

Lawrence Berkeley National Laboratory

Recent Work

Title

POLYMERIC ELECTROLYTES FOR AMBIENT TEMPERATURE LITHIUM BATTERIES

Permalink

<https://escholarship.org/uc/item/8hf7r8bm>

Author

Farrington, G.C.

Publication Date

1984-08-01



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED
LAWRENCE
BERKELEY LABORATORY

OCT 9 1984

LIBRARY AND
DOCUMENTS SECTION

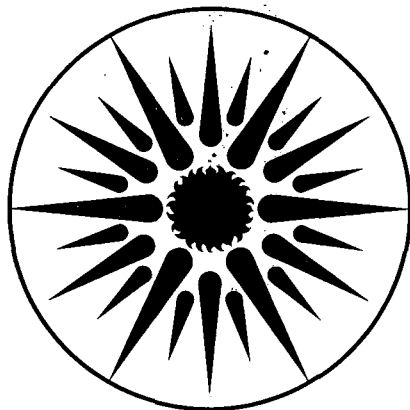
APPLIED SCIENCE DIVISION

POLYMERIC ELECTROLYTES FOR
AMBIENT TEMPERATURE LITHIUM BATTERIES
Final Report

G.C. Farrington

August 1984

TWO-WEEK LOAN COPY
*This is a Library Circulating Copy
which may be borrowed for two weeks.*



**APPLIED SCIENCE
DIVISION**

LBL-18288
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

POLYMERIC ELECTROLYTES FOR
AMBIENT TEMPERATURE LITHIUM BATTERIES

Final Report

August 1984

by

Gregory C. Farrington
University of Pennsylvania
Philadelphia, Pennsylvania

for

Technology Base Research Project
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Systems Research, Energy Storage Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, subcontract no. 4505210 with the Lawrence Berkeley Laboratory.

Final Report

Polymeric Electrolytes for
Ambient Temperature Lithium Batteries

Gregory C. Farrington
Department of Materials Science
University of Pennsylvania
3231 Walnut St.
Philadelphia, PA 19104

Subcontract Number: 4505210

Reporting Period: 3/1/83 - 2/29/84

Summary

Polyacetylene can be electrochemically oxidized in a cell of the type, Li/LiX in propylene carbonate/(CH)_x, with nearly 100% coulombic efficiency for doping levels x in [CH(ClO₄)_y]_x, of less than 0.10. At higher values, the electrochemical potential of the oxidized film is above 3.9 V vs. Li/Li⁺, and the electrolyte is unstable. Reduced polyacetylene (Li_yCH)_x can serve as an anode in a non-aqueous electrolyte battery in the traditional role of lithium. However, stable voltages and high coulombic efficiency for the reduction/oxidation process in an electrolyte of LiClO₄ in tetrahydrofuran are only observed at reduction levels of y < about 0.10. In addition, the potential of a polyacetylene anode doped with Li⁺ is 0.5 to 1.5 V positive to that of Li in the same solution. At present, polyacetylene electrodes are rather unstable, sensitive to impurities, and characterized by low volumetric energy density, and low-moderate gravimetric energy density. They do not appear to offer major advantages for use in high energy density, rechargeable, non-aqueous electrochemical cells.

I. Introduction

Polyacetylene is a simple conjugated organic polymer which can easily be prepared as a film by the catalytic polymerization of acetylene. When polyacetylene films are exposed to oxidants, such as iodine and bromine, the films oxidize to form compounds of the type, $(CHX_y)_x$. Films can also be reduced to compounds of the type, $(M_yCH)_x$ in which M is typically Na and Li. The oxidation or reduction of polyacetylene transforms it from an electronic insulator to a lustrous polymer with an electronic conductivity typical of metals [1-3].

These oxidation and reduction reactions can also be carried out electrochemically in non-aqueous electrolytes containing appropriate dissolved anions and cations. The electrochemical potentials of the oxidized films are 3-4 V vs. a Li electrode. The potentials of the reduced films are about 0.5-1.0 V positive to that of Li. Polyacetylene can therefore function as either an anode or cathode in a non-aqueous battery.

The critical questions concerning the attractiveness of polyacetylene for actual electrochemical energy storage concern its volumetric and gravimetric capacity (value of y that can be attained), voltage as a function of y , and stability.

Over the past several years, our research has explored these aspects of the chemical and electrochemical reactions of polyacetylene. Much of this work on the stability [4], oxidation [5], and reduction [6] of polyacetylene has been described in separate publications. This report briefly reviews the preparation and properties of polyacetylene and summarizes our findings.

II. Physical and Chemical Characteristics of Polyacetylene

Preparation

The polymerization of acetylene into polyacetylene was first described by Natta et al. [7], who produced polyacetylene powder by bubbling acetylene through a solution of $TiCl_3-AlEt_3$ catalyst. The resulting polyacetylene was found to be a linear polymer predominantly in the trans form. The preparation of films of polyacetylene was first

described by Shirakawa et al. [8]. They reported that polyacetylene films can be synthesized by wetting the walls of a glass reactor with a toluene solution of $\text{Al}(\text{C}_2\text{H}_5)_3\text{-Ti}(\text{n-C}_4\text{H}_9)_4$ Ziegler catalyst and then admitting acetylene gas at pressures ranging from a few torr to an atmosphere. A film of polyacetylene grows on the surface of the catalyst solution and on any surface which has been wet by it.

Physical Characteristics

The physical characteristics of polyacetylene films depend on the temperature, pressure, and time involved in their synthesis. Thicker films are produced at higher acetylene pressures and longer polymerization times. In general, polyacetylene films have a randomly-oriented fibrillar structure. The fibrils are typically 50A to 200A in diameter. Shirakawa's original work [8] found that film morphology varied slightly with temperature. Films prepared at -78°C had fibril diameters of about 200A, while the average fibril diameter in films prepared at 100°C was about 300A. The bulk density of typical polycrystalline polyacetylene is approximately 0.4 g/cm^3 [9]. Polymer fibrils fill only about one-third of the total geometric film volume. The actual surface area of the films is quite large, about $40\text{-}60 \text{ m}^2/\text{g}$.

Polyacetylene occurs in either cis or trans isomers. The cis/trans ratio depends on the polymerization temperature. The cis isomer can be produced at -78°C , but it is unstable toward isomerization, which can be induced by heating or by chemical doping [10].

The cis and trans isomers are quite different in their superficial physical properties. Cis films are flexible and can be easily stretched at room temperature to about three times their original length [1]. Trans films are relatively brittle. Stretching cis-polyacetylene tends to orient the films along the lines of stretch [8].

Stability

Various authors have investigated the stability of polyacetylene [11-14]. Virgin, undoped cis-polyacetylene isomerizes spontaneously, as has just been described, and

self-reacts forming cross-links and defects. These reactions occur rapidly at elevated temperatures (150-260°C) [10].

Polyacetylene, when not in contact with an electrolyte, reacts rapidly with oxygen [4]. Oxidation takes two general forms. When exposed to small concentrations of oxygen at low pressures, it does not irreversibly attack the polymer backbone. Under these conditions, oxygen reversibly reacts with the conjugated polymer chain in the prototypical reaction generally referred to as 'p-doping'. However, upon exposure to oxygen for longer periods of time, the polymer becomes brittle and even more insulating than either virgin trans or cis film. The latter reactions involve the irreversible oxidation of the polymer chain and degradation of the conjugated bond network.

We have carried out extensive thermogravimetric analysis, differential scanning calorimetry, and conductivity measurements to determine the stability of doped-polyacetylene films. All of the results indicate that such films are unstable at moderately elevated temperatures. Films doped with iodine or bromine decompose between 45 and 55°C. Films which contain AsF_6^- as the guest ion are somewhat more stable. The decomposition reactions are irreversible. They decrease the electronic conductivity of the material and ultimately destroy its usefulness for electrochemistry.

III. Electrochemical Investigations

Interest in the electrochemistry of polyacetylene began with the demonstration by Nigrey et al. [2] that polyacetylene can be electrochemically oxidized. They produced the first perchlorate-doped polyacetylene by oxidizing a sample in a 0.5 M solution of tetrabutylammonium perchlorate in methylene chloride at 9 V vs. a counter electrode. After one hour, the film had the composition, $[CH(ClO_4)_{0.0645}]_x$ [2]. They extended their investigations to show that the electrochemical oxidation of polyacetylene can be reversed and the oxidized material reduced to the original composition [15]. This reversibility is critical to the application of polyacetylene in batteries.

Subsequent work demonstrated that polyacetylene can be electrochemically reduced to the n-doped form. McInnes et al. [3] showed that a polyacetylene electrode is

spontaneously reduced when connected to a lithium electrode in tetrahydrofuran containing LiClO_4 . Similarly, polyacetylene can be reduced in a solution of tetrabutylammonium salts in propylene carbonate or tetrahydrofuran to form n-doped compositions containing the tetrabutylammonium cation [3].

