THIRD QUARTERLY REPORT

22 December 1965 to 21 March 1966

DEVELOPMENT OF HIGH ENERGY DENSITY PRIMARY BATTERIES

by

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Studies of the CuF$_2$-Li system for the development of high energy density primary batteries were conducted. Lithium metal stability in purified PC-LiClO$_4$ electrolyte was studied. Solubility of CuF$_2$ in PC and BL was found to increase with both water contamination level and LiClO$_4$ concentration. X-ray studies of dried CuF$_2$ and CuF$_2$$\cdot$2H$_2$O showed formation of CuOHF, CuOHF$\cdot$CuF$_2$ and an unknown compound. Good capacity retention was obtained with CuF$_2$-Li cells with PC-LiClO$_4$ electrolyte after six weeks wet stand at -15°C.
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1. SUMMARY

Experimental work toward development of high energy density CuF₂-Li primary cells was conducted.

**Electrolyte Systems Studies.** Lithium metal stability in purified propylene carbonate and in 1M LiClO₄ solution was studied. Stability was better in the LiClO₄ solution at ca. 150 ppm H₂O than in the solvent alone at ca. 25 ppm H₂O. Treatment with lithium powder was effective in reducing the water content in the electrolyte but did not improve lithium stability significantly.

The maximum specific conductance of NaClO₄ in propylene carbonate was found to be $6.8 \times 10^{-3}$ mho/cm at 1.2 mols solute per liter of solvent. The highest conductance for LiClO₄ solutions in redistilled DMF was found to be $14.7 \times 10^{-3}$ mho/cm at a concentration of 1.4 mols/liter of solvent.

The vapor pressure of 4.7M LiClO₄ solution in methyl formate was found to be 1.7 atm. abs. at 72°C.

**Positive Electrode Studies.** The solubility of CuF₂ in LiClO₄ solutions in propylene carbonate and butyrolactone was found to increase with the degree of water contamination of the solution. Increasing the LiClO₄ concentration increased solubility of CuF₂ to a lesser degree. The solubility was larger in butyrolactone than in propylene carbonate electrolytes.

X-ray studies of dried CuF₂ showed the main decomposition products to be CuOHF and CuOHF₂·CuF₂. Decomposition of CuF₂·2H₂O yielded primarily CuOHF and/or an unknown compound with a major peak intensity at 4.15 Å.

Preliminary tests have shown the unknown CuF₂·2H₂O decomposition product to have a low solubility in LiClO₄-PC electrolyte compared to CuF₂.

**Cell Systems Studies.** Tests performed with Ag₂O₂-Li cells showed more than 70% loss of capacity after two weeks of open circuit stand at 35°C. Loss of electrolyte solvent was observed during stand, but appearance of Li electrodes was metallic at the end of open circuit stand.
CuF₂-Li cells with PC-LiClO₄ electrolyte were tested for wet shelf life capability at -15°C and +35°C. Capacity retention was good after six weeks stand at -15°C. After two weeks stand at 35°C, only two of six cells retained any capacity above 2.5V discharge potential.

Tests with CuF₂-Li cells having butyrolactone electrolyte solvent gave poor CuF₂ utilization efficiency at the 200-hour rate (20-30 percent) compared to performance of cells having propylene carbonate solvent (60-80 percent efficiency).
2. INTRODUCTION

The purpose of this program is the development of high energy density primary battery systems suitable for space flight applications. Two types of batteries, differing in energy density and discharge rate requirements, are being sought: 1) batteries capable of delivering 200 watt hours per pound at the 100-1000 hour discharge rate, and 2) batteries capable of delivering 50 watt hours per pound at the 1 hour discharge rate. For both types of batteries, the CuF$_2$-Li couple is being considered. For the low-rate battery, a propylene carbonate-lithium perchlorate electrolyte system is of primary interest, while for the high rate system a methyl formate-lithium perchlorate electrolyte is being considered. These systems emerged as the most promising at the conclusion of two previous yearly contract periods (NAS 3-2775 and NAS 3-6004).

At the present time, the limited shelf life capability continues to constitute the main problem in the evolution of the Li-CuF$_2$ battery system. At least moderately good wet stand performance has been demonstrated for cells having PC-LiClO$_4$ electrolyte (6 weeks at -15°C), but at temperatures only slightly above ambient (35°C), shelf life for these cells is no better than a few days.

