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1-Pyrrolyl-10-decylammoniumphosphonate monolayer: a molecular nanolink between electropolymerized pyrrole films and nickel or titanium surfaces

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Among the various conducting polymers, polypyrrole (PPy) is one of the most studied systems for electrochemical synthesis on active metals due to its interesting properties (low oxidation potential, corrosion resistance and biocompatibility). The present work investigates the electropolymerization of pyrrole (Py) on Ni and Ti substrates modified with 1-pyrrolyl-10-decylammoniumphosphonate (PyDPA) (graphical abstract). The self-assembled monolayers (SAMs) of PyDPA improve the corrosion resistance of Ni and Ti and the adherence of the PPy films. The characteristics of the electropolymerized Py films on the PyDPA SAMs appear to be significantly dependent on the nature of the underlying modified substrate (Ni or Ti). A faster electropolymerization process with longer and more stable polymer chains is obtained in the case of Ni, while a slower electropolymerization process due to an incomplete nucleation step (after 30 min in potentiostatic conditions) is observed for Ti modified by PyDPA.

1. Introduction

Since their discovery, conducting polymers [1] constitute a widely studied topic due to their potential applications in sensors [2–5], protection against corrosion [6–9], battery [10–12], catalysis [13], electromagnetic shielding [14–16] or electrochromic devices [17–19].

It is known that the formation of a conducting polymer film on a metal support depends on the conditions of the electropolymerization process (temperature, current density, potential), composition of the electrolyte (anions, cations, solvent) and nature of the metal support [13,20–22]. At the beginning, such conducting polymer layers have been formed on noble metals, Pt [23,24] and Au [5,23,25] in particular. Later, this has been transposed to active metals such as Al [26–28], Ti [23,29–31], Ni [32–34], Cu [23], Fe [23,35], Zn [36], steel [23,37] due to their much wider applications as well as their lower cost. Electrodeposition on active metal is challenging because of the competition between the oxidation of the monomer and the metal.

In this context, pyrrole is of particular interest due to its relatively low oxidation potential (~ 0.8 V/SCE), effectiveness to act as a corrosion inhibitor [8,32,34,37], biocompatibility [29,38–41] and potential implication in biomedical applications [29,38–40,42,43]. The corrosion inhibition provided by conducting polymer is due to barrier protection but also to passivating oxide layer produced by the oxidation of metal by the conducting polymer (which changed to under its reduced form) due to galvanic coupling [44,45]. Nevertheless, this galvanic coupling can also lead to excessive oxidation and enhanced corrosion [46] especially in presence of defects within the conducting polymer coating [45].

However, for numerous active metals the oxidation potential is reached before the start of the pyrrole electropolymerization. Hence, surface treatments must be carried out first to prevent corrosion during the pyrrole electropolymerization. An attractive way to inhibit/control the metal corrosion is its modification by self-assembled monolayer (SAM) [47–50]. Furthermore, in the present work, a SAM with a pyrrole terminal function is expected to enhance the electropolymerized pyrrole film adhesion [31,51–53]. Indeed, functionalized phosphonic acids [52–54], silane [31,51,55,56] and thiol [32] have already been used successfully as adhesion promoter for conducting polymer.

The nature of the anchoring group leading to the SAM formation on the substrate is a critical parameter not only to achieve a strongly bonded SAM but also to improve corrosion inhibition. A wide variety of anchoring groups have been successfully used to bind metal oxide surfaces: thiols [57–59], carboxylic acids [47,50,60–63], silanes [50,64] and phosphonic acids [50,60,62,63,65–68]. Thiols grafting requires a metal in its reduced

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form [57,58] and is therefore unsuitable for oxidizable metals. Carboxylic acids, silanes and phosphonic acids directly graft on the oxide layers. Thanks to their stronger affinity and better stability, phosphonic acids based chains are usually more efficient than their carboxylic [50,60–63] and silane [50,64,69] analogs. 1-Pyrrolyl-10-decylammoniumphosphonate (PyDPA) has been preferred here to minimize degradations of the surface oxide layer the phosphonic acids could cause. In another context, phosphonate based SAMs have indeed been shown to lead to good corrosion resistance and grafting quality [70].

Among oxidizable metals, Ni is of a great interest due to its wide applications in areas such as batteries [71], catalysis [72], alloys [73], biomaterials [74], etc. Furthermore, despite its recognized cytotoxicity [75], Ni is one of the two elements composing Nitinol (NiTi), an important shape-memory alloy in the biomedical field [74,76]. Hence, Ni corrosion inhibition is critical to prevent Ni ions release from NiTi and improve its biocompatibility. Ti, the other constituent of NiTi, is predominant at the surface of NiTi [74,77–79] and is also used in various biomedical applications [80–82] such as in cardiovascular [74,83–86] and orthopaedic fields [76,74,87–90]. Considering the fact that Ni is a problematic element in biological applications and Ti the major surface constituent of NiTi, Ni and Ti surfaces have been chosen in this study which focuses on the enhancement Ni and Ti corrosion resistance while imparting biologically active surface functions through polypyrrole electropolymerization on PyDPA modified surfaces (graphical abstract).

