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INVESTIGATION OF THE ELECTROCHEMICAL FORMATION OF LI-C
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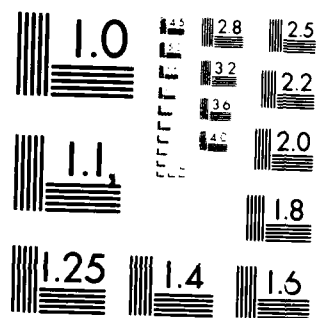
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INVESTIGATION OF THE ELECTROCHEMICAL FORMATION OF Li-C INTERCALATION COMPOUNDS

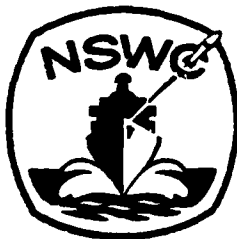
BY PATRICIA H. SMITH LARRY DeVRIES JASON N. SHIH STANLEY D. JAMES
WILLIAM P. KILROY

RESEARCH AND TECHNOLOGY DEPARTMENT

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NSWC TR 83-30	2. GOVT ACCESSION NO. AD A122 879	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) INVESTIGATION OF THE ELECTROCHEMICAL FORMATION OF Li-C INTERCALATION COMPOUNDS		5. TYPE OF REPORT & PERIOD COVERED Final Report--FY82
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Patricia H. Smith, Larry DeVries, Jason N. Shih, Stanley D. James and William P. Kilroy		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Surface Weapons Center (Code R33) White Oak Silver Spring, MD 20910		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61152N; ZR00001; ZR01301; R01AA
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE May 1983
		13. NUMBER OF PAGES 28
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the Abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Carbon Black Lithium Intercalation Batteries		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This investigation re-examines the possible undervoltage electrochemical formulation of Li-C intercalation compounds. The conditions simulated that of a cell which has failed due to depolarizer starvation. Carbon black cathodes were subjected to constant-current electrolysis in 1 M LiAsF solutions in propylene carbonate or 2-methyltetrahydrofuran. Cathode V-t curves displayed plateaus around +1 V versus Li in which the cathode absorbed ~16 coulombs per cm ² before falling to 0.05 V where the runs were terminated.		

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Aqueous extracts of the cathodes contained little or no hydroxide indicating the absence of Li-C compounds. However, the present work also showed that LiC_6 rapidly reduces propylene carbonate to carbonate ion. Hence it remains possible that the undervoltage plateaus originated in the formation of intermediate Li-C compounds which rapidly reduce the solvent.

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FOREWORD

This work was undertaken as part of a program to investigate safety hazards in nonaqueous ambient temperature lithium batteries. In order to ascertain the manner in which potentially hazardous Li-C mixtures may occur in electrochemical cells, a cell containing a lithium anode, carbon cathode, and a depolarizer free aprotic solvent was discharged and analyzed. Initial investigations reveal that no undervoltage formation of a Li-C intercalation compound could be detected by our technique.

We acknowledge the financial support of the Independent Research Program of the Naval Surface Weapons Center and the Electrochemical Technology Block Program of NAVSEA.

Approved by:

Jack R. Dixon
JACK R. DIXON, Head
Materials Division



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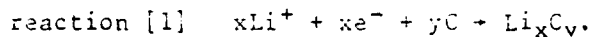
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CHAPTER 1

INTRODUCTION

Recently, considerable attention has been given to the possible formation and potential hazards of lithium/carbon matrices in Li/SO₂ and Li/SOCl₂ batteries.^{1,2} Thermal investigations have revealed such components to be very reactive toward battery electrolyte^{3,4} and may have an impact on the safe use of lithium batteries. Intimate mixtures of carbon and lithium can result from a variety of mechanisms: (a) severe mechanical distortion of the cell could shear Li and C components together; (b) overvoltage deposition of Li could produce Li dendrites. This can occur when cathode failure in one out of a string of cells causes Li to be plated out in the carbon of the failed cell; and (c) undervoltage deposition of lithium resulting in the formation of Li-C intercalation compounds.

