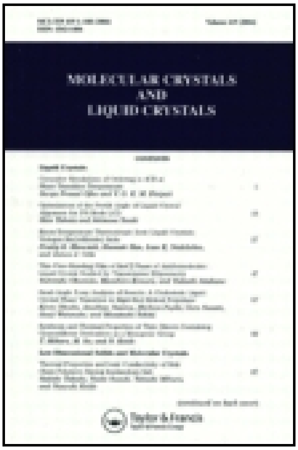

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Electrochemical Doping of Polycyanoacetylene, A New Conducting Polymer

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ELECTROCHEMICAL DOPING OF POLYCYANOACETYLENE, A NEW CONDUCTING POLYMER

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Abstract Polycyanoacetylene was prepared by dehydrochlorination of poly-α-chloroacrylonitrile at low temperature. Thin films were simply obtained by spreading a DMF solution onto a stainless steel substrate. Transmission electron microscopy revealed a highly crystalline structure. Two different morphologies were observed : large isolated single crystals and numerous small crystals dispersed in the precursor matrix. The electrochemical behaviour of polycyanoacetylene was studied using a $(\text{-CH=C(CN)-})_n/(\text{PEO})_8\text{LiClO}_4/\text{Li}$ cell. Cyclic voltammetry indicated a very reversible behaviour. Lithium intercalation/deintercalation occurred at ca 2.6 V vs Li/Li^+. This high value compared to polyacetylene may be attributed to the electron withdrawing effect of the cyano- group. These properties make polycyanoacetylene suitable for use as a positive electrode in batteries.

INTRODUCTION

Within the framework of new materials syntheses exhibiting ionic and electronic transport properties [1], we have focused our attention on the family of conjugated polymers derived from the hypothetical linear form of carbon $(\text{-C}\equiv\text{C-})_n$. Here, we report preliminary results on polycyanoacetylene synthesis, structure and properties.

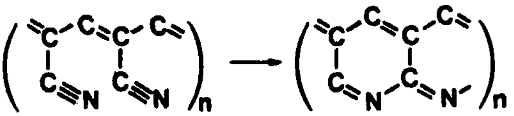
SYNTHESIS

In a paper describing the preparation of cyanoacetylene, Moureu and Bongrand [2] have reported the formation of a tarry product resulting from reaction with potassium hydroxide. More recently, MacNulty [3] has shown that cyanoacetylene polymerization can be initiated by triethylamine and Manassen and Wallach [4] have described polycyanoacetylene preparation using NaCN as a catalyst in DMF. In both cases, the products obtained were partially soluble in acetone, probably due to their relatively low molecular weight.

Another method, using poly-α-chloroacrylonitrile as a precursor, has been devised by Grassie and Grant [5]. Thermal degradation produces dehydrochlorination in the temperature range 150-195°C :

$$(\text{-CH}_2\text{-CCl(CN)-})_n \rightarrow (\text{-CH = C(CN)-})_n + n\,\text{HCl} \qquad (1)$$

According to Chukhadzhyan et al [6], dehydrochlorination can also take place at lower temperatures (ca 60°C) in DMF solution with LiCl or organic bases. The resulting polymer cyclises at 150-200°C, giving a product structurally similar to "black Orlon".



(2)

We preferred the latter method because it enabled us to produce polycyanoacetylene samples in the form of thin films. In practice, the poly-α-chloroacrylonitrile precursor prepared by the method of Grassie and Grant [5] was initially colourless and very viscous, subsequently becoming dark and fluid. DMF was removed under vacuum (T = 170°C).

STRUCTURE

The product obtained after dehydrohalogenation was studied by transmission electron microscopy. Polycyanoacetylene constitutes the major part of the product with two different morphologies present. We observed large isolated lamellae (Fig. 1) and small particles dispersed in the precursor phase (traces). The latter is soluble in the solvent used for dispersion and looks like a foam [1]. The product is unstable under the electron beam and transforms into polycyanoacetylene.