The objective of the major portion of the work performed during the past quarter of the contract period was the development and evaluation of methods for improving the open circuit capability of the CuF$_2$-Li system.
3. DESCRIPTION OF EXPERIMENTAL WORK

3.1. ELECTROLYTE SYSTEMS STUDIES

3.1.1. Lithium Stability Tests

The detrimental effect of small amounts of water contamination on the chemical stability of lithium test strips in butyrolactone and propylene carbonate has been reported previously (NASA CR-54920). During the past quarter, stability of Li strips in propylene carbonate treated with lithium powder was studied.

Propylene carbonate was distilled at 10 mm Hg, and the water content was ascertained to be below 25 ppm. A portion of this solvent was retained, and the remainder was agitated for 40 hours with powdered lithium, filtered, and re-distilled. Lithium test strips were cut to size 1 x 1/2 x 1/16 inch, and one side of each strip was abraded to expose fresh metal. The strips were then placed in test tubes containing 5 ml of solvent or 1M LiClO₄ solution under argon. The tubes were sealed and stored at 35°C, and the appearance of the lithium samples was recorded periodically.

Results of the stability tests are listed in Table I, page 5. In both lithium treated and untreated solvents, presence of 1M LiClO₄ enhanced chemical stability. In the solvent alone, lithium treatment appeared to improve stability, but this could also be a result of a lower water contamination level of this material, since additional drying probably occurs during lithium treatment. In presence of 1M LiClO₄, the stability was not significantly different with the treated and untreated materials, indicating that impurities which are not removed by distillation are not particularly reactive with metallic lithium. However, lithium treatment is used at the present time in the preparation of PC electrolytes for cell tests, since this procedure produces water contamination levels below the sensitivity of the Karl Fisher test (25 ppm) and is not particularly cumbersome to apply.
<table>
<thead>
<tr>
<th>Time, Hours</th>
<th>Propylene Carbonate purified by distillation alone</th>
<th>Propylene Carbonate purified by lithium treatment and distillation</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>No solute H$_2$O = (25±20) ppm 1N LiClO$_4$</td>
<td>No solute H$_2$O &lt; 25 ppm 1N LiClO$_4$</td>
</tr>
<tr>
<td>45</td>
<td>Cut and rough surfaces are tarnishing</td>
<td>No attack</td>
</tr>
<tr>
<td>70</td>
<td>No noticeable changes</td>
<td>No attack</td>
</tr>
<tr>
<td>160</td>
<td>Same</td>
<td>Same</td>
</tr>
<tr>
<td>210</td>
<td>Same</td>
<td>Roughened side slightly tarnished</td>
</tr>
<tr>
<td>330</td>
<td>Trace of gelatinous material in bottom of tube</td>
<td>Trace of gelatinous material in bottom of tube</td>
</tr>
<tr>
<td>540</td>
<td>All surfaces dulled except the cut ones</td>
<td>All surfaces dulling except the cut ones</td>
</tr>
<tr>
<td>1250</td>
<td>Gelatinous material and some powdery white material in bottom of tube; liquid phase cloudy; cut surfaces black; roughened surfaces black.</td>
<td>All surfaces dulled and tarnished except cut ones; gelatinous material in bottom of tube.</td>
</tr>
</tbody>
</table>

TABLE I
LITHIUM STABILITY TESTS IN PROPYLENE CARBONATE SOLUTIONS (+35°C)
3.1.2. Specific Conductance Measurements

Specific conductance-concentration data for NaClO₄ solutions in propylene carbonate were obtained. This salt was chosen for study because of the relatively higher solubility (in water) of NaF compared to LiF. Assuming that this trend holds in PC, the dissolution of CuF₂ could be expected to be suppressed by substituting NaClO₄ for LiClO₄ as the electrolyte salt.

Sodium perchlorate showed a higher maximum conductivity than LiClO₄, which was included in the test for comparison (6.8 x 10⁻³ mho/cm compared to 5.2 x 10⁻³ mho/cm). The specific conductance-concentration relationships for the two salts in PC are given in Figure 1, page 7.

The specific conductance-concentration data for LiClO₄ in dimethyl formamide were also obtained and are shown in Figure 2, page 8. In previous tests, spectroquality DMF showed poor stability toward metallic lithium; however, this solvent is to receive further evaluation after redistillation and/or other purification to see if it may be applicable in the 1-10 hour battery.
3.1.3. Vapor Pressure of LiClO₄-Methyl Formate Electrolyte

The vapor pressure of a 4.7M LiClO₄ in methyl formate solution was determined in order to obtain an estimate of what type of case construction may be employed for a methyl formate electrolyte battery. The solution was placed in a sealed glass tube equipped with a pressure gauge, and heated in a water bath. In order to test the apparatus for proper operation, the vapor pressure of the pure solvent was measured first and compared to data in the literature.*

Results of the vapor pressure determination are listed below.

