

# Positive polyacetylene electrodes in aqueous electrolytes

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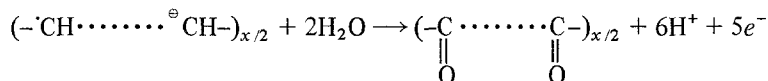
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Polyacetylene films, contacted with platinum mesh, have been polarized anodically in aqueous H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub>, HBF<sub>4</sub> and H<sub>2</sub>F<sub>2</sub> of medium concentrations (30-70 wt%). Two oxidation peaks are observed, the equivalents of which are



The potential of the Process 1 decreases linearly with increasing acid concentration by 20-40 mV mol<sup>-1</sup> dm<sup>-3</sup>, while the potential of Peak 2 exhibits normal Nernst behaviour (about + 60 mV decade<sup>-1</sup> a<sub>H</sub><sup>+</sup>). Process 1 is partially reversible, while Process 2 is totally irreversible.

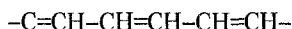
From these findings for Process 1 we conclude the reversible insertion of anions into the polyacetylene host lattice, which is primarily oxidized to the polyradical cation, with the co-insertion of acid molecules HA to yield the insertion compound [(CH)<sup>+</sup><sub>x</sub>·yA<sup>-</sup>·νyHA]<sub>x</sub> y ≤ 4.5% and ν = 1.5 for H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub>. In the course of Process 2, the polymer is irreversibly oxidized according to



As this process occurs to some extent even in the potential region of Process 1, a continuous degradation of the host lattice occurs upon cycling.

## 1. Introduction

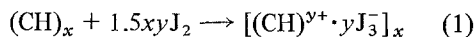
Acetylene is polymerized in the presence of Ziegler-Natta or Luttinger catalysts to yield polyacetylene (CH)<sub>x</sub>, which is the most simple organic polymer from a stoichiometric point of view. In the ground state, the black polymer is an insulator in spite of the presence of chains with extended conjugation (*cis* at low temperatures, *trans* at room temperature):



Practical electrical conductivities are in the order of 10<sup>-8</sup>-10<sup>-10</sup> S cm<sup>-1</sup>. However, 'doping' of polyacetylene via reaction with oxidizing or reducing compounds leads to high-conductivities well above 1 S cm<sup>-1</sup> [1-3].

In the former case, insertion compounds of the

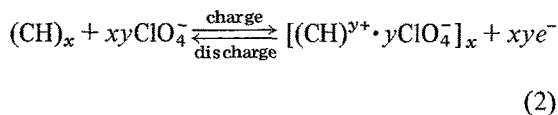
acceptor-type are established via oxidation of the (CH)<sub>x</sub>-chains to the radical cation, and anions from the redox system are inserted in the lattice to sustain electroneutrality. The anions provide a regular ionic sub-lattice. As an example, the reaction with iodine vapour can be written as:



where y is called the degree of insertion, a stoichiometric number between 0 and 1. The high electronic conductivity is explained as an improvement of interchain charge transfer in the new, polar structure [4] of the solid as well as improved intrachain charge transport. The existence of stable iodine compounds, contrary to graphite intercalation compounds [5, 6], is indicative for a relatively low oxidation potential of the polyacetylene chain.

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As 'doping' is essentially a redox process, it can be performed by direct electrochemical oxidation or reduction as well [7, 8]. In the presence of perchlorate ions, anodic insertion leads to the following equation:



This type of electrochemical reaction is highly reversible, that is cathodic desorption ('undoping') is occurring at low overvoltages with reference to the insertion potential. The idea of using systems of this kind as electrodes for new secondary batteries was a consequence of this [9, 10]. However, the practicality of such a battery highly depends on factors such as stability and costs of the host lattice material as well as the degree of insertion  $y$ , which must be related to  $y = 0.042$  as a maximum for graphite intercalation compounds.  $y$  for polyacetylene is reported to be in the range of 0.09–0.17 at maximum.

Laboratory experiments are performed with Shirakawa foil, the usual product of heterogenous polymerization [11, 12]. The fibrillar structure greatly facilitates mass transport in the system. The diameter of  $(\text{CH})_x$  fibrils is about 200 nm. The medium density of the foil is  $0.4 \text{ g cm}^{-3}$ . For technical application, composite electrodes with powder polymer products, e.g. those found by Hocker, Wieder and Dhein [13] with the addition of small amounts of carbon black to improve initial conductivities [14] seem to be more feasible.

