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Matrix rank analysis of spectral studies on the electropolymerisation and discharge process of conducting polypyrrole/dodecyl sulfate films

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Abstract

The polymerisation of pyrrole in aqueous sodium dodecyl sulfate (SDS) solution was studied systematically by in situ spectroelectrochemical technique including the optical changes during the reduction of the freshly prepared film. In order to determine the number of species formed during the anodic oxidation, the spectra registered during the deposition and the electrochemical reduction were evaluated by matrix rank analysis (MRA). This treatment of the data led to the conclusion that the spectral changes can be interpreted only by assuming five independent absorbing species, which could be uniformly detected during both the regular and irregular reduction reported in our recent work. The results were completed by a study on the pH and SDS concentration dependence of the solution phase oligomerisation during the chemical 'aging' of the monomer solution, which leads to a product absorbing also in the visible range. On the basis of the observations, the two extra species found beyond the neutral, monocationic and dicationic species were identified as a protonated neutral segment and its oxidized form.

Keywords: Electropolymerisation; Pyrrole; UV–vis spectroelectrochemistry; Matrix rank analysis; Protonation

1. Introduction

Since the discovery of conducting polymers, the mechanism of the electrooxidation and film formation of aromatic compounds has received much attention. In spite of the great amount of work, the description of the process is widely simplified, and authors mainly agree [1] in the very first steps of the overall reaction. According to this generally accepted but frequently critically treated mechanism, the electrochemical polymerisation starts evidently with the oxidation of the monomer, generating cation radicals, followed by radical–radical coupling. The chain propagation takes place according to an ECCE mechanism where protons are eliminated during each second chemical step. The exclusive validity of this simplified polymerisation mechanism was questioned already more than 12 years ago by Qian and Pei [2], who concluded that the polymerisation is based on protonated pyrrole, formed in a reaction of the monomer with the deliberated protons. On the basis of elementary analysis, they assumed the presence of one proton on each third aromatic unit. According to their mechanism, the observation that conducting polypyrrole (PPy) could not be prepared in buffered solutions above pH 7 can be explained. By referring to the results obtained by Diaz and Bargon [3], they interpreted the lack of polymerisation by the proton scavenger inhibition of added nucleophylic pyridine and protophylic di-*tert*-butyl pyridine [4]. Later, the inhibiting effect of Brönsted base on the polymerisation of thiophene was explained by the larger reactivity and consequently smaller selectivity of the neutral radical intermediate formed in the deprotonation of the cation radical [5]. The mixed mechanism through the classical ECCE and the parallel process via protonated forms was assumed to explain the preference of tetrafluoro-borate over perchlorate counter ion present in the polymerisation solution [6].

Modern complementary techniques gave opportunity to find evidences in favour of the occurrence and effect of the in situ protonation of the polymer segments. On the basis of studies on the effect of the electrolyte concentration, Li and Qian concluded the existence of two types of doping places

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in polypyrrole: beside the charge carriers generated along the chains by oxidation, positively charged segments originated from protonation are to be compensated by the doping anions [7]. According to Otero and Rodriguez, the addition of 1% water to AN solutions—found advantageous many years ago [8]—can promote the deprotonation improving this way the quality of the film [9]. They concluded that deliberated protons can reach relatively large concentration in the neighbourhood of the film depending on the composition of the solution, and can initiate chain polymerisation of the monomer molecules in AN, while this parallel process was assumed negligible in solvents of high basicity like water.

Recently, Sadki et al. gave a summary of the reports on the mechanism of the electropolymerisation, and as a conclusion the acidity of the solution was made responsible for the worst quality of the films, which determines also the morphology of the layers [10].

