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STUDY OF THE SECONDARY Li ELECTRODE
IN ORGANIC ELECTROLYTE

M. Eisenberg

April 1981

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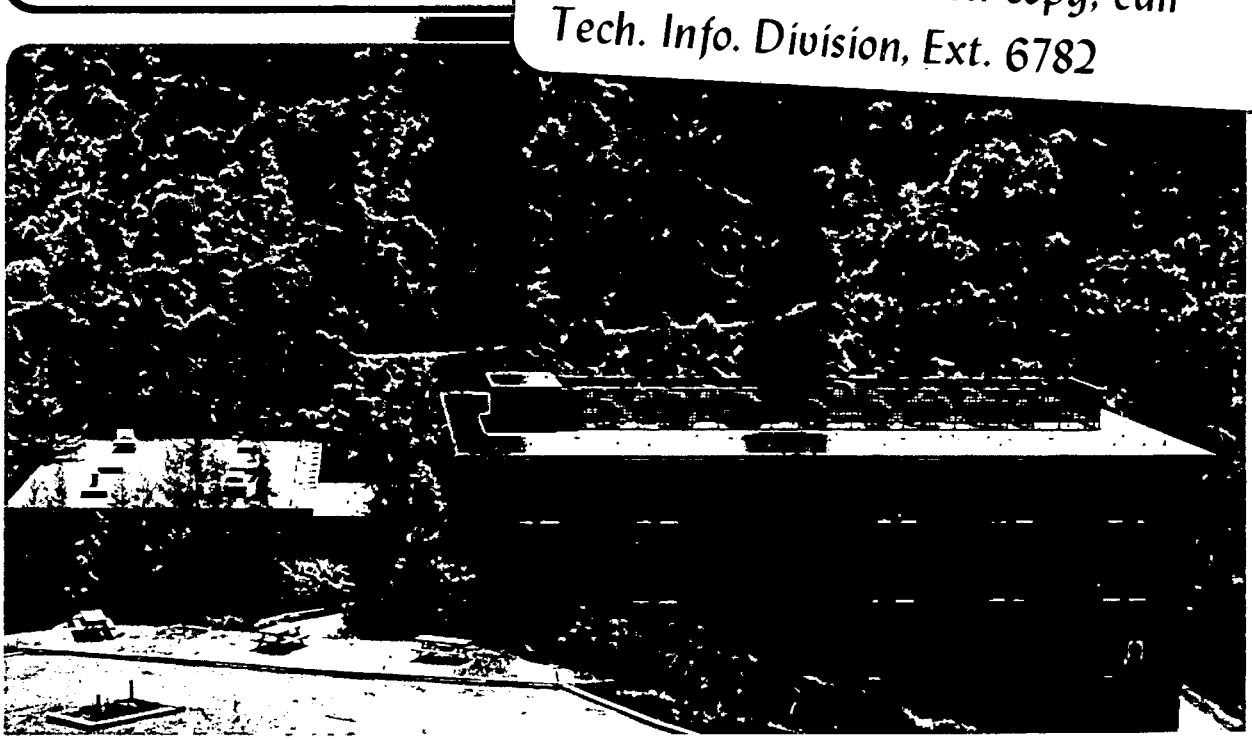

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Study of the Secondary Li Electrode in Organic Electrolyte

Final Report on LBL Subcontract 4507210

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FINAL TECHNICAL REPORT - LITHIUM ANODE STUDY - PHASE I

1.0 INTRODUCTION AND SUMMARY

The objective of this eight-month program was a preliminary Phase I study of the electrochemical and morphology aspects of lithium anode rechargeability in organic electrolyte ambient temperature systems. It is now increasingly recognized that the limitation of lithium anode rechargeability may have a serious effect on the future development and capabilities of ambient temperature high energy secondary lithium batteries.

To provide a basis for future reliable evaluation of electrolyte systems, it was necessary to examine the technique of stripping efficiency studies for lithium with particular reference to the effect of substrates, amount of charge passed, current density and other conditions. Next was a development of a technique for lithium electrode preparation for electrodedeposition for scanning electron microscopy (SEM) studies. With these techniques, a number of basic electrolyte systems were examined in order to elucidate directions in which future efforts in this area should be emphasized. Two additional techniques, namely capillary cells for microscopic observation of electrocrystallization of lithium and an apparatus for the analytical determination of the metallic lithium content on electrode surfaces have been worked on and designed, but were not ready for employment at the conclusion of this Phase I effort.

2.0 EXPERIMENTAL STUDIES AND RESULTS

2.1 Morphological Studies

2.1.1 Electrolytes

Prior work at Electrochimica Corporation over a number of years has established the general fact that the choice of solutes and solvent systems is critically important for the behavoir of the lithium electrode. From these prior studies, it emerged that certain anions such as ClO_4- and AsF_6- are fairly acceptable for the rechargeable lithium electrode, and that certain solvents such as:

Tetrahydrofuran	(THF)
2-Me- THF	
Dimethoxyethane	(DME)
Dioxolane	(DIOX)
Propylene Carbonate	(PC)

are reasonably stable ionizing solvents. More recently, certain tetra alkyl boron salts have been suggested, particularly, Li $B(C_6H_5)_4$.[1] However, these salts are not commercially available and involve special order synthesis by specialized laboratories. They may be considered in a future program, however.

The electrolytes used during the Phase I program are listed in Table 1. These were prepared in volumetric flasks inside a dry box from doubly distilled solvents, and vacuum dried in anhydrous salts. In addition, molecular sieves 5A and lithium chips were used for further treatment of the electrolyte. In Table 1 when co-solvents were used, they were first blended with the main solvent typically in a 30% volumetric ratio. Electrolytes were normally stored in a dry box for additional protection, and all transfer to experimental cells were performed in the same box.

TABLE 1. COMPOSITIONS OF ELECTROLYTES (SERIES J-3155)

Electro-lyte No.	Solute M/L	Solvent System
1-A	1m $LiClO_4$	DIOX
1-B	1m $LiClO_4$	DIOX - 30 DME
1-C	1.5m $LiClO_4$	DIOX - 30 DME
1-E	1.5m $LiClO_4$	2 Me - THF
2-A	1m $LiAsF_6$	DIOX
2-B	1m $LiAsF_6$	DIOX - 30 DME
2-C	1m $LiAsF_6$	2 Me - THF
2-D	1m $LiAsF_6$	2 Me - THF - 30 DME
2-G	1.5m $LiAsF_6$	70 DIOX - 30 DME
2-H	1.5m $LiAsF_6$	2 Me - THF
4-A	1m $LiClO_4$	PC
4-B	1m $LiClO_4$	PC - 30 DME
4-C	1.5m $LiClO_4$	PC - 30 DME
5-A	1m $LiAsF_6$	PC
5-B	1m $LiAsF_6$	PC - 30 DME
5-C	1m $LiAsF_6$	DIOX - 30 PC

DIOX = 1.3 dioxolane
2 ME-THF = 2-methyl tetrahydrofuran
PC = Propylene Carbonate
DME = dimethoxyethane

2.1.2 Bell Jar Glass Cell Studies

A glass cell design previously developed at Electrochimica Corporation was employed for these studies. A heavy walled pyrex jar is equipped with a grove for an O-Ring, which provides a seal to a machined polypropylene cover, in which four packing glands are provided for four electrical lead-throughs for three working electrodes, and one reference electrode.

