Study on thiolation of polyaniline with 2-mercaptoethanol in HCl and KCl at constant potential

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ABSTRACT

Thiolation of polyaniline (PANI) films with 2-mercaptoethanol was studied by cyclic voltammetry (CV) and chronoamperometry (CA). The sulfur content in the PANI films thiolated in acidic and neutral conditions at different applied potentials was used as the measure of the degree of thiolation. FTIR spectroscopy was used to study the changes in the PANI structure after thiolation. The thiolation experiments were performed in 1.0 M HCl and 0.1 M KCl with three different thiol concentrations. Thiolation provides an easy and straight-forward method to bind covalently molecules, even biomolecules to the PANI backbone. Optimization of the thiolation conditions is the key issue when designing PANI-based biosensors. The results show that with the CA technique it is possible to bind thiolated molecules on PANI both in HCl and in KCl. Furthermore, the results indicate that the potential applied, the thiolation medium and the concentration of the added thiol affect the thiolation process. CA offers an opportunity to enhance the thiolation allowing to some extent also to control the entire process opening up new possibilities to prepare PANI based biosensor substrates.

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1. Introduction

It is possible to functionalize polyaniline, an electrically conducting polymer, by adding molecules to its backbone [1,2]. Functionalization offers a possibility to change the properties of PANI, e.g. to overcome the pH sensitivity of PANI or to increase its solubility [3], but this is often gained in the expense of lower electroactivity compared with unmodified PANI. Functionalized PANI has also different chemical properties than unmodified PANI and therefore it is important to characterize these new materials properly. Functionalization would also enable covalent binding of ion-selective groups to PANI. Thiol molecules, even thiolated biomolecules, can easily bind to PANI. They bind to the aromatic ring creating substituted PANI [4–12]. Thiolation takes place when PANI is in the conducting, emeraldine salt or in the non-conducting emeraldine base or pernigraniline forms [4–8,11,12]. Thiolation of PANI with 2-mercaptoethanol (MCE) has intensively been studied in our group and the reaction mechanism was also proposed [4,5].

The thiolation reaction to take place was verified by using several analytical techniques, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), ex situ FTIR and Raman spectroscopies, X-ray photoelectron spectroscopy (XPS) as well as elemental analysis. Thiol groups break the conjugation of PANI and the backbone will partially become reduced. Therefore, thiolation partially decreases the electroactivity of PANI and extensive thiolation leads even to a complete electroinactive material. Thiolation, however, is a lucrative way to bind molecules to PANI and the method can be used to generate substrates for biosensor, e.g. potentiometric biosensors where even modest conductivity is sufficient. PANI can be used to create stable, disposable, cheap and easy-to-make sensor substrates. The rough, porous and uneven layer of electrochemically synthesized PANI on a metal surface gives, however, very different properties compared with those substrates with metal layers of smooth surface. Therefore it is important to study how the surface immobilized thiols affect the electrochemical properties of PANI and whether it is even possible to control the thiolation process. Optimization of the thiolation conditions is very important in applications where PANI is used as the substrate of a biosensor.

We have earlier studied thiolation of PANI with 2-mercaptoethanol by immersion and potential cycling, which creates a thiol surface on top of the PANI substrate [5]. The degree of thiolation is difficult to control with the immersion technique and the time

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needed for proper thiolation is also relatively long. Thiolation can also be performed by chronoamperometric technique (CA). In this work we will study thiolation by CA in 1.0 M HCl and 0.1 M KCl because it would allow an easier control of the thiolation process than when it is done by the direct immersion technique.

2. Experimental

2.1. Chemicals

Aniline was obtained from Sigma-Aldrich and distilled before use. HCl was obtained from J. T. Baker and diluted with deionized water to the desired concentration. KCl was purchased from J.T. Baker and dissolved in deionized water and diluted with it to the desired concentration. 2-Mercaptoethanol (MCE) was purchased from Aldrich and used as received. Deionized water (resistivity ca. 18 MΩ·cm) was used throughout this work.

2.2. Cyclic voltammetry

The experiments were done by using glassy carbon (GC) disc ($A = 0.077$ cm^2) in a polytetrafluoroethylene (PTFE) body as the working electrode (WE) in a three-electrode cell. Prior to electropolymerization, the GC disc electrodes were polished with 400/600, 1200 and 4000 dpi sandpaper, with 1 μm diamond paste and finally with 0.3 μm Al$_2$O$_3$ powder, sonicated, rinsed with deionized water and dried. A GC rod served as the counter electrode (CE) and a Ag|AgCl|3 M KCl as the reference electrode (RE) (Metrohm). The potential was controlled with an Autolab potentiostat (PGSTAT20 or PGSTAT100) using the GPES software. Prior to all measurements, the solutions were purged with nitrogen and during the measurements nitrogen was passed over the solutions.