The lamellar structured compounds are believed to form when cathodic reduction of Li⁺ to Li is accompanied by compound formation between Li and the carbon black cathode:^{1,2}



This theory derives support from several investigators who have reported that lithium can be intercalated into graphite foils when the electrochemical

¹Kilroy, W. P., and James, S. D., "Promotion by Carbon of the Reactivity of Lithium with SOCl₂ and SO₂ - Effect on Lithium Battery Safety," J. Electrochem. Soc., 128, 1981, p. 934.

²Kilroy, W. P. James, S. D., and Milliken, J., "Investigation of the Nature and Reactivity of Compounds Formed Between Lithium and Carbon Black," NSWC TR 81-127, Sep 1981.

³Dallek, S., James, S. D., and Kilroy, W. P., "Exothermic Reactions Among Components of Lithium-Sulfur Dioxide and Lithium-Thionyl Chloride Cells," J. Electrochem. Soc., 128, 1981, p. 508.

⁴James S. D., Smith, P. H., and Kilroy, W. P., "Effect of Carbon on the Reactivity of Lithium with SO₂ and SOCl₂ Electrolytes," submitted to J. Electrochem. Soc.

reaction is carried out in polar aprotic organic solvents containing Li^+ salts.⁵⁻⁸ During this process the reduction of carbon occurs in a step-wise course, and it has been concluded that the quantity of one reduced species does not increase continually. Instead, reduction occurs until formation of a defined stoichiometric structure is complete, at which time the succeeding thermodynamically less stable Li_xC_y is formed.⁵ However it must be noted that Li_xC_y did not form when substituting carbon felt for graphite foils.⁸ Here results indicate that in the case of carbon felt, a solvent decomposition rather than an intercalation of alkali metal occurred. This was attributed to the fact that carbon felt possessed no undisturbed layered structure.

Although most studies pertaining to lithium-carbon intercalation compounds have dealt with carbon in the graphite phase as opposed to carbon black, several papers have suggested that well defined intercalation compounds can form with non-graphitic carbons.^{9,10} However the generally accepted rule is that only graphitic carbons form regular interstitial compounds. If lithium-carbon black intercalation compounds should form within the carbon (Shawinigan Acetylene Black) cathode of lithium batteries, such a formation could result in a potentially hazardous condition. For example it has recently been demonstrated in this laboratory that intimate mixtures of carbon and lithium are extremely reactive toward battery (SOCl_2 - 1.5M LiAsF_6) electrolyte. A 1:1 weight ratio mixture of Shawinigan carbon black and lithium generates $3,550 \pm 616$ calories per gram of mixture when added to battery electrolyte.

In order to investigate the manner in which mixtures of lithium - Shawinigan Acetylene Black form at undervoltage potentials (> 0 Volts versus Li reference) in a lithium battery the following study was undertaken.

⁵Besenhard, J. O., "The Electrochemical Preparation and Properties of Ionic Alkali Metal and NR_4 -Graphite Intercalation Compounds in Organic Electrolytes," Carbon, 14, 1976, p. 111.

⁶Besenhard, J. O., and Fritz, H. P., "Cathodic Reduction of Graphite in Organic Solutions of Alkali and NR_4^+ Salts," J. Electroanal. Chem., 53, 1974, p. 329.

⁷Besenhard, J. O., and Theodoridou, E., "Electrochemical Applications of Graphite Intercalation Compounds," Synth. Met., 4, 1982, p. 211.

⁸Eichinger, G., "Cathodic Decomposition of Propylene Carbonate," J. Electroanal. Chem., 74, 1976, p. 183.

⁹Hérinckx, C., Perret, R., and Ruland, W., "Interstitial Compounds of Potassium with Carbon Fibers," Carbon, 10, 1972, p. 711.

¹⁰Hookey, J. G., "Aluminum Chloride," Carbon, 13, 1975, p. 469.

CHAPTER 2

EXPERIMENTAL

I. PREPARATION OF THE CELLS

Propylene carbonate (PC) obtained from Burdick and Jackson (distilled in glass), and 2-methyltetrahydrofuran (2Me-THF) obtained from Aldrich were used as received or distilled off CaH_2 under argon. Both solvents were degassed with argon for approximately 30 minutes prior to use.