We report our results with polyacetylene electrodes in *aqueous* electrolytes. Most experiments reported hitherto have been conducted in nonaqueous electrolytes. Sometimes, polyacetylene insertion compounds are believed to be unstable in the presence of water. However, this is not compatible with former experimental findings [7, 8, 15, 16]. The practical impact of the application of aqueous electrolytes is understandable. We have found high reversibility in a wide range of aqueous electrolytes in the case of graphite intercalation compounds [17–19] and of poly-*p*-phenylene insertion compounds [20, 21]. It should be of interest to discuss polyacetylene in the light of these results.

## 2. Experimental details

Polyacetylene Shirakawa foil was provided by BASF AG, Ludwigshafen. The free-standing film of brass-like colour had a thickness of  $50 \mu\text{m}$  and a density of  $0.36 \text{ g cm}^{-3}$ . It was stored under pure argon.

Handling of the film and the experimental set-up was under pure argon inside a glove box (Atmos Bag, Aldrich Chemical Co.). Pieces ( $1 \text{ cm}^2$  area) of the film were contacted with platinum by 'enveloping' it into a 'pocket' of platinum mesh, 225 mesh  $\text{cm}^{-2}$  (Fig. 1). This experimental know-how was transferred from VARTA AG, Kellkheim. The metal point contacts pressed onto the film are schematically represented in Fig. 1. The upper part of the platinum mesh was contacted with a brass holder well above the electrolyte level. Two platinum counter-electrodes were arranged in parallel. The potentials were measured with the aid of a Luggin capillary versus the  $\text{Hg}/\text{Hg}_2\text{SO}_4/1 \text{ M H}_2\text{SO}_4$  reference electrode (+ 674 mV vs SHE). The measured potentials are denoted as  $U_s$  and those calculated vs SHE as  $U_H$ . In the case of  $\text{H}_2\text{F}_2$  as electrolyte the reference electrode was separated from the cell by two discs of porous polyethylene [22]. The diffusion potential between 1 M  $\text{H}_2\text{SO}_4$  in the reference electrode and the acids in the cell of higher concentration was well below 50 mV. This was experimentally evaluated by combination with an electrode of the second or first kind in the corresponding acids on the basis of Hg, Pb and Cu [23].

The electrolytes were prepared by diluting the following acids with distilled water:

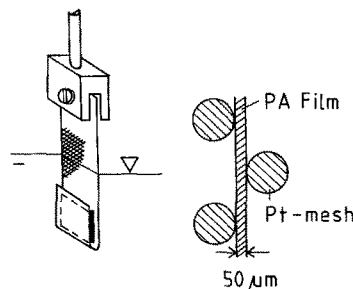


Fig. 1. Experimental polyacetylene electrode. Contacting Shirakawa PA film with platinum mesh.

sulphuric acid, 95–98% (Merck, p.a.)  
 perchloric acid, 70% (Merck, p.a.)  
 tetrafluoboric acid, 50% (Fluka, purum)  
 hydrofluoric acid, 40 and 70%  
 (Merck and Fluka, reinst)

The electrolyte was stirred slightly and was thoroughly purged with pure argon prior to insertion of the electrode. The wettability of the film was excellent; a strip of the material contacted at one end with the liquid seemed to be drawn into the electrolyte. The cell was made of glass and in the case of  $\text{H}_2\text{F}_2$  it was made of polypropylene. The temperature was  $20^\circ\text{C}$ . The measuring equipment for slow cyclic voltametry was conventional, consisting of a potentiostat (Wenking LT 73), a voltage scanner (AMEL 566) and an  $X$ - $Y$ -recorder, (Rhode & Schwarz, ZSKT). The scan rate was in the range of  $0.5$ – $10\text{ mV s}^{-1}$ , mostly at  $1\text{ mV s}^{-1}$ .

### 3. Results

#### 3.1. Total irreversible oxidation

**3.1.1. General behaviour.** On starting with an electrode containing pristine polyacetylene, the anodic current–voltage curve reveals in general two oxidation processes of the substrate. The more negative process (1) involves about 15% of the total charge for oxidation. The film remains smooth and coloured brass in the course of anodic oxidation (1). However, it becomes roughened, brittle and deep black after tracing the more positive process (2).

