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# *In Situ* X-RAY DIFFRACTION OF SURFACE LAYERS ON LITHIUM IN NONAQUEOUS ELECTROLYTE

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For Reference

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# In Situ X-Ray Diffraction of Surface Layers on Lithium in Nonaqueous Electrolyte

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X-ray diffraction, combined with electrochemical techniques, has been used for the in situ identification of materials on electrode surfaces based on their crystal structure during the progress of electrochemical reactions. This approach avoids some long-recognized problems of ex-situ measurements, which may not represent the nature of electrode materials because changes can occur upon transfer out of the electrochemical environment, when potential control is not possible.[1-3] The combination of different in situ techniques has been reviewed by several authors.[4-8]

Previous studies with x-ray diffraction from electrodes includes work by Salkind et al.,[9] who obtained x-ray patterns of iron electrodes during cycling in alkali using sealed polyethylene bags. Salkind and Bruins used in-situ x-ray diffraction to study the Ni electrode in Ni-Cd cells during charge and discharge.[10] Uno Falk determined x-ray diffraction patterns of submerged positive and negative electrodes of Ni-Cd cells during charge and discharge.[11] Recently, Fleischmann et al. used a position-sensitive proportional counter as x-ray detector to study the UPD of Pb on Ag and the adsorption of $I_2$ on graphite.[12,13] Fleischmann's work indicates that with use of a sensitive detector, x-ray diffraction is capable to determine diffraction from a monolayer. Unlike LEED, Auger and ESCA, for which the electrode must be removed from the electrochemical environment and exposed to ultrahigh vacuum, the specimen can remain under electrochemical control during in-situ x-ray diffraction. Another in-situ x-ray technique is

represented by the use of high-intensity beams, usually provided by an electron storage ring for EXAFS electrode studies.[14] EXAFS is able to provide information on short-range order such as distance and number of nearest neighbors and is particularly useful for amorphous compounds and clusters with short-range order.

In this work, in situ x-ray diffraction, using a conventional x-ray source and detector, has been applied to the study of surface layers formed on lithium in nonaqueous electrolytes. The properties of these surface layers are important for the charge and discharge behavior of lithium electrodes in ambient-temperature batteries. Because of the high reactivity of lithium, use of in situ techniques for the characterization of surface layers is essential.

## EXPERIMENTAL

The arrangement for in situ x-ray diffraction from electrode surfaces is illustrated in Fig. 1. A commercial diffractometer (Siemens Model D500) has been used. A collimated x-ray beam is directed toward the electrode surface at a fixed, glancing angle ($6^{o}$ from the surface), and the diffracted x-rays are measured by a rotating detector. In contrast to traditional x-ray diffraction, in which sample and detector are rotated, this arrangement enhances sensitivity for the surface region, although it does not detect monolayer films. The cell containing the electrode is shown in more detail in Fig. 2. The cell body was made of polypropylene and contained the working electrode of 1.9 cm diameter in the center, surrounded by a 3 mm wide counter electrode. A lithium reference electrode of 3 mm diameter was located between working and counter electrodes. Electrolyte could be

injected and removed from the cell by the use of two syringes, which were connected to the cell with Teflon spaghetti tubing. Electrodes and electrolyte were separated from the atmosphere by a polyethylene or Mylar window of 0.3 mm thickness. The x-ray beam enters and exits through this window, which is sealed by use of an O-ring and a washer.

The cell is assembled in an inert atmosphere box where the nonaqueous solution (1.5 M $LiCl_4$ in propylene carbonate) is also prepared. Permeation of water through the cell window in air over the time of the measurements was found to be negligible (no change in water concentration observed by cyclic voltammetry).[15,16]

## RESULTS AND DISCUSSION

Results are illustrated by the formation of surface layers on lithium during its cathodic deposition at 1 $mA/cm^2$ from 1.5 M $LiCl_4$ on a nickel substrate. Figure 3 shows a broad peak at low diffraction angle ($20^0$) which is characteristic of polymeric compounds. This peak cannot be caused by adsorbed electrolyte because the present arrangement is not sensitive to monolayers. Also, the peak remains after evaporation of the electrolyte in vacuum. Figure 4 shows the much sharper diffraction peak characteristic of lithium carbonate. Both peaks increase with time. The identification of the two film materials agrees with earlier analyses by IR spectroscopy, SIMS and ESCA.[17] In the presence of trace amounts of water, the formation of $Li_2O$ has also been observed. Use of a position- sensitive x-ray detector would make it possible to detect monolayer films and to collect diffraction data on a millesecond time-scale, which would be of interest for mechanistic studies of nucleation, film formation and phase transformation during the application of potential or current pulses.[18-21]