1" x 1" lithium (supported on nickel X-met in the center) and nickel foil cathodes were disposed between two lithium anodes, 1/8" apart. Small lithium reference electrodes were employed in a side wall compartment connected through a Luggin capillary to the central compartment exactly in the plane of the central cathode held within a P.P. frame. In this manner, an almost negligible iR-drop is involved between the working electrode and the reference. The same electrolyte was of course, employed in the reference electrode compartment.

After cell assembly in an argon box, the cells were sealed, the packing glands tightened, and experiments carried out either in the dry box through electric wall feed throughs for power and instrumentation or outside the dry box.

Prior to the start of each deposition experiment, the cathode was given a 5 min - 5 mA/cm^2 anodic treatment to remove surface films. This was followed by a 5 min OCV period.

The first experimental series designed for these cells was electrodeposition of lithium onto a lithium electrode or a nickel electrode at a series of current densities beginning with 1 mA/cm^2 for a period of time such that a theoretical deposit thickness would result of $\underline{4.87 \times 10^{-3}\ cm}$ (assuming a 100% density of the deposited lithium and a 100% current efficiency.)

This is considered to be desirable to provide for a more meaningful basis for comparison of deposits and avoid confusion which would result by depositing significantly different amounts during different runs.

The results of studies on several electrolytes at 1 mA/cm^2 are shown in Table 2. There are three electrolytes illustrated in this table of compositions: 1 m/L $LiClO_4$ in dioxolane (DIOX), 1 m/L $LiCO_4$ in solvent mixture of 70 DIOX-30 DME (1.2-dimethyoxyethane) and 1 m/L $LiAsF_6$ in DIOX which is shown with both lithium and nickel cathode substrate.

It should be noted that during the first four runs, initial gassing was observed on all working electrodes, cathodes and anodes. This was only noticed during the first hour of the first run on the solutions and later gassing ceased (and was not observed on subsequent runs reusing the same electrolytes). This is obviously due to electrolysis of small residual amounts of water not quite removed despite careful preparation and drying of electrolytes.

The first three runs on lithium substrates showed a very small net cathode polarization and small cell voltages decreasing from electrolytes 1-A to 2-A. The quality of the deposit improved in going from electrolyte 1-A to 2-A. Thus the AsF_6- anion is preferable.

A completely different story developed for the nickel substrate (Run #4, Table 2).

The deposition of lithium on nickel substrate involves a large cathode polarization starting at 0.400 volts and remaining as high as 0.121V (Line 10, Table 2) towards the end. This must be predominantly a considerable charge transfer or chemical polarization (not concentration polarization). The mass

TABLE 2. Li-Deposition Experiments at 1 mA/cm^2 (Glass Cells)

1. Run No.	#1	#2	#3	#4
2. Electrolyte No.	1-A	1-B	2-A	2-A
3. Composition	1 m $LiClO_4$ DIOX	1 m $LiClO_4$ 70 DIOX - 30 DME	1 m $LiAsF_6$ DIOX	1 m $LiAsF_6$ DIOX
4. Cathode Substrate	Li	Li	Li	Ni
5. CD mA/cm^2	1	1	1	1
6. Time, Hrs.	10.8 hrs	10.8 hrs	10.8 hrs	10.8 hrs
7. Cathodic Charge, mAH/cm^2	10.8	10.8	10.8	10.8
8. Theo. dep. thickness, cmx10^3(@ 100% den. & 100% C.E.)	5.26	5.26	5.26	5.26
9. V_{cell} V	0.12+0.125	0.090+0.088	0.052+0.050	0.480_0.234
10. Li-cathode net polarize (iR-free) (vs. Li-ref)	0.008	0.035+0.008	0.007	0.400+0.121
11. Visual Observation	Initial gassing on both electrodes	-	-	-
	Smooth grey deposit later found not well adherent in solvent storage	Smooth but more lumpy deposit	Much smoother deposit & adherent	Small Li deposit but mostly larger white crystalline mass
	Cloudy gelatinous electrolyte in cell bottom	Some gell	No gelling	No gelling

transfer situation is identical in all these cells and there is, obviously, not much of a mass transfer problem (vertical electrodes, natural convection and a relatively low C.D.), hence not much of a concentration polarization. Since total polarization is low (and remains low during the entire extended runs) on lithium substrates the polarization related to the electrocrystallization process is obviously low too. However, on a nickel substrate the deposition frequently starts with a very large polarization which decreases only slowly as deposition takes place (see Lines 10, Runs #4 & 8, Tables 2 and 3).

The kinetic conclusion is, therefore, that the nucleation process which is the first step in electrocrystallization, occurs with difficulty on nickel. Later, as deposition proceeds on nickel, it tends to occur preferably on the small crystallites which are already on the surface rather than cover the entire nickel surface uniformly. Thus the electrodeposition of lithium on the nickel atoms occurs with much greater difficulty (i.e., polarization) than on lithium atoms. This is in agreement with the visually observable non-uniformity of lithium deposits on the nickel surface. Net cathodic polarization measurements are therefore a valuable tool in the study of the electrocrystallization process and may have a practical significance in future studies and designs of anode support grids.

Table 3 shows a similar series of experiments at 2.5 and Table 4 at 5.0 mA/cm^2. Again, the nickel substrate (Run #8) showed a very large initial potential which decreased to a value of 0.035v still much higher than the 0.005v. for lithium substrates. The nickel cathode, as noted under Run #8, showed two deposits: one, a gelled material, and the other a grey metallic lithium deposit.

With the third use of the same electrolyte in Run #12 the gelled white materials no longer appear in the 5 mA/cm^2 run

TABLE 3. Li Deposition Experiments at 2.5 mA/cm^2 (Glass Cells)

1. Run No.	#5	#6	#7	#8
2. Electrolyte No.	1-A	1-B	2-A	2-A
3. Composition	1 m $LiClO_4$ DIOX	1 m $LiClO_4$ 70 DIOX-30 DME	1 m $LiAsF_6$ DIOX	+
4. Cathode Substrate	Li	Li	Li	Ni
5. CD mA/cm^2	2.5	2.5	2.5	2.5
6. Time, hours	4	4	4	4
7. Cathodic Charge mAH/cm^2	10	10	10	10
8. Theo. Deposit Thickness, cm x 10^3	4.87	4.87	4.87	4.87
9. V_{cell} V	0.060+0.054	0.540+1.006(!)	0.020+0.017	0.410+0.063
10. Li-cathode polariz. (iR- free) (vs. Li-Ref)	0.005+0.033	0.007+0.007	0.011+0.005	0.360+0.035
11. Visual Observation	almost no deposition	Some more deposition (coherent?)	Comparatively most dense deposit	El-yte almost gelled ——— Top edge covered with gell, some Li deposit near lower edge of Vertical cathode
	No electrolyte gelling observed			

