Organic Batteries: Reversible *n*- and *p*-Type Electrochemical Doping of Polyacetylene, $(CH)_x$

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Summary Films of polyacetylene, $(CH)_x$, may be reversibly electrochemically doped *n*-type and *p*-type with a variety of species to give a series of organic metals which may be utilized as the anode- and/or cathode-active material in the fabrication of lightweight rechargeable storage batteries of various types.

We have shown previously that films of polyacetylene, $(CH)_x$, may conveniently be *p*-doped electrochemically through the semiconducting to the metallic regime with the concomitant incorporation of anions such as $(I_3)^-$, $(ClO_4)^-$, $(AsF_4)^-$, *etc.* to give material of general composition $[CH^{y+}A^-_y]_x$ (A^- = anion).[1] The most common electrolyte combination used consisted of a tetrabutylammonium salt dissolved in CH_2Cl_2. Subsequent electrochemical studies have shown that oxidation of $(CH)_x$ commences at $+0{\cdot}8$ V (*vs.* standard calomel electrode, S.C.E.).[2] We now find that $(CH)_x$ can be reversibly electrochemically doped *n*-type or *p*-type and that electrochemical 'undoping' of various combinations of *p*- and/or *n*-doped $(CH)_x$ can also be achieved and may be utilized for the fabrication of lightweight rechargeable storage batteries of three principal types: (i) those in which only the anode discharge reaction involves polyacetylene derivatives; (ii) those in which only the cathode discharge reaction involves polyacetylene derivatives; and (iii) those in which both the cathode and anode discharge reactions involve a polyacetylene derivative.

(i) *Polyacetylene Anodes: Electrochemical* n-*Type Doping of* $(CH)_x$.—We have reported previously[3,4] that $(CH)_x$ film may be doped *n*-type to the metallic state by immersing it in a solution of lithium, sodium, or potassium naphthalide ($Npth^-$) in tetrahydrofuran (THF), *e.g.* reaction (1). We

$$(CH)_x + xyLi^+(Npth)^- \rightarrow [Li^+_y(CH^{y-})]_x + Npth \qquad (1)$$

now find that *spontaneous* electrochemical doping occurs with 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. (See Table, type 1). This configuration therefore acts as a battery during the doping process. The reaction given by the net equation for type 1 can be reversed, *i.e.*, the battery can be 'recharged' if an appropriate potential is applied.

n-Type doping, accompanied by *p*-doping of $(CH)_x$, may be also accomplished by immersing two strips of $(CH)_x$ film in a solution of $LiClO_4$ in THF and attaching them to a d.c. power supply. Simultaneous oxidation and reduction of the films attached to the positive and negative terminals respectively of the power supply occurs to yield, for example, $[CH^{0{\cdot}05+}(ClO_4^-)_{0{\cdot}05}]_x$ and $[Li^+_{0{\cdot}05}(CH^{0{\cdot}05-})]_x$, respectively. These doping reactions may also be regarded as the charging reactions of a storage battery. Upon connecting the anode and cathode of this battery in its charged state, a voltage and current are generated, V_{OC} (initial) = $2{\cdot}9$ V; I_{SC} (initial) = $1{\cdot}9$ mA (oc = open circuit; sc = short circuit). The electrodes become 'undoped' and are ultimately reconverted into $(CH)_x$.

