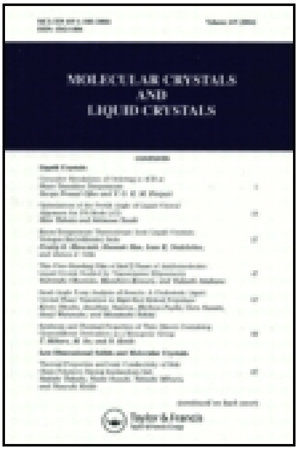

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Electrochemistry of $(CH)^x$: Lightweight rechargeable batteries using $(CH)^x$ as the Cathode- and anode-active materials

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ELECTROCHEMISTRY OF $(CH)_x$: LIGHTWEIGHT RECHARGEABLE BATTERIES USING $(CH)_x$ AS THE CATHODE- AND ANODE-ACTIVE MATERIALS

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Polyacetylene, $(CH)_x$, can be controllably doped p-type (oxidized) or n-type (reduced) by simple electrochemical procedures. Cyclic voltammetry studies on free-standing films of cis-$(CH)_x$ show that $(CH)_x$ can be reversibly oxidized at ~+3.6V vs. Li and reversibly reduced at ~+1.4V vs. Li. The spontaneous electrochemical "undoping" of p- and/or n-doped $(CH)_x$, which occurs when appropriate combinations and configurations of $(CH)_x$ are employed, permits $(CH)_x$ to be used in the fabrication of lightweight rechargeable batteries having large energy and large power densities. Cis-$(CH)_x$ can be readily isomerized to the trans-isomer by electrochemical p-doping followed by electrochemical reduction to $(CH)_x$.

INTRODUCTION

In this report, we summarize some of our studies which show that $(CH)_x$ can be electrochemically p-doped (i.e., oxidized) or n-doped (i.e., reduced) and that spontaneous electrochemical "undoping" readily occurs under appropriate conditions. This permits the use of doped $(CH)_x$ in the fabrication of high energy density, high power density, lightweight rechargeable "organic" batteries.

RESULTS AND DISCUSSION

Electrochemical p-type doping (oxidation)

We have shown previously that $(CH)_x$ film can be doped readily to composition $[CH(ClO_4)_{0.0645}]_x$ in a 0.5M solution of $(Bu_4N)(ClO_4)$ in CH_2Cl_2 when it is used as the anode with an applied potential difference, between the anode and cathode, of approximately 9V.[1] In the present study, we have shown that doping may also be carried out conveniently to values greater than 6% using a 0.3M solution of $LiClO_4$ in propylene carbonate (PC) at an applied potential of ~+3.8V vs. a Li reference electrode during ca. 1 hour. Other dopant anions such as $(I_3)^-$, $(ClO_4)^-$, $(AsF_4)^-$, etc. have been incorporated electrochemically.[6]

When $LiClO_4$ is used instead of $(Bu_4N)^+(A)^-$ and Li metal is used as the cathode, the reaction occurring at the anode is

$$(CH)_x \rightarrow (CH^{+y})_x + xye^- \qquad (1)$$

and the reaction at the cathode is

$$xyLi^+ + xye^- \rightarrow xyLi^o \qquad (2)$$

so that the overall doping reaction is

$$(CH)_x + xyLi^+(ClO_4)^- \rightarrow [(CH^{+y})(ClO_4)_y^-]_x + xyLi^o. \qquad (3)$$

It will be noted that the A^- ion is not oxidized or reduced during the electrochemical reaction. It serves only as a negative counter ion to preserve electrical neutrality in the system.

Subsequent cyclic voltammetry experiments by Diaz and Clarke,[2] using very thin films of $(CH)_x$ (polymerized directly on a platinum surface) in acetonitrile containing 0.1M $(Et_4N)(BF_4)$, showed that oxidation of $(CH)_x$ occurred at a value of $E^{\circ\prime}$~+0.74V (vs. a standard calomel electrode, SCE). We wished to ascertain if free-standing films of $(CH)_x$ could also yield useful information from cyclic voltammetry studies. We have found that when a free-standing film of cis-$(CH)_x$ having a ca. 500Å layer of evaporated gold on one side was used as the electrode in a PC solution containing 1.0M $LiClO_4$, oxidation of the $(CH)_x$ occurred at a value of $E^{\circ\prime}$~+3.6V vs. a lithium reference electrode (~+0.3V vs. SCE).