**TABLE II**

**VAPOR PRESSURE OF LiClO₄-MF ELECTROLYTE**

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Solvent Literature</th>
<th>Solvent Test</th>
<th>4.7M LiClO₄ Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>52</td>
<td>2.0</td>
<td>---</td>
<td>1.2</td>
</tr>
<tr>
<td>58</td>
<td>2.5</td>
<td>2.4</td>
<td>---</td>
</tr>
<tr>
<td>63</td>
<td>2.9</td>
<td>---</td>
<td>1.5</td>
</tr>
<tr>
<td>72</td>
<td>3.8</td>
<td>---</td>
<td>1.7</td>
</tr>
</tbody>
</table>

As expected, substantial reduction in vapor pressure has resulted in the 4.7M LiClO₄ solution compared to the pure solvent. The approximately 10 psig pressure at 72°C would not appear to be prohibitive for the construction of a lightweight battery case for this system.

3.2. POSITIVE ELECTRODE STUDIES

3.2.1. CuF₂ Solubility Studies

The studies of CuF₂ solubility in propylene carbonate and butyrolactone electrolytes described previously (NASA CR-54920) were completed during the past quarter. The solvents (propylene carbonate and butyrolactone) were prepared by agitating with excess amounts of lithium powder until no further hydrogen pressure was produced; at this point, the residual water in both solvents was below the sensitivity of the Karl Fischer test (20 ppm). The lithium treatment was followed by distillation, rejecting the first and last 10 volume percent of the distillate.

The lithium perchlorate used in these tests was vacuum-dried at 110°C for 24 hours, and water content (Karl Fischer analysis) was approximately 600 ppm. Anhydrous CuF₂ was used as received from Ozark Mahoning Company. X-ray analysis of this material showed the water level in this material to be about 0.33 percent (3300 ppm).

A series of 60 ml serum bottles equipped with hermetic stoppers were filled with 40 ml of solvent, 1.0g of CuF₂, and 4.0, 8.0, or 12.0 grams of LiClO₄. Distilled water was added to the bottles in quantities designed to produce water contamination levels in the range of 150 to 5000 ppm. The samples were agitated on a laboratory shaker with appropriately timed interruptions to allow the solid phase to settle. The samples were then compared for color, and the concentration of Cu⁺⁺ in solution was determined by the thiosulphate titration.

Results of the copper ion determinations and the observed solution colors are listed in Tables III and IV, pages 12 and 15. The solutions which had the lower water contamination levels can be seen to have reached equilibrium at between 650 and 1000 hours of agitation, while those with the higher water levels still appeared to increase in copper concentration.

At equal LiClO₄ concentration, increasing water content increased the copper concentration in the solution. For example, increasing water content from 180 ppm to 5000 ppm increased the copper concentration after 1000 hours of agitation from 710 ppm to 7300 ppm. At approximately equivalent water contents, solubility of CuF₂ was more pronounced in the solutions having the higher LiClO₄ concentrations. However, the effect of LiClO₄ on the solubility of CuF₂ was much less pronounced that that of water contamination level. The solubility of CuF₂ was also found to be larger in butyrolactone than in propylene carbonate electrolyte.
The above results further demonstrate the need for very low water concentration in the CuF₂-Li system in order to minimize loss of capacity during wet shelf life of the cells. The solubility tests may prove of value for evaluation of CuF₂ drying methods, since the X-ray examination is of limited utility where low water contents are encountered. To make this approach practical, a method for decreasing the time required for the analysis would have to be developed.
TABLE III

SOLUBILITY OF CuF₂ IN PROPYLENE CARBONATE ELECTROLYTE

Materials: Propylene Carbonate, MC & B, Li dried and distilled; H₂O = (10 ± 10) ppm.
Lithium Perchlorate, Foote Mineral Co., vacuum dried at 110°C for 24 hours; H₂O = (600 ± 300) ppm.
Cupric Fluoride, Ozark Mahoning Co., as received; H₂O = (3300 ± 500) ppm.
Distilled Water, Sunbeam Water Co.

Series A — 10 gm. LiClO₄/100 ml PC; Solution Density = 1.25 gm/ml.

