

## The Electrochemical Oxidation of Polyacetylene and Its Battery Applications

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# The Electrochemical Oxidation of Polyacetylene and Its Battery Applications

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## ABSTRACT

When oxidized in a nonaqueous cell containing 1.0M LiClO<sub>4</sub> in propylene carbonate, polyacetylene develops a voltage of 3.4-4.0V vs. Li/Li<sup>+</sup> ClO<sub>4</sub><sup>-</sup>. Oxidation levels at least as high as [CH(ClO<sub>4</sub>)<sub>0.10</sub>]<sub>x</sub> can be produced electrochemically and then reduced to the undoped state with nearly 100% coulombic efficiency. The electrochemical doping (oxidation) process is only efficient when carried out with a minimum of liquid electrolyte under ultraclean conditions. Similar results are observed with a LiAsF<sub>6</sub> electrolyte. Polyacetylene is an extraordinary material of great importance for electrochemistry. However, on the basis of this and other published research, it is not yet clear that it offers major advantages over current electrodes for high energy density nonaqueous batteries.

Polyacetylene is a fascinating new material with extraordinary electrochemical properties. It is a simple conjugated organic polymer which can easily be synthesized by the catalytic polymerization of acetylene. Polyacetylene films can be chemically oxidized and reduced by a variety of species, such as halogens (I and Br) and various organo-alkali metal reagents, such as n-butyl lithium and sodium naphthalide. These reactions are generally referred to as p-doping (oxidation) or n-doping (reduction). They produce compounds of the type (CHX<sub>y</sub>)<sub>x</sub> and (M<sub>y</sub>CH)<sub>x</sub>, in which y is typically in the range of 0-0.1. What is most unusual about polyacetylene is that p- or n-doping transforms it from a virtual electronic insulator into a lustrous polymer with an electronic conductivity typical of metals (1).

The reversible oxidation and reduction of polyacetylene can also be carried out electrochemically in nonaqueous electrolytes containing appropriate dissolved anions or cations. These reactions were first described by Nigrey *et al.* (2). The electrochemical potentials of oxidized polyacetylene films (X = I, AsF<sub>6</sub>, Br, ClO<sub>4</sub>) are typically 3-4V vs. the Li/Li<sup>+</sup> electrode. The potentials of the reduced films (M = Li, Na) are about 0.5-1.5V vs. that of Li/Li<sup>+</sup>. Nigrey *et al.* (2) and MacInnes *et al.* (3) first suggested that the oxidized and reduced polyacetylenes might be used as high voltage anode/cathode couples in nonaqueous electrochemical cells.

The general goals of our research have been to examine those aspects of the chemistry and electrochemistry of polyacetylene which influence its potential application in batteries. This paper summarizes our investigations of the stability and electrochemical oxidation of polyacetylene in propylene carbonate containing LiClO<sub>4</sub> or LiAsF<sub>6</sub>.

## Stability

Polyacetylene exists in *cis* and *trans* isomers (Fig. 1). *Trans* polyacetylene is the thermodynamically stable form. The *cis* isomer can be produced by polymerization at low (-78°C) temperatures, but it is unstable toward isomerization, which can be induced by heating or by doping with various chemical species (5, 6, 7). Polyacetylene also self-reacts, forming cross-links and defects. These reactions occur rapidly at elevated temperatures (150°-260°C) (5).

The stability of polyacetylene has been studied by various authors (8, 9, 10, 11). In the absence of a

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supply of counterions, virgin and doped polyacetylene are extremely reactive with oxygen. When films are exposed to small concentrations of oxygen for short times, the reaction appears to be reversible. However, during longer exposure, oxygen irreversibly attacks the polymer chain and degrades the conjugated bond network. Oxidation also embrittles the material. Similar reversible and irreversible reactions are observed with other oxidants. We have observed that iodine-doped polyacetylene irreversibly degrades above 60°C, and films doped with bromine irreversibly degrade above about 40°C (11). There are initial indications (11, 12) that films doped with AsF<sub>6</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup> are somewhat more stable.

