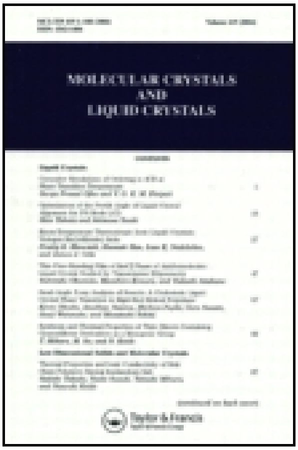

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ELECTROCHEMICAL STUDY OF POLYANILINE IN AQUEOUS AND ORGANIC MEDIUM. REDOX AND KINETIC PROPERTIES.

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I. INTRODUCTION

The polyaniline (PANI) is an interesting material because it can be a very stable electronic conductive polymer. It shows several electrochemical redox systems which have to be elucidated. For the application as battery material, it is the polymer probably which has the larger charge density (Ah/kg).

II. PREPARATION

To be a good conductor, the PANI must be prepared by oxidation of aniline in acidic medium electrochemically or by using chemical oxidants. The yield of polymerization, the electrochemical, physical, mechanical properties and the stability of the PANI depend very much on the nature of the acidic medium and of the electrolyte in the solution of preparation. One of the more common medium is dilute sulfuric acid with sodium sulfate. If the PANI has to be transferred to an other solvent for different purpose, it is very important that the process retains some acidity in the polymer. If the polymer is completely neutralized, it becomes almost electroinactive and insulator. In organic solvent, the residual acidity of the PANI remains in the polymer.

According to our electrochemical study of aromatic amines[1], the reasonable mechanism of formation of PANI in acidic medium is presented in the scheme 1. The ortho positions are also concerned because p-fluoroaniline can also polymerize.

III ELECTROCHEMICAL SYSTEMS OF THE PANI

The figure 1 shows the cyclic voltammetry (CV) of a solution of aniline (.2M) in concentrated HF solution at 20 mV s^{-1}. It shows the perfect growth of the film with two important electrochemical systems. The prepeaks in the middle is attributed to a solvatation-desolvatation phenomenon of ions insertion. The two electrochemical systems are also clearly visible when we transfer the electrode of PANI in organic medium The figure 2 shows the CV of a paste of chemically prepared PANI (polyvinylene fluoride + carbon black + PANI). To interpret ours results we propose the scheme 2 for the redox systems in PANI.

The first system is protoelectronic and the second is purely electronic (ions insertion as in $(CH)_x$). Such mechanism demonstrates, if x = .5 e^- that the charge density must correspond to 1.5 e^- (y) per ring of aniline. In fact, we observe about 50 % less.

IV CHRONOCOULOMETRIC DETERMINATION OF THE CHARGE DENSITY

The figure 3 shows the chronocoulometric curves obtained in a solution as for the figure 1. The potential of the Pt electrode is stepped from -.1 V to 1 V and reversed to .2 V and then to -.1 V. The ratio of available charge on the charge used for the electropolymerization is .25 to .3. This has to be compared to the value of .11 to .14 for the polypyrrole. If we admit that at least 2 e^- are necessary to polymerize the aniline and y to oxidize the film, we obtain .66 to .85 e^- per ring of available charge. The study of the ratio of charge observed after the inversion of potential at different values indicates that about half of the charge is required for the protoelectronic transfer and the remaining for the ions insertion.

Concerning the charge density, the polyaniline must give according to the scheme 2 : 400 Ah/kg (without anion), from the chronocoulometric experiments (.66) we calculate 200 Ah/kg, 170 Ah/kg with F^- and 113 Ah/kg with ClO_4^-. By weight measurements, we obtain 140 Ah/kg with F^- .

V DETERMINATION OF MOLECULAR WEIGHT OF PANI

Since we observe that polyaniline is slightly soluble in DMF giving blue solution, we carried out a gel permeation chromatography - figure 4a - of PANI in DMF + 1% HAC on a SEPHADEX LH60 column. The comparison of the elution time for PANI and other molecules (4b) on the same column indicates that the soluble part of PANI has an average molecular weight of about 80,000. So, PANI is not an octamer as emeraldine.

