The Cyclic Voltammetry of Pristine, Isomerized, Deuterated, and Partially Hydrogenated "P-Type" Polyacetylene

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ABSTRACT

The cyclic voltammetry of ultrathin films of polyacetylene comprised of 2-3 nm microfibrils and their aggregate 20 nm fibrils in methylene chloride, acetonitrile, propylene carbonate, and sulfolane shows many similarities, including a background oxidation of electrolyte that leads to serious coulombic inefficiency in rechargeable polyacetylene battery applications. Reversible charging in neutral aqueous solution is limited by the poor separation between the reversible and irreversible oxidations. Comparison of ultrathin and free-standing 100 μm thick films showed they have the same maximum reversible doping level and thus energy density of 280 Wh/kg. Pristine, isomerized, deuterated, and hydrogenated [CH], show similar electrochemistry. Both n and p-type chemical doping caused isomerization of cis-[CH], to trans-[CH].

The partial, reversible electrochemical oxidation or reduction of polyacetylene, [CH], forms the basis for its potential use as an electrode material in rechargeable batteries (1-3). Used in conjunction with lithium in a non-potential use as an electrode material in rechargeable batteries and the discovery (5) that oxidized [CH] has demonstrated discouragingly low coulombic efficiency for a greatly accelerated battery charge/discharge experiment. Also studied were the effects of isomerization, deuteration, or partial hydrogenation on the electrochemistry of [CH].

Experimental

[CH], for use in cyclic voltammetry was prepared in two morphologies: the first was the free-standing film form made by the method of Ito et al. (15). These 100 μm thick films gave rather cumbersome-looking voltamograms with high currents which tend to exaggerate the effects of ohmic resistance. The second was ultrathin films of polyacetylene on gold EM grids made by short polymerization time (< 1 min), low pressure of acetylene (ca. 10 torr), and dilute catalyst concentrations of few ng/mL, used originally for the purpose of morphological and structural investigations (16). These films, were ca. 0.1 μm thick and contained 10-1000 ng of [CH], per grid. Such films are ideally suited for cyclic voltammetry because of the minute currents involved in the experiment.

Electron micrographs show that [CH], prepared directly on grids and free-standing films are both comprised of a loosely packed network of fibers about 20 nm in diameter. However, in the ultrathin films one can discern “microfibrils” down to 2 nm in which is the ultimate morphological entity of [CH], (17). These microfibrils aggregate to form the thicker fibrils. The gold mesh of the EM grids seems to provide a good support for polyacetylene since the polymer does not detach when the grid is handled and cycled in the electrolytes used for this work.

Materials.—Propylene carbonate (Burdiick and Jackson, glass distilled) was vacuum distilled from calcium hydride. Solvent distilled in this way, after several weeks of standing in the dry box, had 10-34 ppm water as determined by Karl Fischer titration (Galbraith Laboratories). Acetonitrile was purified by cryogenic distillation on the vacuum line from HPLC grade (99.9+%) acetonitrile (Fisher) and 3A molecular sieves. Spectrograde methylene chloride (Fisher) was redistilled cryogenically from molecular sieves. Tetramethylene sulfone (sulfolane, Aldrich) was vacuum distilled from NaOH pellets with a slow argon bleed. Lithium perchlorate (Aldrich) was melt-dried under vacuum using a salt bath. Electrolytes made with this salt and propylene carbonate had a total water content of less than 40 ppm, determined by Karl Fischer titration. Tetraethylammonium perchlorate, tetrabutylammonium perchlorate, lithium trifluoro-methysulfonate, and lithium tetrafluoroborate were obtained from Alpha and dried under vacuum at 90°C for 18h. Lithium hexafluoroarsenate, water content less than 50 ppm, was used as received from U.S. Steel. All dried salts were stored in a Vacuum Atmospheres dry box.

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Electrolytes were made in 50 and 100 ml quantities by adding the appropriate degassed solvent to the dried salt in the dry box. Solvents were stored in Teflon-sealed glass storage bulbs in the dry box.