2. Experimental Part

2.1. Chemicals

All reagents used for the synthesis of the PyDPA were purchased from Sigma-Aldrich: pyrrole (98%), 1,10-dibromodecane (95%), dry sodium hydride (95%), citric acid (99+%), tristrimethylsilyl phosphite (98%), ammonium hydroxide solution (30%), diethylether, acetone and dimethylformamide (DMF). Pyrrole was distilled before use, DMF dried on 4 Å molecular sieves while all the other reagents and solvents were used without further purification. Absolute ethanol was purchased from VWR Prolabo.

Lithium perchlorate (Acros, 99%), sodium chloride (Fluka, ≥99,5%), sodium hydroxide (Acros, purum pellets) and acetonitrile (Chem-Lab HPLC grade) were used for the electrochemical characterizations. All aqueous solutions were prepared with ultra-pure milli-Q water (18.2 MΩ.cm).

2.2. Synthesis of the 1-Pyrrolyl-10-decylammoniumphosphonate

The synthesis of the 1-pyrrolyl-10-decanephosphonic acid has been reported previously [91]. The conditions were adapted to form 1-pyrrolyl-10-decylammoniumphosphonate (PyDPA) by recrystallization in a 1 M NH_3 solution in methanol. PyDPA was obtained with an overall yield of 35%.

2.3. Substrates preparations

Ni substrates, purchased from Goodfellow (99.99% temper as rolled), were cut into $15 \times 10 \times 1$ mm^3 rectangular coupons. They were first mechanically polished down to 1 μm on a Buehler Phoenix 4000 instrument, using silicon carbide papers (P1200) and diamond pastes (9, 3 and 1 μm) from Struers.

Ti substrates, purchased from Advent (99.98%), were cut into $15 \times 10 \times 1$ mm^3 rectangular coupons. They were first mechanically polished down to 9 μm using silicon carbide papers (P1200) and diamond paste of 9 μm. Coupons were then etched down to 0.02 μm using a 4/1 v/v mixture of colloidal silica polishing suspension and hydrogen peroxide (Fluka, 30%).

The Ni and Ti plates were then cleaned in absolute ethanol under ultrasonication for 15 min before being blown dry under nitrogen and stored before use or analysis. Just before their modifications the substrates were further cleaned in absolute ethanol under ultrasonication for 15 min, blown dry under nitrogen, submitted to UV-ozone for 30 min (Jelight 42-220), and ultrasonically treated in absolute ethanol for 15 min, before being blown dry under nitrogen and used for analysis or modification.

2.4. SAM formation of PyDPA on Ni and Ti

The PyDPA monolayers are formed by immersion of the substrate (Ni and Ti) in a 1 mM of PyDPA aqueous solution at 90 °C during various modifications time (4, 8 and 16 h) for Ni and 8 h for Ti. These modified substrates, referred to as Ni|PyDPA and Ti|PyDPA in the sequel, are rinsed copiously with ethanol, cleaned by sonication 15 minutes in the same solvent, blown dry in a nitrogen flow before characterization or pyrrole electropolymerization.

2.5. Electropolymerization of pyrrole on modified and bare Ni and Ti

Electropolymerization of pyrrole is carried out by cyclic voltammetry and chronoamperometry in a three electrodes electrochemical setup including a saturated calomel electrode (SCE) as reference electrode, a platinum foil as the counter electrode and Ni, Ti, Ni|PyDPA or Ti|PyDPA as working electrode. The electrochemical medium is acetonitrile containing 0.1 M $LiClO_4$ and 10 mM of pyrrole. Cyclic voltammetry is carried out by sweeping the potential from -1 V to 1 V at 50 mV/s during 10 cycles. Chronoamperometry is performed by applying a potential of 1 V during 1800 s. After pyrrole electropolymerization the substrates modified with PyDPA, referred to as Ni|PyDPA|PPy and Ti|PyDPA|PPy in the sequel, are cleaned by sonication 15 min in ethanol, blown dry in a nitrogen flow and then characterized. Due to their lack of adhesion under sonication, the pyrrole electropolymerized films on the bare substrates (referred to as Ni|PPy and Ti|PPy) are just copiously rinsed with ethanol.

2.6. Substrates characterizations

The modified substrates were characterized by X-ray photoelectron spectroscopy (XPS), infrared spectroscopy, cyclic voltammetry (CV), linear sweep voltammetry (LSV), water static contact angle measurements, scanning electron microscope (SEM), and a standardized peeling test (ASTM D3359).

XPS is used to study the elemental composition of the modified substrates. The spectra have been recorded on a SSX-100 spectrometer using the monochromatized X-ray Al Kα radiation (1486.6 eV), the photoemitted electrons being collected at 35° take-off angle. Nominal resolution was measured as full width at half-maximum of 1.0 and 1.5 eV for core levels and survey spectra, respectively. The binding energy of core levels was calibrated against the C 1s binding energy set at 285.0 eV, an energy characteristic of alkyl moieties. Peaks were analysed using mixed Gaussian-Lorentzian curves (80% of Gaussian character), the relative peak areas being measured on core levels spectra. Quantitative XPS analyses were carried out by calculating the relevant abundance ratios on the basis of the analysis of the core levels spectra and taking into account the corresponding Scofield sensitivity factors (SF). Sensitivity factor values used for the different atoms are: C_{1s} 1.00, O_{1s} 2.49, Ni_{2p} 14.04, Ti_{2p1} 2.41, Ti_{2p3} 4.69, P_{2p} 1.29, and N_{1s} 1.68.

Polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) data were collected from a Bruker Equinox55