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THE AQUEOUS AND NON-AQUEOUS ELECTROCHEMISTRY OF
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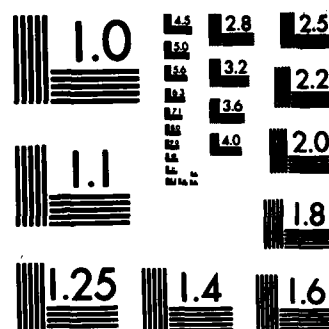
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The Aqueous and Non-Aqueous Electrochemistry of Polyacetylene:

Application in High Power Density Rechargeable Batteries

by

A. G. MacDiarmid, R. B. Kaner, R. J. Mammone and A. J. Heeger

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APPLICATION IN HIGH POWER DENSITY
RECHARGEABLE BATTERIES

by

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Résumé - Le polyacétylène peut être dopé par des moyens chimiques ou électrochimiques au solution aqueuse au regime metallique. Les caracteristiques de certaines batteries rechargeables sélectionnées, qui emploient des electrodes de $(CH)_x$ dans des electrolytes non-aqueux, sont décrites.

Abstract - Polyacetylene can be doped either chemically or electrochemically in aqueous solution to the metallic regime. The characteristics of selected rechargeable batteries employing $(CH)_x$ electrodes in non-aqueous electrolytes are described.

I - p-DOPING OF $(CH)_x$ IN AQUEOUS SOLUTION

It is generally believed that p-doped $(CH)_x$ reacts readily with water. Until the present study was undertaken, the only apparent exception to this water instability involved the electrochemical p-doping (oxidation) of $(CH)_x$ film in an aqueous 0.5 M solution of KI. Doping took place in a few minutes to give $(CHI_{0.07})_x$ having a conductivity in the metallic regime /1/. The sum of the elemental analyses for C, H, and I was 99.8%. This showed that no reaction with water, to incorporate oxygen into the $(CH)_x$ had taken place, at least during the time needed for doping. This observation was most surprising. The absence of reaction with water would at first sight appear to be inconsistent with the fact that p-doped $(CH)_x$, i.e., $(CH^+yA_y^-)_x$, is a polycarbonium ion delocalized within solitons and polarons, since all other carbonium ions react instantly with neutral water and are stable only in certain concentrated acids or "super-acid" solutions. We wished to ascertain whether $(CH)_x$ doped with iodine was unique or whether other dopants would behave similarly with respect to its relative stability in aqueous solutions.

A piece of cis $(CH)_x$ film and a piece of Pt foil were placed in a saturated solution of ca. 0.5 M NaAsF₆ in 50% aqueous HF. The $(CH)_x$ was attached to the positive electrode and the Pt to the negative electrode, respectively, of a d.c. power supply. A constant potential of 1.0V was applied between the electrodes for ca. 30 minutes and the film was then washed in 50% HF and pumped in the vacuum system for 18 hours. In several different experiments, carried out under slightly different conditions, flexible, golden films having good metallic conductivity (ca. 10 to 100 ohm⁻¹cm⁻¹) were obtained. It was most surprising to find that the films contained no oxygen. The fluorine content varied from one preparation to another, e.g. $[CH^{+0.026}(AsF_5.1)^-]_{0.0261x}$, (sum

of C + H + As + F analyses = 100.2%) and $[\text{CH}^{+0.029}(\text{AsF}_{4.7})^{-0.029}]_x$ (sum of C + H + As + F analyses = 100.3%). The nature of the dopant species and the cause of the variable fluorine content is currently being investigated. It is believed that the dopant probably consists of a mixture of the $(\text{AsF}_6)^-$ and $(\text{AsF}_4)^-$ ions.