VI Electrochemical study of PANI

Many experiments have been done to understand the kinetic of electron transfer throught a PANI film. By CV in CH_3CN with several electroactive soluble species as anthraquinone, ferrocene and phenothiazine, we observe that PANI is perfectly insulator in reduced form, slightly conductor after the protoelectronic transfer and good conductor in full oxidized form. The figure 5 shows the voltamperometric curve of ferrocene and a rotating disc electrode (RDE) at several values of rotation per minutes (rpm). The figure 6 shows the inverse of the LEVICH criterium ($1/i_{lim} = f(rpm)^{-1/2}$). It gives according to MURRAY relation[2] a rate constant of electron transfer between the film and the ferrocene which is about 10^8 $mole^{-1}$ cm^{-1}.

VII CONCLUSION

The electrochemical study of PANI shows that this material is very stable with a good conductivity[3] in oxidized and protonated forms. The utilisation of PANI as material for positive battery electrode is interesting. With propylene carbonate ($2M LiClO_4$)

and LiAl as negative electrode, we obtain the following characteristics : $V_{OC} = 3.7$ V, $I_{CC} = 18$ mA with $A = 1$ cm^2 and .8 cm of path length solution and 18 coulombs cm^{-2}. The stability is very good upon cycling and storages[4].

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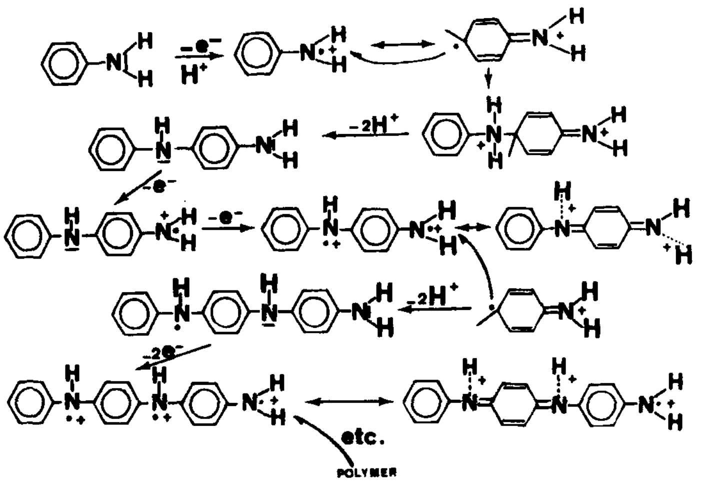
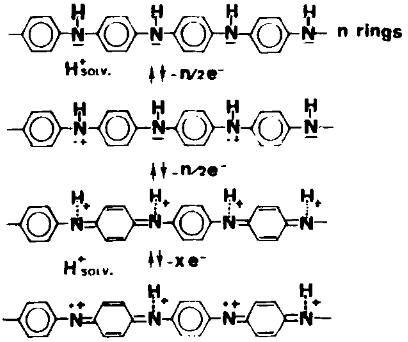


