

ENERGY SYSTEMS BASED ON POLYACETYLENE:
RECHARGEABLE BATTERIES AND SCHOTTKY BARRIER SOLAR CELLS

Final Report

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200 Word Summary

The chief thrust of the research has been directed towards the evaluation of polyacetylene $(CH)_x$, the prototype conducting polymer as an electrode-active material in novel, rechargeable batteries employing non-aqueous electrolytes. The p-doped material, $[(CH^{+y})A_y^-]_x$, (where A^- is an anion) in conjunction with a Li anode, shows excellent discharge characteristics, e.g. very little change in discharge voltage with change in discharge current and a high power density. Its energy density is also good but it shows poor shelf life. When $(CH)_x$ is used as a cathode (Li anode), which results in the formation of the n-doped polymer, $[Li_y^+(CH^{-y})]_x$, during discharge, good discharge plateaus and power densities are obtained together with excellent shelf life and good recyclability. The energy density is, however only moderate. Cells employing a $[M_y^+(CH^{-y})]_x$ (where $M = Li, Na$) anode and a TiS_2 cathode show very good discharge and recycling characteristics but their energy density is poor. Work supported by this contract has been in large part responsible for five major companies world wide, embarking upon, and continuing an active R. and D. program on rechargeable batteries employing conducting polymers as one and/or both electrodes.

Final Report

The electrochemistry of organic polymers involving oxidation or reduction of the polymer backbone and its application to electrical storage is still a very new field of endeavor, the first preliminary paper on this subject appearing in 1979. The discovery that the backbone of an organic polymer having an appropriate type of bonding can be reversibly oxidized and reduced electrochemically with, in certain cases, little irreversible degradation, opens up a new potential field for electrical energy storage. It shows that certain types of organic polymers can act as a storage medium for electricity and that the stored charge can be delivered on demand at a rate which could be useful in practical cells. In view of the newness of the field, and the potentially enormous number of synthesizable new polymers, it seems improbable that the best polymers have necessarily yet been found. Real long-term advances can only be accomplished by detailed chemical and electrochemical studies of different types of polymers and of the principal and side reactions which occur during their storage and recycling under a wide variety of experimental conditions.

Research supported in whole or in part by this contract has resulted in the publication of 26 papers in scientific journals in addition to one which has been submitted for publication. The work has developed into two related chief thrust areas as it progressed:

(1) A study of the chief characteristic chemical and physical properties of polyacetylene, $(CH)_x$ necessary to obtain a solid scientific foundation to permit the performance of studies in the second thrust area. Exploratory studies on other potentially important conducting polymers has also been performed (Reprints: 1, 3, 4, 5, 10, 14, 16, 23).

(2) Detailed electrochemical studies of $(CH)_x$, p-doped polyacetylene i.e. $[(CH^{+y})A_y^-]_x$ (where A^- is an anion), and n-doped polyacetylene i.e. $[M_y^+(CH^{-y})]_x$

(where M^+ is Li^+ or Na^+) have been carried out, many of them in a battery mode of charging and discharging, in order to evaluate the polymer in its various forms as potential anode-active or cathode-active materials in novel rechargeable batteries. Very preliminary studies were also performed on the study of fundamental properties of polyaniline with a view to its possible use as an electrode-active material (Reprints: 2, 6, 7, 8, 9, 11, 13, 15, 17, 18, 19, 20, 21, 22, 24, 25, 26, 27).

Patents on the possible use of polyacetylene in its various forms as an electrode-active material in novel rechargeable batteries has been filed previously on behalf of the University of Pennsylvania. These were based on studies performed by the present principal investigator either alone (together with appropriate students) or in collaboration with a previous co-principal investigator, Professor A. J. Heeger. Work under this contract has involved detailed electrochemical studies, based on our previous discoveries, with a view to providing sufficient data to permit industry to make a decision whether or not to launch a program of their own to evaluate the possible commercial application of polyacetylene and conducting polymers in general, as electrode-active materials in rechargeable batteries. The success of the project is evidenced, at least in part, by the announcement that Allied Corporation, which holds the University's exclusive patent rights in this field for North America and Japan had entered into an agreement with the Japanese Companies, Showa Denko K. K. and Hitachi Ltd. for research and development of rechargeable polymer batteries. Similarly, the West German Companies, B.A.S.F. AG. and Varta Batterie have announced a collaborative R. and D. program on polymer batteries. B.A.S.F. AG. holds the University's patent rights for Europe.

(1) Study of Chief Characteristic Chemical and Physical Properties of Polyacetylene and other Conducting Polymers. (Reprints: 1, 3, 4, 5, 10, 14, 16, 23).