The two peaks are well separated at higher concentrations of the acids. However, with decreasing acid concentration, peak 1 is shifted strongly in the positive direction, while Peak 2 becomes more negative. Thus, the two peaks merge at lower concentrations to virtually one peak. This is demonstrated by the representative current–voltage curves shown in Figs. 2–4.

There is an upper limit for acid concentration in the case of oxidizing acids such as  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$ . In  $18\text{ M H}_2\text{SO}_4$  the film dissolves partially yielding a brown solution.

If the voltage scan direction is reversed after

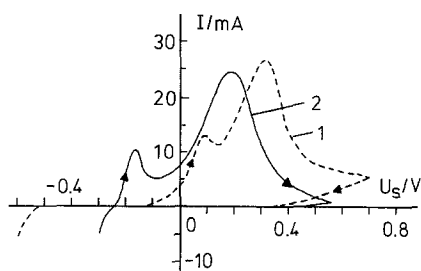


Fig. 2. Slow cyclic voltametry of  $1\text{ cm}^2$  polyacetylene foil in  $\text{H}_2\text{SO}_4$  electrolyte:  $v_s = 2\text{ mV s}^{-1}$ ; 1 - - - -  $12\text{ M H}_2\text{SO}_4$ ; 2 - - - -  $15\text{ M H}_2\text{SO}_4$ .

Peak 2, no reduction processes can be observed in the whole potential region. The total oxidation of the material is a strongly irreversible reaction.

The average charges derived from the oxidation peaks are

$$Q_1 = 0.60\text{ C} \quad Q_2 = 3.0\text{ C}$$

As  $1\text{ cm}^2$  of the film weighs  $1.8\text{ mg}$ , which corresponds to  $0.138\text{ mM 'CH'}$ , the average electrochemical equivalents are

$$m_{e,1} = 0.045\text{ F mol}^{-1}\text{ 'CH' } (y = 4.5\%)$$

$$m_{e,2} = 0.23\text{ F mol}^{-1}\text{ 'CH'}$$

Besides the four acids mentioned in Section 2, other acids were investigated:  $85\%\text{ H}_3\text{PO}_4$ ,  $98\%\text{ CH}_3\text{SO}_3\text{H}$  and  $100\%\text{ CH}_3\text{COOH}$ . These

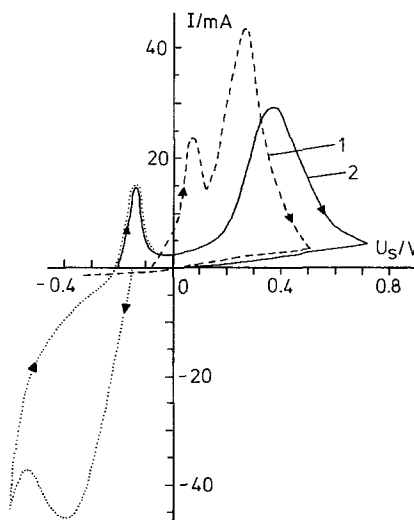


Fig. 3. Slow cyclic voltametry of  $1\text{ cm}^2$  polyacetylene foil in  $\text{HClO}_4$  electrolyte:  $v_s = 2\text{ mV s}^{-1}$ ; 1 - - - -  $8\text{ M HClO}_4$ ; 2 - - - -  $11.3\text{ M HClO}_4$ . Dotted line shows experiment with primary scan in the cathodic direction.

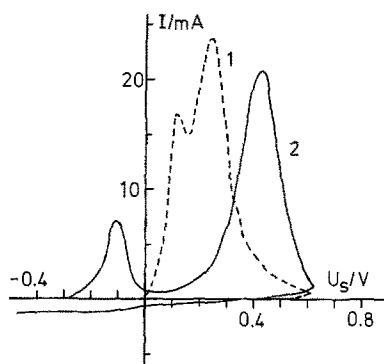


Fig. 4. Slow cyclic voltammetry of 1 cm<sup>2</sup> polyacetylene foil in H<sub>2</sub>F<sub>2</sub> electrolyte:  $v_s = 1 \text{ mV s}^{-1}$ ; 1 - - - - 13 M H<sub>2</sub>F<sub>2</sub>; 2 - - - - 22 M H<sub>2</sub>F<sub>2</sub>.

candidates exhibited only one irreversible oxidation peak at about  $U_s = 300 \text{ mV}$ . The charge of this peak was as high as 10 C in the case of phosphoric acid.