## ACKNOWLEDGMENT

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## FIGURE CAPTIONS

1. Arrangement for combined electrochemical technique and x-ray diffractometer for in-situ x-ray diffraction. X-ray source Cu K-$\alpha$ with Ni filter. The angle of incident x-ray beam with the electrode (CE), and reference electrode (RE) were connected to a potentiostat for electrochemical studies.

2. Electrochemical cell for in-situ x-ray diffraction. (A) cell body, polypropylene, (RE) reference electrode, (WE) working electrode and (CE) counter electrode; leads connected to potentiostat. (1) working electrode with Li deposited on Ni 1.9 cm diameter. (2) Li reference electrode, 0.3 cm diameter, (3) Li counter electrode, 0.3 cm wide and (4) Groove for O-ring. (B) O-ring, (C) polyethelene window, (D) Cu washer, (E) syringe for electrolyte delivery to cell, and (F) syringe for electrolyte removal from cell.

3. In-situ x-ray diffraction from the surface layer formed on Li electrochemically deposited on a Ni substrate at 1 $mA/cm^2$, observed during deposition after (A) 5 min., (B) 10 min., (C) 15 min. and (D) 20 min. Electrolyte PC, 1.5 M $LiClO_4$. Peak indicative of polymer formation.

4. <u>In-situ</u> x-ray diffraction from the surface layer formed on Li electrochemically deposited on a Ni substrate observed during deposition, after (A) 5 min., (B) 10 min., (C) 15 min., (D) 20 min., (E) 25 min. Peak indicative of $Li_2CO_3$ formation.