TABLE 4. Li Deposition Experiments at 5.0 mA/cm^2 (Glass Cells)

1. Run No.	#9	#10	#11	#12
2. Electrolyte No.	1-A	1-B	2-A	2-B
3. Composition	1 m $LiClO_4$ DIOX	1 m $LiClO_4$ 70 DIOX-30 DME	1 m $LiAsF_6$ DIOX	+
4. Cathode Substrate	Li	Li	Li	Ni
5. CD mA/cm^2	5.0	5.0	5.0	5.0
6. Time, Hrs.	2	2	2	2
7. Cathode Charge mAH/cm^2	10	10	10	10
8. Theo. dep. thickness cm^x10^3	4.87	4.87	4.87	4.87
9. V_{cell}, V	0.067	0.073→0.115	0.032	0.043
10. Li-cathode net polarization (iR-free) (vs. Li Ref) V.	0.006	0.003	0.033	0.036
11. Visual Observations	Thin granular uniform deposit (darkish)	Thicker uniform deposit (light gray)	Thicker uniform deposit (some dark spots and flakes)	Very thin smooth uniform deposit (can be scraped) (no gelling)

(Table 4). Of the lithium substrate runs 9 - 12, again electrolyte 1-B (with DME addition) gave a better deposit than 1-A. Electrolyte 2-A (run #11) gave the thickest deposit, however, some dark spots and flakes have been observed.

The cathodes from these and similar experiments were washed in pure ether solvent and stored in ground glass or sealed jars under solvent until their mounting on specially designed stainless steel SEM holders for introduction into the SEM machine.

An additional series of runs were performed at relatively high current density at 10 mA/cm^2 with four electrolytes designed to compare the perchlorate anion and the hexofluoroarsenate anion as well as the effect of 30% DME addition, as shown in Table 5. The addition of DME increased the polarization towards the end of the deposition. This coincides also with the observation with more uniform deposits, although all deposits were adherent. Generally, the increase of current density in going from 1 to 10 mA/cm^2 significantly lowered adhesion.

From the visual observations (before SEM examinations) the following initial conclusions were drawn:

1. Pre-electrolysis of an electrolyte to remove last traces of water may be a beneficial procedure for all secondary lithium batteries.

2. A lithium substrate is definitely more favorable (and shows substantially lower polarization) for deposition of lithium than does a nickel substrate. The nickel substrate gives non-adherent deposits with small crystallite morphology. This obvious non-adhesion makes nickel a very poor substrate for studying stripping efficiencies.*

*It was this finding which later was the basis for investigations of the reliability of the nickel substrate for stripping efficiency studies compared to other materials.

TABLE 5. Li-Deposition Experiments at 10 mA/cm^2 (Glass Cells)

1. Run No.	#15	#16	#18	#17
2. Electrolyte No.	1-A	1-B	2-A	2-B
3. Composition	1 m $LiClO_4$ DIOX	1 m $LiClO_4$ DIOX-30 DME	1 m $LiAsF_6$ DIOX	1 m $LiAsF_6$ DIOX - 30 DME
4. Cath. substrate	Li	Li	Li	Li
5. C.D., mA/cm^2	10	10	10	10
6. Time, hours	1.093	1.093	1.093	1.093
7. Cathodic charge, mAH/cm^2	10.93	←	←	←
8. Theo. Deposit thickness, cmx 10^3	5.32	←	←	←
9. V_{cell} V.	0.955 1.800 (!)	0.740 1.45(!)	0.441 0.363	0.521 0.555
10. Li-cath. polarization (iR-free) (vs. Li-ref), V.	0.100→ 0.050	0.070→ 0.115	0.077→ 0.061	0.084→ 0.080
11. Li cath. net polariz. final scans, volts				
at 1 mA/cm	0.026	0.012	0.010	0.019
at 2 mA/cm	0.044	0.032	0.017	0.032
at 5 mA/cm	0.094	0.051	0.036	0.069
at 10 mA/cm	0.094	0.086	0.065	0.117
12. Visual observations	Plates shorted lumpy non-adherent dep.	loose crumbly dep. purplish tinge →turned yellow	Thick layer non-adherent dep. non-uniform	Even layers of non-adherent dep. more uniform

3. DME addition to DIOX is probably beneficial

4. A more dense deposit (not necessary more adherent) results from $LiAsF_6$ compared to $LiClO_4$.

5. Gel formation in the electrolyte may occur already at low current densities and may be related to initial water impurities or result from electrode reaction products of such impurities (e.g., polymerization reaction catalyzed by radicals or intermediates).

2.1.3 SEM Electrode Examinations

Electrodes with lithium deposits on both nickel and lithium substrates from the cell studies discussed in the previous section and from many other runs covering also additional electrolytes shown in Table 1, were, as pointed out previously, mounted on specially designed stainless steel SEM holders and then stored in tight jars under a pure ether solvent layer in such a way that the deposits did not touch any of the walls of the jar. When the jars were moved to the SEM machine, the jars were quickly opened, the holders with the samples were removed while still wet with the solvent, and quickly introduced into the sample holding chamber which was promptly evacuated to evaporate the solvent from the electrode surface. It was found that this transfer procedure did not significantly affect by oxidation the morphology to be studied.

It should be understood that this initial study was in the nature of a preliminary survey designed to obtain rapidly an initial idea of the effects of solutes, solvents and substrates, and current densities; therefore, most of the conclusions in this section are somewhat tentative based on visual and SEM observations, and qualitative observations of adherence. It is considered, however, as a very important initial study designed to funnel future efforts in the direction of desirable electrolytes and deposition conditions.

Out of 35-40 photographs, 12 were selected and presented in Figs. 1, 2, and 3.

Figure 1 shows several interesting comparisons of deposits obtained at 1 mA/cm^2 for 2 hrs. The following should be noted:

a. (From R-26 and R-27) In DIOX AsF_6- anion gives larger crystallites and a more massive deposit, while ClO_4- yields smaller crystals, with dendrite tendency even at the modest current density of 1 mA/cm^2 (see below at 2,000 X magnification).

b. (From R-27 and R-28) For the same Electrolyte #2A, the nickel substrate leads to a substantially smaller crystallite and greater non-uniformity (poor adhesion to the nickel substrate was also determined).

Figure 2 compares deposits obtained also at 1 mA/cm^2 for 2 hrs. in several AsF_6- electrolytes, all on lithium substrates. Here comparisons lead to the following observations:

a. (From R-27 and R-29) Electrolytes 2A and 2B yields similar deposits, although the particle sizes seem to be larger,

R-26 in 1A (ClO_4^- in DIOX) on Li-Sub.

R-27 in 2A (AsF_6^- in DIOX) on Li-Sub.

