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PC, LiClO<sub>4</sub> OF VERY LOW WATER CONTENT

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April 1985

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LBL-18197 Rev.

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COMPOSITION OF SURFACE LAYERS ON Li ELECTRODES  
IN PC,  $\text{LiClO}_4$  OF VERY LOW WATER CONTENT

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ABSTRACT

Surface layers formed on Li in PC,  $\text{LiClO}_4$  with less than 1 ppm of water have been analyzed by use of IR Spectroscopy, SIMS, ESCA, low-angle x-ray diffraction, and SEM. Electrodeposited Li showed a highly porous micromorphology with surface layers containing primarily a partially chlorinated hydrocarbon polymer and lithium carbonate. The carbonate is mostly present in the inner film regions, the polymer in the outer. Perchlorate decomposes to chlorine compounds of lower valences, with higher-valent chlorine found in the outer film regions, lower-valent in the inner.

## INTRODUCTION

The electrochemistry of the alkali and alkaline earth metals in ambient temperature nonaqueous electrolytes has been reviewed by several authors.<sup>1-6</sup> The electrolytic deposition and dissolution of Li from aprotic electrolytes with high efficiency is of interest for the operation of ambient-temperature high energy-density rechargeable Li batteries. Surface layers which spontaneously form on the metal protect it to varying degrees from corrosion but are mainly responsible for the poor rechargeability of the lithium electrodes.<sup>7,8</sup>

Great efforts have been made during the last decade to prevent or minimize the formation of surface layers. Improvements have been achieved by the molecular modification of solvents<sup>9,10</sup> and the use of lithium alloys as anodes,<sup>11-14</sup> while the effectiveness of solvent purification to improve electrode performance has not been uniform. In some cases, trace amounts of water or reactive gases such as  $\text{SO}_2$ ,  $\text{O}_2$ , and  $\text{N}_2$  have been found to improve the cycling efficiency of the lithium anodes.<sup>6</sup> Reaction products of Li with solvent have been reported to be more detrimental to the Li morphology and cycle life than the products formed by Li-protic reactions.<sup>15</sup> Dey and Sullivan showed that propylene carbonate (PC) decomposes on a graphite electrode below + 0.6V vs. Li.<sup>16</sup> Rauh and Brummer claim that one of the reasons for the poor rechargeability of Li electrodes is the corrosion of the lithium anode at grain boundaries resulting in an electrical isolation of lithium particles from the substrate by corrosion products. This isolated metal is not available for stripping during the next anodic cycle.<sup>17</sup> Dey

also showed that a lithium electrode after charge and discharge had a porous structure. Epelboin et al.<sup>13</sup> found that surface layers are formed on Li electrodes in PC, 1M LiClO<sub>4</sub> during charge, discharge and at open-circuit. Yen et al.<sup>18</sup> carried out ESCA studies of the surface layer on lithium which had been cycled in a 2Me-THF, 1.5M LiAsF<sub>6</sub> electrolyte. They found Li, C, O, As and F on the surface of discharged Li. A polymerization of AsOF on the surface has been proposed.<sup>13</sup> The effect of light on the polarization on lithium electrodes in PC has been studied by Povarov and Sitnina.<sup>19</sup> They found that the anodic current of Li decreases and the cathodic current increases during exposure of the electrode to visible light. They concluded that a passive film formed on Li in PC possesses semiconducting properties. The sign of the effect indicates a p-type semiconductor. Although the electrons and holes are formed under the influence of light, the main carrier of current through the passive film is Li ions.<sup>19</sup>

Understanding the structure and composition of surface layers on lithium is important for further progress in the development of the rechargeable ambient-temperature Li batteries. The objective of this work was to elucidate the nature of the films on lithium and their role during charge and discharge of Li electrodes by use of different experimental techniques, in particular, IR spectroscopy, x-ray diffraction, ESCA, SIMS, and SEM.

## EXPERIMENTAL

Propylene carbonate (PC) (Burdick and Jackson) has been used as a solvent. After vacuum distillation, GC analysis usually showed a water content of 20-30 ppm (Propac column, 110°C injection temperature). Treatment of the distilled solvent with Li amalgam resulted in a water content which was below the detection limit of GC (1 ppm).

The  $\text{LiClO}_4$  (G. Frederick Smith) used for the experiments has been recrystallized three times from ultrapure water and dried under vacuum at 240°C for 12 hours. The water content of  $\text{LiClO}_4$  before and after vacuum drying has been measured by use of a vacuum oven with differential pressure change equipment, a digital pressure gauge and a mass spectrometer. The sample was placed in the vacuum oven in a ceramic crucible with a thermocouple in its center. The temperature of the oven was scanned from 25°C to 800°C at 3 deg/min. After each sudden change in pressure, the mass spectrum of the released gas was monitored to determine its chemical composition. Thus, the water content of vacuum dried  $\text{LiClO}_4$  ( $10^{-4}$  torr, 160°C) was found to be much below 1 ppm. Cyclic voltammetry in the PC,  $\text{LiClO}_4$  electrolyte with Pt electrodes also showed a water content below 1 ppm.

Cyclic voltammetry with platinum electrodes of 1.0 and 1.5M  $\text{LiClO}_4$  solutions with PC solvent prepared as described above, indicated a water content of less than 1 ppm for the solutions. Before each experiment, two auxiliary electrodes of Li (2 x 2 x 0.3 cm), placed in the same cell, were used to further purify the solutions by potentiostatically cycling these electrodes between ±2V vs. a Li reference electrode at 50 mV/s for 15-20

cycles. The resulting electrolyte has been used for the experiments reported here.