The influence of scan rate was tested with 8 M HClO<sub>4</sub> in the range of  $v_s = 0.5\text{--}5 \text{ mV s}^{-1}$ . The values of  $Q_1$  and  $Q_2$  derived from these experiments were practically independent of  $v_s$ .

The geometry of the platinum contacts allows for the fact that at a specific conductivity of  $10^{-4} \text{ S cm}^{-1}$  the ohmic voltage drop is below 100 mV. The corresponding doping level is attained very rapidly. Thus, current-voltage curves are not significantly influenced by ohmic polarization.

**3.1.2. Influence of acid concentration.** The chemical potential of the anion (and eventually the undissociated acid as a solvate molecule) is greatly influenced by the change of acid concentration. We have varied this parameter in an appropriate range. An upper limit is already described in the previous section, where a general discussion of the influence of acid concentration is involved as well. A lower limit is given by excessive irreversible oxidation of the substrate.

The insertion potentials, derived from the steep rise of current at the beginning of Peak 1 [20], and the oxidation potentials, derived from the peak maximum of Process 2, are plotted versus the molar acid concentration in Fig. 5. For comparison, former results for intercalation potentials on graphite [17, 19] and for insertion potentials on poly-*p*-phenylene (PPP) [20, 21] are included

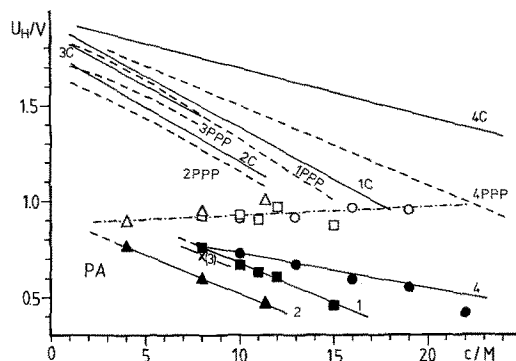
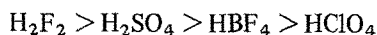


Fig. 5. Oxidation potentials of polyacetylene (PA), poly-*p*-phenylene (PPP) and graphite (C) vs molar acid concentration,  $c$ : 1 ■ — ■ PA, H<sub>2</sub>SO<sub>4</sub>, insertion potentials; 2 ▲ — ▲ PA, HClO<sub>4</sub>, insertion potentials; 3 □ — □ PA, HBF<sub>4</sub>, insertion potentials; 4 ● — ● PA, H<sub>2</sub>F<sub>2</sub>, insertion potentials; — — — — PA, corresponding peak potentials of Peak 2. For comparison from literature: 1-4 — — — — C, intercalation potentials in the corresponding acids; 1-4 - - - - PPP, insertion potentials in the corresponding acids.

in the diagram. The potentials on polyacetylene are much more negative than the other ones. At a given acid concentration, the relative order is maintained and the insertion potentials are shifted in the negative direction in the following order:



Exactly the same order has been found with graphite [17, 21] and with PPP [20, 21].

While the insertion potentials (Peak 1) are shifted linearly in the negative direction with increasing acid concentrations, the peak potentials are shifted quasi-linearly to the positive side. The slope of the curves are much smaller than the previously observed slopes.

### 3.2. Partial reversible oxidation, 'inner cycles'

**3.2.1. Cyclic behaviour.** Even if the electrode is cycled in the limited potential region of Peak 1, it shows only partial reversible behaviour. Fig. 6 represents a typical example. In these 'inner cycles', the first oxidation peak, starting with pristine polyacetylene, which is also shown in Figs. 2-4, is appreciably higher than the subsequent peaks, and it is shifted to more positive potentials. The capacity of the electrode, derived from the charge in the oxidation peak  $Q$ , is continuously lessened in the course of cycling. The

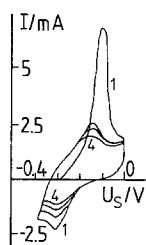


Fig. 6. Slow cyclic voltammetry of PA in 22 M  $\text{H}_2\text{F}_2$  in the potential region of Peak 1 ('inner cycles'). Potential range:  $U_s = -400-0$  mV; cycle 1-4;  $v_s = 1$  mV  $\text{s}^{-1}$ .

current efficiency, c.e. =  $Q_{\text{disch}}/Q$ , is low in the course of the first cycles, but it increases to a value slightly below 100%. In the steady state, the capacity loss per cycle seems to be equivalent to the loss indicated by the current efficiency, which is indicative of an irreversible attack of the host lattice.

