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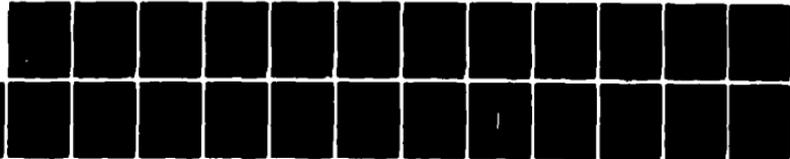
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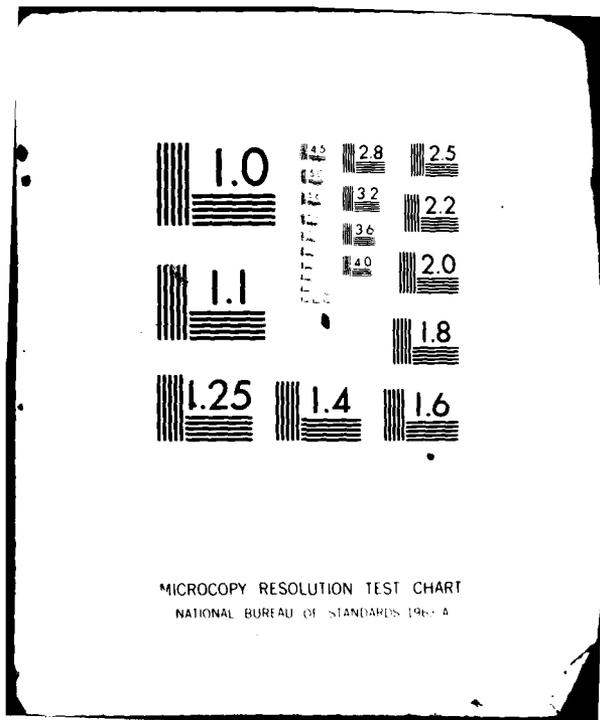
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**INVESTIGATIONS OF THE NATURE AND REACTIVITY
OF COMPOUNDS FORMED BETWEEN LITHIUM
AND CARBON BLACK**

BY WILLIAM P. KILROY, STANLEY D. JAMES AND JOANN MILLIKEN

RESEARCH AND TECHNOLOGY DEPARTMENT

1 SEPTEMBER 1981

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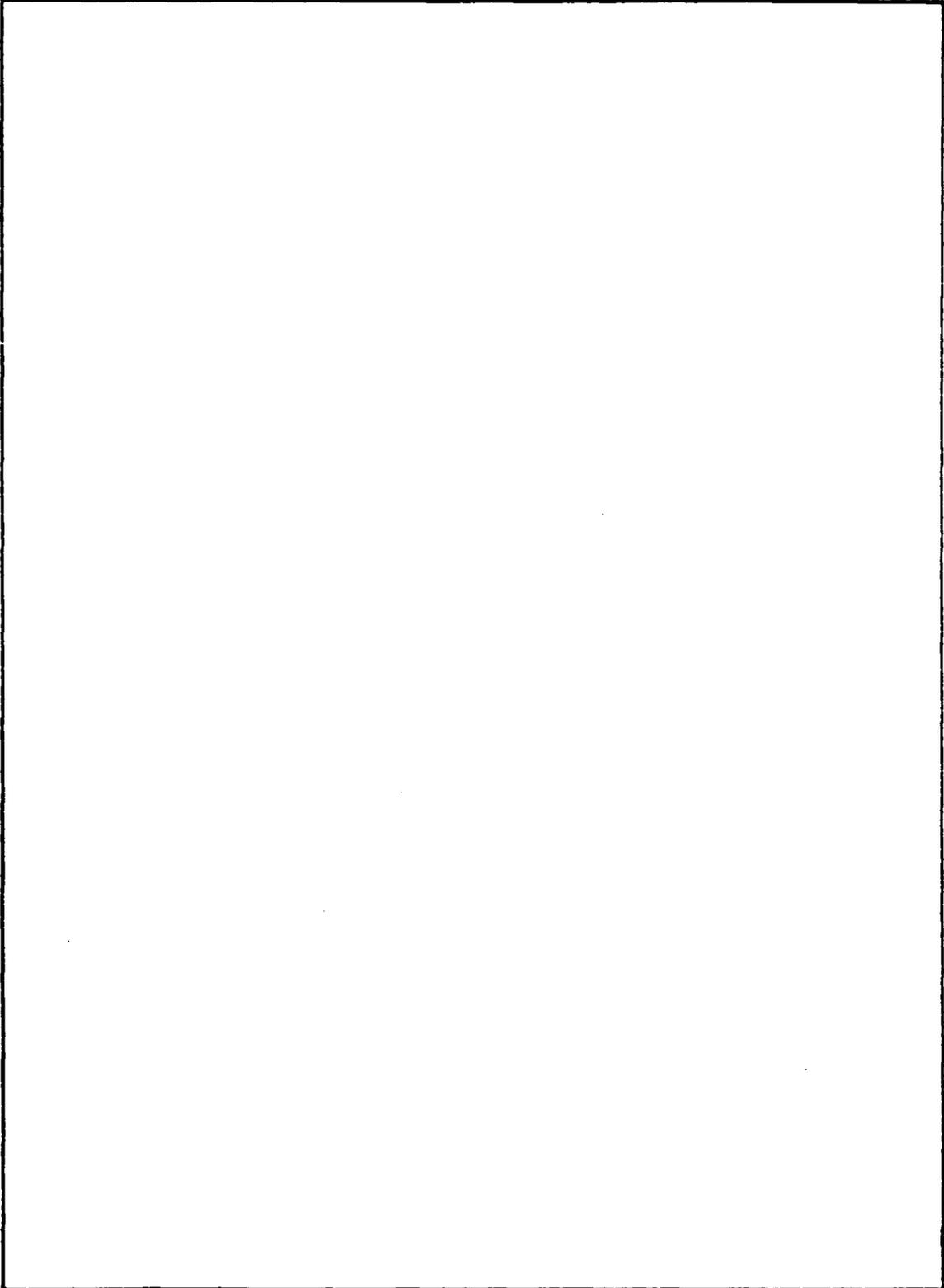
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FOREWORD