Electrochemical experiments have been performed in a dry box (Vacuum Atmospheres) equipped for removal and analysis of oxygen, water and nitrogen. The  $O_2$  and  $H_2O$  content of the He in the inert atmosphere box was measured continuously with a calibrated  $O_2$  fuel cell sensor (Vacuum Atmospheres A 0 316-H) and a solid state moisture sensor (Vacuum Atmospheres AM-2), both of them sensitive to less than 0.1 ppm. These components, in addition to  $N_2$ , were also measured with a calibrated gas chromatograph (Vacuum Atmospheres AN-1). Concentrations of about 10 ppm of  $O_2$  and  $H_2O$  and 50 ppm of  $N_2$ , normally achieved, were lowered to less than 1 ppm by use of a stirred pool of lithium amalgam exposed to the dry box atmosphere (He). Li sheet of 3 mm thickness (Foote Mineral 99.99%) has been used for the preparation of electrodes, unless the metal was cathodically deposited on Cu or Ni substrates. Reference and counter electrodes were always made of solid Li.

The composition of surface layers on bulk or electrodeposited Li has been analyzed by transmission IR spectroscopy after removal from the surface with a glass rod. Surface layers on electrochemically deposited Li have been characterized by ESCA, SIMS, AES and SEM. For these studies, the electrode was washed with dry PC after formation of the surface layer. The electrode was then entered into a He-filled transfer chamber which had been placed inside the dry box. After connection to the pre-evacuation chamber of the ESCA/SAM/SIMS system, the transfer chamber was purged 3-4 times with ultrapure Ar for removal of He, and evacuated for transfer of the specimen to the main vacuum chamber with a magnetic transfer rod. XPS spectra for Li, O, C and Cl have been collected after different times of Ar ion bombardment.

The Li and O spectra were broad and are not shown here. The sputtered area was chosen to be much (about 8 times) larger than the observed area in order to minimize redeposition and surface diffusion of sputter products. X-ray diffraction also has been employed for the analysis of surface layers. The morphology of the Li deposit and the electrode after cycling has been studied by SEM.

## RESULTS AND DISCUSSION

Li amalgam (approx. 2%) has been used to investigate the behavior of PC in contact with film-free lithium before and after removal of water. The formation of a solid, black material on the amalgam surface, and a transparent material with a scale type structure on top of it was observed. A viscous material was present at the interface of scales and electrolyte. Spectrum C in Fig. 1 represents the scale type material, spectrum D the dark solid material. Comparison with spectra A and B of  $\text{Li}_2\text{CO}_3$  and PC included in Fig. 1 shows that most of the functional groups of PC, in particular covalent  $\text{CO}_3$  ( $1030, 1170, 1790 \text{ cm}^{-1}$ ) and  $\text{CH}_3$  ( $3000 \text{ cm}^{-1}$ ) are preserved in the precipitate. A small amount of  $\text{Li}_2\text{CO}_3$  is possibly indicated in spectrum D by absorption at  $500$  and  $860 \text{ cm}^{-1}$ . The presence of residual PC in the film is not a likely cause of the observed spectral features because the procedure used for removing the solvent from the film material involved heating in vacuum. The sample chamber of the IR spectrometer was purged with Ar during the measurements.

An IR spectrum of the surface layer formed on a Li electrode in PC, 1M  $\text{LiClO}_4$  during cathodic deposition at  $1\text{mA/cm}^2$  on a Cu substrate is shown in

Fig. 2, curve B. The spectrum of this material differs from those of the precipitate formed on the amalgam (Fig. 1) in that many of the functional groups of PC are no longer present, such as covalent  $\text{CO}_3$  (700, 760, 1030). Comparison with the two calibration spectra for PC and  $\text{Li}_2\text{CO}_3$  (A and C) indicates the formation of  $\text{Li}_2\text{CO}_3$  by the presence of ionic  $\text{CO}_3$  peaks (500, 860, 1430 and  $1500\text{ cm}^{-1}$ ). Additional peaks around  $600\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$  and the special feature of the spectrum at around  $200\text{ cm}^{-1}$  show formation of other materials. The band at  $620\text{ cm}^{-1}$  may show the presence of a carbon-chlorine bond.

Previous studies<sup>20</sup> on the effect of residual water on film formation during charge and discharge of Li electrodes have shown a peak at  $3560\text{ cm}^{-1}$  due to lithium oxide in addition to the peaks due to  $\text{Li}_2\text{CO}_3$  and polymer found here. The formation of oxidic and polymeric films on bulk lithium at open circuit had been postulated earlier.<sup>21</sup> Those layers are probably too thin for observation by the present techniques.

The composition of the surface layer has also been investigated by use of ESCA with Li deposited electrochemically from PC, 1M  $\text{LiClO}_4$  on a Cu substrate. After deposition, the electrode has been washed with dry PC and evacuated. Without exposure of the electrode to air, it was inserted in the vacuum chamber of the ESCA equipment with a transfer rod (High Vacuum Apparatus Mfg.). Two different carbon 1s peaks have been observed, one at 290 eV related to  $\text{Li}_2\text{CO}_3$  and another at 284 eV typical of polymeric carbon (Fig. 3). The latter peak is often seen as a result of surface contamination, and it rapidly disappears upon sputtering (after about  $10\text{ \AA}$  removal). However, the depth profiling of the surface layer showed the peak at 284 eV decreasing only gradually while that at 290 eV increased with

sputter time. It can be concluded that  $\text{Li}_2\text{CO}_3$  is mostly present in the inner film regions, polymer in the outer, although the large internal surface of the porous deposit makes it difficult to distinguish inner and outer regions and does not allow us to derive film thicknesses from sputter times. The slight shift of the peaks in Fig. 3 at different sputter times is probably due to charging of the film and change in its thickness. The ESCA spectrum for chlorine 2p (Fig. 4) showed the presence of five different chlorine compounds in the film indicating that  $\text{LiClO}_4$  decomposes during electrochemical deposition of Li. Literature data given in Table I have been used for identifying the peaks. Depth profiling showed that chlorine of higher valence, such as perchlorate, is mostly present in the outer regions of the film, while chloride and chlorinated polymeric compounds are present in the inner regions. The mechanism of polymer formation from PC or some of its decomposition products and the chlorination of the polymer are not clear. Since propylene had been identified as a reaction product of PC with  $\text{Li}^{16}$ , it is a likely participant in polymerization reactions. Epelboin et al. concluded that  $\text{LiCl}$  exists in the film.<sup>13</sup> It is also possible that Cl ions are formed by the decomposition of  $\text{ClO}_4$ ,  $\text{ClO}_3$ ,  $\text{ClO}_2$  or  $\text{ClO}$  ions due to the sputtering.

