

AD-A145 477

P-DOPING OF (CH)₃N TO THE METALLIC REGIME WITH GASEOUS
OXYGEN APPLICATION T. (U) PENNSYLVANIA UNIV
PHILADELPHIA DEPT OF CHEMISTRY R J MAMMONE ET AL.

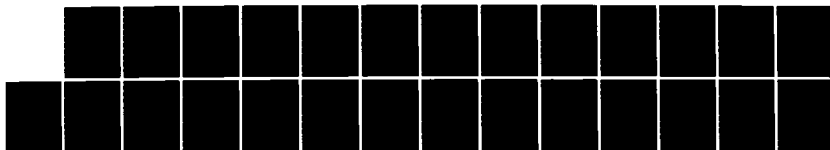
1/1

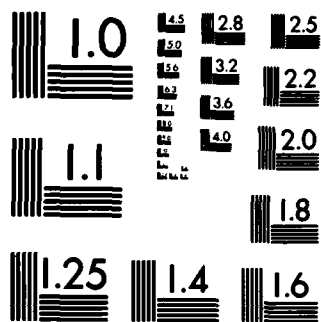
UNCLASSIFIED

MAY 84 TR-84-5 N00014-83-K-0209

F/G 11/9

NL





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD-A145 477

DTIC FILE COPY

OFFICE OF NAVAL RESEARCH

Contract N00014-83-K-0209

Task No. NR-356-842

TECHNICAL REPORT NO. 84-5

p-Doping of $(CH)_x$ to the Metallic Regime with Gaseous Oxygen:

Application to Oxygen Fuel Cell Type Electrodes

by

R. J. Mammone and A. G. MacDiarmid

Submitted to:

Journal of the Chemical Society, Faraday Transactions I

March, 1984, in press

Department of Chemistry
University of Pennsylvania
Philadelphia, Pennsylvania 19104

SEP 13 1984

May 1984

Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited

84 09 12 014

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 84-5	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) p-Doping of $(CH)_x$ to the Metallic Regime with Gaseous Oxygen: Application to Oxygen Fuel Cell Type Electrodes	5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report	
	6. PERFORMING ORG. REPORT NUMBER	
7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s) N00014-83-K-0209	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Pennsylvania Philadelphia, PA 19104	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-356-842	
11. CONTROLLING OFFICE NAME AND ADDRESS Department of the Navy Office of Naval Research Arlington, VA 22217	12. REPORT DATE May 1984	
	13. NUMBER OF PAGES 18	
14. MONITORING AGENCY NAME & ADDRESS (If different from Controlling Office)	15. SECURITY CLASS. (of this report) Unclassified	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Submitted to: Journal of the Chemical Society, Faraday Transactions I, March 1984, in press		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) polyacetylene, doping, fuel cells, electrodes, counter anion, reduction potentials, electrochemistry, catalyst electrode		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Trans-polyacetylene, $(CH)_x$, can be p-doped (oxidized) to the metallic regime by gaseous oxygen in the presence of an aqueous solution of a non-oxidizing acid such as HBF_4 . The oxygen oxidizes the $(CH)_x$ to $(CH^+y)_x$ while the HBF_4 supplies a stable fluoroborate counter anion to give a species such as $[CH^+yA^-]_x$ ($y \sim 0.02$; A^- = fluoroborate). The doping process is consistent with the reduction potentials of $(CH)_x$ and O_2 in acid solution.		

In the absence of the acid, oxygen reacts irreversibly with the semiconducting $(CH)_x$ to destroy its conductivity. The $[CH^{+y}A_y^-]_x$ formed above may be connected to a lead anode in a HBf_4 electrolyte whereupon it is reduced to $(CH)_x$ with concomitant production of an electric current. If oxygen is bubbled over the $(CH)_x$ during this process it is continuously electrochemically reduced by the lead as rapidly as it is oxidized chemically by the oxygen. The $(CH)_x$ therefore acts as a catalyst electrode - a "fuel cell" electrode for the room temperature reduction of O_2 to H_2O at atmospheric pressure. The overall reaction does not occur to any significant extent in the absence of the $(CH)_x$.



A1

p-Doping of $(\text{CH})_x$ to the Metallic Regime with Gaseous Oxygen:

Application to Oxygen Fuel Cell Type Electrodes

by

Robert J. Mammone and Alan G. MacDiarmid

Department of Chemistry

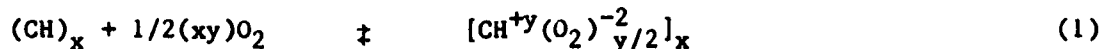
University of Pennsylvania

Philadelphia, Pennsylvania 19104

Abstract

Trans-polyacetylene, $(CH)_x$, can be p-doped (oxidized) to the metallic regime by gaseous oxygen in the presence of an aqueous solution of a non-oxidizing acid such as $HB\dot{F}_4$. The oxygen oxidizes the $(CH)_x$ to $(CH^{+y})_x$ while the $HB\dot{F}_4$ supplies a stable fluoroborate counter anion to give a species such as $[CH^{+y}A^-]_x$ ($y \sim 0.02$; A^- = fluoroborate). The doping process is consistent with the reduction potentials of $(CH)_x$ and O_2 in acid solution. In the absence of the acid, oxygen reacts irreversibly with the semiconducting $(CH)_x$ to destroy its conductivity. The $[CH^{+y}A^-]_x$ formed above may be connected to a lead anode in a $HB\dot{F}_4$ electrolyte whereupon it is reduced to $(CH)_x$ with concomitant production of an electric current. If oxygen is bubbled over the $(CH)_x$ during this process it is continuously electrochemically reduced by the lead as rapidly as it is oxidized chemically by the oxygen. The $(CH)_x$ therefore acts as a catalyst electrode - a "fuel cell" electrode for the room temperature reduction of O_2 to H_2O at atmospheric pressure. The overall reaction does not occur to any significant extent in the absence of the $(CH)_x$.