Electropolymerization of 0.5 M aniline was done in 1.0 M HCl by cycling the potential between −0.15 V and 0.74 V for 50 cycles at a scan rate of 50 mV s^{-1}. The polymerization process was initiated by holding the potential first at 0.85 V for 10 s before starting the potential cycling. By performing the electropolymerization in this way we can avoid the second oxidation/reduction transition of polyaniline (emeraldine to pernigraniline). This transition is known to destroy, at least partly, the electroactivity of the film. After polymerization, the films were characterized within the same potential interval in a monomer-free 1.0 M HCl solution by cycling the film 5 times (scan rate 50 mV s^{-1}, the 5th cycle is shown).

Aniline films for CHNS-analysis were prepared on SnO$_2$-glass electrodes (TO-glass, Lasiluoto Oy, Finland) on a surface of approximately 1.6 cm^2. The electropolymerization of 0.5 M aniline in 1.0 M HCl was done by cycling the potential between −0.3 V and 0.825 V 50 times with a scan rate of 50 mV s^{-1}. The polymerization process was initiated also in this case by holding the potential at 0.825 V for 10 s before starting the potential cycling. An Autolab potentiostat (PGSTAT20) using the Nova 2.0.2 software was used to control the potential. The TO-glass electrodes were washed by detergent, rinsed with copious amounts of deionized water, sonicated and at last rinsed with acetone before use.

2.3. Chronoamperometry

The CA measurements were performed at six different potentials (0 V, 0.2 V, 0.4 V, 0.5 V, 0.6 V and 0.7 V) in 1.0 M HCl and in 0.1 M KCl for 1800s in both electrolytes. In 0.1 M KCl the thiolation experiment was also performed at −0.15 V. The chronoamperometric measurements were performed in the following sequence: first the current response of the PANI film at each potential value studied without any added thiol was measured for 1800s both in 1.0 M HCl and in 0.1 M KCl to determine the background current. Second, the film was reduced at −0.15 V for 600 s without any added thiol in order to transform the film into the so called zero-current form, i.e. reduced state. This was done as a pretreatment step for the CA experiments. Third, the current response of the PANI film was measured at the selected potentials for 1800s but in this case the thiol was added at 400 s after the start of the experiment. In this thiolation experiment a given amount of MCE (to make the solution 0.05 M, 0.1 M or 0.2 M in respect to MCE) was added to the solution of the experiment (1.0 M HCl or 0.1 M KCl). During the experiment the solution under study was slowly stirred to ensure that the thiol was evenly spread in the solution and not depleted at the electrode surface. After the thiolation process the electrode was immediately removed from the thiol solution and rinsed with copious amount of water to remove any unbound thiols. The film was then reduced for 600 s at −0.15 V and a CV was recorded in thiol free 1.0 M HCl in order to study the effect of thiolation to the electroactivity of PANI.

For the thiolation of the PANI films on TO-glass electrodes the films were prepared the same way as the films on the glassy carbon surface. The only difference is that prior the CA experiments they were first reduced at −0.15 V for 400 s in order to transform the films into the reduced state and thereafter 0.1 M MCE was added at the same time (at 400 s from the start of the experiment) when the potential of 0.4 V or 0.6 V was applied for 1400s. The CA measurements were done in 1.0 M HCl and in 0.1 M KCl under mild stirring.

2.4. Ex situ FTIR measurements

The ex situ FTIR-ATR spectra were recorded using a Harrick's VideoMVP single reflection diamond ATR accessory (incidence angle 45°) with a horizontal sampling area ($\phi = 500$ μm) and a built-in pressure applicator. Small pieces of the PANI films were tightly pressed against the diamond crystal and 32 interferograms were recorded with a resolution of 4 cm^{-1}. The ATR accessory was attached to a Bruker IFS 66S spectrometer equipped with a DTGS detector. In order to convert the non-thiolated PANI film into its conducting ES form the film was oxidized at 0.4 V for 9 min and to convert the film into the non-conducting LE form it was reduced at −0.15 V for 9 min.

2.5. Elemental analysis

The elemental analysis of C, H, N and S was conducted with the Flash 2000 Organic Elemental Analyzer (Thermo Scientific). Four PANI films, which after preparation were stored in a desiccator, were peeled off the TO-glass electrodes, combined and carefully weighed with a microbalance before the analysis. Two parallel determinations, each with four PANI films were done (eight films were used for each analysis at the potentials of the experiments). The sample mass varied between 0.29 mg and 0.67 mg in the analysis.

3. Results and discussion

According to our earlier results both the emeraldine salt (ES) and the emeraldine base (EB) forms of PANI can be thiolated [4,5]. The techniques used in those studies were immersion and potential cycling. The thiolation process was found to be slow, when the film was thiolated by the immersion technique. The thiol molecules attach covalently onto the quinoid rings of PANI and as a consequence break the conjugation. After thiolation the redox peak currents in the CV of PANI decreased and an increase in the current at higher potentials was observed. It was also found that the rate of thiolation could be increased by potential cycling. The changes in the electrochemical properties were also found to be