The surface layer formed on electrochemically deposited Li on Cu has been studied using SIMS. A complex spectrum was obtained, which was difficult to fully interpret. In the low-mass range (Fig. 5) fragments of PC can be recognized. They include among hydrocarbons  $\text{CH}$  (13) and  $\text{CH}_2$  (14),  $\text{C}_2$  (24),  $(\text{CH}_2)_2$  (28),  $\text{CH}_3\text{CH}_2$  (29),  $\text{CH}_3\text{CH}_3$  (30), propylene or  $(\text{CH}_2)_3$  (42), and propane (44). Possible oxygen compounds are  $\text{CO}$  (28),  $\text{CO}_2$  (44) and ethylene oxide (44). Chlorine appears as fragments of residual perchlorate, such as  $\text{HCl}$

(36), LiCl (42) and ClO (51), but also as chlorinated organic compounds such as CHCl (48), CH<sub>2</sub>Cl (49), possibly CH<sub>3</sub>Cl (51) and (not shown in the figure) CH<sub>3</sub>CH<sub>2</sub>Cl (64). Small amounts of water may be indicated by OH<sub>3</sub> (19), LiOH (24), LiO (or Na) (23), Li<sub>2</sub>O (30) and Li<sub>2</sub>OH (31). Other lithium compounds are possibly LiC (19) and LiCH<sub>2</sub>CH<sub>2</sub> (49). After Ar ion bombardment of the surface layer, the residual gas analysis of the SIMS chamber always showed a strong Li (7) and an Li<sub>2</sub> (14) peak, which indicates the presence of occluded metallic Li in the film. Most of the low-mass SIMS spectrum had also been observed previously from surface layers on bulk Li.<sup>21</sup> In the high-mass range (Fig. 6), fragments with mass higher than that of PC (102) were observed. These are indicative of the presence of a polymeric material in the film. Most of the mass units can be represented by fragments from a partially chlorinated hydrocarbon polymer and their Li adducts such as LiCHClCHCl (103), Li-PC (109), LiCH<sub>2</sub>CHClCH<sub>2</sub>Cl (118), CH<sub>3</sub>CH<sub>2</sub>CHClCH<sub>2</sub>Cl (127), CH<sub>3</sub>CH<sub>2</sub>CHClCH<sub>2</sub>ClLi (134) and CH<sub>3</sub>CH<sub>2</sub>CHClCHClCH<sub>2</sub>Li (147).

Surface layers on electrochemically deposited Li have also been studied by in-situ x-ray diffraction. Data for galvanostatic deposition on a Ni substrate are shown in Fig. 7. The experimental procedure and the cell design used have been discussed elsewhere.<sup>22</sup> A broad peak at low 2θ angle (14-24°) which is characteristic of polymeric compounds, has been observed as was a narrow peak at 32° (2θ) characteristic of Li<sub>2</sub>CO<sub>3</sub>. In the presence of residual water diffraction lines characteristic of the oxide have been observed.<sup>20</sup>

The morphology of electrochemically deposited Li on metallic substrates has been studied using SEM. Li deposited on a Ni substrate from PC, 1.5M LiClO<sub>4</sub> is shown in Fig. 8. The electrode was washed with PC and transferred

(36), LiCl (42) and ClO (51), but also as chlorinated organic compounds such as CHCl (48), CH<sub>2</sub>Cl (49), possibly CH<sub>3</sub>Cl (51) and (not shown in the figure) CH<sub>3</sub>CH<sub>2</sub>Cl (64). Small amounts of water may be indicated by OH<sub>3</sub> (19), LiOH (24), LiO (or Na) (23), Li<sub>2</sub>O (30) and Li<sub>2</sub>OH (31). Other lithium compounds are possibly LiC (19) and LiCH<sub>2</sub>CH<sub>2</sub> (49). After Ar ion bombardment of the surface layer, the residual gas analysis of the SIMS chamber always showed a strong Li (7) and an Li<sub>2</sub> (14) peak, which indicates the presence of occluded metallic Li in the film. Most of the low-mass SIMS spectrum had also been observed previously from surface layers on bulk Li.<sup>22</sup> In the high-mass range (Fig. 6), fragments with mass higher than that of PC (102) were observed. These are indicative of the presence of a polymeric material in the film. Most of the mass units can be represented by fragments from a partially chlorinated hydrocarbon polymer and their Li adducts such as LiCHClCHCl (103), Li-PC (109), LiCH<sub>2</sub>CHClCH<sub>2</sub>Cl (118), CH<sub>3</sub>CH<sub>2</sub>CHClCH<sub>2</sub>Cl (127), CH<sub>3</sub>CH<sub>2</sub>CHClCH<sub>2</sub>ClLi (134) and CH<sub>3</sub>CH<sub>2</sub>CHClCHClCH<sub>2</sub>Li (147).