It is well established that the conductivity of parent polyacetylene, $(CH)_x$, the prototype conducting polymer or that of its p- or n-doped forms is rapidly and irreversibly destroyed on exposure to oxygen or air.^(1,2) A more detailed understanding of the oxidation (p-doping) process by which the conductivity of cis- or trans- $(CH)_x$ can be increased through the semiconducting to the metallic regime⁽³⁾ has now enabled us to use gaseous oxygen to "dope" $(CH)_x$ under appropriate experimental conditions to the metallic regime. It has been reported previously that when cis- $(CH)_x$ or trans- $(CH)_x$ is exposed to oxygen or air for more than approximately one hour irreversible oxidative degradation of the material occurs.⁽¹⁾ However, during the first few minutes of exposure the conductivity increases by one to two orders of magnitude (from $\sim 10^{-9}$ to 10^{-7} ohm⁻¹cm⁻¹) for cis- $(CH)_x$ in a reversible process, viz.,



During this time the O_2 -doping reaction may be reversed by pumping off the oxygen. It is believed the material probably consists of delocalized polycarbonium ion in combination with an O_2^{-2} ion.⁽¹⁾ This system is intrinsically unstable in view of the strongly oxidizing nature of the anion. It may be regarded as the transition state for the irreversible oxidation of the $(CH)_x$ to an insulating material containing carbonyl and other oxygen-containing groups.

The degradation by oxygen of $(CH)_x$ p-doped to the metallic regime, e.g. $[CH^{+0.07}(I_3)^{-}_{0.07}]_x$ ⁽²⁾ presumably occurs in a similar manner, the oxygen oxidizing the material still further to give $[CH^{+(0.07+y)}(I_3)^{-}_{0.07}(O_2)^{-2}_{y/2}]_x$ which then spontaneously decomposes. It is not surprising that reduced (n-doped) polyacetylene, e.g. $[Na^+_{0.1}CH^{-0.1}]_x$ reacts instantly and irreversibly with air in view of the

strongly reducing nature of the $(\text{CH}^{-0.1})_x$ polycarbanion. This results in complete loss of conductivity.⁽⁴⁾

Experimental

Polyacetylene film was synthesized as previously described.⁽⁵⁾ For the O_2 -doping studies, a piece of cis-rich $(\text{CH})_x$ (ca. 85% cis isomer) was thermally isomerized to the more stable trans isomer by heating at 160°C for 20 minutes.⁽⁶⁾ This piece was cut into several small pieces ($\sim 5 \times 20 \times 0.1$ mm; ~ 4 mg) and several large pieces ($\sim 20 \times 30 \times 0.1$ mm; ~ 20 mg) which were later sent out for elemental analysis.⁽⁷⁾ All the pieces were placed in a 48% (7.4 mol dm^{-3}) aqueous solution of the strong non-oxidizing acid, HBF_4 (Aldrich Co.) in two polyethylene containers. The solutions were previously deaerated by bubbling argon through them for 2 h. Oxygen was then bubbled continuously through one container so that the samples of film were constantly floating and moving throughout the solution. After a selected time interval one piece of the film was removed and dried in the vacuum system for 2 h by dynamic pumping and its conductivity (4-probe) was measured. Passage of oxygen was continued for an additional period of time and another sample of film was removed and treated in a similar manner. This process was repeated until all pieces of film had been examined. The solution in the other container was covered with an argon atmosphere and was used as a control. Samples of film were removed at intervals and treated as described above.

For the O_2 -electrode studies, cis-rich $(\text{CH})_x$ (ca. 85% cis isomer) was first electrochemically isomerized in the following manner. A strip of $(\text{CH})_x$ film, to the top of which a platinum wire had been attached by mechanical pressed contact, was placed in a solution of 0.5 mol dm^{-3} $[\text{Bu}_4\text{N}]^+[\text{BF}_4]^-$ in methylene chloride

under a dry, nitrogen atmosphere. A platinum counter electrode (1.5 cm²) was placed in the solution at a distance of ~ 5 cm from the (CH)_x electrode. Electrochemical oxidation (p-doping) of the (CH)_x to [CH^{+0.06}(BF₄)_{0.06}]_x was accomplished by having it serve as the anode. It was held at a constant potential of +9.0 V with respect to the Pt counter electrode. Oxidation of the (CH)_x was discontinued after a set number of coulombs, corresponding to 6 mol% oxidation had been passed. The (Bu₄N)⁺ ion was reduced at the cathode, with the production of hydrocarbons and amines.(8) This step took ~ 15 min. The film was then washed with methylene chloride and dried in vacuo with constant pumping. Oxidation as described above results in spontaneous isomerization of the cis isomer to the trans isomer.(9)

A strip of the [CH^{+0.06}(BF₄)_{0.06}]_x (~ 10 x 10 x 0.1 mm; ~ 5.1 mg), to the top of which a platinum wire had been attached by mechanical pressed contact, was then placed in one leg of a polyethylene H-cell containing a solution of 48% aqueous HBF₄. The platinum wire attached to the film and the area of the film touching the platinum was covered with molten paraffin wax. The latter step was done to insure that the platinum current collector was isolated from the electrolyte solution. A lead counter electrode (~ 10 x 40 x 0.13 mm) was placed in the solution in the other leg of the H-cell at a distance of ~ 5 cm from the [CH^{+0.06}(BF₄)_{0.06}]_x electrode. Electrochemical reduction of the [CH^{+0.06}(BF₄)_{0.06}]_x was accomplished by having it serve as the cathode by holding by holding it at a constant potential of 0.01 V with respect to the lead counter electrode for 1 h. The net electrochemical reaction which occurred is expressed by the equation



