widens the electrode potentials, within which such a polymer can be used. Moreover, it is evidenced that even though the electrolyte concentration is lowered, the redox activity and the electrical properties of the PPy film are retained.

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1. Introduction

The use of biodegradable, metallic, cardiovascular stents is becoming an alternative to the currently used permanent forms [1,2]. One of the promising materials for this application is iron (Fe) [3–6]. Iron possesses very good mechanical properties similarly to 316L stainless steel (used in permanent cardiovascular stents) [1], favourable biological properties and a high biocompatibility [2]. However, its degradation rate and the biological performance need to be controlled and optimized [1,2]. One promising solution is to modify the surface of the metal with conducting polymer films [5,7].

Recently, electrically conducting polymers have attracted attention of many researchers from different fields of science [8–10]. One of the most promising among conducting polymers is polypyrrole (PPy) [11–14]. Polypyrrole exhibits very good environmental stability [11], high biocompatibility [14], good adhesion to the substrate [12], very good mechanical and thermal properties and higher conductivity compared to many other conducting polymers [11]. Because of its unique properties, PPy can be used in various applications including biosensors [15,16], anti-corrosive coatings [17–19], organic electronics [20] or gas sensors [21].

Polypyrrole can be electrochemically synthesized on different metallic substrates under various synthesis conditions [22–27]. Depending on the synthesis conditions, especially on the type of the doping agents, the chemical, physical and electrical properties, including the PPy electroactivity, can be altered [14,28]. Poly-pyrrole behaviour depends strongly on its oxidation state [29], and like other conducting polymers it exhibits redox switching ability between its reduced and oxidized states [30]. Many studies have been performed in order to examine the redox properties of polypyrrole synthesized in a presence of different electrolytes based on cyclic voltammetry measurements [24,29,31–34]. It has been reported that in aqueous solutions under anodic potentials such polymeric materials can undergo an irreversible oxidative degradation (overoxidation) [34–40]. The overoxidized PPy irreversibly loses its unique properties, such as electrochemical activity, charge storage ability, conjugation, conductivity, mechanical properties, and adhesion to the substrate [34,36–39]. In fact, all the beneficial features of the conducting polymers are destroyed by this process [41]. The specific reason responsible for PPy oxidative degradation is related to the hydroxyl radicals formed during the water oxidation [35,42]. The potential at which the PPy overoxidation begins has been reported to be around +(0.3–0.4 V) vs. Ag/AgCl in solution of pH 7 [34,39]. PPy is relatively stable in its oxidized (doped) state as long as overoxidation is avoided [43]. Different studies have been performed in order to inhibit or avoid the PPy film to become easily overoxidized [35,39]. It has been reported that overoxidation process of PPy can be inhibited by

lowering the pH of the aqueous solution in which the polymer is studied [39]. It has been shown that the higher the pH of the solution, the lower the overoxidation potential of the polymer [39]. On the other hand, use of the organic compounds, such as dodecyl sulphate or ionic liquids in the solution, is reported to increase the PPy stability [35].

Since the overoxidation process of PPy leads to loss of its conductive properties, it is also important to monitor its electrical properties. Some studies have been performed in order to examine the resistance behaviour of conducting polymers in different solutions, as a function of electrode potential during its doping/dedoping [34,38,44]. This allows for the determination of the potential ranges in which the studied polymer can be used. Lankinen et al. [38] reported that poly(3-methyl thiophene) (PMeT) has a minimum resistance between 0.5 and 0.7 V in acetonitrile solution of tetrabutylammonium perchlorate (Bu$_4$N-ClO$_4$). At higher potentials the resistance increased, which was ascribed to its oxidative degradation [38]. Our own studies showed that PPy films synthesized from aqueous sodium salicylate solution retained their electroactive and conductive properties in a potential window between −0.6 and 0.3 V [34]. At more positive potentials the polymer was overoxidized and became an insulator [34]. A study of the redox and electrical properties of the polymer coatings could give information about a potential range in which the polymer is electrochemically active, and whether it exhibits insulating or conductive properties. Knowledge about this could help controlling the degradation of metallic cardiovascular stents and drug release process from polymeric films coated on such implants [34]. The possibility of using PPy film at higher potentials is especially important when there is a need to additionally tailor the morphological and electrical properties of the polymer film (by applying certain potentials). However, the challenge is to do it in such a way which does not lead to the electrochemical degradation of polymeric material.

