



# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED  
LAWRENCE  
BERKELEY LABORATORY  
APR 8 1985  
LIBRARY AND  
DOCUMENTS SECTION

## Materials & Molecular Research Division

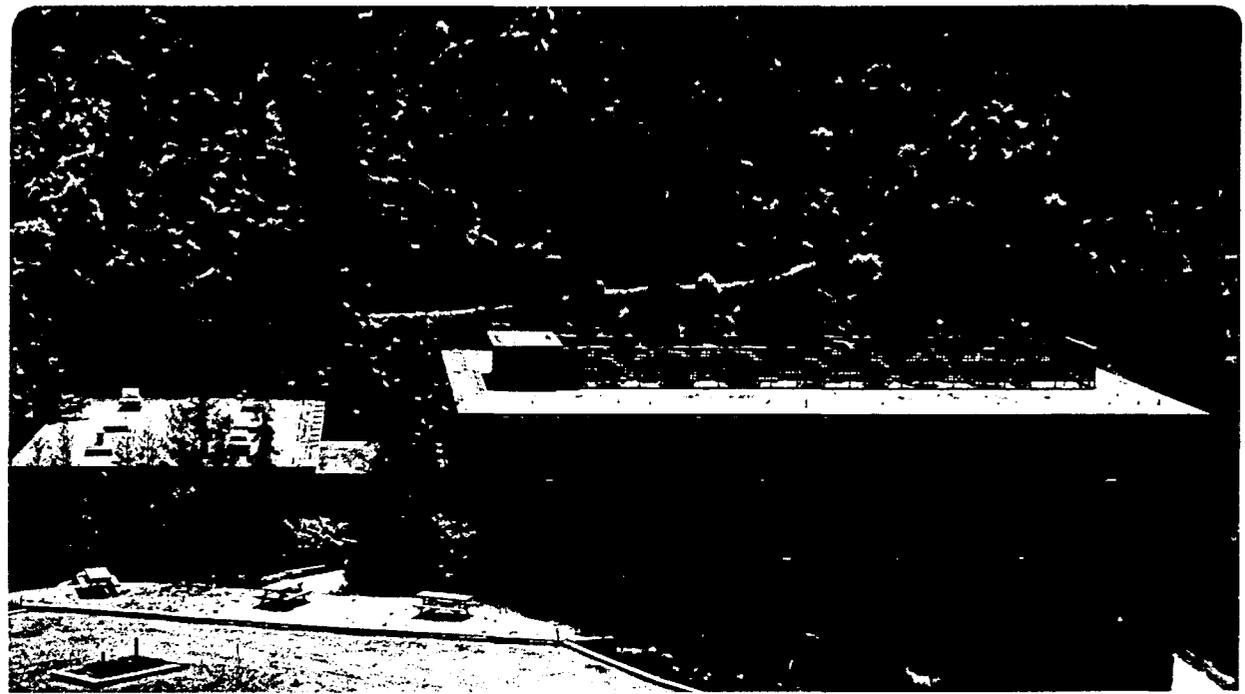
Submitted to Chemical Engineering Communications

STABILITY OF NONAQUEOUS ELECTROLYTES FOR AMBIENT  
TEMPERATURE RECHARGEABLE LITHIUM CELLS

Gh. Nazri and R.H. Muller

February 1985

**For Reference**  
Not to be taken from this room



LBL-18497 Rev.  
c.1

## **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.

STABILITY OF NONAQUEOUS ELECTROLYTES  
FOR AMBIENT TEMPERATURE RECHARGEABLE LITHIUM CELLS

Gh. Nazri,<sup>\*</sup> and R.H. Muller

Materials and Molecular Research Division  
Lawrence Berkeley Laboratory  
University of California  
Berkeley, CA 94720

ABSTRACT

Three tests have been used to determine the stability of solutions of two nonaqueous solvents, propylene carbonate and 2-methyl-tetrahydrofuran and their solutions of  $\text{LiAlCl}_4$ ,  $\text{LiAsF}_6$  and  $\text{LiClO}_4$  in contact with lithium. The procedures identify the effect of surface layers, open-circuit stand, anodic and cathodic polarization. They employ (1) contact with liquid Li amalgam and solid sheet Li; (2) open circuit potential measurements of cathodic deposits and (3) anodic dissolution of deposits with ramped potential. The stability of solvents is found to depend on the dissolved electrolyte. Polymeric materials containing other products of the reaction between metal and electrolytes have been identified by x-ray diffraction.

\* Present address: Electrochemistry Department, Research Laboratories, General Motors Corp., Warren, MI 48090

## Introduction

The remarkable stability of cyclic esters, particularly propylene carbonate (PC), introduced for electrochemical process with alkali metals by Harris and Tobias in 1958, has subsequently made these solvents attractive for use in ambient-temperature lithium batteries. Among several other classes of solvents, cyclic ethers have also received considerable attention, particularly 2-methyl-tetrahydrofuran (2-Me-THF) which was introduced by EIC Corp. (Goldman et al., 1980). While these and other solvents in combination with different electrolytes, particularly  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$  and  $\text{LiAlCl}_4$ , have been quite successful for use in primary cells, they have not provided satisfactory performance for secondary (rechargeable) cells, although some have been found more stable than others (Besenhard et al.). Reaction of lithium with the electrolytes, which often results in the formation of protective surface layers, appears to be responsible for the poor rechargeability of lithium electrodes. Studies of these reactions are complicated by the extremely high reactivity of lithium. It is, therefore, necessary to remove surface layers by mechanical or electrochemical means immediately before measurement or to use fresh electrochemical metal deposits. The difficulties of preparing reproducibly clean lithium electrodes is illustrated by the large spread of exchange current densities reported for PC, 1 M  $\text{LiClO}_4$  solutions, ranging from 1 to 240  $\text{mA/cm}^2$  (Butler et al., 1969; Jasinski, 1971; Scarr, 1970; Jorne and Tobias 1974; Meibur, 1971).