Both X-ray analysis of Li-carbon black grinds and electrochemical analysis of cathodized carbon black are consistent with the presence of Li-C compounds, probably intercalates. Both mechanically and cathodically formed Li-C mixtures are highly reactive with Li battery electrolytes with obvious implications for Li battery safety. At voltages above +0.9 V versus Li, in depolarizer-free solution, carbon black absorbs about 500 coul/g of cathodic charge in the form of a Li-C compound. The large total charge absorbed down to 0, V versus Li (3000 coul/g, equivalent to $C_{2.7}Li$) and big mass gains (>100%) of the cathodized carbon suggest that at the lower voltages cyclic reaction occurs in which cathodically formed Li-C reduces the electrolyte. Future work is expected to concentrate in the electrochemical side and should confirm and extend the above preliminary conclusions.

This work was undertaken as part of a program to investigate safety hazards in nonaqueous ambient temperature lithium batteries.

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W. Carson Lyons
W. CARSON LYONS
By direction

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CHAPTER 1

INTRODUCTION

Safety hazards in both the SO_2 and SOCl_2 batteries have delayed the development of future advanced weapons systems. Despite continued investigations, no clear indication of the origins of these hazards has been forthcoming. Work in our laboratory¹ has indicated carbon to be a powerful catalyst in promoting the reactivity of the lithium with battery oxidants.

In a recent report, we examined various parameters that might influence this reactivity².

The basic reaction under study was that between Li-C mixes and battery electrolytes. We found reactivity was relatively low and quite variable if the Li and carbon were merely mixed or lightly pressed together. However, vigorous mixing by grinding or hammering together substantially raised reactivity and made it more reproducible.

Reactivity was recorded upon addition of 71 ± 21 ul of SOCl_2 or SO_2 electrolyte to weighed amounts of Li (~ 7 mg) and various weighed amounts of carbon black (Shawinigan) that were ground together in a Pyrex Ignition Tube. Accordingly, mixture reactivity was characterized using the following qualitative scale: (1) no reaction; (2)-(5) exothermicity increasing to hot vigorous boiling at level (5); (6) sparks; (7)-(10) spontaneous ignition generating fires ranging in height from a small localized fire at level (7) to one over 100 cm high at level (10). If no fire occurred, we explored the mixture's shock sensitivity by dropping a 25 g, 8 inch steel needle from a 3 inch height onto the mixture. Shock sensitivities were characterized as (0) no reaction; (1) fire; (2) explosion.

We found that traces of carbon were insufficient to activate the Li-oxidant reaction. Figure 1 shows that only when the carbon content of Li-C mixes rose above about 10 and 30 wt% respectively for the SOCl_2 and SO_2 electrolytes was perceptible energy liberated. Reactivity then rose sharply with SOCl_2 and more gradually with SO_2 . The SOCl_2 electrolyte was substantially more reactive; spontaneous ignition being consistently observed above about 20 wt%C.

¹Dallek, S., James, S. D. and Kilroy, W. P., "Exothermic Reactions among Components of Li- SO_2 and Li- SOCl_2 Cells," J. Electrochem. Soc., 128, 508, 1981.

²Kilroy, W. P. and James, S. D., "Promotion by Carbon of the Reactivity of Lithium with SOCl_2 and SO_2 - Effect of Lithium Battery Safety," J. Electrochem. Soc., 128, 934, 1981.

Spontaneous ignition was seen also with the SO_2 electrolyte although this is not apparent in curve B which depicts only the average reactivities. Fires were observed with SO_2 electrolyte above about 60% carbon although such fires were relatively rare. For both electrolytes, decreasing carbon content led to a fall in spontaneous flammability accompanied by a rise in shock-sensitivity. At about 13% carbon, violent explosions occur with salt-free SOCl_2 if the mixture is shocked.

We ruled out the participation of other active compounds such as Li_2C_2 , Li_3N , Li_2O , Li_2O_2 by testing their reactivity to battery electrolyte, both alone and after grinding with excess lithium. All were inert. Furthermore we found that Li and carbon ground together in a helium atmosphere was still highly reactive with electrolyte so that combination with air during the prior grinding is not an essential factor.

Preliminary ESCA (XPS) work in our laboratories has shown that the initially Li-free, carbon surface of a 0.5-lmm thick layer of graphite powder, pressed lightly onto a Li substrate, was showing evidence of a Li-C compound within a day or two. Thus Li is very mobile in and reactive with carbon at room temperature.

This report describes some preliminary studies that probe the nature and reactivity of reaction products of lithium and carbon black formed under conditions related to the abusive treatment of lithium batteries.

CHAPTER 2

EXPERIMENTAL

I. Li-C SAMPLE PREPARATION, REACTIVITY TESTING AND X-RAY ANALYSIS

Weighed amounts of Shawinigan carbon black and lithium were ground together in a Pyrex Ignition Tube using the flame polished end of a 5mm Pyrex rod. The compacted mass was broken with a steel spatula and the process repeated once or twice more. Samples were prepared under a helium atmosphere and also in a Dry Room of $< 0.5\%$ relative humidity. After the ground mixture had cooled, 71 ± 21 μ l of SOCl_2 electrolyte were added from a Pasteur pipet and the reactivity noted. The reactivity scale was mentioned in the Introduction. The SOCl_2 was refluxed with lithium for 20 hours under argon followed by distillation under argon. A 1.6 M LiAlCl_4 in SOCl_2 solution was prepared using "Polaroquality" LiAlCl_4 from Matheson - Coleman/Bell. X-ray analysis was performed on samples using Mo K_α radiation. Two samples were analyzed. The Dry Room sample contained Vulcan 6 carbon black 51.4% by weight. The helium prepared sample contained 54.3% by weight of Shawinigan carbon black.

