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ELECTROCHEMICAL REDUCTION OF SOME GRAPHITE FLUORIDES IN PROPYLENE CARBONATE

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SUMMARY

The reduction of graphite fluorides has been carried out in propylene carbonate by the carbon paste electrode technique. Our results confirm the insertion mechanism of Li^+ ions during the reduction of CF_x in lithium batteries. The shift of the reduction peak towards more negative potentials when $LiClO_4$ is replaced by nBu_4NClO_4 as the supporting electrolyte is attributed to the difficulty of the bulky cation to intercalate in the host structure. In this paper, the electrochemical behaviour of several CF_x samples is compared, in relation to their crystallinity and composition.

INTRODUCTION

It has been already established that a passive layer of fluorocarbons generally denoted CF_x is formed on the surface of carbon anodes during the electrolysis of KF,2HF [1a,2] ; it is responsible for the considerable energy loss during the electrolysis of HF whilst generating fluorine. The stability of these electrogenerated compounds to reduction depends strongly on their formation potential [2].

On the other hand, the application of chemically prepared CF_x as an active species in primary lithium batteries, first proposed in 1970 [3] has been extensively reported in the literature [4]. Non-aqueous solvents are always needed because of the reactivity of the Li-metal anodes. However, the reduction of CF_x in Zn batteries has been studied in aqueous alkaline solutions [5] in the presence of a surfactant because graphite fluorides are not 'wetted' by aqueous electrolytes. The reduction of CF_x in acetonitrile and DMSO has been studied since 1968 by several authors [6,7]. In several recent papers, it has been found that the discharge performances of $(CF)_n$ and $(C_2F)_n$ / Li batteries depend strongly on the crystallinity and composition of the graphite fluoride [1b,8].

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The aim of this paper is the study of the electrochemical reduction of CF_x in propylene carbonate (used in lithium batteries) with different supporting electrolytes in order to confirm the hypothesis of the insertion of Li^+ cations during the reduction process. The reduction of several CF_x compounds is compared in relation to their stoichiometry x, structure and method of preparation.

Several problems must be solved :

(i) the necessity to have the solution free of water and oxygen impurities.

The electrochemical properties of propylene carbonate have been investigated by other authors. They recommend argon bubbling and the use of perchlorates as supporting electrolytes [9]. Recent works have shown the large electroactivity domain of solutions of $LiClO_4$ and nBu_4NClO_4 [10, 11].

In this work, three supporting electrolytes have been tested : 1 M $LiClO_4$, 1 M nBu_4NClO_4 and 0.1 M $KClO_4$. The first two solutions have roughly the same conductivity ; it is not possible to obtain 1 M $KClO_4$ solutions.

(ii) the choice of the reference electrode

A lithium electrode in $LiClO_4$ (1 M) may be used as a reference electrode ; however instabilities are observed due to oxidation of the metal when working without a glove box [11]. Other reference electrodes have been proposed : Li/LiCl [11] ; mercury/calomel [12, 13] ; $Ag/AgClO_4$ [14] and $Ag/AgNO_3$ [15].

For our experiments, we have adopted an Ag / AgI reference electrode, dipped in a saturated NaI solution in propylene carbonate separated from the electrochemical cell by a junction similar to that described in reference [16] (gelatinous vinylidene fluoride resin containing propylene carbonate saturated with lithium nitrate). Its stability has been verified for periods as long as three months.

(iii) the choice of a suitable working electrode because graphite fluorides are very insulating compounds. It seems to us that the best way to investigate the electrochemical properties of CF_x is to use a carbon paste electrode which permits the study of insoluble and insulating compounds drowned in a conductive carbon paste [17-23]. Nevertheless, kinetics in the solid phase are very slow, and it is often necessary to choose a low sweep rate.

EXPERIMENTAL

Graphite fluoride samples

Several graphite fluorides have been investigated :

* two industrial samples from CENTRAL GLASS COMPANY, Japan :

- white $(CF_x)_n$ with x = 1.1 (trade name : Cefbon-CM), denoted 'Sample 1' hereafter, prepared from petroleum coke. Its decomposition temperature lies between 400 and 450°C.

