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### Authors

Nazri, G.  
Muller, R.H.

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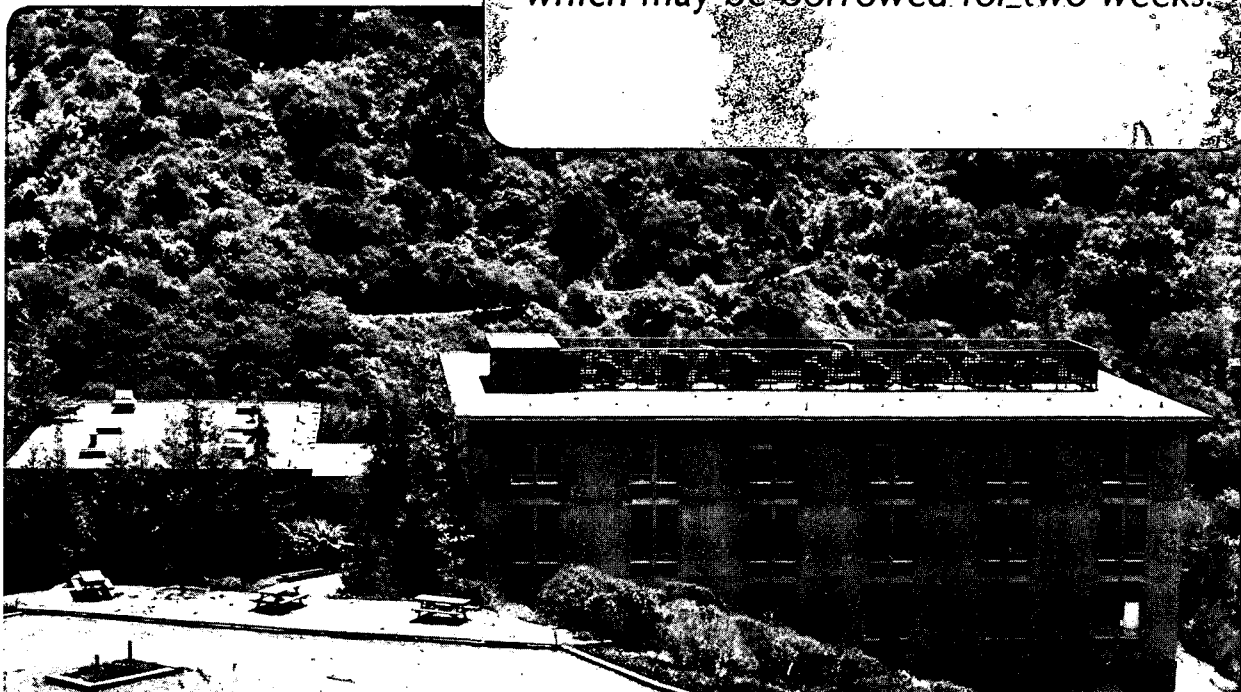
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EFFECT OF RESIDUAL WATER IN PROPYLENE CARBONATE  
ON FILMS FORMED ON LITHIUM

Gholamabbas Nazri and Rolf H. Muller

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

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## ABSTRACT

Low concentrations of water in propylene carbonate solutions result in the formation of protective surface layers on lithium electrodes. Increasing concentrations of water have been found by infrared spectroscopy and x-ray diffraction to result in increasing lithium oxide and decreasing carbonate and polymer content in the layers. The oxide layers are protective and greatly reduce the rate of corrosion reactions of the metal with the electrolyte. They represent the principal resistance to current passage and can be removed by breakdown at high potential. Water-free solvent interacts differently with lithium resulting in the continuous formation of lithium carbonate and polymeric materials. Use of a thin-layer cell with 10  $\mu\text{m}$  electrode separation has been shown to eliminate the effect of low concentration of water.

The structure and composition of surface layers are a major controlling factor in the dissolution and deposition of Li in ambient-temperature non-aqueous electrolytes.<sup>1-4</sup> Peled<sup>5</sup> proposed migration of  $\text{Li}^+$  in a solid electrolyte interphase as a controlling factor in the electrochemistry of lithium. The surface layers formed on Li in 1M  $\text{LiClO}_4$  and  $\text{LiAsF}_6$  in propylene carbonate (PC) have been investigated using potential pulse techniques and electrochemistry.<sup>6-8</sup> Semiconductor properties of the surface layer on Li due to defects in the crystal lattice have also been reported.<sup>9</sup> However, despite the use of various techniques, structure and composition of the surface layer formed on a Li electrode exposed to propylene carbonate (PC) containing residual water is still not definitely known. Decomposition of the PC in contact with lithium and formation of  $\text{Li}_2\text{CO}_3$  as a surface layer has been postulated by several authors.<sup>10,11</sup> However, such a composition cannot fully explain the behavior and properties of the layers, and is not in agreement with optical observations.<sup>7,8</sup> The effect of electrolyte impurities on the performances of Li batteries, although extensively investigated, is not well understood.<sup>11,12</sup> Some trace impurities such as  $\text{H}_2\text{O}$ ,  $\text{O}_2$ , and  $\text{N}_2$  have been found to favorably affect the cycle life of lithium anodes.<sup>11,12</sup>

One of the major problems in electrochemical studies of Li is the purification of the electrolytes. Distillation of solvents does not remove traces of water and more than 10 ppm of residual water is often detected. Several procedures for purification of electrolytes have been established.<sup>10,13,14</sup> These procedures include the pre-electrolysis of salts, recrystallization of salts and drying under vacuum, storage of solvents on molecular sieves and distillation of solvent along with the treatments with Li amalgam or Na/K (50/50) alloy. Distillation of solvent after treatment with

amalgam or NaK alloy is desirable to remove decomposition products of the solvents which may form during treatment. Purification of non-aqueous electrolytes is a tedious and time consuming process. Since most of the procedures being used today are open to questions, an effective way to minimize the effect of impurities is to use a small amount of electrolyte (less than a drop) after reasonable purification. A thin-layer cell has been used for that purpose. Another difficulty in electrochemical studies of Li is the existence of an initial film on the Li electrode. Even in an inert atmosphere box with less than 1 ppm  $O_2$ ,  $H_2O$ , and  $N_2$  a film will form on the surface in less than one second. Some research groups produced clean electrode surfaces in-situ by mechanical removal of the surface layer, electrochemical pulse cleaning, or deposition of Li on metallic substrates.<sup>15,19</sup>

The objective of this work is to understand the structure and composition of the surface layer formed on Li in PC, 1M  $LiClO_4$  containing residual water. The effect of impurities has been minimized by use of a thin-layer cell. The composition and structure of the surface layers has been analyzed using ex-situ and in-situ X-ray diffraction and transmission IR spectroscopy. The role of the residual water was also studied using potential cyclic voltammetry and potential pulse measurements.