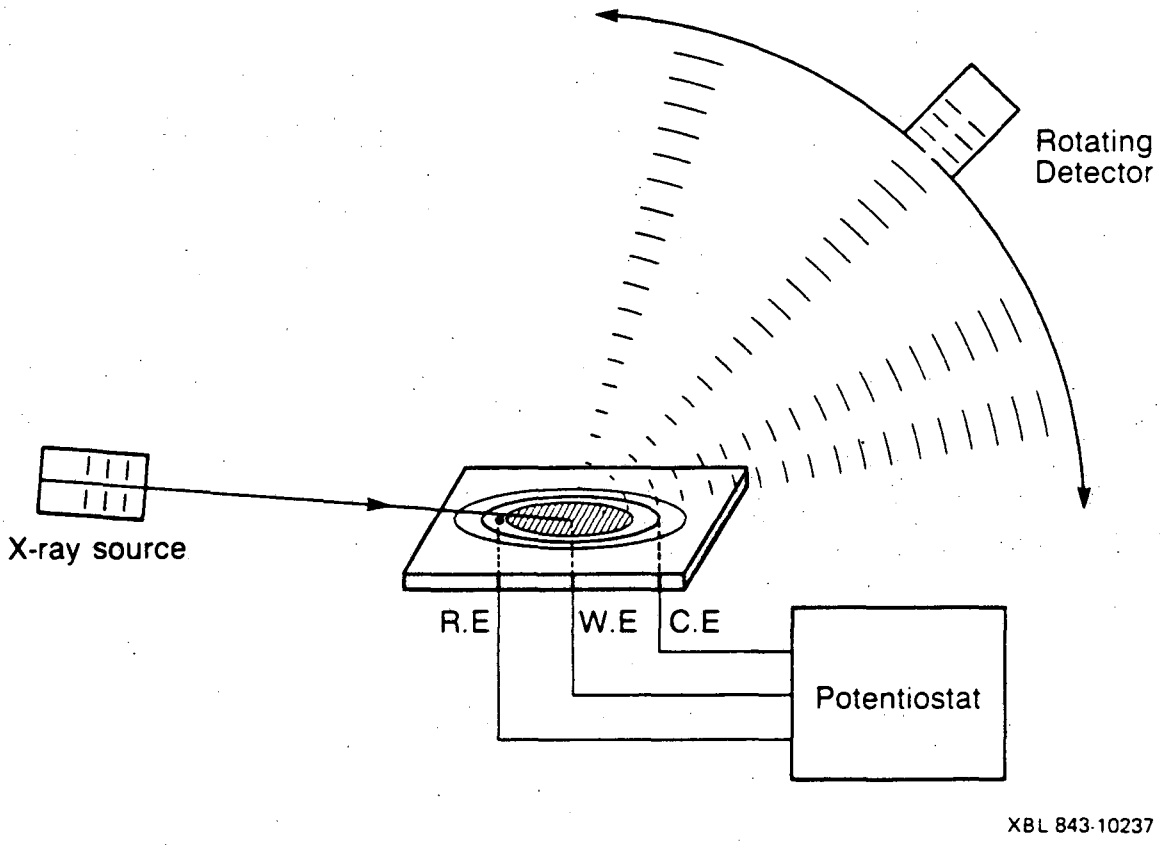
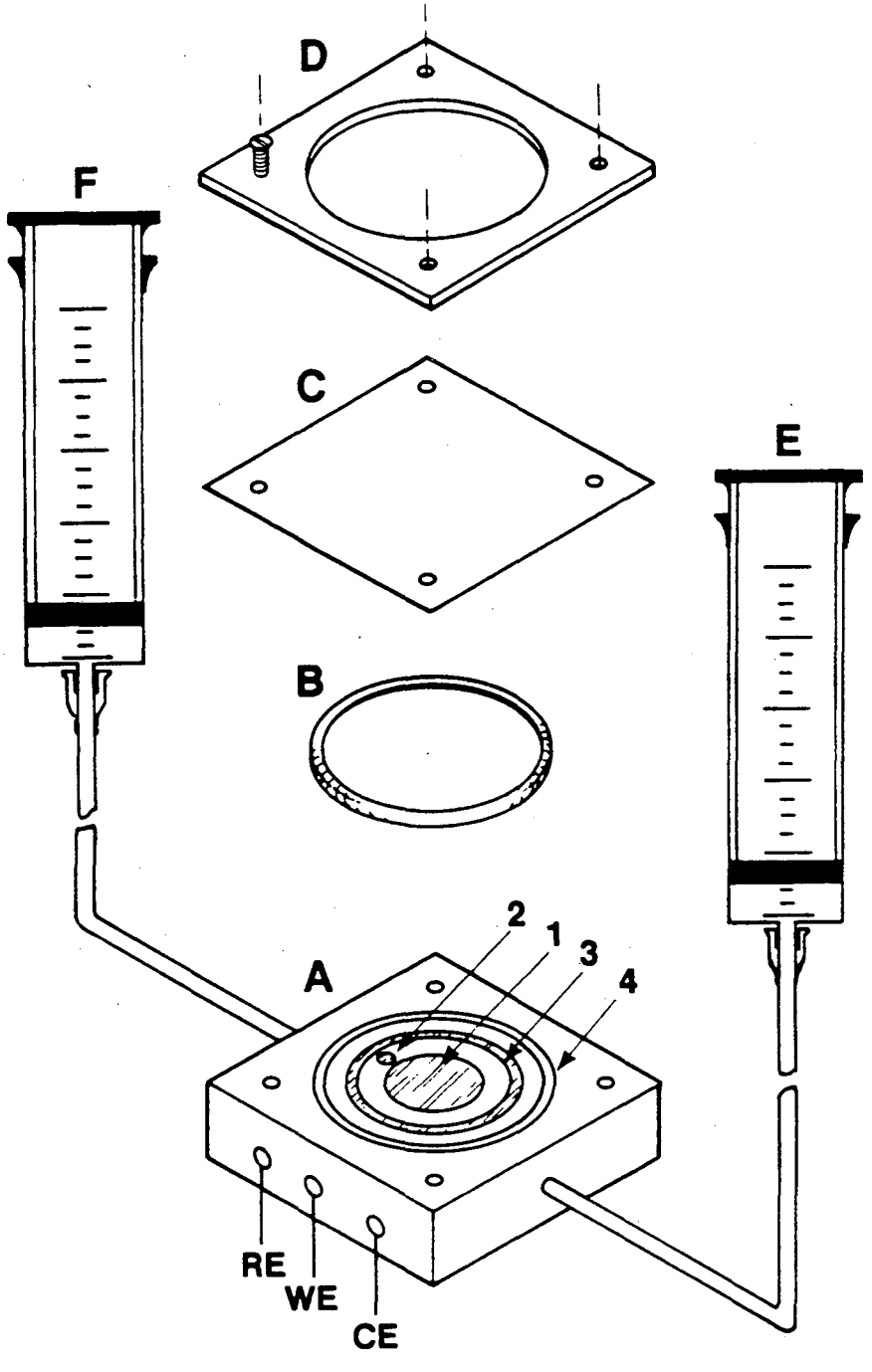