II. ELECTROCHEMICAL PREPARATION OF Li-C MIXTURES

We tried to simulate the way in which a polarizing carbon cathode could become electrochemically impregnated with Li. Each preparation was done in an enclosed glass "research type" cell containing a Li anode, polypropylene cloth separator and (except with samples E and E') a 80% Shawinigan Black - 20% Teflon cathode having about 3.4 cm^2 projected area supported on a Al Exmet grid. Figure 2 shows schematically the set-up normally used.

SAMPLE A. Electrolyte was a 0.3M LiBF_4 in THF. Li and C were shorted through an ammeter. A single sheet of Li was used as anode. Short-circuit current fell from about 4 mA initially, to a pseudo steady value of 0.76 mA, 69h later at the end of treatment. At this time cathode voltage was still 9 mV positive of the Li.

SAMPLE B. Electrolyte was 1.0M LiAsF_6 in 1:1 volume mixture of PC-AN. A single sheet of Li was used as anode. The carbon was cathodized at a constant current of 25 mA using a power supply for a period of 15h. Its voltage stayed about 1V positive of the Li for the first 7h and was driven into reversal (about -14V to the Li) for the remaining 8h.

SAMPLE C. Electrolyte same as for Sample B. Two sheets of Li were used as anode one on either side of the carbon cathode. The carbon was cathodized at

8 mA constant current and its voltage monitored versus an unpolarized Li reference electrode. Electrolysis was terminated after 21.3h when this voltage was -0.02V. The carbon's voltage approached zero after 1lh.

SAMPLE D. Electrolyte was 1M LiBr in 1:1 volume mixture of PC and AN. Two sheets of Li were used as anode, one on either side of the carbon cathode. A separate sheet of Li formed a reference electrode. Carbon was cathodized at a constant current of 10 mA. Electrolysis was terminated when the cathode voltage was +0.1 V versus Li reference.

SAMPLES E AND E'. Electrolyte was 1M LiAsF₆ in PC. Two sheets of anode surrounded the carbon cathode. The electrolyte was deoxygenated. This electrolysis dispensed with the Al Exmet support and Teflon-free carbon black was contained in a 80 x 80 mesh, Stainless Steel screen bag. A separate sheet of Li formed a reference electrode. Electrolysis at about 1.3 mA/cm² of cathode surface was ended after cathode voltage fell from +1.3 to +0.9V versus Li reference electrode. Samples E and E' contained 0.633 and 0.210 g respectively of Shawinigan carbon black.

After electrolysis, all samples were removed from the cell in the Dry Room, washed repeatedly on a glass filter with THF to free them from salt then dried by evacuation at 22°C and weighed. Portions of the cathodized carbons were then separated and subjected to reactivity testing with battery electrolyte as described in the previous section. In two cases (samples D and E) the major portion of the carbon was chemically analyzed as follows. Sample D--after THF-washing and pumping to constant weight, Sample D was found to be 75% heavier as a result of its cathodization. The sample was acidified with excess standard HCl then digested at 80°C until supernatant acidity no longer fell, indicating no more Li was being leached from the carbon. The indicator employed was phenolphthalein. From this constant titre, the amount of leached Li was calculated. Flame tests showed that the extract contained much Li⁺ while the extracted carbon was Li-free. Sample E--After washing with propylene carbonate (PC) and pumping to constant weight, it was observed that this sample had gained in weight by 27% as a result of its cathodization. The carbon was first extracted in water for four days at 80°C and the extract potentiometrically titrated with a glass electrode. The extract contained about 0.0002 moles of OH⁻ and no evidence of carbonate or fluoride was seen. Acidification with HCl and prolonged digestion with HCl at 80°C occasioned no further release of alkalinity from the carbon. Flame tests showed the extract contained Li⁺ and also that some lithium remained in the carbon.

CHAPTER 3

RESULTS AND DISCUSSION

I. REACTIVITY OF Li-C MIXTURES

Table 1 compares the reactivity of electrochemically prepared Li-C mixtures with that of Li and C physically mixed (Li/C ~ 0.1) by pressing or grinding as described in "Experimental". We divided the electrochemical preparations into "H" and "L" referring to the (relatively) high and low voltage of the intermediate, undervoltage plateau during their formation. The "H" material prepared at +1.0V versus Li was significantly more reactive to $\text{LiAlCl}_4\text{-SOCl}_2$ than was "L" formed just above the Li potential. We presently have no explanation of this fact. "H" was more reactive (5.0) than the pressed mixture (3.3), in fact it boiled the SOCl_2 electrolyte. This is especially noteworthy as "H" contained Teflon. Table 1 demonstrates that Teflon significantly decreases the reactivity. In contrast to its behavior with SOCl_2 electrolyte, the electrochemical preparation "H" was virtually inert to the SO_2 electrolyte.

The observed exothermicities of "H" and "L" probably considerably underestimate the heat they would have evolved if generated in an actual battery. The discussion (in the next section) of the large mass gains experienced by these cathodized carbons suggests they had already undergone extensive reaction even before the reactivity tests reported in Table 1. This reaction was either with the electrolyte during their cathodic preparation or with solvent in the subsequent washing.