The trans-(CH)_x prepared using the above method gave better results in the O₂-electrode studies than those obtained from a cell constructed using either

cis-(CH)_x or trans-(CH)_x obtained by thermal isomerization of cis-(CH)_x in vacuo. This may be related to the fact that trace amounts of dopant remained in the trans-(CH)_x after the above electrochemical treatment, which would tend to make it more hydrophilic and therefore give higher currents with aqueous electrolytes.

Current versus time curves were recorded continuously for the above 1 h electrochemical reduction of the $[\text{CH}^{+0.06}(\text{BF}_4)^{-}_{0.06}]_x$ and for all subsequent studies. Oxygen was then permitted to bubble for 1 h over the (CH)_x, still held at a constant applied potential of 0.01 V versus the lead counter electrode. This resulted in the continuous chemical oxidation and electrochemical reduction of the partly oxidized polyacetylene electrode. The oxygen stream was then turned off and the current was recorded as a function of time. These two steps were repeated several times. In order to confirm that the effect being observed was due to the polyacetylene and not to the current collector, the exposed portion of the polyacetylene was cut off parallel to the current collector (see Figure 1). A thin cross section (~ 0.1 mm) of film was still exposed to the solution. The experiment was repeated once utilizing this configuration.

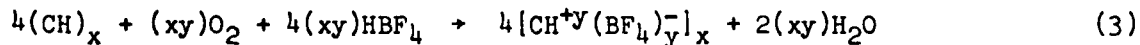
Constant potential oxidation and reduction (for electrochemical doping and O₂-electrode studies) was carried out utilizing a Princeton Applied Research (PAR) Model 363 potentiostat/galvanostat in conjunction with an Electro-Synthesis Company (ESC) Model 630 digital coulometer. Voltages and currents (for conductivity studies) were measured with a Keithley 169 or 177 microvolt digital multimeter. Current-time curves (for O₂-electrode studies) were recorded with a Houston Instruments Series D500 strip-chart recorder.

Results and Discussion

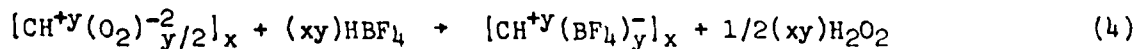
The relationship between the conductivity of the (CH)_x samples and the length of their exposure to their environments is given in Figure 1. The

initial conductivity of the trans-(CH)_x was $2.3 \times 10^{-5} \text{ ohm}^{-1}\text{cm}^{-1}$. The conductivity of the film exposed to oxygen increased by $\sim 10^5$ during the first day to the beginning of the metallic regime ($3 \pm 2 \text{ ohm}^{-1}\text{cm}^{-1}$) and remained constant within experimental error at this value for the following seven days. The increase in conductivity of the (CH)_x in the control experiment was significantly less, reaching a maximum of only $\sim 2 \times 10^{-3} \text{ ohm}^{-1}\text{cm}^{-1}$. Elemental analysis (Figure 1, footnote i; Table I, sample 1) of a piece of (CH)_x from the control experiment under argon shows that the HBF₄ used in these studies undergoes negligible reaction with (CH)_x under the experimental conditions employed. The (much smaller) increase in conductivity which does occur is probably related to the presence of minute traces of oxygen remaining in the HBF₄ solution since upon doping, the conductivity of (CH)_x increases very rapidly at first, even at extremely low doping levels(10). As can be seen from the footnotes to Figure 1, the data given in the graphs were obtained from several different experiments carried out under slightly different conditions. In one of the 7-day experiments the same HBF₄ solution was used throughout the experiment. In the other 7-day experiment a fresh solution was used every 2 days.

The overall reaction which occurs can be expressed by the following equation:

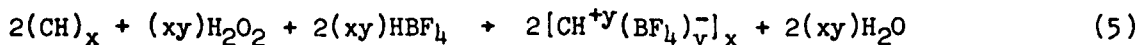


and is consistent with a mechanism involving first the oxidation of (CH)_x to (CH⁺_y)_x by the oxygen as given by equation (1) followed by reaction of the [CH⁺_y(O₂)⁻²_{y/2}]_x so formed with the HBF₄, viz.,



Since the O₂⁻² ion is a hard base it is expected to react preferentially with the hard acid, H⁺ (or its aquated form) rather than with the soft acid, (CH⁺_y)_x. We

have shown in a separate study that a $\sim 0.1 \text{ mol dm}^{-3}$ solution of H_2O_2 in 48% HBF_4 will oxidize trans-(CH) $_x$ to the metallic regime ($\sigma \sim 12 \text{ ohm}^{-1}\text{cm}^{-1}$; Table I, sample 2) during $\sim 30 \text{ min}$ as given by equation (5):

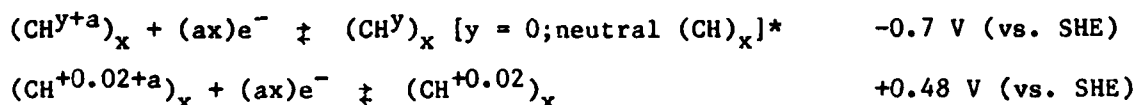


A combination of the reactions given by equations (1), (4) and (5) results in the net reaction represented by equation (3).

