

Short communication

Electrochemically deposited polyethyleneimine films and their characterization

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ABSTRACT

Polyethyleneimine films have been deposited on platinum electrode surfaces by electrochemical oxidation of ethylenediamine $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ (EDA) in acetonitrile solutions. This electrochemical synthesis was realized by cyclic voltammetry and gravimetry techniques. Then, the characterization of the thin solid polyethyleneimine film was performed using X-ray photoelectron spectroscopy and infrared spectroscopy. It was also shown, using atomic force microscopy, that the solid polymeric coating has a granular and homogeneous structure. The influence of EDA concentration on the electropolymerization process was studied leading to the conclusion that the reaction is easier for high EDA concentration. Then, the influence of the nature and concentration of the supporting salt was investigated, showing that its nature is not very important, contrary to its concentration.

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1. Introduction

Polyethyleneimine is a polymer containing amino groups and existing in two forms. Linear polyethyleneimine, L-PEI, contains only secondary amines and is made of $-(\text{CH}_2-\text{CH}_2-\text{NH})-$ repeating units, in contrast to branched polyethyleneimine, B-PEI, which contains primary, secondary and tertiary amino groups. The linear polyethyleneimine is solid at room temperature where branched polyethyleneimine is liquid at all molecular weights.

B-PEI, which has been produced since the early 1940s by acid-catalyzed aziridine-based aqueous solutions, is a very frequently used polymer for applications as chelating agent for heavy metals removal or retention [1–3], as copolymer in solid polymeric electrolyte for electrical energy storage devices [4–6], as non-viral vector for gene transfection [7–9], as adhesion promoter in cell culture [10] and as active layer of (bio)sensors [11–13].

L-PEI was first synthesized by chemical route in 1970 by Dick and Ham [14]. This polymer can be obtained by the cationic polymerization of 2-substituted-2-oxazolines [15] or by aqueous polymerization of aziridine [16]. However, we have recently shown that the anodic oxidation of pure ethylenediamine-based electrolytes yields L-PEI polymer films on metallic or semi-conducting electrode surfaces [17]. However, this latter synthesis is not easy

since it needs the use of pure EDA ($\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$) and consequently must be done in a glove box under a dehydrated atmosphere. That is why, it seems interesting to develop a new way to synthesize L-PEI from an electrolyte containing a small amount of EDA dissolved in an organic solvent.

But, looking at the literature, such a synthesis seems difficult to realize since other works dedicated to the oxidation of amines in organic solvents led to the formation of a monolayer on the electrode surface and not to a polymer. Indeed, before this study, the electrochemical oxidation of aliphatic primary, secondary and tertiary amines has been investigated in acetonitrile solutions on glassy carbon, Au and Pt surfaces by cyclic voltammetry, X-ray photoelectron spectroscopy and infrared reflection-absorption spectroscopy but no electropolymerization occurred. In fact, it was only possible to show that the amine led to a radical cation, then to a radical, obtained after deprotonation, which reacts with the electrode surface, leading first to the creation of a covalent bond between carbon, Au or Pt and the organic radical, and second to a monolayer of oxidized EDA molecules bonded to the electrode by both nitrogen atoms [18–21].

However, in this work, the electrochemical oxidation of ethylenediamine (EDA) in acetonitrile solutions was studied and the conditions leading to linear polyethyleneimine were determined, showing that it is possible to electropolymerize amines in organic solvents such as acetonitrile. Then, the synthesized coatings were characterized using X-ray photoelectron spectroscopy and infrared spectroscopy, and imaged by atomic force microscopy.

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Finally, different parameters (concentration in EDA, presence, nature and concentration of a supporting salt) that could influence the oxidation of both types of EDA solutions were also tested.

2. Materials and methods

2.1. Electrochemistry

All cyclic voltammetry analysis experiments were performed using an Autolab, model PGSTAT 20 (Ecochemie, The Netherlands), controlled by a PC computer via a GPES software interface. The electrochemical cell consisted of a classic three-electrode setting with an Ag wire as pseudo-reference electrode, a platinum disk as the counter electrode and a smooth platinum electrode (0.785 mm² area) as the working electrode. The Electrochemical Quartz Crystal Microbalance (EQCM) from Maxtek-USA, model PM 710 using AT-cut 5 MHz platinum-plated quartz as the working electrode (1.37 cm²), was coupled to cyclic voltammetry measurements. All electrochemical experiments were carried out at room temperature (293 K). Ethylenediamine, LiClO₄, LiCF₃SO₃, LiNO₃, NaBF₄ and KBF₄ were from Sigma–Aldrich.

2.2. XPS

The polymer surface was characterized by X-ray photoelectron spectroscopy (XPS, Thermo VG spectrometer). XPS was used to control elemental composition and to determine the oxidation state of elements. All spectra were recorded at a 45° take-off angle relative to the substrate with a spectrometer using the monochromatized Al K_α radiation (1486.6 eV). The binding energies of the core-levels were calibrated against the C_{1s} binding energy set at 285.0 eV, an energy characteristic of alkyl moieties. The peaks were analyzed using mixed Gaussian–Lorentzian curves (80% of Gaussian character).