- grey $(CF_x)_n$ with x = 0.65 (trade name : Cefbon-DM), denoted 'Sample 2', prepared from artificial graphite powder (decomposition temperature : $450 < t_d < 500°C$);

* graphite fluoride CF_x with x = 1.03, denoted 'Sample 3', synthesized in Professor N. Watanabe's Laboratory by direct fluorination of flaky natural graphite, at 600°C, under an atmosphere of a fluorine-argon mixture (1:1). Its decomposition temperature is above 610°C.

Electron diffraction patterns of these samples were obtained with a JEOL JEM 100 CX II high resolution Transmission Electron Microscope.

As recommended by other authors [23], carbon tetrachloride was used to wet the samples.

Experiments must be carried out rapidly in order to avoid disintegration of the CF_x. We report below data obtained from Debye-Scherrer patterns, on the assumption of a hexagonal crystal structure, as reported by several authors [23-25] who have given structural information deduced from X-ray powder data.

- Sample 1 usually shows diffuse lines. The electron beam contributes to a partial recrystallization of the compound before destroying it.

- Sample 2 presents the same behaviour ; Fig. 1 shows the impact of the electron beam after diffraction experiments.

- Sample 3, which is a crystalline compound shows well-defined patterns (see Fig. 2). The crystallographic parameters were found to be : a = 2,54 Å and c = 6,968 Å. However, the disintegration of the compound may occur.

Other chemicals

- Propylene carbonate for synthesis MERCK
- Tetrabutylammonium perchlorate (purum) FLUKA ($H_2O < 0.2$ %)
- Lithium and potassium perchlorate (purum) FLUKA
- Lithium nitrate and sodium iodide R.P. RHONE-POULENC (PROLABO).

Electrochemical apparatus

Experiments were carried out at 25°C in a polypropylene cell (Fig. 3 a) fitted with three electrodes :

- a carbon paste working electrode (Fig. 3 b)
- an Ag / AgI reference electrode separated from the main compartment by a PVDF bridge [16].
- an auxiliary platinum electrode ($S = 5\ cm^2$).

The solid electroactive compound CF_x (0.02 g) is mixed with JOHNSON MATTHEY graphite powder (0.1 g) ; addition of a few drops of the propylene carbonate solution provides the 'carbon paste'. Silica powder is placed over the paste in order to avoid mixing with the electrolyte. Potentials were imposed by a PAR 273 potentiostat ; the I-V curves were plotted on a XY recorder.

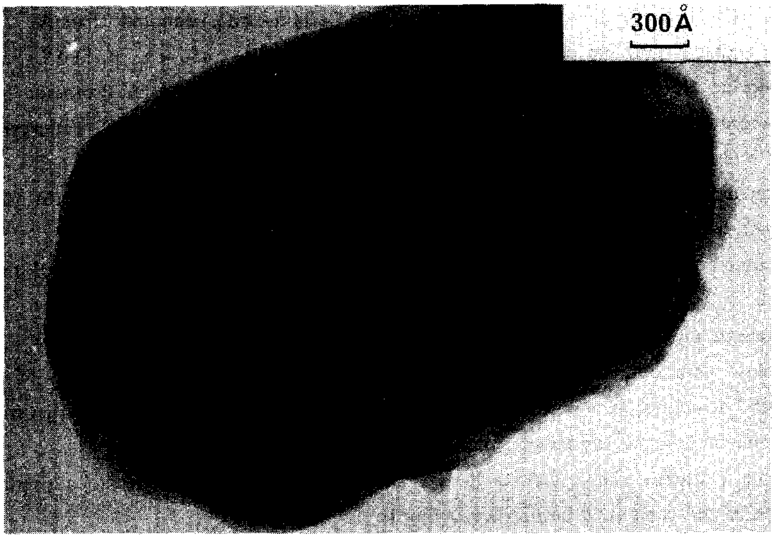

Fig. 1 . T.E.M. micrograph of a crystal of CF_x (Sample 2)
The impacts are due to the electron beam.