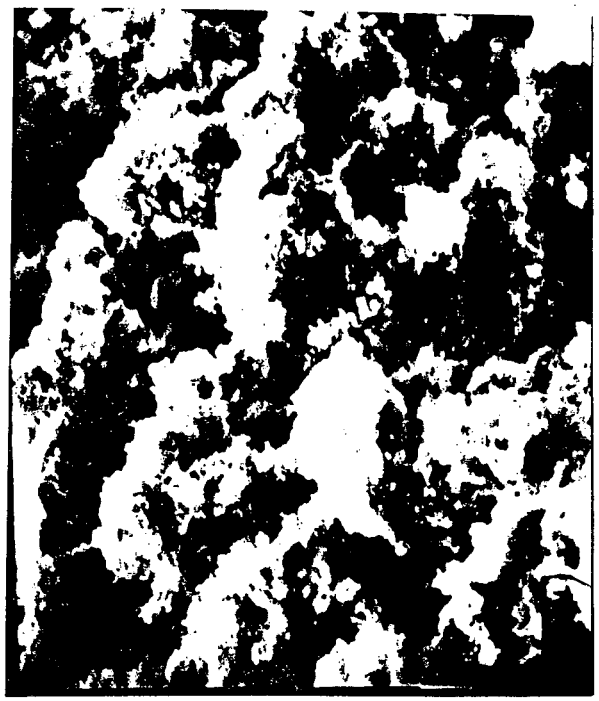
R-26 (same at 2000X)

R-28 in 2A (AsF_6^- in DIOX) on Ni-sub.

Fig. 1. SEM Micrographs (at 500X) of lithium deposited at 1 mA/cm^2 for 2 hours in several electrolytes.

R-29 in 2B (AsF_6^- in DIOX-DME)

R-32 in 5A (AsF_6^- in P.C.)



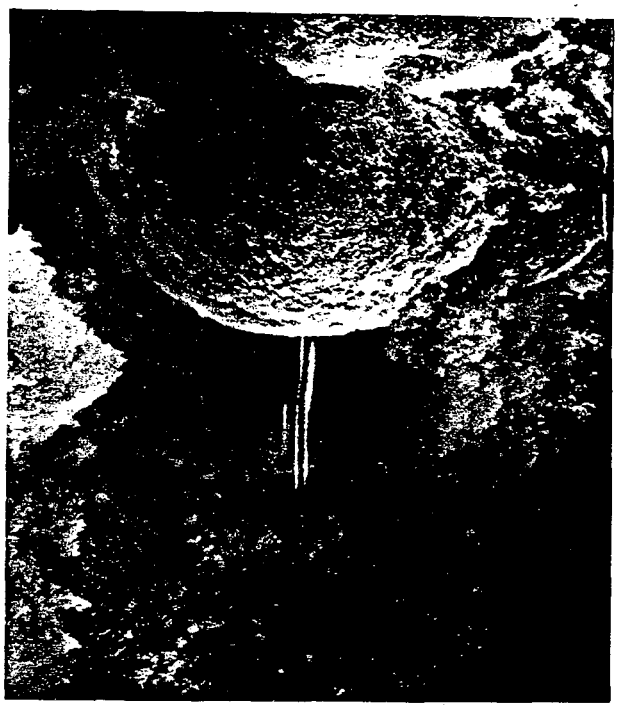
R-33 in 5C (AsF_6^- in DIOX-30PC)

R-31 in 5B (AsF_6^- in PC-30DME)

Fig. 2. SEM Micrographs (at 500X) of lithium deposited at 1 mA/cm^2 for 2 hours in several AsF_6^- electrolytes on Li substrates.

R-17 in 2B (DIOX - 30 DME)

R-51 in 2D (Me-THF-30 DME)



R-24 in 5B (PC - 30 DME)

R-25 in 5C (DIOX - 30 PC)

Fig. 3. SEM Micrographs (at 500X) of lithium deposited 10 mA/cm^2 for 0.2 hours on Li substrates in several AsF_6^- electrolytes.

closer to 20 μ rather than 10 in Electrolyte 2B with the DME addition.

b. (From R-29 and R-32 or R-27 and R-32) For the same anion P.C. radically changes the deposit from spherical particles of 10-20 μ to a foam-like very porous structure composed of fingers (2-4 μ diameter X 20-40 μ long). This structure was later found to have very poor adhesion to the solid lithium substrate.

c. (From R-32 and R-31) An addition of 30% DME to PC has little effect on the porous finger-like structure.

d. (From R-32, R-31, and R-33) Only when PC is down to 30% with DIOX does the finger-like structure disappear, but it still remains foamy and less crystalline in particular than in DIOX or DIOX-DME (it was also found to be less adherent).

Figure 3 shows results obtained with a tenfold increase of the current density, namely, to 10 mA/cm^2 for 0.2 hrs. so that theoretically the same amount of total deposit would result. Several observations can be made from this figure and the preceding ones:

a. (R-29, Fig. 2 and R-27) There is very little change in the nature of the spherical deposit in Electrolyte 2B ($AsF6^-$ in DIOX-DME) except there was a decrease in particle size to 7-10 μ from typically 20 μ which is expected at high current densities; the deposit remained adherent.

b. (From R-17 and R-52) Electrolyte 2D with 2 Me-THF is substantially different from the globular material from 2B. THF yields a very non-uniform deposit with platelets and deep

crevices. It may contain other materials besides lithium metal. It was found to be also non-adherent.

c. (From R-25, R-24, and R-27) The propylene carbonate containing electrolytes result in non-uniform cluster of very fine particles, deep crevices, and non-adherent deposits.

The preliminary conclusions from this phase of the study are therefore as follows:

1. A nickel substrate is undesirable, leads to non-uniform and non-adherent deposits with small crystallites(this may have practical consequences in future fabrication of secondary lithium anodes in which exposure of even support grids made of nickel may need to be avoided).

2. The perchlorate anion yields a good deposit, finer in structure but with some dendritic tendency, even at 1 mA/cm^2. The AsF_6^- is more desirable.

3. Of the solvents, PC is totally undesirable, 2 Me-THF also probably not, and so far DIOX with and without DME additions yields the best results.

4. The AsF_6^- DIOX system is capable of deposition on a lithium substrate in an adherent desirable crystalline structure, at least over the range of 1 - 10 mA/cm^2.

2.2 Anodic Stripping Efficiency Studies

2.2.1 General

In any secondary battery system employing a metallic anode the Faradaic efficiency for its charge and discharge steps is an important consideration. It is particularly important in case of metal anodes which during the discharge form species that are soluble in the electrolyte. The ratio of the Faradaic efficiency for the anodic dissolution step to the Faradaic efficiency for the preceding cathodic deposition step is commonly referred to as stripping efficiency.

Generally, soluble anode systems are, of course, not desirable for long cycle life secondary batteries, since the inherent mass transport limitations during the recharge step result in dendritic or powdery deposits with poor adhesion and in shape change of the entire anode surface, as this is the case in well-known battery systems employing aqueous alkaline zinc anodes.

However, while in alkaline systems the solubility of zinc anode products in the electrolyte is not a necessary, but a burdensome, fact of nature one has to contend with, a different situation exists with a lithium anode in organic, aprotic electrolyte systems. Here a relatively high solubility of lithium ion salts is necessary since they provide for the necessary ionic transport through the electrolyte and in case of many cathode materials they are necessary for interstitial or intercalation processes involved in the cathode reduction steps. Thus with lithium organic electrolyte secondary battery systems, the solubility of the lithium anode product in the electrolyte appears to be an unavoidable fact of life.