In the above equations, the anion has been represented, for convenience, as $(\text{BF}_4)^-$. However, it is known that $(\text{BF}_4)^-$ tends to undergo pH dependent hydrolysis⁽¹¹⁾ to give species such as $[\text{BF}_3(\text{OH})]^-$, $[\text{BF}_2(\text{OH})_2]^-$, etc. Hence it is not surprising to find that elemental analyses for samples of the oxygen-doped film (Figure 1, footnotes g,h; Table I, samples 3,4) indicate compositions such as e.g. $[\text{CH}^{+0.018}(\text{BF}_3\text{OH})_0.0057(\text{BF}_2(\text{OH})_2)_0.0123]_x$ and $[\text{CH}^{+0.019}(\text{BF}_4)_0.0083(\text{BF}_3\text{OH})_0.0110(\text{OH})_0.067]_x$. The conductivities of 2.9 and 1.4 $\text{ohm}^{-1}\text{cm}^{-1}$ obtained for these $\sim 2 \text{ mol\%}$ oxidized materials fall in the same range as that observed for similar levels of doping of trans-(CH) $_x$ with iodine ($\sim 0.2 \text{ ohm}^{-1}\text{cm}^{-1}$)⁽¹²⁾ and AsF_5 ($\sim 10 \text{ ohm}^{-1}\text{cm}^{-1}$)⁽¹³⁾. An elemental analysis obtained after exposing a sample of (CH) $_x$ to oxygen continuously for 7 days in the HBF_4 solution (Figure 1, footnote h; Table I, sample 4) indicated the presence of additional oxygen. This is believed to be caused by partial hydrolysis of the $(\text{CH}^{+\text{y}})_x$ ion to form $[\text{CH}(\text{OH})_y]_x$ groups which occurred to a greater extent during this more lengthy experiment.

We have recently determined thermodynamic (equilibrium) reduction potentials for polyacetylene in a number of different oxidation states.⁽³⁾ Since oxidation of (CH) $_x$ occurs in a continuous manner, rather than in a series of distinct integral steps, as for example, in the electrochemical intercalation of graphite with HSO_4^- , etc.⁽¹⁴⁾, we define the reduction potential of a polyacetylene

couple for a given level of oxidation of the polyacetylene as that potential such that the application of an infinitesimally small potential greater or smaller than that of the couple will result in the removal or addition, respectively, of an infinitesimally small amount of negative charge, $(ax)e^-$, from or to the couple.⁽³⁾ Values of the reduction potentials for polyacetylene couples determined in nonaqueous solution versus the Li^+/Li couple may be arbitrarily converted to values in aqueous solution versus the Standard Hydrogen Electrode (SHE) by the subtraction of 3.05 V. In the non-aqueous solvents employed for studying the polyacetylene couples the error introduced by this approach is not greater than ~ 0.1 V.⁽³⁾ Hence the reduction potentials can be used to rationalize qualitatively the expected thermodynamically permitted reactions. Two representative reduction potentials for the polyacetylene system⁽³⁾



when compared to the standard oxygen reduction potential



shows qualitatively that $(CH)_x$ should be oxidized by oxygen in the presence of acid, even though the hydrogen ion concentration differs from unity. This is consistent with the reaction given by equation (3). Similarly the reduction potential of the couple



is consistent with the reaction given by equation (5).

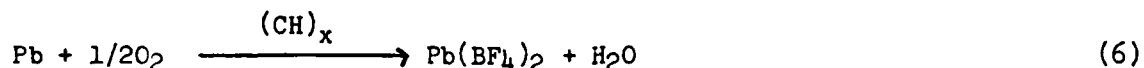
*y refers to the degree of oxidation or reduction of the polyacetylene; it is a positive number for p-doped (oxidized) polyacetylene and a negative number for n-doped (reduced) polyacetylene.

The effect of gaseous oxygen on the current produced by the O_2 -electrode is shown in Figure 2. The initial current, given in the decreasing left-hand curve is the initial electrochemical reduction of the $[CH^{+0.06}(BF_4)^{-}_{0.06}]_x$ described previously. When the film had been almost completely reduced to $(CH)_x$ the oxygen stream was turned on and the current was recorded as given in Figure 2. After a period of 1 h the oxygen stream was turned off and the current was again recorded. The oxygen stream was then turned on and off several times as shown in Figure 2. The number of coulombs released during the time oxygen was bubbled over the $(CH)_x$ as well as the current observed after 1 h exposure to oxygen is given in Table II for each individual oxygen treatment. Note that a total of 6.715C was released during the time oxygen was bubbled over the $(CH)_x$. This corresponds to the passage of 0.249 electrons per CH unit in the $(CH)_x$. A significant current flowed only when oxygen was bubbled over the $(CH)_x$ electrode. When the oxygen stream was stopped, the current immediately dropped from ~ 0.5 mA leveling off at ~ 0.1 mA after 1 h. After four trials, the film was severed from the platinum wire by means of a razor blade, by cutting through the wax-covered portion of the film as shown by the dotted line on the electrode configuration given in the inset to Figure 2. When oxygen was bubbled over what then remained of the $(CH)_x$ electrode only a minute increase in current was observed (see Figure 1) thus proving that the $(CH)_x$ film, not the platinum current collector, was responsible for the observed phenomenon. In another experiment, after turning the oxygen stream off, argon was bubbled through the solution to remove dissolved oxygen. The current fell to an even lower value (~ 0.03 mA/cm²). Experiments are now in progress to determine the optimum acid strength to be used in the electrolyte in order to obtain maximum currents, voltages and recyclability, etc.