## Electrochemical Experiments

MacDiarmid *et al.* first demonstrated that films of polyacetylene prepared by the Shirakawa technique can be readily doped to semiconducting and metallic states with a wide variety of chemical species (13, 14, 15). Interest in the electrochemistry of polyacetylene began with the demonstration by Nigrey *et al.* (2) that polyacetylene can be electrochemically oxidized to

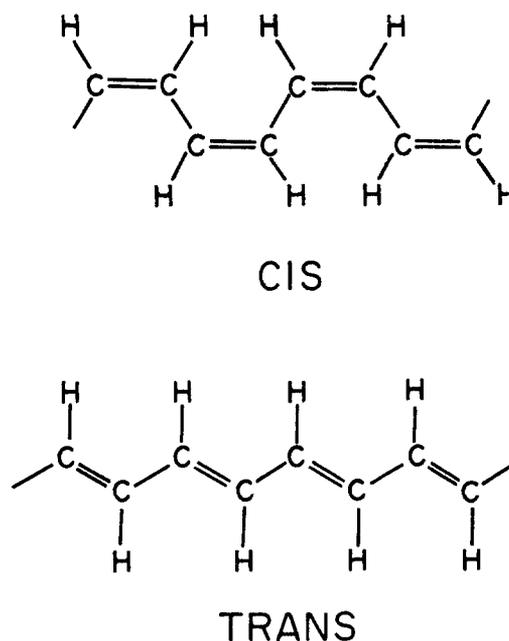


Fig. 1. Polyacetylene isomers

the metallic state in reactions that are the electrochemical equivalents of the chemical doping reactions. Many additional investigations of the electrochemical reactions of polyacetylene have been reported (16-21).

Our research has examined the oxidative (p-doped) electrochemical reactions of polyacetylene in propylene carbonate containing  $\text{LiClO}_4$  or  $\text{LiAsF}_6$ . Its principal goals have been to explore the reversibility, coulombic efficiency, and electrochemical potentials associated with the reactions at various levels of doping (values of  $y$  in  $[\text{CHX}_y]_x$ ).

The polyacetylene films used in these experiments were prepared by the technique first described by Shirakawa (4). Polyacetylene was transferred and stored under vacuum, and manipulated and studied in an inert atmosphere dry box.

Experiments were carried out with electrochemical

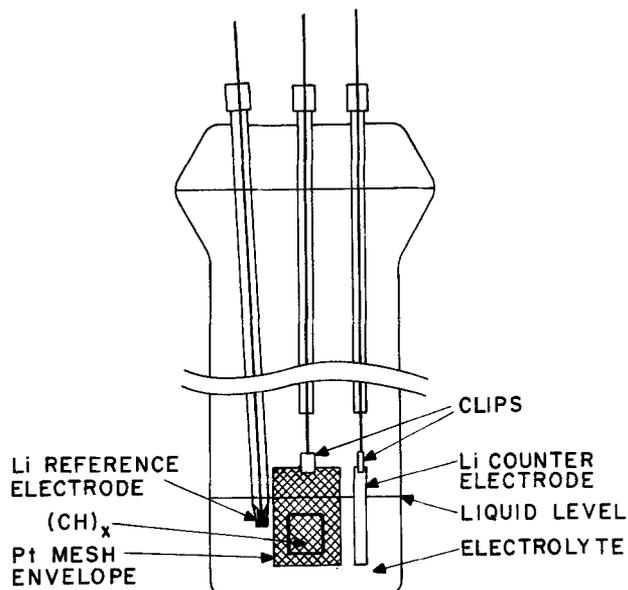


Fig. 2. Larger volume electrochemical cell

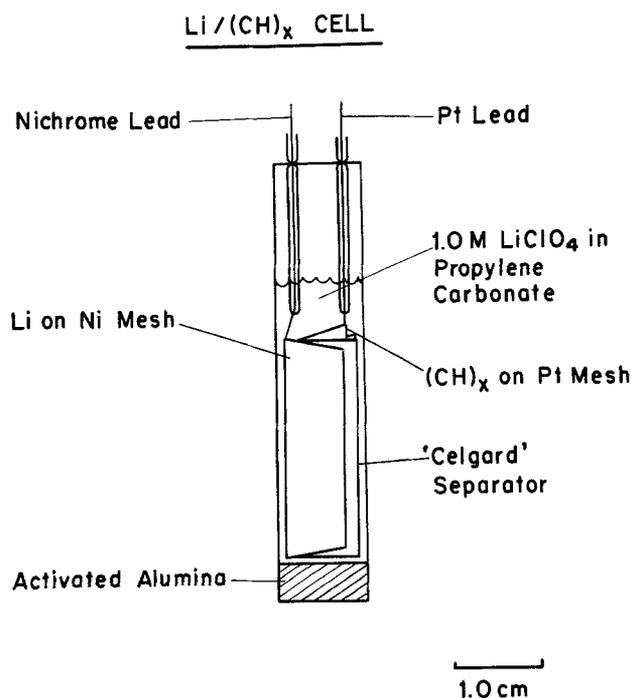


Fig. 3. Sealed electrochemical cell of small electrolyte volume

cells of the types shown in Fig. 2 and Fig. 3. Electrolytes were prepared from Burdick and Jackson propylene carbonate which was distilled and then percolated through neutral activated alumina (Fisher or Woelm). The electrolyte salts were  $\text{LiAsF}_6$  (U.S. Steel, Electrochemical Grade),  $\text{LiClO}_4$  (Alfa-Ventron), and  $\text{LiClO}_4$  (Anderson Physics). The salts were dried at  $180^\circ\text{C}$  before use. After the salts were dissolved, the electrolyte solutions were purified by a second percolation through activated alumina.