The powerful catalysis by carbon black of the lithium/battery oxidant reaction evident above is important because, in polarized cathodes, Li and C may become intimately mixed (a) by undervoltage deposition to form reactive Li-C intercalates which react continuously with the electrolyte accumulating heat to possibly dangerous levels and (b) by normal overvoltage deposition of passivated Li dendrites. Subsequent shear or shock could then grind dendrites and carbon together causing violent reaction. Furthermore, severe mechanical distortion of fresh or normally discharged Li batteries could shear Li and C components together with the same dangerous result. With this in mind we are currently testing carbons that have the promise of combining a greatly reduced reactivity in Li-C mixes with unimpaired efficiency as cathodes.

II. NATURE OF THE Li-C MIXTURES

A. ELECTROCHEMICAL STUDIES. Figure 3 shows some of our V-t curves for carbon electrodes (Shawinigan Black) cathodized in solutions free of battery-cathode depolarizer. This situation simulates that of battery cathodes that have failed due to SO_2 or SOCl_2 -starvation. High OCV's of +3V versus

Li fall rapidly to plateaus whose length and voltage-level (+0.2 to +1.2V versus Li in the present work) depend on electrolyte composition and current density. No Li deposit is seen on the carbon in this undervoltage region. Then there is a final fall to an overvoltage plateau where Li dendrites are seen to grow on the carbon surface. We suspect that the intermediate plateaus originate in the cathodic reduction of Li^+ to Li, accompanied by compound formation, between Li and the carbon substrate. The undervoltage generation of Li-C compounds at carbon cathodes has been shown in melts at 450°C by James.³ Other workers have demonstrated the same effect in organic solvents at graphite foil^{4,5,6} and spectroscopic graphite rods.⁷ The present data is apparently the first to indicate the undervoltage deposition of Li may occur also at ungraphitized carbon black.

Cathodically generated Li-C intercalates react much faster with organic solvents than pure Li does.⁴ Thus if these compounds are formed in the carbon substrates of polarizing Li battery cathodes, significant quantities of heat can accumulate as they react with the battery electrolyte and may become hazardous.

Under our conditions intermediate plateaus like those of Figure 3 might have arisen from a variety of cathodic reductions: AsF_6^- to AsF_3 ; Teflon to F^- ; AN to CN^- ; PC to CO_3^{2-} ; dissolved oxygen to OH^- ; or Li^+ to LiAl in the Al Exmet cathode support (See Table 3). Using samples E and E' we excluded these possibilities by showing that such voltage plateaus persisted in deoxygenated solution containing PC only (no AN) at carbon black free of Teflon, supported on Stainless Steel instead of Al. Also, SS mesh without carbon on it could support no significant cathodic current in LiAsF_6 -PC without falling immediately to the Li potential. The alkaline aqueous extract of carbon black (sample E) cathodized at undervoltage contained no carbonate or fluoride, so neither PC nor AsF_6^- were being reduced, at least in this case.

The above data suggest strongly that the primary electrode reaction is undervoltage deposition of Li into carbon black. Only this process (reaction 1, Table 3) can account for the 500 coul/g, C passed between +1.3 and +0.9V versus Li in curve E and presumably also the charge passing in this voltage region of the other curves (reaction 2 does not occur above about +0.3V versus Li). However the total charge passed down to 0, V versus Li is on the order of 3000 coul/g of carbon which would correspond to a formula of $\text{C}_{2.7}\text{Li}$. Since the

³James, S. D., "Undervoltage Deposition of Alkali Metal at Carbon Electrodes in the LiCl-KCl Eutectic Melt," J. Electrochem. Soc., 122, 921, 1975.

⁴Besenhard, J. O., "The Electrochemical Preparation and Properties of Ionic Alkali Metal and NR - Graphite Intercalation Compounds in Organic Electrolytes," Carbon, 14, 111, 1976.

⁵Besenhard, J. O. and Fritz, H. P., "Cathodic Reduction of Graphite in Organic Solution of Alkali and NR Salts," J. Electroanal. Chem., 53, 329, 1974.

⁶Eichinger, G., "Cathodic Decomposition Reactions of Propylene Carbonate," J. Electroanal. Soc., 74, 183 1976.

⁷Dey, A. N. and Sullivan, B. P., "The Electrochemical Decomposition of Propylene Carbonate on Graphite," J. Electrochem. Soc., 117, 222, 1970.

richest Li intercalate known is C_4Li^8 and Li_2C_2 is not known to form below about $400^\circ C$,⁹ we believe the cathodically formed Li-C compound reacts at lower voltages with electrolyte regenerating free carbon surface. Thus the capacity of carbon to absorb charge at undervoltage is not limited by the relatively small Li content of a particular Li-C compound. One would expect Li-C compounds to be more reactive as their potential of formation approaches that of free Li. Thus the Li-C compound can act as an intermediate in the reduction of electrolyte species according to reactions 3-6 of Table 3. Direct cathodic reduction of electrolyte may also occur at the lower voltages.

The observed large mass gains (up to 134%) listed in Table 2 support the occurrence of such secondary reactions generating solvent-insoluble products (Table 3) which become weighed with the washed and dried cathode. Mass gain rises with cathodic charge, leveling off at about 130% after passage of 5000 coul/g carbon.

In the case of samples D and E, the aqueous extracts of the solvent-washed cathodes contained only 63 and 12% respectively of the alkalinity expected from the presence of Li-C equivalent to the cathodic charge passed. Sample D's extract was titrated using phenolphthalein indicator which would have missed bicarbonate and fluoride if present from reactions 2 and 6 of Table 3. So reaction of Li-C with PC or Teflon could explain the discrepancy in this case. Potentiometric titration of sample E's extract showed that neither carbonate nor fluoride was present thus ruling out reactions 3 and 4 of Table 3. Flame tests revealed that lithium remained in the extracted carbon but reaction 1 cannot account for the observed mass gain. So this discrepancy remains unresolved.