Lithium hexafluoroarsenate (LiAsF_6) (U.S. Steel Agri-Chemicals, electrochemical grade) was used as received.

Electrolytic solutions were made of 1 M LiAsF_6 in PC and 2Me-THF.

Lithium metal (Foote Mineral) pressed on Ni Exmet was used as a reference and counter electrode. A nickel tab was spot-welded to the Exmet for electrical contact.

The carbon cathodes (10% Teflon) were prepared from Shawinigan carbon black, du Pont TFE-30 emulsion, and a sufficient amount of water to yield a stiff paste. The latter was then applied to a 9.5 cm x 4 cm (5 Ni6-3/0) Exmet (Exmet Corporation) while still moist. The electrodes were pressed to a thickness of $.035'' \pm .003''$ prior to vacuum drying for approximately 24 hours at 120°C . All cathodes were trimmed to a 2.5 cm x 1.5 cm dimension then spotwelded to nickel wire.

A schematic diagram of the cell is shown in Figure 1. The cathode was placed between two lithium anodes. Polypropylene served as a separator between cathode and lithium, while two glass slides and a nickel wire secured the cell components. A lithium electrode placed in the same plane as the cell served as a reference. After assembling the cell, 50 mL of 1 M LiAsF_6 propylene carbonate solution was added.

II. DISCHARGE PROCEDURE

Galvanostatic experiments were accomplished with an Electronic Measurements model C612 constant current power supply. The potential of the carbon cathode versus lithium reference and carbon cathode versus lithium working electrode was recorded as a function of time as was the current. Runs were terminated when the carbon versus lithium working electrode reached a voltage of +0.05V.