TABLE. Polyacetylene batteries [using $(CH)_x$ film, $0\cdot5\ cm^2 \times 0\cdot01$ cm; *ca.* 2 mg]

Class A battery discharging ('doping') reactions		
Type 1	Cathode reaction:	$(CH)_x + 0\cdot06xLi^+ + 0\cdot06xe^- \rightarrow [Li^+_{0.06}(CH^{0\cdot06-})]_x$
	Anode reaction:	$0\cdot06xLi \rightarrow 0\cdot06xLi^+ + 0\cdot06xe^-$
	Net reaction:	$(CH)_x + 0\cdot06xLi \rightarrow [Li^+_{0.06}(CH^{0\cdot06-})]_x$
	Electrolyte:	$0\cdot3$ M $LiClO_4$ in THF
	Charge characteristics:	$V_{oc}(max.) = 1\cdot9$ V; $I_{sc}(max.) = 0\cdot5$ mA
Class B[a] battery discharging ('undoping') reactions		
Type 2[b,c]	Cathode reaction:	$[(CH)^{0\cdot06+}(ClO_4^-)_{0\cdot06}]_x + 0\cdot06xe^- \rightarrow (CH)_x + 0\cdot06x(ClO_4)^-$
	Anode reaction:	$0\cdot06xLi \rightarrow 0\cdot06xLi^+ + 0\cdot06xe^-$
	Net reaction:	$[(CH)^{0\cdot06+}(ClO_4^-)_{0\cdot06}]_x + 0\cdot06xLi \rightarrow (CH)_x + 0\cdot06xLi^+(ClO_4)^-$
	Electrolyte:	$0\cdot3$ M $LiClO_4$ in PC
	Discharge characteristics:	$V_{oc}(initial) = 3\cdot7$ V; $I_{sc}(initial) =$ *ca.* 25 mA
Type 3	Cathode reaction:	$[(CH)^{0\cdot024+}(ClO_4^-)_{0\cdot024}]_x + 0\cdot024xe^- \rightarrow (CH)_x + 0\cdot024x(ClO_4)^-$
	Anode reaction:	$[Bu^n_4N)^+_{0.024}(CH^{0\cdot024-})]_x \rightarrow (CH)_x + 0\cdot024x(Bu^n_4N)^+ + 0\cdot024xe^-$
	Net reaction:	$[(CH)^{0\cdot024+}(ClO_4^-)_{0\cdot024}]_x + [(Bu^n_4N)^+_{0.024}(CH^{0\cdot024-})]_x \rightarrow 2(CH)_x + 0\cdot024x(Bu^n_4N)^+(ClO_4)^-$
	Electrolyte:	$0\cdot5$ M $(Bu^n_4N)^+(ClO_4)^-$ in PC
	Discharge characteristics:	$V_{oc}(initial) = 2\cdot5$ V; $I_{sc}(initial) = 11\cdot1$ mA
Type 4	Cathode reaction:	$[(CH)^{0\cdot06+}(PF_6^-)_{0\cdot06}]_x + 0\cdot06xe^- \rightarrow (CH)_x + 0\cdot06x(PF_6)^-$
	Anode reaction:	$[(Bu^n_4N)^+_{0.06}(CH^{0\cdot06-})]_x \rightarrow (CH)_x + 0\cdot06x(Bu^n_4N)^+ + 0\cdot06xe^-$
	Net reaction:	$[(CH)^{0\cdot06+}(PF_6^-)_{0\cdot06}]_x + [(Bu^n_4N)^+_{0.06}(CH^{0\cdot06-})]_x \rightarrow 2(CH)_x + 0\cdot06x(Bu^n_4N)^+(PF_6)^-$
	Electrolyte:	$0\cdot3$ M $(Bu^n_4N)^+(PF_6)^-$ in THF
	Discharge characteristics:	$V_{oc}(initial) = 2\cdot5$ V; $I_{sc}(initial) = 4\cdot1$ mA
Type 5	Cathode reaction:	$[(CH)^{0\cdot050+}(ClO_4^-)_{0\cdot050}]_x + 0\cdot015xe^- \rightarrow [(CH)^{0\cdot035+}(ClO_4^-)_{0\cdot035}]_x + 0\cdot015x(ClO_4)^-$
	Anode reaction:	$[(CH)^{0\cdot020+}(ClO_4^-)_{0\cdot020}]_x + 0\cdot015x(ClO_4)^- \rightarrow [(CH)^{0\cdot035+}(ClO_4^-)_{0\cdot035}]_x + 0\cdot015xe^-$
	Net reaction:	$[(CH)^{0\cdot050+}(ClO_4^-)_{0\cdot050}]_x + [(CH)^{0\cdot020+}(ClO_4^-)_{0\cdot020}]_x \rightarrow 2[(CH)^{0\cdot035+}(ClO_4^-)_{0\cdot035}]_x$
	Electrolyte:	$0\cdot5$ M $(Bu^n_4N)^+(ClO_4)^-$ in PC
	Discharge characteristics:	$V_{oc}(initial) = 0\cdot5$ V; $I_{sc}(initial) = 0\cdot3$ mA
Type 6	Cathode reaction:	$[(Bu^n_4N)^+_{0\cdot02}(CH^{0\cdot02-})]_x + 0\cdot025x(Bu^n_4N)^+ + 0\cdot025xe^- \rightarrow [(Bu^n_4N)^+_{0.045}(CH^{0\cdot045-})]_x$
	Anode reaction:	$[(Bu^n_4N)^+_{0\cdot07}(CH^{0\cdot07-})]_x \rightarrow 0\cdot025x(Bu^n_4N)^+ + [(Bu^n_4N)^+_{0.045}(CH^{0\cdot045-})]_x + 0\cdot025xe^-$
	Net reaction:	$[(Bu^n_4N)^+_{0\cdot07}(CH^{0\cdot07-})]_x + [(Bu^n_4N)^+_{0\cdot02}(CH^{0\cdot02-})]_x \rightarrow 2[(Bu^n_4N)^+_{0\cdot045}(CH^{0\cdot045-})]_x$
	Electrolyte:	$0\cdot5$ M $(Bu^n_4N)^+(ClO_4)^-$ in PC
	Discharge characteristics:	$V_{oc}(initial) = 0\cdot66$ V; $I_{sc}(initial) = 1\cdot9$ mA