The purpose of this study is to apply three test procedures to combinations of two solvents (PC and 2-Me-THF) with three salts ( $\text{LiClO}_4$ ,

LiAsF<sub>6</sub> and LiAlCl<sub>4</sub>). In the first test, each electrolyte is brought in contact with stirred liquid Li-Hg and solid sheet lithium. This test shows the effect of surface layers since their protective effect is avoided on the amalgam. The stability of the electrolyte can be estimated by measuring the reaction products or the amount of Li consumed. In the second test, Li is deposited electrochemically on a conductive (Cu) substrate, then the potential of the deposit is measured vs. a Li reference as a function of time. As the freshly deposited Li reacts with the electrolyte under formation of corrosion products and exposure of the substrate, the electrode potential changes. The delay time for this change is a measure of the stability of the electrolyte. The delay time can also demonstrate the degree of protection by surface layers and provides information about the wet-stand behavior of the lithium electrode. The third test involves the anodic stripping by potential-sweep cyclic voltammetry of a cathodic Li deposit after different wet-stand periods. This test provides information on cycling efficiency, the stability of the electrolyte during deposition, dissolution and at open circuit, and the protective and conductive properties of surface layers.

The composition and structure of surface layers formed on Li-Hg and Li electrodes were studied by use of different analytical techniques, primarily in situ and ex situ x-ray diffraction (Nazri and Muller 1984 i).

### Experimental

Propylene carbonate (PC, Burdick and Jackson) and 2-methyl-tetrahydrofuran (2-Me-THF, Aldrich) have been used as solvents. The

purification of PC and removal of residual water have been described previously (Nazri and Muller 1983). 2-Me-THF has been stirred over liquid Li-Hg to remove reactive impurities. The salts were dehydrated in vacuum for 24 hours;  $\text{LiAlCl}_4$  (Foote Mineral), and  $\text{LiAsF}_6$  (Alfa P.A.), at  $80^\circ\text{C}$ , and  $\text{LiClO}_4$  (G. Frederick Smith) at  $160^\circ$ . All solutions were 1 molar. Li (Foote Mineral, high purity foil 99.99%), was used without further purification.

For the first test, all six solutions were stirred in contact with Li-Hg, inside a dry box for 20 hours. Amalgam of 2% Li content was prepared by dissolving Li in Hg. Relative amounts of decomposition products were evaluated visually. In addition, a Li disc (1.2 cm diameter and 0.3 cm thickness) was exposed to the electrolytes for 20 hours. Samples of decomposition products formed on Li-Hg were collected, dried in vacuum, and transferred to the x-ray diffractometer (Siemens D-500) without exposure to air by use of a transfer cell. The surface layers formed on the Li sheet were examined by x-ray diffraction with and without removal from the metal. Diffraction patterns of  $\text{LiClO}_4$  and  $\text{LiAlCl}_4$  powder in He atmosphere were generated for comparison. In the case of PC,  $\text{LiClO}_4$  the surface layer was also analyzed by ESCA, IR and SIMS (Nazri and Muller 1984 i). For the second test, Li was galvanostatically deposited at  $1\text{ mA/cm}^2$  on Cu from 2-Me-THF,  $\text{LiClO}_4$ , and PC,  $\text{LiClO}_4$ . Based on charge passed, the deposit thicknesses for a compact layer ranged from 100 to  $2000\text{ \AA}$ . Potential measurements at open circuit were initiated immediately after deposition. For the third test, Li was deposited galvanostatically on a Cu substrate at  $1\text{ mA/cm}^2$  for a thickness of  $1000\text{ \AA}$ , then stripped anodically after remaining at open circuit for different periods of time.

## Results and Discussion

For all the solutions, the reaction between Li-Hg and solvents in the first test was accelerated by the presence of salts, with the rate of reaction increasing in the order  $\text{LiAlCl}_4$ ,  $\text{LiAsF}_6$ , and  $\text{LiClO}_4$ . The reaction resulted in the formation of a gelatinous, transparent material. With the same salt, 2-Me-THF was more stable than PC, and pure solvents were more stable than their solutions. Mixed solvents have not been studied in this work. With 2 Me-THF,  $\text{LiClO}_4$  the amount of reaction product was approximately 1/3 of that formed with PC,  $\text{LiClO}_4$ . PC,  $\text{LiAlCl}_4$  reacted with Li-Hg to form a transparent solid material which after evacuation turned white. 2-Me-THF tends to polymerize after adding  $\text{LiAlCl}_4$ , with only about 1/10 of the electrolyte remaining in liquid form and most changed to a solid, gelatinous material after 30 minutes of agitation. This polymerized material has been studied by x-ray diffraction in a He atmosphere (Fig. 1). Comparison of this diffractogram with that of  $\text{LiAlCl}_4$  powder, (Fig. 2) shows the presence of  $\text{LiCl}$  in addition to a small amount of  $\text{LiAlCl}_4$  in the polymerized material. The diffraction pattern of solid material formed by 2-Me-THF, 1M  $\text{LiClO}_4$  in contact with Li-Hg, given in Fig. 3, shows  $\text{LiCl}$  as a reaction product. A solid-sheet Li disc (1.2 cm x 0.3 cm) was removed from 2-Me-THF, 1 M  $\text{LiAlCl}_4$  before complete polymerization of the solution. The resulting surface layer was removed from the disc for analysis by x-ray diffraction. A broad band between  $24^\circ$  and  $34^\circ$ , indicative of a polymeric material, was observed (Fig. 4; the band between  $6^\circ$  and  $12^\circ$  is an artefact caused by diffraction from the polymeric cell material). The formation of polymeric material on Li electrodes has been observed in previous work,

where diffraction patterns for film materials formed in PC,  $\text{LiClO}_4$ , had been shown (Nazri and Muller 1984 i, 1984 ii and 1984 iii) and has been reported by Epelboin et al. (1980). Peled (1979) has, however, postulated formation of ionic solids termed "solid electrolyte interface." The formation of a polymeric surface layer impregnated with electrolyte and reaction products, proposed by Froment et al. (1979), results in a more complex film structure. Such a composition may account for observed optical properties (Schwager et al. 1980 and Geronov et al. 1982) and semiconductor behavior (Povarov and Sitnina, 1981) of surface layers on Li. Films formed on Li in 2-Me-THF,  $\text{LiClO}_4$  showed a polymer band between  $26^\circ$  and  $42^\circ$  (Fig. 5).

