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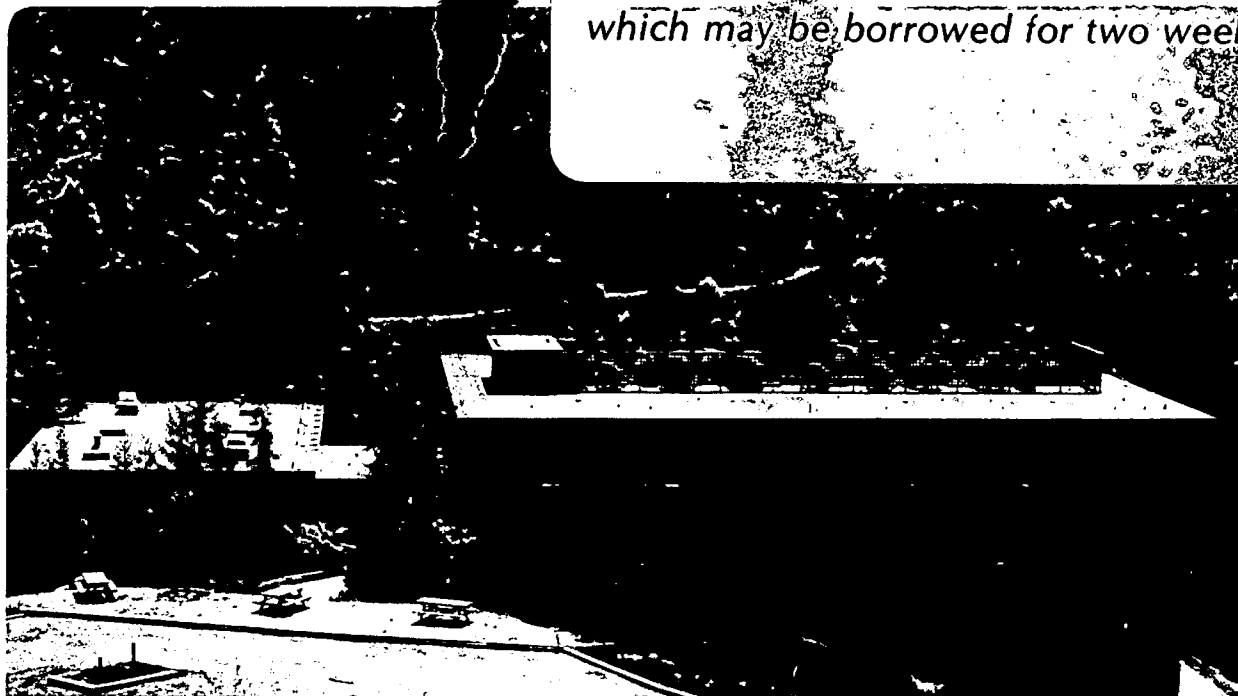
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To be submitted to J.E.C.S.

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.

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Abstract

Surface layers formed on Li in LiClO₄ with <1 ppm water content have been analyzed. IR spectroscopy showed the formation of Li₂CO₃ and a polymeric compound. ESCA analysis of the surface layer on electrochemically deposited Li on a Cu substrate indicated the formation of two types of carbon compounds, related to the formation of Li₂CO₃ and polymer. ESCA analysis also showed that LiClO₄ decomposes to chlorine compounds with lower valency; with higher-valent chlorine found in the outer film regions, lower-valent in the inner. In-situ x-ray diffraction confirmed the formation of Li₂CO₃ and polymeric compounds. SEM study of the surface of electrodeposited Li showed a porous structure.

Introduction

The electrochemistry of the alkali and alkaline earth metals in ambient temperature nonaqueous electrolytes has been reviewed by several authors.¹⁻⁶ 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.^{7,8}

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^{9,10} and the use of lithium alloys as anodes,¹¹⁻¹⁴ 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 SO₂, O₂, and N₂ has been found to improve the cycling efficiency of the lithium anodes.⁶ 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.¹⁵ Dey and Sullivan showed that propylene carbonate (PC) decomposes on a graphite electrode above +0.6V vs Li.¹⁶ 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 anode cycle.¹⁷ Dey also showed that a lithium electrode after charge and discharge had a porous structure. Epelboin et al.¹³ found that surface layers are formed on Li electrodes in PC, 1M LiClO₄ during charge, discharge and at open-circuit. Yen et al.¹⁸ carried out ESCA studies of the surface layer on lithium which had been cycled in a 2Me-THF, 1.5M LiAsF₆ electrolyte. They found Li, C, O, As and F on the surface of discharged Li. A polymerization of AsF₆⁻ on the surface has been proposed.¹³ The effect of light on the polarization of lithium electrodes in PC has been studied by Povarov and Sitnina.¹⁹ 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.¹⁹

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. Treatment of the distilled solvent with Li amalgam resulted in a water content which was below the detection limit of GC (1 ppm). Cyclic voltammetry with platinum electrodes of 1.0 and 1.5 M LiClO_4 solutions prepared with this solvent 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 $\pm 2\text{V}$ vs. a Li reference electrode at 50 mV/s for 15–20 cycles. The resulting electrolyte has been used for the experiments reported here.