Under these circumstances it becomes necessary to develop electrolyte systems conducive to a desirable electrocrystallization of adherent lithium deposits despite the mass transfer situation discussed above.

Stripping efficiencies need to be studied as a function

of electrolyte composition, current density, substrate effect, and effect of cycling. Past work in this field universally involved such studies on nickel substrates. On the basis of initial observations on the structure and adherence and non-adherence of lithium deposit to a nickel substrate have led the staff of Electrochimica Corporation to consider the effect of substrate and the validity of work in this area. The other important effect looked into in these studies was that of subsequent cycling. Profound effects have been found usually resulting in a worsening of obtained stripping efficiency. It was decided that this, too, must be looked at if the work was to be significant for future practical development work of such batteries.

2.2.2 Glass Cell Stripping Efficiency Studies

Six glass cells of the same type as described previously in Section 2.1, 2. were employed for this program. Since there is no way to deposit lithium on a lithium substrate and strip only the amount deposited, conductive but inert substrates are necessary for such experimentation. Nickel remains stable and does not dissolve at the dissolution potentials of lithium and therefore it is a good starting point for a substrate. Electrodes 1 x 1" were cut abraded with a #320 mesh grit washed with MEK and employed in the glass cells between 2 lithium anodes. The cells were also equipped with lithium reference electrodes to permit following the electrode potential when desirable.

As a result of initial experiments it was found that past work of many investigators involved the deposition of a very small amount (much less than 1 Coulomb/cm^2) and this was on the one hand unrealistically low to what happens in a real battery, and on the other hand this tended to yield optimistically high

stripping efficiency results. After several investigations the work was standardized to deposit 2 Cb/cm^2 (i.e., 33.3 $mA\text{-}min/cm^2$). This is a realistic value for practical battery operation without involving excessive mechanical losses which excessively thick deposits would involve.

In addition to the traditionally employed nickel electrodes it was decided to investigate other substrates, and gold and aluminum were considered for this purpose. Aluminum is of potential interest because its alloying capabilities with lithium may facilitate the nucleation process for the deposition of lithium (gold which may not be practical but technically of interest would be investigated in the future).

The results for 4 cells connected in series and studied simultaneously with the same current density for the deposition and for the stripping step are summarized in Table 6. In addition to the stripping efficiency, $\eta\%$, tabulated is the net anodic polarization for the stripping portion of the cycle, ΔE, to see if there is a possible correlation. The first 3 cycles were performed at 1 mA/cm^2, the next at 2.5 and 5, and the last two at 10 mA/cm^2.

A number of interesting observations can be made from these results:

1. The first 3 cycles are somewhat erratic-probably due to water removal effects.

2. Considering that successful operation of a secondary battery requires very high stripping efficiency all values obtained from nickel substrates are discouraging. There are a number of sources of inefficiencies such as side reactions of water and other impurities, solvent cleavage, polymeriza-

TABLE 6. LITHIUM STRIPPING EFFICIENCY STUDIES AT 2 Cb/cm^2

η - Faradaic Stripping Efficiency, %

ΔE - Anodic Polarization, Volts

Cell No.	2		3		4		5	
	N I C K E L						ALUMINUM	
Electrolyte No.	2 C		2 G		2 H		2 G	
Composition	1m $LiAsF_6$		1.5 $LiAsF_6$		1.5 $LiAsF_6$		1.5 $LiAsF_6$	
	DIOX		DIOX-30 DME		ME-THF		DIOX - 30 DME	
	ΔE V.	η %	ΔE V.	η %	ΔE V.	η %	ΔE V.	η %
at 1 mA/cm^2								
Cycle #1	-	81.7%	-	78%	-	75.1%		76.4%
Cycle #2	.22	82	.09	58	.05	68.4	.21	82.0
Cycle #3	.22	77.2	.07	74.9	.06	75.3	.27	91.6
at 2.5mA/cm^2								
Cycle #4	.25	72.4	.16	75.2	.17	70.2	.21	80.3
at 5.0mA/cm^2								
Cycle #5	.51	66.3	.10	77.1	.25	61.5	.14	91.1%
at 10 mA/cm^2								
Cycle #6	.62	59	.18	82.8	.34	41.0	.12	96.6%
Cycle #7	0.58	48	0.15	79	.32	41.9	.10	92.7%

tion, etc., and mechanical losses of just plated lithium from the electrode surface. While these must all eventually be considered, comparisons between electrolytes can be made.

3. Electrolyte No. 2H (with Me-THF) appears to be the poorest.

4. Electrolyte No. 2G (with DIOX-30 DME) becomes superior to electrolyte 2C (without DME). This is especially true after several cycles (the first 2 cycles seem to be helpful in removing initial impurities in analogy to a pre-electrolysis.)

5. The most startling and important conclusion is that of the superiority of aluminum as a substrate over nickel. This becomes especially dramatic beginning with Cycle 3. This is possibly due to easier nucleation on the aluminum surface than on nickel and avoidance of catalytic processes which obviously take place on nickel (gel and white deposit formations). The lithium deposited aluminum plates are smooth, uniform, blue-gray and free of any gells or white deposits.

6. On aluminum stripping efficiency has clearly improved with current density.

7. While it is not clear at this point how stripping efficiency relates to the anodic polarization, we note from Table 1 that for nickel substrates polarization rises with current density significantly but remains small and drops somewhat in case of aluminum.

In a more extensive study on both aluminum and nickel, it was decided to compare with freshly prepared electrolytes #2G and #2H the stripping efficiencies. As can be seen from Table 7, rather inconsistent results were obtained on nickel substrates for both electrolytes, and this was even true for the first 3 cycles at 1 mA/cm^2. In fact, electrolyte #2H yielded at 10 mA/cm^2 (Cycle 7 & 8) efficiencies of 0%. On the aluminum substrate the efficiency improves during the first 4 cycles (probably removal of water impurities) and is consistently higher for electrolyte #2G (with DIOX-DME). It should be noted however that the stripping efficiency dropped off considerably from Cycle #6 (at 5 mA/cm^2) to 77%in Cycle #8 (at 10 mA/cm^2). The drop off for electrolyte #2H (with 2 Me-THF) is however much steeper, down to 57%.

Aside of the question of safety considerations which may preclude future use of percchlorate containing electrolytes in practical batteries, the perchlorate anion is known to function well and to give reasonably good deposits as has been observed previously. It was therefore of interest to compare 2 electrolytes with the same concentration of perchlorate by varying in respect to the solvent. Table 8 illustrates the stripping efficiencies obtained in the 2 solvent systems, DIOX-DME and 2 Me-THF. As shown in Table 8, while efficiencies are generally low (in the range of 60-70%) more consistent and higher results are obtained with DIOX-DME than with Me-THF. After 7 cycles the drop-off of the efficiency of Me-THF down to only 37% is particularly note worthy.