<table>
<thead>
<tr>
<th>Water Content, ppm</th>
<th>Agitation Time, Hours</th>
<th>Copper (II) Concentration, µ moles/ml</th>
<th>Solution Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>25</td>
<td>2.5</td>
<td>Off White</td>
</tr>
<tr>
<td>125</td>
<td>6.6</td>
<td>335</td>
<td>Off White</td>
</tr>
<tr>
<td>290</td>
<td>7.0</td>
<td>355</td>
<td>Off White</td>
</tr>
<tr>
<td>650</td>
<td>12.5</td>
<td>635</td>
<td>Light Tan</td>
</tr>
<tr>
<td>1000</td>
<td>12.5</td>
<td>635</td>
<td>Tan</td>
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<tr>
<td>400</td>
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<td>125</td>
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<td>355</td>
<td>Off White</td>
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<td>290</td>
<td>11.5</td>
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<tr>
<td>650</td>
<td>14.2</td>
<td>720</td>
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</tr>
<tr>
<td>1000</td>
<td>15.0</td>
<td>765</td>
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</tr>
<tr>
<td>810</td>
<td>25</td>
<td>6.0</td>
<td>Off White</td>
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<td>125</td>
<td>11.0</td>
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<tr>
<td>290</td>
<td>15.7</td>
<td>800</td>
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<td>650</td>
<td>20.0</td>
<td>1015</td>
<td>Light Yellow Green</td>
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<tr>
<td>1000</td>
<td>25.0</td>
<td>1270</td>
<td>Yellow Green</td>
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<td>2220</td>
<td>25</td>
<td>18.0</td>
<td>Light Green</td>
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<tr>
<td>125</td>
<td>32.5</td>
<td>1650</td>
<td>Light Green</td>
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<td>290</td>
<td>40.0</td>
<td>2030</td>
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<tr>
<td>650</td>
<td>40.0</td>
<td>2030</td>
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<td>1000</td>
<td>52.0</td>
<td>2640</td>
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<td>6050</td>
<td>25</td>
<td>101</td>
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<td>113</td>
<td>5750</td>
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<td>145</td>
<td>7400</td>
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<tr>
<td>1000</td>
<td>175</td>
<td>8900</td>
<td>Green</td>
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</table>
### TABLE III (Continued)

**SOLUBILITY OF CuF₂ IN PROPYLENE CARBONATE ELECTROLYTE**

**Materials:** Propylene Carbonate, MC & B, Li dried and distilled; 

\[ H₂O = (10 \pm 10) \text{ ppm}. \]

Lithium Perchlorate, Foote Mineral Co., vacuum dried at 

110°C for 24 hours; \( H₂O = (600 \pm 300) \text{ ppm}. \)

Cupric Fluoride, Ozark Mahoning Co., as received; 

\( H₂O = (3300 \pm 500) \text{ ppm}. \)

Distilled Water, Sunbeam Water Co.

**Series B** - 20 gm. LiClO₄/100 ml PC; Solution Density = 1.30 gm/ml.

<table>
<thead>
<tr>
<th>Water Content, ppm</th>
<th>Agitation Time, Hours</th>
<th>Copper (II) Concentration, ( \mu \text{ mols/ml} )</th>
<th>Solution Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>25</td>
<td>4.6</td>
<td>224</td>
</tr>
<tr>
<td>125</td>
<td>6.2</td>
<td>303</td>
<td>Off White</td>
</tr>
<tr>
<td>290</td>
<td>6.5</td>
<td>317</td>
<td>Off White</td>
</tr>
<tr>
<td>650</td>
<td>12.5</td>
<td>610</td>
<td>Light Tan</td>
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<tr>
<td>1000</td>
<td>13.0</td>
<td>635</td>
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<td>430</td>
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<td>245</td>
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<td>125</td>
<td>6.8</td>
<td>333</td>
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<td>290</td>
<td>9.5</td>
<td>465</td>
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<td>650</td>
<td>17.5</td>
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<td>1000</td>
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<td>416</td>
<td>Off White</td>
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<td>650</td>
<td>25.0</td>
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<td>1000</td>
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<td>1760</td>
<td>25</td>
<td>4.8</td>
<td>235</td>
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<td>125</td>
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<td>Light Green</td>
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<td>36</td>
<td>1770</td>
<td>Olive Green</td>
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<td>650</td>
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</tr>
<tr>
<td>1000</td>
<td>135</td>
<td>6600</td>
<td>Green</td>
</tr>
</tbody>
</table>
TABLE III (Continued)

**SOLUBILITY OF CuF₂ IN PROPYLENE CARBONATE ELECTROLYTE**

**Materials:**
- Propylene Carbonate, MC & B, Li dried and distilled; 
  $\text{H}_2\text{O} = (10 \pm 10)$ ppm.
- Lithium Perchlorate, Foote Mineral Co., vacuum dried 
  at 110°C for 24 hours; $\text{H}_2\text{O} = (600 \pm 300)$ ppm.
- Cupric Fluoride, Ozark Mahoning Co., as received; 
  $\text{H}_2\text{O} = (3300 \pm 500)$ ppm.
- Distilled Water, Sunbeam Water Co.