Two features are apparent in the curves of Figure 3. Firstly there appears to be a very pronounced anion effect. Curve D (LiBr-PC-AN) lies over a half a volt lower than curve C (LiAsF₆-PC-AN). This striking difference should be confirmed and investigated. Secondly, none of our curves (except the start of D) shows any arrests in voltage corresponding to the formation of Li-C compounds successively richer in Li. These would have appeared at the points marked on the abscissa of Figure 3. Such steps in voltage have been observed at natural graphite cathodized in DMSO solutions of salts of all the alkali metals.⁴ Our smooth curves suggest a continuous spectrum of interaction energies of Li with the carbon structure as was observed in LiCl-KCl melts at synthetic graphite and glassy carbon.³ This difference is presumably related to the more highly developed graphite crystallinity of natural graphite versus carbon black, glassy carbon or synthetic graphite.

B. X-RAY ANALYSIS. X-ray diffraction is one of the common methods used to characterize intercalation compounds of carbon. Normally, highly oriented pyrolytic graphite (HOPG) is studied and only the 001 reflections are observed

⁸Novikov, Y. N. and Volopin, M. E., "Lamellar Compounds of Graphite with Alkali Metals," Russ. Chem. Rev., 40, 733, 1971.

⁹Basu, S., Zeller, C., Flanders, P. J., Fuerst, C. D., Johnson, W. D. and Fischer, J. E., Synthesis and Properties of Lithium-Graphite Intercalation Compounds," Mat. Sci., Eng., 38, 275, 1979.

⁴See footnote 4 on page 12.

⁵See footnote 5 on page 12.

from which the new c-axis repeat distance and hence the stage of the material is determined. The lack of orientation in the powdered Li-C mixture makes it more difficult to characterize intercalation. We are further limited by the increased disorder in the carbon black relative to graphite.

X-ray diffraction data for Shawinigan carbon black and Li-C mixtures prepared under helium and in a Dry Room are compared in Table 4. The two Li_xC_y samples are similar to each other and different from the starting materials, lithium and the carbon black. Computed 2θ values for lithium graphite (tabulated in Table 5) are based on Bragg equation $n\lambda = 2d\sin\theta$ where d corresponds to the c-axis repeat distance (001 reflections). The values for lithium, carbon black, and the Li-C products correspond to all hkl reflections. The most intense reflection occurs where n is equal to the stage number, i.e., $n = 1$ for Stage 1 (11.02°), $n = 2$ for Stage 2 (11.57°), etc.

Table 4 reveals that a $\Delta 2\theta$ value of 2.40 is obtained from the strong lines (10.53 and 12.93) for the Li-C material prepared under helium. A similar value of approximately 2.40 is calculated from the strong lines (10.54, 12.92, 15.35, 22.49 and 24.88) of Li_xC_y prepared in the Dry Room. From the data in Table 5, this would appear to correspond to a Stage 5 lithium-graphite compound. However, the 2θ values differ by approximately 1° . Perhaps this difference is due to the fact that we are dealing with carbon black rather than graphite. It is interesting to note that Guerard and Herold¹⁰ prepared samples of stage 1-4 lithium graphite (depending on the Li:C ratio used) by compressing mixtures of lithium and graphite powders at room temperatures.

The strongest reflection for carbon black at $d = 4.90 \text{ \AA}$ does appear very weakly in the Li_xC_y prepared under helium, suggesting a small amount of unreacted carbon may be present.

A sample of Li_2C_2 was analyzed. The characteristic reflections of the carbide did not appear in the diffraction pattern of the Li-C mixtures. Thus the amount of carbide present if any, is negligible.

¹⁰Guerard, D., and Herold, A., "Intercalation of Lithium into Graphite and Other Carbons," Carbon, 13, 337, 1975.

CHAPTER 4

CONCLUSIONS AND FUTURE WORK

Both X-ray analysis of Li-carbon black grinds and electrochemical analysis of cathodized carbon black are consistent with the presence of Li-C compounds, probably intercalates. Both mechanically and cathodically formed Li-C mixtures are highly reactive with Li battery electrolytes with obvious implications for Li battery safety. At voltages above +0.9V versus Li, in depolarizer-free solution, carbon black absorbs above 500 coul/g of cathodic charge in the form of a Li-C compound. The large total charge absorbed down to 0, V versus Li (3000 coul/g, equivalent to $C_{2.7}Li$, and big mass gains (>100%) of the cathodized carbon suggest that at the lower voltages cyclic reaction occurs in which cathodically formed Li-C reduces the electrolyte.

Future work is expected to concentrate in the electrochemical side and should confirm and extend the above preliminary conclusions. We intend a systematic study of V-Q undervoltage deposition curves as in Figure 3 as a function of electrolyte composition, current density and temperature. Data will be analysed in terms of:

1. Curve Morphology. Do the curves contain V-steps indicating presence of Li-C intercalates? Is the large anion effect reproducible and does it extend to other anions?

2. Cathode Composition and Reactivity. Measure composition, reactivity and mass gain of cathodized carbon black at various points of the V-Q curves, i.e., versus the final voltage of their preparation. Analyze the extracted carbon to distinguish Li-C compounds, the primary cathode product, from secondary products of reaction with the electrolyte.