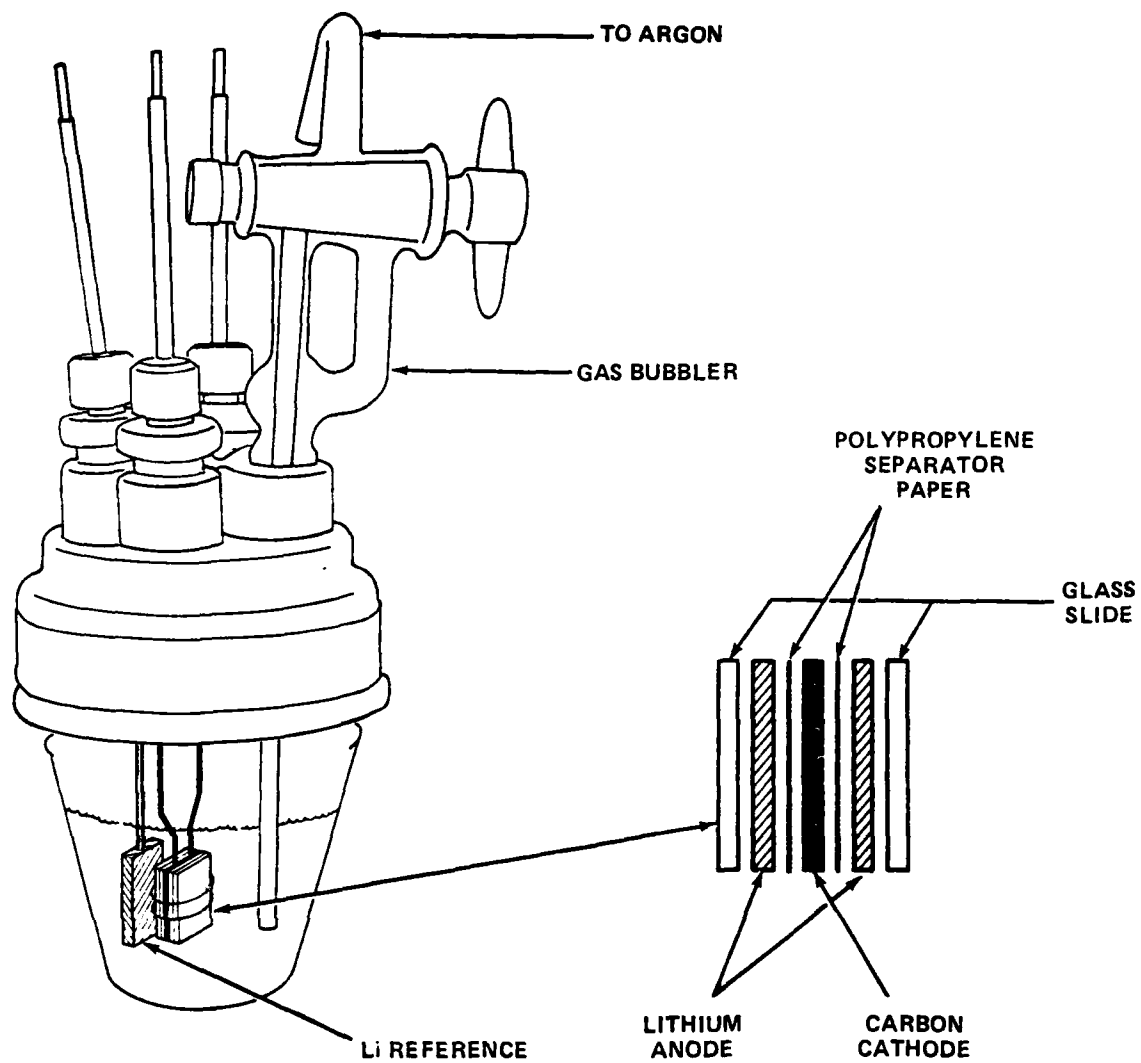


FIGURE 1. SCHEMATIC DIAGRAM OF THE ELECTROCHEMICAL CELL

Controlled potential operations (+0.05 and +0.10V) were maintained using a Princeton Applied Research (PAR) model 371 Potentiostat/Galvanostat in series with a PAR model 379 digital coulometer.

III. POTENTIOMETRIC DETERMINATION OF CO_3^{2-}

After electrolysis to a cut off voltage of +0.05 V versus Li reference, the cells were disassembled and the carbon cathodes refluxed for 8-10 hours in 50 mL of distilled carbonate-free water. All transfers and procedures were done under a blanket of argon to avoid contamination by atmospheric CO_2 . After refluxing, the carbon-water mixtures were filtered and an aliquot of the extract was potentiometrically titrated with .1N HCl using a Metromm potentiograph Model E535. Blanks were run of the carbonate-free water used in this analysis and that volume was deducted from the total volumes prior to calculations. A combination glass electrode was used to measure the pH changes during the titration. Using this procedure both hydroxide and carbonate were determined in one titration. Titration curves were made in the derivative mode as well as pH mode.

IV. ATOMIC ABSORPTION DETERMINATION OF Li^+

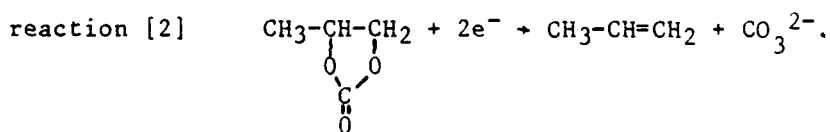
In order to ensure that the above experimental procedure (refluxing the carbon cathode for 8-10 hours) accounted for all lithium deposited inside the pores of the carbon, the carbon was acidified with a 2.5% nitric-water solution. This mixture was boiled for 30 minutes then filtered. The extract was analyzed for Li^+ concentration using a Perkin Elmer Model 5000 Atomic Absorption Spectrophotometer. The carbon was then ashed in a Pt crucible. The remaining residue was analyzed using atomic absorption.