#### EXPERIMENTAL PROCEDURE

$LiClO_4$  has been recrystallized from water and dried under vacuum at  $150^\circ C$ . The dehydration of  $LiClO_4$  has been studied by thermogravimetry. All physically and chemically adsorbed water is released below  $150^\circ C$  at  $10^{-3}$  torr. After treatment with Li amalgam, the concentration of water in PC was below the

detection level of the GC (1 ppm).

A cylindrical cell and a thin layer cell have been used in this work. The cylindrical cell<sup>7,8</sup> contains two parallel disc electrodes of 1.9 cm diameter, 3 cm apart from each other. One of these discs served as working electrode, the other as counter electrode. The reference electrode was a Li wire with diameter of 3 mm forced into the polypropylene in such a way that only its cross-section was exposed to the electrolyte. The distance between reference and working electrode was about 2 mm. The two optical windows on this cell have been used in previous ellipsometric studies.

A thin-layer cell has also been used. Its design is shown in Fig. 1. A pellet of lithium (Foot Mineral Co., 1.22 cm diameter and 0.6 cm height) is held between two stainless steel current collectors contained in polypropylene rods. This lithium is cut in half by use of a stainless steel wire of 0.5 mm diameter with the two halves serving as working and counter electrodes. A drop of electrolyte was placed between the two electrodes and the gap between them was adjusted to 10  $\mu\text{m}$  using a micrometer which carried one of the electrodes on its non-rotating tip. Although the thin-layer cell was operated inside the inert atmosphere box (Vacuum Atmospheres Co.), with concentration of  $\text{O}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{N}_2$  of less than 1 ppm, a polyethylene bag was placed around the cell for further isolation. This bag could be collapsed by evacuation and refilled with ultrapure He from a separate supply. This system also enabled us to expose the electrodes to any gas without contaminating the dry box atmosphere. An application of the capability will be reported separately.

The formation of surface layers on Li has been studied potentiostatically and galvanostatically using a PAR potentiostat, programmer and coulometer. During potentiostatic pulse measurements the results have been monitored by a



storage oscilloscope, then recorded by an X-Y recorder (H-P 7044B). Copper was mostly used as a substrate because of its optical properties, although alloy formation occurred with Li, as was the case for Ag, Au and Pt and to a lesser degree with Ni and stainless steel. The Cu substrates were successively polished with 600 emery paper, 1  $\mu\text{m}$  and 0.25  $\mu\text{m}$  diamond paste. They were then cleaned in ethanol, dried in pure He and washed with dry PC in the glove box. Electrode potentials have been corrected for IR drop in the solution, determined at the beginning of an experiment by conventional current interruption techniques.

The composition of surface layers formed on Li in PC, 1M  $\text{LiClO}_4$  with different water concentrations has been analyzed by transmission IR spectroscopy. The Li electrode was washed with dry PC and then evacuated for evaporating the solvent. The surface layer on the electrode was collected from the dried electrode by a glass rod and ground with KBr in the dry box. A pellet of the mixed powder was made for transmission IR spectroscopy. During the measurement, the sample chamber of the IR machine was purged with pure Ar gas. The decomposition products of the PC on Li amalgam have also been analyzed using the IR spectrometer. The IR spectrum of the surface layer was compared to the spectra of PC,  $\text{Li}_2\text{CO}_3$  and  $\text{Li}_2\text{O}$ . The Li electrode was potentiostatically cycled 20 times by sweeping the potential ( $\pm 2\text{V}$  vs. Li) at a rate of 20 mV/s. The electrode was removed from the electrochemical cell, washed with dry PC and isolated inside a propylene transfer cell with a Mylar window for the collection of X-ray diffraction data from the electrode surface. The design of the transfer cell for x-ray diffraction analysis is shown in Fig. 2.

In-situ x-ray diffraction of surface layers formed on Li electrodes

during anodic and cathodic polarization has been presented separately.<sup>20</sup>

## RESULTS AND DISCUSSION

The effect of residual water in PC, 1M LiClO<sub>4</sub> on Li electrodes has been studied using sampled current voltammetry.<sup>21</sup> The experiments have been performed with dry and wet PC in both the cylindrical and the thin-layer cells. A potential step has been imposed on the working electrode and the current response as a function of time has been measured for each potential step. The current observed 1 sec. after application of the potential step is shown in Fig. 3 as a function of the potential. In these measurements the double-layer charging does not affect the measured current. The advantage of this technique is that at the beginning of each potential step the concentration of electrolyte at the interface is the same because the bulk concentration is allowed to be reestablished before the next pulse is applied. As shown in Fig. 3, the current density observed with dry electrolyte is much higher than that in the presence of water. This result may be due to the presence of an oxide film on the electrode surface which forms by reaction of Li with H<sub>2</sub>O before application of the potential step. The film appears to break down at higher potentials. The resulting current density depends on the concentration of water in the electrolyte and the time for which the electrode has been exposed to it before the measurements are taken. The formation of an oxide layer on the electrode surface by trace amounts of water has been credited for the higher cycling efficiency of Li anodes in the presence of residual water.<sup>10</sup>

The ability of the thin-layer cell to discriminate against the effect of residual water in the electrolyte is illustrated in Fig. 4. Cyclic voltammetry of Li in PC, 1M LiClO<sub>4</sub> containing 300 ppm water, using thin-layer cell and cylindrical cell, are compared. Higher current densities are obtained in the thin-layer than in the cylindrical cell. In addition, the anodic dissolution of Li in the thin-layer cell does not show the passivation seen with the cylindrical cell. Similarly, experimental results from the thin-layer cell for electrolyte with 500 ppm water have been found to be almost the same as those with dry solution (less than 1 ppm water) obtained in the cylindrical cell which contains 20 cc of solution.

Delay-time phenomena in the passivation and activation are illustrated in Fig. 5. Four successive potential pulses of 40 s duration have been applied to the Li working electrode in the cylindrical cell containing 20 ml of dry PC, 1M LiClO<sub>4</sub>. The current response to each subsequent potential pulse at different potential varies as

$$i_1 < i_2 < i_3 < i_4 \quad \text{for } 0.2 < E < 1.6V \text{ vs. Li}$$

and

$$i_1 > i_2 > i_3 > i_4 \quad \text{for } 1.6 < E < 3.0V \text{ vs. Li}$$

where  $i_1$ ,  $i_2$ ,  $i_3$ , and  $i_4$  are currents corresponding to the first, second, third, and fourth pulses. Up to a pulse height of 1.6V the current increases with time and the response to the first pulse is smaller and builds up more slowly than the response to subsequent pulses. This behavior indicates that

film removal (or breakdown) takes place during the first pulse and continues to a lesser degree during the succeeding pulses. These results are in agreement with a diffusion-limited migration of Li ions through the interface. For potential steps higher than 1.6V the current decreases with time and the initial current response to the first pulse is lower than the initial response to subsequent pulses, indicative of a film-removal process, as in the low-potential regime. However, after a few seconds, the current for the first pulse remains higher and declines less rapidly than that of subsequent pulses. This behavior indicates a limitation of the dissolution rate by mass transfer or film formation at high current densities. Below 0.2V the current densities are the same for the four pulses, showing that the film remains intact and Li ions migrate through it. Removal of the film from the electrode surface by successive anodic pulses can be used for cleaning the Li surface in-situ.