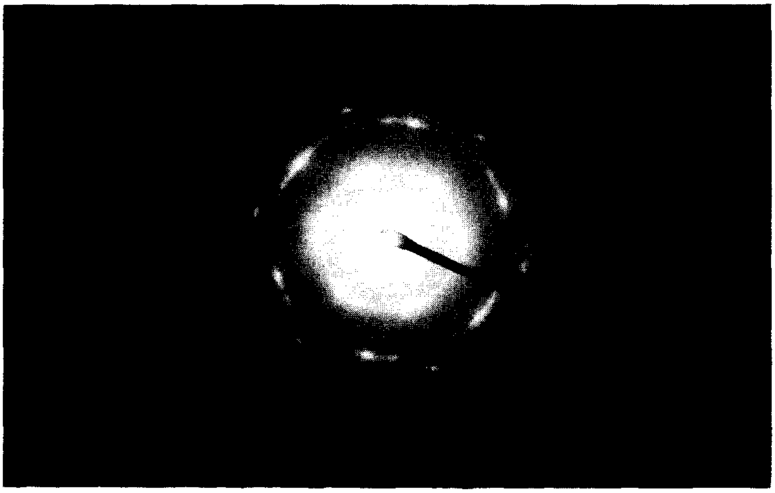

Fig. 2 . Electron diffraction pattern of a CF_x compound (Sample 3).

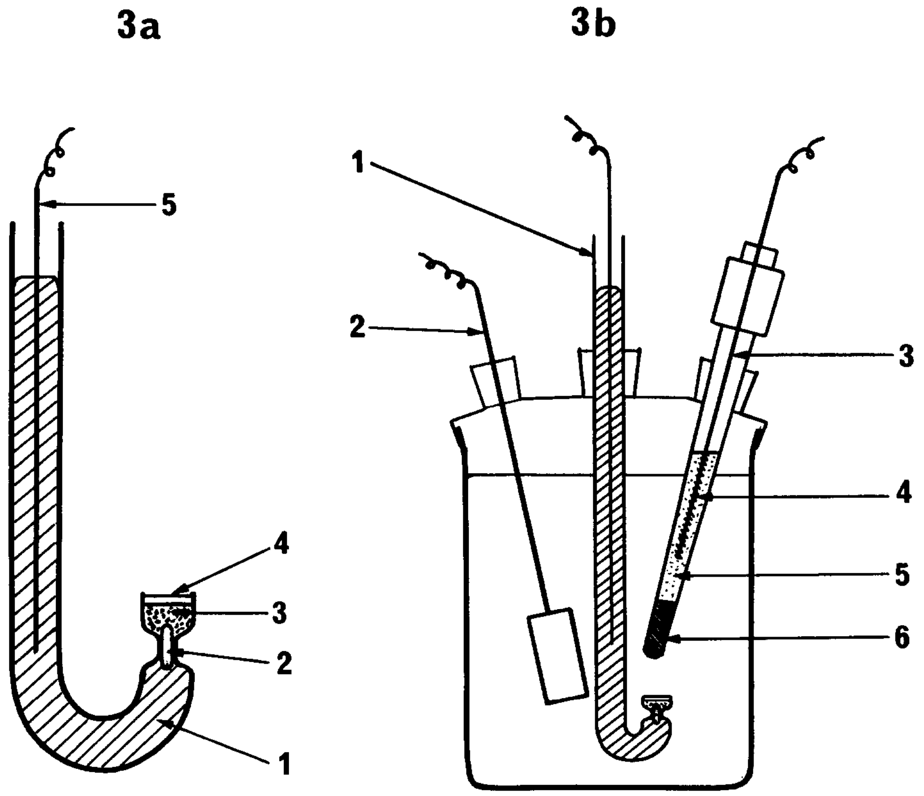

Fig. 3 a . Carbon paste electrode

1 : Hg ; 2 : vitreous carbon rod ;

3 : carbon paste (graphite + solid electroactive compound + electrolyte ;

4 : silica powder ; 5 : Pt wire.

b . Electrochemical cell

1 : carbon paste electrode → working electrode

2 : Pt electrode → auxiliary electrode

3 : Ag wire

4 : solid AgI

5 : NaI solution in P.C.