CHAPTER 3

RESULTS AND DISCUSSION

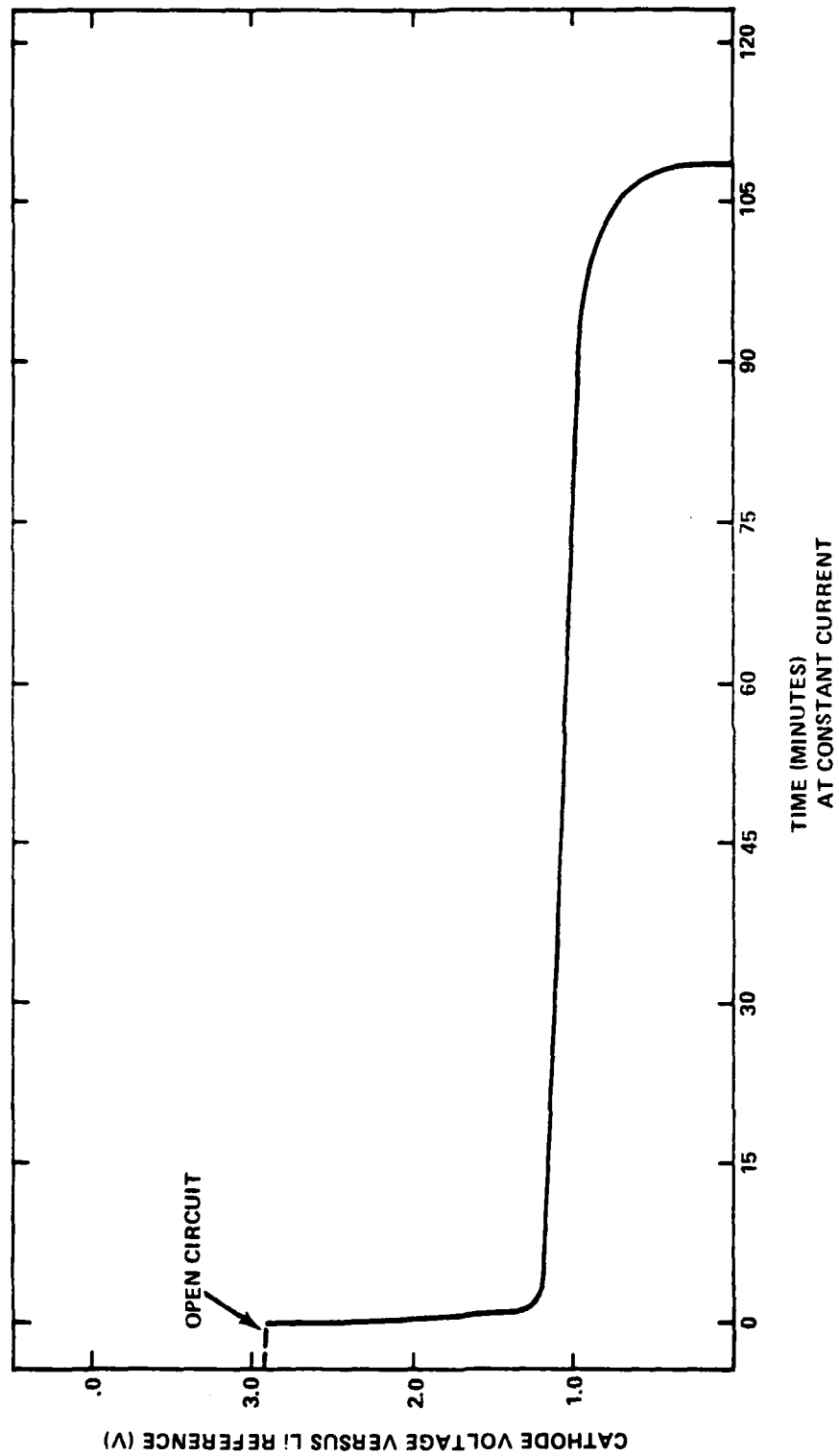
Typical voltage-time curves for Shawinigan carbon black electrodes cathodized in solutions free of battery cathode depolarizer are shown in Figures 2 and 3. These situations may simulate that of a battery cathode which has failed due to SO_2 or SOCl_2 starvation. The open circuit voltage of approximately 3V versus Li reference dropped sharply on the passage of cathodic current ($2\text{mA}/\text{cm}^2$) and appears to plateau around 1.3 V for 2-MeTHF and 0.9-0.7 V for PC. The decrease in potential down to +0.5 volts is the result of blockage of the active surface of the carbon by insoluble reaction products (Li_2CO_3) and is not the consequence of a reactant depletion. This was verified by submerging a new cathode and anode into the existing electrolytic solution. A new voltage-time curve similar to the first curve was obtained.