[a] Charging was generally carried out during *ca.* 30 min by one of the following methods: (i) a potentiostat was used to apply a constant potential of 1·0 V (*vs.* an Ag/Ag^+ standard electrode); (ii) a galvanostat was used to supply a constant current of 1 mA; (iii) a d.c. power supply was used to apply a potential of 4·0 V. [b] The metal electrode during charging can be Li, Al, Pt, *etc.* The Li metal formed on the electrode during charging is then consumed in the discharge reaction. The I_{sc} value given involves the use of a film pre-doped in a separate experiment. If parent, undoped $(CH)_x$ film is used in the initial charging operation, the I_{sc} values are usually *ca.* 50–70% of the given value. [c] An analogous experiment (stainless steel electrodes) employing a piece of glass filter paper sandwiched between two pieces of $(CH)_x$ film, all saturated with a 0·1 M solution of NaI in solid polyethylene oxide, gave an initial $V_{oc} = 1\cdot3$ V and an initial $I_{sc} = 1\cdot0$ mA.

An extension of the above experiment permits, for the first time, the *n*-doping of $(CH)_x$ with non-metallic species such as tetra-alkylammonium cations. This occurs, for example, when strips of $(CH)_x$ and Pt [or $(CH)_x$] in a solution of $(Bu^n_4N)^+(ClO_4)^-$ or $(Bu^n_4N)^+(PF_6)^-$ [in either THF or propylene carbonate (PC)] are attached to the negative and positive terminals respectively of an appropriate d.c. power source. The *n*-doping reactions are the reverse of those given by the anode reactions in the Table, types 3 and 4. The discovery that the $(CH^{y-})_x$ anion may be used as an electrochemically reversible anode in a battery employing a nonaqueous electrolyte is of particular interest since hitherto the only lightweight anode material of any potential significance has been metallic Li. As is well known, the Li anode is fraught with many problems, particularly those associated with dendrite formation of Li metal during recharging operations.[5]