## Results

**Series A.**—The first series of experiments was carried out using the electrochemical cell shown in Fig. 2 and electrolytes prepared from  $\text{LiAsF}_6$  and from  $\text{LiClO}_4$  obtained from Alfa-Ventron. Data from one set of experiments using  $\text{LiAsF}_6$  are described first. These experiments used a sample of polyacetylene of about  $0.7\text{ cm}^2$  in area (2.8 mg), held in Pt mesh, along with approximately  $10\text{ cm}^3$  of  $0.95\text{M}$   $\text{LiAsF}_6$  in propylene carbonate.

The cell was first studied without any polyacetylene in order to determine the electrochemical stability of the electrolyte. The working electrode was a large piece of Pt mesh, about  $2\text{ cm}^2$  in area, normally used to hold the sample of polyacetylene. While the potential was slowly swept from 2.7 to  $4.0\text{V}$  vs.  $\text{Li/Li}^+$  at  $2\text{ mV/sec}$ , background currents of less than  $3\text{ }\mu\text{A/cm}^2$  were observed between 3.2 and  $3.75\text{V}$ . Around  $3.8\text{V}$ , the current began to rise and reached a value of about  $20\text{ }\mu\text{A/cm}^2$  at  $4.0\text{V}$ . The solvent had a good window of stability in the potential range of 3.2 to  $3.75\text{V}$  vs.  $\text{Li/Li}^+$ , but decomposed at an increasing rate at higher potentials.

With the polyacetylene sample in place, appreciable oxidation began at around  $3.4\text{V}$  and the current rose to just over  $3\text{ mA/cm}^2$  at  $4.0\text{V}$ . Reduction was observed when the sweep was reversed.

The polyacetylene sample was then repeatedly oxidized and reduced to determine the maximum oxidation level which could be achieved and the reversibility of the reaction. To oxidize the film, the potential was increased in  $100\text{ mV}$  steps from 3.5 to  $3.9\text{V}$ . The experiment was first carried out without a sample of polyacetylene. The control experiment demonstrated that negligible background current passed up to potentials of  $3.9\text{V}$ . With a sample in place, currents upon initial polarization were much larger, typically  $0.5\text{--}1\text{ mA/cm}^2$ , on the basis of the geometric area of one side of the polyacetylene. At each potential, the current decayed rapidly to a value that remained approximately constant. The magnitude of the limiting current increased with increased polarization voltage (see Table I).

A separate experiment under essentially identical conditions was designed to determine the coulombic efficiency of the oxidation/reduction process. This experiment started with a fresh sample of polyacetylene, which attained an open-circuit voltage of  $2.49\text{V}$  vs.  $\text{Li/Li}^+$ . The film was oxidized (charged) by increasing its potential from 2.6 to  $3.7\text{V}$  in  $100\text{ mV}$  steps. At any given potential, the potential was increased when the current had decayed to approximately 10% of its peak value. To reduce the film (discharge), the po-

Table I.

Potential (V) (Charge)	I Limiting ( $\mu\text{A/cm}^2$ )
3.5	20
3.6	24
3.7	57
3.8	157
3.9	571
Total	

tential was stepped immediately to 3.6V and then to 3.0V in 100 mV steps. Again, the potential was decreased whenever the current decreased to 10% of its initial value at any potential. A final discharge step at 2.5V was carried out for 24 hr. Table II summarizes the results. The maximum oxidation level attained ( $y$  in  $[\text{CHX}_y]_x$ ) was 0.11, based on the total charge passed. However, the total charge recovered during discharge indicated a real  $y$  value of only 0.023. This yielded an apparent efficiency of charge storage and recovery only about 22%.

We observed similar results in other experiments of this type. Because this behavior might have been the result of some curious chemistry of the  $\text{AsF}_6^-$  ion, the experiments were repeated with an electrolyte of 1.0M  $\text{LiClO}_4$  in propylene carbonate. However, all of the results were consistent, regardless of the electrolyte salt. In all cases, the coulombic efficiency of the polyacetylene electrode was very low. The charge recovered upon reduction indicated that a maximum oxidation level of no greater than 0.02-0.03 could be achieved before the oxidation process became very inefficient.