In a similar experiment employing PC as the solvent, an investigation¹¹ has suggested that during the plateau region, cathodic reduction of Li^+ to Li occurs accompanied by compound formation between lithium and carbon black to produce Li-C intercalation compounds (reaction 1). Although a variety of cathodic reductions could account for the observance of such a plateau (AsF_6^- to AsF_3 ; Teflon to F^- ; dissolved oxygen to OH^- or Li^+ to LiAl in the aluminum Exmet cathode support) the authors rejected these possibilities by systematically excluding each component and observing the effect on the plateau. Cathodic reduction of the solvent (propylene carbonate) was ruled out because aqueous extracts of the carbon black electrodes cathodized at undervoltage potentials contained no observable carbonate but rather a substantial amount of hydroxide. (It has been postulated that electrochemical reduction of propylene carbonate generates carbonate ion via reaction 2)¹²



¹¹Kilroy, NSWC TR 81-127.

¹²Dey, A. N., and Sullivan, B. P., "The Electrochemical Decomposition of Propylene Carbonate on Graphite," J. Electrochem. Soc., 117, 1970, p. 222.

FIGURE 2. VOLTAGE-TIME CURVE FOR SHAWINIGAN CARBON BLACK ELECTRODE CATHODIZED IN 1M LiAsF₆-2 Me-THF

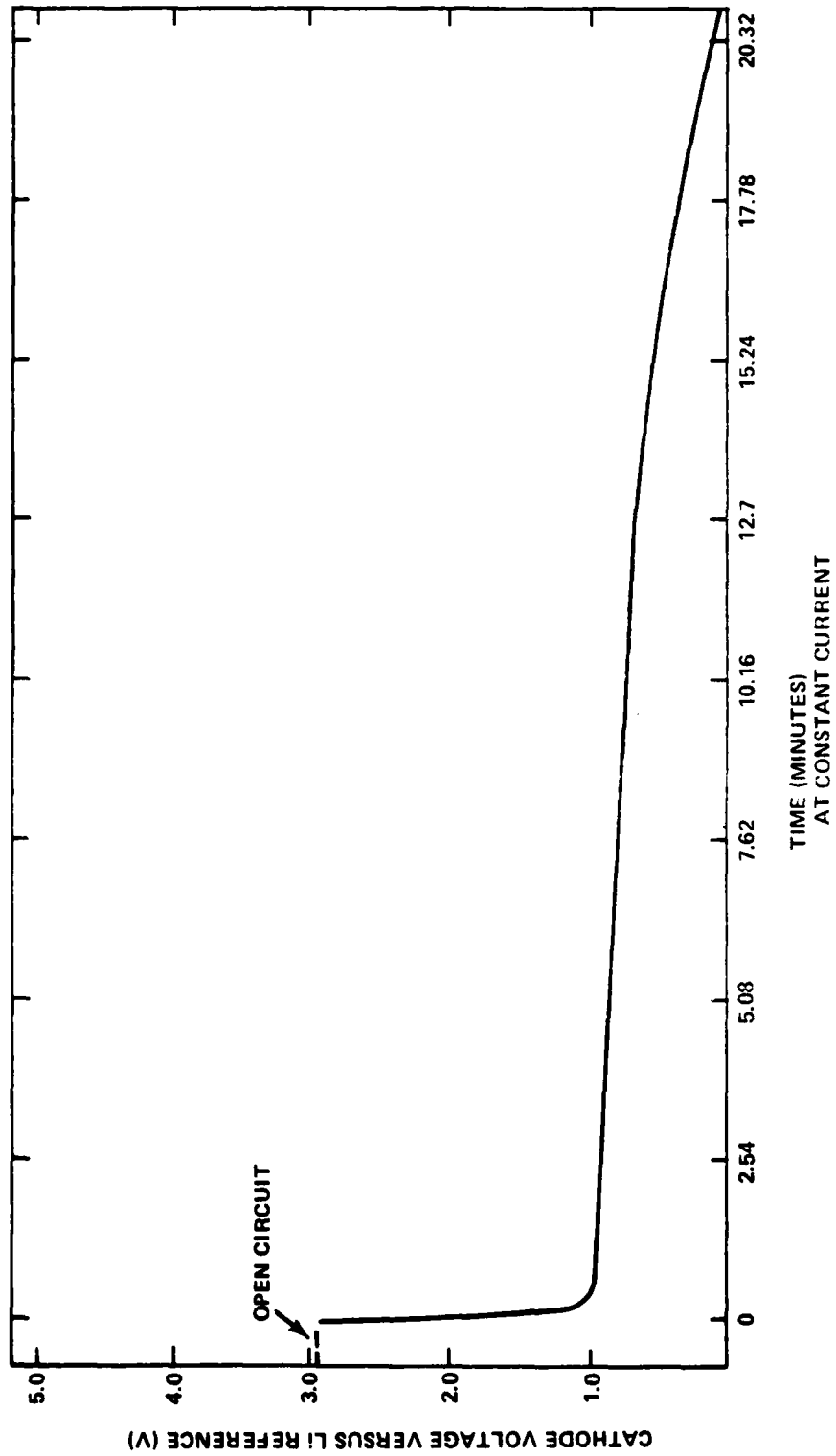


FIGURE 3. VOLTAGE-TIME CURVE FOR SHAWINIGAN CARBON BLACK ELECTRODE CATHODIZED IN 1M LiAsF₆-PC SOLUTION

Although the authors' conclusions¹¹ are in agreement with similar studies employing graphite foil electrodes instead of Shawinigan black cathodes,¹³ both studies appear to be in disagreement with an earlier investigation by Dey and Sullivan¹⁴ which proposed the plateau region as the voltage at which the solvent (PC) is electrochemically reduced.

Results obtained in the present investigation indicate that during the voltage plateau, a substantial amount of carbonate is indeed formed, as witnessed by Dey and Sullivan. This was determined by a potentiometric titration of the aqueous extracts of the carbon cathode. The results are shown in Table 1.

TABLE 1. POTENTIOMETRIC TITRATION OF Li_2CO_3 AND LiOH IN THE CATHODE AFTER ELECTROLYSIS IN 1M LiAsF_6 -PC SOLUTIONS

