STUDY OF PROTONATION STATE OF POLYANILINE THIN FILM IN DEPENDENCE ON STORAGE CONDITIONS

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Abstract
Conducting polymers are nowadays in forefront of the interest because of its very good electrical conductivity combined with other beneficial properties. Polyaniline is one of the widely studied conducting polymers due to its light weight, low cost, excellent environmental stability and reversible acid-base switching of its electrical conductivity. This study is focused of polyaniline thin films prepared from anilinium sulfate by its chemical polymerization using ammonium peroxodisulfate. During the polymerization process, polyaniline was deposited on glass slides where it formed thin film. Different polymerization times were used (10, 20, 30 and 40 minutes). Two sets of polyaniline thin films were prepared. The first set was kept in dry in desiccator; the second set was freely exposed to air moisture. Influence of storage to protonation state of polyaniline films was revealed after long time observation. Samples kept in desiccator hold longer its protonation state as well as its color, which is the marker of protonation state. Protonation is also dependent on the polymerizations time, longer polymerization time leads to better protonation of polyaniline film. Raman spectroscopy, which is sensitive to chemical bonds and changes in structure, was used for the characterization of protonation state.

Keywords:
Conducting polymers, polyaniline, Raman spectroscopy, protonation

1. INTRODUCTION
Polyaniline (PANI) is most studied conducting polymer, because of its low cost, easy preparation and very good properties which allows wide field of applications [1]. Two basic forms of PANI are known, the blue pernigraniline form and green emeraldine protonated form [2]. Many applications require thin films (sensors, antistatic, and anticorrosive coatings). Advantage of PANI is also ability to cover any surface in contact with reaction mixture, thickness of the PANI film depends on reaction conditions [3]. This work deals with PANI thin films coated onto glass slides. The possible arrangement of PANI polymer onto the glass slide is shown in Fig. 1.

For the practical utilization, it is very important to know degradation mechanisms and the stability under various conditions, e.g. thermal stability [4]. To characterize protonation state of PANI thin films was used Raman spectroscopy, which provides information about molecular vibrations, which are specific to symmetry of molecules and chemical bonds. Such kind of information is a powerful tool for determine the structural changes in PANI thin films.
The aim of the study was to perform dependence of protonation state of PANI thin films on storage conditions and time of polymerization.

Fig. 1: Optimized atomistic model containing three PANI oligomers anchored on the glass surface.

2. EXPERIMENTAL

2.1 Sample preparation

Simple oxidative chemical polymerization of the solution of aniline in concentrated sulfuric acid by strong oxidizing agent at room temperature was used for preparation PANI thin films. Two solutions: i) aniline solution in sulfuric acid (cationic source), and ii) solution of ammonium persulfate in distilled water (oxidizing agent) were mixed. Polymerization started immediately after the mixing of both solutions, the time of the polymerization was 10, 20, 30 and 40 minutes. PANI thin films were deposited onto the surface of the glass slides by their rinsing into the reaction mixture. Two sets of samples were prepared at same conditions in two independent reaction mixtures. The first set was kept dry in desiccator; the second set was freely exposed to air moisture.

2.2 Raman microspectroscopy

Smart Raman Microscopy System XploRA™ (HORIBA Jobin Yvon, France) was used for measuring Raman spectra. Raman spectra were acquired with 532 nm excitation laser source, 100x objective and using 1200 gr./mm grating in the range from 80 to 2000 cm\(^{-1}\). Spectra of two sets of slides were measured on the day of preparation and next four days each day. Next spectra were measured second, third and fourth week from the preparation and then for one month and six months from the preparation. Before each measurement, the slides were photographed. Each slide was measured in five points (see Fig. 2).

Fig. 2: Measured points on glass slides coated with PANI thin film

3. RESULTS AND DISCUSSION

3.1 Color change of PANI thin films over the time

Each day of measurements were taken photographs of the PANI thin films. Fig. 3 shows photos for both sets of samples of those days: day of preparation, one month and six months from preparation. On the day of preparation the colors of the PANI thin films are same, dark blue for 10 minutes of polymerization and green color for other times of polymerization (20, 30 and 40 minutes). Colors correspond to protonation state of PANI thin film, blue belongs to deprotonation state and green to protonation state, which confirm Raman spectroscopy (see chapter 3.2 Raman spectra of PANI thin films). Thus, 10 minutes of polymerization was not sufficient time for creation protonated PANI thin film. Color changes were occurred over the time, which were more noticeable for PANI thin films kept in air moisture (see Fig. 3). An interesting thing appears in
slides of polymerization time 10 minutes, blue color of this slide became lighter, which could be probably caused by ongoing protonation (see chapter 3.2).

3.2 Raman spectra of PANI thin films

Two sets of samples were prepared in two reaction mixtures at same conditions, as you can see at Fig. 4 - A PANI thin film with time of polymerization 20, 30 and 40 minutes had same spectra. Contrary to spectrum of PANI thin film with time of polymerization 10 minutes, which is different. The two reaction mixtures produced two identical sets of samples, which confirm Fig. 4 – B, C.

Fig. 3: Photographs of PANI thin films kept in desiccator A - day of preparation, B - one month from preparation, C - six months from preparation, and photographs of PANI thin films kept in air moisture D - day of preparation, E - one month from preparation, F - six months from preparation.