The LiClO_4 (G. Frederick Smith) used for the experiments has been recrystallized from water and dried under vacuum at 240°C for 12 hours. Electrochemical experiments have been performed in a dry box (Vacuum Atmospheres) equipped for removal and analysis of oxygen, water and nitrogen. 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) 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 and transferred to the vacuum chamber by use of a He-filled transfer chamber. XPS spectra for Li, O, C and Cl have been collected after different times of Ar ion bombardment. 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 the spectra of Li_2CO_3 and PC included in Fig. 1 shows that IR absorption bands characteristic of Li_2CO_3 are present in the spectra of the film materials and similarities with the spectrum of PC indicate the possible presence of polymerized PC which is also supported by the physical appearance of the precipitate. The presence of residual PC in the film is not a likely cause of the observed spectral features because of the procedure used for removing the solvent from the film material by 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 LiClO_4 during cathodic deposition at $1\text{mA}/\text{cm}^2$ on a Cu substrate

is shown in Fig. 2. Comparison with the two calibration spectra indicates the formation of Li_2CO_3 . Additional peaks around 600 cm^{-1} and 1600 cm^{-1} and the special feature of the spectrum at around 200 cm^{-1} show formation of other materials. It is interesting to note the absence of the peak at 1800 cm^{-1} , characteristic of the carbonyl group in propylene carbonate, which would indicate the absence of PC in the film after evacuation. The band at 650 cm^{-1} may show the presence of a carbon-chlorine bond.

Previous studies²¹ on the effect of residual water on film formation during charge and discharge of Li electrodes have shown a peak at 3550 cm^{-1} due to lithium oxide in addition to the peaks due to Li_2CO_3 and polymer found here. The formation of oxidic and polymeric films on bulk lithium at open circuit had been postulated earlier.²² 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 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 Li_2CO_3 and another at 284 eV typical of polymeric carbon (Fig. 3). The depth profiling of this surface layer showed the peak at 284 eV decreasing and that at 290 eV increasing with sputter time. It can be concluded that Li_2CO_3 is mostly present in the inner film regions, polymer in the outer. 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 showed the presence of five different chlorine compounds in the film indicating that 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 polymerization of PC and chlorination of the polymer are not clear. Epelboin et al. concluded that LiCl exists in the film.¹³ It is also possible that Cl ions are formed by the decomposition of ClO_4 , ClO_3 , ClO_2 or 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 (Figs. 5 and 6). Fragments with mass higher than that of PC were observed. These are indicative of the presence of a polymeric material in the film. The residual gas analysis of the SIMS chamber after Ar ion bombardment of the surface layer showed a strong peak that coincided with the mass of Li. The significance of this observation is not clear at the moment.

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.²⁰ A

broad peak at low 2θ angle ($14-24^\circ$) which is characteristic of polymeric compounds, has been observed as was a narrow peak at 32° (2θ) characteristic of Li_2CO_3 . In the presence of residual water diffraction lines characteristic of the oxide have been observed.²¹

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_4 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. 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.

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 a polymerized product and Li_2CO_3 . When water is present, Li_2O is also formed. Surface layers are of complex composition and structure. LiClO_4 decomposes during potential cycling of Li electrode between $\pm 2\text{V}$. 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.