No significant change of this general behaviour could be observed for other polyacetylene samples such as a *cis*-rich one (cf. Fig. 7) or after activation by charging and discharging in an aprotic system.

Chemical doping of polyacetylene was demonstrated in 11.3 M (70 wt%)  $\text{HClO}_4$ . On scanning primarily in the negative direction, a large reduction peak (in the potential range of Peak 1) was detected with an unusual capacity of 8.0 C. This cathodic peak is indicated in Fig. 3 as a dotted line. However, subsequent cycles exhibited only the normal partial reversibility.

If the experiments were not performed under Ar, but after a short exposure of the film in the open air, only rather small changes of the current-voltage and capacity-time behaviour was observed. These experiments were done with 8 M  $\text{HBF}_4$ .

**3.2.2. Capacity losses upon cycling.** Fig. 7 shows the capacity  $Q$  in  $\text{H}_2\text{F}_2$  as a function of cycle number  $Z$ . The capacities are normalized to the initial capacity  $Q_0$ . For one example, the current efficiency c.e. vs  $Z$  is included. The curves show a continuous decrease of capacity upon cycling. The initial large fall off is lessened later but no constant value is attained. The c.e. increases to nearly 100% and the small deficit of c.e. per cycle is reflected in the capacity loss in the later stages of the experiment.

In Fig. 8, some results in 8 M (50%)  $\text{HBF}_4$

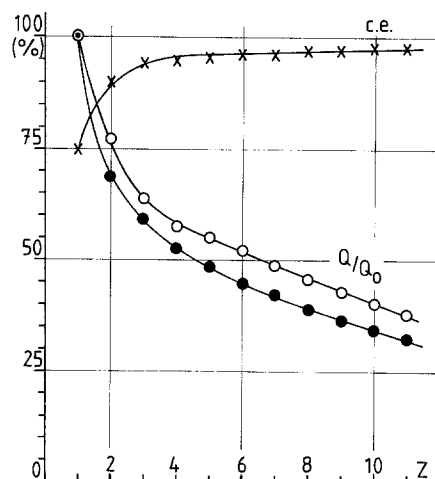


Fig. 7. Continuous cyclic voltammetry. Charging capacity,  $Q$ , and current efficiency, c.e., vs cycle number,  $Z$ . Electrolyte: 22 M  $\text{H}_2\text{F}_2$ ,  $v_s = 1$  mV  $\text{s}^{-1}$ ;  $\circ$ — $\circ$   $Q/Q_0$  (%),  $Q_0 = 0.6$  C,  $y_0 = 4.5\%$ , potential range,  $U_s = -400-0$  mV;  $\bullet$ — $\bullet$   $Q/Q_0$  (%),  $Q_0 = 0.42$  C,  $y_0 = 3.2\%$ , potential range,  $U_s = -400+80$  mV for *cis*-rich PA material;  $\times$ — $\times$  current efficiency, c.e., for curve  $\bullet$ — $\bullet$ .

are presented. By changing the scan rate, the conversion ( $y$ ) is varied. Once again, the capacity decays rapidly for  $v_s = 0.2$  and 1 mV  $\text{s}^{-1}$ . In the latter experiment, current efficiencies are shown in addition. With the highest scan rate (10 mV  $\text{s}^{-1}$ ), where conversion is rather low, an initial increase of capacity is observed, which may be due to a formation process.