**Apparatus.**—A PAR 173 potentiostat/galvanostat driven by a PAR 175 Universal Programmer was used to generate potential ramps for cyclic voltammetry. Current-voltage curves were recorded on a Hewlett-Packard 700-A X-Y recorder. Fast (> 1000 V/s) voltammograms were recorded on a Tektronix 564B storage oscilloscope fitted with a Polaroid camera. Electrochemistry using the nonaqueous solvents was performed in an argon-filled dry box (Vacuum Atmospheres). Aqueous electrochemistry was done on the lab bench using deoxygenated solutions under a blanket of argon.

**Electrochemical procedure.**—Electrical contact to an EM gold grid was made by passing the end of a short length of 3 ml platinum wire through a hole in the tab of the grid and twisting the wire until the connection was firm. The platinum wire was gripped at the distal end by a dolphin-nosed clip and lowered, along with the reference and counter electrodes, into 1.5 ml of electrolyte in a small beaker. Care was taken never to short the working electrode to either of the other electrodes. The open-circuit potential ($V_{oc}$) was recorded before CV's were taken.

IR compensation was generally not used for the ultrathin films, since there was a possibility that the polyacetylene could be partially doped during the brief period that potentiostatic control was lost when setting the IR compensation. For most cases, where the current was less than 100 µA, the IR drop was estimated at less than 1 mV. In fact, IR compensation made no observable difference in the voltammetry. At the highest scan rate used, where the current was on the order of a milliampere, IR compensation shifted the peak position by less than 10 mV.

Cyclic voltammetry on free-standing films was recorded using a Teflon stopcock doping cell described previously (18). Sample sizes of a few mg gave voltammograms with much larger currents than seen in ultrathin films. Since there was a large (ca. 2000Ω) resistance through the glass frit of the doping cell, IR compensation was set, though it was not possible to achieve 100% compensation.

Reference and counter electrodes were lithium for electrolytes consisting of lithium salts in propylene carbonate or sulfolane. The counter electrode was a Corning platinum-button electrode for acetonitrile, methylene chloride, and water electrolytes. A silver/0.1M silver nitrate in acetonitrile, Vycor-fritted reference electrode was used for acetonitrile and methylene chloride, and a potassium-saturated calomel electrode was employed in aqueous solutions.

**Results and Discussion**

**Background currents.**—For both thick and ultrathin films the background currents on the metal support in the region where the polymer was electroactive was less than 5% of the peak height due to the polymer. Unfortunately, the background on the polymer itself could not be measured independently of the [CH]₄, electrochemistry in the potential range where the polymer was electroactive. It will be shown below that this background actually accounts for a substantial fraction of charge passed during the oxidation of [CH]₄, which has important implications when projected to battery systems.

**Cyclic voltammetry of free-standing films.**—Figure 1 shows a cyclic voltammogram of 1.5 mg of freestanding trans-[CH]₄ films. A broad, featureless ramp was obtained on the positive sweep, which ran up to 4.5V. A very broad cathodic peak is seen on reversal. These data are similar to those of Chiang et al. (10) for 30 µm [CH]₄ film clamped with platinum. The excessive broadness of these features when compared to CV's for ultrathin films is due to the uncompensated ohmic resistance, estimated to be about 400Ω, through the solution, through the glass frit of the electrochemical cell and through the film, it is not due to mechanistic differences. The fact that it is possible to obtain anodic peaks with thick films if the scan rate is slow enough (14), or intimate contact is made by evaporating gold on one side of the film (8) supports the idea the IR drops are responsible for the unusual shape of the voltammetry in Fig. 1. It was not deemed worthwhile to continue using thick films in cyclic voltammograms since the undetermined ohmic effects would hinder any attempts at quantitative analysis. Furthermore, it was soon discovered that ultrathin films on EM grids were far superior for voltammetry.