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

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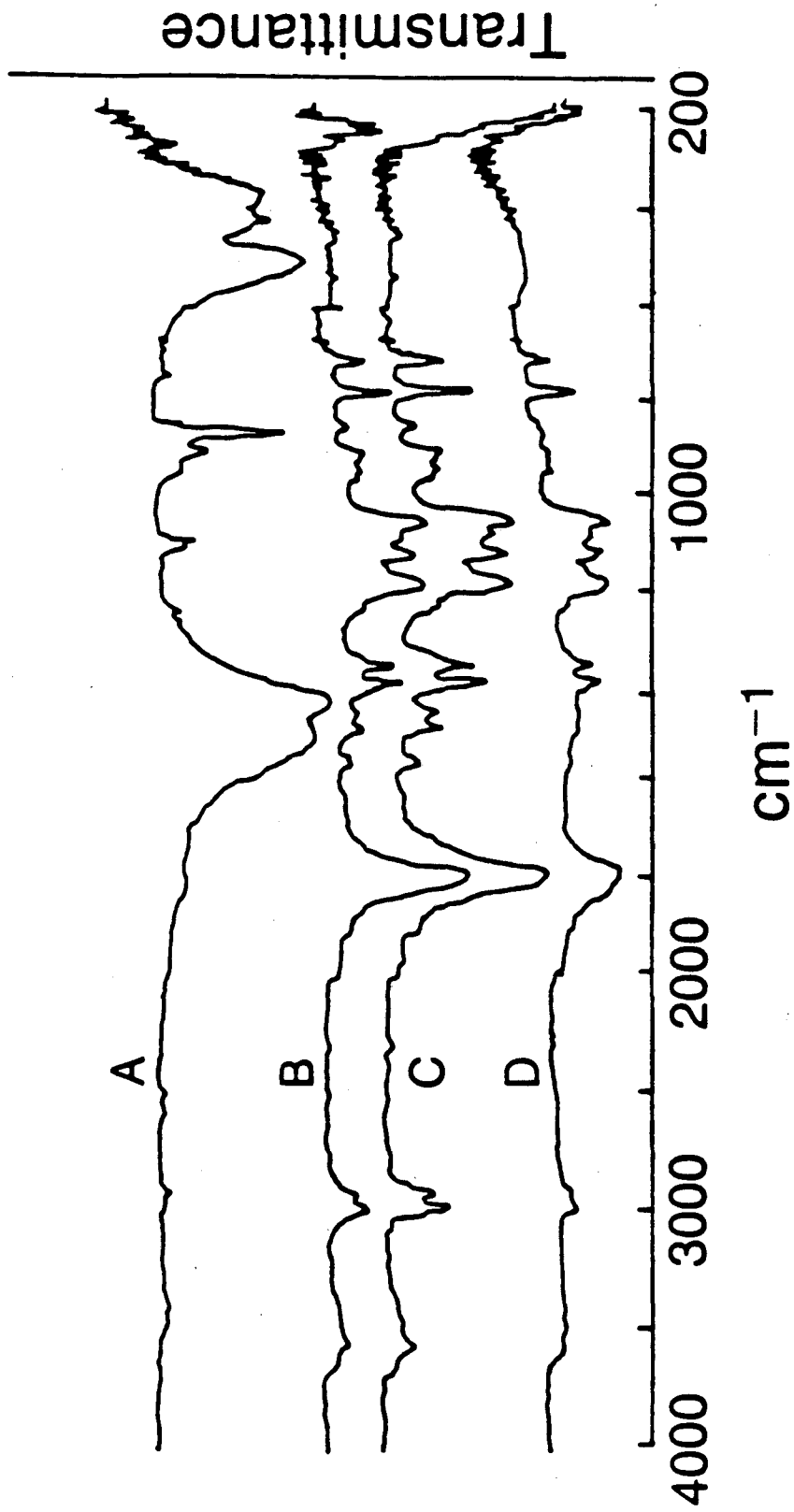
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Table I. Identification of Cl 2p ESCA Peaks

Compound	Binding Energy (eV) Cl 2p
LiCl	198
Poly Vinyl Chloride	200
ClO_2^-	206
ClO_3^-	208
ClO_4^-	209