The few studies of n-doping that have appeared include those of Kaner et al. [16] and Shacklette et al. [17]. Kaner et al. [16] concluded that polyacetylene can be reduced to doping levels of 0.06 with excellent stability and reversibility. The reduction/oxidation coulombic efficiency was found to be about 99% with lithium, sodium and $(\text{Bu}_4\text{N})^+$ dopants at y levels of up to 0.06. Shacklette and co-workers [17] observed considerable swelling of polyacetylene when it was reduced in tetrahydrofuran (THF) with Li^+ as the doping ion. Unreduced, neutral polyacetylene did not swell in the presence of THF.

These initial experiments led to the suggestion that polyacetylene films might be used as polymeric ion-insertion electrodes in batteries. MacInnes et al. [3] have described batteries using polyacetylene anodes, polyacetylene cathodes, and both anodes and cathodes of polyacetylene.

IV. Summary of Our Research

Our research has examined the oxidation (p-doping) of polyacetylene in propylene carbonate containing LiClO_4 and LiAsF_6 and the reduction (n-doping) in tetrahydrofuran containing LiClO_4 . Its principal goals have been to explore the reversibility, coulombic efficiency, and electrochemical potentials associated with the reactions at various levels of doping.

The polyacetylene films used in these experiments were kindly provided by Prof. A. MacDiarmid and co-workers from the Department of Chemistry of this University.

The electrochemical measurements were carried out in a miniature glass cell having three compartments separated by glass frits. The polyacetylene film electrodes (approximately 1 cm^2 and 0.01 cm thick) were sandwiched in Pt mesh and housed in the central compartment of the cell. The lithium reference and lithium counter electrodes were located in the two side compartments. About 1 ml of electrolyte was required to fill

all three compartments. The electrolyte used in these investigations was 0.8-1.0 M LiClO_4 in THF.

Electrolytes were prepared from Burdick and Jackson solvents which were distilled and percolated through neutral activated alumina (Woelm). The electrolyte salts were LiAsF_6 (U.S. Steel, Electrochemical Grade), LiClO_4 (Alfa-Ventron), and LiClO_4 (Anderson Physics). The salts were dried at 180°C before use. After the salts were dissolved, the electrolyte solutions were purified by a second percolation through activated alumina.

All experimental procedures were performed in an argon-atmosphere drybox (Vacuum Atmospheres). Standard electrochemical equipment was used for carrying out the cyclic voltammetry and constant current/potential experiments.

Electrochemical Oxidation of Polyacetylene

When a polyacetylene film is electrochemically oxidized in propylene carbonate with ClO_4^- or AsF_6^- as the anion, its open circuit potential varies from about 3.6 V (vs. Li/Li^+) at $y=0.01$ to about 3.9 V at $y=0.10$. Oxidation is typically carried out at $50\mu\text{A}/\text{cm}^2$. Subsequent reduction at $500\mu\text{A}/\text{cm}^2$ extracts about 40-60% of the stored charge before the potential reaches 2.5 V. Nearly all of the remaining charge can be recovered by an extended (10-20 hours) controlled potential discharge at 2.5 V. Within the composition range of $0 < y < 0.10$, the oxidation/reduction coulombic efficiency ($Q_{\text{out}}/Q_{\text{in}}$) is 90-100%.

At least two factors strongly influence the coulombic efficiency of oxidation/reduction. If the liquid electrolyte is not purified scrupulously, the efficiency drops. Polyacetylene does not forgive casual handling and requires extreme care in the preparation of the electrochemical cell and electrolyte. Also, if the initial oxidation is carried out to doping levels above about $y=0.10$, the electrode potential enters the region in which the propylene carbonate electrolyte is increasingly unstable, and the oxidation/reduction coulombic efficiency drops dramatically. An oxidation level of about $y=0.10$, therefore, appears to be an approximate upper limit for efficient cycling in the propylene carbonate electrolytes used in this work.

Oxidized polyacetylene appears to be quite unstable toward reaction with the propylene carbonate electrolyte. A sample oxidized to $y=0.03$ lost about 40% of its stored charge during 40 hours stand on open circuit.

Electrochemical Reduction of Polyacetylene

Controlled Potential Studies

1. Cyclic Voltammetry:

These experiments used samples of polyacetylene which had areas of $0.3-1.0 \text{ cm}^2$ (single side) and weighed about 0.00475 g/cm^2 . Cyclic voltammograms were recorded between 0.5 and 2.5 V vs. Li/Li^+ under the following conditions: (a) Pt mesh electrode in fresh electrolyte; (b) fresh polyacetylene in fresh electrolyte; (c) reduced polyacetylene; and (d) polyacetylene after various reduction/oxidation cycles. The results are shown in Figures 1-3.

Cyclic voltammograms using the Pt mesh electrode without polyacetylene were carried out to monitor the level of background current and the stability of the electrolyte. Fresh electrolyte (Fig. 1a) showed an good window of stability from 2.5 V to 0.6 V, but increasing decomposition at potential less than 0.5 V. The same solvent after eleven reduction/oxidation cycles on a polyacetylene sample (Fig. 1b) showed essentially identical cyclic voltammetry behavior. No evidence of electrolyte degradation was observed over this number of cycles.

The cyclic voltammogram of fresh polyacetylene (Fig. 2a) shows that both the reduction and oxidation peaks increase with cycling. This behavior is expected, since the polyacetylene is initially neutral and non-conductive. For polyacetylene reduced to $y=0.047$ (Fig. 2b), both the reduction and oxidation peaks become broad. The oxidation peak current increased from 5 mA/cm^2 for polyacetylene at $y=0.00$ after four cycles to 10.5 mA/cm^2 for polyacetylene reduced to $y=0.047$.

After six cycles (Fig. 3a), the voltammogram is similar to that for fresh polyacetylene, although the peak currents have fallen somewhat. However, after the eleventh cycle (Fig. 3b), the peak current has decreased dramatically and the shape of the voltammogram has changed. Since there was no change in the background voltammogram of the electrolyte after the eleventh cycle (Fig. 1b), it is reasonable to

conclude that these changes are the result of processes within the polyacetylene electrode.

2. Controlled Potential Reduction of Polyacetylene

Samples of polyacetylene were reduced and then re-oxidized under two different controlled potential conditions. In the first, the potential was decreased in 100 mV steps from 2.2 V (or the rest potential) to 0.7 V. At each point, the current was allowed to decrease to a steady value of about 20-25 μA . When the series of reduction steps was complete, at a potential of 0.7 V, the potential was stepped to 2.5 V to oxidize and undope the film.

Figure 4 shows the cumulative doping level, y , achieved at each controlled potential. The points on the curve are not the true maximum doping levels attainable at each potential, since the current was not allowed to decay beyond 20-25 μA . However, they are quite close to the maxima that would be observed after longer doping times.

Very little doping takes place between 2.2 and 1.3 V; but, from 1.2 to 1.0 V the rate of doping increases rapidly. By 0.7 V the maximum doping level of 0.09-0.10 is reached. It may be possible to achieve higher levels by decreasing the potential below 0.7 V. Unfortunately, below 0.6 V the electrolyte is increasingly unstable, and the reduction process would be very inefficient.

Another set of experiments was carried out in which the polyacetylene was electrochemically cycled by reduction at either 1.1 V or 0.7 V followed by oxidation at 2.5 V. The oxidation was considered complete when the current decayed to about 0.5 $\mu\text{A}/\text{cm}^2$.

The current decay curves during controlled potential reduction at 1.1 V show an interesting evolution with increasing cycle number (see Fig. 5). The current levels upon initial polarization were typically 4-5 mA/cm^2 , on the basis of the geometric area of one side of the electrode, regardless of cycle number. In the earlier cycles, the current decreased to a plateau (0.75-1.2 mA/cm^2) after which it decayed to much smaller values. The magnitude of the plateau current decreased steadily with cycling. High current densities were only observed in early

cycles. By the tenth cycle, the current plateau was in the range of $200 \mu\text{A}/\text{cm}^2$.

Because the average reduction current decreased dramatically with cycling, it took longer and longer to reach the same doping level. For example, 60 minutes reduction time in the second and fifth cycles yielded 3.32 and 3.2% doping, respectively. However, by the tenth cycle, the same reduction time produced only 2% doping. Not only did the doping time increase with cycling, it became necessary to reduce at lower potentials to achieve the same doping levels. For example, 3.8% doping was achieved at 1.1 V during the second cycle, but the potential had to be decreased to 0.8 V to reach the same doping level during the tenth cycle. All of these results are consistent with the cyclic voltammogram study which showed a dramatic decrease in the peak current by the tenth cycle.

3. Controlled Potential Oxidation of Polyacetylene at 2.5V

After doping to 3.8%, polyacetylene was re-oxidized at 2.5 V. The variation of oxidation current with time for the second and tenth cycles is shown in Fig. 6. Upon initial oxidation, very high currents, in the range of $10 \text{ mA}/\text{cm}^2$ were observed. This current level remained steady for about 30 seconds (not shown clearly in graph because of the scale). Then a quasi-exponential decay curve is observed.