**Series B.**—The results of Series A are inconsistent with previous reports by MacDiarmid and co-workers (see, for example, 2, 16-21) which have indicated that polyacetylene can be oxidized to  $y$  values of 0.07 with coulombic efficiencies of over 90%. They obtained these results with electrochemical cells containing very small amounts of electrolyte.

We evaluated one cell of this type, which was prepared by members of Professor MacDiarmid's research group. It contained a polyacetylene electrode about 1.12  $\text{cm}^2$  in area (2.7 mg). The polyacetylene was separated from a lithium electrode with Celgard™, a porous polymeric separator. The electrode package was packed into the upper part of a small glass cell (see Fig. 3). The lower part was filled with activated alumina.

The cell had undergone five charge-discharge cycles before it was given to us under the conditions of 0.050  $\text{mA}/\text{cm}^2$  charge followed by discharge at 0.500  $\text{mA}/\text{cm}^2$  and an additional exhaustive controlled potential discharge at 2.5V vs.  $\text{Li}/\text{Li}^+$ . We then carried out seven additional cycles. Table III summarizes the results.

In each cycle, the polyacetylene electrode film was oxidized at a constant current of 50  $\mu\text{A}/\text{cm}^2$ . During

Table II.

Potential (V) (Charge)	$^*Q$ (C)	% Cumulative oxidation or reduction
2.6	0.0002	
2.7	0.0004	
2.8	0.0005	
2.9	0.0005	0.01
3.0	0.0010	0.02
3.1	0.0020	0.03
3.2	0.0045	0.07
3.3	0.0095	0.14
3.4	0.0190	0.23
3.5	0.1017	1.10
3.6	0.1070	1.90
3.7	1.1740	11.00
Total charge:	1.4203	
(Discharge)		
3.6	0.0001	
3.5	0.0124	0.09
3.4	0.0211	0.25
3.3	0.0211	0.41
3.2	0.0117	0.50
3.1	0.0046	0.53
3.0	0.0033	0.56
2.5	0.2425	2.30
Total charge:	0.3168	
Efficiency:	22%	

\* Not cumulative.

Table III.

% Oxidation*	Reduction current ( $\text{mA}/\text{cm}^2$ )	$Q_0/Q_1$ (%)**	$Q_0/Q_1$ Total %†
6.96	0.56	48.7	92.1
6.96	0.56	48.6	92.2
7.00	0.56	52.7	92.1
6.00	0.56	45.3	94.3
3.00	0.28	50.0	90.0
6.00	0.28	66.5	90.7
6.00	0.14	60.5	84.8

\* 100y in  $(\text{CHX}_y)_x$ , oxidized at 0.050  $\text{mA}/\text{cm}^2$ ; \*\* at constant current; † constant current plus additional controlled-potential discharge at 2.5V.

oxidation, the potential of the cell slowly rose from about 3.79V at  $y = 0.03$  to 3.9V at  $y = 0.07$ . The cell was then discharged at three different currents: 500  $\mu\text{A}/\text{cm}^2$ , 250  $\mu\text{A}/\text{cm}^2$ , and 120  $\mu\text{A}/\text{cm}^2$ , in separate experiments. At all three discharge currents, the cell potential immediately fell to about 3.4V. It then continued to decrease until it reached 2.5V. The constant-current discharge was changed to an extended controlled-potential discharge at that potential.

About 50% of the charge could be removed during the constant current discharge at 500  $\mu\text{A}/\text{cm}^2$  before the cell potential reached 2.5V. At the lower discharge currents, 60-65% of the charge was removed before the potential reached 2.5V. The initial peak currents during controlled potential discharge were 500-800  $\mu\text{A}/\text{cm}^2$ . After about 1 hr, the current decayed to less than 50  $\mu\text{A}/\text{cm}^2$ . After 15 hr at 2.5V, the current was less than 1  $\mu\text{A}/\text{cm}^2$ . The controlled potential discharges extracted an additional 30-40% of the initial oxidation charge, which yielded overall coulombic efficiencies of 85-95%.

**Series C.**—Another cell of this design (Fig. 3) was prepared. It used a polyacetylene sample of 1.3  $\text{cm}^2$  (2.86 mg) supported on Pt mesh of about 2  $\text{cm}^2$ . The lithium counterelectrode was formed by pressing lithium ribbon into a nickel support mesh, and was about 3  $\text{cm}^2$  in area. The electrodes were separated by a Celgard K-442 polypropylene sheet. The cell contained about 1g of activated alumina (Woelm) as a continuous getter for impurities and about 1  $\text{cm}^3$  of electrolyte prepared from Burdick and Jackson UV-grade propylene carbonate which had been vacuum distilled and contained 1.0M  $\text{LiClO}_4$ . After one freeze-pump-thaw cycle, the cell was sealed under vacuum.