Run	Current Density (mA/cm ²)	Grams of Carbon	Initial Open Circuit Voltage (V)	Coulombs Passed	Equivalents Passed	% Found as Carbonate	% Found as Hydroxide
1	1	-	2.80	185	1.92×10^{-3}	74	1
2	2	.1127	2.95	107	1.11×10^{-3}	80	1
3	2	.0783	2.98	60	6.22×10^{-4}	76	0
4	2	.1268	2.97	105	1.09×10^{-3}	74	0
5*	2	.1632	3.10	114	1.18×10^{-3}	84	0

*propylene carbonate was triple distilled

Electrolysis of the propylene carbonate- LiAsF_6 solution appears to generate carbonate at almost 80% coulombic efficiency.

The failure to account for the total number of equivalents passed could be the result of electrochemical decomposition of other reactive species within a PC-1M LiAsF_6 solution. Impurities such as H_2O , O_2 , propylene oxide, propylene glycol, and other organics are known to be present in commercially obtained PC.¹² It is interesting to note that the greatest coulombic efficiency for carbonate occurred in Run #5 where the solvent had been distilled

¹³Eichinger, J. Electroanal. Chem.

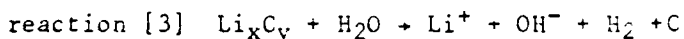
¹⁴Dey, J. Electrochem. Soc.

¹⁵Jasinski, R., "Electrochemistry and Application of Propylene Carbonate," Advances in Electrochemistry and Electrochemical Engineering, 8, Wiley Interscience, 1971, p. 261.

prior to use. A second explanation of this phenomenon may be that the aqueous extract procedure did not remove all the lithium located within the porous cathode structure. This possibility was rejected when lithium atomic absorption analysis on the extract of a second HNO_3 leaching and on the extract of the remaining carbon residue after leaching proved too low to explain the discrepancy

Run #3 % Li found in HNO_3 extract = 0; % Li found after ashing = 0
Run #4 % Li found in HNO_3 extract = 2; % Li found after ashing = 0

The results of this study (Table 1) suggest that undervoltage deposition of lithium may not be occurring in this system. If lithium-carbon intercalates had been formed in the carbon cathode, then a potentiometric titration of the aqueous extract of the carbon should reveal the presence of hydroxide ion:



As indicated in Table 1 less than 1% of the lithium was determined as hydroxide.