We have shown previously that $(\text{CH})_x$ can be doped readily to the metallic regime when exposed to the vapor from 98% sulfuric acid or 72% perchloric acid /2/. In view of the surprising electrochemical results obtained above, we wished to ascertain if $(\text{CH})_x$ could be doped in aqueous solutions of these acids. We therefore studied the (d.c.) conductivity of a strip of $(\text{CH})_x$ film immersed in acid solutions of different strengths. At all concentrations except the lowest, the conductivity of the partly doped $(\text{CH})_x$ was much greater than that of the ionic conductivity of the solution. As can be seen from Fig. 1 and Fig. 2, the conductivity of the $(\text{CH})_x$ increased rapidly at first and then increased only very slowly for a period of ca. 24 hours, presumably due to slow diffusion of the oxidizing acids into the interior of the $(\text{CH})_x$ fibrils. The quasi-equilibrium conductivity values shown

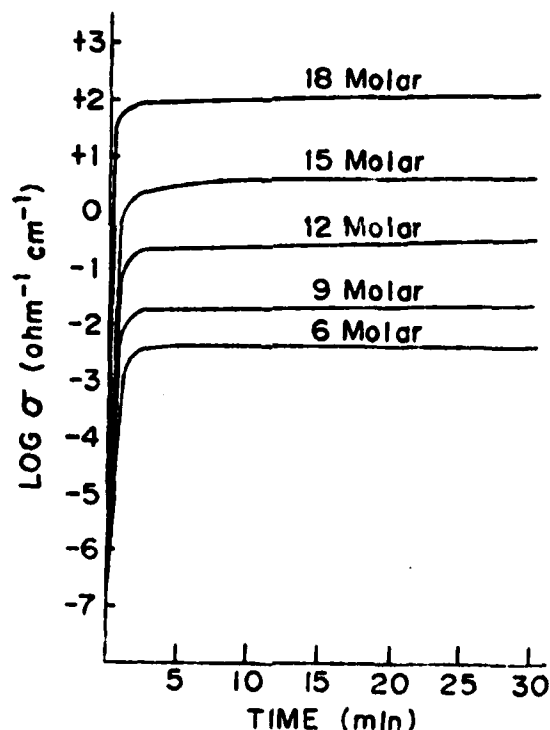


Fig. 1 - Conductivity of cis-(CH)_x film immersed in aqueous sulfuric acid solutions of different concentrations.

in Fig. 1 and Fig. 2 are plotted in Fig. 3 and Fig. 4 as a function of acid concentration (molarity). In each case, the conductivity increases over five orders of magnitude to metallic levels! It is most interesting to find that $(\text{CH})_x$ can actually undergo a semiconductor-metal transition in aqueous solution and that the stability of the (CH^+Y) ion to water is exceptionally great under certain conditions. When the film doped in 18 M sulfuric acid

was washed with cyclohexene to remove free acid, it was flexible and golden and had a conductivity of $1 \times 10^2 \text{ ohm}^{-1} \text{ cm}^{-1}$.

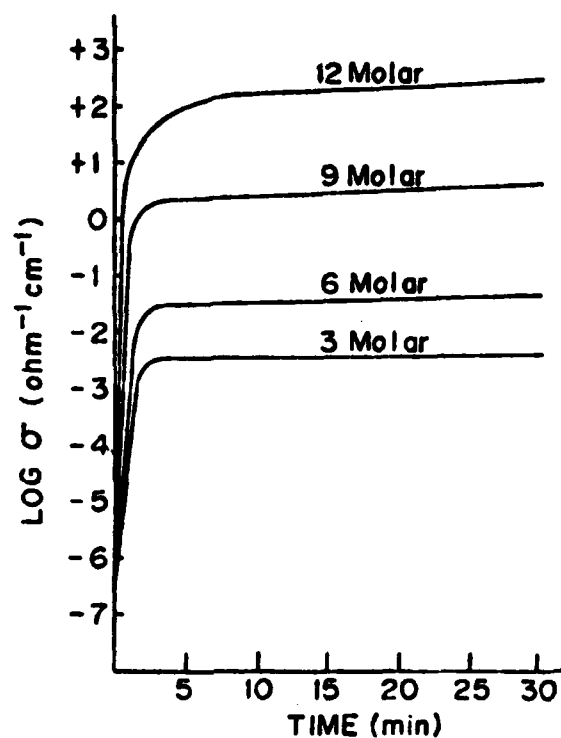


Fig. 2 - Conductivity of cis-(CH)_x film immersed in aqueous perchloric acid solutions of different concentrations.