TABLE 1 AVERAGE REACTIVITIES¹ OF ELECTROCHEMICALLY VERSUS
PHYSICALLY PREPARED Li-C MIXTURES (Li/C~0.1)

TYPE OF MIXTURE	REAGENT		
	SOCl ₂ -LiAlCl ₄	SO ₂ -AN-LiAsF ₆	H ₂ O
ELECTROCHEMICAL (H,L) ²	5.0(H);3.0(L)	2.0(H)	3.5(H)
PHYSICAL	PRESSED	3.3	---
	GROUND	9.7	5.8
	GROUND & TEFLON	7.8	3.8

¹See "Introduction" for Reactivity Scale

²H and L refer to preparation at about +1.0 and 0.1 V versus Li reference respectively

TABLE 2 MASS GAIN AND EXTRACTED ALKALINITY FOR CARBON BLACKS¹
CATHODIZED ABOVE THE LITHIUM POTENTIAL

Sample/Run	Electrolyte	Final V of carbon vs Li	Cathodic Charge Passed Above 0, V vs Li (Coul/g C)	Mass Gain of Cathodized Carbon (%)	Extracted Alkalinity as Coul/g C ²
B/E ₂	LiAsF ₆ PC-AN	-16	4850	128	--
C/E ₃	LiAsF ₆ PC-AN	0.0	2400-4700	134	--
D/E ₄	LiBr PC-AN	+0.1	1170	75	739(63) ³
E/E ₆	LiAsF ₆ PC	+0.9	480	27	58(12) ³

¹Samples B, C, D: 80% Shawinigan Black, 20% Teflon
Sample E: 100% Shawinigan Black

²One mole of alkali in aqueous extract of carbon derives from F coulomb of cathodic charge

³Figures in parenthesis express extracted alkalinity as a % of that expected from the cathodic charges of column 4

TABLE 3 REACTIONS THAT COULD INCREASE MASS OF CATHODIZED CARBON

Reaction	Calculated % mass gain due to passage of 1000 coul/g, carbon
(1) $\text{Li}^+ + \text{C} + \text{e}^- \longrightarrow \text{Li} - \text{C}$	7
(2) $\text{Li}^+ + \text{Al} + \text{e}^- \longrightarrow \text{LiAl}$	7
(3) $\text{AsF}_6^- + 3\text{Li}^+ + 2\text{e}^- \longrightarrow \text{AsF}_3 \downarrow + 3\text{LiF} \downarrow$	105
$\text{AsF}_6^- + 2\text{e}^- \longrightarrow \text{AsF}_3 \downarrow + 3\text{F}^-$	66
(4) $\text{PC} + 2\text{Li}^+ + 2\text{e}^- \longrightarrow \text{P} + \text{Li}_2\text{CO}_3 \downarrow$	37
(5) $\text{CH}_3\text{CN} + \text{Li}^+ + \text{e}^- \longrightarrow \text{CH}_3 \cdot + \text{LiCN}$	33
$\text{CH}_3 \cdot \longrightarrow \text{Polymers}$?
(6) $(-\text{CF}_2-) + 2\text{Li}^+ + 2\text{e}^- \longrightarrow \text{C} + 2\text{LiF}$	7
$(-\text{CF}_2-) + 2\text{e}^- \longrightarrow \text{C} + 2\text{F}^- \downarrow$	-19

OBSERVED MASS GAINS

Sample B	Carbon - Teflon LiAsF_6 -PC-AN	26
C	Carbon - Teflon LiAsF_6 -PC-AN	29-56
D	Carbon - Teflon LiBr -PC-AN	64
E	Carbon only LiAsF_6 -PC	56

TABLE 4 X-RAY DATA. A. SHAWINIGAN CARBON BLACK. B. Li_xC_y PREPARED UNDER He. C. Li_xC_y PREPARED IN A DRY ROOM (< 0.5% RELATIVE HUMIDITY).

<u>A</u>		
°		
<u>2 (Mo)</u>	<u>d(A)</u>	<u>Intensity*</u>
8.32	4.90	vs
11.76	3.46	s, vbr
14.44	2.83	vw
16.80	2.43	vw, br
18.71	2.19	vw
19.56	2.09	vw, br

<u>B</u>		
°		
<u>2 (Mo)</u>	<u>d(A)</u>	<u>Intensity*</u>
8.29	4.91	vw
10.53	3.87	s
12.93	3.15	s
13.95	2.92	vw, br
15.16	2.69	vw, br
16.70	2.45	vw
17.47	2.34	vw
20.62	1.99	vw
21.17	1.93	w
22.51	1.82	m
24.89	1.65	w
31.09	1.33	vw

<u>C</u>		
°		
<u>2 (Mo)</u>	<u>d(A)</u>	<u>Intensity*</u>
9.83	4.15	vw
10.54	3.87	vs
11.30	3.61	w
11.98	3.40	m
12.92	3.16	vs
13.42	3.04	vw
13.99	2.92	vw
15.35	2.66	s
16.70	2.45	vw
17.70	2.31	vw
20.58	1.99	vw
21.20	1.93	m
22.49	1.82	s
24.88	1.65	m
25.16	1.63	m

* s - strong; m - medium; w - weak; br - broad; v - very

TABLE 5 COMPUTED 2θ VALUES FOR LITHIUM GRAPHITE
 (Mo radiation, $\lambda K_{\alpha} = 0.71069$)

<u>STAGE 1</u> (d=3.70 A)	<u>STAGE 2</u> (d=7.05 A)	<u>STAGE 3</u> (d=10.40 A)	<u>STAGE 4</u> (d=13.75 A)	<u>STAGE 5</u> (d=17.10 A)
<u>11.02</u>	5.78	3.92	2.96	2.38
22.15	<u>11.57</u>	7.84	5.93	4.76
33.49	17.39	<u>11.77</u>	8.89	7.15
45.18	23.26	15.71	<u>11.87</u>	9.54
57.40	29.19	19.67	14.85	<u>11.93</u>
70.37	35.21	23.66	17.84	14.32
84.49	41.32	27.68	20.84	16.73
100.41	47.56	31.73	23.86	19.14
119.62	53.95	35.82	26.90	21.56
147.64	60.53	39.96	29.95	23.99
	67.34	44.15	33.03	26.43
	74.44	48.41	36.13	28.88
	81.88	52.74	39.26	31.35
	89.76	57.16	42.42	33.83