In our previous studies [34], the redox properties of PPy coated Fe electrodes in aqueous solution of sodium salicylate were studied by cyclic voltammetry measurements. It was shown that such electrodes cannot be used at potentials higher than +(0.3–0.4) V [34]. In this work, PPy films are electrochemically polymerized from sodium salicylate aqueous solution under conditions, which have been previously optimized to provide an increase in corrosion resistance of iron [17]. The salicylate molecules incorporated in the PPy layer during the coating process could act as a drug, which can be released into the body during the implant degradation. Here, we demonstrate, for the first time, that by lowering the salicylate concentration in the electrolyte, the electrode potential window for the use of the PPy/salicylates can be significantly increased. This is achieved without degradation of the electroactivity and the electrical properties of the PPy film. This provides the possibility of additional tailoring the polymer properties by applying certain potential in aqueous solution of salicylates. Because the PPy film is synthesized here in a presence of the salicylate ions, a possible tailoring of the polymer properties should be also performed in a solution of such ions in order to avoid introduction of the new species in a system. The latter could change the overall properties and the performance of the PPy/Fe material.

2. Experimental

Polypyrrole film was galvanostatically (2.5 mA cm^{-2}) polymerized on iron (≥99.5%) (Chempur Feinchemikalien und Forschungsbedarf GmbH) in a one step process (Q = 4.72 C cm^{-2}) from aqueous solution of 0.1 M pyrrole monomer (Sigma Aldrich) and 0.1 M sodium salicylate (EMSURE). Such polymerization condition is the optimum condition of PPy synthesis providing the increase of corrosion resistance of iron, as demonstrated in our earlier study

on the complex optimization procedure of the PPy polymerization process on Fe [17].

The construction of working electrodes allowed obtaining reproducible electrode surface after grinding and polishing processes. The iron electrodes were mechanically polished with abrasive papers: 220, 500, 1200 SiC grade, respectively, rinsed with ethanol and dried. After the experiments, the samples were rinsed with distilled water and dried (for approximately one minute in a warm air stream).

The coating process and cyclic voltammetry measurements were performed in a one-compartment cell with a three electrode system controlled by the potentiostat VersaSTAT 4. The working electrode for these measurements was an iron sheet (36 mm^2) surrounded by epoxy resin with lead attached at the one side of the electrode. An Ag/AgCl electrode in 3 M KCl solution was used as a reference electrode and a platinum sheet (10 mm × 10 mm) as a counter electrode. Impedance measurements were carried out in a 2-electrode system controlled by Gamry Instrument – Interface 1000. Because the resistance measured in-situ is a combination of polymer resistance, the supporting electrolyte and the double layer capacitance [30,34,45], here the impedance measurements were conducted in the air. A working electrode (Fe double-band) for this measurement was prepared based on description provided by Kankare and Kupila [46]. Such electrode consists of two separated iron sheets (each with dimension of 18 mm × 1.5 mm) with a gap between the sheets of 80 μm. All surrounded by epoxy resin with leads attached to each iron sheet. The construction of a double-band electrode allows for resistance measurements of a polymer film deposited between the iron sheets.

The cyclic voltammetry measurements of the PPy coated Fe electrodes were performed in monomer free aqueous solution of 0.1, 0.05, 0.02, 0.01, 0.005, 0.003, 0.002 or 0.001 M sodium salicylate in different potential windows (from −1.2 to 1.2 V, from 1.2 to −1.2 V, from −0.6 to 0.3 V and from −0.9 to 0.9 V) vs. Ag/AgCl with a scan rate of 10 mV s^{-1} (5 or 100 cycles). The resistance measurements were based on impedance measurements which were performed in the air at frequency range of 10 kHz–0.01 Hz with an amplitude of 20 mV (Gamry – Interface 1000) without DC bias. Determination of the polymer resistance from the impedance spectra was performed at frequency of 10 Hz (it is the impedance value for which the phase angle is 0°, and therefore, the modulus of impedance was assumed to be resistance of the polymer film) [34,45]. Because the resistance of the conducting polymer film is dependent on its dry state [45], each sample was measured at the same condition (after the polymer deposition, each sample was immediately removed from the solution, dried in a warm air stream for approximately one minute and then the impedance was measured). In order to determine the relation between the resistance of the PPy film and the electrode potential, the impedance measurements were conducted in air, periodically with the doping/dedoping processes. For this purpose, the polymer film was gradually re-oxidized (doped) (from −0.9 to 0.9 V) and reduced (dedoped) (from 0.9 to −0.9 V) during linear sweep voltammetry in 0.01 M sodium salicylate aqueous solution with the scan rate of 10 mV s^{-1}. More details about the method of polypyrrole resistance determination can be found in our earlier work [45].

3. Results and discussion

3.1. Electroactivity and stability of optimized PPy coatings on Fe

The redox properties (electrochemical activity) of the polypyrrole (PPy) film on iron were investigated by applying different parameters of the cyclic voltammetry measurements in our previous study [34]. It was shown that PPy films subjected to a