Results of the second test are illustrated in Figs. 6 and 7. Li was deposited on Cu from 2-Me-THF,  $\text{LiClO}_4$  and PC,  $\text{LiClO}_4$  to thicknesses (for a compact layer, based on charge) of 100, 200, 500, 1000, and 2000 Å. The subsequent behavior of open circuit potential with time is shown in the figures. In contrast to the greater reactivity of PC with lithium amalgam compared to 2-Me-THF, the corrosion of the Li deposits proceeds more slowly in PC. For example, the rise in electrode potential, indicating exposure of the substrate, sets in after 150 s with PC and 100s with 2-Me-THF for a deposit thickness of 1000 Å. While the electrode potential with the latter solvent approached that of the Cu substrate, a lower potential, indicative of reaction products, was reached in PC solutions. The results show the protective properties of surface layer formed in PC solutions.

The third test, the anodic stripping of Li deposits after different wet-stand periods, is illustrated in Figs. 8 and 9. In these experiments, Li layers of 1000 Å thickness were deposited galvanostatically on Cu at 1

$\text{mA/cm}^2$ , then stripped potentiostatically at 50 mV/sec. It can be seen that after 60 s at open circuit, about 1/4 of the deposit is still available for dissolution in PC while none is left in 2-Me-THF. The two peaks which appear in Fig. 8 represent dissolution of Li from bulk and alloy phases, respectively. It can be seen that while the amount of bulk metal available for anodic stripping decreases with time, the alloy is practically unaffected by corrosion reactions with the solution. The formation of Li alloys with substrates of Pt, Au, Cu and stainless steel has resulted in a degradation of the surfaces under powder formation, in agreement with literature reports (Dey, 1971; Nicholson, 1976; Rao, et al., 1977).

The stability of electrolytes for rechargeable lithium batteries can be estimated by the three tests. The first test, exposure of the electrolyte to Li amalgam, provides information about the chemical stability of the electrolyte toward Li. Because the amalgam surface is liquid, reaction products do not passivate it. The chemical stability of the electrolyte can therefore be studied without the effect of protective surface layers, which often form on solid Li. The second test provides information on the chemical stability of the electrolyte toward deposited Li, which is more reactive than bulk Li. This test allows one to estimate the behavior of Li electrodes during recharge and wet stand. The third test provides a measure of charge retention and rechargeability of a Li electrode in the electrolyte. The test simulates the electrode behavior during charge and discharge and may be the most important of the three for the choice of an electrolyte. The tests can equally be used for the efficient screening of electrolytes with mixed solvents, as well as electrolytes containing additives.

Acknowledgment

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. This paper is dedicated to Charles W. Tobias, who has introduced the use of cyclic esters as solvents for electrochemical processes with reactive metals.

References

- Besenhard, J.O., and G. Eichinger, J. Electroanal. Chem. 68, 1 (1976).
- Butler, J.N., D.R. Cogley and J.C. Synott, J. Phys. Chem. 73, 4026 (1969).
- Dey, A.N. J. Electrochem. Soc. 118, 1547 (1971).
- Epelboin, I., M. Froment, M. Garreau, J. Thevenin and D. Warin, J. Electrochem. Soc. 127, 2100 (1980).
- Froment, M., M. Garreau, J. Thevenin and D. Warin, J. Microsc. Spectrosc. Electron 4, 111 (1979).
- Geronov, Y., F. Schwager and R.H. Muller, J. Electrochem. Soc., 129, 1422 (1982).
- Goldman, J.L., R.M. Mank, J.H. Young and V.R. Koch, J. Electrochem. Soc. 127, 1461 (1980).
- Harris, W.S. (with C.W. Tobias), Ph.D Thesis, Dept. of Chem. Engr., University of California, Berkeley, 1958 (UCRL-8381).
- Jasinski, R., Collect. Czech., Chem. Commun., 36, 1079 (1971).
- Jorne, J. and C.W. Tobias, J. Electrochem. Soc. 121, 994 (1974).
- Meibuhr, S.G., J. Electrochem. Soc. 118, 709 (1971).
- Nazri, Gh. and R.H. Muller, Electrochem. Soc. Meeting, Washington, DC, Oct. 9-13, 1983, Ext. Abstr. No. 61; submitted to J. Electrochem. Soc.
- Nazri, Gh. and R.H. Muller, submitted to J. Electrochem. Soc. (1984 i).
- Nazri, Gh. and R.H. Muller, submitted to J. Electrochem. Soc. (1984 ii).
- Nazri, Gh. and R.H. Muller, Int. Soc. Electrochem. Meeting, Berkeley, CA, Aug. 5-10, 1984 iii, Ext. Abstr. No. A4-16.
- Nicholson, M.M., J. Electrochem. Soc. 121, 736 (1976).
- Peled, E., J. Electrochem. Soc. 126 2047 (1979).
- Povarov, Yu. M., and E.N. Sitnina, Elektrokimiya 17, 633 (1981).

Rao, B.M.L., R.W. Francis and M.A. Christopher, J. Electrochem. Soc. 124, 1490 (1977).