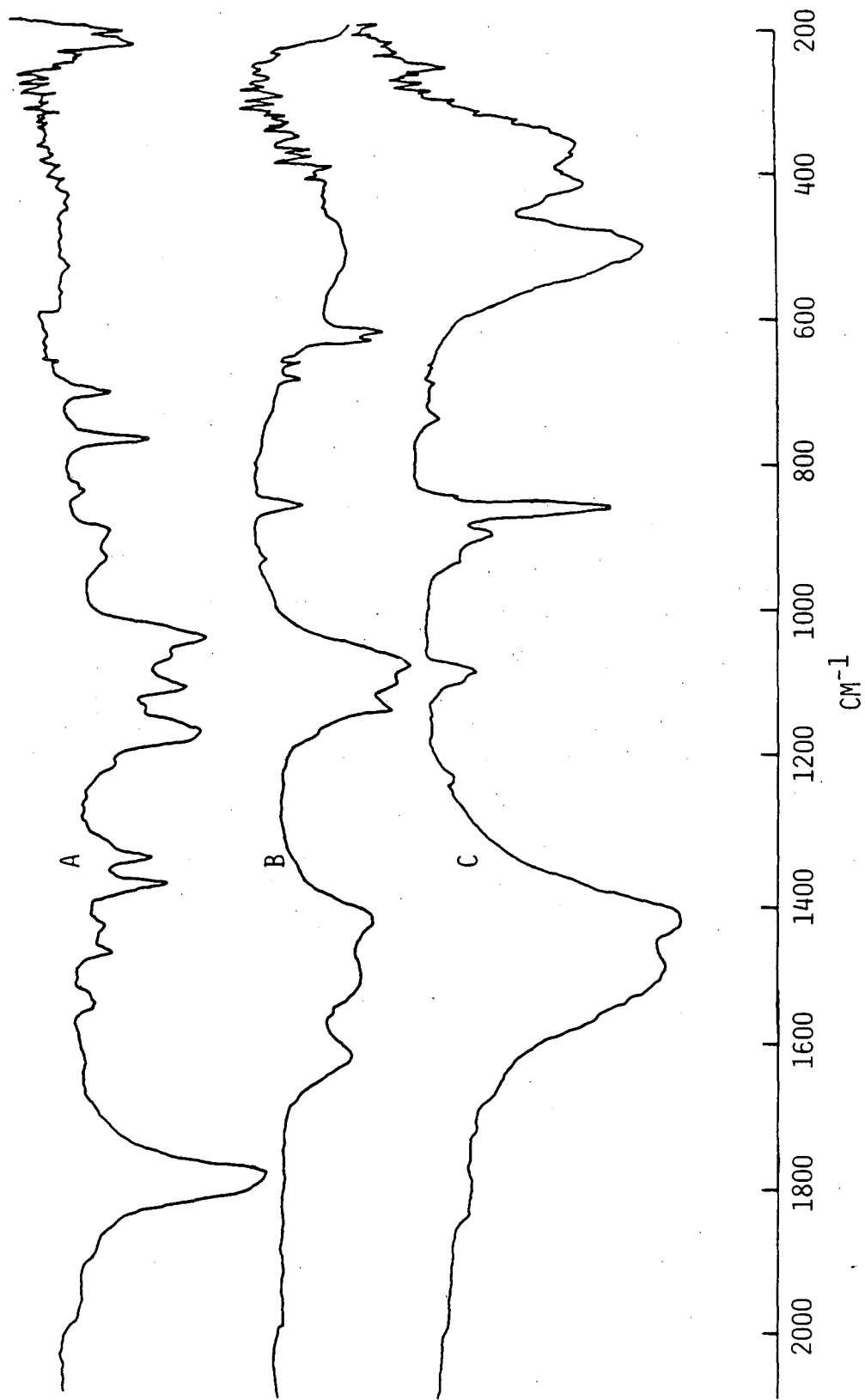
Figure Captions

- Fig. 1 Infrared transmission spectra of (A) Li_2CO_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 LiClO_4 and (C) Li_2CO_3 .
- Fig. 3 XPS spectra of carbon 1s in the surface layer formed on a Li electrode, electrochemically deposited on Cu from PC, 1M 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 Cl_{2p} in the surface layer formed on Li, electrochemically deposited from PC, 1M LiClO_4 indicating the decomposition of 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 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. Li_2CO_3 and polymeric compounds are identified.
- Fig. 8 SEM showing the micro morphology of Li deposited on a Cu substrate from PC, 1M LiClO_4 .