This value, not unexpectedly, differs from that obtained by Diaz and Clarke[2] since different solvents were used in the two experiments and correction factors are involved in converting from one reference electrode to another. Figure 1 shows that free-standing films of $(CH)_x$ can be reversibly oxidized (p-doped) and then reduced back to $(CH)_x$ electrochemically.

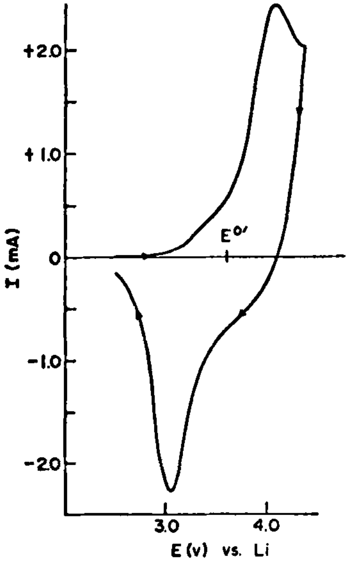

FIGURE 1 Cyclic voltammogram of free-standing cis-$(CH)_x$ film ($0.5cm^2$ x 0.01cm) in 1.0M $LiClO_4$/PC (scan rate=10 mV/sec).

From the charge passed, as determined by integrating the area under the oxidation and reduction peaks, it was found that the $(CH)_x$ was doped to 1% levels under these conditions, in agreement with the results of Diaz and Clarke.[2] The E°' value (+3.9V vs. Li) of a model compound such as β-carotene which has 12 conjugated double bonds is very similar to that obtained above for $(CH)_x$.[7] The small difference in the E°' values is undoubtedly related to the higher doping levels (~8%) obtained with β-carotene.

The reaction given by equation (3) may also be regarded as a battery charging reaction to produce a doped polymer which could be utilized as a cathode-active battery material, the discharge reaction being the reverse of that given by equation (3). The simplest battery configuration is shown diagrammatically in Figure 2.

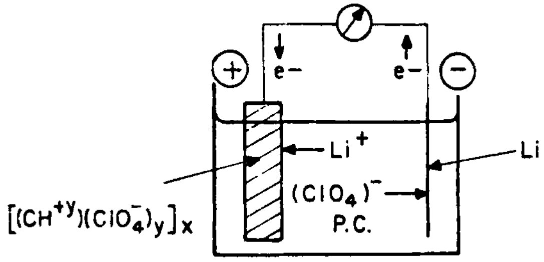

FIGURE 2 Schematic representation of the discharge process in a $(CH)_x/LiClO_4/Li$ rechargeable storage battery cell.

It consists basically of a piece of $(CH)_x$ film ($0.5cm^2$ x 0.01cm) immersed in a PC solution of $LiClO_4$. The top of the film is attached by means of a wire to the positive terminal of a galvanostat (a constant current d.c. power source). The negative terminal is attached to a lithium metal electrode immersed in the solution. In a typical experiment the battery was charged at 1 mA for ca. 30 min. to give a film of approximate composition $[CH(ClO_4)_{0.06}]_x$. The overall charge reaction is given by equation (3), (y=0.06).

The initial open circuit voltage, (V_{oc}), of a 6% predoped film, $[CH(ClO_4)_{0.06}]_x$, ($0.5cm^2$ x 0.01cm; 3mg), was 3.7V and the initial short-circuit current (I_{sc}), was 23 mA. The I_{sc} value varied from 15mA to ~200mA/cm^2 in different cell constructions, depending primarily on the distance between the $(CH)_x$ and the Li electrode. The exceptionally high current density is probably related to the large effective surface area of the $(CH)_x$ fibrils in the film, approximately $2.5x10^3$ cm^2 for a piece of film 1cm x 1cm x $0.01cm^3$.