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The morphology of electrochemically deposited Li on metallic substrates has been studied using SEM. Li deposited on a Ni substrate from PC, 1.5M LiClO<sub>4</sub> is shown in Fig. 8. The electrode was washed with PC and transferred

to the SEM chamber by use of a He-filled transfer rod. Special care was taken not to expose the specimen to air by inserting it into the Ar-filled SEM air lock surrounded by an Ar-purged plastic bag. A porous structure of the deposit was observed in most cases. This porous deposit may be responsible for rapid film formation and poor rechargeability of the Li electrodes. In this structure, one can well imagine the formation of isolated regions of lithium by localized corrosion, as postulated in the literature.<sup>17</sup>

#### CONCLUSIONS

In-situ and ex-situ studies of surface layers on Li electrodes in PC-based electrolytes demonstrate that PC reacts with Li under formation of several products, primarily what appears to be a chlorine-containing polymer product and  $\text{Li}_2\text{CO}_3$ . When water is present,  $\text{Li}_2\text{O}$  is also formed.  $\text{LiClO}_4$  decomposes during potential cycling of Li electrode between  $\pm 2\text{V}$ . Surface layers are of complex composition and structure. Depth profiling of the surface layers indicates an inhomogeneous structure with concentration gradients of different components across film. Electrodeposited Li shows a highly porous micromorphology. The use of advanced in-situ techniques, such as x-ray diffraction with a position sensitive detector, with its high sensitivity and short time response, promises to provide new insight into the initial step of film formation.

### ACKNOWLEDGMENTS

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.

We wish to thank Kenneth A. Gaugler for assistance with the ESCA and SIMS measurements.

This paper is dedicated to the 60th birthday of Professor E.B. Yeager, September 26, 1984.

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Table I. Identification of C1 2p ESCA Peaks

Compound	Binding Energy (eV) C1 2p
LiCl	198
Poly Vinyl Chloride	200
$\text{C1O}_2^-$	206
$\text{C1O}_3^-$	208
$\text{C1O}_4^-$	209

Figure Captions

- Fig. 1 Infrared transmission spectra of (A)  $\text{Li}_2\text{CO}_3$ , (B) PC, (C) scale-type transparent material near Li-Hg/PC interface, and (D) precipitated dark material on Li/Hg surface.
- Fig. 2 IR spectra of (A) PC, (B) film formed on 1000Å thick Li, electrochemically deposited on Cu from PC 1M  $\text{LiClO}_4$  and (C)  $\text{Li}_2\text{CO}_3$ .
- Fig. 3 XPS spectra of carbon 1s in the surface layer formed on a Li electrode, electrochemically deposited on Cu from PC, 1M  $\text{LiClO}_4$ . (A) top surface, (B) after 10 min. sputtering, and (C) after 20 min. sputtering. Sputtering rate 8Å/min.
- Fig. 4 XPS spectra of  $\text{Cl}_{2p}$  in the surface layer formed on Li, electrochemically deposited from PC, 1M  $\text{LiClO}_4$  indicating the decomposition of  $\text{ClO}_4$  ions. (A) top surface, (B) after 10 min. sputtering, and (C) after 20 min. sputtering. Sputtering rate 8Å/min.
- Fig. 5 SIMS spectrum of surface layer on Li electrochemically deposited from PC, 1M  $\text{LiClO}_4$  on Cu. Two different sensitivities shown; low mass range.
- Fig. 6 As Fig. 5, high mass range.
- Fig. 7 In-situ x-ray diffraction of the surface layer on electrochemically deposited Li on a Ni substrate.  $\text{Li}_2\text{CO}_3$  and polymeric compounds are identified.
- Fig. 8 SEM showing the micro morphology of Li deposited on a Cu substrate from PC, 1M  $\text{LiClO}_4$ .