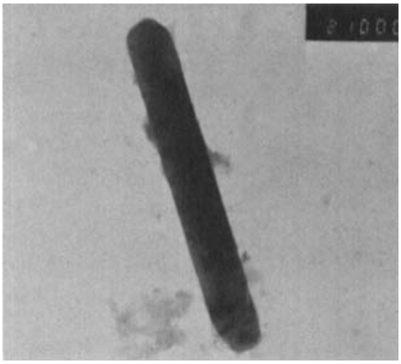


Fig. 1 : Polycyanoacetylene isolated crystal (BF Image, mag. 21 000 x)

As can be seen in the microdiffraction patterns, polycyanoacetylene is a crystalline polymer. Diagrams (2 a) and (2 b) probably correspond to beam diffraction by a fcc lattice along axis [001] and [111] respectively. The lattice parameter was calculated (a = 6.22 Å). A more detailed structural study is underway in our laboratory.

a : Zone axis [001] *b : Zone axis [111]*

Fig. 2 : Polycyanoacetylene microdiffraction patterns

ELECTROCHEMICAL BEHAVIOUR

The electrochemical behaviour of polycyanoacetylene was studied using the Li / PEO_8LiClO_4 / $(\text{-CH} = \text{C(CN)-})_n$ chain. The polymer electrolyte is particularly suited to such preliminary studies. It presents many advantages compared to organic electrolytes, namely its wide electroactivity domain, the simplicity of electrode reactions and the absence of side reactions due to impurities [7].

The three electrode cell was designed and built in our laboratory (Fig. 3). The sample studied was deposited on the working electrode support (stainless steel).

The electrochemical behaviour of polycyanoacetylene was investigated using cyclic voltammetry (Fig. 4). The curves obtained were stable during repetitive cycling and the anodic and cathodic charges passed (as measured by the areas of the corresponding peaks) were equal, denoting the reversibility of the electrode process.

Based on the analogy of graphite and polyacetylene, the crystalline state of polycyanoacetylene leads us to postulate an intercalation/deintercalation mechanism :

$$1/n\ (\text{-CH} = \text{C(CN)-})_n + x\ Li^+ + x\ e^- \underset{\text{intercalation}}{\overset{\text{deintercalation}}{\rightleftharpoons}} 1/n\ (Li_x\text{-CH} = \text{C(CN)-})_n \quad (2)$$

The variation of the reduction current may correspond to the formation of two different phases with a low miscibility.

The potential difference between the anodic (e = 2.85 V) and cathodic (e = 2.40 V and e = 2.10 V) peaks is rather small, especially for a solid state system.

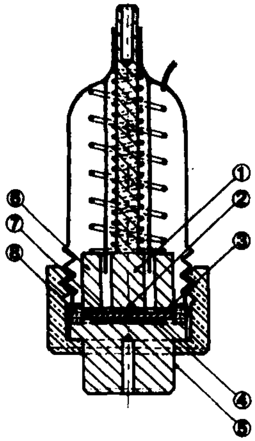


Fig. 3 : Electrochemical cell (1) WE current lead,(2) Working electrode (WE), (3) Reference electrode (RE), (4) Counter electrode (CE), (5) CE current lead, (6) RE current lead, (7) Polymer solid electrolyte, (8) Viton O'ring.

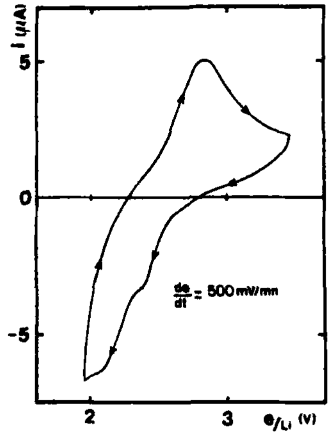


Fig. 4 : Cyclic voltammogram for polycyanoacetylene Ref. : Li° , Temperature : 85°C, Electrolyte : PEO_8LiClO_4

CONCLUSION

From a practical viewpoint, these initial results indicate the possibility of using polycyanoacetylene as a positive electrode material in solid state batteries. Regarding this application, the theoretical and practical features of this material will be extensively studied (structure, implementation, coulometry).

From a theoretical viewpoint, the comparison between polyacetylene [8] and polycyanoacetylene illustrates the influence of the electron withdrawing cyano- group on electrochemical properties. This substitution produces a shift of the redox potential toward higher values.

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