Scheme 1: Mechanisme of formation of conductive PANI



Scheme 2: redox systems in PANI

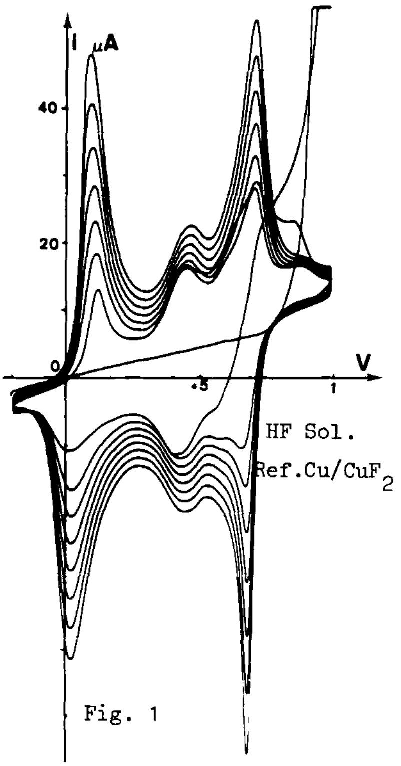


Fig. 1

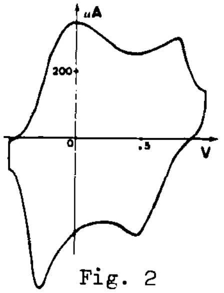


Fig. 2

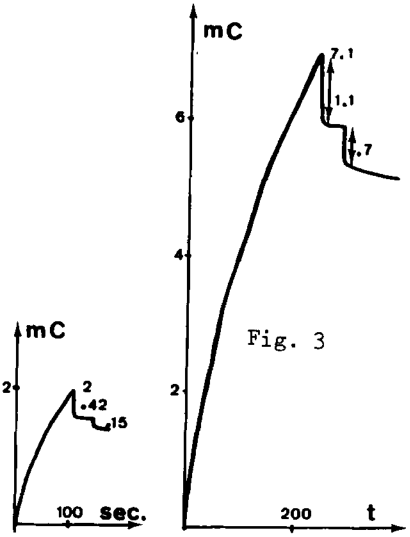


Fig. 3

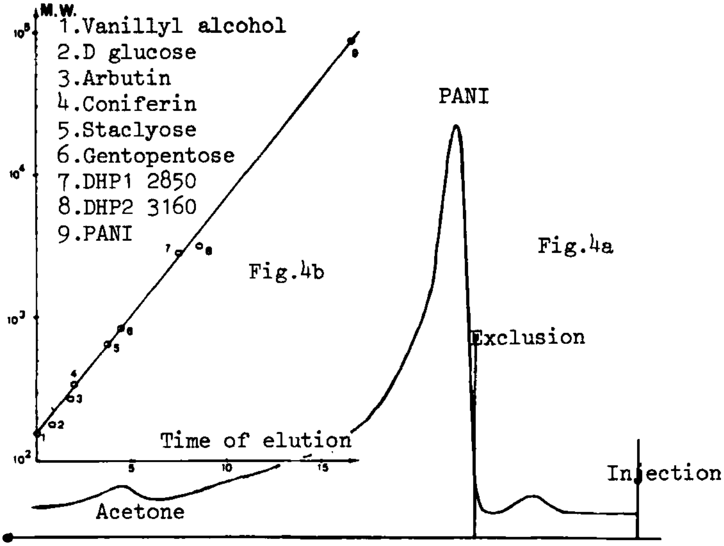


Fig.4b

Fig.4a

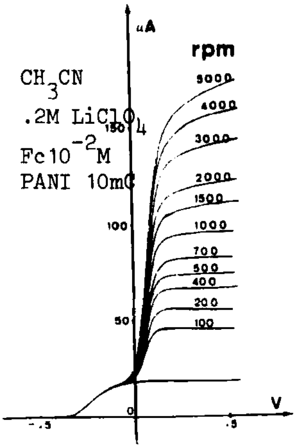


Fig.5

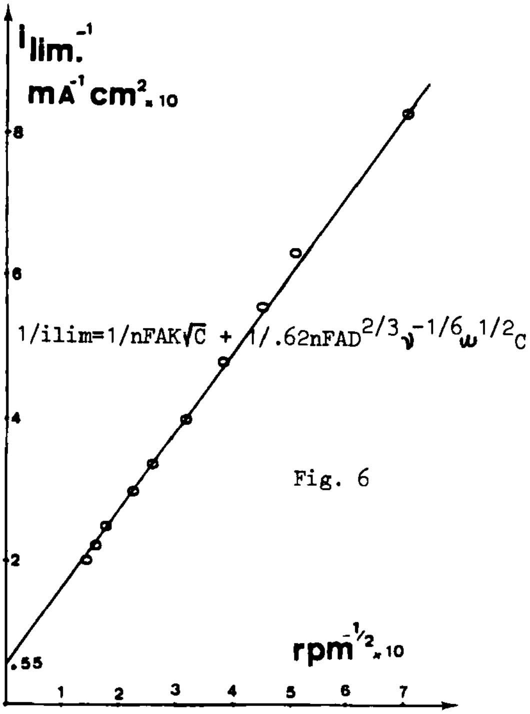


Fig. 6