Lithium was galvanostatically deposited on a Cu substrate from PC, 1M  $\text{LiClO}_4$  at  $30 \text{ mA/cm}^2$  with a Li counter electrode for a thickness of  $1000 \text{ \AA}$  based on Li bulk density. The formation of Li deposits on Cu with 60-70% current efficiency was determined by immersion in water and measurement of  $\text{H}_2$  evolved. Higher current efficiencies had been found with stainless substrates. In-situ x-ray diffraction also showed the presence of Li metal. The open circuit potential of the Li electrode, vs. Li reference, has been monitored with electrolytes of different water content (Fig. 6). Immediately after deposition, the cell voltages were almost independent of water content. The potential of the electrodeposited Li is different from that of bulk Li (used as reference) probably because it represents a mixed potential of alloy, corrosion products, UPD and substrate. Similar anomalous potentials have been observed for Li deposits on Cu in 2 Me-THF,  $\text{LiClO}_4$ . At later times, a potential

characteristic of the substrate is reached much faster when no water is present. This observation shows that no protective film is formed on the electrode surface in the absence of water, allowing Li to continue to react with the electrolyte. The resistivity of the Li electrode is much higher with higher concentrations of water in the electrolyte, in agreement with the formation of a thicker, more resistive and protective oxide film. The oxide film does not fully protect the Li electrode but greatly reduces the rate of reaction with the electrolyte.

The surface layers formed on Li in PC, 1M LiClO<sub>4</sub> containing different concentrations of water have been analyzed by transmission IR spectroscopy. Comparison to the spectra of Li<sub>2</sub>O and Li<sub>2</sub>CO<sub>3</sub>, obtained by the same procedures, shows that increasing concentrations of water result in increased Li<sub>2</sub>O (3560 cm<sup>-1</sup>), and decreased Li<sub>2</sub>CO<sub>3</sub> (860, 1430, 1500 cm<sup>-1</sup>) and C-Cl (620 cm<sup>-1</sup>) content (Fig. 7). This result is consistent with the view that a partially-protective oxide layer reduced the rate of lithium corrosion and solvent decomposition. Cyclic voltammetry with a Cu electrode in PC, LiClO<sub>4</sub> showed that PC decomposes anodically above 3.5V vs. Li (Fig. 8). Similar results have been obtained with Ni, Ag and SS electrodes; with Pt decomposition occurs at a lower anodic potential.

A Li electrode that had been cycled anodically and cathodically in PC, 1M LiClO<sub>4</sub> 20 times between ±2V vs. Li at a sweep rate 20 mV/s was subjected to analysis by x-ray diffraction. For this purpose, the electrode was removed from the cell, washed with dry PC and inserted in the transfer cell with Mylar window for placement in the diffractometer. A diffraction pattern of this electrode, shown in Fig. 9, confirms the presence of Li<sub>2</sub>O, and Li<sub>2</sub>CO<sub>3</sub> apart from Li. A noncrystalline (probably polymeric) material, which appears to

result from reactions of the solvent, is indicated by a broad peak at low  $2\theta$ . The same film materials have been identified by in-situ x-ray diffraction.<sup>20</sup> The formation of a polymeric membrane has been reported by Epelboin et al.<sup>23</sup>

### CONCLUSIONS

Composition and properties of surface layers on lithium electrodes in propylene carbonate solutions, which are mainly responsible for the performance of this electrode, have been analyzed. The layers are strongly affected by small amounts of water in the solutions. The formation of an oxide in an earlier-postulated<sup>8</sup> inner layer in the presence of water, has been confirmed. This layer greatly reduces the rate of Li corrosion, which occurs in its absence under formation of carbonate and polymer products. At low current density migration of Li ion through this film appears to control the rate of dissolution and deposition of Li. The effect of low to moderate concentrations of water (and other electrolyte impurities) on the lithium electrodes can be avoided by use of a small electrolyte volume in a thin-layer cell.

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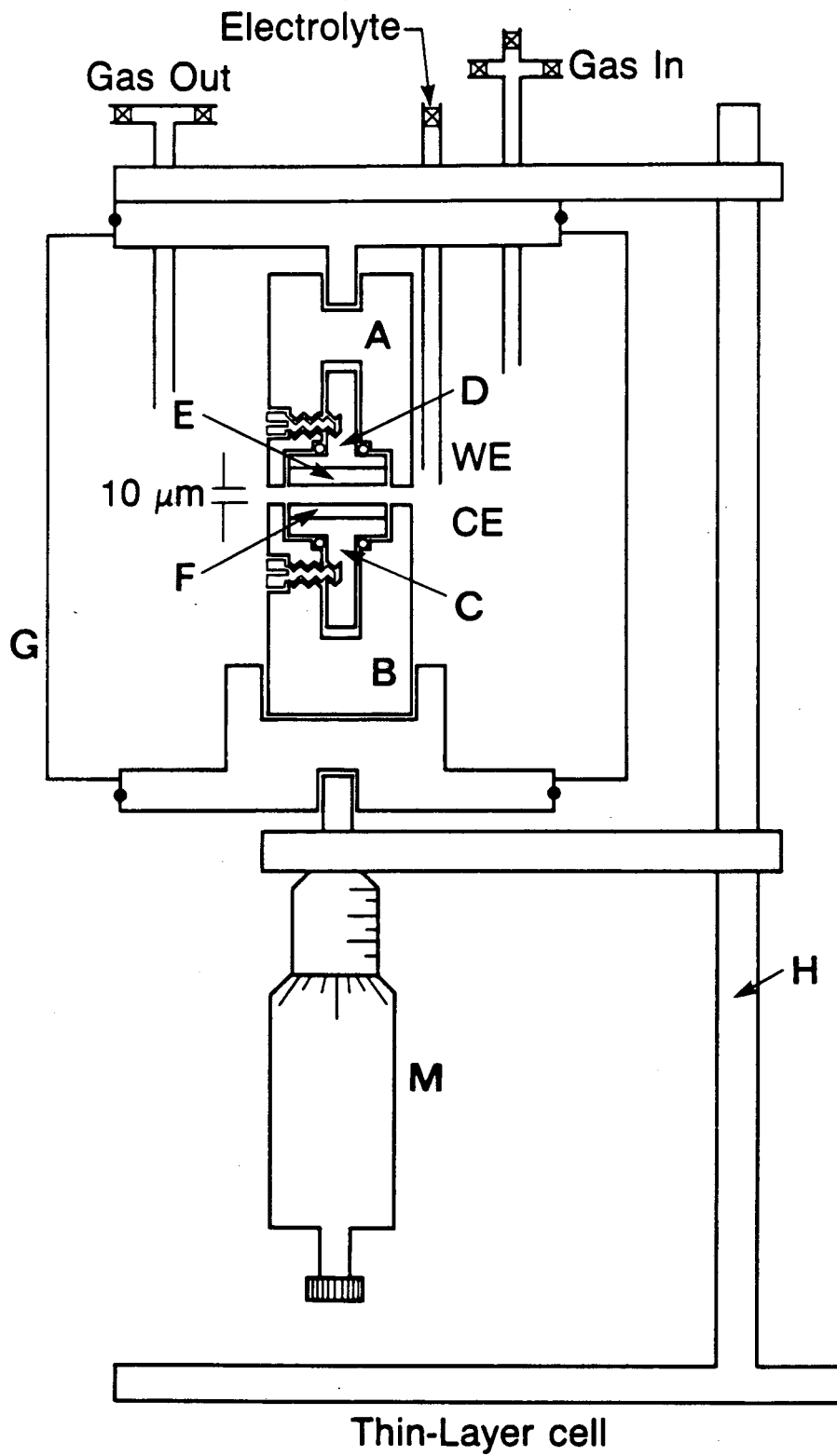
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### Figure Captions