About 30-50% of the charge initially passed during reduction was recovered at current densities greater than $1 \text{ mA}/\text{cm}^2$. After one hour, the oxidation current level had decayed to less than $0.1 \text{ mA}/\text{cm}^2$, and the fraction of charge recovered was 60-70%. After exhaustive oxidation until the current level was less than $2 \mu\text{A}/\text{cm}^2$, which typically required 40-60 hours, the apparent coulombic efficiency, $Q_{\text{in}}/Q_{\text{out}}$, was 93% or greater.

Controlled Current Studies

1. Constant Current Reduction

Samples of polyacetylene were reduced at a constant current of $0.1 \text{ mA}/\text{cm}^2$ until the desired doping level was reached. They were then oxidized (discharged) at $1 \text{ mA}/\text{cm}^2$ until the cell potential reached 2.5 V. Oxidation was then continued but under constant potential control at 2.5 V.

Fig. 7 shows the open circuit and cell potential for $(Li_yCH)_x$ during reduction and the open circuit potential after one minute current interruption for the second and eleventh cycles as a function of the doping level, y . The electrode establishes a reasonable voltage plateau in the second cycle. But, by the eleventh cycle, it decreases sharply with increasing doping level. If 0.5 V is considered a cutoff point below which the solvent is increasingly unstable, then it is clear that the capacity of the polyacetylene electrode which can be efficiently cycled decreases with cycling, and is about 0.04 by the eleventh cycle.

The overvoltage for the reduction process is also much greater in the eleventh cycle than in the second cycle. An examination of the rate of potential rise after current interruption made this point clear. In the third cycle, the current was interrupted at the 4% doping level. The open circuit potential then gradually rose 120 mV over 17 hours. When the current was interrupted at 4% doping during the twelfth cycle, the potential rose about 300 mV within 5 seconds, and then gradually rose another 200 mV over 12 hours.

These observations are consistent with the cyclic voltammogram and constant potential results just discussed. They indicate the polyacetylene electrode is changed by cycling. The behavior of the electrode changes from that which resembles a well-defined redox couple with an extended voltage plateau, which is desirable for a battery electrode, to a steeply-decreasing potential with increasing charge, which is undesirable in a battery electrode. The gradual decrease of the open circuit potential of polyacetylene doped to 4% with cycle number is shown in Fig. 9. The effect of this decrease is to severely limit the capacity of the electrode which can be efficiently cycled.

2. Constant Current Oxidation

The rate at which Li-doped polyacetylene can be oxidized back to undoped polyacetylene decreases with cycle life. For example, samples of polyacetylene were reduced to an n-doping level of 4-6% at 0.100 mA/cm^2 . They were then oxidized at 1 mA/cm^2 until the potential reached 2.5 V. In earlier cycles, the third and fourth, about 60% of the charge could be extracted in this way. By the eleventh

cycle, only about 40% of the charge could be recovered before the potential reached 2.5 V. In each case, the remaining charge could be almost completely recovered by an extended (40-60 hours) oxidation at a controlled potential fo 2.5 V.

The total coulombic efficiency for the reduction/oxidation process (Q_{out}/Q_{in}) was measured by reducing polyacetylene to various doping levels at 0.1 mA/cm^2 , and then reoxidizing, first at a constant current of 1 mA/cm^2 and then exhaustively at a constant potential of 2.5 V. Table 1 summarizes the results obtained in one set of experiments.

Polyacetylene reduced to 4% doping maintains a coulombic efficiency of nearly 100% to the fifteenth cycle, and perhaps beyond. These high coulombic efficiencies were observed when there was no delay between the reduction and oxidation reactions. The reactions are very efficient despite the clear decrease in the open circuit potential of the polyacetylene at the 4% doping level. If this gradual decrease in open circuit potential in fact continues, the potential will ultimately enter the region of solvent instability, and the coulombic efficiency of the reduction reaction will decrease.

Reducing to levels higher than 4% or allowing the sample to stand on open circuit both decrease the fraction of charge which can be recovered upon oxidation, as Figure 10 demonstrates. When polyacetylene is oxidized immediately after reduction, a coulombic efficiency of nearly 100% is maintained until about 6% doping. It then drops off sharply, and reaches about 80% at 9% doping. An 18-20 hour stand on open circuit after reduction decreases the overall coulombic efficiency at doping levels above about 4%. For example, for polyacetylene doped to 7%, the coulombic efficiency drops from 93% upon immediate discharge to 76% after and 18 hour delay. It appears that 6% doping is about the cutoff for efficient rapid cycling of fresh polyacetylene, and 4% for delayed oxidation.

Conclusions

On the basis of this and other research, polyacetylene does not appear to major advantages over current electrodes for high energy density, rechargeable, non-aqueous electrochemical cells. It suffers principally from instability, sensitivity to impurities, low volumetric

energy density, and low-moderate gravimetric energy density.

Polyacetylene's instability and sensitivity to impurities clearly are problems for the manufacture of practical electrochemical cells. Polyacetylene is not a forgiving material. In the dry state, it is rapidly attacked by oxygen at moderate ($>40^{\circ}\text{C}$) temperatures. Polyacetylene that has been n-doped with Li^+ appears to be quite stable, but the p-doped compositions are unstable toward oxidation or halogenation of the double bond network comprising the polymer backbone. With some dopants these irreversible oxidations proceed at relatively low temperatures. In addition, achieving high coulombic efficiencies for the oxidation of polyacetylene requires extraordinarily clean electrolytes. Perhaps some oxidized forms, such as those containing ClO_4^- or AsF_6^- , are sufficiently stable to find application at low temperatures, and it may be possible to attain the degree of cleanliness necessary for the successful operation of a polyacetylene battery. Nevertheless, polyacetylene's instability and sensitivity to impurities are concerns that must be considered in any technological application of the material.

The low-moderate gravimetric and low volumetric energy densities which can be achieved with either n- or p-doped polyacetylene are the result of the relatively low levels of doping that can be efficiently attained and the intrinsically low density of the polymer. The equivalent weight and density of $[\text{CH}(\text{ClO}_4)_{0.10}]_x$ are 229 g and about 1 g/cc, respectively. Corresponding values for LiTiS_2 are 118g and 3.3 g/cc. $[\text{Li}_{0.10}\text{CH}]_x$ has an equivalent weight of 137 g, while that of Li is 6.9 g. It takes 8-12 times more volume to store the same charge in the form of Li-doped polyacetylene as in lithium metal.

Large scale commercial development of polyacetylene for the purpose of creating a rechargeable battery with unusually high energy or power densities seems of questionable value at this time. Nevertheless, a battery using polyacetylene as one or both electrodes could be made, and it is possible that its development would be justified for a specialized application.

Regardless of the present commercial outlook for polyacetylene, it is critical that fundamental research into its properties and those of other conducting polymers is

continued. It is truly a revolutionary electrochemical material. That alone justifies its further exploration. In addition, the prospects for polyacetylene as a commercial, high energy density battery material might be much brighter if its stability were improved and maximum doping levels increased.

Acknowledgement

This work was supported the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Systems Research, Energy Storage Division of the U.S. Department of Energy under Contract No. DE-ACO3-76SF00098.

References

1. A.G. MacDiarmid and A.J. Heeger, Syn. Met., 1, 101 (1979/80)
2. P.J. Nigrey, A.G. MacDiarmid, and A.J. Heeger, J. Chem. Soc., Chem. Comm., 1979, 594
3. D. MacInnes, Jr., M.A. Druy, P.J. Nigrey, D.P. Nairns, A.G. MacDiarmid, and A.J. Heeger, J. Chem. Soc., Chem. Commun., 1981, 317
4. R. Huq and G.C. Farrington, J. Electrochem. Soc., in press
5. G.C. Farrington, B. Scrosati, D. Frydrych, and J. DeNuzzio, J. Electrochem. Soc., 131, 7 (1984)
6. R. Huq and G.C. Farrington, submitted for publication
7. G. Natta, G. Mazzanti, and P. Corradini, Atti. Acad. Nazl. Lincei Rend. Classe Sci. Fis. Mat. Nat., (8), 25, 3 (1958)
8. T. Ito, H. Shirakawa, and S. Ikeda, J. Polymer Sci., Polym. Chem. Ed., 12, 11 (1974)
9. M.A. Druy, C.H. Tsang, N. Brown, A.J. Heeger, and A.G. MacDiarmid, J. Polym. Sci. Polym. Phys. Ed., 1979, in press
10. M. Rolland, P. Bernier, S. Lefrant, and M. Aldissi, Polymer, 21, 1111 (1980)
11. M. Aldissi, M. Rolland, and F. Schue, phys. stat. sol., 733 (1982)
12. J.M. Pochan, H.W. Gibson, F.C. Bailey, and D.F. Pochan, Polym. Commun., 21, 250 (1980)
13. D.J. Berets and D.S. Smith, Trans. Faraday Soc., 64, 823 (1968)
14. M. Rolland, S. Lefrant, M. Aldissi, P. Bernier, E. Rzepka, and F. Schue, J. Electronic Mat., 10, 619 (1981)
15. P. Nigrey, D. Macinnes, Jr., D.P. Nairns, A.G. MacDiarmid, and A.J. Heeger, J. Electrochem. Soc., 128, 1651 (1981)
16. R.B. Kaner and A.G. MacDiarmid, Extended Abstracts, The Electrochemical Society, May 1983, Abstract No. 550
17. L.W. Shacklette, R.H. Baughman, and J.M. Sowa, ibid., Abstract No. 558