**Series C** — 30 gm. LiClO₄/100 ml PC; Solution Density = 1.34 gm/ml.

<table>
<thead>
<tr>
<th>Water Agitation Copper (II) Concentration Solution</th>
<th>Concentration</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content, Agitation Time, Copper (II) Concentration</td>
<td>Solution Color</td>
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TABLE IV
SOLUBILITY OF CuF₂ IN BUTYROLACTONE ELECTROLYTE

Materials: Butyrolactone, MC & B, Li dried and distilled;
H₂O = (10 ± 10) ppm.
Lithium Perchlorate, Foote Mineral Co., vacuum dried at
110°C for 24 hours; H₂O = (600 ± 300) ppm.
Cupric Fluoride, Ozark Mahoning Co., as received;
H₂O = (3300 ± 500) ppm.
Distilled Water, Sunbeam Water Co.

Series A — 10 gm. LiClO₄/100 ml BL; Solution Density = 1.18 gm/ml.

<table>
<thead>
<tr>
<th>Water Content, ppm</th>
<th>Agitation Time, Hours</th>
<th>Copper (II) Concentration, μmoles/ml</th>
<th>Solution Color</th>
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</table>
TABLE IV (Continued)

SOLUBILITY OF CuF₂ IN BUTYROLACTONE ELECTROLYTE

Materials: Butyrolactone, MC & B, Li dried and distilled;
H₂O = (10 ± 10) ppm.
Lithium Perchlorate, Foote Mineral Co., vacuum dried at
110°C for 24 hours; H₂O = (600 ± 300) ppm.
Cupric Fluoride, Ozark Mahoning Co., as received;
H₂O = (3300 ± 500) ppm.
Distilled Water, Sunbeam Water Co.

Series B - 20 gm. LiClO₄/100 ml BL; Solution Density = 1.22 gm/ml.

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<tr>
<th>Water Content, ppm</th>
<th>Agitation Time, Hours</th>
<th>Copper (II) Concentration μ moles/ml</th>
<th>Solution Color</th>
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<tbody>
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</tr>
<tr>
<td></td>
<td>290</td>
<td>15.0</td>
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</tr>
<tr>
<td></td>
<td>650</td>
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<td>Pale Yellow Green</td>
</tr>
<tr>
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<td>290</td>
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<tr>
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<td>34.5</td>
<td>Olive</td>
</tr>
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<td>1000</td>
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</table>
### TABLE IV (Continued)

**SOLUBILITY OF CuF₂ IN BUTYROLACTONE ELECTROLYTE**

**Materials:** Butyrolactone, MC & B, Li dried and distilled; 
H₂O = (10 ± 10) ppm. 
Lithium Perchlorate, Foote Mineral Co., vacuum dried at 
110°C for 24 hours; H₂O = (600 ± 300) ppm. 
Cupric Fluoride, Ozark Mahoning Co., as received; 
H₂O = (3300 ± 500) ppm. 
Distilled Water, Sunbeam Water Co.

**Series C** — 30 gm. LiClO₄/100 ml BL; Solution Density = 1.27 gm/ml.

<table>
<thead>
<tr>
<th>Water Content, ppm</th>
<th>Agitation Time, Hours</th>
<th>Copper (II) Concentration, μ moles/ml</th>
<th>Solution Concentration, ppm</th>
<th>Solution Color</th>
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<td>250</td>
<td>12500</td>
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</table>
3.2.2. Copper Fluoride Drying Studies

The removal of trace water from CuF₂ has been of major importance on this program, since the detrimental effect of water on the properties of CuF₂ has been repeatedly demonstrated. The main effect of presence of water appears to be the increased dissolution of the CuF₂ in the electrolyte which results in poor cell performance after wet stand at normal temperature.

Two basic procedures have been employed in this laboratory for the removal of water from CuF₂. The first method involves heating of the material under vacuum, while the second consists of placing the material in a vertical tube heated by a constant temperature bath and continuously purging the tube with dry argon.

To study the effect of the various drying conditions, eight batches of anhydrous CuF₂ were treated. The method of treatment and the X-ray patterns obtained before and after drying are presented in Table V, page 19. The relative concentration of each material in the sample is proportional to the peak intensity (counts/second), but the actual percentage figures can only be calculated for the materials which are available in pure form for calibration (CuF₂ and CuF₂·2H₂O).