2.3. AFM

Examinations of polymer topographies and morphologies were performed by an atomic force microscope (AFM PicoSPM from Molecular Imaging, USA), in contact mode with gold coated Si₃N₄ tip (200 μm-long triangular cantilever and 0.1 N/m force constant).

2.4. Infrared spectroscopy

The spectroscopic study was done with glass substrates previously coated first with a thin layer of Ti/Pt, and second with the oxidized EDA film obtained by electrochemistry. A magnetron sputtering (Alcatel SCM 441 apparatus) was used to coat glass substrates with titanium (30 nm, used to improve platinum layer), then plat-

inum (150 nm). The fabrication parameters for Pt and Ti films were the following ones: base pressure: 4.6×10^{-7} mbar, pressure (Ar) during sputtering: 5×10^{-3} mbar, power: 150 W, target material purity: 99.99%, film thickness: 150 nm for Pt films and 30 nm for Ti films.

Polarization Modulation-Infrared Reflection Absorption (PM-IRRAS) spectra were recorded using a Bruker IFS 66 S with a Bruker PMA 37 polarization modulator. The same spectrometer was used, with a Bruker SpectraTech Baseline DRIFT module, for doing DRIFT (Diffuse Reflectance Infrared Fourier Transform) spectra. PM-IRRAS spectra were recorded between 4500 and 750 cm⁻¹, when DRIFT spectra were recorded between 4000 and 650 cm⁻¹.

3. Results and discussion

3.1. Electrochemical oxidation of ethylenediamine

Electrochemical oxidation of acetonitrile solutions containing 0.1 M ethylenediamine and 0.1 M LiClO₄ was performed by cyclic voltammetry on a platinum microelectrode. The resulting figure (Fig. 1a) exhibits an oxidation peak at +1.9 V/Ag, corresponding to the oxidation of the terminal amino groups of ethylenediamine. The peak location and its broadness are characteristic of the oxidation of primary aliphatic amines but renders the experimental study of the electrochemical mechanism impossible. However, since EDA contains two amino groups in its molecular structure, it can easily be oxidized at a positive potential to produce cationic radicals and further reacts with other monomers to form linear polyethyleneimine from EDA. The mechanism of this electropolymerization is probably similar to the one established for the electropolymerization of pure EDA in L-PEI using ab initio calculations at the Hartree–Fock level of theory [22,23]. For subsequent scans, there is a drastic drop of current and all the peaks disappear. So the anodic oxidation of EDA in acetonitrile leads to the formation of a passivating film at the electrode surface.

Electrochemical Quartz Crystal Microbalance was also coupled to cyclic voltammetry since EQCM allowed us to access, through measurements of the quartz's frequency changes and according to the Sauerbrey's equation [24], to the deposited mass as a function of oxidation time. Thus, the gravimetric curve obtained during the oxidation of EDA (Fig. 1b) shows that as soon as the intensity increases, the mass at the platinum-coated quartz electrode increases too, leading to an important deposited mass during the 1st scan of oxidation. For subsequent scans, there is a drastic drop of current and consequently the deposited mass still increases but slower. By using the Sauerbrey equation [24], the deposited mass was evaluated to 4.07 μg cm⁻². This deposited mass corresponds to a coating thickness of 27 nm, assuming a polymer density of 1.5 g cm⁻³.

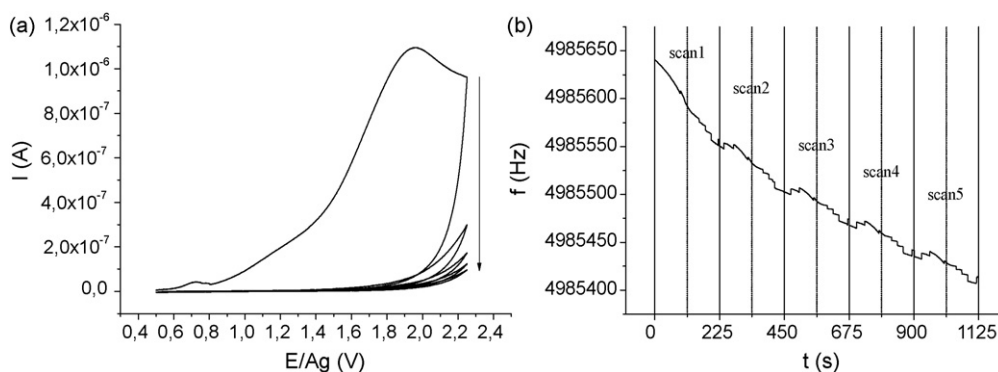


Fig. 1. Cyclic voltammogram (a) and gravimetric curve (b) at a platinum electrode of acetonitrile solution containing 0.1 M EDA and 0.1 M LiClO₄ M. Scan rate: 20 mV/s.

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