Publications

During this contract year we submitted three manuscripts for publication in the Journal of the Electrochemical Society. The first, "Electrochemical Reactions of Polyacetylene," by R. Huq and G.C. Farrington, appeared in February; the second, "Stability of Undoped and Oxidized Polyacetylene," by G.C. Farrington, D. Frydrych, J. DeNuzzio, and B. Scrosati, has been accepted for publication; and the third, "Electrochemical Characteristics of n-Doped Polyacetylene," by R. Huq and G.C. Farrington, is being reviewed. Another manuscript entitled, "Polyacetylene Electrodes for Non-Aqueous Electrolyte Batteries", by G.C. Farrington and R. Huq has been submitted to the Journal of Power Sources.

B. Scrosati and G.C. Farrington were co-authors of "An Electrochemical Investigation of Polyacetylene Electrodes in Lithium Organic Electrolyte Cells," which was presented at the 4th International Conference on Solid State Ionics, Grenoble, France, July 1983. The manuscript has appeared in Solid State Ionics.

In addition, G.C. Farrington presented an overview of the electrochemistry of polyacetylene and its potential battery applications at the 2nd International Meeting on Lithium Batteries, which was held in Paris in April, 1984.

Figure Captions

1. (a-top) Voltammogram of a Pt mesh electrode in fresh LiClO_4 -THF electrolyte. Scan rate of 20 mV/sec.

(b-bottom) Voltammogram of same Pt mesh electrode in same solution after eleventh reduction/oxidation cycle of a polyacetylene film. Scan rate of 20 mV/sec.

2. (a-top) Voltammogram of a fresh polyacetylene sample in LiClO_4 -THF electrolyte. Scan rate of 20 mV/sec.

(b-bottom) Voltammogram of 4.7% reduced polyacetylene sample in LiClO_4 -THF electrolyte.

3. (a-1) Voltammogram of polyacetylene after sixth reduction/oxidation cycle. Scan rate of 20 mV/sec.

(b-2) Voltammogram of same electrode after eleventh reduction/oxidation cycle. Scan rate of 20 mV/sec.

4. Reduction level, y , as a function of controlled reduction potential in 100 mV steps.

5. Curves 1, 2, and 3 are current decay curves for the second, fifth, and tenth constant potential reduction cycles, respectively.

6. Curves 1 and 2 are current decay curves for the second and tenth constant potential oxidation cycles, respectively. Curves 1' and 2' show the coulombic efficiencies ($Q_{\text{out}}/Q_{\text{in}}$) upon immediate oxidation for 3.8% reduced polyacetylene for the second and tenth cycles, respectively.

7. Open circuit and cell potential of $(\text{Li}_y\text{CH})_x$ as a function of y for the second and eleventh cycles. The sample was reduced at a constant current density of $100\mu\text{A}/\text{cm}^2$.

8. Change in open circuit potential with time after the twelfth reduction/oxidation cycle. The polyacetylene electrode was reduced to 3.5%.

9. Open circuit potential as a function of cycle number for a 4% reduced polyacetylene sample.

10. Coulombic efficiency (Q_{out}/Q_{in}) as a function of y upon immediate and delayed (18-20 hr) oxidation.

Table 1

Coulombic Efficiency for Reduction/Oxidation of $(\text{CH})_x$

Cycle	y(1)	% Out at 1 mA/cm ² (2)	Total % Out (3)
1	0.040	57	67
2	0.038	75	93
6	0.038	77	100
7	0.085	50	63
8	0.038	78	106
9	0.040	85	105

(1) value of y in $(\text{CHLi}_y)_x$

(2) $Q_{\text{out}}/Q_{\text{in}} \times 100\%$

(3) same as 2 except after exhaustive oxidation at 2.5 V.