It is important to remember that impurity levels particularly the amount of water in the electrolyte introduced through the solute or through the solvent or from the operating enviornment will have an effect on the stripping efficiency values obtained. It is for this reason that in this

TABLE 7. Li-STRIPPING EFFICIENCIES (%) AT 2Cb/cm^2 (ASN-10) ON FRESHLY PREPARED ELECTROLYTES 2G and 2H

	Ni - SUBSTRATE		Al - SUBSTRATE	
Electrol. No.	2G	2H	2G	2H
Composition:	1.5m $LiAsF_6$ DIOX-30 DME	1.5m $LiAsF_6$ 2 Me-THF	(SAME)	
Stripping Eff., % at 1 mA/cm^2				
Cycle #1	85%	52%	72%	75%
Cycle #2	78	41	91	85
Cycle #3	30	69	92	88
at 2.5 mA/cm^2				
Cycle #4	30	78	99	93
Cycle #5	-	-	-	-
at 5.0 mA/cm^2				
Cycle #6	11	46	97	94
at 10 mA/cm^2				
Cycle #7	7	0	78	63
Cycle #8	10	0	77	57

TABLE 8. STRIPPING EFFICIENCY ON ALUMINUM SUBSTRATE AT 2 Cb/cm^2 WITH FRESH PERCHLORATE ELECTROLYTES IN TWO SOLVENT SYSTEMS

Electrolyte No.		1 C	1 E
Composition		1.5m $LiClO_4$ DIOX-30 DME	1.5m $LiClO_4$ 2 Me-THF
Cycle #	C.D. mA/cm^2		
1	1	59%	66%
2	1	57	73
3	1	57	76
4	1	71	69
5	2.5	78	47
6	1	69	65
7	2.5	65	37

work an effort was made to use the same salts, solvents or dry box make-up procedures. Cells were operated simultaneously on the same circuit in the same place and at the same time to minimize variability. In this manner effects of variable parameters could be studied more reliably, even if a different stripping efficiency value could be obtained for the same electrolyte for a similar electrolyte in another experimental series.

In an additional experimental series it was decided to investigate the possible effects which sulfur dioxide additions to the electrolyte might have on the stripping efficiency. The benefit of such small additions have been established for at least primary batteries in U.S. Patent 3,891,458[(2)]. SO_2 forms with the lithium surface dithionite film which is the basis for long term stability of the lithium anode in primary cells. If a thin non-insulating protective film which would minimize attack of the freshly deposited lithium by the solvent could be established, the stripping efficiency could possibly be enhanced. The results of the first effort in this direction are shown in Table 9 for 3 electrolytes #1C, #1E, and and #2G, with and without SO_2 additions, i.e., for a total of 6 electrolytes on aluminum substrates. A number of observations can be made on the results obtained:

a. In every case, additions of 3 molar SO_2 lowered the stripping efficiency except in one case, for Cycle #1 which is typically inconsistent.

b. The lowering of the efficiency is particularly significant for electrolyte #1E (see e.g., cycle #4) in which the drop is almost to half.

c. The comparatively best stripping efficiencies were

Table 9 Li-Stripping Efficiency Electrolyte Studies On Aluminum Substrate-Effects of 3 m SO_2 Additions (ASN-9)

Electrolyte No.	1 C	1 C $+SO_2$	1 E	1 E $+SO_2$	2 G	2 G $+SO_2$
Composition	1.5 m $LiClO_4$ DIOX-30DME		1.5 m $LiClO_4$ 2 Me-THF		1.5 m $LiAsF_6$ DIOX-30DME	
Stripp. Eff. % @ 1 mA/cm^2						
Cycle #1	70%	64%	84%	52%	79%	86%
Cycle #2	61	62	73	63	91	78
Cycle #3	73	57	95	52	97	79
@ 2.5 mA/cm^2						
Cycle #4	71	51	86	44	87	76

obtained with electrolyte #2G (as high as 97%) but these too, would drop 12 to 18% upon the addition of SO_2.

It is of course possible that a 3 molar addition is too large and it would be interesting to explore what additions in the range of 0.1 - 0.5 molar SO_2 would accomplish. It would also be desirable to explore any changes of the morphology with SEM.

2.3 Design of a Capillary Cell for Electrocrystallization Studies

As part of this program, it was considered desirable to develop a technique for future studies of the electrocrystallization phenomena for lithium in organic electrolyte systems. A capillary cell has been designed with a 1 millimeter I.D. which would fit under the objective of a microscope and permit observation and photography of lithium crystallite formation on a solid lithium substrate, filling the cross-section of the capillary tube, in the center. The other half of the tube would be filled with an electrolyte under investigation. The counter electrode would a lithium wire in a side compartment connected at the end of the capillary tube. In addition, the design provides for another side compartment to accommodate a reference electrode. All 3 compartments of the cell would be sealed with ground joints to permit operation in air after dry box assembly of the cell.

This proposed procedure requires a 1 millimeter extruded lithium wire to fill the capillary cross-section entirely. Both vendors of metallic lithium are unable to supply such a small diameter lithium wire. Another possibility which is being considered is the melting in of lithium into the cell cross-section in such a way as to have the lithium fill the capillary

somewhere to the center of its length. This would require a differential heating and cooling of the cell before pouring in molten lithium. Such a procedure would be contemplated in a future program.

2.4 Apparatus and Procedure for Determination of Metallic Lithium In Deposits

It is well-known that the solute or solvent may participate in cathodic and anodic reactions in parallel with the or dissolution of lithium metal. For instance, there is evidence that upon discharge, the lithium AsF_6^- salt decomposes to some extent, yielding degradation products which react with, or are catalyzed by impurities in the salt. SEM/EDAX studies have revealed a white fluffy product[3], containing As and Si. Similar white co-deposits have been found in this work. It is also known that the solvents can undergo polymerization; for instance, through free radical mechanism (e.g., Dioxolane)[4].

In any event it is deemed important to develop a reliable analytic procedure for determination of the metallic content of lithium in the lithium deposit on the electrode as an important independing research tool in addition to stripping efficiency studies. We have undertaken on the basis of past experience at Electrochimica Corporation to design and develop such equipment and procedure. The design and approach are discussed below.