The cell was charged at a constant current density of 50  $\mu\text{A}/\text{cm}^2$  (based on the area of one side of the polyacetylene) and later discharged in two steps, first at 500  $\mu\text{A}/\text{cm}^2$  until the potential reached 2.5V, and then in an extended controlled-potential discharge at 2.5V. The controlled-potential discharge was generally carried out for about 16 hr, during which the cell current decayed to less than 1  $\mu\text{A}/\text{cm}^2$ . A typical plot of current vs. time during controlled-potential discharge is shown in Fig. 4.

The results of this experiment are summarized in Table IV, which presents the final open-circuit voltage attained after charging as a function of oxidation level. It also indicates the fraction of charge recovered during constant-current discharge and the total charge recovered at constant current and controlled potential. The data are listed in the order of increasing oxidation level. The real order in which the experiments were carried out is indicated by the numbers in brackets after each value of  $y$ . Figure 5 plots the open-circuit voltage after charging as a function of oxidation level.

The results on coulombic efficiency clearly demonstrate that nearly all of the charge injected during oxidation can be recovered if the reduction begins immediately. However, regardless of the oxidation level, only about half of the charge can be recovered under the constant-current conditions used (500  $\mu\text{A}/$

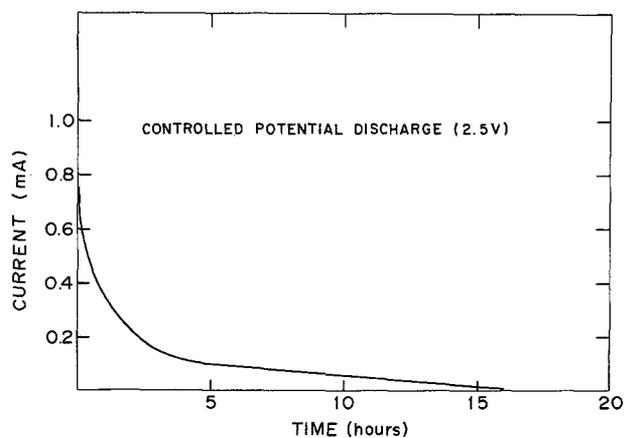


Fig. 4. Discharge of polyacetylene cathode at controlled potential of 25V vs. Li/Li<sup>+</sup>.

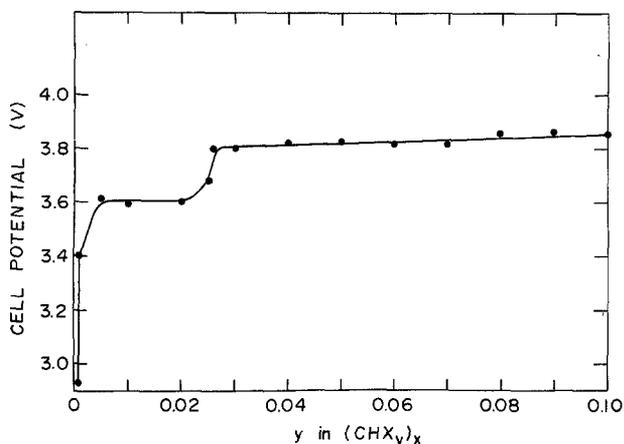


Fig. 5. Open-circuit potential of Li/[CH(ClO<sub>4</sub>)<sub>y</sub>]<sub>x</sub> as function of y. Cell oxidized at 50 μA/cm<sup>2</sup> constant current.

cm<sup>2</sup>). The remainder can only be extracted at lower rates.

To measure the rate of self-discharge of the cell, the polyacetylene was first charged to a  $y$  level of 0.03 and then discharged using the usual constant-current/controlled-potential sequence. In one experiment the discharge began immediately, in the other it was delayed while the cell stood on open circuit for 40 hr. The results are summarized in Fig. 6. Immediate constant current discharge recovered 41% of the