**Cyclic voltammetry (CV) of ultrathin films.**—General characteristics.—Figure 2 shows a steady-state CV (a CV obtained with continuous cycling) of about 400 ng [CH]₄ on an EM grid in a perchlorate/propanol carbonate electrolyte. Both oxidation and reduction peaks are seen. Anodic and cathodic peak heights are proportional to scan rate in the range 1-50 mVs, demonstrating thin film behavior (19). At low scan rates, such as those used by Diaz and Clarke (8), the cathodic peak exhibits a shoulder. At high scan rates the anodic peak has a clear shoulder. The peaks are nearly symmetrical though somewhat broader than theoretically predicted for an irreversible one- or two-electron system. The first anodic peak in the first CV on any sample is always larger and narrower than peaks in the subsequent CV's for both pristine cis and trans [CH]₄. Steady-state CV can be achieved by using an upper potential limit of less than 4.0V vs. lithium; under this condition there is less than 1% decrease in peak height per cycle. There are no diffusion limitations to the electrochemistry of polyacetylene at low scan rate. If anions had a diffusion coefficient of $10^{-18}$ cm²/s (20) (giving a diffusion time constant of 13h for 20 nm fibrils) one would expect semi-infinite rather than thin-film behavior. The diffusion coefficient must clearly be orders of magnitude larger than $10^{-18}$ cm²/s. Cycling of these small amounts of polyacetylene could be achieved much more rapidly than was possible for thick films, allowing numerous battery-oriented experiments to be performed quickly. Cis-to-trans isomerization can be achieved with one electrochemical cycle as reported previously (11, 21). Ex-
tending the positive limit of a CV to more than 5 V vs. Li results in a second, large anodic peak (11). This type of oxidation is irreversible and results in the loss of all polymer electroactivity.

Detection limits.—Figure 3 shows a CV of 1.1 ng of polyacetylene on an EM grid. The small polymer peaks are clearly discernable on a rapidly rising background. Since there was no measurable noise on the CV it was estimated that the minimum detectable amount of [CH₄] is of the order of 100 pg by the electrochemical technique. The important point here is that the amounts of polyacetylene used for the present work were always in the hundreds of ng range, which is well above the detection limit.

Background reactions.—Figure 2 shows a clear anodic peak superimposed on a rising portion of the voltammogram. Diaz and Clarke (8) assumed that “since current increases in the potential region beyond +0.9 V [vs. SCE], it is clear polyacetylene can be oxidized further.” It has been shown (11) that polyacetylene can indeed be oxidized further, but irreversibly. The CV in Fig. 2 represents steady-state cycling of [CH₄]. The anodic area of the CV is consistently about 30% greater than the cathodic area. Therefore, an irreversible expenditure of charge occurs on each cycle. If this consumption of coulombs were used in oxidizing [CH₄], the polymer would very soon be exhausted and one would expect no further electroactivity. In fact, cycling has very little effect on the activity of the [CH₄], as demonstrated by Fig. 4, which shows the anodic peak height, which is proportional to peak area (19), vs. the cycle number for polyacetylene cycled numerous times in propylene carbonate. Even after hundreds of cycles (each cycle showing 30% more positive area than negative area) a large proportion of the electroactivity of the polymer remains. The only conclusion that can be drawn from this result is that a large fraction of the charge that is used to oxidize the polymer is consumed in the irreversible oxidation of the electrolyte (which is available in infinite abundance relative to [CH₄]). Such an observation has extremely important implications for the construction of polyacetylene batteries. The system has a large inherent coulombic inefficiency because even on the short time scale used to charge the ultrathin polyacetylene films, about 30% of charge is wasted on irreversible oxidation of the electrolyte.

The nature of this side reaction is not clear. Delahay (22) has recently shown, by photoelectron emission techniques, that the standard potential for perchlorate oxidation is 2.6 V vs. hydrogen or about 5.6 V vs. Li. By the process of elimination the side reaction can therefore be reasonably attributed to oxidation of solvent only, i.e. propylene carbonate. The side reaction is not the oxidation of impurities such as water since the addition of up to 1000 ppm water or propane diol had no effect on the...
The appearance of voltammograms in propylene carbonate. The mechanism of this reaction and eventual product is worth investigating since such a study may lead to a solvent which is more oxidatively stable than propylene carbonate.

Returning to Fig. 4 a few advantages of using ultrathin films should be mentioned. Cycling for Fig. 4 was done at 10 V/s, which gave well-defined voltammograms. Numerous cycles could be performed in a short time, minimizing the effects of reaction of solvent with doped polycetylene (18). Some decrease in capacity is seen with cycling. It was observed on samples cycled extensively that squares of polymer had detached from the interbar spaces of the EM grid (see Fig. 5). The polymer perhaps becomes brittle upon cycling.