6 : PVDF junction

} reference electrode

The potential range studied was between +0.5 V and -3.5 V. Usually, only the forward sweep is done, since the reverse sweep is not really significant with the carbon paste electrode technique (electroactive products which have diffused in the solution may not be reoxidized) and, for graphite fluoride, the electrochemical reduction reaction is irreversible [6].

It is necessary to adopt a very slow sweep rate ($v = 2 . 10^{-5}$ V/s) in order to reduce a large proportion of the electroactive compounds ; the current peak strongly depends on the value of v as in classical cyclic voltammetry experiments.

Due to the resistivity of the electrolyte and the geometry of the cell, the uncompensated resistance between the working electrode and the reference is high but is constant for all our experiments.

RESULTS AND DISCUSSION

Several preliminary experiments have been carried out in the absence of electroactive compound (i. e. only with graphite powder). The residual current is very weak in the potential range of CF_x reduction (see Fig. 4 and Fig. 5, curve D). We attribute the cathodic peak observed at potentials lower than -1.2 V to the reduction of water, since the intensity of this peak increases when water is added to the electrolyte.

TABLE I

Electrical conductivity of solutions used in this work

Supporting electrolyte	$LiClO_4$ (1M)	$KClO_4$ (0,1M)	nBu_4NClO_4 (1M)	NaI (Saturated)	$LiNO_3$ (Saturated)
Conductivity ($S.cm^{-1}$)	$7.13\ 10^{-3}$	$1.39\ 10^{-3}$	$7.05\ 10^{-3}$	$6.70\ 10^{-3}$	$2.02\ 10^{-3}$

The electrical conductivity of our solutions, reported in Table I, have been measured at 25°C and f = 100 kHz with a TACUSSEL cell (cell constant : k = 0.75 cm).

Table II summarizes the values of the intensity and the potential of CF_x reduction peaks in the electrolytic solutions mentioned above (See curves in Fig. 5).