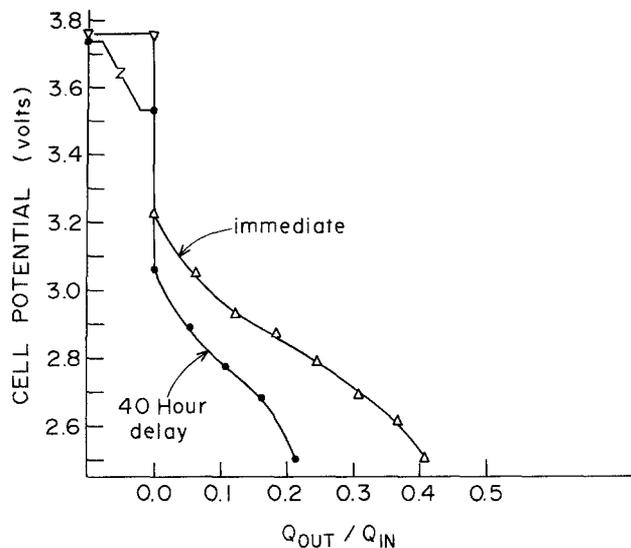


Fig. 6. Immediate and delayed constant current (500 μA/cm<sup>2</sup>) reduction of polyacetylene originally oxidized to a level of  $y = 0.03$  at 50 μA/cm<sup>2</sup> in an LiClO<sub>4</sub>-PC electrolyte. Charge fraction refers to fraction of the original doping level recovered upon reduction.

charge; an additional 56% was recovered during the subsequent controlled-potential discharge for a total coulombic efficiency of 97%. The initial open-circuit potential was high, but dropped sharply as the result of cell resistance when the discharge current was applied. In the other experiment, the 40 hr delay resulted in a decrease in the open-circuit potential of the cell. No change in the cell IR drop was observed. But, constant current discharge recovered only 21% of the initial charge. A total of 61% was recovered after the controlled-potential step.

## Discussion

Our experiments confirm previous reports of MacDiarmid *et al.* (16-19) that polyacetylene can be reversibly oxidized (p-doped) to compositions of (CH[ClO<sub>4</sub>]<sub>0.10</sub>)<sub>x</sub> and then reduced with nearly 100% coulombic efficiency. The results also illustrate several aspects of the stability, variation in electrochemical potential, and electrochemical reversibility of polyacetylene. These are discussed in this section, which also reviews the prospects for polyacetylene as a cathode material in nonaqueous batteries.

Our results confirm that the oxidation of polyacetylene is highly efficient if carried out with a minimum of electrolyte under ultraclean conditions (for example, 2-3 mg of polyacetylene with about 1 cm<sup>3</sup> of electrolyte sealed under vacuum with Al<sub>2</sub>O<sub>3</sub>—experimental Series B and C). However, poor coulombic efficiencies were observed when the same amount of film was in contact with about 10 cm<sup>3</sup> of electrolyte in a cell which was not sealed under vacuum, but merely operated in a dry box. We assume that the inefficiency observed with the latter cell was the result of impurities in the electrolyte, although no thorough study of the impurity content of the various electrolytes used in this investigation has been carried out.

The observation that even cells which use a minimum of electrolyte can yield poor coulombic efficiencies during initial oxidation/reduction cycles (see, for example, Table IV, cycle 1) suggests that polyacetylene is extremely sensitive to the presence of traces of impurities in the electrolyte. The first oxidation/reduction cycles with a polyacetylene electrode may actually help purify the electrolyte. Whether impurities are in fact the major cause of poor efficiency, however, cannot be confirmed without a more detailed study of electrolyte/polyacetylene interactions.

Table IV.

% Oxidation*	Final potential (V)	Q <sub>o</sub> /Q <sub>i</sub> (%)**	Q <sub>o</sub> /Q <sub>i</sub> Total %†	Cycle
0.50	3.61	19.7	100.0	18
1.00	3.59	2.1	100.0	12
2.00	3.60	2.4	100.0	16
2.50	3.68	3.5	93.2	20
2.69	3.80	46.3	96.9	3
3.00	3.80	39.2	73.1	1
3.00	3.80	21.3	62.0	2
3.00	3.80	41.6	96.8	8
4.00	3.81	43.3	89.0	4
4.00	3.83	45.5	92.5	5
4.00	3.84	45.5	94.4	6
5.00	3.84	46.6	89.7	7
5.00	3.84	46.9	92.5	9
5.00	3.82	46.1	93.0	10
6.00	3.82	44.2	95.4	14
7.00	3.82	41.6	95.6	19
8.00	3.86	50.9	88.9	11
8.00	3.86	46.9	94.1	15
9.00	3.86	44.6	91.2	17
10.00	3.85	48.7	87.6	13

\* 100y in (CHX<sub>y</sub>)<sub>x</sub>; \*\* at constant current of 500 μA/cm<sup>2</sup>; † constant current plus additional controlled potential discharge at 2.5V.