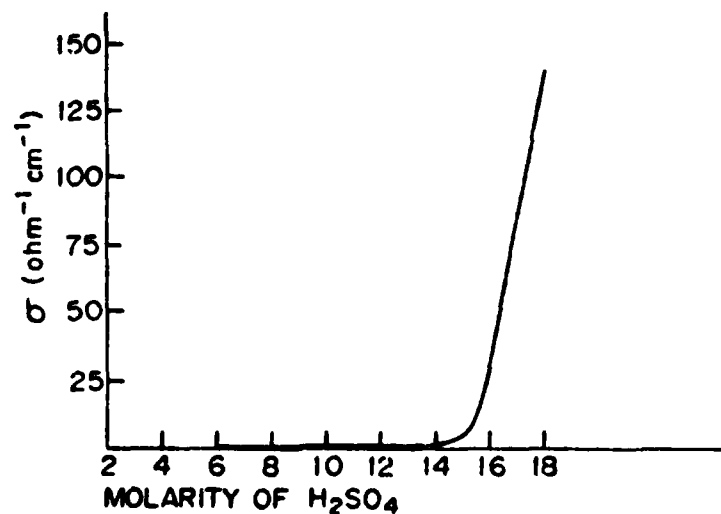


Fig. 3 - Relationship between quasi-equilibrium values of conductivity of cis-(CH)_x film immersed in aqueous sulfuric acid solutions of different concentrations.

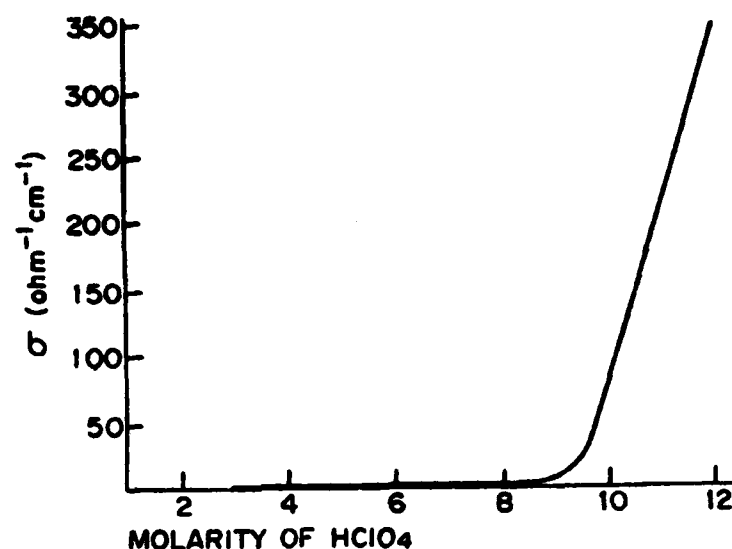
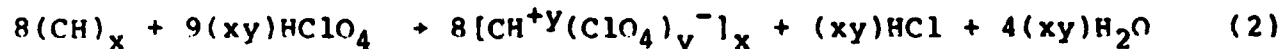
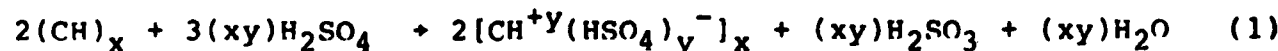


Fig. 4 - Relationship between quasi-equilibrium values of conductivity of cis-(CH)_x film immersed in aqueous perchloric acid solutions of different concentrations.

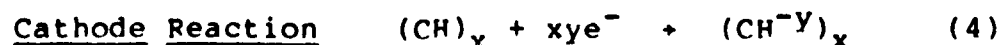
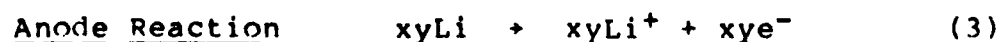
In view of the known oxidation potentials (vs. Li/Li⁺) of (CH)_x/(CH⁺_a)_x, H₂SO₃/SO₄⁻², and Cl⁻/ClO₄⁻ which are -2.4V, -3.2V and -4.36V, respectively, the expected doping (oxidation) reactions which occurred are:



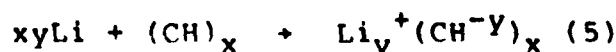
The greater the concentration of the acids, the greater will be the value of y in each case. The high stability of (CH⁺_y)_x to water in certain cases is believed to be due to the extensive delocalization of charge which varies according to the nature of the dopant anion associated with the (CH⁺_y) ion.