Capacitance currents.—Classically, an electrical double layer exists when a solid electrode is placed in an electrolyte. When potential is changed charge must be added to or removed from this capacitance. The resulting "capacitance current" was recognized in the initial work on electroactive polymers such as polypyrrrole (23). Feldberg (24) has dealt with the issue of capacitance in conducting polymers more extensively and has pointed out that it may be difficult to separate capacitive from faradaic processes in cyclic voltammograms. The major clue which suggested that capacitance could be involved in the electrochemistry of polypyrrrole was the existence of a level portion of the cyclic voltammograms after the peak. Assuming (incorrectly) capacitance does not depend on potential the capacitance current ($I_c$) is given simply by

$$I_c = Cv$$

where $v$ is the scan rate in V/s, $C$ is the capacitance in farads, $I_c$ is the current which would be a constant value for a particular scan rate.

Capacitance has little importance in the cyclic voltammetry of polycetylene according to the following evidence. First, it is a strict requirement of Feldberg's theory that the level portion after the anodic peak be symmetrical about the voltage axis. That is, the capacitance current should be the same magnitude (opposite sign) scanning in the positive and negative directions. The voltammograms of polycetylene are not symmetric in the area positive of the oxidation and reduction peaks. This asymmetry is reflected in the coulombic inefficiency of the charging process and is more consistent with an irreversible background reaction. Second, the actual value of the capacitance may be estimated knowing the surface area of the polymer. Surface areas have been measured for thick films by BET to be about 60 m$^2$/g. The thin films used for CV's have thinner fibers and thus have higher specific surface area. The specific surface area, $A_s$, is given by

$$A_s = 2/Dr$$

where $D$ is the density (1.16 g/cm$^3$) and $r$ is the average radius of fibers. From electron micrographs of polycetylene on EM grids one can estimate a fiber diameter of 10 nm which gives a surface area of ca. 340 m$^2$/g. Using a "typical" double layer capacitance of 10$^{-5}$ F/cm$^2$ the capacitance arrives at a value of less than 1 $\mu$A for the contribution of charging current to the cyclic voltammogram in Fig. 2, which represents less than 2% of the peak current. Capacitance may therefore be neglected.

Drawing a base line.—It has been shown that polycetylene electrochemistry is superimposed on a rapidly rising background of solvent oxidation. In order to draw any quantitative conclusions from the cyclic voltammograms of [CH$_x$]$_r$ it is necessary to determine a base line, from which peak heights and areas can be measured. For the anodic branch of the CV a base line can be conveniently drawn using the inflection at 3.95 V as shown in Fig. 2. Estimating a base line for the cathodic half is more difficult; it was done by assuming the positive peak area measured from the base line to be equal to the negative peak area because the CV's are steady state. The positive peak area was determined with the base line drawn as described. Next, several straight lines were drawn across from the shallow inflection point on the negative end of the cathodic peak. The line which gave an integrated peak area the same as that determined for the positive peak was used as the base line for the cathodic peaks.

As a test of the estimated base line, background scans of solvent oxidation only were run on a gold grid without [CH$_x$]$_r$ at several current sensitivities. The scan which best fit the right half of the CV is drawn in Fig. 2 as a dotted line. A reasonable fit is obtained with the background on the right-hand side of the CV where the polycetylene is conducting. As the [CH$_x$]$_r$ is undoped the background drops to the level seen on a bare EM grid. This approach to justifying the base lines drawn assumes that the background on a bare EM grid has the same shape as the background on a conducting polymer over the same potential range.

Mechanism of oxidation.—The cyclic voltammetry of these films of [CH$_x$]$_r$ shows thin film behavior. The peaks are, however, wider than the 90/n mV (19), where n is the number of electrons transferred, predicted for reversible systems or 62.5/(1 - $a$), where $a$ is the transfer coefficient, for an irreversible anodic peak at room temperature. The peak widths at half-height range from 200 to 150 mV, depending on the solvent. It is therefore difficult to determine an "$n" value for the reaction from cyclic voltammetry. Laviron (25) has treated the broadening of surface-localized waves in terms of electrostatic repulsion between electroactive sites. Bard and others (26) have pointed out that a broad peak could be obtained from a collection of electroactive sites with nonequivalent redox potentials caused, for example, by small differences in environment. If these nonequivalent sites were close enough in potential they would not be resolved and it would be difficult to predict which effect was causing peak broadening. In the present case a...
shoulder appears on either the cathodic or anodic peak of \([\text{CH}]_r\) at the appropriate scan rate. It is evident that some broadening is caused by the presence of two inequivalent electroactive species. However, the magnitude of the shoulder is still much smaller than the main peak and cannot completely account for all the peak broadening. Since it has been shown that polyacetylene is about 80% crystalline it is tempting to assign the shoulder to the amorphous part of the polymer, which would be expected to oxidize more rapidly than the crystalline part.