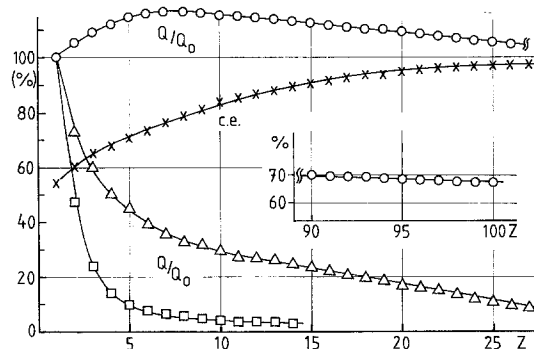


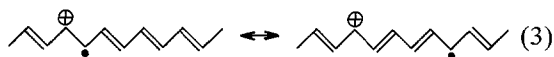
Fig. 8. Continuous cyclic voltammetry. Charging capacity,  $Q$ , and current efficiency, c.e., vs cycle number,  $Z$ . Electrolyte: 8 M  $\text{HBF}_4$ ,  $v_s$  as variable;  $\square$ — $\square$   $Q/Q_0$  (%),  $Q_0 = 0.58$  C,  $y_0 = 4.4\%$ ,  $U_s = -400+120$  mV for  $v_s = 0.2$  mV  $\text{s}^{-1}$ ;  $\triangle$ — $\triangle$   $Q/Q_0$  (%),  $Q_0 = 0.69$  C,  $y_0 = 5.2\%$ ,  $U_s = -500+90$  mV for  $v_s = 1.0$  mV  $\text{s}^{-1}$ ;  $\times$ — $\times$  c.e. vs  $Z$  curve for this experiment;  $\circ$ — $\circ$   $Q/Q_0$  (%),  $Q_0 = 0.028$  C,  $y_0 = 0.2\%$ ,  $U_s = -400+120$  mV for  $v_s = 10$  mV  $\text{s}^{-1}$ .

Nevertheless, capacity decreases continuously even in this case, starting with the seventh cycle. As the fall off in capacity is strongest in the case of small scan rates, transport limitation cannot be the reason for it.

#### 4. Discussion

If we assume that anions of the corresponding acids ( $\text{HSO}_4^-$ ,  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{HF}_2^-$ ) are anodically inserted in the potential region of Peak 1 according to Equation 2, the (primary) degree of insertion (for the average  $\gamma = 4.5\%$ ) is relatively low. It is about 50% of that value, which is found under aprotic conditions with a corresponding experimental technique [24], and it is even less than 50% with reference to values reported elsewhere. Similar to this, with graphite intercalation compounds of the acceptor type,  $y_{\text{max}} = 4.2\%$  (1st stage) is attained under anhydrous conditions, but only  $y_{\text{max}} = 2.1\%$  (2nd stage) can be realized in aqueous electrolytes [25, 26].

The primary step in Process 1 is the anodic oxidation of the polyacetylene molecule to a radical cation:



The positive charge as well as the unpaired electron moves through the chain. The insertion of an anion according to Equation 2 into the host lattice provides electroneutrality.

The time constant of the experiment

$$\tau = \frac{\Delta U}{v_s} \quad (4)$$

where  $\Delta U$  is the potential range of Peak 1 and  $v_s$  is the scan rate, must be adapted to the time constant of diffusion of the anion in the solid in order to prevent transport limitation:

$$\tau = \frac{L^2}{4D} \quad (5)$$

where  $L$  is the transport length and  $D$  is the diffusion coefficient.

As  $D$  is in the order of  $10^{-11} \text{ cm}^2 \text{ s}^{-1}$  [27] and as no concentration polarization can be detected at  $v_s = 1 \text{ mV s}^{-1}$ , the standard scan rate in our experiments,  $L$  must be lower than  $10^{-4} \text{ cm}$ . This leads to the conclusion, that the fibrils of a radius

of  $10^{-6} \text{ cm}$  are wetted within the macroscopic film thickness.

The insertion process is about 0.7–1 V more negative than the corresponding process on graphite or poly-*p*-phenylene, cf. Fig. 5. In spite of this fact, the radical cation of polyacetylene seems to be rather reactive, and the stability of the insertion compound, which is discussed below, is appreciably lessened.

The insertion potential for Process 1 is shifted in the *negative* direction linearly with increasing molar concentration of the acid. We have observed the same virtual strong deviation from the Nernst law formerly in the case of graphite and poly-*p*-phenylene as host lattices. The explanation was found in terms of kinetic involvement of solvate molecules in the anodic insertion process [19].

The kinetic equation is given by

$$\frac{j}{F} = k_+ a_A^- c_{\text{HA}}^\nu \exp\left(\frac{\alpha F \eta}{RT}\right) \quad (6)$$

where  $a_A^-$  is the activity of the free anions and  $\nu$  is the reaction order of solvate acid.