Figure 3 shows the change in voltage during a constant current discharge of 0.55mA of a cell consisting of a ($0.5cm^2$ x 0.01cm, 3mg) piece of $[CH(ClO_4)_{0.06}]_x$ immersed in a 1.0M solution of $LiClO_4$ in PC. It should be noted that the voltage remains relatively constant during the discharge process even with the very small weight of film employed, and then decreases rapidly. The charge released gives an

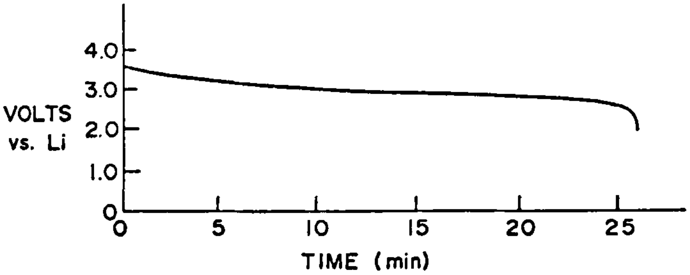

FIGURE 3 Constant current (0.55mA for a $0.5cm^2$ film) discharge curve for a $(CH)_x/LiClO_4/Li$ cell.

energy density of 176 W-hr/Kg. Empirical rules may be applied to obtain a rough estimate of the expected energy density of a packaged battery, (including the weight of electrolyte, solvent, and casing), from an experimental energy density such as the above. A reduction factor of six gives a reasonably conservative estimate and results in a value of ~30 W-hr/Kg for a completely packaged battery of the above type. This is approximately the same value as that found for the average lead/acid automobile battery. Although these energy densities are interestingly large even with 6% doped film, they are not the maximum obtainable. Higher doping levels are presently being studied in detail with $(ClO_4)^-$ and other dopant anions.

Power densities obtained from the $[CH(ClO_4)_{0.06}]_x/Li$ cells are very high. Thus initial $V_{discharge}$ (2.5V) and $I_{discharge}$ (208mA) using ~18mg of $[CH(ClO_4)_{0.06}]_x$ were observed when the current was passed through a load resistor having a resistance similar to that of the cell (~10Ω). These values give a power density of ~30,000 watts/Kg based on the weight of $[CH(ClO_4)_{0.06}]_x$ initially employed and the weight of lithium consumed in the discharge process. This gives an approximate power density for a completely packaged battery, using the empirical reduction factor described above, of ~5,000 watts/Kg.[8] This is approximately 25 times that of an automobile lead/acid battery.

Electrochemical n-type doping (reduction)

We have shown previously that $(CH)_x$ may be doped n-type to the metallic state by immersing it in a solution of lithium, sodium, or potassium naphthalide in tetrahydrofuran (THF).[4,5] We now find that spontaneous electrochemical doping occurs with the concomitant production of an electric current when a strip of $(CH)_x$ and a strip of Li are placed in a solution of $LiClO_4$ in THF and the two strips are then connected through an ammeter.[6] This configuration therefore acts as a battery during the doping process. The reaction occurring at the cathode is

$$(CH)_x + xye^- \rightarrow (CH^{-y})_x \qquad (4)$$

and at the anode

$$xyLi \rightarrow xyLi^+ + xye^- \qquad (5)$$

so that the overall reaction is

$$(CH)_x + xyLi \rightarrow [Li^+_y(CH^{-y})]_x \qquad (6)$$

The reaction can be reversed, i.e., the battery can be "recharged" if an appropriate potential is applied. An extension of the above experiment permits, for the first time, the n-doping of $(CH)_x$ with non-metallic species such as tetraalkylammonium or tetraphenylphosphonium cations when $(Bu_4N)(ClO_4)$, $(Bu_4N)(PF_6)$ or $(Ph_4P)(ClO_4)$ in THF or PC are substituted for the $LiClO_4$ electrolyte.[4]

The reduction potential of free-standing films of $(CH)_x$, supported on a platinum grid in 0.5M $LiPF_6$ in THF was determined by cyclic voltammetry. Figure 4 shows $(CH)_x$ can be reduced at a value E°'~+1.4V vs. a Li reference electrode (~-1.9V vs. SCE). The broad shoulders on the main cathodic and anodic peak near +1.5V appear to be due to traces of impurities in the electrolyte. By integrating the area under the reduction peak, it was found that $(CH)_x$ was n-doped to ~2% under these conditions. The reduction potential of a model compound such as β-carotene (E°'~+1.4V vs. Li)[7], has an essentially identical value. These preliminary studies show that free-standing films of $(CH)_x$ can be reversibly reduced (n-doped) and then oxidized back to $(CH)_x$.