The apparatus shown in Fig. 4 would be evacuated and flashed with Argon to remove all air in the system. Separately, in an Argon Box the lithium electrode or the lithium deposit holding the substrate would be removed from the cell, gently dabbed with tissue to remove excess electrolyte or solvent and placed

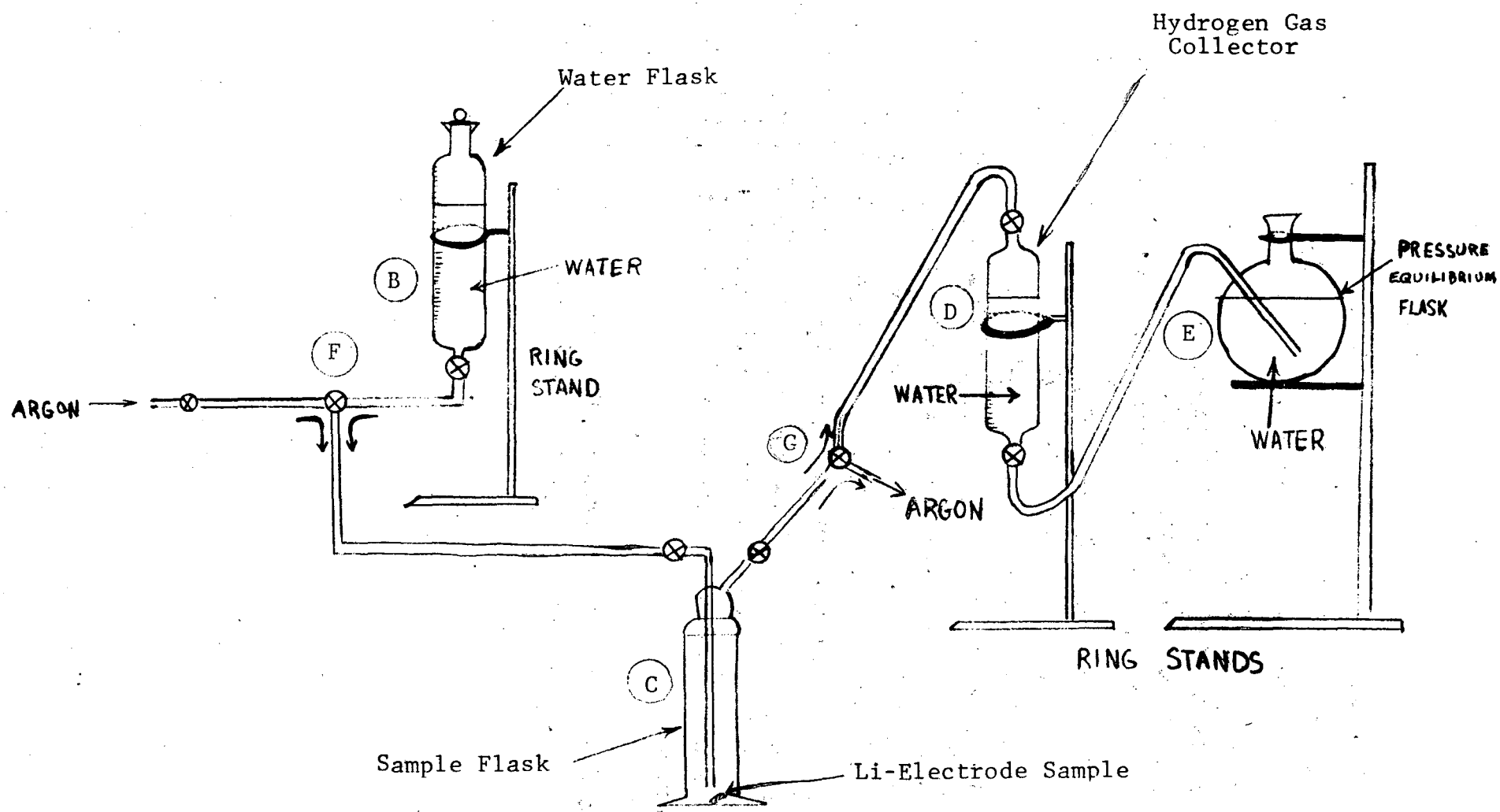


Fig. 4 Lithium Determination Apparatus via H_2 Evolution

in a 500 cc gas washing bottle C (see Fig. 4) which is then sealed with a stopper, removed from the dry box, and assembled to the hydrogen collection apparatus. The next step is to equilibrate water levels in the wide burette D and in flask E by moving burette D up and down to adjust the water level to approximately 450 cc level. After recording the water levels in burettes D and B, opening the three-way stop cock E allows water from B gradually to flow into C where it reacts with the metallic lithium content of the electrode. At the same time, the three-way stop cock G is opened to D where the evolved hydrogen enters. Stop and record the water level B before the first drop of water goes into wash bottle C (the connection tube should be filled with water by now). Slowly add 25 cc of water into C. The collected amount of hydrogen is finally determined by equilibrating the levels of water in vessels D and E. From the temperature and barometric pressure, the volume of hydrogen collected is converted into moles of hydrogen and correspondingly into moles of metallic lithium on the electrode.

The design of the equipment has been completed, parts ordered, and the setup should be available for a future program.

3.0 DISCUSSION

Despite its limited effort, this Phase I program has succeeded in the establishment of several research techniques important for future progress in the area of rechargeable ambient temperature lithium anodes and in obtaining valuable initial results in the area of promising electrolytes.

In the area of techniques, the following have been established:

1. A method for stripping efficiency studies on an aluminum substrate which gives reproducible results by alloying with the deposited lithium in a reversible manner. At the same time, it was demonstrated that prior studies employing nickel substrates cannot be considered reliable and that the nickel surface catalyzes side reactions and polymerization.

2. A SEM holder and handling method was developed to facilitate morphology studies of lithium electrodeposits.

3. An analytical technique for determination of the metallic content of electrodeposits by decompositon with water was developed.

4. A preliminary design for a 3 compartment capillary cell for microscopic studies for the electrocrystallization process was initiated.

From the results of the SEM electrode studies (Sec. 2.1.3) and of the anodic stripping efficiencies (Sec. 2.2.2), the following conclusions and observations can be made:

1) For morphological studies with SEM, a nickel substrate is undesirable (compared to a solid lithium or aluminum substrate) since it leads to non-uniform and non-adherent deposition of smaller crystallites often accompanied by co-deposition of gells, polymers, and other materials which have nothing to do with metallic lithium.

2) For stripping efficiency studies, an aluminum substrate was found to be reliable and reproducible and provide significantly higher efficiency values than did nickel under the same conditions.

3) It was found that meaningful stripping efficiency studies should be conducted in the range of 2-5 coulomb/cm^2 for the deposition step and that a number of cycles should be performed to first remove water impurities and then to observe the effect of cycling on the resulting stripping efficiency.

4) Of the two anions so far studied, both perchlorate and AsF_6^- can operate (although perchlorate shows a greater dendritic growth tendency). The results of obtained stripping efficiencies, SEM observations and, of course, safety considerations make the AsF_6^- anion so far more desirable.

5) Of the solvents so far studied, P.C. with any co-solvents has been found to be totally undesirable, 2 Me THF was undesirable from the point of view of stripping efficiencies, and DIOX preferably with 30% DME to yield the best overall results.

6) Additions of SO_2 to the electrolyte at the 3 molar level, motivated by the desire to protect freshly deposited lithium from solvent attack, resulted in a lowering of stripping

efficiency. It is possible that the concept still has merits but lower concentrations of SO_2 or other additives might be more desirable.

7. In summary, the AsF_6^--Dioxolane electrolyte system (with and without co-solvents such as DME) offers the most adherent desirable crystalline deposits, and is a good point of departure for future development.