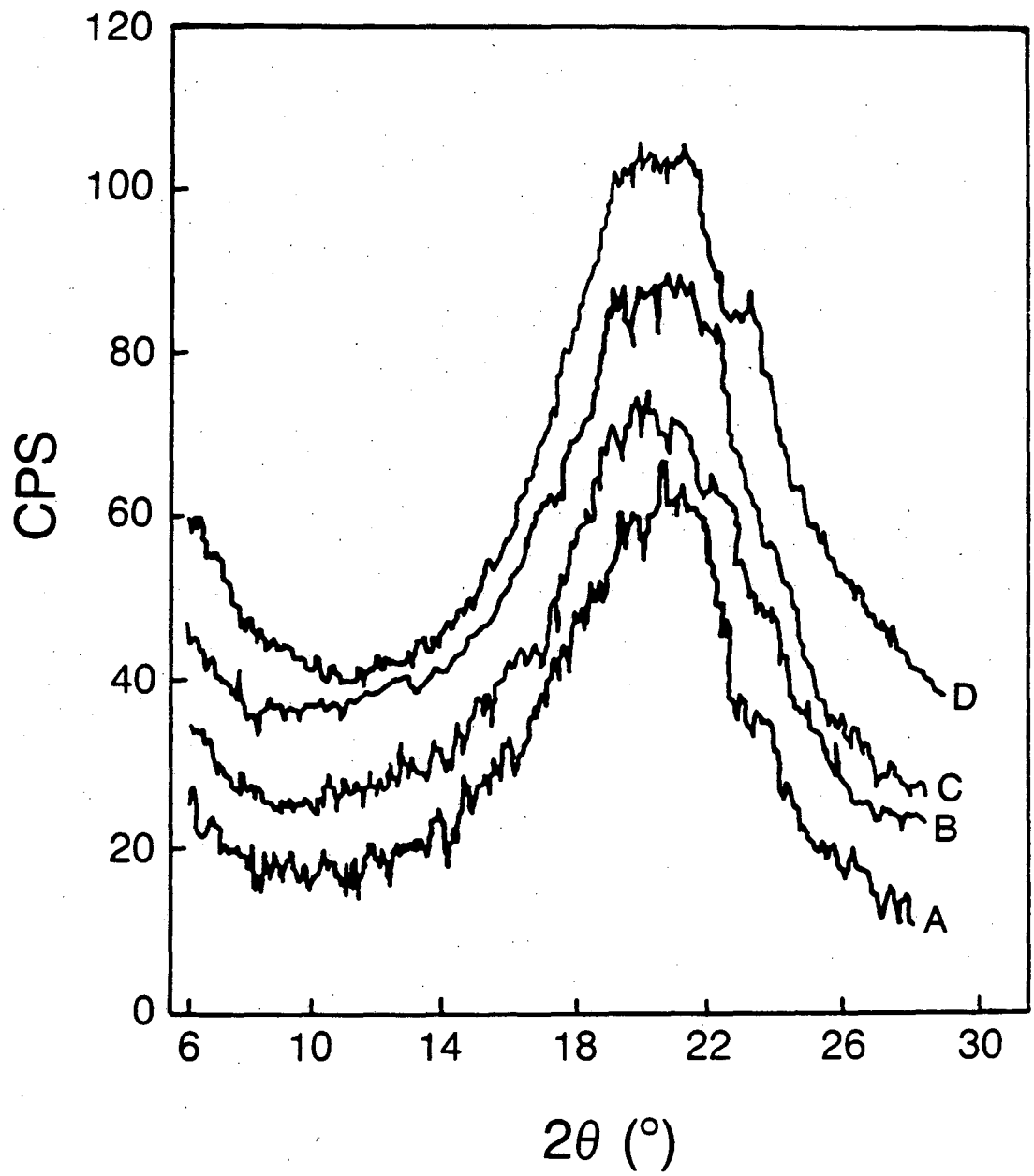