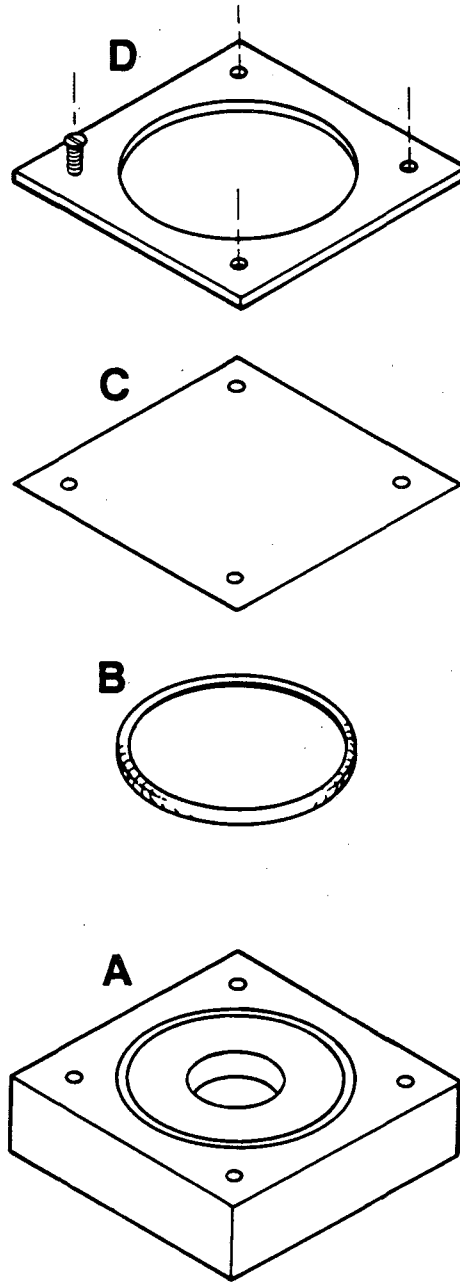
- Fig. 1 Schematic of the thin-layer cell for non-aqueous electro-chemistry. WE - working electrode; CE - counter electrode, 10  $\mu\text{m}$  gap set after cutting of electrodes from single piece in inert atmosphere, M - non-rotating tip micrometer, A and B - polypropylene electrode holder, C and D - Stainless steel current collectors, E and F - Li electrodes, G - polyethylene bag for control of atmosphere at the electrodes by use of gas inlet and outlet, and H - aluminium stand.
- Fig. 2 Schematic of the transfer cell for X-ray diffraction analysis of surface layers on Li electrodes; A - cell body made of polypropylene, with a cylindrical cavity in the center for the electrode and a groove around the cavity for O-ring seal, B - O-ring, C - Mylar window, and D - Cu washer.
- Fig. 3 Effect of water content and volume of the electrolyte on sampled-current voltammetry of Li electrodes in (A) dry PC, 1M  $\text{LiClO}_4$ , 20 cc cylindrical cell, (B) same solution containing 300 ppm water, 20 cc cylindrical cell, (C) same solution containing 500 ppm water, thin-layer cell. Potentials (A) and (B) corrected for IR drop in solution; (C) represents cell voltage.
- Fig. 4 Cyclic voltammetry of Li electrodes in PC, 1M  $\text{LiClO}_4$  containing 300 ppm water using ——— thin layer cell, and - - - - cylindrical cell containing 20 cc electrolyte. The electrode surface areas were the same in both cells. IR-free electrode potential shown for cylindrical cell, cell voltage for thin layer cell.

- Fig. 5 Potential pulse measurements (I vs. t). Response to first pulse —, second pulse - - - -, third pulse - · - · - ·, and fourth pulse - · - · - ·. Height of anodic pulse listed in Volts; potentials corrected for IR drop in solution (dry PC < 1 ppm H<sub>2</sub>O, 1M LiClO<sub>4</sub>); pulse duration 40s, current response shown only for first 20s.
- Fig. 6 Effect of water content in the electrolyte on the potential of electrochemically deposited Li (1000Å) on a Cu substrate at open circuit vs. Li reference electrode. PC, 1M LiClO<sub>4</sub> with different H<sub>2</sub>O content.
- Fig. 7 IR spectra of the surface layers on a Li electrode formed after 20 cycles ± 2V vs. Li in PC, 1M LiClO<sub>4</sub> containing (A) less than 1 ppm, (B) 500 ppm, and (C) 1% water; (D) spectrum of the Li<sub>2</sub>O.
- Fig. 8 Cyclic voltammetry of Cu electrode in PC, 1M LiClO<sub>4</sub> showing decomposition of PC above 3.5 V vs. Li.
- Fig. 9 X-ray diffraction of the surface layer formed on a Li electrode electrochemically cycled in PC, 1M LiClO<sub>4</sub> containing 700 ppm water, showing presence of Li<sub>2</sub>CO<sub>3</sub>, Li<sub>2</sub>O and a polymeric compound.