II - BATTERY CELLS USING (CH)_x AND/OR p-DOPED (CH)_x

(1) Neutral (CH)_x cathode + Li anode: Selected electrochemical characteristics of a cell constructed from cis-polyacetylene film (thickness ca. 0.1mm; ca. 3.5mg/cm²) and lithium metal immersed in electrolyte of 1.0M LiClO₄ in THF have been studied. A spontaneous electrochemical reaction occurs when the (CH)_x and Li electrodes are connected by a wire external to the cell. The discharge reactions are:



giving the overall net reaction



where $y < 0.1$. It should be noted that the reaction given by equation (5) is the discharge reaction of a voltaic cell and that the cell, in its completely charged state consists of parent, neutral $(CH)_x$ which appears to be stable indefinitely in the electrolyte. (See Fig. 5) Reversal of the reaction given by equation (5) may be obtained on charging at a fixed applied potential of 2.5V, the potential (vs. Li) of the parent, neutral $(CH)_x$ in this electrolyte.

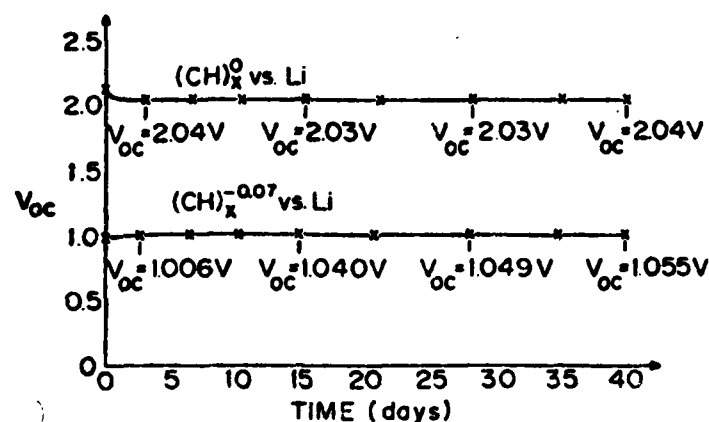


Fig. 5 - Open circuit voltage, V_{oc} , values of $(CH)_x$ (upper curve), and $[Li_{0.07}(CH^{-0.07})]_x$ (lower curve), in a 1M $LiClO_4$ solution in THF. The V_{oc} value for $(CH)_x^0$ was determined on a previously reduced film which had then been reoxidized to $(CH)_x^0$. The small initial decrease in V_{oc} is caused by diffusion of traces of remaining dopant from the interior to the exterior of the $(CH)_x$ fibrils.

Although reduction occurs spontaneously, most studies were carried out at a constant applied potential at various selected values in order to study the system in a controllable manner. Significant reduction of the $(CH)_x$ occurs only at an applied potential less than 1.7V. After the onset of reduction, the open circuit voltage, V_{oc} , falls rapidly up to a reduction level of ca. 1% and then decreases more slowly.

The relationship between cell potential and degree of reduction has been studied up to 10% reduction levels. The reduction process was stopped at intervals and the V_{oc} value (vs. Li) was measured immediately. The cell was then allowed to stand for a period of 24 hours in order to permit partial equilibration of the Li^+ ions within the 200Å $(CH)_x$ fibrils. The V_{oc} values were again recorded. An increase in potential was observed on standing. This is caused by a decrease in the degree of reduction of the outside of the $(CH^{-Y})_x$ fibrils as the counter Li^+ ions diffuse towards the center of a fibril together with their attendant negative charge on the polyacetylene. Exactly the opposite effect is observed after a partial electrochemical oxidation (charge reaction) of $(CH^{-Y})_x$ to a less reduced state. In this case, the V_{oc} falls on standing.