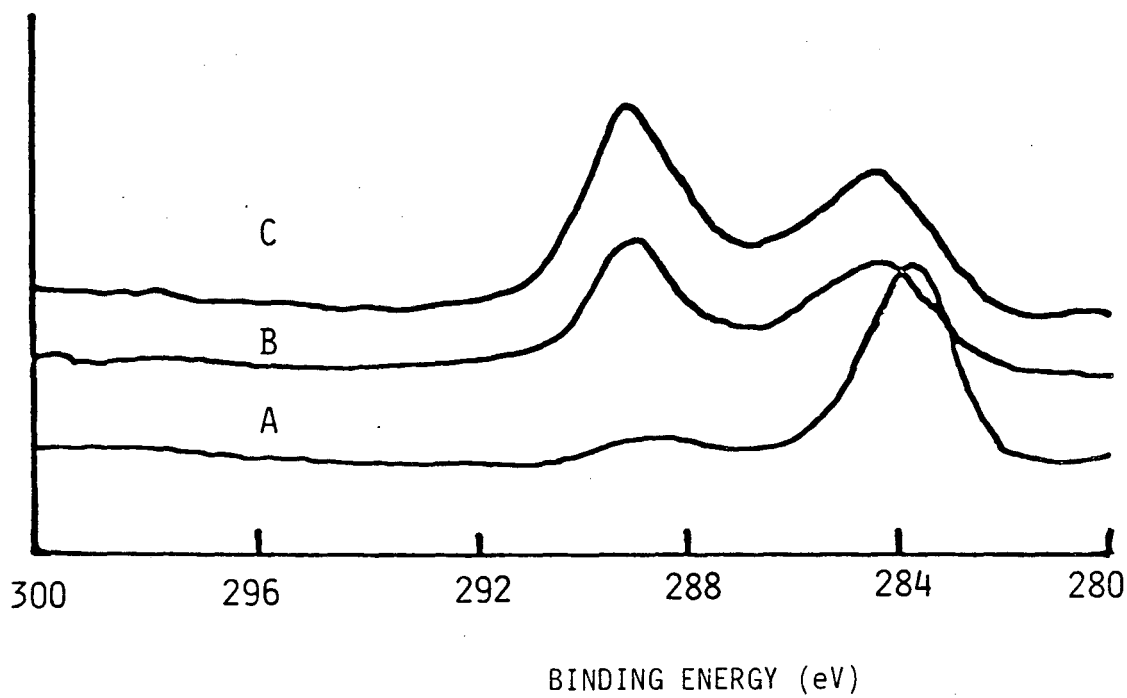
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Fig. 1



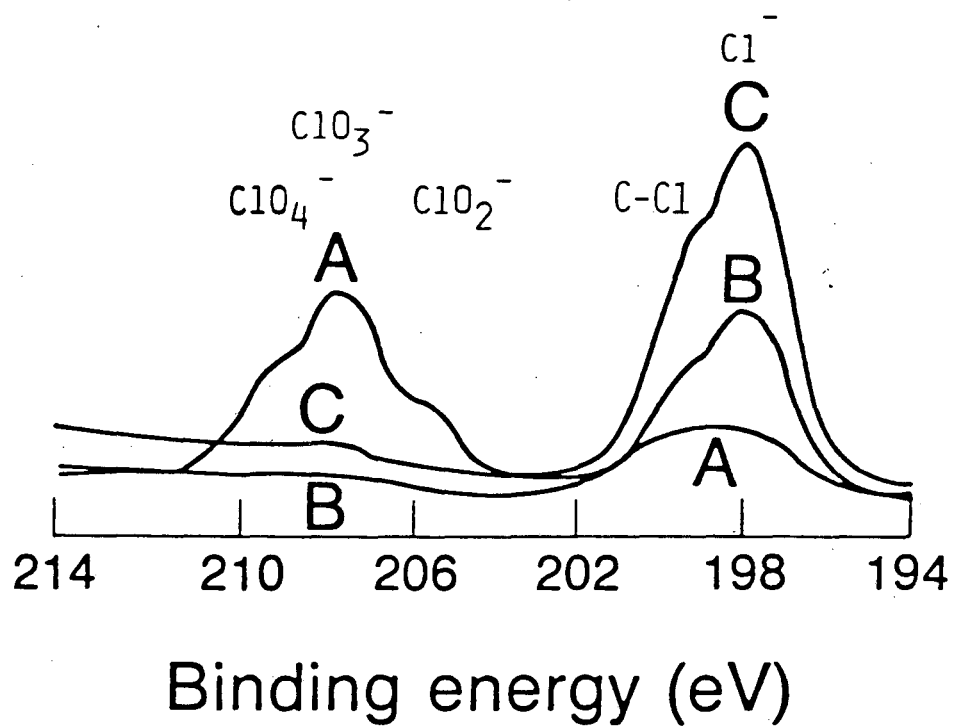
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Fig. 2



