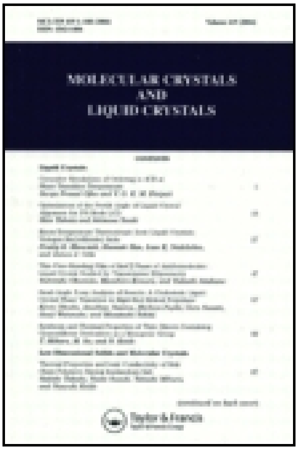

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Reversible and Non Reversible Oxidation of Polyacetylene In Aqueous and Non Aqueous Media : An Electrochemical Study

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REVERSIBLE AND NON REVERSIBLE OXIDATION OF POLYACETYLENE IN AQUEOUS AND NON AQUEOUS MEDIA : AN ELECTROCHEMICAL STUDY

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Abstract Cyclic voltammetry has been applied to study the reversibility of the oxidation of polyacetylene in sulfuric acid solutions and in lithium salts - nitromethane solutions. The intensity-potential curves indicate generally two steps of oxidation : the first one, corresponding to the doping, is reversible and is characterized by a dramatic increase of the electrical conductivity ; the second one, called overoxidation, is due to the irreversible destruction of the carbon-carbon double bonds by formation of sp^3 carbon atoms and is evidenced by the lowering of the conductivity.

INTRODUCTION

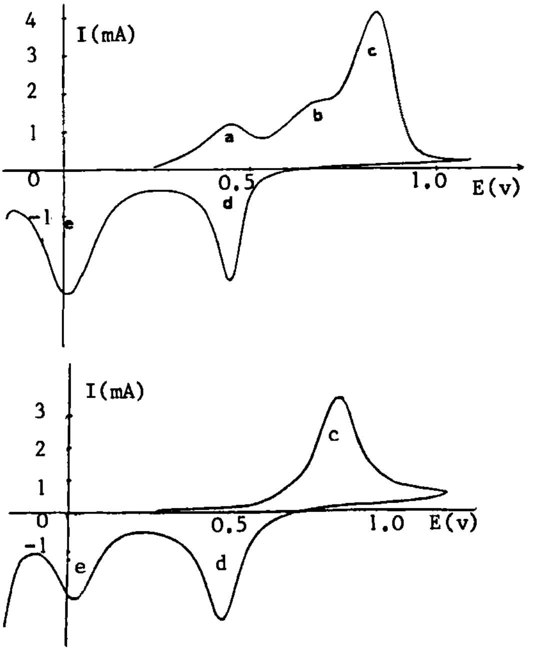
Polyacetylene, the simplest conjugated polymer, can react either with electron donating or accepting species. Some of its properties (low density, high specific area, fibrillar morphology) are interesting for utilisations as electrode materials. However undoped and doped $(CH)_x$ are usually unstable towards chemical oxidation with oxygen or electrochemical oxidation. This paper deals with some aspects of the reversibility of $(CH)_x$ doping in aqueous sulfuric acid solutions and in $LiAsF_6$-CH_3NO_2 solutions using a cyclic voltammetry (CV) technique.

RESULTS

System $(CH)_x$-H_2SO_4

Different behaviours have been observed depending on the concentration of acid solutions.

For concentrated solutions (95 % H_2SO_4), the CV curves obtained are represented in figure 1. It is established that $(CH)_x$ can react spontaneously with concentrated H_2SO_4 [1]. However, an extra doping can be achieved by electrochemical oxidation. Figure 1 shows intensity-potential curves obtained after cycling the potential immediately after immersing the strip of Ito's$(CH)_x$ film [2] into H_2SO_4 solution (fig. 1a) or after the 15 hours reaction of $(CH)_x$ with the solution (fig. 1b). Fig. 1a shows two peaks a+b observable during the oxidation process. They correspond to the spontaneous chemical doping which has not been achieved immediately because of kinetic reasons related to the slow intrafibrillar diffusion of the dopant. This chemical doping is reversible from a chemical viewpoint as evidenced by the existence of the e peak. A doping level of around 8 molar per cent of the dopant is involved in this process.