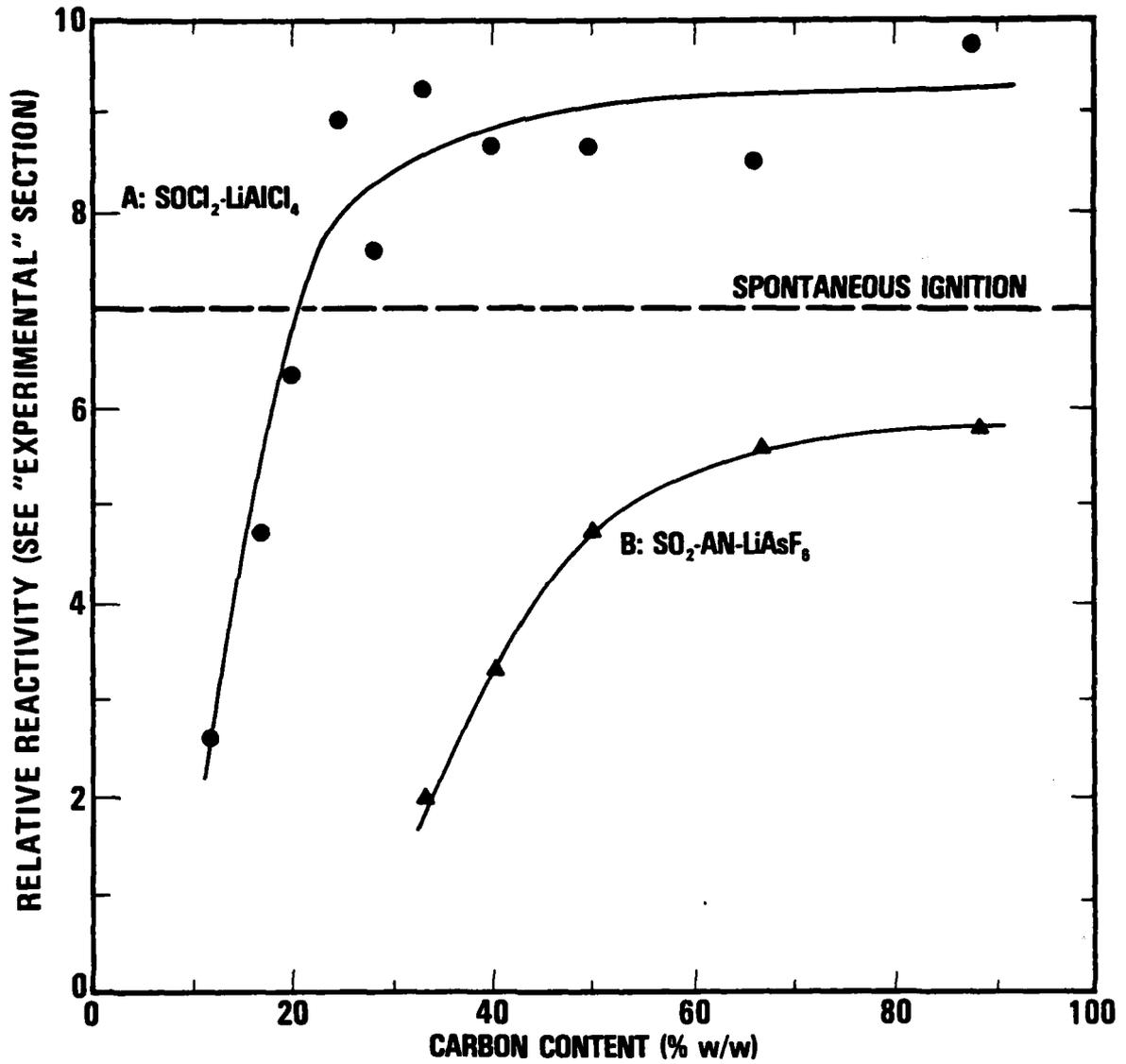


FIGURE 1 EFFECT OF THE CARBON CONTENT IN GROUND Li-C MIXTURES ON THEIR REACTIVITY TO BATTERY ELECTROLYTES. A: SOCl₂-LiAlCl₄ B: SO₂-AN-LiAsF₆.