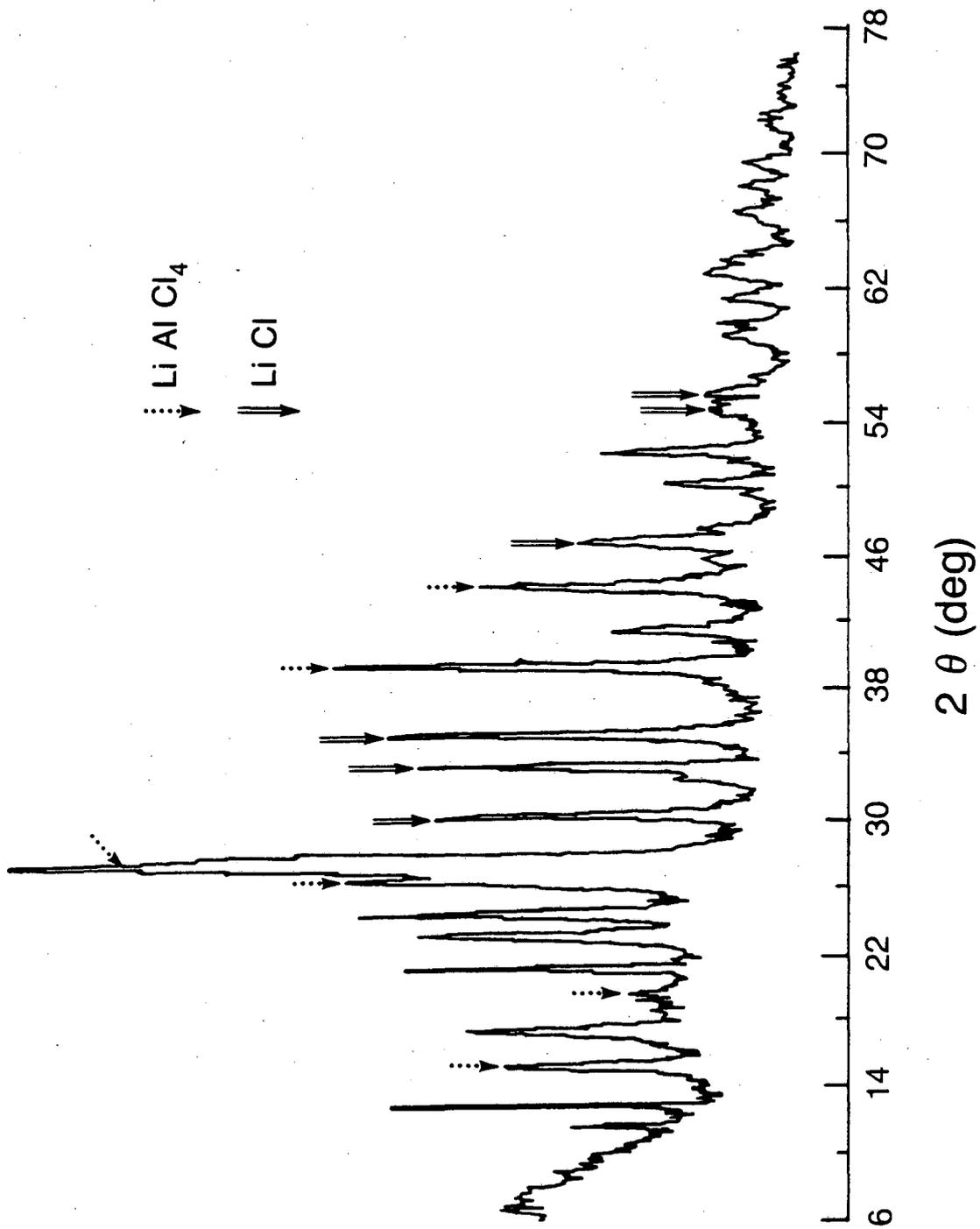
Scarr, R.F., J. Electrochem. Soc. 117, 295 (1970).

Schwager, F., Y. Geronov and R.H. Muller, Electrochem. Soc. Meeting, Hollywood, FL, Oct. 5-10, 1980, Ext. Abstr. No. 37; J. Electrochem. Soc. 132, 285 (1985).

Figure Captions

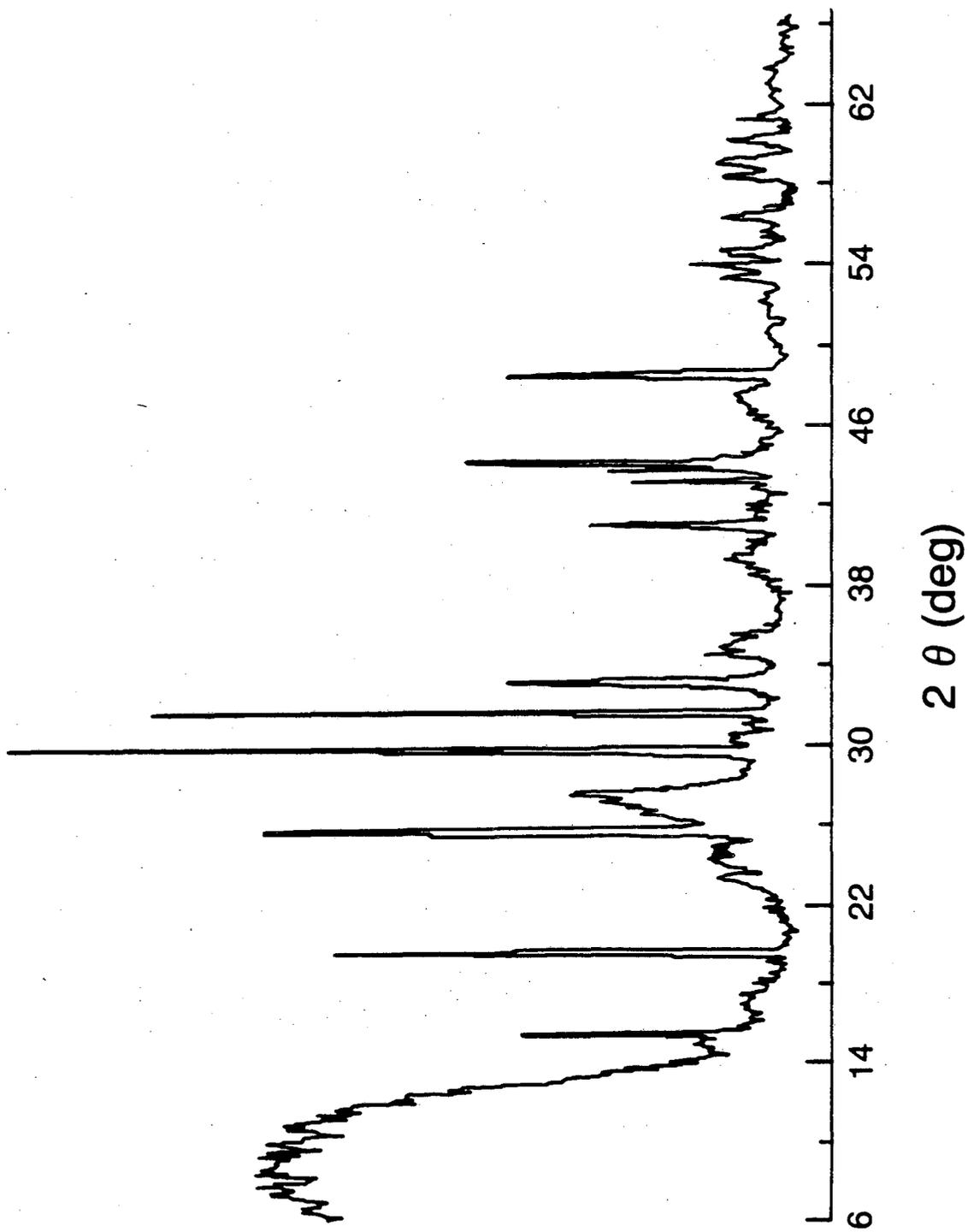
- Fig. 1. X-ray diffraction of solid material formed in 2-Me-THF, 1 M  $\text{LiAlCl}_4$  after 30 min. (measured in He-filled transfer-cell).
- Fig. 2. X-ray diffraction of  $\text{LiAlCl}_4$  powder (measured in He atmosphere).
- Fig. 3. X-ray diffraction of solid material formed after 20 h on Li-Hg in 2-Me-THF, 1 M  $\text{LiClO}_4$ .
- Fig. 4. X-ray diffraction of material formed after 10 min on bulk Li electrode at open circuit in 2-Me-THF, 1 M  $\text{LiAlCl}_4$  (material removed from electrode).
- Fig. 5. X-ray diffraction of surface layer formed on bulk Li at open circuit in 2-Me-THF, 1 M  $\text{LiClO}_4$  (material left on electrode).
- Fig. 6. Open-circuit potential vs. Li reference of electrochemically deposited Li on Cu in PC, 1 M  $\text{LiAlCl}_4$ . Deposit thickness for compact layer, based on charge passed (A) 100  $\text{\AA}$ , (B) 200  $\text{\AA}$ , (C) 500  $\text{\AA}$ , (D) 1000  $\text{\AA}$ , (E) 2000  $\text{\AA}$ .
- Fig. 7. Open-circuit potential vs. Li reference of electrochemically deposited Li on Cu in 2-Me-THF, 1 M  $\text{LiClO}_4$ . Deposit thicknesses for curves A to D as in Fig. 5.
- Fig. 8. Anodic stripping of 1000  $\text{\AA}$  Li deposit on Cu electrode in PC, 1 M  $\text{LiClO}_4$ , after different periods at open circuit before stripping (A) 0, (B) 15, (C) 30 and (D) 60 sec. Sweep rate, 50 mV/sec.