Effect of solvent.—Cyclic voltammograms were recorded using the same EM grid in different electrolytes. 1M lithium perchlorate in propylene carbonate (PC) or sulfolane (SL), and tetraethylammonium perchlorate in methylene chloride (MeCl) or acetonitrile (AN) was used. The grid was rinsed in pure solvent before being transferred to the new electrolyte. A silver/silver nitrate in acetonitrile reference electrode was used. Figure 6 shows the steady-state CV's obtained in each case. Changing the solvent evidently has little effect on the shape or position of the peaks. The level of background current remains roughly constant between each solvent. The coulombic efficiency, given in Table I by the ratio of the negative to the positive branch of the CV, is low for all the solvents tested, which implies that polyacetylene batteries made with these solvents will also show low coulombic efficiency.

The kinetics of oxidation of \([\text{CH}]_r\) are faster in MeCl$_2$ and acetonitrile as demonstrated by narrower peaks and anodic peak areas for each solvent system. It is noted that reversibility scales inversely with solvent viscosity. It is also evident, by comparing the $E^*$ values and peak areas, that each solvent will provide \([\text{CH}]_r\) battery electrodes with similar energy densities.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>MeCl$_2$</th>
<th>AN</th>
<th>PC</th>
<th>SL</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E^<em>$ vs. Li/Li$^+$</em></td>
<td>3.58</td>
<td>3.57</td>
<td>3.59</td>
<td>3.58</td>
</tr>
<tr>
<td>Rel. anodic peak area</td>
<td>1</td>
<td>1.1</td>
<td>0.9</td>
<td>0.8</td>
</tr>
<tr>
<td>Ratio area – ve to + ve branch</td>
<td>0.53</td>
<td>0.50</td>
<td>0.71</td>
<td>0.77</td>
</tr>
<tr>
<td>Peak separation (mV)</td>
<td>285</td>
<td>285</td>
<td>332</td>
<td>411</td>
</tr>
<tr>
<td>Anodic peak width at half height (mV)</td>
<td>95</td>
<td>95</td>
<td>140</td>
<td>160</td>
</tr>
</tbody>
</table>

* Converted from the Ag/Ag$^+$ reference by adding 3.36V.
* Area relative to MeCl$_2$ cyclic.
* Separation between anodic peak and larger of the cathodic peaks.

Toluene was added to the propylene carbonate electrolyte to give a 0.5M LiClO$_4$, 50/50 toluene/PC mixture. The CV's in this solvent were identical to those in the pure PC electrolyte.

Effect of salt.—The following dried salts were used in 0.5M or 1M concentrations in propylene carbonate: LiClO$_4$, LiAsF$_6$, LiBF$_4$, LiSO$_2$CF$_2$. CV's are given in Fig. 7. The BF$_4$ and ClO$_4$ electrolytes gave identical CV's and AsF$_6$ and SO$_2$CF$_2$ gave similar CV's. Importantly, the backgrounds are all the same, demonstrating that they are probably not due to anion oxidation. As further evidence to support the assertion that anion oxidation is not taking place at these potentials, elemental analysis of thick films of \([\text{CH}]_r\) doped with ClO$_4$ or AsF$_6$ shows that the anion is unchanged upon doping. A small difference in the larger cathodic peak is seen on going from ClO$_4$ to AsF$_6$, perhaps because the latter ion is larger. However, elemental analysis on free standing films shows that both ions have a maximum reversible electrochemical doping level of 5.5%.
that ClO₃⁻ is expelled on undoping polyacetylene in condoping of polypyrrole is accompanied by migration of in situ of [CH],. remained unchanged on switching from LiClO₄ in PC to Bu₄NClO₄ in PC. Results on thick films show ing/undoping in LiClO₄ electrolyte and found that contrast to the behavior of polypyrrole (28). showed that the choice of cation of the salt affected the chlorate out. In the present work the cyclic voltammetry cyclic voltammetry. Kaufman et al. (27) performed mass measurements on polypyrrole during doping/undoping in LiClO₄ electrolyte and found that undoping of polypyrrole is accompanied by migration of lithium into the polymer rather than diffusion of perchlorate out. In the present work the cyclic voltammetry of [CH] remained unchanged on switching from LiClO₄ in PC to Bu₄NClO₄ in PC. Results on thick films show that ClO₄⁻ is expelled on undoping polypyrrole in contrast to the behavior of polypyrrole (28).