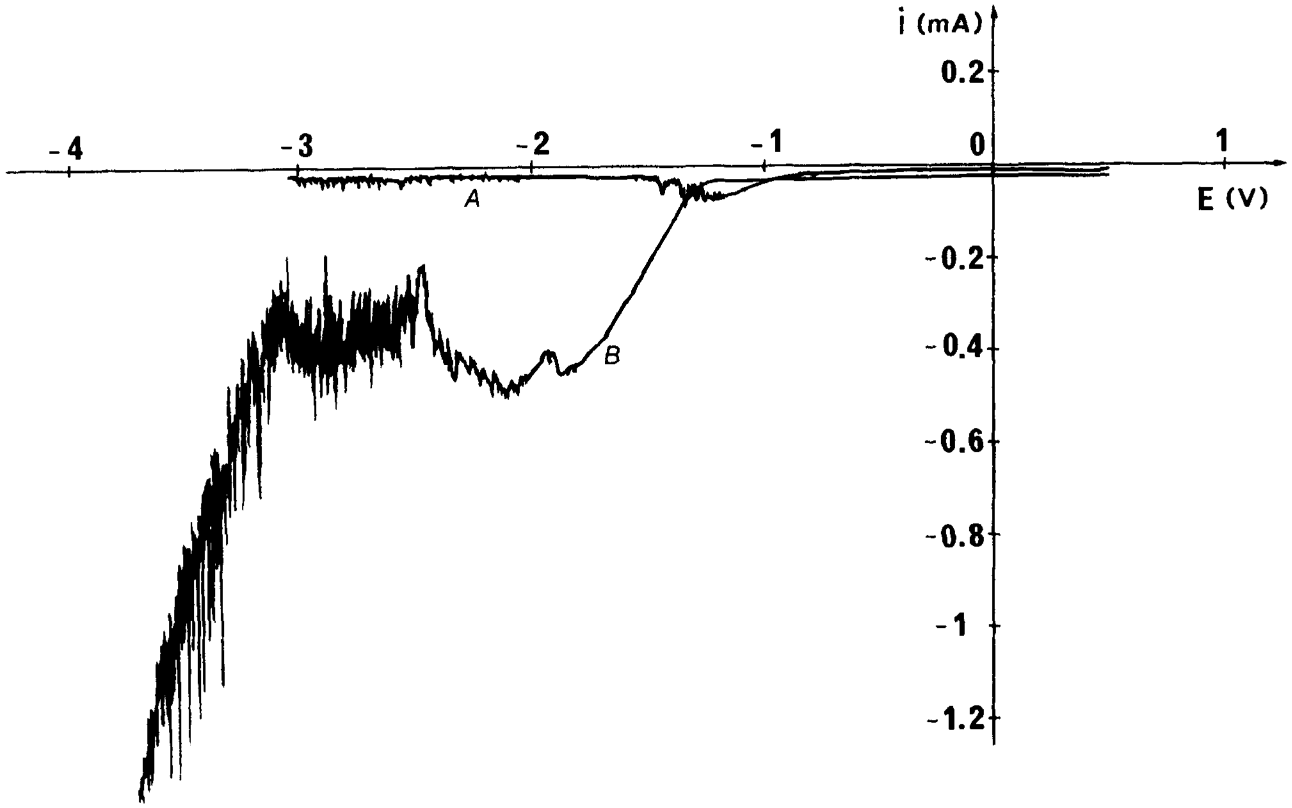

Fig. 4 . Residual current for the carbon paste electrode without electroactive CF_y :

A : using $LiClO_4$ as the supporting electrolyte; B : using nBu_4NClO_4 as the supporting electrolyte.

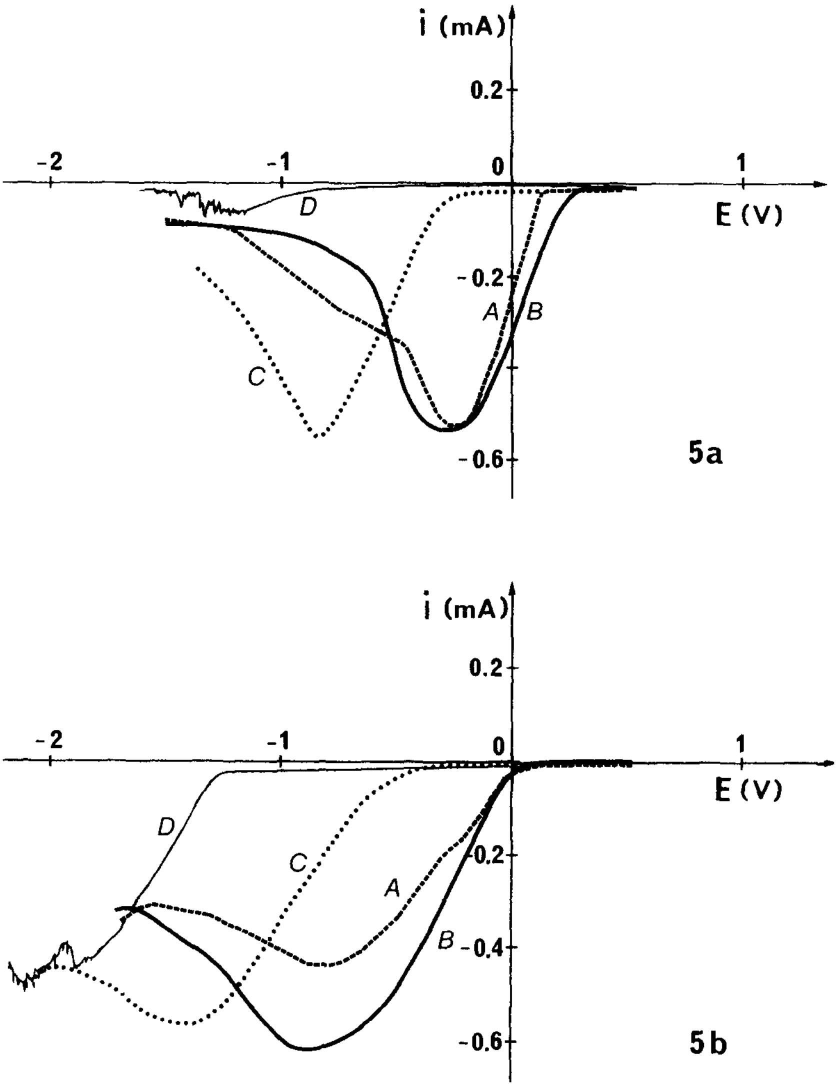

Fig.5 : Voltammograms for the reduction of CF_x compounds in Propylene carbonate

A : Sample 1 ; B : Sample 2 ; C : Sample 3 ; D : residual current;