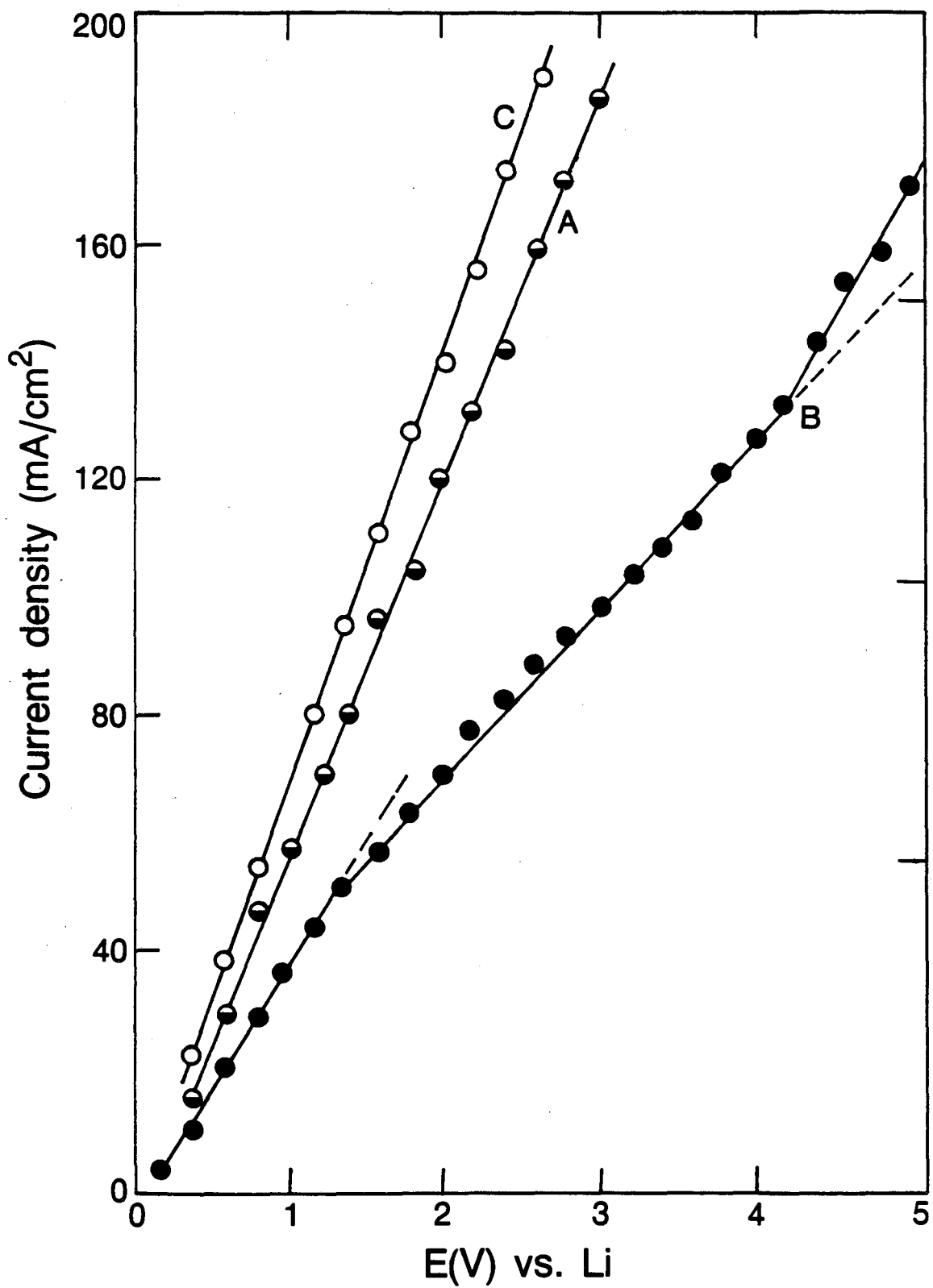
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Fig. 1