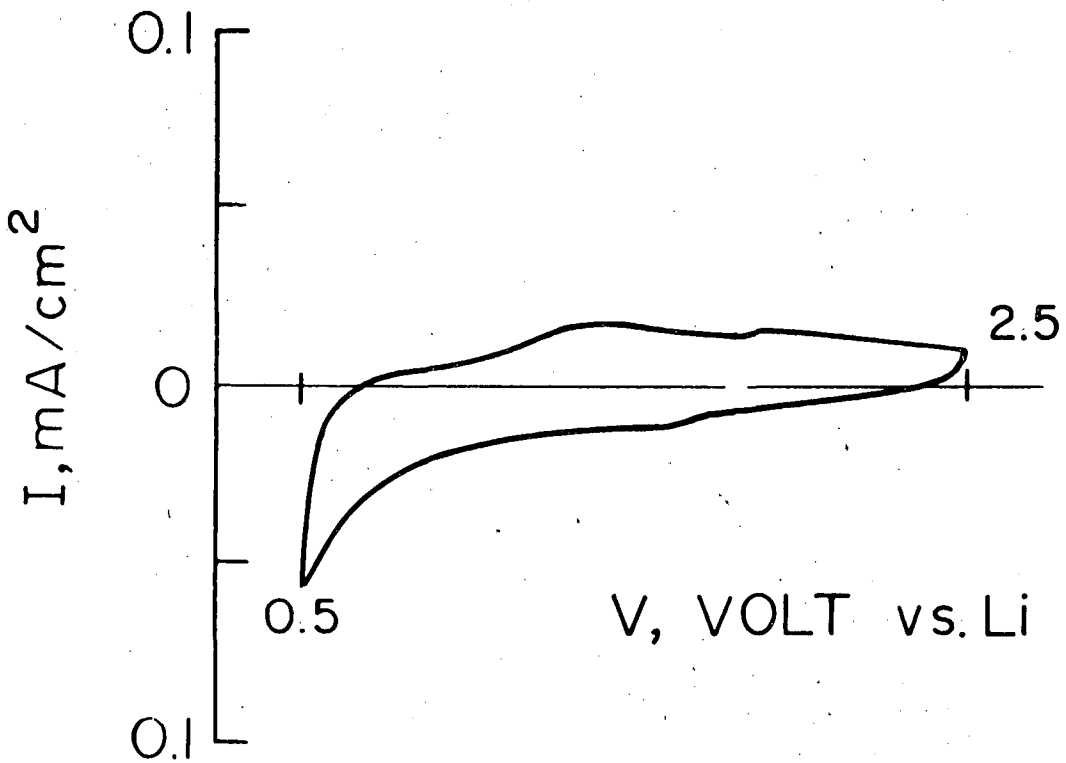
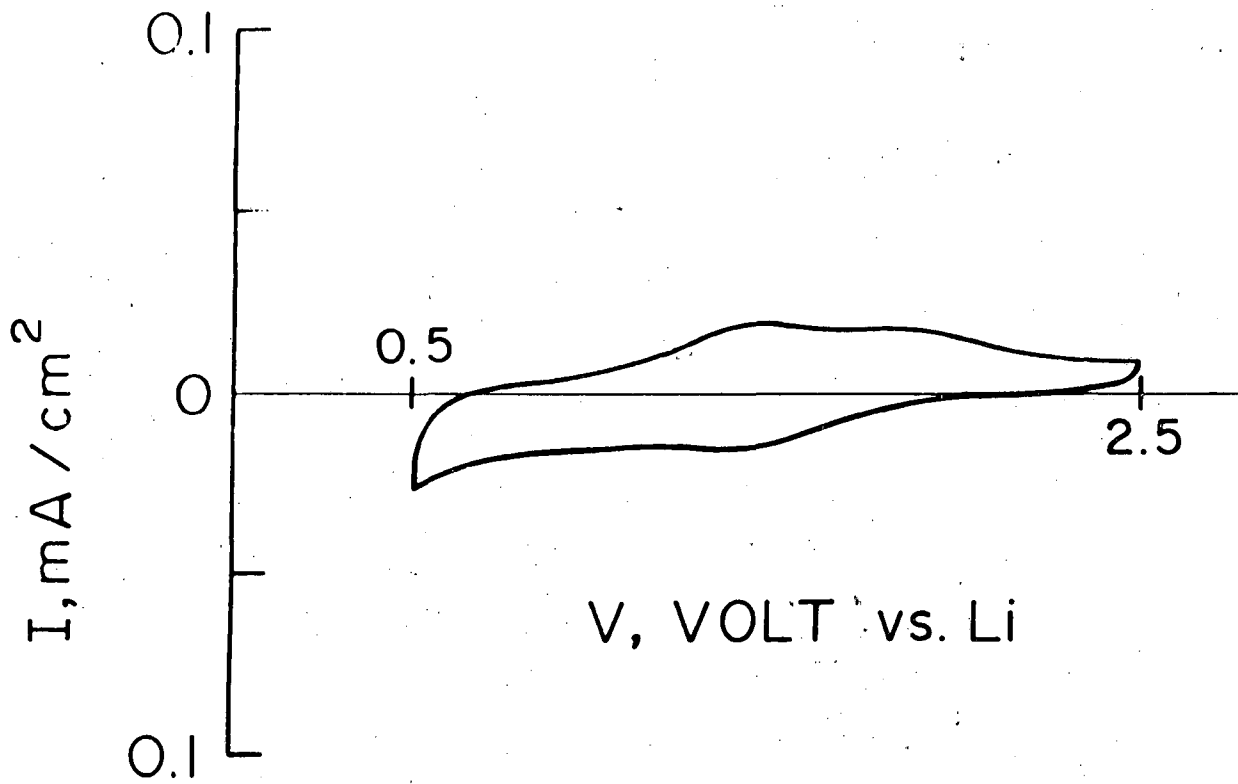
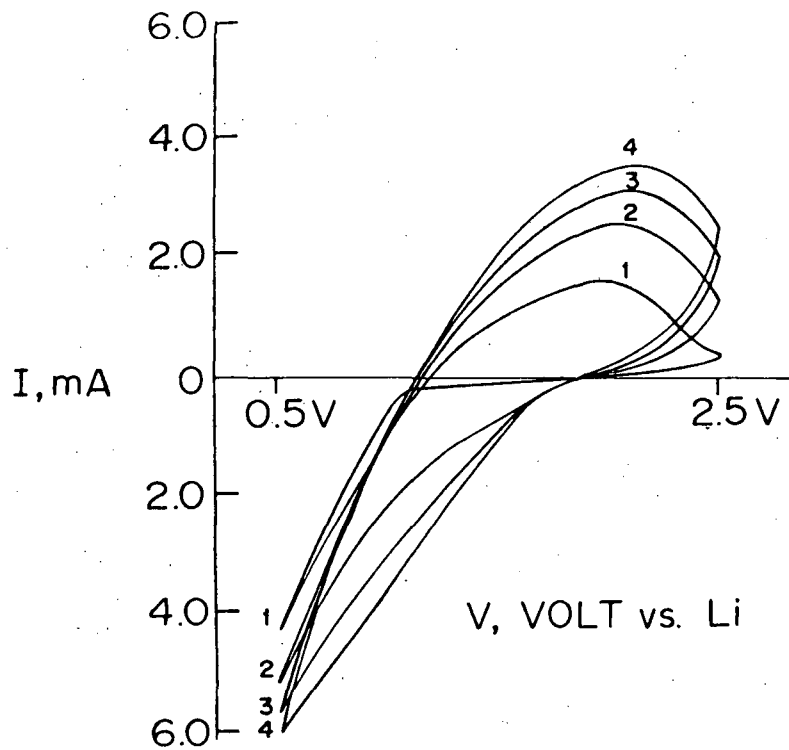
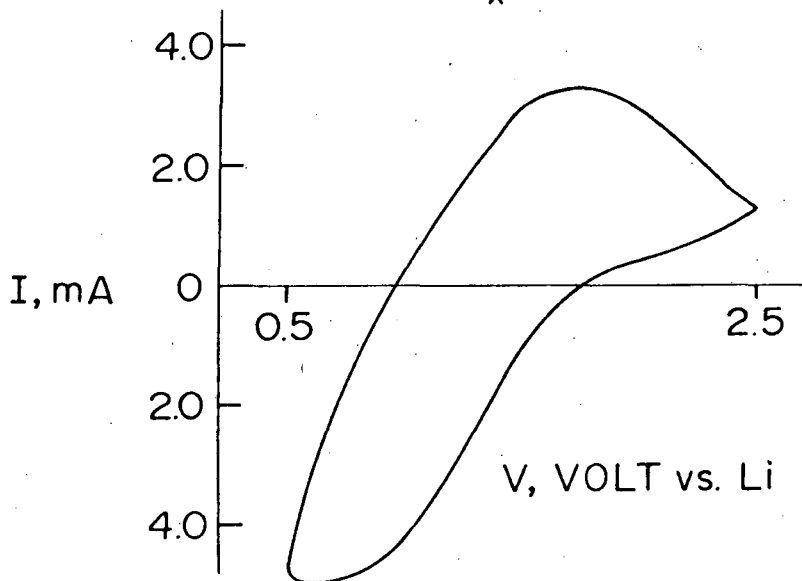


FIGURE 1

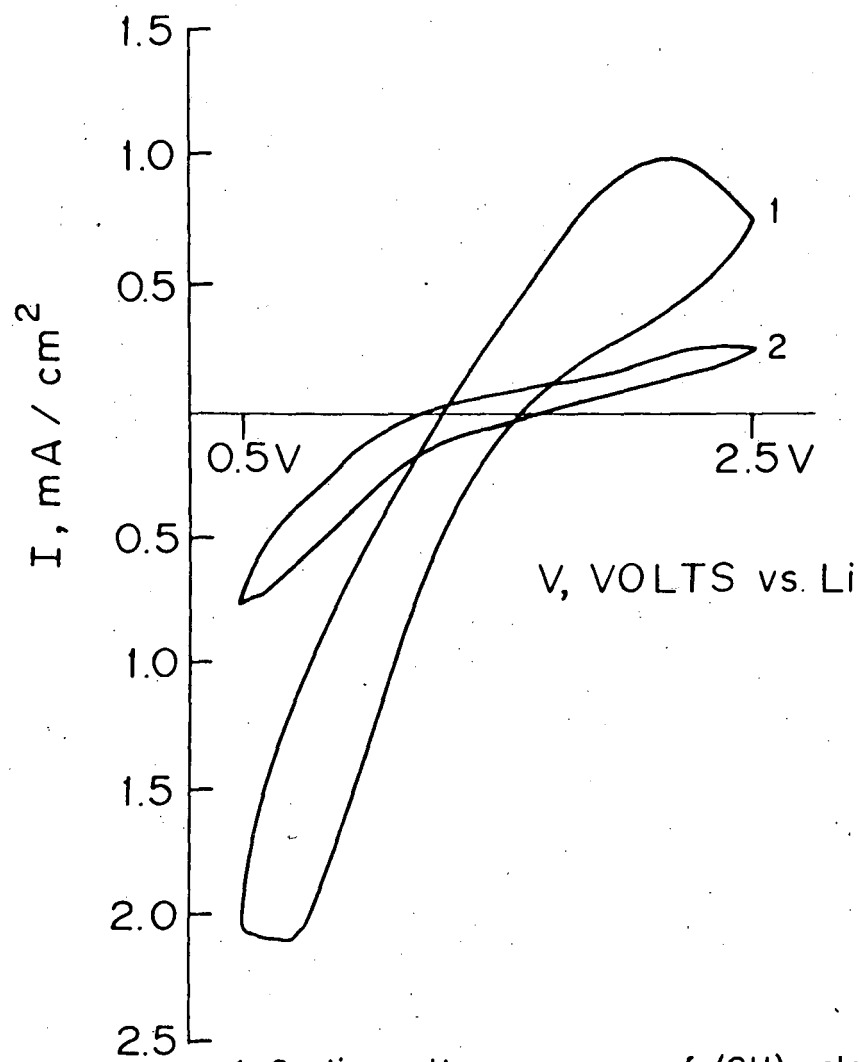


Cyclic voltammogram of a fresh $(CH)_x$ film electrode in the $LiClO_4$ -THF solution. Scan rate 20 mV/sec
Size of $(CH)_x = 0.7 \text{ cm}^2$



Cyclic voltammogram of a 4.7% doped $(CH)_x$ film electrode in the $LiClO_4$ -THF solution. Scan rate 20 mV/sec.
Size of $(CH)_x = 0.3 \text{ cm}^2$

FIGURE 2



1. Cyclic voltammogram of $(\text{CH})_x$ electrode after the sixth discharge-charge cycle. Scan rate: 20 mV/sec. Size of $(\text{CH})_x = 1.0 \text{ cm}^2$
2. Same electrode after eleventh discharge-charge cycle.