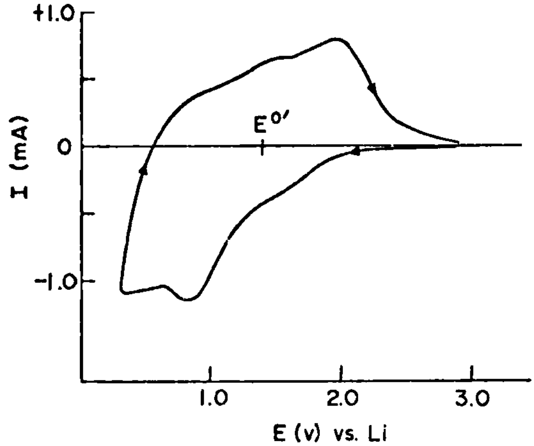

FIGURE 4 Cyclic voltammogram of free-standing <u>cis</u> $-(CH)_x$ supported on platinum grid in 0.5M $LiPF_6$/THF (scan rate= 100mV/sec).

Batteries having p-doped $(CH)_x$ cathodes and n-doped $(CH)_x$ anodes have also been constructed. The simplest cell of this type consists of two strips of $(CH)_x$ film in a solution of $LiClO_4$, $(Bu_4N)(ClO_4)$ or $(Bu_4N)(PF_6)$ in PC. These are attached to a d.c. power supply in the charging reaction. Simultaneous oxidation and reduction of the film attached to the positive and negative terminals, respectively, occurs to yield, for example, $[(CH^{+0.06}(A)^-_{0.06}]_x$ and $[M^+_{0.06}(CH^{-0.06})]_x$ respectively (where $A^-=(ClO_4)^-$ or $(PF_6)^-$ and $M^+=Li^+$ or $(Bu_4N)^+$) as given by equation (7)

$$2(CH)_x+0.06M^+A^- \rightarrow [M^+_{0.06}(CH^{-0.06})]_x+[(CH^{+0.06}(A)^-_{0.06}]_x. \qquad (7)$$

When the anode and cathode of a charged battery cell of this type are connected V_{oc} (initial)=2.7V; I_{sc} (initial)=~100mA/cm^2 [where M^+ is $(Bu_4N)^+$ and A^- is $(PF_6)^-$], are observed. The electrodes become spontaneously "undoped" and are ultimately reconverted to $(CH)_x$ by the reverse reaction to that given by equation (7). Detailed studies of the energy density and power density of these batteries in which $(CH)_x$ is used for both electrodes, using different dopant species are in progress.[9]

Electrochemical Isomerization[10]

There is a considerable body of evidence[11] which suggests that cis-$(CH)_x$ is isomerized to trans-$(CH)_x$ during chemical doping. We wanted to determine whether electrochemical doping followed by electrochemical "undoping" would result in isomerization of $(CH)_x$. Since electrochemical doping is a simple and rapid method of doping and undoping, it represents a potentially ideal method for studying the isomerization of cis-$(CH)_x$. In this study, we used a free-standing film of $(CH)_x$ supported on a platinum grid. The purpose of the grid was to provide a structural support in order to record infrared spectra before and after doping as well as to provide good electrical contact. The doping/undoping cycle was performed on the time scale of one complete cyclic voltammetry scan (~6 minutes) using a 1.0M solution of $LiClO_4$ in PC. Electrochemical oxidation was carried out by sweeping the potential from +3.0V vs. Li to +4.1V followed by returning to 2.0V during which time the oxidized $(CH)_x$ (i.e., $(CH^{+y})_x$) was reduced to neutral $(CH)_x$. The electrode was washed in fresh PC followed by fresh dioxolane and then vacuum dried. The infrared spectra obtained before and after the cyclic voltammetry studies show conclusively that the $(CH)_x$ was converted completely from the cis-isomer to the trans-isomer. In addition, the color of the film, when viewed by transmitted light, changed from the initial characteristic red color of the cis-isomer to the characteristic blue color of the trans-isomer. From these preliminary studies it is apparent that electrochemical isomerization is a convenient and rapid method for converting cis-$(CH)_x$ to the trans-isomer at room temperature.

CONCLUSION

In conclusion, it is apparent that the electrochemistry of $(CH)_x$ and presumably of other organic metals represent an extensive area for further research not only of fundamental scientific interest but of possible technological value.

ACKNOWLEDGMENTS

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