XBL 845-8904

Fig. 2



XBL 848-8556

Fig. 3

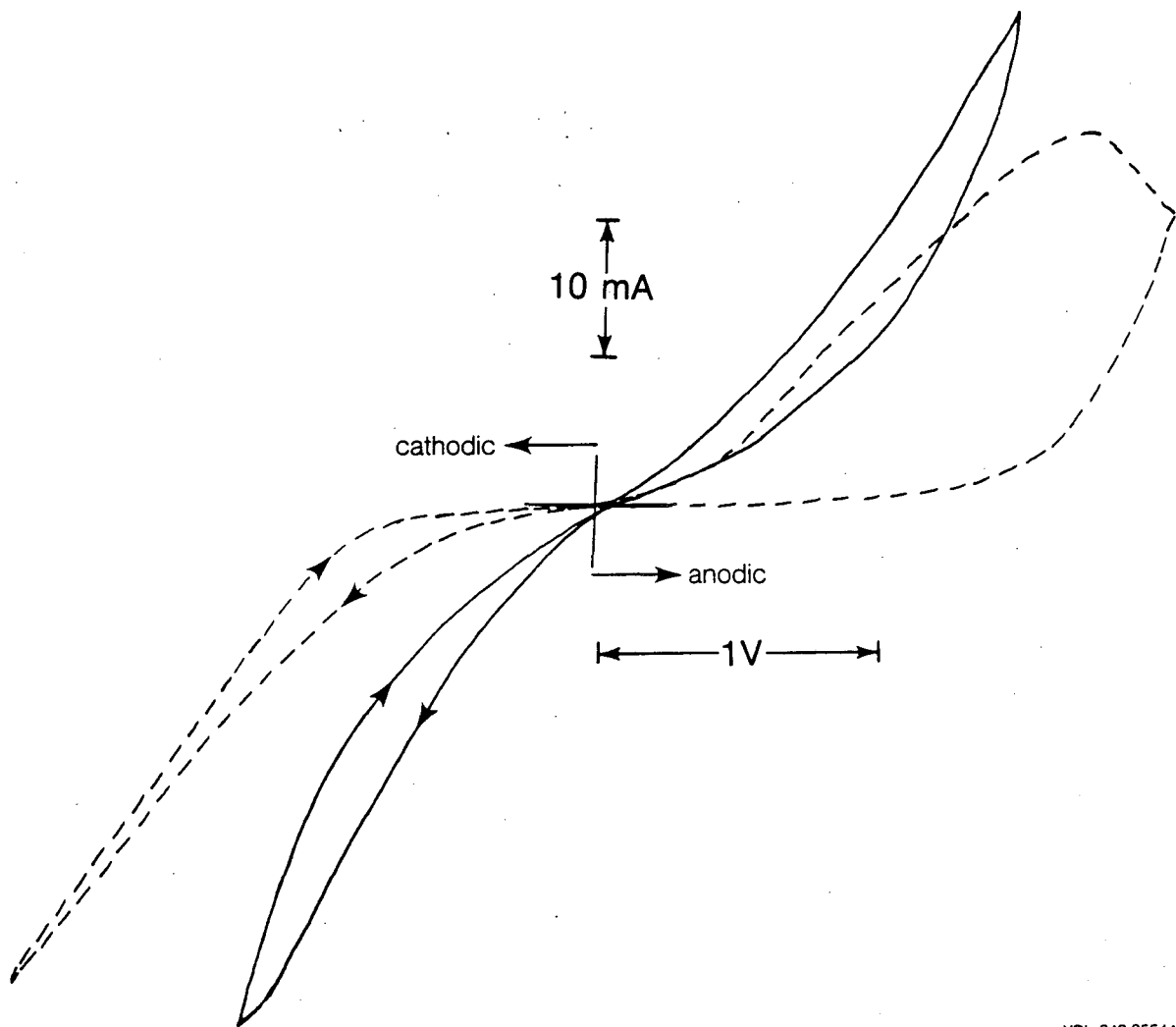
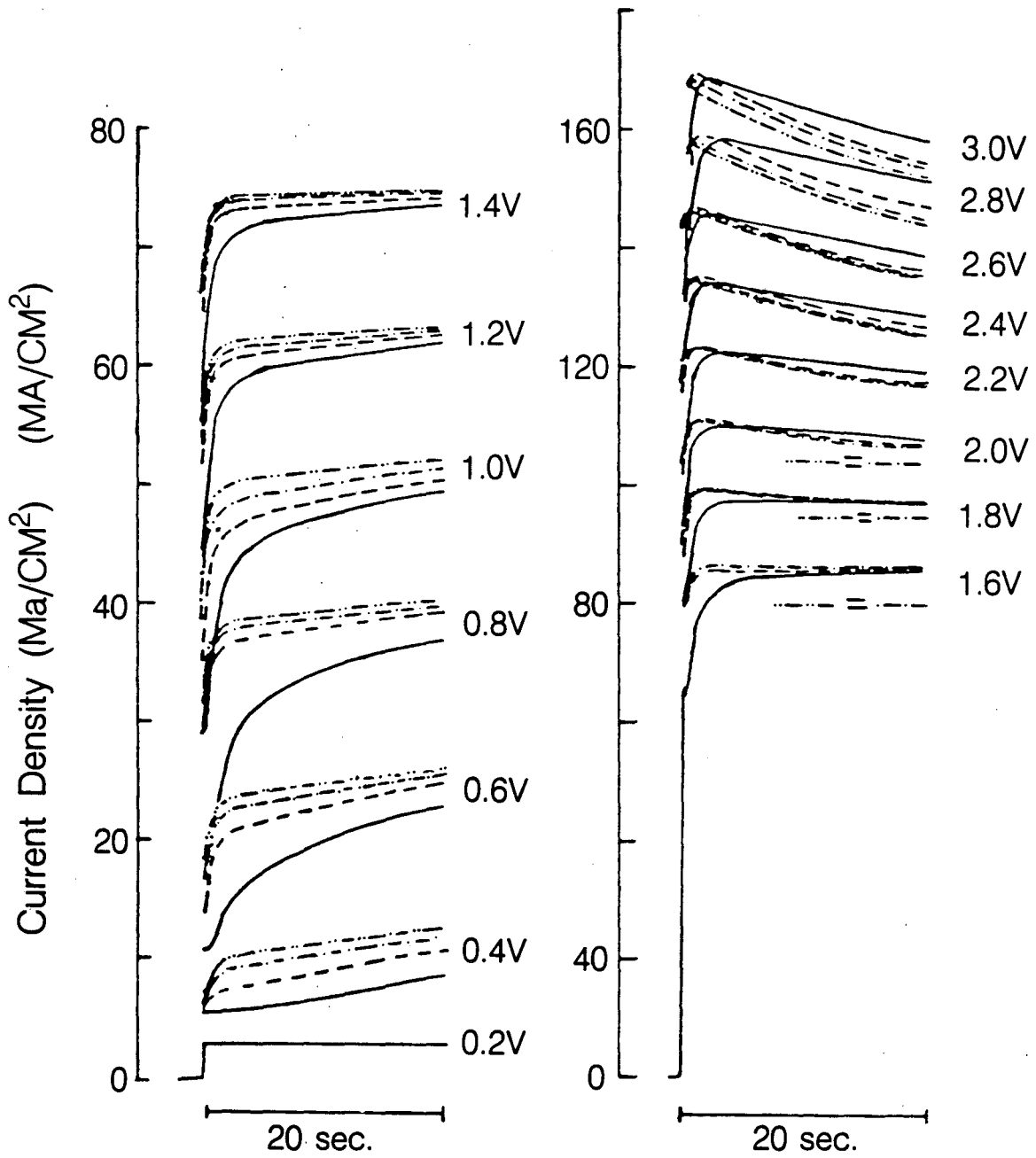