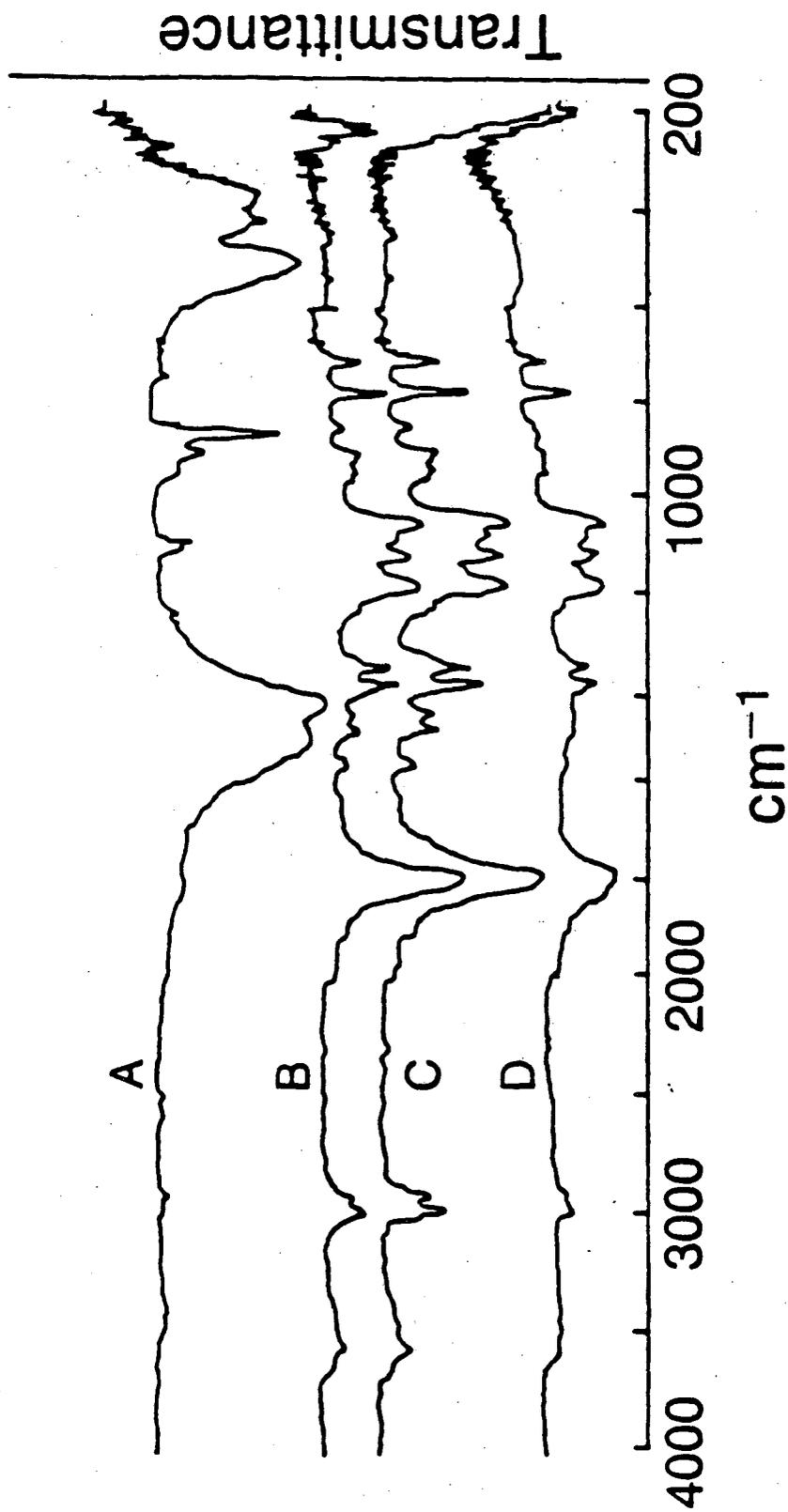


Fig. 1

XBL 839-11550

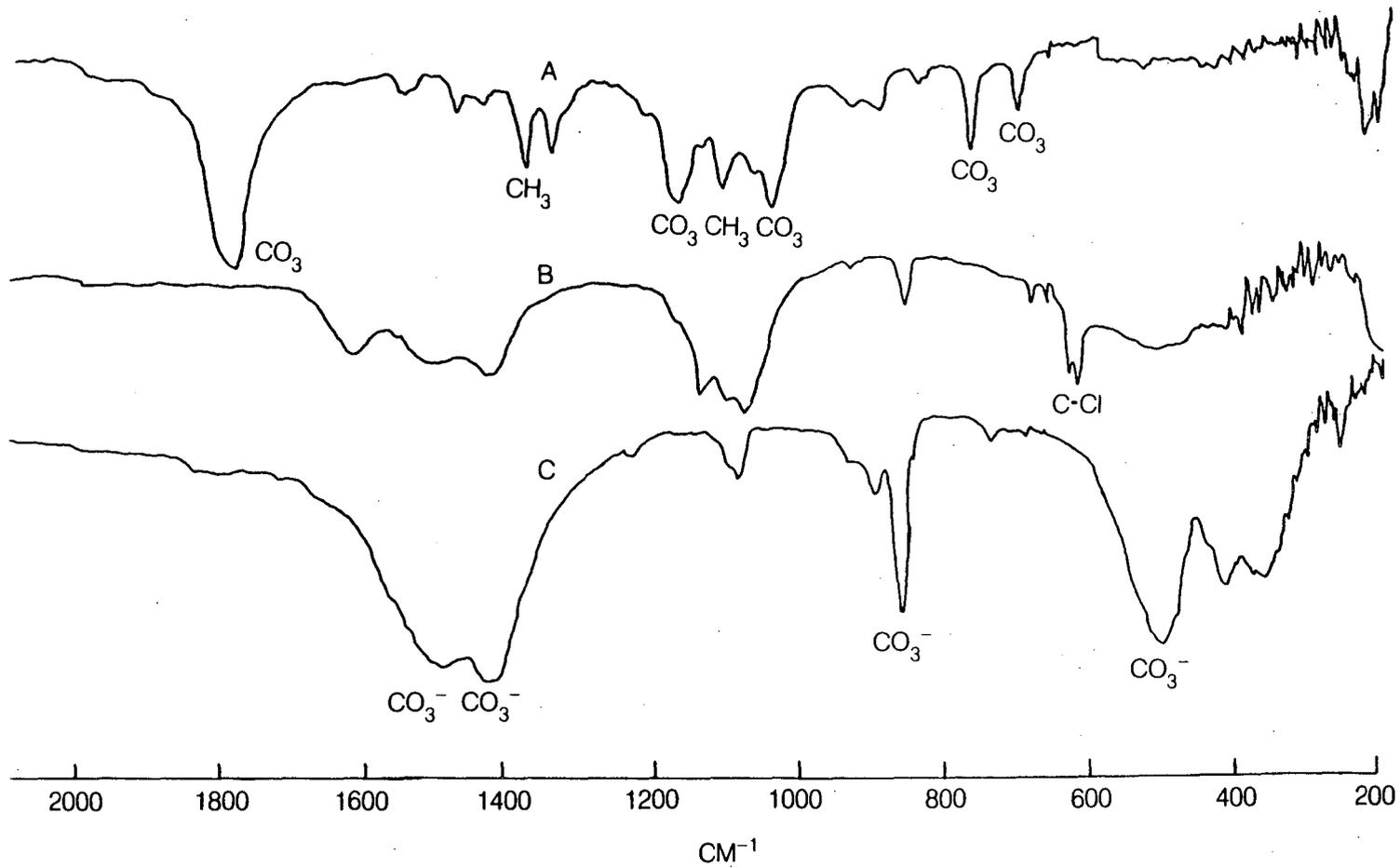