The concentration  $c_{\text{HA}}$  of solvate acid is known from spectroscopic measurements to rise exponentially with increasing molar acid concentration,  $c$ , in a wide range of concentrations:

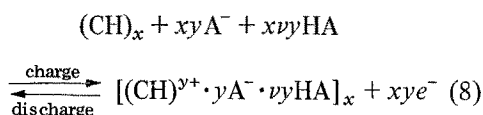
$$c_{\text{HA}} = c_0 \exp(kc) \quad (7)$$

With this model we were able to explain the analytically established stoichiometric numbers for graphite sulphate and perchlorate ( $\nu = 2$  [19]). If we assume, that this model is valid in the case of polyacetylene as well, the conclusions compiled in Table 1 can be drawn.

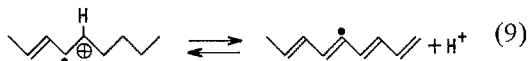
Thus, the lower slopes in the case of polyacetylene lead to a smaller value of  $\nu$  in order of 1.5. The overall reaction for insertion of anions (Process 1) can be written more precisely

Table 1. Slopes in  $\text{mV M}^{-1}$  of  $U_{H,I}$  vs  $c$ -curves and  $\nu$  derived therefrom

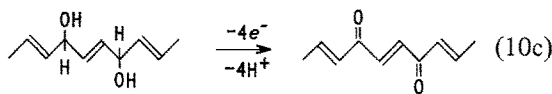
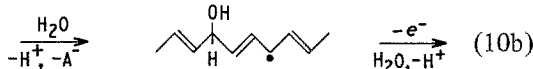
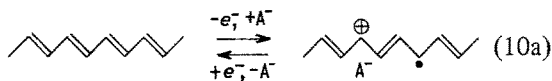
Acid (guest)	Graphite: host lattice		Polyacetylene: host lattice	
	Slope	$\nu$	Slope	$\nu$
$\text{H}_2\text{SO}_4$	55	2	40	~ 1.5
$\text{HClO}_4$	58	2	41	~ 1.4
$\text{HBF}_4$	54	—	—	—
$\text{H}_2\text{F}_2$	26	—	18	—



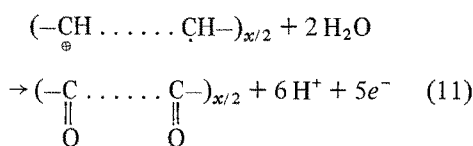
The strong acids should be able to stabilize the radical cation and prevent the splitting off of a proton:



Thus, substitution processes according to a concerted *ec* mechanism [29] should be not very reasonable.\* However, the electrochemically initiated addition of nucleophiles such as water molecules leads to a straightforward explanation of the instability of the system



The first step is Process 1 and subsequent steps constitute Process 2. The overall reaction in Process 2 can be written as



This mechanism is in accordance with the following experimental findings:

1. The formation of an insertion compound as a precursor for the oxidation of the polyacetylene chain. For graphite oxide formation, the graphite intercalation compound as a precursor has been claimed formerly [30].

2. The ratio  $Q_1:Q_2 = 1:5$ .

3. The interruption of bond conjugation in the chain. Electronic conductivity must decrease due to this effect as well as due to consumption of holes.

4. The irreversibility of the process involved in Peak 2.

\* Nevertheless, it would lead, via an en-diol as an intermediate, to the same end-product as outlined below.

5. The *positive* shift of electrode potential by Peak 2 by about 60 mV after increasing of  $a_{\text{H}^+}$  by one order, cf. Fig. 5.

It has been observed, that even the process in Peak 1 is only partially reversible. With increasing  $y$ , that is with increasing concentrations of radical and cationic sites in the chain, the reversibility decreases. The potential increases with  $\log y$  [31]. As the current-voltage curves for both processes overlap more or less, the probability of partition of irreversible processes must increase with increasing  $y$ . Anodic water decomposition is not possible in the potential range of Process 1. Thus, the only side reaction is the irreversible oxidation of the host lattice itself. The findings with phosphoric acid show, that it can even proceed beyond the stage discussed here.

It is clear that the conclusions derived in this work from electrochemical experiments must be confirmed by analytical evaluation of the compounds synthesized in the course of the Processes 1 and 2. However, this was outside the scope of this investigation.

Corresponding work in aprotic solvents [24] shows a quite similar irreversible degradation of the polymer. As the water activity is very low, other nucleophiles must take over its role.

Even if the stability problem did not exist, the  $y$  values found experimentally are in the order of those known for graphite, and the potentials are much more negative. Thus, the preconditions for an application as a positive in a secondary cell in aqueous electrolytes do not appear very favourable.

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