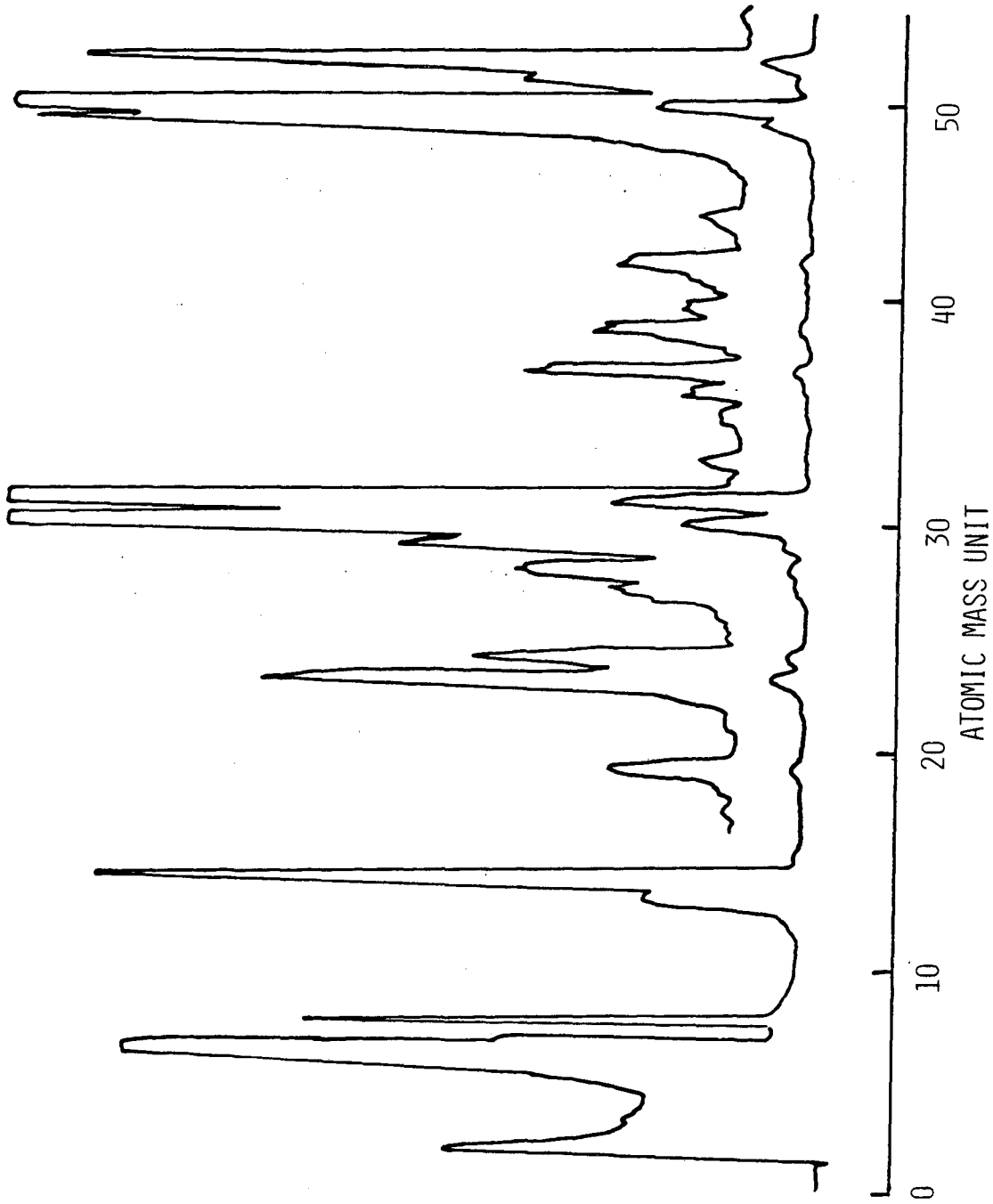
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Fig. 3