Maximum power density of a cell using 4.5 cm^2 (ca. 15mg) of $(\text{CH})_x$ film was obtained by discharging it through an external resistor having the same resistance as the internal resistance of the cell (ca. 15 ohms), (see Fig. 7). Measurement of the initial current (54mA) gave a maximum power density of ca. 2,900 Watts/Kg on the second discharge. After 1 minute the current was 45mA, after 2.5 minutes it was 24mA and after 5 minutes it had fallen to 14mA. Maximum power density values after other discharging times are given in Fig. 7.

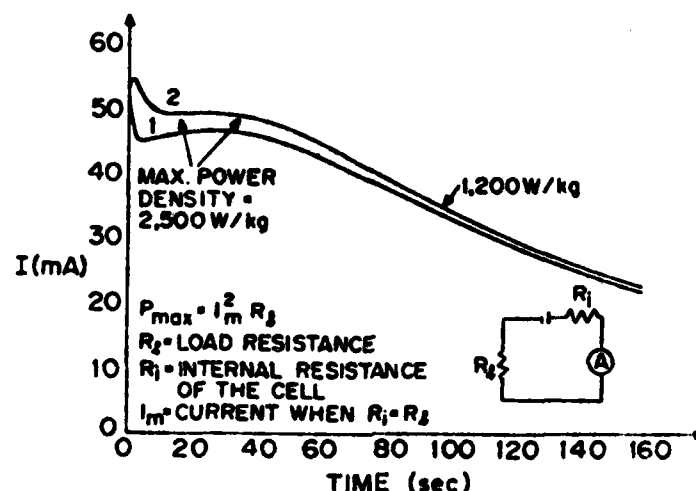
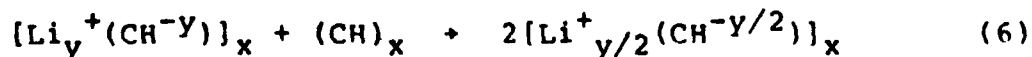


Fig. 7 - Maximum power density characteristics of a $(\text{CH})_x/\text{LiClO}_4$, (THF)/Li cell. Curve 1 refers to the first discharge; curve 2 refers to the second discharge. A coulombic efficiency of 99% was obtained on recharging after the first discharge.

(2) Neutral $(\text{CH})_x$ cathode + n-doped $(\text{CH})_x$ anode: Since both neutral and reduced $(\text{CH})_x$ have good stability in an electrolyte of 1M LiClO_4 in THF a voltaic cell was constructed using $(\text{CH})_x$ as the cathode and $(\text{CH}^{-Y})_x$ as the anode. The overall discharge reaction is:



A cell of this type using 7% electrochemically reduced $(\text{CH})_x$ for the anode and neutral $(\text{CH})_x$ for the cathode has a potential of ca. 1.0V and a short circuit current of ca. 3 mA/cm^2 of $(\text{CH})_x$. The cell shows excellent stability over a 4-5 month period. (See Fig. 8). It is fully rechargeable with coulombic efficiencies of ca. 99%. It is the first stable, rechargeable battery developed in which both the cathode and anode active materials are organic polymers.

The present studies indicate that cells involving neutral and/or partly reduced polyacetylene have excellent stability and coulombic efficiency and some types exhibit interestingly large energy and power densities even at relatively small levels of reduction of the polyacetylene.

Coulombic efficiencies, $(Q_{\text{discharge}}/Q_{\text{charge}})100$ where $Q_{\text{discharge}}$ refers to the total coulombs involved in a given discharge (reduction) process and Q_{charge} refers to the total coulombs involved in a charge (oxidation) process to 2.5V have been determined for several different levels of reduction. Values of ca. 99% were found up to ca. 6.0% reduction levels. Somewhat poorer values were found at higher levels of reduction. These high coulombic efficiencies are undoubtedly related, at least in part, to the excellent chemical stability of $(\text{CH})_x$ and partly reduced polyacetylene in the electrolyte as shown by Fig. 5.