FIGURE 3

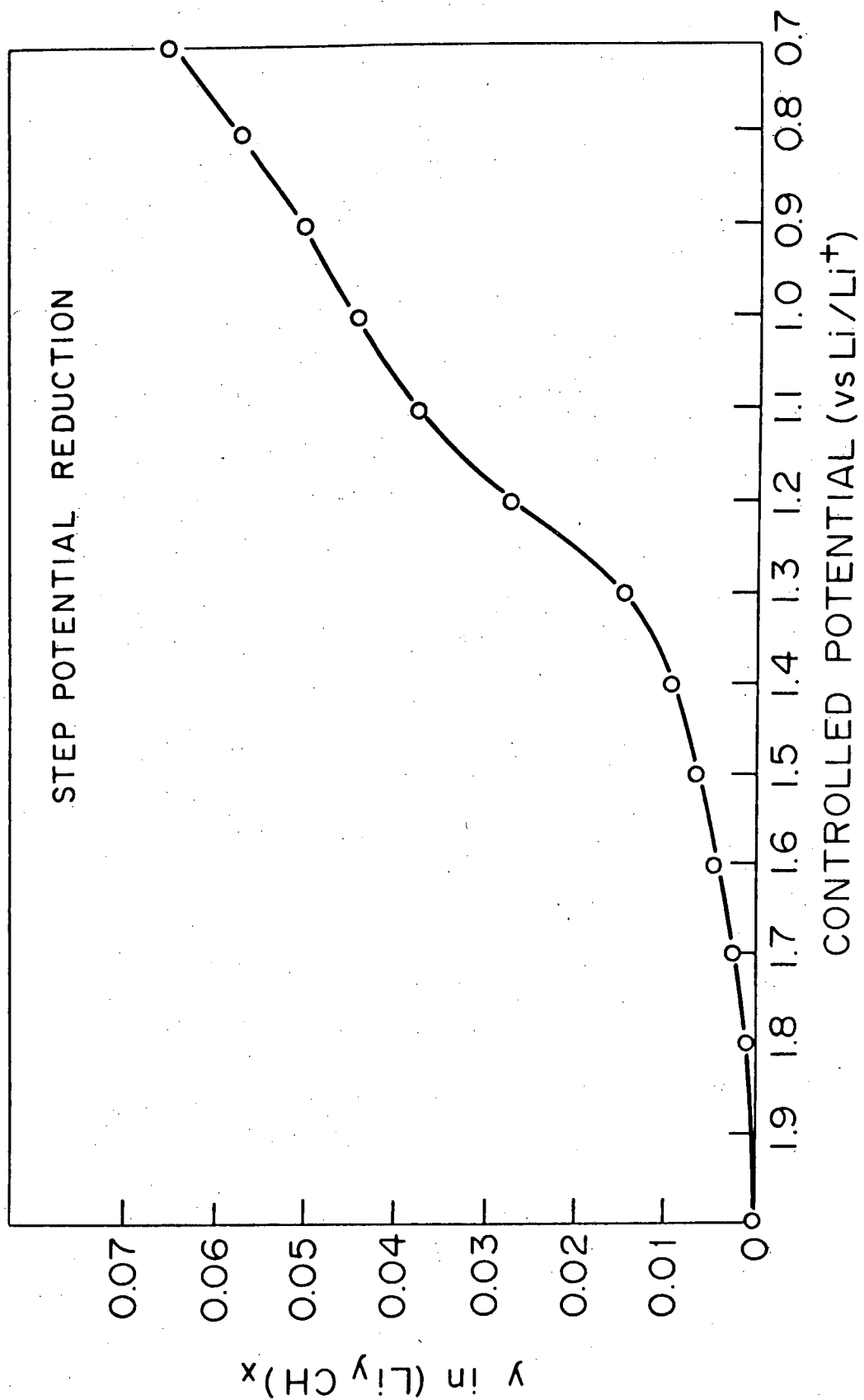


FIGURE 4

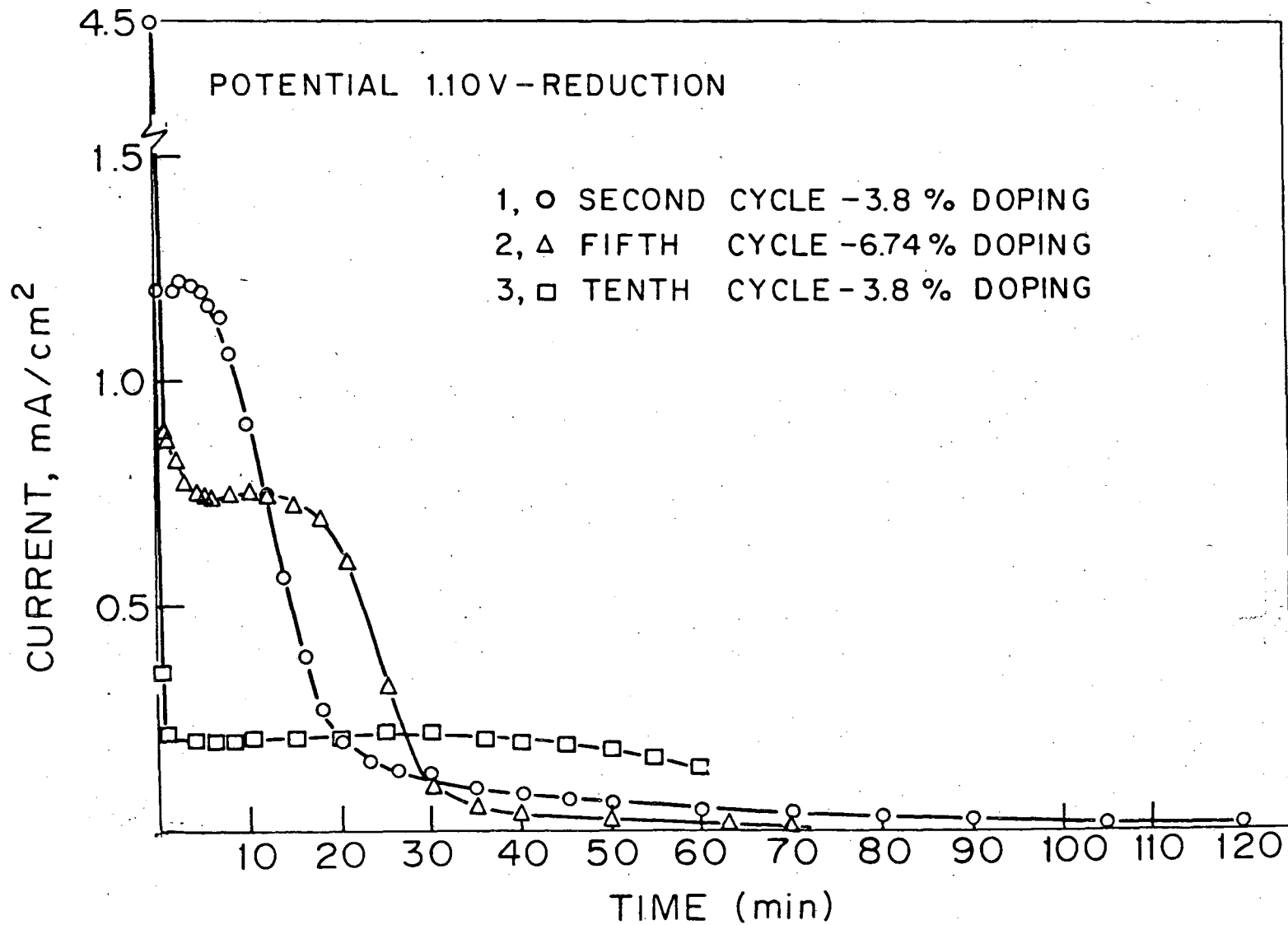


FIGURE 5

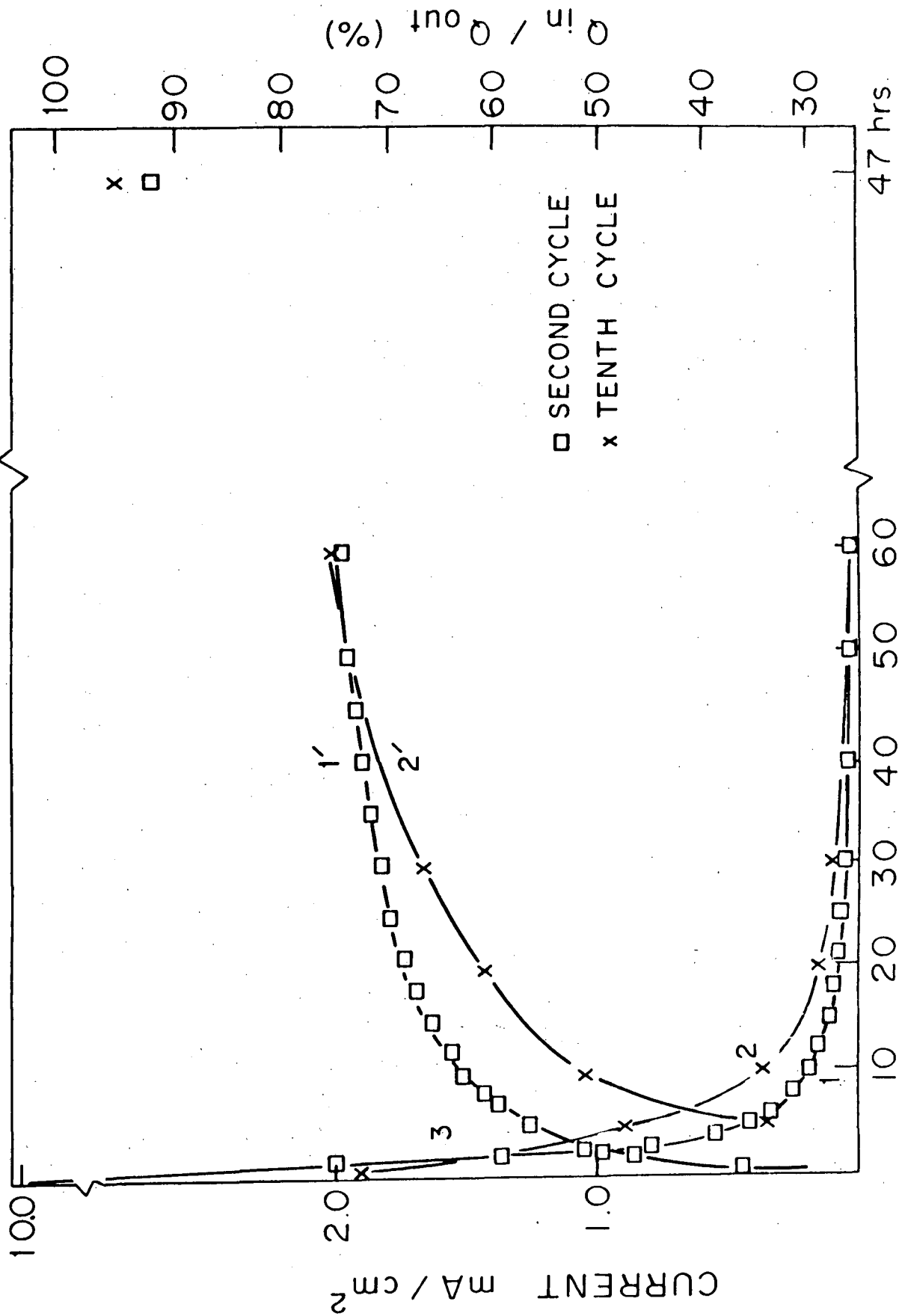