We have also observed that only about 50% of the charge stored in oxidized polyacetylene ( $x = \text{ClO}_4$ ) at a current density of  $50 \mu\text{A}/\text{cm}^2$  can be recovered at a constant-current discharge of about  $500 \mu\text{A}/\text{cm}^2$  before the potential of the electrode drifts sharply toward negative values. The remainder of the stored charge appears to be accessible, but only upon extended controlled-potential discharge at 2.5V vs. Li/Li<sup>+</sup>. These results imply that slow diffusion of  $\text{ClO}_4^-$  in polyacetylene may hinder the recovery of a large fraction of the stored charge. Results which also imply that the slow diffusion of anions in polyacetylene may limit the rate of its electrochemical reactions have been presented by Will (23).

The results shown in Fig. 6 also suggest that even under carefully controlled conditions, oxidized polyacetylene ( $x = \text{ClO}_4$ ) undergoes considerable loss of charge upon standing on open circuit for 40 hr. This might be the result of the diffusion of  $\text{ClO}_4^-$  species deep into the polyacetylene fibrils or of slow self-discharge with the nonaqueous electrolyte. It might also be caused by the irreversible chlorination of polyacetylene by  $\text{ClO}_4^-$ .

There is no doubt that many of the oxidized polyacetylene compositions are thermodynamically unstable toward irreversible oxidation of the conjugated-polymer backbone. As mentioned earlier in this paper, irreversible halogenation begins at 40°-60°C with Br<sup>-</sup> or I<sup>-</sup> as the doping ion. The stability of  $\text{ClO}_4^-$ -doped compositions appears to be considerably greater, although recent reports of Abe *et al.* (24) and Winkle *et al.* (25) indicate that extended electrochemical cycling of polyacetylene with  $\text{ClO}_4^-$  may slowly result in its irreversible chlorination. It may be that the degree of irreversible oxidation of polyacetylene is negligible if it is cycled within a carefully defined potential range. Further investigations of its long-term cycle life as a function of doping level are needed to resolve this point.

In measuring the open-circuit potential of  $\text{ClO}_4^-$ -doped polyacetylene as a function of  $\text{ClO}_4^-$  content (see Fig. 5), we observed two potential plateaus. This behavior contrasts with the smooth increase in open-circuit potential with doping level reported by Kaneto *et al.* (16). Our data were obtained at somewhat lower currents than those used by Kaneto *et al.* ( $20 \mu\text{A}/\text{mg}$  film [ $50 \mu\text{A}/\text{cm}^2$ ] vs. up to  $100 \mu\text{A}/\text{mg}$  film) and are also based on complete oxidation/reduction cycles to oxidation levels chosen in a semi-random order. The data are quite consistent. They were not obtained at inappropriately high current densities or electrode potentials. Why two plateaus are observed is not clear. However, Abe *et al.* (24) have recently reported similar results. Perhaps two plateaus are an artifact, perhaps not. Nevertheless, these results underscore the need for a careful study of the interrelationship of the preparation conditions, structure, and morphology of polyacetylene and its electrochemical characteristics.

All of these results underscore the fact that the most desirable properties of polyacetylene—high electronic conductivity, oxidizing and reducing power, and utility as an electrochemical electrode—are observed with compositions that often are highly reactive or unstable. Polyacetylene is an extremely sensitive electrode material which must be handled carefully during cell assembly, used only with highly pure electrolytes, and cycled within strict potential limits.

Possible battery applications of polyacetylene have been widely discussed. Three types of batteries using polyacetylene as an electrode material have been suggested (3). The first uses p-doped polyacetylene as a cathode material, most likely with a lithium or similarly high energy-density anode; the second uses n-doped polyacetylene as an anode in combination with a cathode such as  $\text{TiS}_2$ ; and the third is an all-poly-

acetylene battery in which the n-doped material is the anode and the p-doped form is the cathode.

On the basis of the information which has been published so far, two major factors appear to impede the application of polyacetylene in high energy-density rechargeable batteries. The first is the instability of both virgin and doped polyacetylene, which has already been discussed in this paper. The other is its apparently low gravimetric- and volumetric-energy-densities, in either the p-doped (cathode) or n-doped (anode) form.

To put polyacetylene in perspective, Table V compares the characteristics of a typical oxidized polyacetylene cathode composition,  $[\text{CH}(\text{ClO}_4)_{0.10}]_x$  with  $\text{TiS}_2$ , and a polyacetylene anode composition,  $[\text{Li}_{0.10}\text{CH}]_x$  with pure Li. Note that it takes about twice the weight and nearly ten times the volume of the oxidized polyacetylene to store the same charge as  $\text{TiS}_2$ . The characteristics of n-doped polyacetylene are similar.