(ii) *Polyacetylene Cathodes: Electrochemical* p-*Type Doping of* $(CH)_x$. $(CH)_x$ film can be doped readily to (*p*-type) $[CH^{y+}A^-_y]_x$ ($A = ClO_4$ or PF_6) by immersing it in a THF or PC solution of $LiClO_4$ or the corresponding $(Bu^n_4N)^+$ salt and attaching it to the positive terminal of an appropriate d.c. power source, the negative terminal being attached to a Li, Pt, Al, or $(CH)_x$ electrode. The doping (charging) reactions which occur are the reverse of those given by the cathode-discharge equations for types 2 and 4 (Table). After charging, each of the above systems acts as a battery and upon discharge exhibits a characteristic open-circuit voltage and short-circuit current.

The $(CH)_x | LiClO_4 | Li$ or Al battery, PC solvent (Table, type 2), has been the most extensively investigated. Even though the weight of the doped $(CH)_x$ film is so small (*ca.* 3 mg), the discharge currents and voltages are remarkably large even after several minutes of short-circuit discharge. For example, after 0·5 min, $V_{oc} = 3\cdot6$ V and $I_{sc} = 4$ mA; after 1 min, $V_{oc} = 3\cdot3$ V and $I_{sc} = 2$ mA; and after 3·5 min, $V_{oc} = 1\cdot3$ V and $I_{sc} = 0\cdot3$ mA. Within the accuracy of the measurements, the $(CH)_x$ electrode was found to be reversible with no observable degradation after a number of charge–discharge cycles. For example, after 20 charge and 20 discharge cycles at constant currents varying from 0·1 to 1·0 mA, a given $(CH)_x$ electrode showed no change in its charging or discharging characteristics. Furthermore, no change in V_{oc} was observed after a charged battery had been permitted to stand for 48 h.

(iii) *Polyacetylene Anodes and Cathodes: Simultaneous Electrochemical Formation of* $(CH)_x$ *in Different Oxidation States.*—The discovery that $(CH)_x$ can be either oxidized or reduced electrochemically permits, in certain cases, the fabrication for the first time of completely organic rechargeable storage batteries involving no free metal or metal ion in their charge or discharge operations. These batteries involve two $(CH)_x$ electrodes having different oxidation states. They are of three types: $(CH^{a+})_x \mid (CH^{b+})_x$, $(CH^{c+})_x \mid (CH^{d-})_x$, and $(CH^{e-})_x \mid (CH^{f-})_x$. During discharge, electrons flow from the less oxidized state to the more oxidized state until both electrodes have the same oxidation state, *i.e.*, the same chemical composition. In those cases where the electrodes in a given battery are both cationic or both anionic, then an appropriately pre-*p*- or -*n*-doped film must be used for the initial charging. Examples of these types of battery are given in the Table, types 3—6. It should be noted that the Li^+, $(Bu^n{}_4N)^+$, $(ClO_4)^-$, and $(PF_6)^-$ ions are not oxidised or reduced in the electrochemical charging or discharging reactions; they serve only as counter-ions to preserve electrical neutrality in the systems.

Higher degrees of oxidation and/or reduction than those given in the Table are attainable electrochemically in certain systems. When these are used in battery configurations, they should result in even higher voltages, currents, energy densities, and power densities. No attempt has yet been made to optimize the open-circuit voltages or short-circuit currents given in the Table. They serve purely to illustrate a possible new area of organic polymer electrochemistry and battery development. The present results suggest that electrochemical studies not only of $(CH)_x$ but also of other organic metals represent an extensive area for further research not only of fundamental scientific interest but of possible potential technological value.

This work was supported jointly by the Office of Naval Research and the Defense Advanced Research Projects Agency (through a grant monitored by the Office of Naval Research), the National Science Foundation, and the National Science Foundation Materials Research Program.

(*Received*, 15*th December* 1980, *Com*. 1326.)

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