a) using $LiClO_4$ as the supporting electrolyte;

b) using nBu_4NClO_4 as the supporting electrolyte.

TABLE II

Peak characteristics (E_p, I_p and Q_{exp}) for the electrochemical reduction of several samples of CF_x

Q_{th} is the theoretical charge needed for the complete reduction of the compounds according to eqn. (1).

		Supporting electrolytes					
		$LiClO_4$ (1M)			nBu_4NClO_4 (1M)		
	Q_{th} (C)	E_p (mV)	I_p (µA)	Q_{exp} (C)	E_p (mV)	I_p (µA)	Q_{exp} (C)
Sample 1	64.5	-200	480	16.5	-775	435	20.0
Sample 2	45.0	-300	555	17.0	-800	460	29.0
Sample 3	63.4	-750	575	12.0	-1400	500	15.0

The results obtained with $KClO_4$ as supporting electrolyte are not given in Table II because reproductibility is poor. The conductivity of this solution is quite different from the conductivity of nBu_4NClO_4 or $LiClO_4$ solutions, and the less intense current peak is shifted towards more negative potentials at the limit of the electroactivity domain as a consequence of the important ohmic drop.

Firstly, it may be seen that the reduction of Sample 3 occurs at lower potentials whatever the nature of the supporting electrolyte. This means that this well-defined crystalline compound is less reactive than the others, in agreement with its higher decomposition temperature.

In Table II, we report the charge Q_{exp} deduced from the I-V curves ; it is compared to the theoretical charge Q_{th} needed for the complete reduction of the electroactive species according to reaction (1) :

$$CF_x + x\,e^- \rightarrow C + x\,F^- \qquad (1)$$

It is often noticed with the carbon paste electrode technique that the reduction yield Q_{exp}/Q_{th} is never equal to unity because of the slow diffusion of the species in the solid phase and because of the geometry of the working electrode. The yield of the reduction of CF_x in batteries is of course higher ; in this work, the ability of the compounds to be reduced more or less easily is deduced from the comparison of the ratios Q_{exp}/Q_{th}.

We observed that the reduction process occurs at higher potentials for experiments with $LiClO_4$ as the supporting electrolyte ; however, the yield is lower than that obtained with nBu_4NClO_4.

Some authors [26] have proposed a two step reduction mechanism according to reactions (2) and (3) :

- formation of an intermediate compound :

$(CF_x) + x\,Li^+ + x\,e^- \rightarrow Li_xCF_x$ (2)

- decomposition of this compound :

$Li_xCF_x \rightarrow C + x\,(LiF)$ (3)

The formation of intercalated compounds, detected by X-ray diffraction, with Li^+ has been observed during the reduction of V_2O_5 [6], Nb_2O_5 [27], MoO_2 [28], TiS_2 [29] and iron-niobium selenide [30] (promising cathode materials for secondary lithium batteries). The intercalation of the cation is often a reversible process. Theoretical studies of this mechanism have been performed for modelling constant current cycling [28] or cyclic voltammetry [31]. However, in the case of the irreversible discharge of CF_x, recent studies have shown that the intermediate compound is not a real intercalation compound because it is not detected by X-ray diffraction ; solvent molecules participate in the cell reaction [32] and the intermediate phase is really composed of carbon, lithium fluoride and solvent molecules.

Our results are in agreement with this mechanism ; the reduction of CF_x in the presence of Li^+ cations is easier because the bulky nBu_4N^+ cations can barely form intercalation compounds ; thus the reduction peak is shifted towards a more negative potential. This shift is not due to a higher ohmic drop because the two electrolytes $LiClO_4$ and nBu_4NClO_4 have the same conductivity.