Fig. 9. Anodic stripping of 1000 Å Li deposit on Cu in 2-Me-THF, 1 M LiClO<sub>4</sub> after different periods at open circuit (A) 0, (B) 5, (C) 15, (D) 30, (E) 60 sec. Sweep rate, 50 mV/sec.



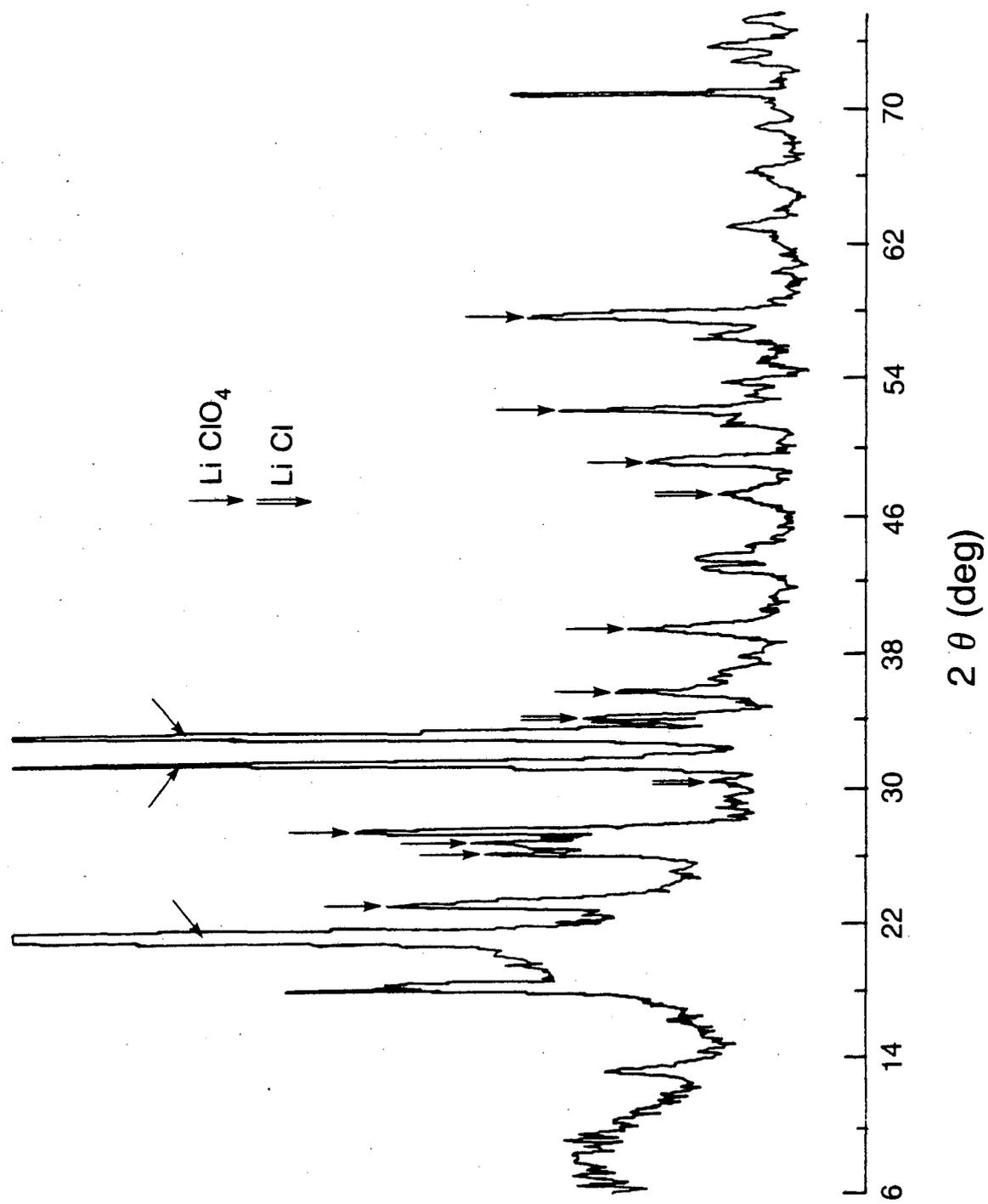
XBL 8410-10894

Fig. 1



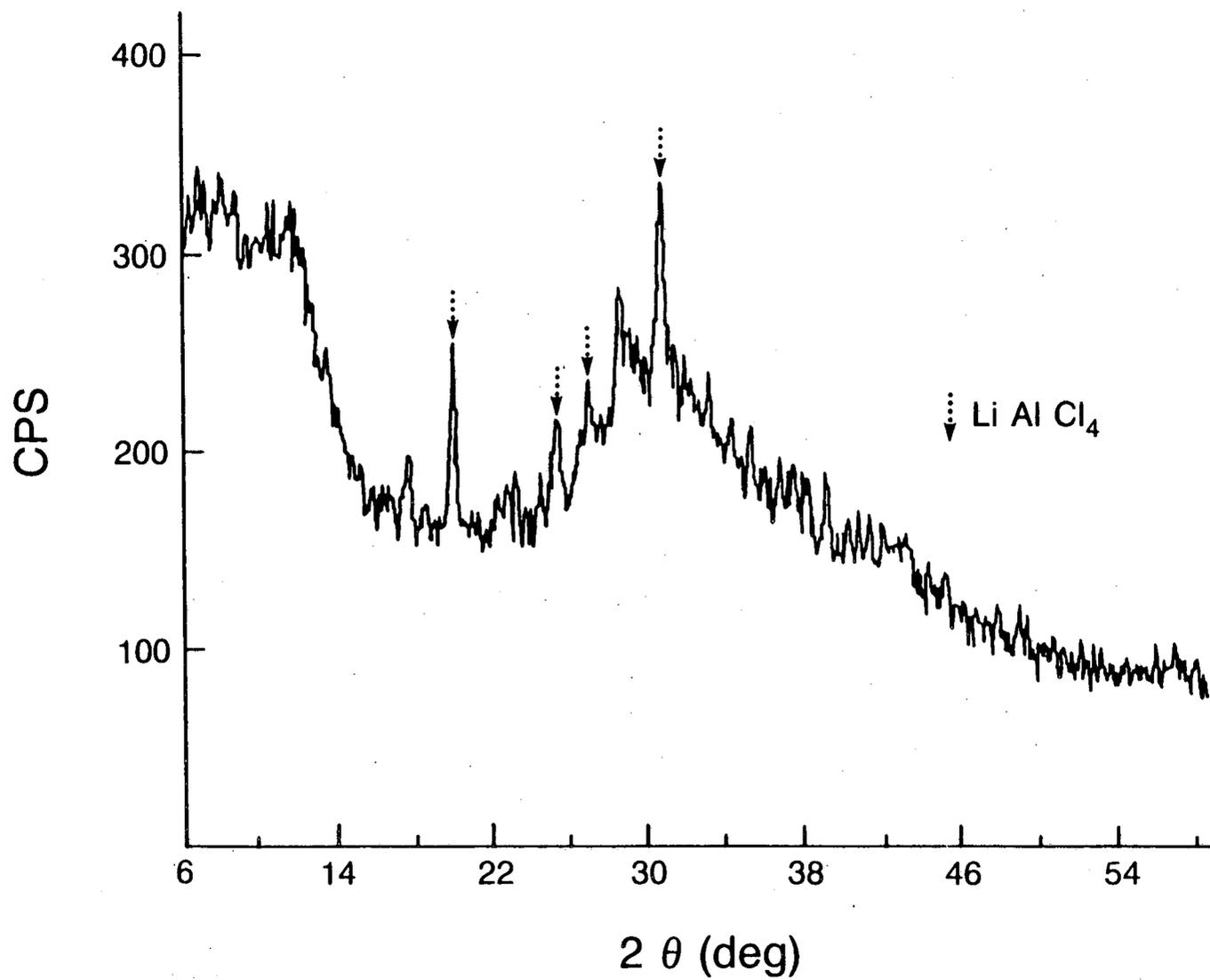
XBL 8410-10895

Fig. 2



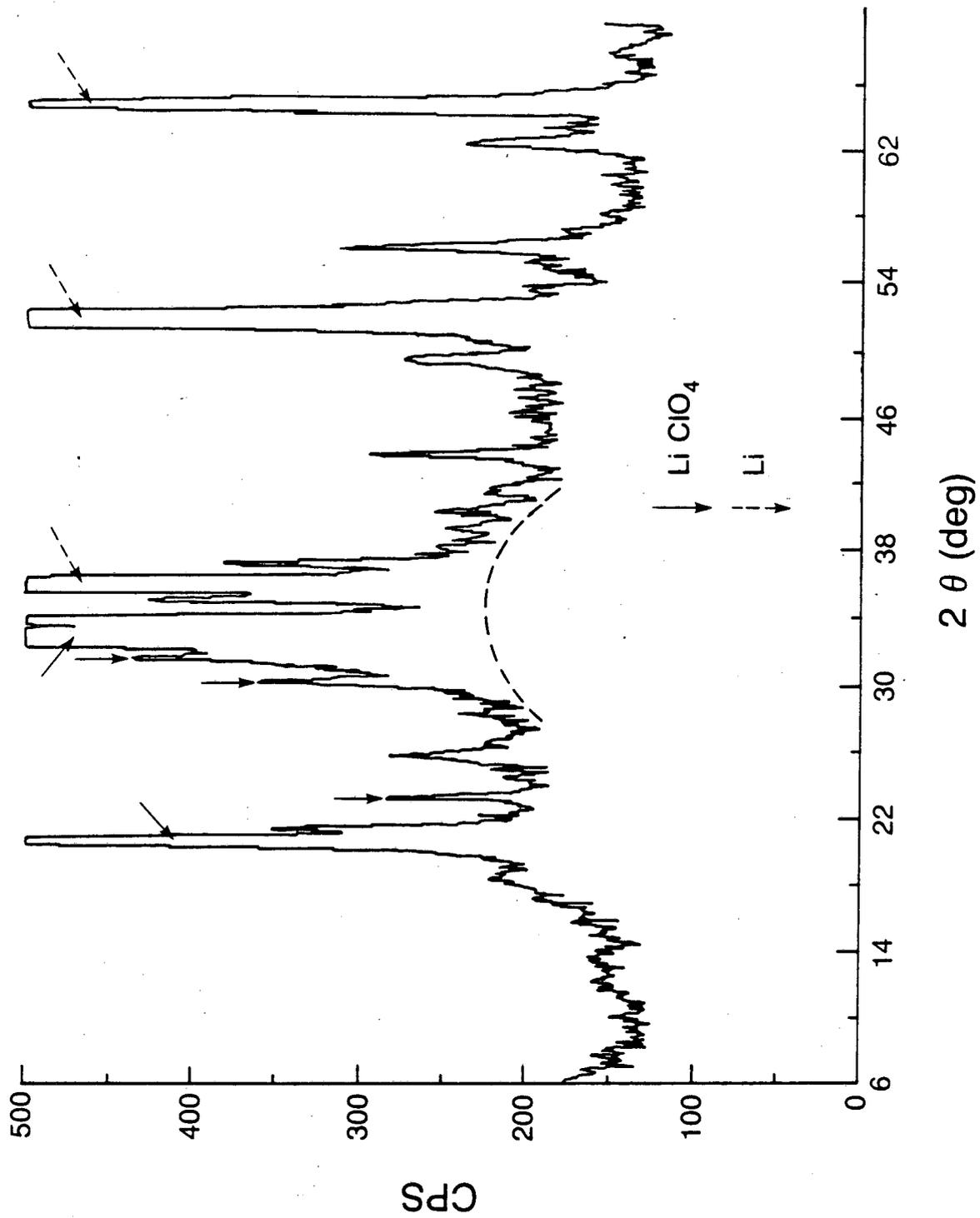