1a Intensity-potential curve obtained immediately after immersion of $(CH)_x$ in concentrated H_2SO_4 solution

1b Intensity-potential curve obtained after 15 hours immersion of $(CH)_x$ in concentrated H_2SO_4 solution

FIGURE 1 Cyclic voltammograms of $Ag/AgCl/H_2SO_4/(CH)_x$

In Fig. 1b, the spontaneous chemical doping occured during 15 hours and, after cycling the potential, no peaks a+b are observable ; during the reduction, the undoping of the chemically doped $(CH)_x$ is evidenced by the e peak similar as the one observed in Fig. 1a. When the potential is increased, an extra c peak appears which is reversible (peak d).

In conclusion, for concentrated H_2SO_4 solutions the two steps of reversible oxidation of $(CH)_x$ could correspond either to the formation of different stages of intercalation or to a different interchain organization of the dopant.

In the case of diluted H_2SO_4 solutions (<10 N), the CV curve (fig. 2) shows only an irreversible peak due to the degradation of the π system of $(CH)_x$ chains. IR studies of such degradated materials indicate the formation of carbonyl groups caused by the evolution of free oxygen on the surface of the $(CH)_x$ electrode during the electrolysis of the solution.

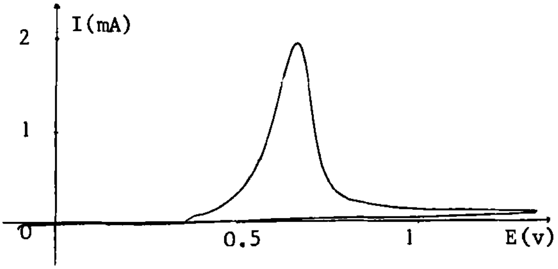


FIGURE 2 Cyclic voltammogram of $Ag/AgCl/H_2SO_4/(CH)_x$ in diluted H_2SO_4 solution

<u>System $(CH)_x$-$LiAsF_6/CH_3NO_2$ solutions</u>

The voltammogram represented in Fig. 3 shows two different steps of oxidation of $(CH)_x$. The first reversible one (peaks a_1, a_2 and a') is due to the doping of $(CH)_x$. The highest level of doping obtained is *ca* 7 % and therefore corresponds to the formula $|CH^{0,07+}(AsF_6^-)_{0,07}|_x$. When the potential is increased over *ca*

3.8 volts vs Li/Li^+, a large irreversible peak b appears up to ca 5.2 volts vs Li/Li^+. Measurements of the area of this peak indicate that $(CH)_x$ is totally degraded (lowering of the electrical conductivity and of the mechanical properties) when around 30 % of CH groups are oxidized by addition of fluorine on the carbon atoms. Similar results have been obtained during the doping with $LiPF_6$ [3].

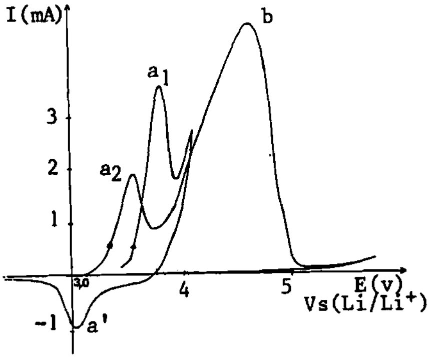


FIGURE 3 Cyclic voltammogram of $Li/Li^+/LiAsF_6-CH_3NO_2/(CH)_x$

CONCLUSIONS

Such an electrochemical study of $(CH)_x$ doping and undoping in aqueous and non aqueous media shows generally two steps :
- a reversible doping characterized by the increase of the electrical conductivity ; - an unreversible doping due to the degradation of the π-system of $(CH)_x$.

In the case of reactions in CH_3NO_2 solutions, the degradation starts before the achievement of the doping process contrary to the reactions in concentrated sulfuric solutions where the different steps of intercalation and the degradation are well separated.

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