In a series of papers, Heinze and coworkers studied systematically the polymerisation process of pyrrole [11–15]. They demonstrated that even a small change in a single parameter might greatly influence the main properties of the resulting polymer [11]. They concluded that three types of polypyrrole units may co-exist in the layer, and their ratio is mainly determined by the pH value [12]. The form PPy II is a shorter chain which may transform into the ‘classical’ type PPy, and can be distinguished on the basis of its different EQCM behaviour, exhibiting the involvement of cation movement which completes the sorption of less mobile doping anions [15]. PPy III is a partially conjugated segment formed through protonation [12].

Spectroscopy has proven to be a good tool to study the composition of the polymer layers [16], and a combination of spectroelectrochemical results with matrix rank analysis was very useful to determine the number of independent absorbing species (NIAS) in the film [17]. Kurosu et al. found by ^{15}N NMR technique that four types of nitrogen can be distinguished in PPy films [18]. On the basis of the deconvolution of optical spectra, Sharifker and coworkers found also four different bands reflecting the presence of two different oxidized and two neutral forms within the film [19].

In our resent work, the history of the film after the polymerisation was found to be a determining factor of the properties of polypyrrole, and the effect of the open circuit time before the first reduction of the film was found to exert a crucial effect on the further behaviour of the PPy films [20]. The well-known regular pattern of reduction could be observed only if a long enough time was allowed for the film to relax. On the contrary, the lack of relaxation led to irregular behaviour, which could be interpreted by the existence of partially protonated film. On the basis of in situ ac conductance, EQCM and pH measurements [21] the open circuit relaxation was interpreted by the deprotonation and desolvation of the polymer.

The goal of the present work was to determine the number of absorbing species forming during the electropolymerisation of polypyrrole films by matrix rank analysis [22] and to look at the eventual differences in the case of the regular and irregular reductions. In order to be able to interpret the results, optically monitored homogeneous kinetic studies on the monomer solution were also carried out. The effect of the different parameters such as the pH and the SDS concentration on the proton-induced chemical polymerisation was also investigated.

2. Experimental

The monomer solutions were prepared using pyrrole (Sigma), distilled freshly under vacuum and sodium dodecyl sulfate (SDS, Merck). MilliQ water solutions were deaerated by nitrogen flow. For the optical measurements polypyrrole films were deposited galvanostatically at a 3 mA/cm^2 current density and 67.5 mC/cm^2 charge density from a solution of 0.05 M for both the monomer and the SDS. For the ac conductance studies the PPy was prepared potentiostatically for a 3 C/cm^2 charge density.

The electrochemical measurements were done on a PGSTAT 10 (Autolab) instrument. In case of the ac conductance studies the reference signal was a 130 Hz sine wave, and the response of the double band electrode with a gap of 15 μm was measured on a lock-in amplifier (SR 830, Stanford Research Instruments). After the electropolymerisation the films were left to relax [21], and rinsed thoroughly with the solvent.

Spectroelectrochemical studies were carried out in a cell described in [22,23]. The film was deposited onto an indium–tin-oxide (ITO) layer covered glass electrode with a surface area of $A = 0.28$ cm^2. In the three-electrode spectroelectrochemical cell, a gold-plated steel and a silver/silver chloride microelectrode served as counter and reference electrodes, respectively. The spectra were recorded on a HP8452A diode array spectrophotometer in the kinetic mode. Owing to the intensity change of the light source, the acquired spectra were evaluated in the wavelength range between 370 and 770 nm. The spectral measurements were taken typically at each 2 s during the polarisations.

2.1. About the MRA technique

Several methods of the matrix rank analysis exist in the literature to determine the number of independent absorbing species. In [24], the authors developed new algorithms not using any statistical information, but monitoring the experimental information content along the absorbance matrix to get the true NIAS. As the first step, it is supposed that the value of NIAS is n, then we calculate the residual absorbance matrix (RAM$_{n+1}$), which contains the unexplained information belonging to further species. If n absorbing species are not sufficient for describing the primary experimental data within the experimental error, the residual absorbances change systematically along the wavelength range, so that it is needed to suppose that NIAS is at least $(n+1)$. By applying this new condition, a new residual absorbance matrix (RAM$_{n+2}$) is