In these preliminary experiments, in which no attempt has been made to optimize conditions for maximum performance, a steady state short circuit current

I_{sc} , of $\sim 0.4 \text{ mA/cm}^2$ of $(\text{CH})_x$ is obtained simply by bubbling oxygen over the surface of the $(\text{CH})_x$ film immersed in the electrolyte. Since the bulk density of the film is $\sim 0.4 \text{ g/cm}^3$ and the density of the $\sim 200\text{\AA}$ fibrils comprising the film is $\sim 1.2 \text{ g/cm}^3$ the material is therefore approximately two-thirds void space. Experiments are now in progress to force the oxygen through the porous film. Such a modification in design is expected to increase the current to significantly higher levels. That higher currents should be obtainable is evidenced by the observation that if oxygen is bubbled over the film for 1 h when it is not connected to the lead anode so as to permit the interior portions of the film to become oxidized to a somewhat similar level to the outer surface, a short circuit current of $\sim 10 \text{ mA/cm}^2$ is obtained. The open circuit voltage, V_{oc} , of the cell after the 1 h exposure to oxygen, immediately before the short circuit current measurements was $\sim 0.74 \text{ V.}$ (15)

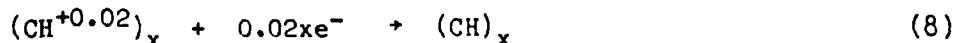
The overall reaction which occurs can be expressed by the following equation:



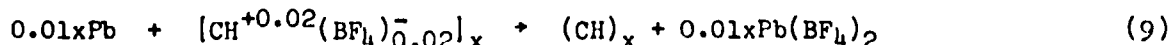
If a piece of $[\text{CH}^{+0.02}(\text{BF}_4)^{-0.02}]_x$ film and a strip of lead are placed in a 48% aqueous HBF_4 solution nothing happens. The overvoltage for H_2 evolution at lead is such that lead does not dissolve spontaneously to any significant extent. If, however, these two electrodes are now connected via an external wire the lead dissolves, liberating electrons:



The electrons flow through the wire and are taken up by the $(\text{CH}^{+0.02})_x$ ion



resulting in the net electrochemical reduction reaction:



which regenerates the $(CH)_x$. The lead, which acts as the reducing agent or "fuel", is converted to $Pb(BF_4)_2$.

The important point to note is that the $(CH)_x$ can be reconverted back to $[CH^{+0.02}(BF_4)_{0.02}^-]_x$ in 48% aqueous HBf_4 by bubbling oxygen over it while it is immersed in the acid solution as given by equation (3). Hence, if oxygen is constantly bubbled over the polyacetylene electrode it is possible to continuously chemically oxidize the polyacetylene to $[CH^{+0.02}(BF_4)_{0.02}^-]_x$ as rapidly as it is reduced electrochemically according to equation (9). Hence, neither the chemical composition nor the total mass of the p-doped polyacetylene electrode changes during the reaction at steady state, i.e., the p-doped polyacetylene acts as a "catalyst electrode" permitting the reaction expressed by equation (6) to occur. The $(CH)_x$ is therefore acting as an electrocatalytic "fuel cell type" electrode for oxygen, the oxidizing agent being elemental oxygen, the "fuel" being lead and HBf_4 . It is clear that the operation of the $(CH)_x$ electrode in this system is completely different from that a battery electrode during either charge or discharge conditions. In a battery the chemical composition and/or the total mass of the electrode changes.

It should be stressed that the potential of the oxygen catalyst electrode is determined by the value of y in the steady-state composition of the $[CH^{+y}(BF_4)_y^-]_x$ comprising the electrode. The value of y will not be affected by the mechanism by which the $(CH)_x$ is converted to $[CH^{+y}(BF_4)_y^-]_x$, i.e., whether it is by a four-electron reduction of O_2 to $2O^{2-}$ (to produce H_2O) as given by equation (3) or whether it is by two two-electron reduction steps as given first by equation (4) (to produce H_2O_2) followed by the reaction given in equation (5). The role of $(CH)_x$ in acting as a catalyst electrode for the net reduction of O_2 is completely different from the catalytic role

of a material such as platinum. In the latter case, the potential of the electrode will depend critically on the degree to which four-electron or two-electron reduction steps are involved.

It should also be stressed that lead has been used in this study of the electrocatalytic properties of a $(\text{CH})_x/\text{O}_2$ electrode purely as a convenient counter and reference electrode. It should not be implied that lead should be considered as a "fuel" in any practical oxygen fuel cell system! Studies are in progress to investigate other "fuels", particularly organic compounds as a replacement for lead, especially at a $(\text{CH})_x$ electrocatalytic counter electrode.

A secondary, very important observation arising from this study is that, contrary to general belief, p-doped polyacetylene in the metallic conducting regime can be stable in aqueous (acid) solution. We believe that this stability arises from the delocalization of the positive charge on the polymer chain over approximately 15 CH units in a positive soliton⁽¹⁶⁾ which makes the material less susceptible to nucleophilic attack than if the charge were localized on one CH unit.

In conclusion, these studies show that contrary to previous belief, gaseous oxygen, rather than destroying the conductivity of $(\text{CH})_x$, can be used to dope it to the metallic regime. This is accomplished by replacing the O_2^{-2} anion in $[\text{CH}^{+y}(\text{O}_2)^{-2}_{y/2}]_x$ by a fluoroborate anion which does not react with the $(\text{CH}^{+y})_x$ cation to destroy its conductivity as does the O_2^{-2} ion. Furthermore the reaction is in qualitative agreement with the reduction potentials of $(\text{CH})_x$ and oxygen in acid solution.