The suggestion of using aluminum or its alloys as a base for a working lithium electrode has recently been mentioned in the literature (see e.g., (5) and (6)). Whether such suggestions are of practical significance for the design of batteries with high energy may be debatable. What was sought in this program was to bring out the fact that traditional nickel substrates which had been used for stripping efficiency evaluation studies were not suitable and tended to give irreproducible results as well as low efficiencies. What is important about the aluminum surface is that the alloying facilitates the nucleation process for the start-up of the lithium deposition. It is very likely that an amalgamated metal surface, e.g., of copper or brass would present an even better substrate for application in the stripping technique, as lithium alloys readily with mercury (compare also (7)). Gold has already been mentioned as another possibility. Ease of nucleation is one consideration. The other is avoidance of local action between a noble substrate and the electropositive lithium.

Another interesting aspect is the finding of this study that the substituted cyclic ether 2-Me-THF yields poorer efficiences than the DIOX solvent systems, despite the high chemical stability claimed for this ether, compared to the unsubstituted THF[8]. What is important in the overall picture is not just

the chemical stability of the solvent but also its effect on the lithium electrocrystallization, mode, the protective filming effects, nature of such films (e.g., whether they are Li^+ ion conducting) etc. Stripping efficiency results one obtains are thus the gross product of a number of phenomena such as nucleation and crystallization processes, adhesion, both chemical and mechanical to the substrate, net Faradaic efficiency for the deposition and dissolution processes, and all possible chemical interactions between solvent and lithium. A typical such interaction as may be involved in a 1 electron transfer from lithium to the lowest unfilled molecular orbital (LUMO) of an ether molecule:

$$Li + R\text{-}O\text{-}R \xrightarrow{slow} R\text{-}\overset{-\cdot}{O}\text{-}R,\ Li^+ \qquad (1)$$

and subsequent C-O clevage and further reduction by lithium to the observed product stoichiometry[9]:

$$2Li + R\text{-}O\text{-}R \longrightarrow R^-Li^+ + RO\text{-}Li^+ \qquad (2)$$

From the point of view of deposit classification and characterization, we find that there is in fact, very little established criteria, at present, to be helpful in battery anode R&D. As a starting point, we may have to resort to the field of electrodeposition of metal for plating purposes, well realizing that in a battery the desirable objectives are different.

H. Fischer[10] divided metal deposits into five categories:

1. Base-oriented reproduction type (BR)
2. Field-oriented texture-type (FT)
3. Non-oriented dispersion type (UD)
4. Twinning type (z)
5. Field-oriented isolation type (FI).

The first four categories relate to compact deposits. Only FI describes deposits in which individual grains do not press against each other to form a solid layer, but rather leave space in between containing electrolyte. If deposition is prolonged, porous deposits are formed. There can be several types of non-adherent deposits. Dendrites and whiskers can be considered to be belonging to the FI types. The deposits of this type show poor adherence (powders and mossy deposits) and still dendritic structure when observed under high magnification. Under some circumstances in the field of zinc depositions (a field from which we hope to learn a lot to guide us in the lithium studies) good adherence is obtained and the crystallites do not exhibit preferential growth directions. They are of similar dimension in all directions and therefore give a granular appearance. This type is designated as the granular isolation type (GI)[11]. In a very preliminary way we can already say that AsF_6^- anion definitely favors this type over ClO_4^-.

Finally, to gain a perspective on the entire question of battery cycle life, it may be useful to consider the effect of both cell design and of Li-stripping efficiency on cycle life.[10] Let:

C_o - be the initial (design) capacity ratio (to nom. capacity) for the Li-anode

C - Capacity ratio of negative after N - cycles

N_1 - Number of cycles till capacity ratio of one ($C=1$ i.e., no excess negative capacity)

N_2 - The number of additional cycles until capacity drops to a defined cell end-of-life (e.g. $1.0<C<0$)

$\bar{E}$ - Av. fraction of capacity recovery each cycle (= stripping efficiency)

While anode excess capacity still exists:

$$Co-1 = N_1(1-\bar{E}) \qquad (3)$$

After it is down to a ratio of 1 or less:

$$C = \bar{E}^{N_2} \qquad (4)$$

Thus for a defined cell end-of-life of 50% of original capacity $C = 0.5$ and

$$N_2 = \log 0.5/\log \bar{E} \qquad (4a)$$

How profoundly both the design factor C_o and the anode recharge efficiency, $\bar{E}$, affect the total number of obtainable cycles (N_1+N_2) can be seen from the sample calculations of equ. (3) and (4a) given in Table 10.

Table 10. Number of Cycles as Function of C_o & $\bar{E}$

Cap. Design Factor C_o	Recharge Efficiency $\bar{E}$	Cycles to 100% nom. Cap. N_1	Cycles to 50% nom. Cap. N_2	Total Cycles N_1+N_2
5	0.99	400	69	469
5	0.97	133	22	155
10	0.99	900	69	969
10	0.97	300	22	322

In alkaline nickel zinc batteries the designer typically provides for design capacity factors (C_o) in the range of 2.5 to 4.5. For a light element like lithium, design factors of 5-10 are therefore not unreasonable. As can be seen, these factors have a profound effect on the number of cycles N_1. At a given design factor dropping in recharge efficiency from 99% to 97% cuts the number of cycles N_1 by a factor of <u>three</u>. Approximately the same happens to the generally smaller number of cycles N_2. In short, we can say that within the range of sensible design factors one could live with recharge efficiencies of 97% and up, but probably not below that figure. This provides an orientation goal for future studies on the lithium anode.

4.0 FUTURE DIRECTIONS

On the basis of the findings of this preliminary program and related considerations, we feel that in order to provide a basis for future successful developments in this area of rechargeable ambient temperature lithium batteries, future efforts should be channeled in the following directions:

1. Development and optimization of solvent systems with particular attention to the lithium ion coordination by co-solvent molecules on the one hand, and the formation of desirable protective films on lithium capable of Li^+ ion transport. A number of ethers even as simple as diethyl ether (DEE) may have sufficiently high oxidation potentials combined with desirable film characteristics to warrant study as co-solvents. DEE, for instance, has proven itself as a good solvent as an electrodeposition of alkaline metals. A number of five-mem-

bered unsaturated heterocyclic hydrocarbon compound having no replaceable hydrogen and having at least one heterocyclic atom selected from the group of oxygen, sulfur and nitrogen would appear meritorious for complexing and/or solvating the Li^+ ion with large molecules.

2. Lithium salts with large but stable anions must be sought. The boron alkyl compounds[1] are just one example providing high oxidation potentials can be assured. The AsF_6^- salt is probably acceptable for limited cycle batteries, so further efforts in this area are necessary.

3. The concept of mixed salts should also be explored so that good electrolyte conductivities can be provided on the one hand, and desirable lithium ion complexing or solvating on the other hand.

4. The initial exploration of the performance of reasonable size lithium anodes in cell designs with limited electrolyte should be undertaken in the next phase program to obtain an early assesment of potential cell behavior problems such as anode shape change, densification and passivation at medium and high operating rates.

5. As progress in the electrode area is made, it is critically important to verify that the optimized electrolyte will be compatible with stable and energetically desirable cathodes of choice.

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