Fig. 4: A - Raman spectra of one set PANI thin films with different time of polymerization (10, 20, 30 a 40 minutes), B – comparison of two slides from two sets with time of polymerization 10 minutes, C – comparison of two slides from two sets with time of polymerization 20 minutes.
Raman spectra measured at five separated points (see Fig. 2) was identical at the day of preparation. Characteristic PANI vibrations (Fig. 4) are at 1610 cm\(^{-1}\) (stretching mode in the phenyl rings), 1587 cm\(^{-1}\) (C=C stretching vibration in quinone), 1503 cm\(^{-1}\) (stretching C=N and C=C in quinone), 1400 cm\(^{-1}\) (protonated oxazine like units and stretching vibration of C-C in quinone), 1322 cm\(^{-1}\) (stretching vibration of C-N\(^+\)), 1253 cm\(^{-1}\) (C-N stretching vibration of benzene, quinone and polaronic forms), 1161 cm\(^{-1}\) (C-H bending vibration of semiquinone rings), 803 cm\(^{-1}\) (benzene ring deformations), 412 and 506 cm\(^{-1}\) (out-of-plane deformations of the ring)\(^\text{[5-11]}\). Very strong band at 1496 cm\(^{-1}\) (C=N)\(^\text{[11]}\) and low intensity of band at 1321 cm\(^{-1}\) (C-N\(^+\))\(^\text{[6]}\) are the biggest differences between the spectrum with time of polymerization 10 minutes and spectra with higher time of polymerization. Spectrum with 10 minutes of polymerization contains also bands at 1410 and 570 cm\(^{-1}\), which correspond to “cross-linking” and phenazine structures\(^\text{[6,8]}\) and broad structural band at 760 cm\(^{-1}\) belongs to deformation vibrations of substituted aromatic rings\(^\text{[10]}\). These findings demonstrate presence of deprotonated form of PANI, which confirm blue color of PANI thin film (see Fig. 3).

All samples were measured over the time (see chapter 2.2). Regarding the measurement of each day in the first week of preparation, for both sets of samples there has been no significant changes. Therefore the results are not listed. To demonstrate what changes occurred in samples were selected slide with time of polymerization 20 minutes (Fig. 5), because slides with times of polymerization 30 and 40 minutes had similar findings and deprotonated PANI form (10 minutes of polymerization) is discussed further.

Samples kept in a desiccator show no significant changes over the time (Fig. 5 - A). Contrary to, the samples kept in air moisture show significant changes (Fig. 5 - B). Intensity of band at 1503 cm\(^{-1}\) (C=N and C=C in quinone) increases and the intensity of band at 1322 cm\(^{-1}\) (C-N\(^+\)) decreases with time. Also the band at 803 cm\(^{-1}\) (benzene ring deformations) becomes wider and structured. These changes are caused by loss of protonated quinones.

Fig. 5: A - Raman spectra of PANI thin films kept in desiccator with time of polymerization 20 minutes measured in day of preparation (1d), second week (2w), third week (3w), fourth week (4w), one month (1m) and six months (6m) from the preparation, B - Raman spectra of PANI thin films kept in air moisture with time of polymerization 20 minutes measured in day of preparation (1d), second week (2w), third week (3w), fourth week (4w), one month (1m) and six months (6m) from the preparation.
As has been already mentioned color of PANI thin film with time of polymerization 10 minutes become lighter, which corresponds to changes at Raman spectra (see Fig. 6). Possible explanation could be slow ongoing protonation of the sample over the time. This is reflected by loss of intensity of band at 1503 cm\(^{-1}\) (C=N and C=C in quinone) and rise intensity of band at 1322 cm\(^{-1}\) (C-N\(^+\)). This changes also pass over at PANI thin film (time of polymerization 10 minutes) kept in air moisture, but the changes are less significant and PANI thin film still stay in deprotonated form, therefore the spectra are not show here. As well as the changes did not pass over homogeneously. Because the spectra from five separated measured points (see Fig. 2) are not same, differ in ratio of intensities in discussed bands.

![Fig. 6: Raman spectra of PANI thin film coated on glass slide during 10 minutes and kept in desiccator measured in day of preparation (1d), second week (2w), third week (3w), fourth week (4w), one month (1m) and six months (6m) from the preparation.](image)

4. **CONCLUSIONS**

Preparation in same conditions at two reaction mixtures gave PANI thin films with same protonation state, which confirm Raman spectroscopy. Protonation state of PANI thin film was influenced by time of polymerization. Polymerization in 10 minutes was not sufficient to produce protonated form of PANI. Other times (20, 30 and 40 minutes) were sufficient to create protonated PANI thin film. Protonation state was clearly visible also at photographs of PANI thin films, where blue color corresponds to deprotonated form and green to protonated form of PANI.

Set of PANI thin films kept in desiccator were more stable than PANI thin films kept in air moisture as evidenced by Raman spectroscopy as well as photographs of PANI thin films. For one week after the preparation PANI thin films with time of polymerization 20, 30 and 40 minutes stay stabile regardless of the storage method.

Samples kept in air moisture exhibit significant changes of intensities at characteristic Raman bands for protonation state, which proved conversion to deprotonated form of PANI thin film. For samples kept in desiccator no significant change of protonation state was observed.

Raman spectroscopy revealed a possible small ongoing protonation of sample PANI thin film with time of polymerization 10 minutes, which was detected at both samples (kept in desiccator and in air moisture). For the sample kept in desiccator were these changes more significant.
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LITERATURE