**Table II. Summary of CV parameters for different types of polyacetylene in perchlorate electrolyte. Scan rate, 50 mV/s**

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>E°C/Li⁺</th>
<th>Epa⁺</th>
<th>Epam</th>
<th>Epc</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH)₂H₂</td>
<td>1M LiClO₄/PC</td>
<td>3.52</td>
<td>3.72</td>
<td>4.56</td>
</tr>
<tr>
<td>(CH)₂H₂</td>
<td>9.3M NaClO₄/H₂O</td>
<td>3.54⁺</td>
<td>3.90</td>
<td>4.18</td>
</tr>
<tr>
<td>(CH)₁H₂</td>
<td>1M LiClO₄/PC</td>
<td>3.51</td>
<td>3.69</td>
<td>4.48</td>
</tr>
<tr>
<td>(CH)₁H₂</td>
<td>1M LiClO₄/PC</td>
<td>3.52</td>
<td>3.63</td>
<td>4.45</td>
</tr>
<tr>
<td>(CH)₂H₂</td>
<td>1M LiClO₄/PC</td>
<td>3.54</td>
<td>3.70</td>
<td>4.49</td>
</tr>
<tr>
<td>(CH)₂H₂</td>
<td>1M LiClO₄/PC</td>
<td>3.52</td>
<td>3.71</td>
<td>—</td>
</tr>
</tbody>
</table>

* “Standard” molecular weight (CH)₂.  
* Low molecular weight (CH).  
* Hydrogenated once.  
* Hydrogenated twice.  
* Converted from SCE by adding 3.27V.

**Low molecular weight polyacetylene.**—Methods have been developed in our group for the synthesis of polyacetylene with variable molecular weight (29). Cyclic voltammetry in propylene carbonate was performed on “low” molecular weight (Mᵣ ~ 500) polyacetylene prepared on EM grids. Figure 8 depicts a representative CV and shows no new details when compared with “regular” molecular weight [CH]₁ (Mᵣ ~ 11,000).

**Deuterated polyacetylene.**—Deuterated polyacetylene, [CD]₁, was made on EM grids from perdeuterated acetylene monomer. A representative cyclic voltammogram of [CD]₁ is shown in Fig. 9. As expected, replacing hydrogen with deuterium has little effect on the electrochemistry of acetylene. The standard potentials of [CD]₁ and [CH] are the same within experimental error. The peak potentials are similar although [CD]₁ appears to be more reversible, since the peak separation is smaller. The shoulder is more evident on [CD]₁ cyclics which, according to the earlier mentioned tentative hypothesis, might suggest a higher percentage of amorphous polymer. Table II summarizes the cyclic voltammetric parameters of [CD]₁. From this study the use of [CD]₁ appears to offer no advantages over [CH]₁ in possible battery applications.

**Partially hydrogenated polyacetylene.**—Polyacetylene on grids was partially hydrogenated using the method of Soga et al. (30). Cis-films of polyacetylene were exposed to 0.1M sodium benzophenone in THF for 1h in the dry box. The grids were then transferred to a glove bag and exposed to methanol for 1h. For some grids the procedure was repeated, yielding polyacetylene with a higher hydrogen content. The same procedure was repeated with thick cis films in order to determine the hydrogen content of polyacetylene treated thus. After doping, films were golden and had 4-probe conductivities of about 140 Ω⁻¹ cm⁻¹. The doping level, determined by weight uptake after pumping on the films for 30 min to remove solvent, was 14 mole percent (m/o) Na. After compensation with methanol the hydrogenation level was determined to be 12% by elemental analysis. The average level of hydrogenation is estimated at about 13% from these two results. It was assumed that this value could be extrapolated to thin films. The hydrogenation level after repeating the process on the same film was not determined.