Fig. 2

XBL 839-11896A

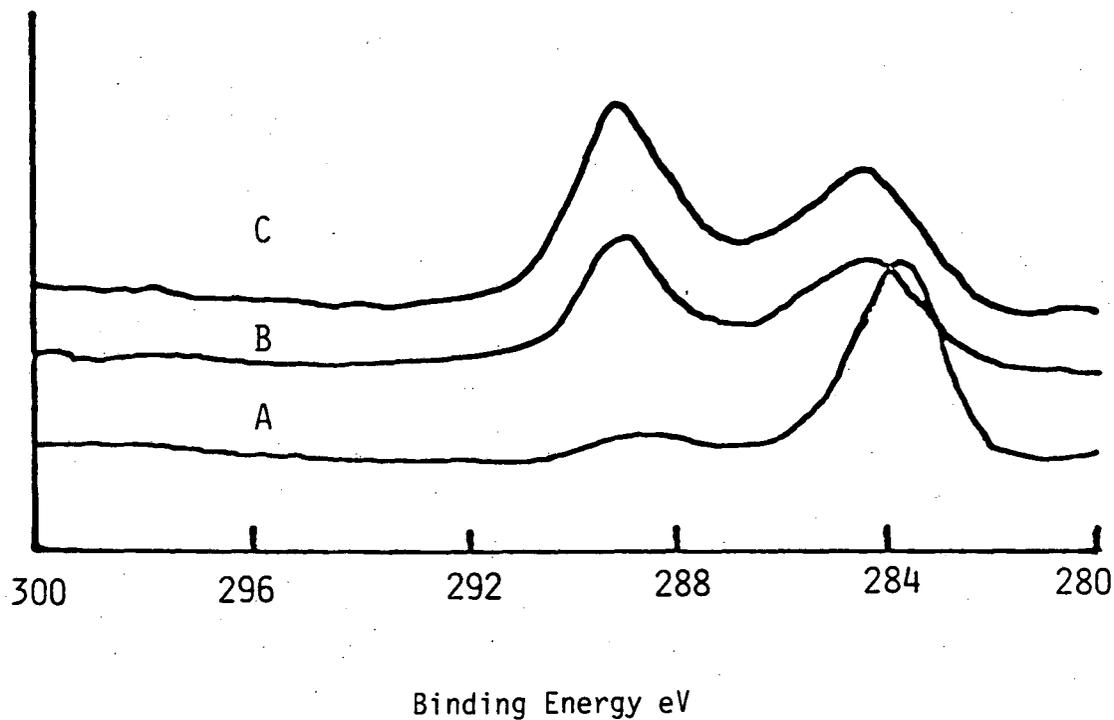


Fig. 3

XBL 839-11549

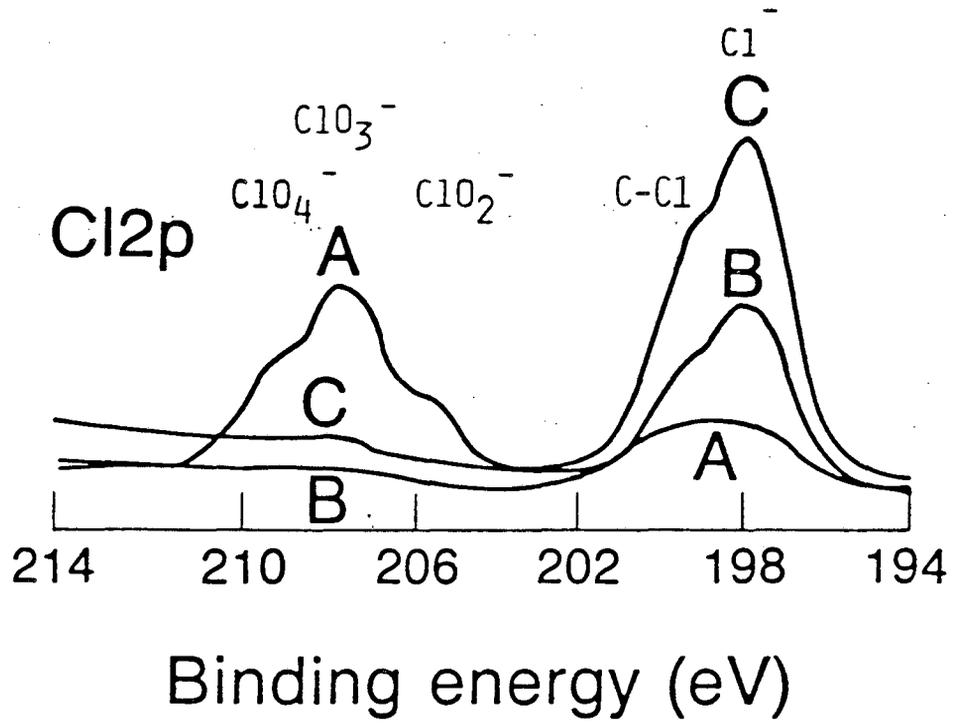