These calculations consider only charge and not cell voltage. To include voltage, Table VI summarizes four possible battery couples involving the anodes and cathodes drawn from Table V. The characteristics presented for polyacetylene n-doped with Li are based on currently available experimental results. Kaner *et al.* (26) and Huq *et al.* (27) have indicated that n-doping of polyacetylene occurs readily in a highly pure electrolyte of 1.0M  $\text{LiClO}_4$  in tetrahydrofuran (THF). Coulombic efficiencies for charge and immediate discharge are nearly 100% for doping levels up to 0.08. Above  $y = 0.08$ , the efficiency decreases in this particular electrolyte. The potential of the  $(\text{Li}_y\text{CH})_x$  electrode varies from about 1.5V at  $y = 0.01$  to 0.5V for  $y = 0.08$ .

As Table VI shows, the voltage of a  $\text{Li}/[\text{CH}(\text{ClO}_4)_{0.10}]_x$  cell is about 50% higher than a comparable  $\text{Li}/\text{TiS}_2$  cell. Its price is increased weight and volume. Similarly, cells involving  $(\text{Li}_y\text{CH})_x$  anodes sacrifice considerable potential, weight, and volume compared to their Li counterparts. One additional difference between the cathode materials is worth noting. Cells using  $\text{TiS}_2$  have an invariant salt concentration in the electrolyte, whereas cells using polyacetylene cathodes inject additional electrolyte salt (here  $\text{LiClO}_4$ ) into the electrolyte during the discharge process. Sufficient solvent must be present to accommodate the additional salt.

We have not attempted to estimate energy densities for complete cells. In such estimates, much depends on the specifics of design. It is especially difficult to extrapolate the characteristics of active materials to the performance of a finished system when a radically different electrode material is being considered. Never-

Table V. Theoretical gravimetric and volumetric energy densities of selected electrodes

Electrode	Gravimetric g/eq	Volumetric cm <sup>3</sup> /eq
$\text{TiS}_2$	111.0	34.2
$[\text{CH}(\text{ClO}_4)_{0.10}]_x$	229.0	327.0
Li	6.9	12.9
$[\text{Li}_{0.10}\text{CH}]_x$	137.0	195.0

Table VI. Theoretical energy densities of selected couples

Couple	Voltage (V)	Energy density (W-hr/kg)
$\text{Li}/\text{TiS}_2$	2.0	454
$\text{Li}/[\text{CH}(\text{ClO}_4)_{0.10}]_x$	3.0	341
$(\text{Li}_{0.10}\text{CH})_x/\text{TiS}_2$	1.0	108
$(\text{Li}_{0.10}\text{CH})_x/[\text{CH}(\text{ClO}_4)_{0.10}]_x$	2.0	146

Voltages are estimated operating voltages.

theless, the results currently available for the electrochemical performance of polyacetylene cathodes and anodes suggest that they are considerably less interesting as high energy density cathode and anode materials than materials such as  $\text{TiS}_2$  (28) and Li.

We have also made no attempt to estimate the potential power densities that might be achieved with polyacetylene electrodes. If energy densities are difficult to estimate, power densities are more so, since power density is largely an engineering parameter. However, current data do not indicate that polyacetylene is a major breakthrough in achieving high power densities.

All of these estimates would be changed if the maximum oxidative doping level of polyacetylene could be increased to 0.20 or 0.30 with high coulombic efficiency. On the basis of what we currently know, increasing the doping level would require either decreasing the voltage of the polyacetylene cathode or identifying a non-aqueous electrolyte that is stable at potentials above 3.9-4.0V vs. Li/Li<sup>+</sup>. Currently, the charging process in propylene carbonate containing LiClO<sub>4</sub> becomes inefficient above  $\gamma = 0.10$ . In this range, the electrode potential is greater than 3.9V vs. Li/Li<sup>+</sup>, and the non-aqueous electrolyte begins to decompose. Similarly, n-doped polyacetylene would be a more attractive anode if it could store more charge at potentials closer to that of pure lithium.

Unfortunately, too little is understood about the electrochemical reactions of polyacetylene to know whether, for example, the present doping levels are limited by an intrinsic characteristic of the doped state or by an extrinsic factor such as the morphology of the polymer. Logical directions for polyacetylene research include a search for new dopants and electrolytes which will permit the material to be cycled efficiently to higher doping levels. In addition, the relationship between the structure of doped polyacetylenes and their electrochemical behavior must be understood to determine whether the currently achieved capacities might be increased by changing the physical characteristics of the material.

To understand the structural/compositional/property relationship in polyacetylene is an exciting challenge for electrochemical research. Perhaps polyacetylene or some other polymer yet to be discovered will revolutionize batteries; perhaps not. Regardless, polyacetylene is a remarkable material which opens up new areas of electrochemistry and deserves continued research.

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