FIGURE 6

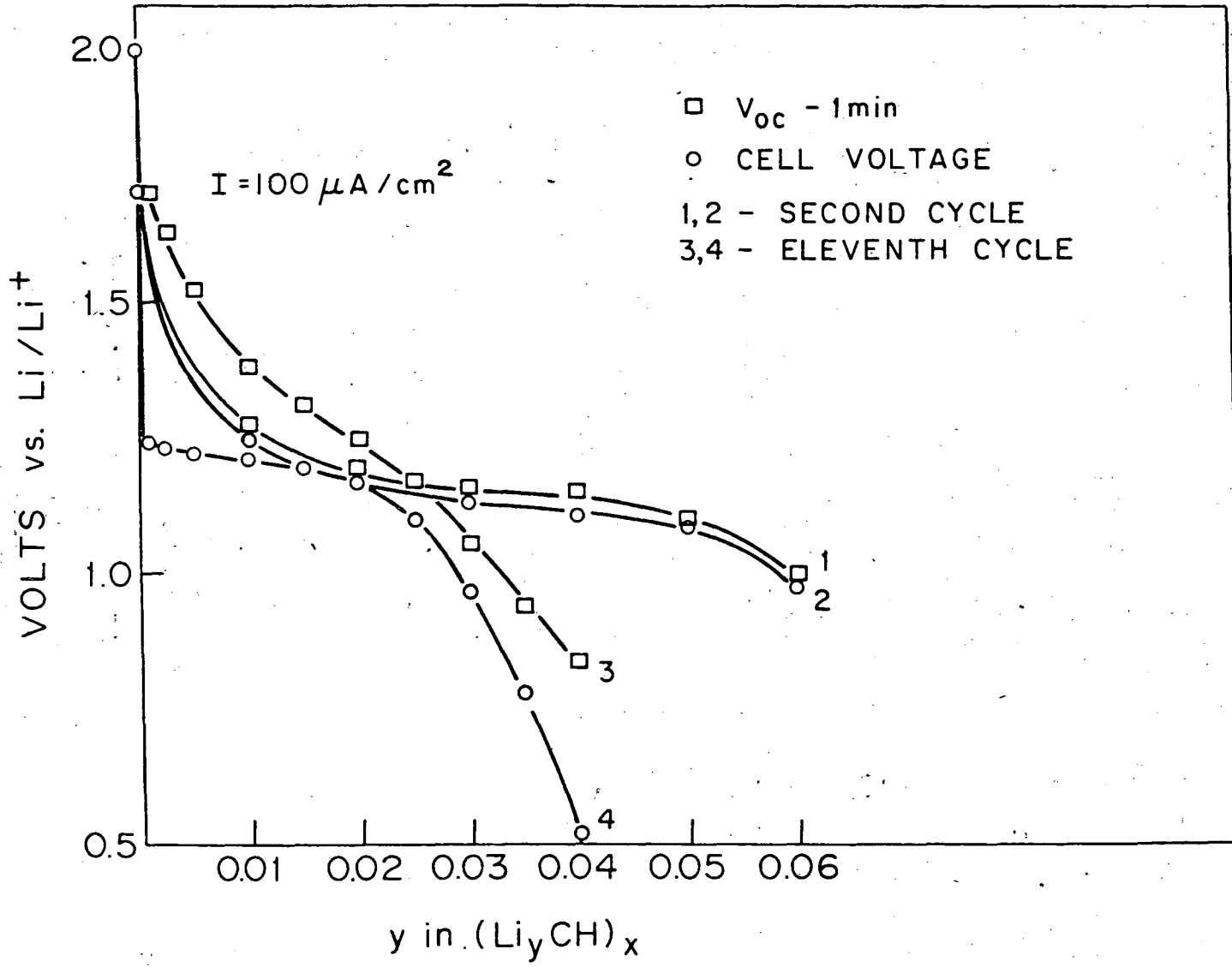


FIGURE 7

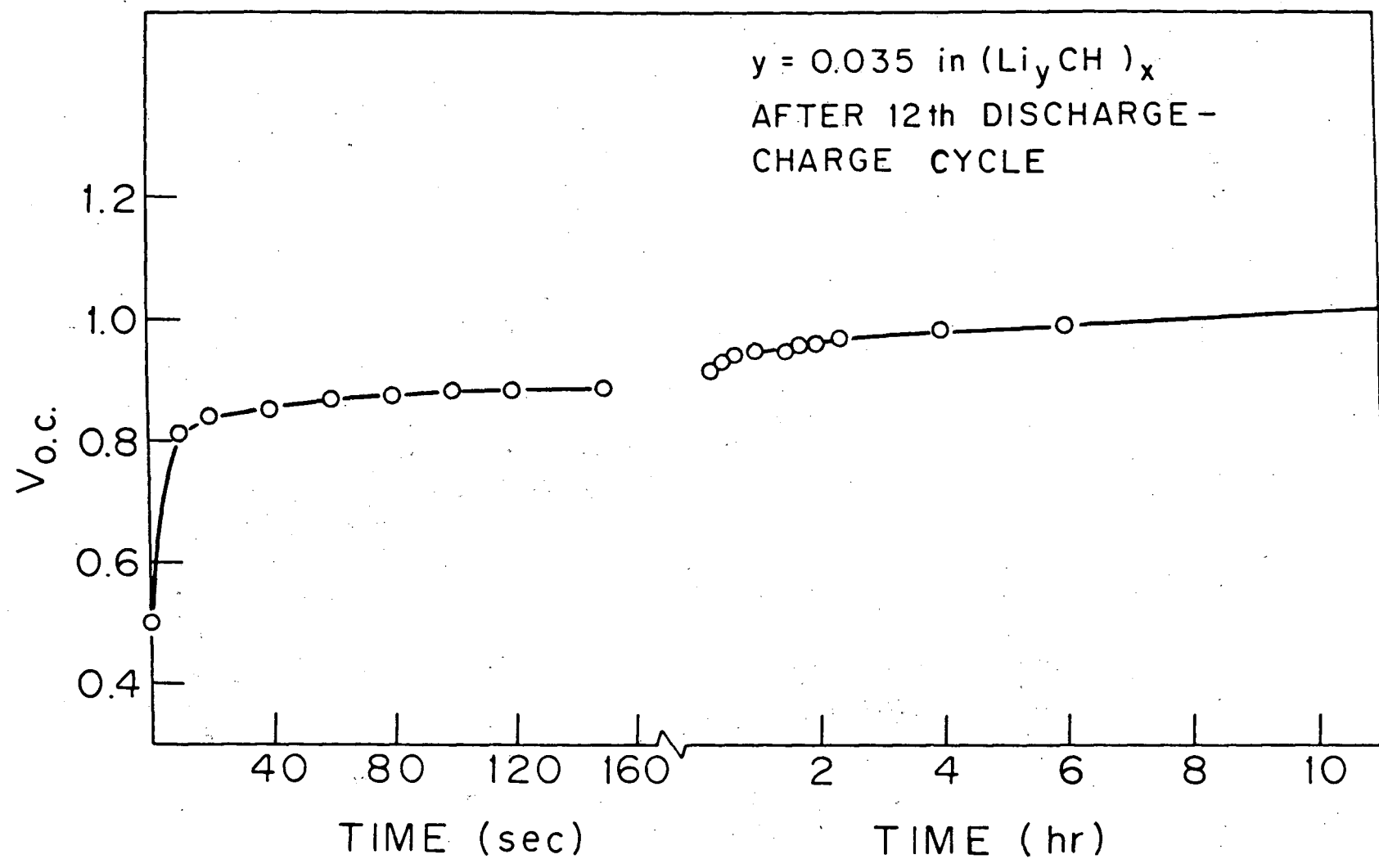


FIGURE 8

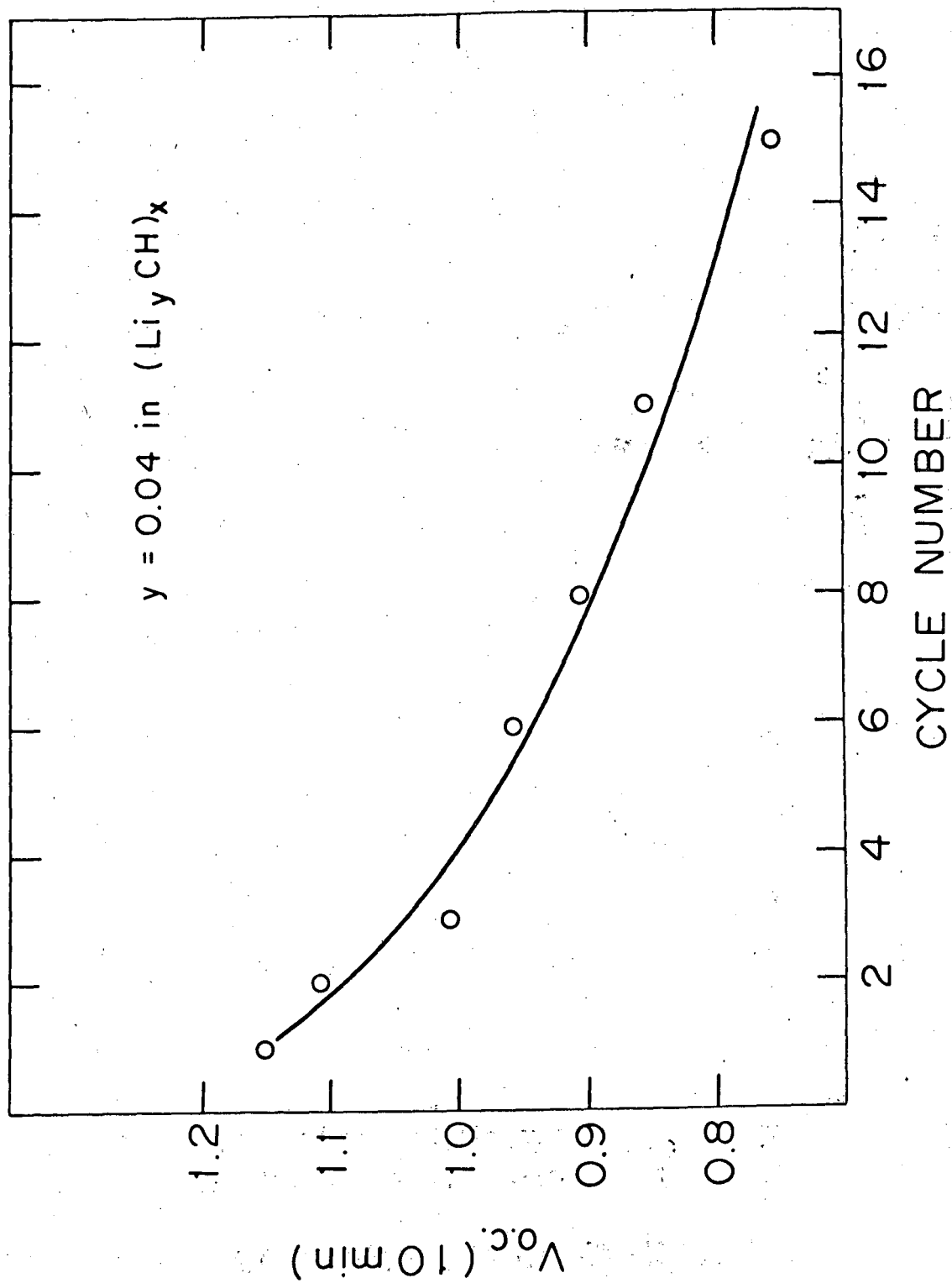