Fig. 4

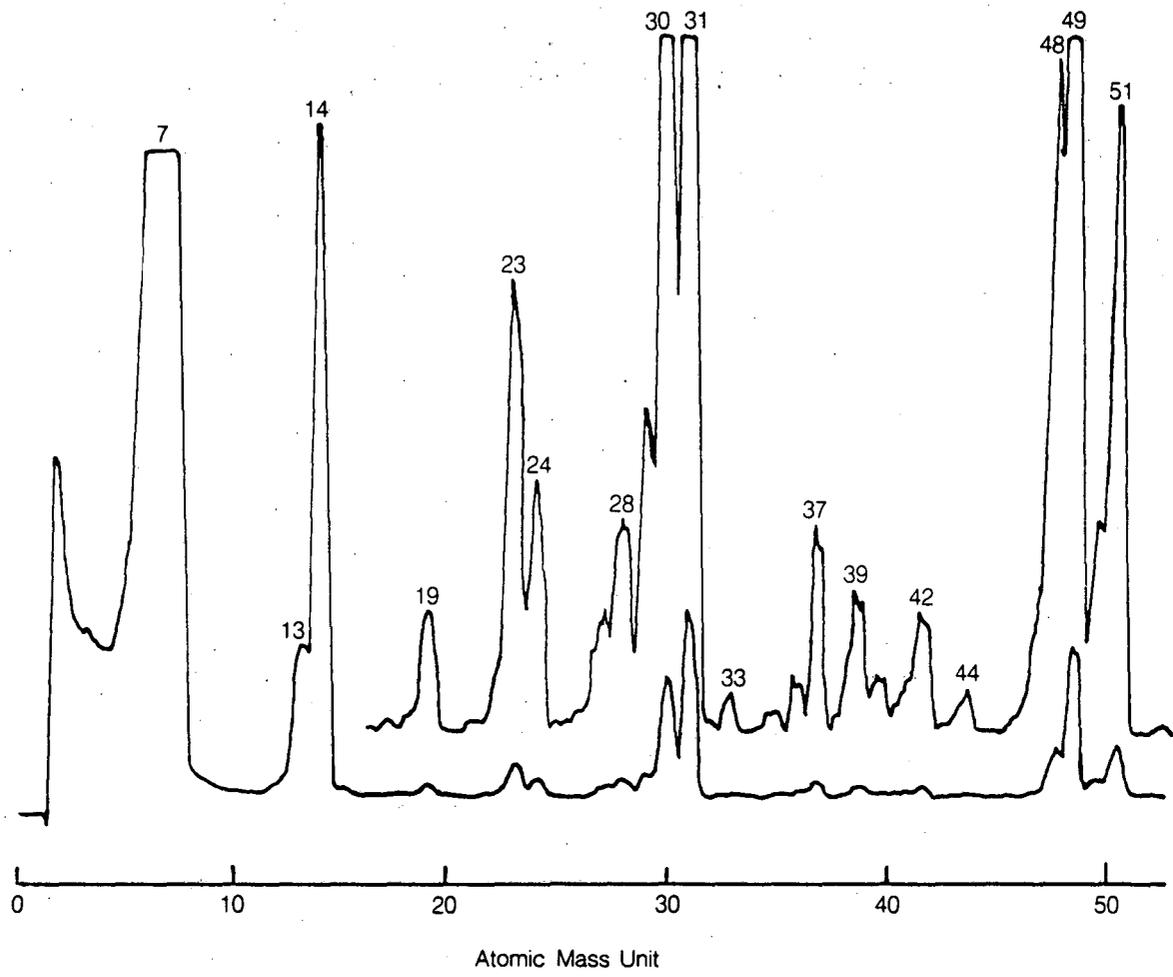
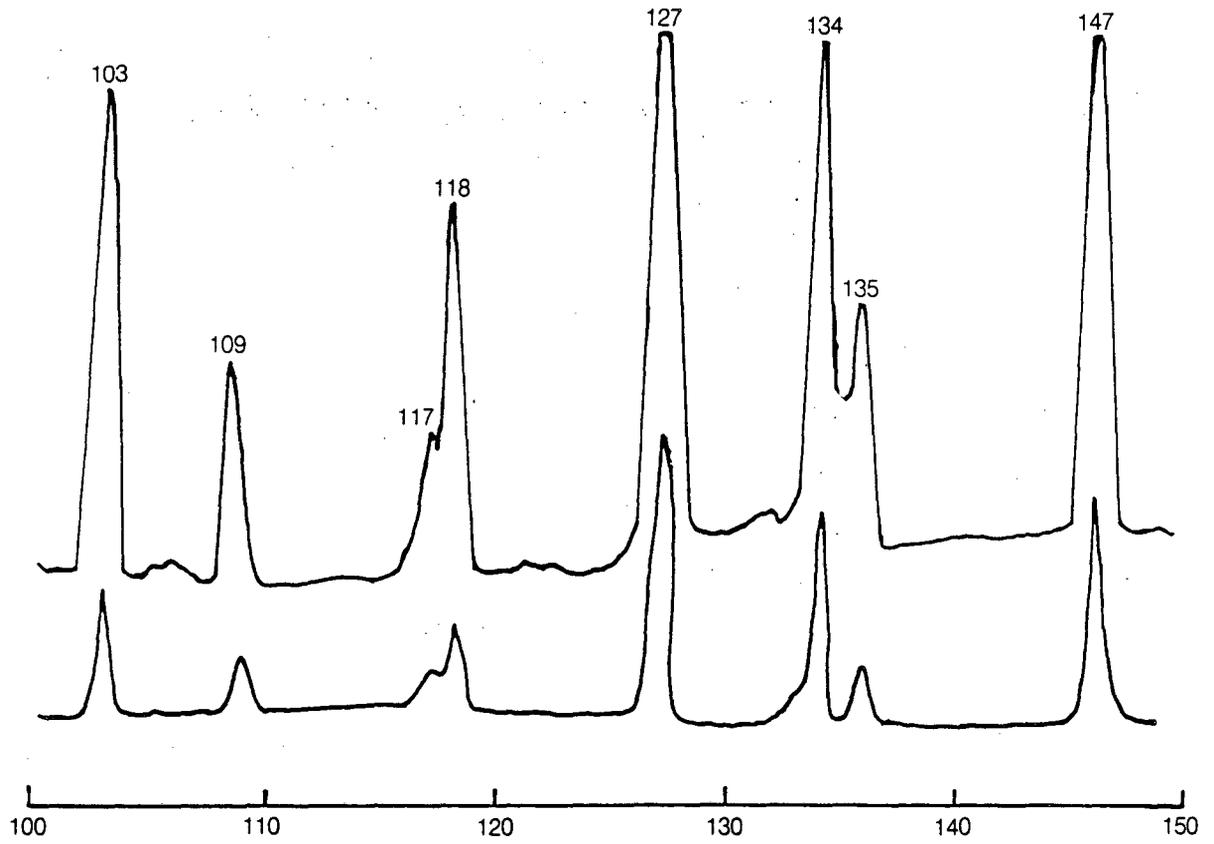