Sample 3, which is a stable crystalline compound, is more difficult to reduce in both supporting electrolytes.

Larger values of the sweep rate do not disturb the general form of the curves but shift the peaks towards more negative potentials (Fig. 6).

Our results are different from those of M. Armand [6], who has worked with another solvent (acetonitrile). However, the CF_x samples were not identical and the preparative method has a great influence on the electrochemical behaviour of these compounds. One may compare results obtained with different CF_x only if experiments are carried out in the same solvent, at the same sweep rate and with the same reference electrode.

CONCLUSIONS

Our study of the reduction of CF_x in propylene carbonate by the carbon paste electrode technique confirms the insertion mechanism of Li^+ cations. The reduction of CF_x is easy when $LiClO_4$ (the supporting electrolyte used in lithium / CF_x primary batteries) is chosen. The shift of the reduction peak towards more negative potentials when $LiClO_4$ is replaced by nBu_4NClO_4 is attributed to difficult insertion of the bulky cation.

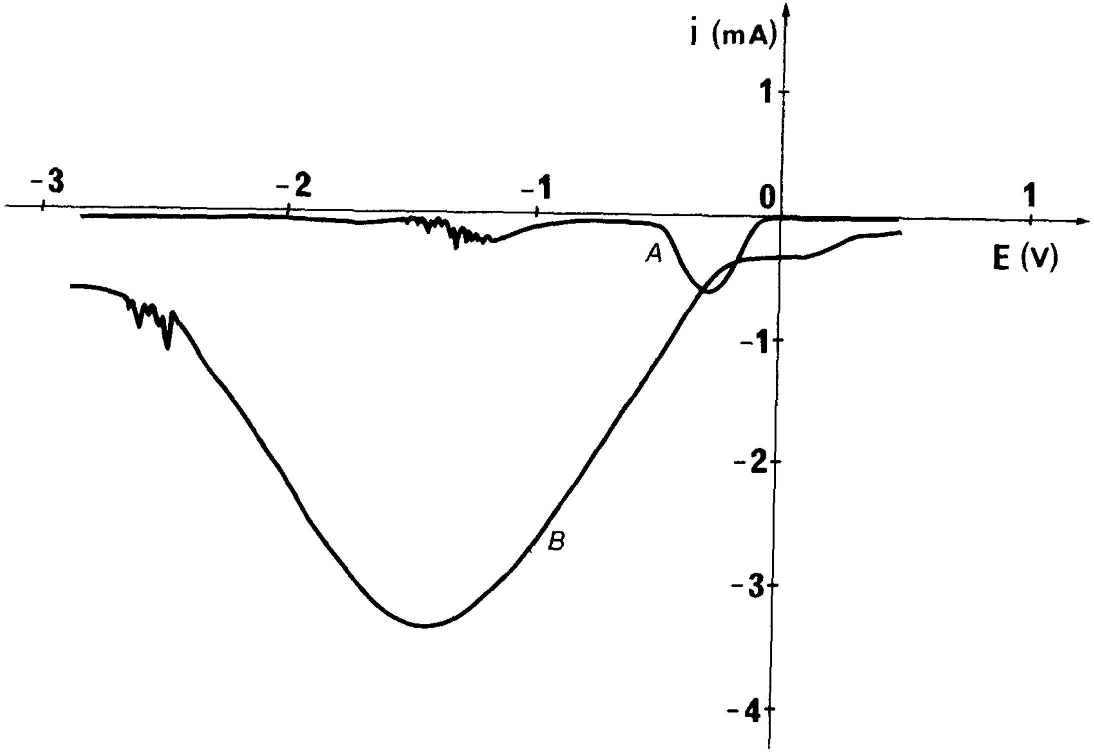

Fig. 6 : Influence of the sweep rate v on the voltammograms : A : v = 2 . 10^{-5} V/s ; B : v = 2 . 10^{-3} V/s (reduction of Sample 2 using $LiClO_4$ as the supporting electrolyte).

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