Although it is as yet far too early to make any realistic predictions, these unexpected catalytic properties of a conducting organic polymer suggest that $(\text{CH})_x$ and possibly other conducting polymers might be useful either in fuel cell type processes for the generation of electricity using oxygen as an

oxidizing agent, or for the facile oxidation of certain organic or inorganic compounds to give useful materials not readily synthesized by other methods.

Acknowledgement

This work was supported by the Office of Naval Research and by the Defense Advanced Research Projects Agency through a grant monitored by the Office of Naval Research.

References

1. J. M. Pochan, H. W. Gibson and F. C. Bailey, J. Polym. Sci., Polym. Lett. Ed., 1980, 18, 447; J. C. Chien, J. Polym. Sci., Polym. Lett. Ed., 1981, 19, 249; J. M. Pochan, D. F. Pochan, M. Rommelmann and H. W. Gibson, Macromolecules, 1981, 14, 110; J. M. Pochan, H. W. Gibson and J. Harbour, Polymer, 1982, 23, 439; H. W. Gibson and J. M. Pochan, Macromolecules, 1982, 15, 242.
2. A. G. MacDiarmid, Y. W. Park, A. J. Heeger and M. A. Druy, J. Chem. Phys., 1980, 73, 946.
3. A. G. MacDiarmid, R. J. Mammone, J. R. Krawczyk and S. J. Porter, Mol. Cryst. Liq. Cryst., 1984, 105, 89; R. J. Mammone and A. G. MacDiarmid, accepted for publication in Synthetic Metals (October, 1983).
4. T. -C. Chung, A. Feldblum, A. J. Heeger and A. G. MacDiarmid, J. Chem. Phys., 1981, 74, 5504.
5. H. Shirakawa and S. Ikeda, Polym. J., 1971, 2, 231; H. Shirakawa, T. Ito and S. Ikeda, Polym. J., 1973, 4, 460; T. Ito, H. Shirakawa and S. Ikeda, J. Polym. Sci., Polym. Chem. Ed., 1974, 12, 11; *ibid.* 1975, 13, 1943.
6. H. Shirakawa, T. Ito and S. Ikeda, Makromol. Chem., 1978, 179, 1565; B. R. Weinberger, H. Ehrenfreund, A. Pron, A. J. Heeger, and A. G. MacDiarmid, J. Chem. Phys., 1980, 72, 4729; P. Bernier, C. Linenya, M. Rolland, and M. Aldissi, J. Phys. Lett., 1981, 42, L-295.
7. Analysis performed by Schwartzkopf Microanalytical Laboratory, Woodside, N.Y., 11377.
8. J. E. Dubois, A. Monvernay and P. C. Locaze, Electrochimica Acta, 1970, 15, 315.
9. T.-C. Chung, A. G. MacDiarmid, A. Feldblum and A. J. Heeger, J. Polym. Sci., Polym. Lett. Ed., 1982, 20, 427.
10. A. G. MacDiarmid and A. J. Heeger, Synthetic Metals, 1979/80, 1, 101.
11. D. W. A. Sharp, Adv. Fluorine Chem., 1961, 1, 68.
12. C. K. Chiang, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis and A. G. MacDiarmid, J. Chem. Phys., 1978, 69, 5089.
13. C. K. Chiang, S. C. Gau, C. R. Fincher, Jr., Y. W. Park, A. G. MacDiarmid and A. J. Heeger, Appl. Phys. Lett., 1978, 33, 18.
14. A. Metrot and J. E. Fischer, Synthetic Metals, 1981, 3, 201; J. O. Besenhard, E. Wudy, H. Mohwald, J. J. Nickl, W. Biberacher and W. Foag, Synthetic Metals, 1983, 7, 185; see also Intercalation Chemistry, M. S. Whittingham and A. J. Jacobsen, ed., Academic Press, New York, New York (1982).
15. J. R. Krawczyk and A. G. MacDiarmid, unpublished results, (1983).
16. W. P. Su, J. R. Schreiffer and A. J. Heeger, Phys. Rev. Lett., 1979, 42, 1698; Phys. Rev. B., 1980, 22, 2099.

Table I
Analytical Data for Doped Trans-(CH)_x Films^a

Sample	Composition	Carbon		Hydrogen		Boron		Fluorine	
		Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
1	[CH(BF ₂ (OH) ₂) ₂ 0.0035(OH)0.0025] _x ^b	89.34	89.96	7.73	7.62	0.56	0.28	0.97	1.0
2	[CH(BF ₂ (OH) ₂) ₂ 0.0560] _x ^c	68.32	68.02	6.75	6.35	3.55	3.43	12.38	12.05
3	[CH(BF ₃ OH)0.0057(BF ₂ (OH) ₂) ₂ 0.0123] _x ^d	83.17	82.71	7.18	7.15	1.47	1.34	6.36	5.
4	[CH(BF ₄) ₂ 0.0083(BF ₃ OH)0.0110(OH)0.067] _x ^e	76.19	75.96	6.50	6.87	1.33	1.32	8.01	

^aSince oxygen analysis of compounds of this type presents certain difficulties, the amount of oxygen was deduced, as is common practice, by assuming that the difference between 100 and the sum of the percentage elemental composition of all other elements represents the percentage of oxygen by weight in the compound.