These studies showed that $(CH)_x$ could be reversibly p-doped (oxidized) electrochemically in the form of thin films. The doping and undoping was followed by a

continuous monitoring of the visible near-ir absorption spectrum of the polymer. It was also shown that the rate of electrochemical oxidation, (followed by reduction) back to neutral $(\text{CH})_x$ far exceeded the rate-controlling diffusion process of the dopant anions within the polymer. A theory was then developed which showed how high power and current densities could be generated by a $(\text{CH})_x$ battery cell (as found experimentally) despite the slow diffusion and low conductivity characteristics of ionic motion in polyacetylene. The presence of a small driving potential (or a load) causes current to flow and generates a large electric field within polyacetylene fibrils. This field dramatically increases the ion transport rate when the electronic screening length is comparable to or greater than the radius of a fibril.

P-doping (oxidation) and also n-doping (reduction) of $(\text{CH})_x$ was studied by means of electrochemical-voltage-spectroscopy. The results showed that the difference between the voltage characteristic of the onset of electrochemical oxidation and the voltage characteristic of the onset of electrochemical reduction was almost exactly equal to the optical band gap of $(\text{CH})_x$. This showed for the first time how the electrochemical properties of $(\text{CH})_x$ were related to its electronic configuration.

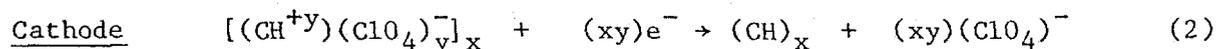
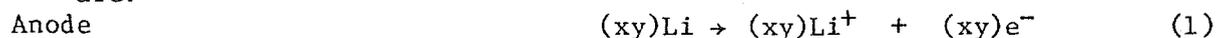
The polymers poly (p-phenylene selenide), $[-(\text{C}_6\text{H}_4)\text{-Se-}]_x$ and poly (2, 5- thienyl selenide) were synthesized. Although the conductivities of these polymers could be increased by doping, their properties did not suggest they would be useful for anode- or cathode-active materials in rechargeable batteries.

(2) Electrochemical Studies of Polyacetylene Directly Related to its Use as an Electrode-Active Material in Rechargeable Batteries in Non-Aqueous Electrolytes.

(A) Use of $[(\text{CH})^{+y}\text{A}_y^-]$ as a Cathode. (See in particular, reprints 2, 25 and 19).

The discharge reactions occurring in a $\text{Li} / \text{LiClO}_4(\text{P.C.}) / [(\text{CH}^{+y})(\text{ClO}_4)_y^-]_x$ cell

are:



(5)

resulting in the net discharge reaction



The charge reactions are the reverse of the above. The cell shows many very good features such as good coulombic efficiency, high power density, flat discharge curves at useful discharge currents, very little change in discharge voltage when the discharge current was varied greatly, etc. However, the cell shows poor retention of charge on standing and poor recyclability. Hence p-doped polyacetylene, $[(\text{CH}^{+y})\text{A}^-]_x$ does not show promise as a useful cathode in a rechargeable battery of this type.

(B) Use of $[\text{M}^+(\text{CH})^{-y}]_x$ as an Anode (See reprints 21 and 22).

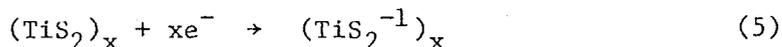
Considerable interest has been shown in recent years in the use of a cell of the type



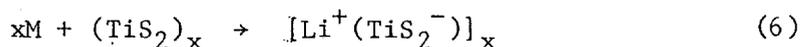
(where M = Li or Na and M^+A^- is a salt of M) as a rechargeable battery. The anode discharge reaction is



the corresponding cathode reaction being



resulting in the overall discharge reaction



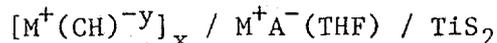
The charge reactions are the reverse of the above.

A particular problem with this type of battery, common to all rechargeable batteries involving Li anodes (which are preferable to Na anodes because of their larger energy density) is the formation of Li dendrites on the Li electrode during charging, especially at high charging rates.

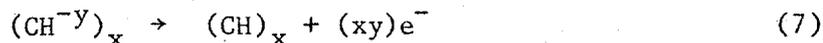
In the present studies, cells have been constructed in which the Li anode

(6)

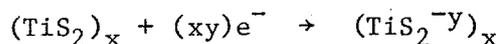
has been replaced by a $[M^+(CH)^{-y}]_x$ anode ($M = Li$ or Na). Such anodes permit high charging rates without dendrite formation and both $(CH)_x$ and $[M^+(CH)^{-y}]_x$ are stable in the electrolyte. The cell is of the type



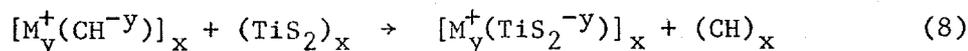
the anode discharge reaction being



and the corresponding cathode reaction being identical to that given by equation (5), viz.,



The overall discharge reaction can be represented by the equation

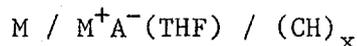


The charge reactions are the reverse of the above.