As seen in Fig. 10, the anodic peak of first scan on [CH], hydrogenated to 13%, H⁺[CH]₁, appears at about 3.76V vs. Li and is very close to, although larger than, the subsequent peaks. This is consistent with the hypothesis that doping — here n-type chemical doping — has induced isomerization of cis-[CH]₁. The rest of the electrochemical parameters are very close to those for nonhydrogenated [CH]₁ for both singly and doubly hydrogenated [CH]₁, as summarized in Table II. Although polycetylene electrochemistry seems independent of the concentration of sp² sites, the conductivity of [CH] decreases rapidly with increasing hydrogenation (31); it is not recommended to use partially hydrogenated [CH]₁ in batteries.
It is interesting that the standard potential remains independent of hydrogenation level. One would expect the potential to increase as conjugation length decreases (as the stability of the cation produced decreases it becomes more difficult to oxidize [CH].). This effect may well be within the experimental error of the E° measurements, (±20 mV). Another possible explanation is that the CH units are not randomly distributed between the CH units and the average conjugation lengths are greater than (CH = CH), for the random distribution of CH, units.

Degradation by reduction in propylene carbonate.— Polyacetylene can also be electrochemically reduced or "n-doped" at lower potentials. Thus, "all-polymer" batteries can be made using polyacetylene as both cathode and anode (4). To see whether the propylene carbonate/LiClO₄ electrolyte is suitable for this application, cyclic voltammograms of [CH], on EM grids were recorded for aqueous solutions of strong acids or in highly concentrated salt solutions, as demonstrated by Wangel et al. (31) and G-Elie and Wnek (32). The possible use of aqueous electrolytes in polyacetylene batteries is significant since aqueous electrolytes have greater conductivity than nonaqueous ones thus allowing for higher currents.

For the present study saturated perchlorate solutions in deionized, distilled, deoxygenated water were used. Wangel et al. (31) have suggested that high salt concentrations reduce the availability of free water, i.e., water not coordinated to ions. For example, they estimated that only 5 moles of water are present per mole of Pb(ClO₄), in a saturated solution of lead perchlorate. The solubility of NaClO₄ in water at 25°C is 67.8 g per 100 g solution, and of LiClO₄ is 37.5 g/100 g (33). From the respective densities of 1.683 and 1.269 g/cm³, the calculated molarities for saturated NaClO₄ and LiClO₄ are 9.8 and 4.5 M, respectively, with watersalt ratios of 3:1 and 10:1.

CV's were run on cis- and trans-[CH], in saturated LiClO₄ and NaClO₄ aqueous solutions in a three-electrode cell provided with an argon blanket. Potentials are vs. potassium SCE. Reversible CV's could not be obtained with either cis or trans (thermally isomerized, 150°, 20 min) polyacetylene using LiClO₄. Only a large irreversible peak at 0.86 V is seen as shown in Fig. 12. It was possible, on the other hand, to obtain some "partially-reversible" behavior with trans-[CH], using the more concentrated NaClO₄ solution by reversing the scan direction immediately after the peak at 0.63 V, as seen in Fig. 12. The implications for battery applications are serious. It was shown that polyacetylene could be oxidized by reduction in propylene carbonate. Cyclic voltammetry (CV) showed that the p-type electrochemistry was recorded after each cathodic scan. The negative region, which allowed by the steady-state p-type electrochemistry taken after single cycles 2, 4, and 8, respectively, into the n-type region. 1M LiClO₄/PC. Scan rate 50 mV/s.

Aqueous cyclic voltammetry.—It is reasonable to suppose that the delocalized carbocation formed as a result of polyacetylene oxidation is susceptible to nucleophilic attack. The stability of polyacetylene is thus expected, and found, to be low in protic solvents such as water and methanol, due to reactions of the type

\[
\text{CH}_n^+ + \text{H}_2\text{O} \rightleftharpoons \text{CH}_n\text{OH} + \text{H}^+ \]

The reaction has been drawn as an equilibrium because oxidized polyacetylene shows a surprising stability in aqueous solutions of strong acids or in highly concentrated salt solutions, as demonstrated by Wangel et al. (31) and G-Elie and Wnek (32). The reaction is given by the equilibrium constant

\[
K = \frac{[\text{CH}_n\text{OH}][\text{H}^+]}{[\text{CH}_n^+][\text{H}_2\text{O}]} \]