^bOxygen determined by difference: found 1.40, calc. 1.14

^cOxygen determined by difference: found 9.00, calc. 10.15

^dOxygen determined by difference: found 1.82, calc. 3.35

^eOxygen determined by difference: found 7.97, calc. 7.90

Table II

Coulombs Released and Currents Observed for a $(CH)_x/O_2/(HBF_4(aq))/Pb$ Cell

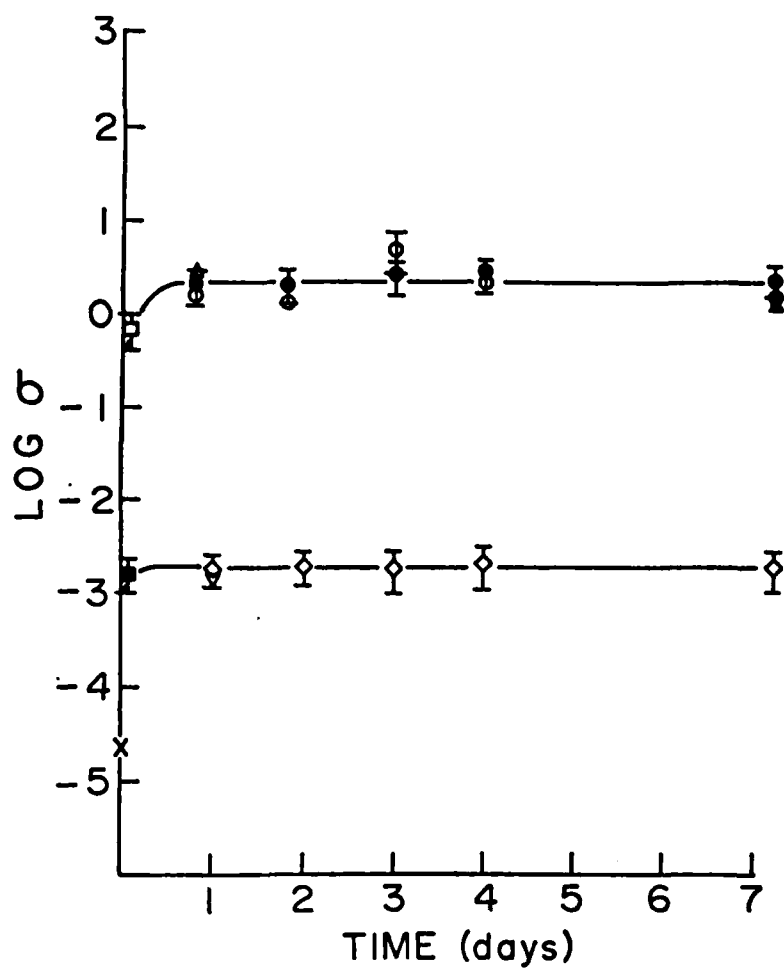
<u>Trial</u>	<u>Coulombs Released^a</u>	<u>Current^b</u>
1	1.802C (0.0668)	0.530mA
2	1.745C (0.0647)	0.483mA
3	1.625C (0.0602)	0.460mA
4	1.543C (0.0572)	0.458mA

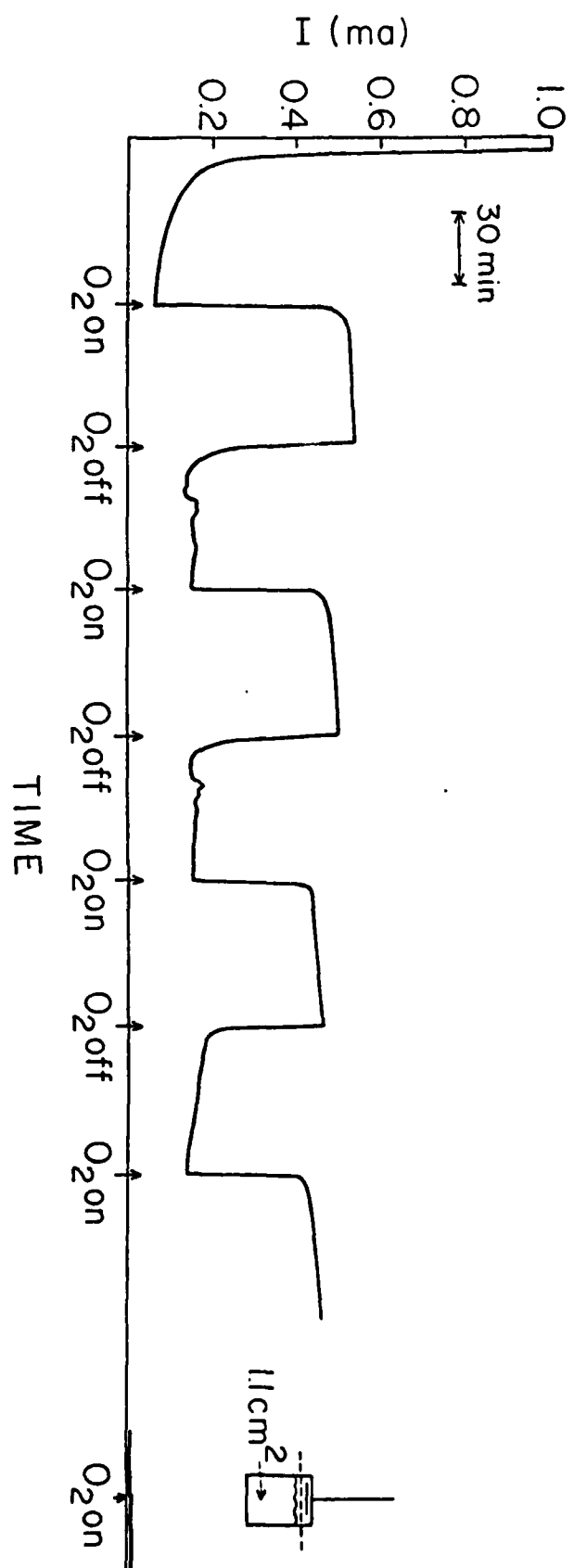
^aCoulombs released during 1 h exposure to oxygen. The number in parentheses is the number of electrons released per CH unit present in the film.