XBL 8410-10964

Fig. 3



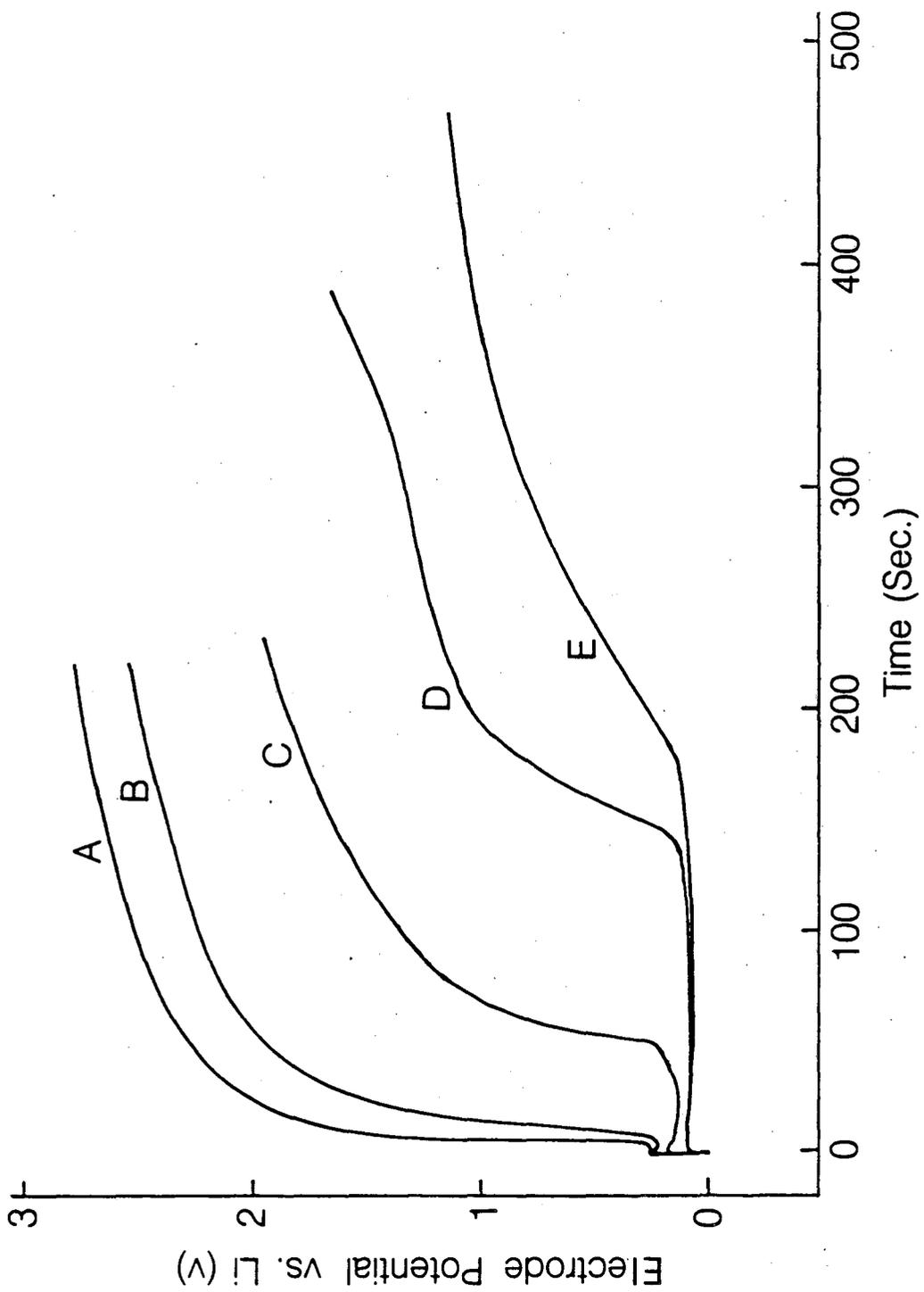
XBL 8410-10898

Fig. 4



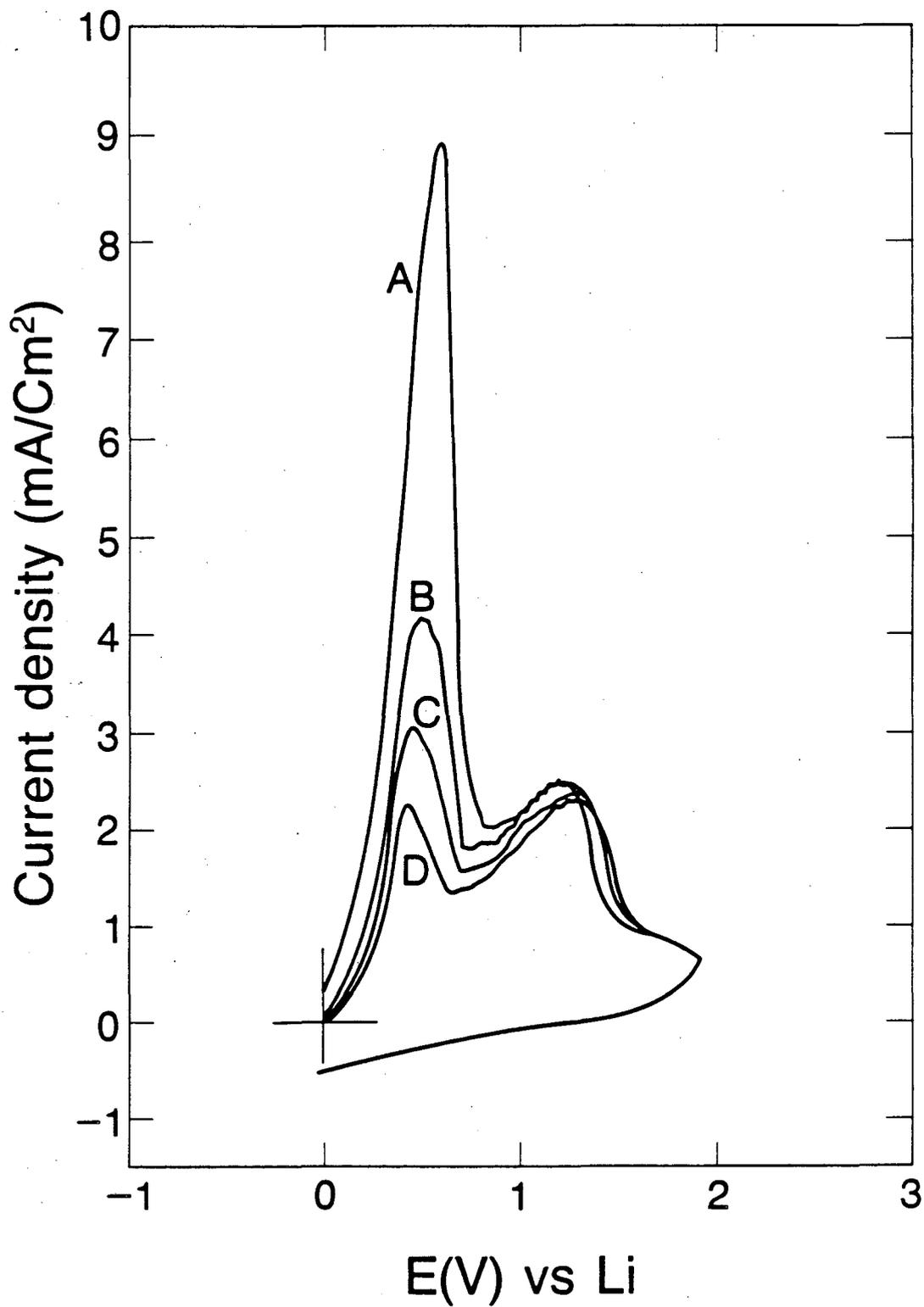
XBL 8410-10897

Fig. 5



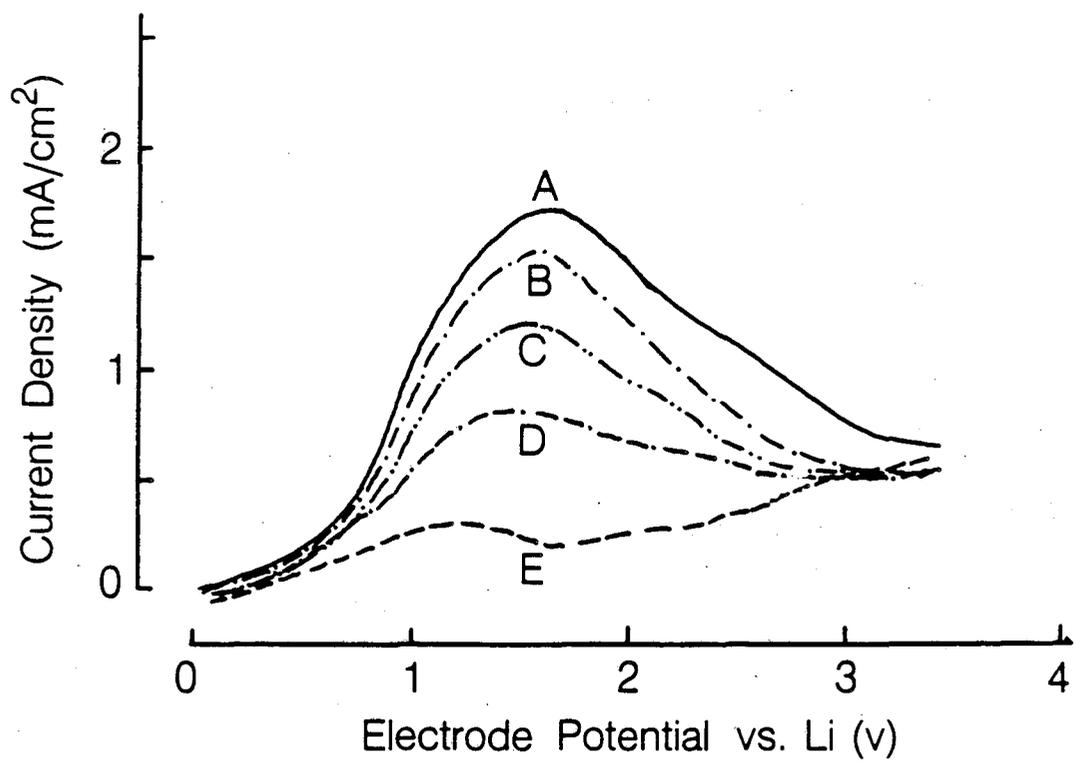
XBL 841-508 A

Fig. 6



XBL 8401-6760

Fig. 8



XBL 841-500 A

Fig. 9

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

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