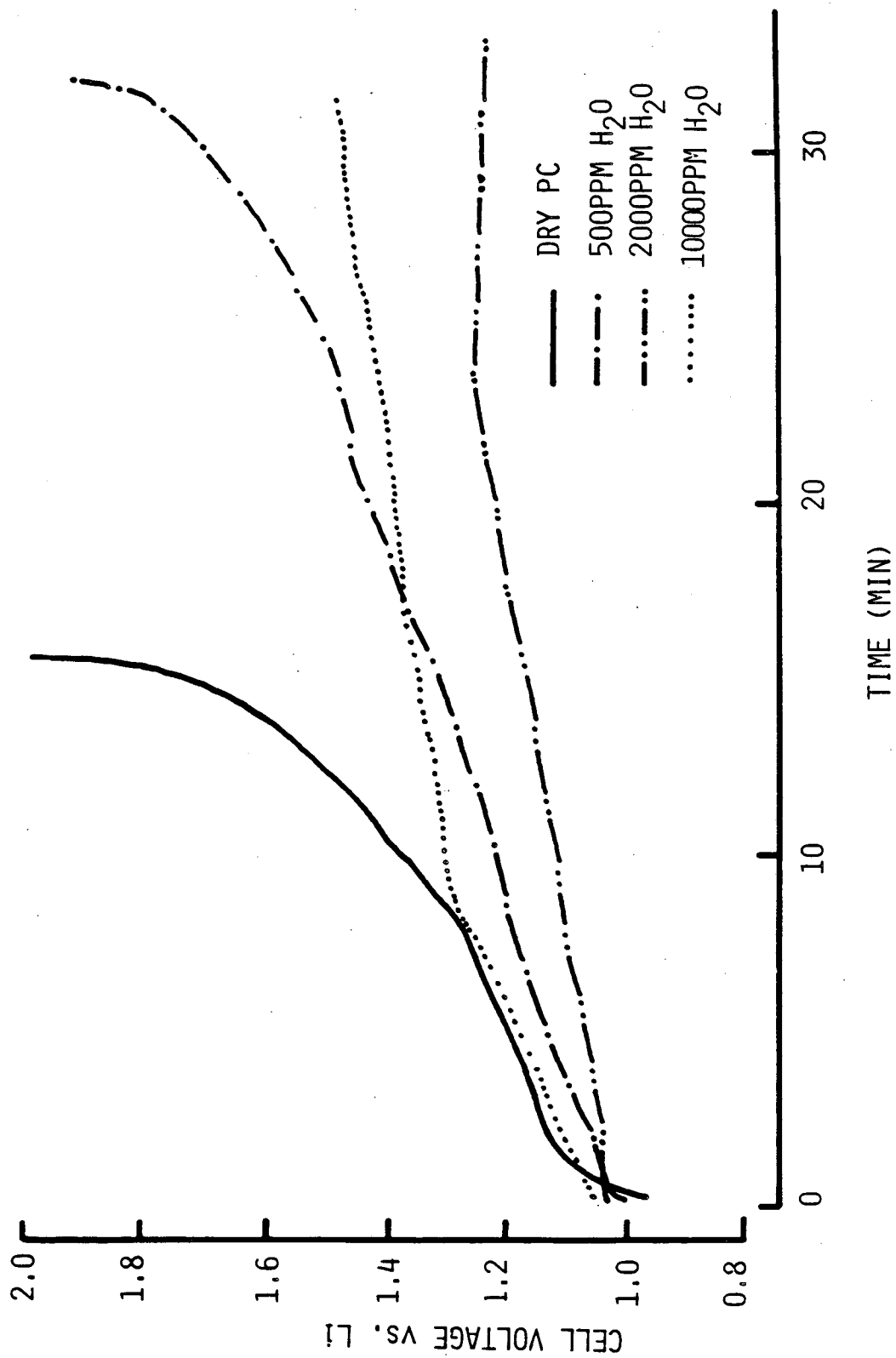
Fig. 4

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XBL 848-3362A

Fig. 5



XBL 839-11894

Fig. 6



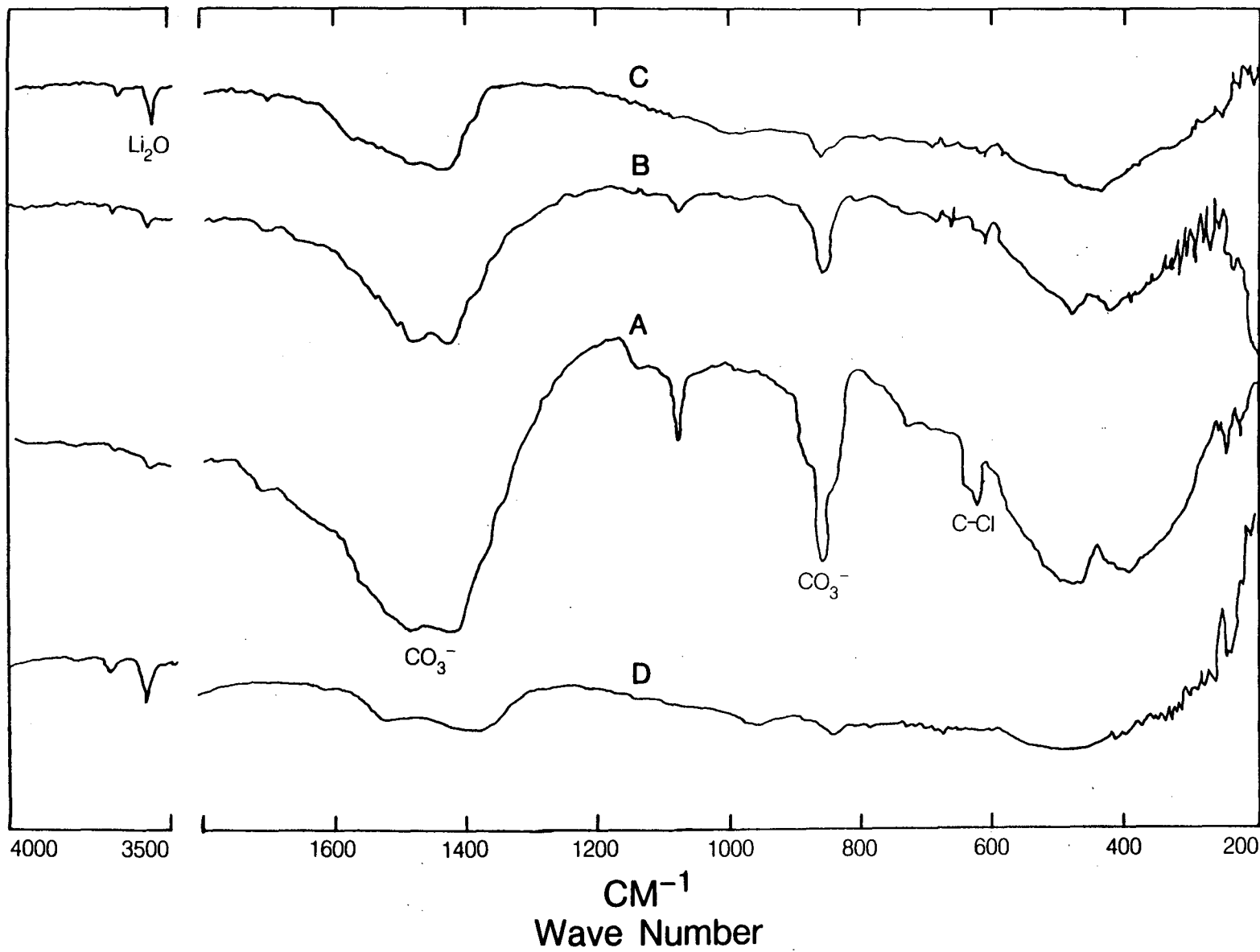
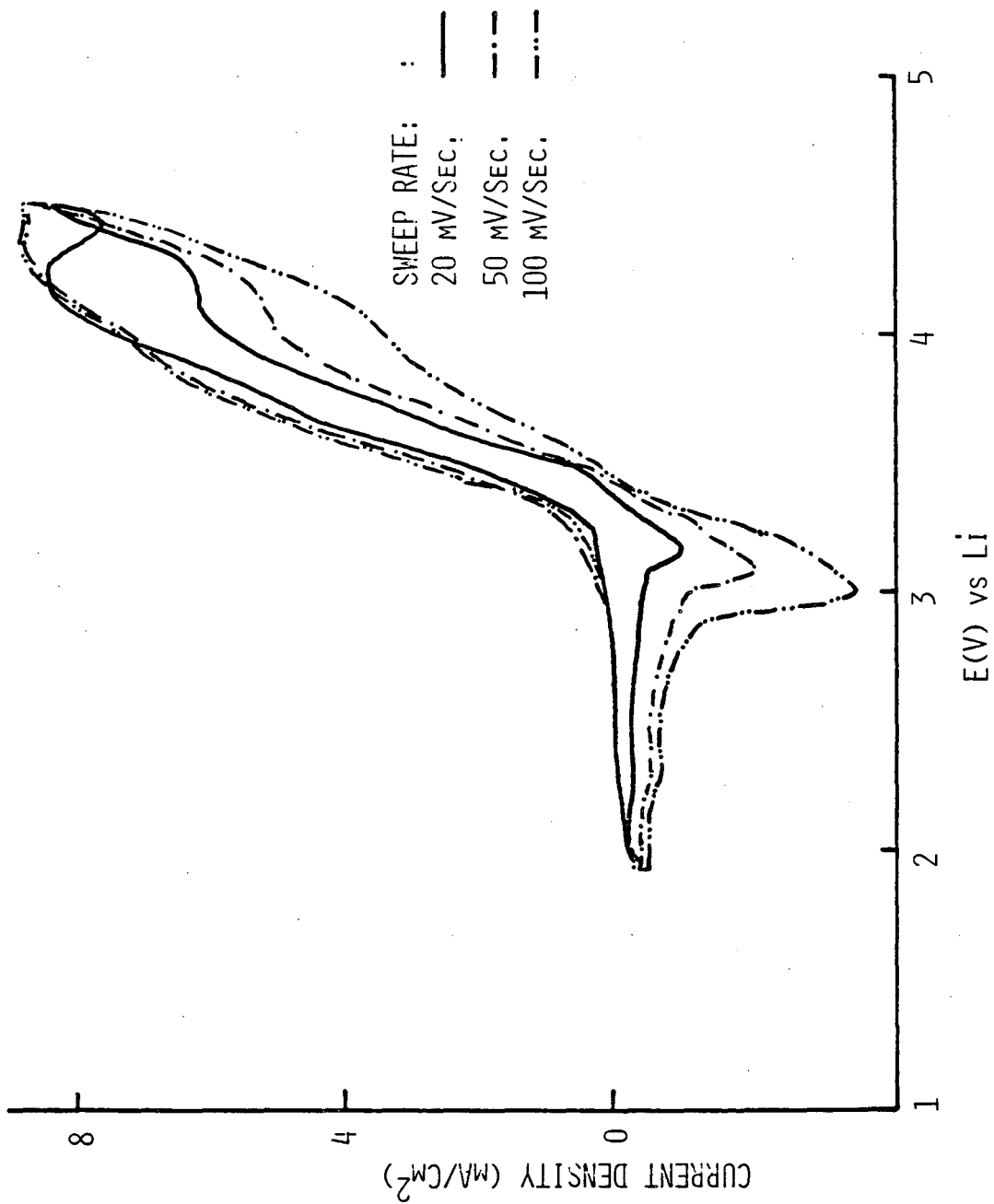