It can be seen from an examination of Table V, page 19, that the main decomposition products which result from heating the salt are CuOHF·CuF₂·H₂O and CuOHF. An unknown compound having a major peak intensity at 4.15 Å is also produced. This material increases in quantity with increasing drying time and also with increasing temperature.
<table>
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<th>Compound</th>
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<th>Lot 7 A.R.</th>
<th>Lot 7 Oven</th>
<th>Lot 7 Argon</th>
<th>Lot 7 Argon</th>
<th>Lot 7 Argon</th>
<th>Lot 7 Argon</th>
<th>Lot 7 Argon</th>
<th>Lot 7 Argon</th>
<th>Lot 7 A.R.</th>
<th>Lot 8 A.R.</th>
<th>Lot 9 A.R.</th>
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<td>12</td>
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<td>----</td>
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<td>12</td>
<td>28</td>
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<td>12</td>
<td>----</td>
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<tr>
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<td>120</td>
<td>60</td>
<td>52</td>
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</tr>
</tbody>
</table>

* As received from manufacturer
3.2.3. Decomposition of CuF₂·2H₂O

Since decomposition of CuF₂·2H₂O is of importance in removing water from CuF₂, this reaction was studied further in a series of decomposition tests performed on the dihydrate. In the first series of experiments, 50 grams of dihydrate were heated in a sealed vacuum oven having a volume of 6.5 L from which air was evacuated prior to application of heat. Results of the X-ray analyses of the initial and resulting materials are given in Table VI, page 21.

A second series of tests was performed by heating the dihydrate in a tube while purging with argon as described in the previous section; results of these runs are presented in Table VII, page 22.

It can be seen from the X-ray data that the main decomposition products obtained by both methods are CuOHF and an unknown compound having a major peak intensity at 4.15 Å, the latter becoming more predominant with longer decomposition time and higher temperature.

Further work under more closely defined conditions is necessary in order to clarify the nature of the decomposition reactions involved. It is of interest to note, however, that preliminary tests indicate a low solubility of the "unknown" decomposition product of CuF₂·2H₂O in LiClO₄-PC electrolyte compared to dried CuF₂. The properties of this unknown compound will be studied further to see if an advantage could be gained by utilizing it as the positive active material of the cell in place of CuF₂.
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<th>B54-1</th>
<th>55-7</th>
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<td>150°C</td>
<td>135°C</td>
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<td>1 Atm. abs.</td>
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</tbody>
</table>

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* Vacuum pump was connected to chamber for 16 hours at which time chamber was sealed.

** Line is obscured by CuOHF line.
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3.3. CELL SYSTEMS STUDIES

3.3.1. Ag₂O₂-Li Cell Tests

Since the solubility of CuF₂ in LiClO₄-PC electrolyte appears to contribute adversely to the wet stand capability of the CuF₂-Li cells, self-discharge tests with cells having Ag₂O₂ instead of CuF₂ in the positive electrode were initiated. The silver oxide was chosen for the tests because it was presumed to have a very low solubility in the electrolyte, thus allowing evaluation of the remaining cell construction for wet stand capability without the complication of a dissolved species (Cu⁴⁺) attacking the lithium electrode from solution.

In order to study the wet stand capability of the Ag₂O₂-Li system, six cells with LiClO₄-PC electrolyte were constructed and tested. Two cells were discharged through 200 Ω loads (ca. 0.5 mA/cm²), while the remaining four cells had wet stands of two and four weeks at 35°C. Construction and discharge data for the cells are summarized in Table VIII, page 24, and voltage-time data for Cells 1, 2, and 4 are plotted in Figure 3, page 25.

Degradation of capacity even after two weeks of stand at 35°C was quite severe and approximately comparable to that observed in CuF₂-Li cells. However, appearance of the lithium electrodes at the end of the test was comparatively very good, with no visible deposits on the surface. The free electrolyte level in the cells as viewed through the transparent polyethylene envelope had completely disappeared after the wet stand period; this condition could easily have affected the discharge performance of the cells. The above tests are scheduled to be repeated in a hermetically sealed test assembly in order to minimize electrolyte loss during open circuit stand and discharge.
TABLE VIII
SELF-DISCHARGE IN Ag₂O₂-Li CELLS
WITH LiClO₄-PC ELECTROLYTE

Stand Temperature: 35°C
Discharge Temperature: 35°C
Load: 200 ohms

<table>
<thead>
<tr>
<th>Cell No.</th>
<th>Stand Time, Weeks</th>
<th>Theoretical Ag₂O₂ Cap. AH *</th>
<th>Hours to 2.5 VF AH</th>
<th>Capacity to 2.5 VF AH</th>
<th>Average Discharge Potential Volts</th>
<th>Cathode Eff. %</th>
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<td>42</td>
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<td>16</td>
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* Based on 100% Ag₂O₂ in active material.
Test No. 540-8
Load: 200 ohms
Temperature: +35°C
Electrolyte: 15 gm LiClO₄/100 ml PC.