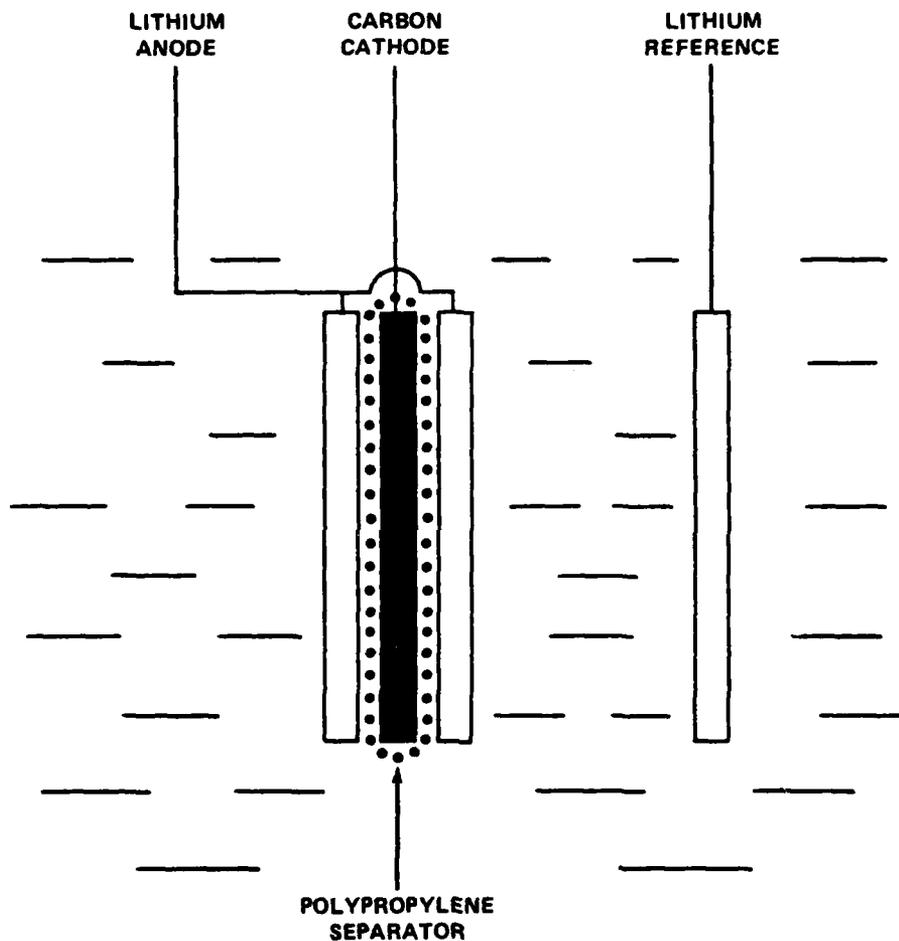


FIGURE 2 ELECTROCHEMICAL PREPARATION OF Li-C MIXTURES (SCHEMATIC DIAGRAM)

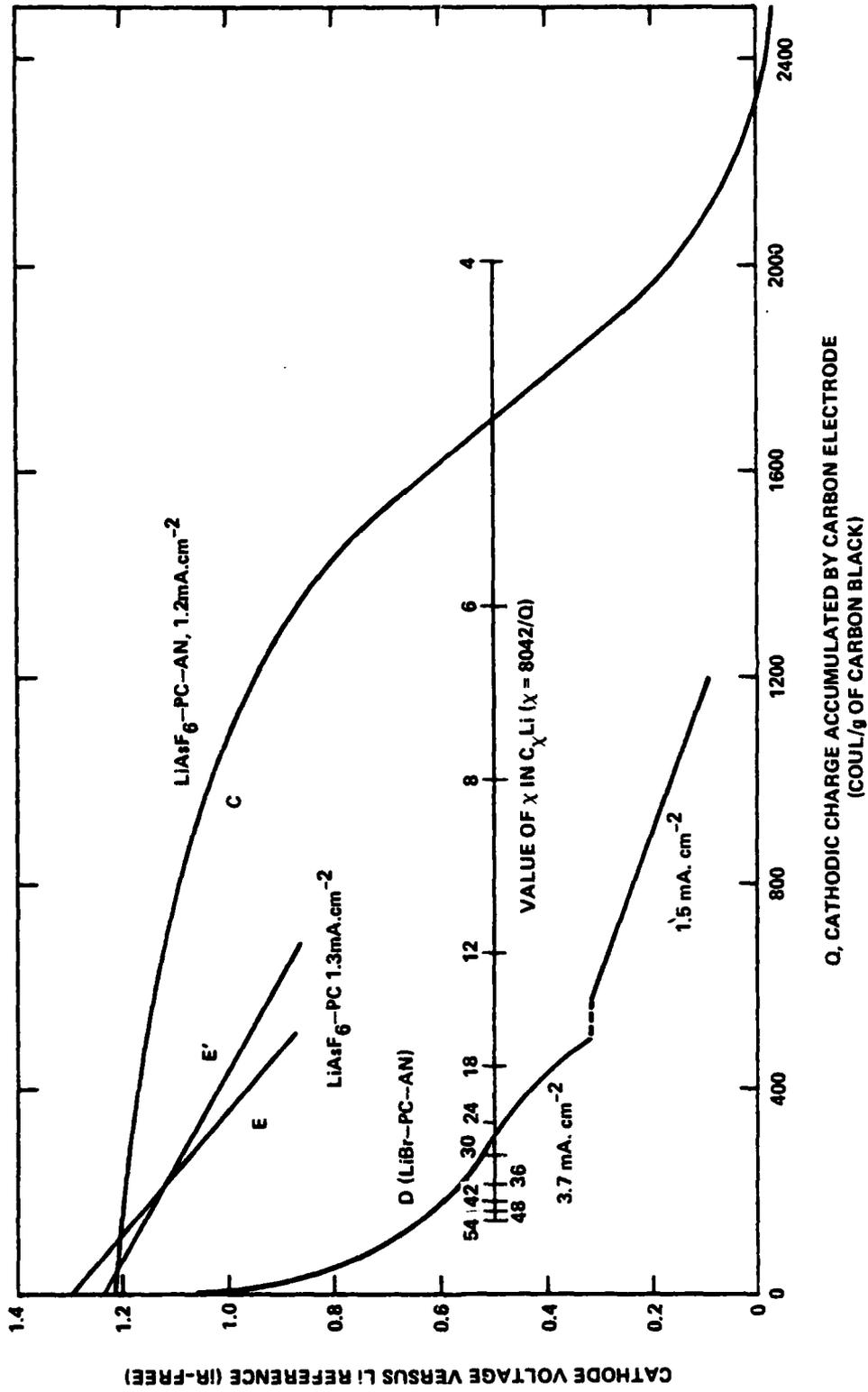


FIGURE 3 UNDERVOLTAGE DEPOSITION ON CARBON BLACK CATHODES

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