Studies have been made of the change in voltage during constant current discharges of 0.1mA (19.8Amps/Kg), 0.5mA (98.8Amps/Kg) and 1.0mA (197.6Amps/Kg) to 6.0% reduction of the $(\text{CH})_x$, i.e., to a composition of $[\text{Li}_{0.06}(\text{CH})_{0.06}]_x$ in each case, (See Fig. 6).

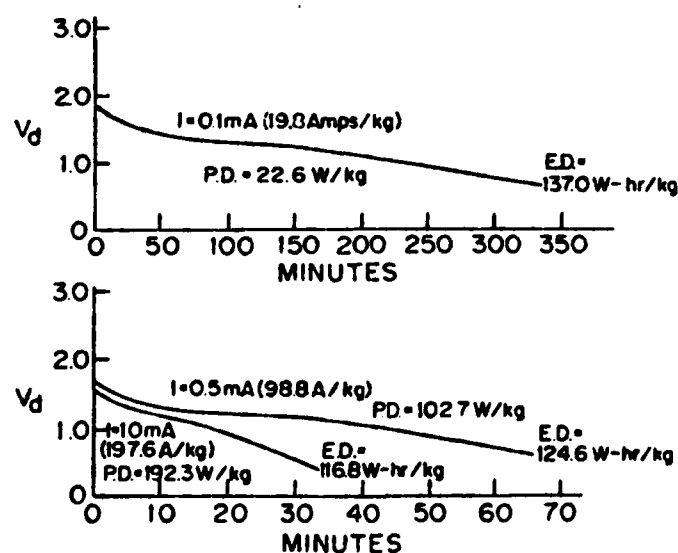


Fig. 6 - Constant current discharge characteristics of a $(\text{CH})_x/\text{LiClO}_4, (\text{THF})/\text{Li}$ cell.

The weight of the $(\text{CH})_x$ employed (4.9mg) and the weight of the Li consumed in the discharge reaction were used to calculate the normalized discharge rates in Amps/Kg given above. Even though each constant current discharge involved the same number of coulombs and hence resulted in the same average percent reduction, the final discharge voltages, V_d , decreased as the discharge currents increased, e.g., $V_d=0.62\text{V}$ at 0.1mA, $V_d=0.52\text{V}$ at 0.5mA and $V_d=0.35\text{V}$ at 1.0mA. This is due to the fact that the diffusion equilibrium involving migration of the Li^+ ions from the exterior to the interior of the $(\text{CH})_x$ fibrils becomes less complete the more rapidly the electrochemical reduction process is carried out.

The energy density and average power density values obtained in each of the above discharges are, respectively, 0.1mA, 137.0 Watt hr/Kg and 22.6 Watts/Kg; 0.5mA, 124.6 Watt hr/Kg and 102.7Watts/Kg; 1.0mA, 116.8 Watt hr/Kg and 192.3 Watts/Kg.

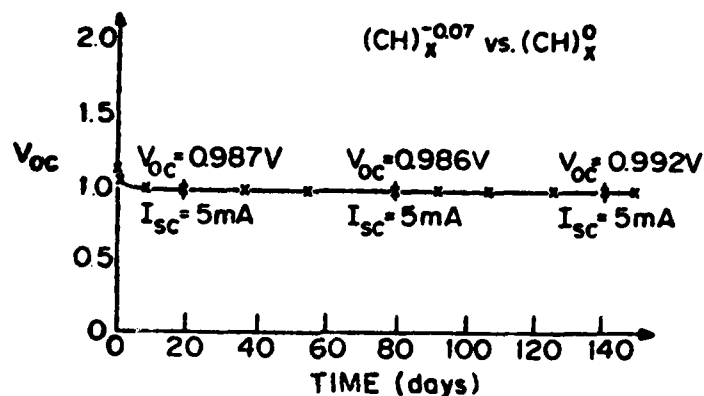


Fig. 8 - Open circuit voltage, V_{oc} , and short circuit current, I_{sc} , characteristics of a $(CH)_x/LiClO_4, (THF)/[Li_{0.07}^{+}(CH^{-0.07})]_x$ cell.

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- [2] GAU, S.-G., MILLIKEN, J., PRON, A., MACDIARMID, A.G., and HEEGER, A.J., J.C.S. Chem. Commun., (1979) 662.

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