^bCurrent observed after 1 h exposure to oxygen. Exposed area of $(CH)_x$ film is 1.1 cm².

Figure 1: Conductivity (4-probe) of trans-(CH)_x film as a function of time when immersed in 48% (7.4 mol dm⁻³) aqueous HBF₄ and exposed either to oxygen or argon: (a) □ One sample treated for 2 h (dried for 2 h); (b) ■ One sample treated for 2 hours under argon (dried for 2 h); (c) ● Five samples treated for varying lengths of time in the same container (dried for 2 h); (d) ○ Five samples treated for varying lengths of time in the same container but HBF₄ replaced by a fresh HBF₄ solution every 48 h (dried for 2 h); (e) ◇ Five samples treated for varying lengths of time under argon in the same container (dried for 2 h); (f) ✕ Conductivity of trans-(CH)_x, (2.3 x 10⁻⁵ ohm⁻¹ cm⁻¹); (g) △ One sample (~20 x 30 x 0.1 mm) treated for 24 h (dried for 24 h); (h) ▲ One sample (~20 x 30 x 0.1 mm) treated for 7 days (dried for 24 h); (i) ▽ One sample (~20 x 30 x 0.1 mm; 18.1 mg) treated for 24 h under argon (dried for 24 h, 18.5 mg).

Figure 2: Change in current produced by a (CH)_x/O₂/HBF₄(aq)/Pb cell when oxygen stream bubbling over the (CH)_x electrode is turned on and off.





TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 413 800 North Quincy Street Arlington, Virginia 22217	2	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Pasadena Detachment Attn: Dr. R. J. Marcus 1030 East Green Street Pasadena, California 91106	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Dean William Tolles Naval Postgraduate School Monterey, California 93940	1
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
U.S. Army Research Office Attn: CRD-AA-IP P. O. Box 12211 Research Triangle Park, N.C. 27709	1	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Mr. Vincent Schaper DTNSRDC Code 2803 Annapolis, Maryland 21402	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1	Mr. A. M. Anzalone Administrative Librarian PLASTEC/ARRADCOM Bldg 3401 Dover, New Jersey 07801	1

TECHNICAL REPORT DISTRIBUTION LIST, 356B

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. C. L. Shilling Union Carbide Corporation Chemical and Plastics Tarrytown Technical Center Tarrytown, New York	1	Dr. G. Goodman Globe-Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Dr. R. Soulen Contract Research Department Pennwalt Corporation 900 First Avenue King of Prussia, Pennsylvania 19406	1	Dr. E. Fischer, Code 2853 Naval Ship Research and Development Center Annapolis Division Annapolis, Maryland 21402	
Dr. A. G. MacDiarmid University of Pennsylvania Department of Chemistry Philadelphia, Pennsylvania 19174	1	Dr. Martin H. Kaufman Code 38506 Naval Weapons Center China Lake, California 93555	1
Dr. H. Allcock Pennsylvania State University Department of Chemistry University Park, Pennsylvania 16802	1	Dr. C. Allen University of Vermont Department of Chemistry Burlington, Vermont 05401	1
Dr. M. Kenney Case-Western University Department of Chemistry Cleveland, Ohio 44106	1	Professor R. Drago Department of Chemistry University of Florida Gainesville, FL 32611	1
Dr. R. Lenz University of Massachusetts Department of Chemistry Amherst, Massachusetts 01002	1	Dr. D. L. Venezky Code 6130 Naval Research Laboratory Washington, D.C. 20375	1
DR. M. David Curtis University of Michigan Department of Chemistry Ann Arbor, Michigan 48105	1	COL R. W. Bowles, Code 100M Office of Naval Research 800 N. Quincy Street Arlington, Virginia 22217	1
NASA-Lewis Research Center Attn: Dr. T. T. Serafini, MS 49-1 21000 Brookpark Road Cleveland, Ohio 44135	1	Professor T. Katz Department of Chemistry Columbia University New York, New York 10027	1
Dr. J. Griffith Naval Research Laboratory Chemistry Section, Code 6120 Washington, D.C. 20375	1	Professor James Chien Department of Chemistry University of Massachusetts Amherst, Massachusetts 01002	1

TECHNICAL REPORT DISTRIBUTION LIST, 356B

	<u>No. Copies</u>		<u>No. Copies</u>
Professor Malcolm B. Polk Department of Chemistry Atlanta University Atlanta, Georgia 30314	1	Dr. Alan J. Heeger Dept. of Physics University of California Santa Barbara, CA 93106	1
Dr. G. Bryan Street IBM Research Laboratory, K32/281 San Jose, California 95193	1	Dr. Frank Karasz Dept. of Polymer Science and Engng. University of Massachusetts Amherst, MA 01003	1
Professor Michael Moran Department of Chemistry West Chester State College West Chester, Pennsylvania 19401	1		
Dr. K. Paciorek Ultrasystems, Inc. P. O. Box 19605 Irvine, California 92715	1		
Dr. D. B. Cotts SRI International 333 Ravenswood Avenue Menlo Park, California 94025	1		
Professor D. Seyferth Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1		
Dr. Kurt Baum Fluorochem, Inc. 680 S. Ayon Avenue Azusa, California 91702	1		

END

FILMED

10-84

DTIC