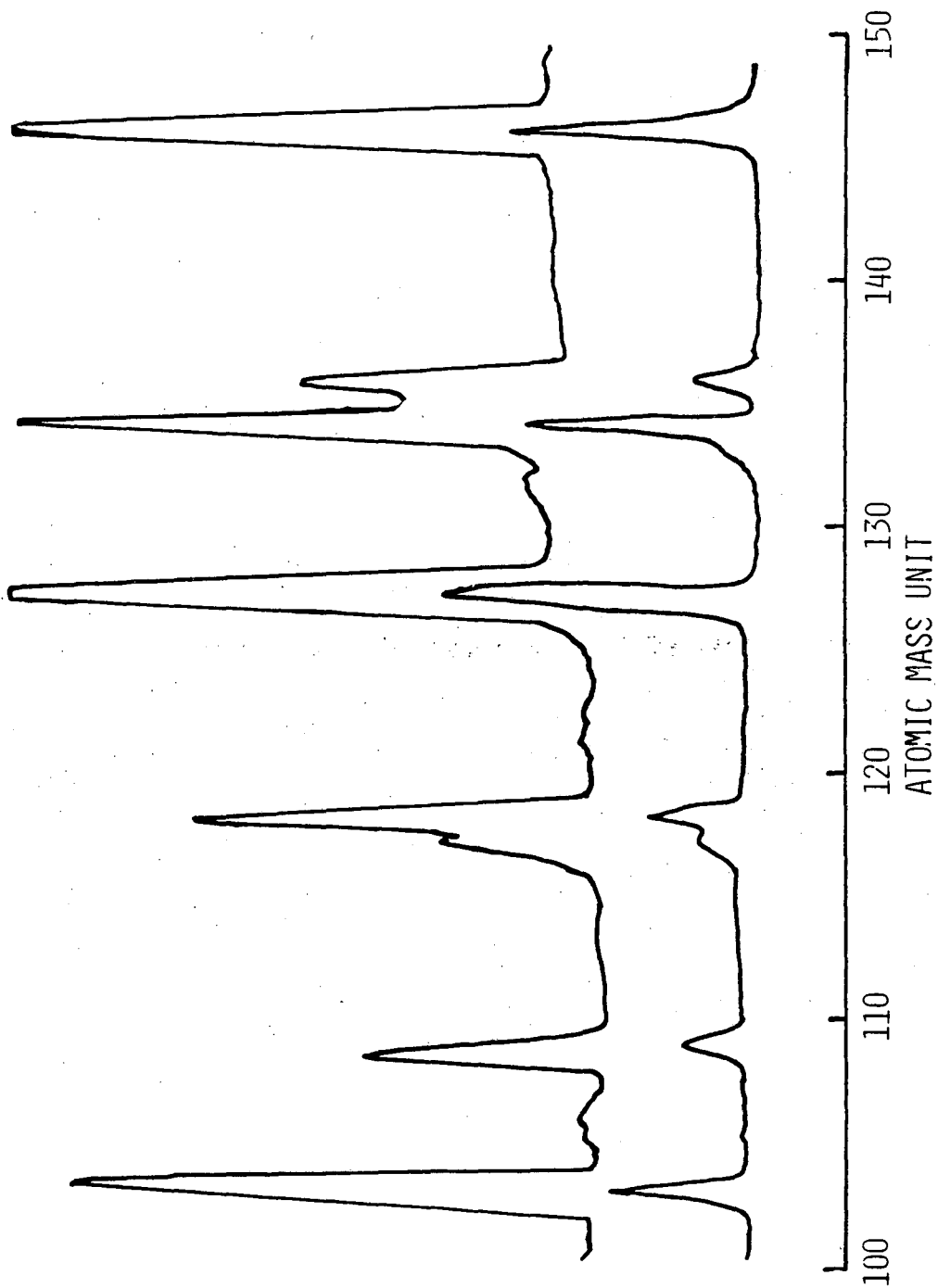
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Fig. 4