Since the reaction is an equilibrium, the stability of polyacetylene will depend on the concentration of the reactants. The concentration of water in the solution will determine the equilibrium constant, and therefore the stability of polyacetylene. The concentration of water in the solution will determine the equilibrium constant, and therefore the stability of polyacetylene. The concentration of water in the solution will determine the equilibrium constant, and therefore the stability of polyacetylene. The concentration of water in the solution will determine the equilibrium constant, and therefore the stability of polyacetylene.
Fig. 12. A, CV's of trans-(CH)$_2$. in saturated LiClO$_4$ aqueous solution at 50 mV/s. 1, first scan; 2, second scan. B, CV's of trans-(CH)$_2$. in saturated NaClO$_4$ aqueous solution showing progressive decrease of reversible peak, r, which is poorly resolved from the irreversible peak, i. Scan 5 was taken at 1/10th the current sensitivity of scans 1–4 (i.e., scale bar is 200 μA).

Fig. 13. Irreversible CV of cis-(CH)$_2$. in saturated NaClO$_4$ aqueous electrolyte at 50 mV/s. 1, first scan; 2, second scan.

Conclusions

The cyclic voltammetry of ultrathin polyacetylene films has proven to be a rapid and convenient method for screening several electrolytes which are of potential use in [CH]$_2$. batteries. A significant coulombic loss occurs on each cycle due to the irreversible oxidation of electrolyte. Unfortunately, the same morphological feature — high specific surface area — that allows high power density also leads to substantially higher background currents and thus to lower coulombic efficiency. Finding an electrolyte that is stable to both n- and p-type [CH]$_2$. appears to be a daunting challenge since similar coulombic inefficiency is present in very different solvents. Charging and discharging is more facile in solvents of low viscosity. Since reversible and irreversible oxidations of [CH]$_2$. are poorly resolved in neutral aqueous electrolytes it is doubtful that they will be useful in [CH]$_2$. batteries.

Polyacetylene is a rather delicate material for p-type battery electrodes since it must be maintained in the narrow potential range 1.7–4.2V; it is more forgiving to overdischarge than to overcharge in the propylene carbonate electrolyte used here.

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Electrochemical Profiling of Ion-Implanted InP

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ABSTRACT

A liquid barrier contact to InP utilizing HCl is described which may be used as a routine contact for the evaluation of carrier concentration profiles in ion-implanted and annealed samples. The basic characteristics of the InP/HCl barrier were explored for undoped n-type material with carrier concentrations of 5 x 10^18 and 1.5 x 10^19 cm^-3, and for S-doped n-type material with 2 x 10^18, 2 x 10^19, and 10^20 electrons cm^-3. The factors which influence the accuracy and the reproducibility of ion-implanted carrier concentration profiling utilizing this technique, in which the sample is dissolved by an electrolytic solvent continuously passing over the specimen in situ, are described in detail. The possibility of using this technique to detect deep levels induced by the process of implantation and subsequent annealing is shown.

Indium phosphide (InP) is increasingly being explored as a material for microwave devices (e.g., PERT's, avalanche diodes), and for use in conjunction with ternary and quaternary alloy semiconductors in optoelectronic devices (e.g., lasers, detectors) for long-range optical communications (1, 2). Ion implantation is used in the fabrication of many of these devices. However, the implant process produces considerable damage in the semiconductor, which must be thermally annealed in order to achieve good electrical activation of the dopant and high mobility of the resulting carriers. The determination of the carrier concentration profile obtained after these procedures is often done by a series of differential Hall measurements, an extremely tedious and difficult process. Another difficulty encountered with InP and related compounds is the formation of high-quality Schottky barriers (2). This problem can be avoided, however, by employing an electrolytic liquid barrier, thus allowing conventional C-V analysis to be performed. A useful extension of this approach is to take advantage of the electrolytic Schottky barrier to perform capacitance-voltage profiling measurements, which are critically examined. Attention is centered upon the capacitance contributions from the edge regions of the electrolyte-contact area, and their influence on profile determination. It is shown that the carrier profile evaluation is very sensitive to a small amount of residual damage remaining after implantation and annealing. The possibility of using this technique to detect deep levels induced by the process of implantation and subsequent annealing is shown.

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