Rotating
Detector
X-ray source
R.E
W.E
C.E
Potentiostat
XBL 843-10237

Fig. 1




XBL 845-8903

Fig. 2




XBL 848-8557

Fig. 3

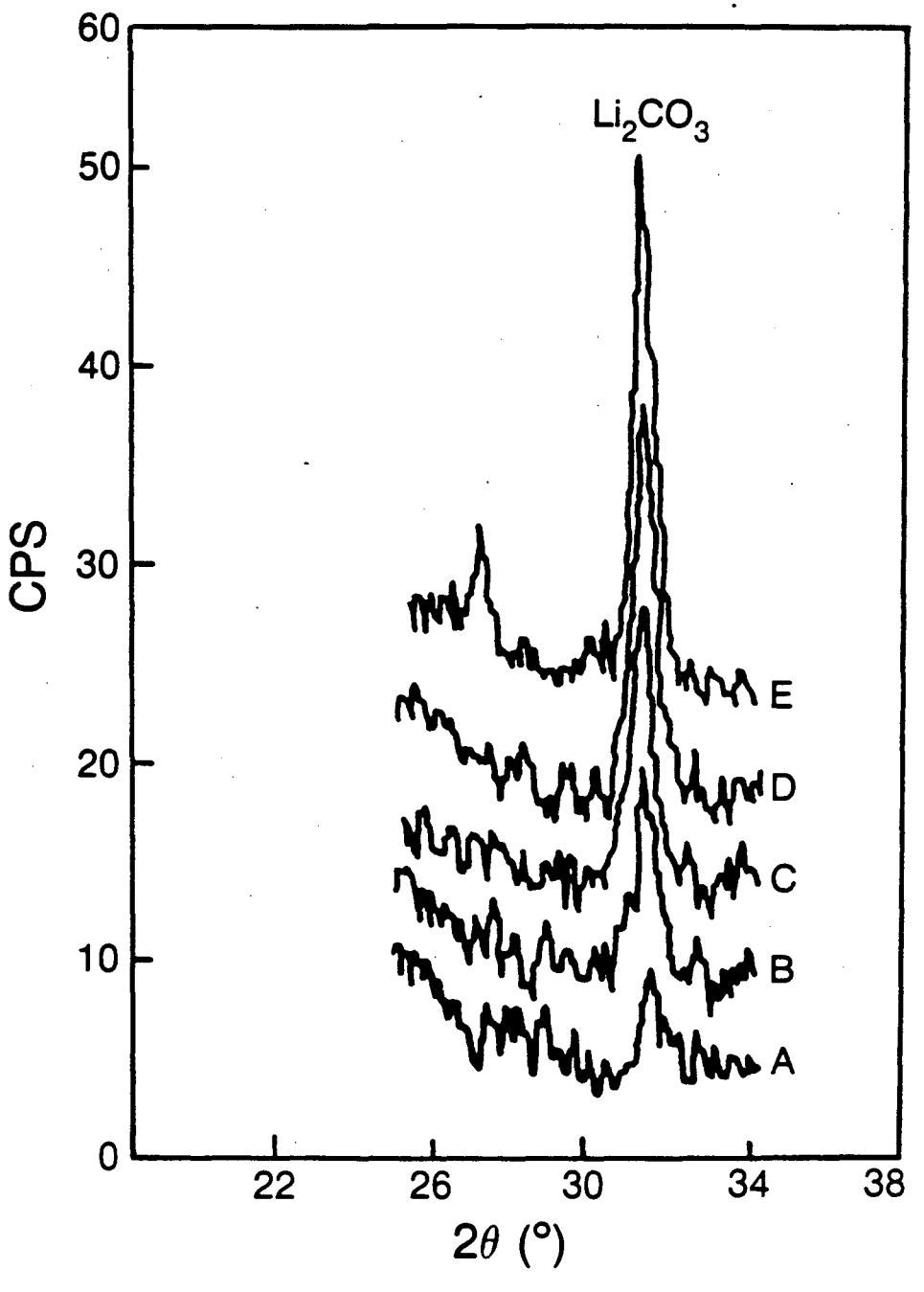



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Fig. 4

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