However, the analytical procedure used to verify the existence of the Li-C intercalation compounds is only valid if these substances have substantial life times. Dousek et al.¹⁶ have reported that lithium amalgam reacts vigorously and quantitatively with PC forming propene and carbonate. If the cathodically generated Li-C intercalates react in a similar fashion, then detection of these compounds would be extremely difficult.

To examine the stability of Li-C intercalation compounds, 10 mg of LiC_6 [obtained from Dr. J.E. Fisher, University of Pennsylvania] was placed in 10 ml of propylene carbonate and allowed to react for 2 hours. Upon subversion a gaseous substance evolved from the surface of LiC_6 . Subsequent analysis of the mixture revealed a 98% conversion of the LiC_6 to Li_2CO_3 . This indicates that if Li_xC_y compounds had been formed during electrolysis, their rapid decomposition via reaction with PC may complicate any attempts at qualitative identification of these compounds.

It has been recently demonstrated that tetrahydrofurans methylated at α position are chemically and electrochemically stable toward Li. For example, lithium stored in 2-methyltetrahydrofuran (2Me-THF) at 71°C is stable for over 10 months.¹⁷ If this solvent is equally stable toward lithium intercalation

¹⁶Dousek, F. P., Jansta, J., and Rhiha, J., "Electrochemical Systems for Galvanic Cells in Organic Aprotic Solvents," J. Electroanal. Chem., 46, 1973, p. 281.

¹⁷Goldman, J. L., Mank, R. M., Young, J. H., and Koch, V. R., "Structure-Reactivity Relationships of Methylated Tetrahydrofurans with Lithium," J. Electrochem. Soc., 127, 1980, p. 1461.

compounds, then isolation of these compounds may be achieved by substituting PC in the previous experiment with 2Me-THF. However, results obtained with Shawingan black electrodes cathodized in 2Me-THF proved inconclusive (Table 2 and 3). Analysis of the aqueous extracts of the cathodes indicated that lithium was not deposited in the carbon. However, again the possibility of formation of Li_xC_y compounds followed by immediate chemical decomposition by the solvent (2Me-THF) can not be ruled out.

TABLE 2. POTENTIOMETRIC DETERMINATION OF LiOH IN THE CATHODE AFTER ELECTROLYSIS IN $1\text{M LiASF}_6 - 2\text{Me-THF}$ SOLUTIONS (AQUEOUS EXTRACTION)

Run	Constant Current mA/cm^2	Constant Voltage (v)	Grams of Carbon	Initial Open Circuit Voltage	Coulombs Passed	Equivalents Passed	% Found as Hydroxide
6	4	-	.158	3.09	121	1.25×10^{-5}	1
7	2	-	.166	2.89	142	1.47×10^{-3}	0
8	-	0.05	.153	2.80	83	8.6×10^4	0
9	-	0.10	.163	2.90	93	9.6×10^{-4}	0

TABLE 3. ATOMIC ABSORPTION DETERMINATION OF Li REMAINING AFTER AQUEOUS EXTRACTION

Run	Coulombs Passed	% Li Found When Leaching with HNO_3	% Li Found When Ashing
6	121	0	0
7	142	18	0
8	83	1	0
9	93	1	0

CHAPTER 4

CONCLUSIONS

No evidence was observed for the undervoltage formation of Li-C intercalation compounds during electrolysis of a depolarizer-free electrolytic solution.

Propylene carbonate and 2-methyltetrahydrofuran decompose quite efficiently on Shawinigan Acetylene Black cathodes at potentials substantially positive to the lithium potential. However at the present time it is unclear if this mechanism is a direct chemical reaction or electrolysis.

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