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Fig. 5



XBL 848-3439

Fig. 6

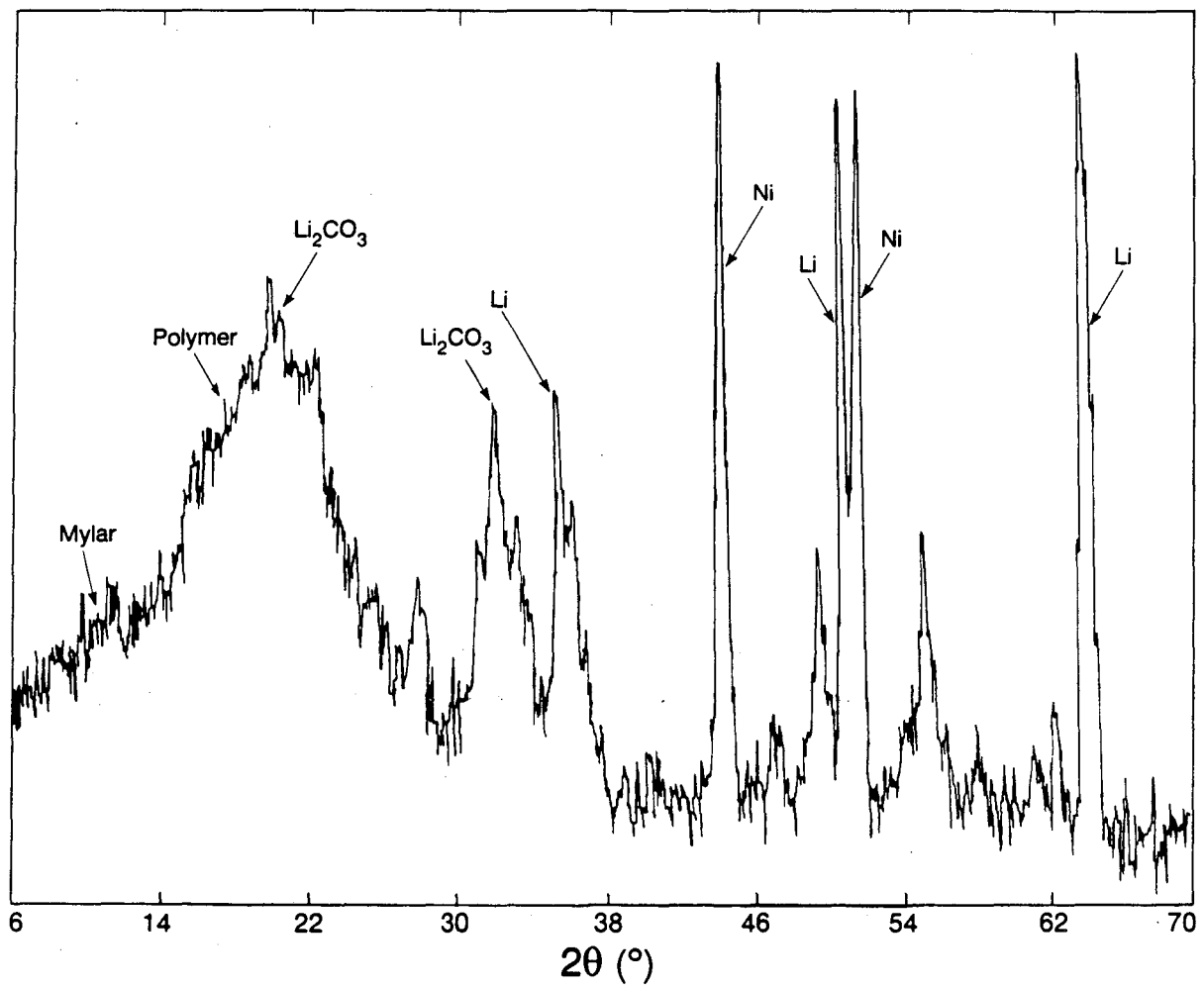
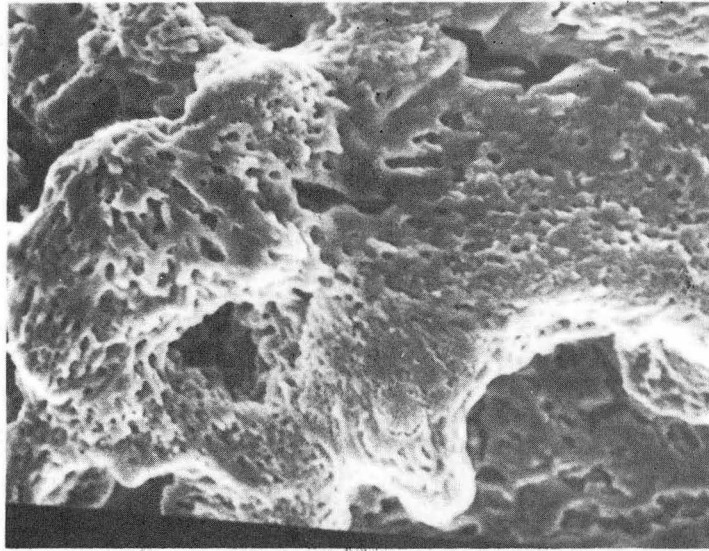
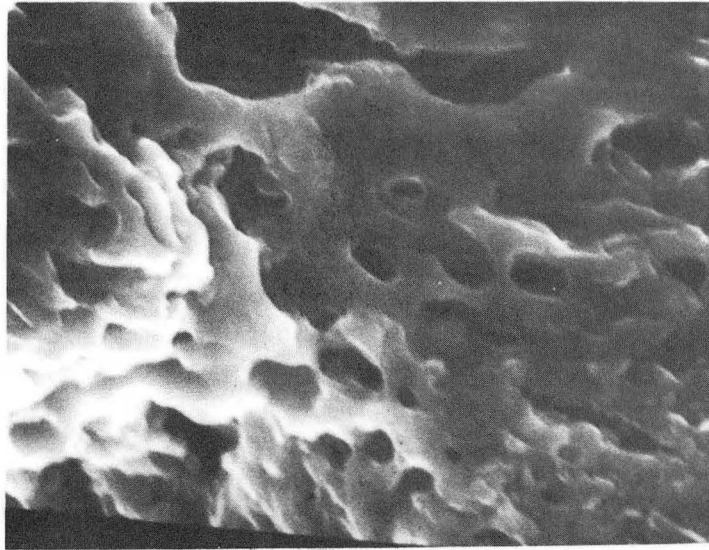


Fig. 7



20 μ



4 μ

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Fig. 8

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