E1-09: Polyaniline prepared in aqueous media: influence of polymerization current density

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Polyaniline (PANI) is one of the widely studied electronically conducting polymers because of the possibility of using it in technological applications such as electrochromic windows, rechargeable batteries, sensors etc. It has been shown earlier that highly conjugated PANI films can be electrochemically synthesized from non aqueous media using low polymerization current densities. The films synthesized at low current density have a higher conjugation length and a more regular structure than those prepared using higher current densities. In this study an attempt was made to verify whether similar results can be obtained when aqueous media are used and to determine the conditions required to prepare such highly conjugated PANI films from aqueous media. Polyaniline films have been synthesized in aqueous medium by galvanostatic electrochemical polymerization at current densities between 16 and 500μA/cm^2 and their behaviour was investigated using cyclic voltammetry. Also the effect of changing the pH of the electrolyte solutions on the cyclic voltammograms of polyaniline have been studied.

It is necessary to separate the 2 processes of synthesis and characterization in order to work with a well defined system. Since PANI needs to be synthesized in the presence of acid in order to be electrochemically active, all polymer films were synthesized in the same medium: 0.5M Aniline monomer, 2.0M CF_3COOH and 1.0M $LiClO_4$ in distilled water. Based on the experience from the PANI in non aqueous system, the syntheses were performed galvanostatically with current densities ranging from 16 to 500μA/cm^2. The potential relative to a Ag/AgCl reference electrode during synthesis was 0.6V at both current densities. The films were formed on platinum wires of length 1 cm and diameter 0.5mm. After synthesis the films were rinsed in monomer free solution containing salt plus acid. The thickness of the films (usually 0.25μm) was calculated by assuming 240 mC/cm^2 leads to a 1μm film as assumed for polypyrrole.

Cyclie voltammetry was performed on the rinsed films in 0.5M $LiClO_4$ aqueous solution and pH of the solutions were adjusted using CF_3COOH acid.

Because of high potential of polymerization for PANI, it was not possible to use current densities higher than 500μA/cm^2. The voltammograms for low current density films are found to be different to those of high current density films. The voltammograms for films prepared with current density of 16 μA/cm^2 had the largest capacity with well defined peaks and detailed structure. In contrast the high current density films have featureless voltammogram curves. The results show the same effect earlier observed for polypyrrole and polyaniline prepared and cycled in non aqueous solutions. Polypyrrole and polyaniline films polymerized with low current densities showed voltammograms with detailed structure and narrow peaks and such voltammograms have been attributed with high degree of conjugation. The high degree of conjugation in such films was confirmed by the observed low value for π-π* transitions in the optical absorption studies. It can be concluded that in aqueous media too the low current densities of the order of 16μA/cm^2 produce films which have high conjugation with well defined crystal structure.

When the same low current density polyamine films were cycled in electrolytes with different pH ranging from 1 to 5 the voltammograms corresponding to pH 1 showed the highest capacity.

Galvanostaic polymerization of polyaniline at low current densities in either aqueous or non aqueous media produces films which have a more regular structure with a high degree of conjugation than those prepared at higher current densities.