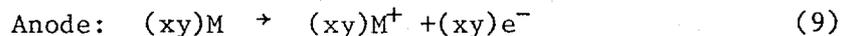
Such cells show very good retention of charge, discharge and recycling characteristics but their energy density is poor because the maximum value of y which can be obtained in the $LiClO_4/THF$ electrolyte employed was ~ 0.1 . However, since these studies were completed, very important information has been released by Allied Corporation (L. W. Shacklette et al., *J. Electrochem. Soc.*, 132, 1529 (1985)) which shows that the value of y can be increased to ~ 0.18 by replacing the $LiClO_4$ by $LiBR_4$ ($R =$ phenyl, n -butyl). In view of these recent findings it appears that this type of cell may have real potential technologically.

(C) Use of $(CH)_x$ as a Cathode (See in particular reprints 20, 26 and 27)

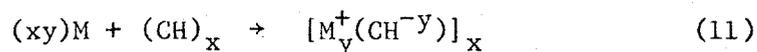
The discharge reactions occurring in a cell of the type



(where $M = Li$ or Na and M^+A^- is a salt of M) are:



resulting in the discharge reaction



These cells show good discharge plateaus, power densities, recyclability and excellent retention of charge both in the charged and partly discharged states.

The cells employing a Li anode naturally exhibit a greater power density than those employing sodium, but even so their energy density is only moderate when they are discharged to a value of $y \sim 0.1$ in the above electrolyte. However, in view of the recent announcement by Allied Corporation, mentioned in the previous section, where values of $y \sim 0.18$ can be obtained by use of an electrolyte consisting of $Li^+(BR_4)^-$ in THF, it appears that the energy density of these types of cells could probably be increased to a value which could have real technological significance.

(3) Use of Forms of Polyaniline as Electrode Active Materials. (See reprint: 24).

Towards the termination of this contract, preliminary studies supported in part by the contract, were performed on the use of the emeraldine form of polyaniline as an electrode-active material in rechargeable cells employing a zinc anode and a polyaniline cathode in an aqueous electrolyte. The cell showed many desirable features such as excellent recyclability, coulombic efficiency and retention of charge. The gravimetric energy density was $\sim 62\%$ that of a Ni/Cd cell; however, the volumetric energy is probably not sufficiently large for this type of battery to be useful technologically.

Continuing studies, commenced after termination of this contract, have involved a Li/polyaniline cell using a propylene carbonate/ $LiClO_4$ electrolyte. The preliminary results suggest this may be the best rechargeable battery to date involving a conducting polymer as an electrode-active material.

(4) Present Status of Rechargeable Batteries Employing Polymer Electrodes

Since the commercial development of a successful battery often takes more than

10 years from the first laboratory discovery of the phenomenon on which it is based, it would be most surprising if a battery employing an electroactive polymer were already in production. Not only is new chemistry and electrochemistry involved, but also new engineering aspects concerning, for example, something as apparently simple as the method of attachment of an organic polymer to a current collector. A disadvantage of all polymer electrodes is that they will, in general, be expected to exhibit smaller volumetric energy densities than conventional batteries since organic materials are usually less dense than metals and inorganic substances. To what extent this is a serious disadvantage will depend on the use to which the cell in which they are incorporated might be put.

Electrodes using polymers as electrode-active materials differ from conventional materials in that the polymer does not dissolve and is not re-deposited during charge/discharge cycles, although some swelling of the polymer does occur during oxidation or reduction. This absence of dissolution and redeposition is expected to promote longer life for polymer electrodes due to the absence of relatively large mechanical changes in electrode dimensions, etc., such as those observed with many conventional electrodes. Also, in most batteries, complete deep discharge leads to rapid deterioration. Hence, only partial utilization of the energy density of a battery can be achieved if it can only be partly discharged in order to prolong its effective operating life. The energy density of a polymer electrode, can, however, in many cases be completely utilized in repeated deep discharges at good discharge rates without adverse effects. For practical use this may in many instances compensate for the smaller gravometric and/or volumetric energy density of polymer batteries as compared to some conventional rechargeable batteries. If the charge/discharge cycles are held between potentials such that the polymer always retains sufficient conductivity to permit appropriately rapid charging and discharging,

both the effective gravometric and volumetric energy densities in a completely packaged battery may be larger than otherwise expected. This is because the necessity of introducing a conductive filler such as a carbon black will be reduced. It may be noted that the flexibility of polymeric films may be significant in their use in certain types of thin batteries.

The number of different types of batteries possible with inorganic materials is limited whereas the number of potential electrode-active materials involving organic substances is essentially "unlimited" in view of the enormous number of different types of organic materials which are potentially synthesizable. It would appear that the use of organic substances as electrode-active materials in batteries for certain specific types of uses is still in its infancy.

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