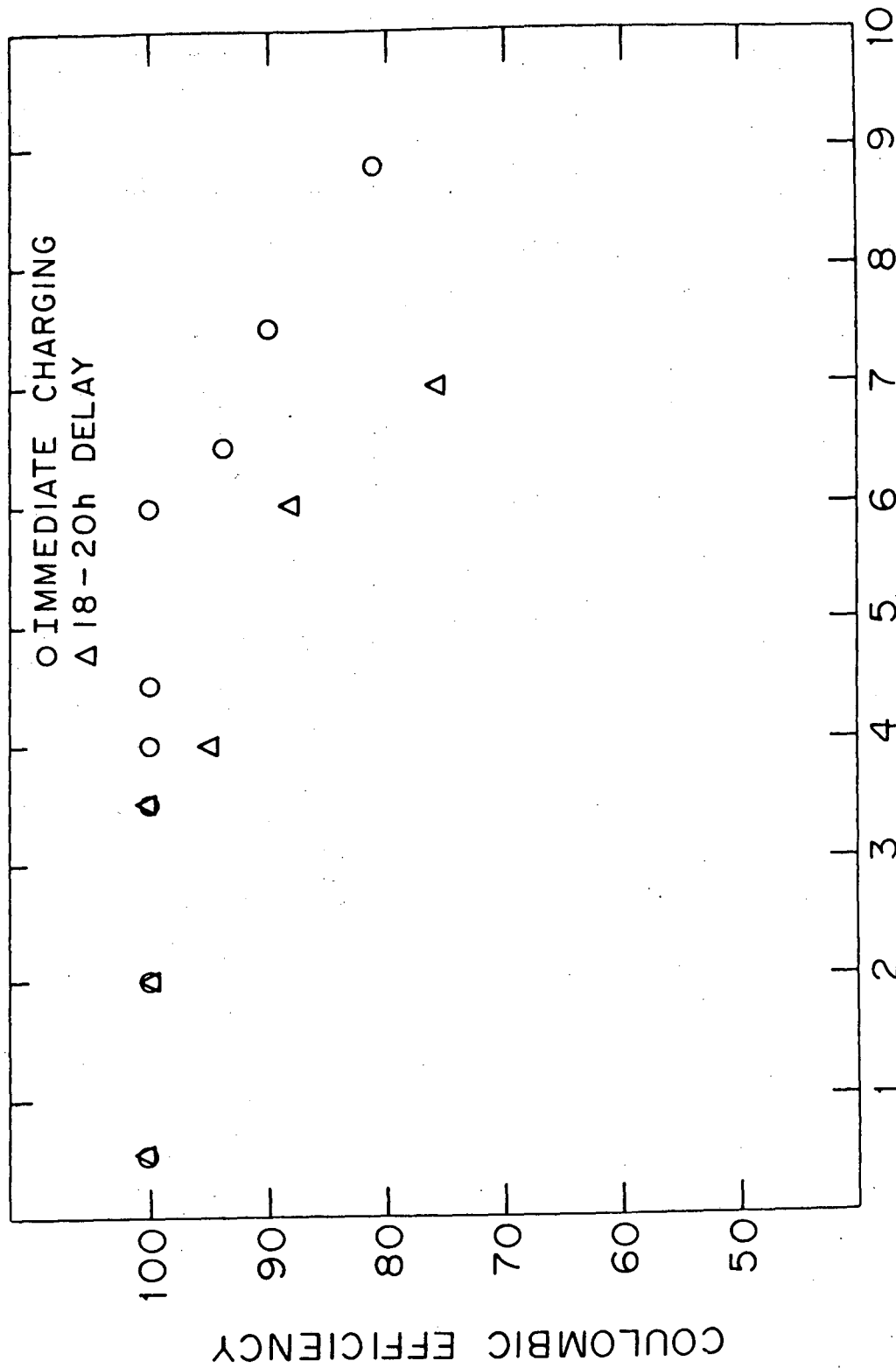


FIGURE 9



y in $(Li_yCH)_x$

FIGURE 10

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720