Fig. 5

XBL 848-3438A



Atomic mass unit

Fig. 6

XBL 848-3439A

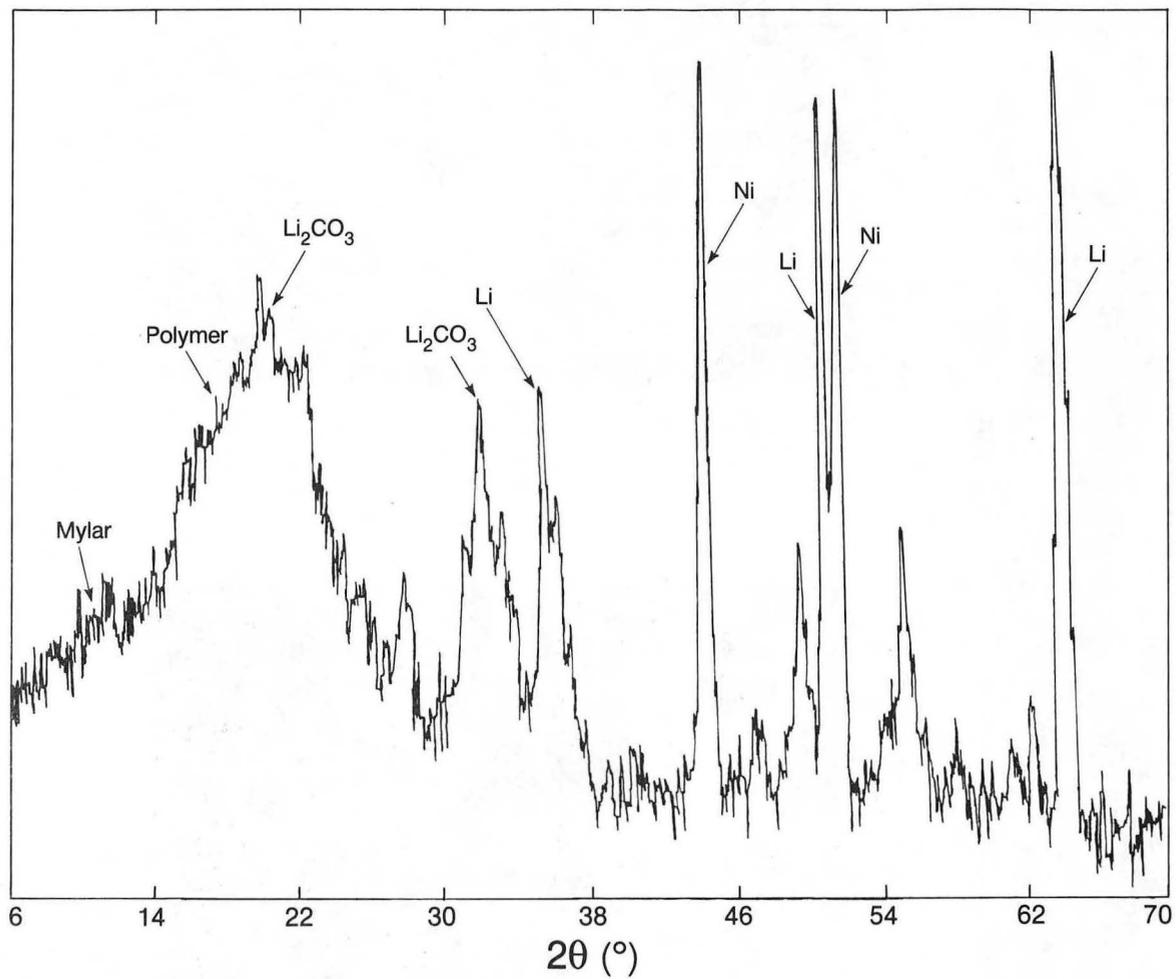
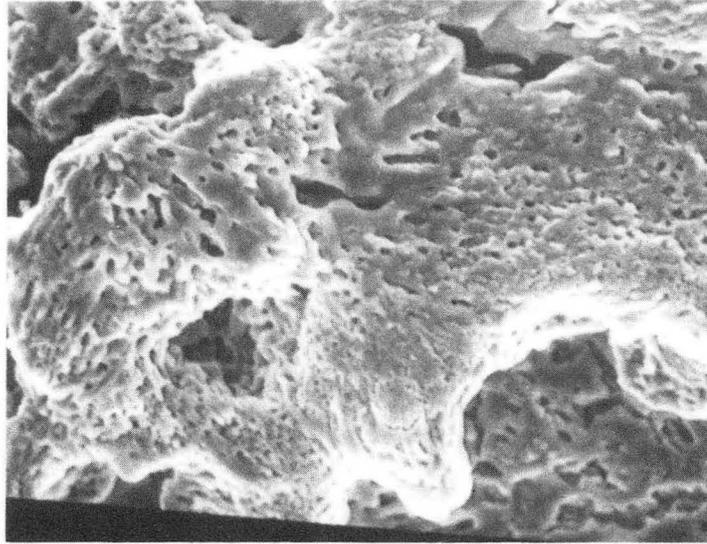
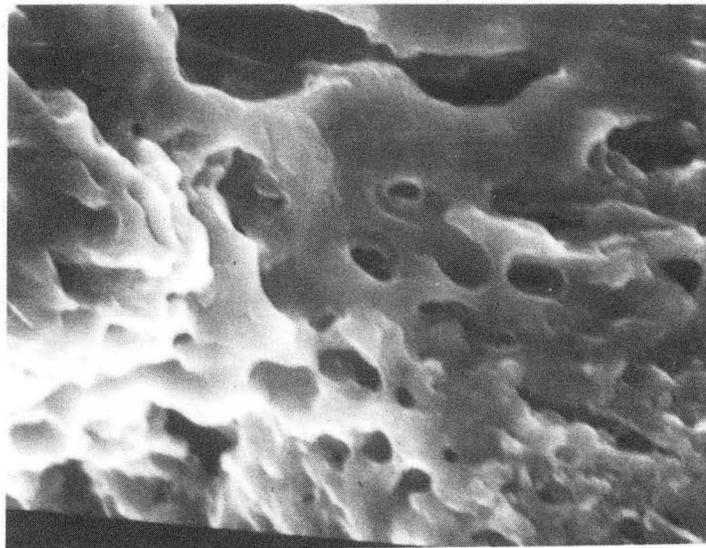


Fig. 7

XBL 848-8560



20 $\mu$



4 $\mu$

XBB 839-8205-B

Fig. 8

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