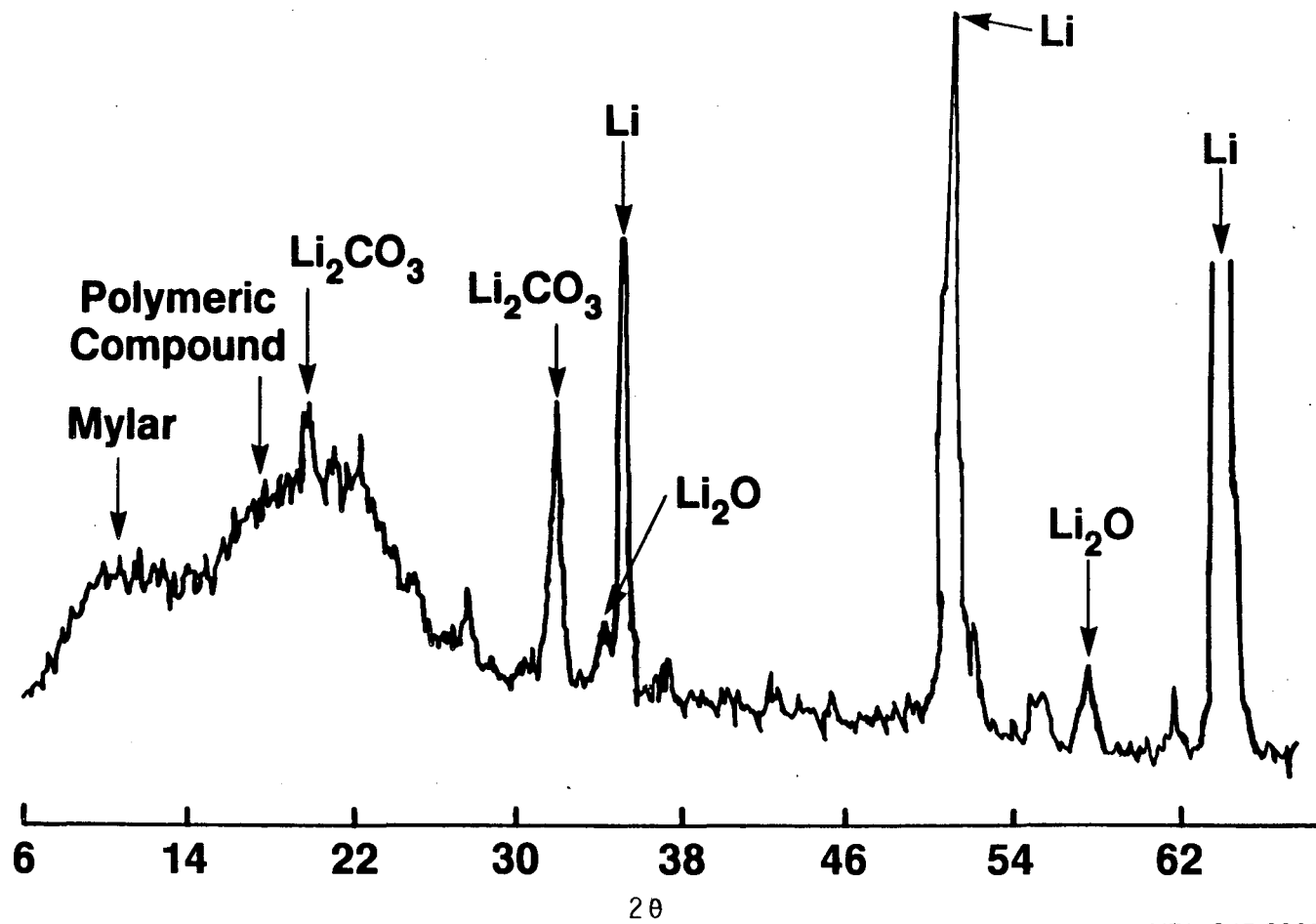
Fig. 7

XBL 848-8555A



XBL 841-497

Fig. 8



XBL 845-8905

Fig. 9

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