Theoretical Capacity, AH: 1 - 2.90
2 - 2.75

No open circuit stand

Two weeks stand at +35°C.

Theoretical Capacity, AH: 4 - 2.62

PERFORMANCE OF Ag₂O₂-Li CELLS

FIGURE 3.
3. 3. 2. Self Discharge Tests in Propylene Carbonate

Further evaluation of the wet stand capability of CuF₂-Li cells with propylene carbonate electrolyte was conducted during the past quarter. The main variable under study was the water content of the CuF₂ used in constructing the positive electrodes. One lot of CuF₂ was dried with argon at 130°C for 16 hours, and a second lot was dried under the same conditions for 113 hours. Subsequent X-ray analysis of the treated materials indicated water contents of below 0.3 and below 0.1 percent, respectively.

Copper fluoride test electrodes were constructed by the filter mat technique employed in previous self discharge tests (CuF₂: 82 percent, graphite: 12 percent, paper fiber: 6 percent, 29 cm² geometric electrode area, 4-5 AH theoretical capacity). Three-plate cells with lithium sheet electrodes and 0.03 inch microporous rubber separation were constructed and filled with propylene carbonate electrolyte (15g LiClO₄/100 ml PC). Cells were discharged thru 200 Ω resistors at 35°C immediately after filling with electrolyte, and after wet stand at 35°C and -15°C.

Without open circuit stand period, capacity was somewhat higher for the cells which had CuF₂ dried for the shorter period (16 hours), indicating that some decomposition of CuF₂ may have taken place during the drying period. After a two-week stand at 35°C, only two of the six cells with each type of CuF₂ had any significant capacity above 2.5 volts. After stand periods of 2, 4, and 6 weeks at -15°C, cell performance was not significantly different than had been obtained from cells which had received no open circuit stand. Results of the discharge tests are summarized in Tables IX and X, pages 27 and 28. The voltage-time data for the cells are presented in Figures 4 to 8, pages 29 and 33, and the extent of self discharge under the various test conditions for the highest performance cell in each group is displayed graphically in Figure 9, page 34.

Inspection of the cells at the end of test did not reveal clearly why the cells failed to discharge after the open circuit stand period at 35°C. All cell components appeared to be in good condition, and no evidence of short-circuiting could be found. However, the unabsorbed portion of the electrolyte had disappeared during the stand period, and an ester-like odor was always evident in the constant temperature chamber. This suggests loss of solvent by decomposition and evaporation, which contributes to the loss of capacity after stand. Also, the loss of electrolyte is more pronounced in the cells which show more extensive capacity loss during stand. This factor will be studied further utilizing hermetically sealed cell assemblies.
### TABLE IX

**SELF-DISCHARGE IN CuF$_2$-Li CELLS**

CuF$_2$ Dried 16 Hours at 130°C under Argon

<table>
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<th>Cell No.</th>
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<th>Hours to 2.5 VF</th>
<th>Capacity to 2.5 VF, AH</th>
<th>Average Discharge Potential, Volts</th>
<th>Cathode Eff., %</th>
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$^1$ Test in progress.

$^2$ Cell had internal short circuit.
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</tr>
</tbody>
</table>

¹ Test in progress.
LTA #640-35

Stand Conditions: 2 hours, +35°C
Discharge Condition: 200 mA, +35°C

Theoretical CuF₂ Capacity:
1 3.72 AH
2 3.93 AH

Theoretical CuF₂ Capacity:
3 3.93 AH
4 4.18 AH

Performance of CuF₂-Li Cells

Figure 4
PERFORMANCE OF CuF₂-Li CELLS

FIGURE 5
THEORETICAL CuF$_2$ CAPACITY:

- Cell 13: 3.52 AH
- Cell 14: 3.50 AH

THEORETICAL CuF$_2$ CAPACITY:

- Cell 29: 4.11 AH
- Cell 30: 4.27 AH

PERFORMANCE OF CuF$_2$-Li CELLS

FIGURE 6
PERFORMANCE OF CuF$_2$-Li CELLS

FIGURE 7
PERFORMANCE OF CuF$_2$-Li CELLS

FIGURE 8

LTA #646-3B

Stand Conditions: 1/2 hours; +35°C

Theoretical CuF$_2$ Capacity:

Cell 17 4.57 AH
Cell 18 4.58 AH

Cell 19 4.77 AH
Cell 20 4.24 AH

Time, Hours
SELF-DISCHARGE IN CuF₂-Li CELLS

FIGURE 9
3.3.3. Butyrolactone Cell Tests

Butyrolactone had been tested during previous work on this program as a possible electrolyte solvent for CuF₂-Li cells. It showed generally less desirable properties in compatibility and cell discharge tests compared to propylene carbonate. However, the solvent purity level in these earlier tests was not comparable to that presently obtained in PC. Since butyrolactone possesses certain desirable properties compared to propylene carbonate (higher specific conductance, lower viscosity), it was decided to study cell performance with BL-LiClO₄ electrolyte having water content comparable to that presently obtained in PC-LiClO₄ electrolyte.

Test cells were assembled using the argon stream dried CuF₂ and cell construction described in Section 3.3.2. The butyrolactone electrolyte had a concentration of 15g LiClO₄/100 ml solvent, and the water content as determined by Karl Fischer analysis was 150 ppm. The cells were discharged thru 200 Ω loads at 35°C after filling with electrolyte and after wet open circuit stand periods of one week at 35°C and two weeks at -15°C.

No capacity was retained by the four cells which experienced active stand at 35°C. Inspection of the components showed a large amount of copper colored deposit in the positive electrode matrix, although no evidence of short circuits thru the microporous rubber separation could be found. After the two-week stand period at -15°C, capacity was somewhat higher than without stand. Results of the discharge tests are summarized in Table XI, page 36, and voltage-time curves for some cells are given in Figures 10 to 12, pages 37 to 39.

The discharge performance of butyrolactone electrolyte cells was poor compared to similar cells having propylene carbonate electrolyte solvent. The CuF₂ reduction efficiency was only 20-30 percent compared to 60-80 percent obtained with propylene carbonate electrolyte. This reduction of efficiency is probably associated with the greater solubility of CuF₂ in butyrolactone electrolyte, although the exact mode of failure could not be determined from inspection of discharged cells. In view of the above results, no further tests with butyrolactone electrolyte are contemplated at this time.
TABLE XI

PERFORMANCE OF CuF₂-Li CELLS
WITH BUTYROLACTONE ELECTROLYTE

Electrolyte: 15g LiClO₄/100 ml BL
Water Content: 150 ppm
Discharge Temperature: 35°C
Discharge Load: 200 Ω
Electrode Area: 29 cm²
Separation: 0.03" MPR

<table>
<thead>
<tr>
<th>Cell No.</th>
<th>Temp. °C</th>
<th>Time, wks.</th>
<th>Theo. CuF₂ Capacity, AH</th>
<th>Hours to 2.5 VF</th>
<th>Capacity to 2.5 VF, AH</th>
<th>Average Discharge Potential, Volts</th>
<th>Percent Cathode Efficiency</th>
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</thead>
<tbody>
<tr>
<td>1*</td>
<td>--</td>
<td>--</td>
<td>3.71</td>
<td>70</td>
<td>1.07</td>
<td>3.05</td>
<td>29</td>
</tr>
<tr>
<td>2*</td>
<td>--</td>
<td>--</td>
<td>4.18</td>
<td>76</td>
<td>1.17</td>
<td>2.99</td>
<td>28</td>
</tr>
<tr>
<td>3*</td>
<td>--</td>
<td>--</td>
<td>3.59</td>
<td>74</td>
<td>1.98</td>
<td>2.92</td>
<td>30</td>
</tr>
<tr>
<td>4*</td>
<td>--</td>
<td>--</td>
<td>3.44</td>
<td>75</td>
<td>1.16</td>
<td>3.01</td>
<td>34</td>
</tr>
<tr>
<td>9**</td>
<td>--</td>
<td>--</td>
<td>3.90</td>
<td>64</td>
<td>1.00</td>
<td>3.12</td>
<td>26</td>
</tr>
<tr>
<td>10**</td>
<td>--</td>
<td>--</td>
<td>4.50</td>
<td>70</td>
<td>1.10</td>
<td>3.13</td>
<td>24</td>
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<tr>
<td>11**</td>
<td>--</td>
<td>--</td>
<td>4.67</td>
<td>62</td>
<td>0.96</td>
<td>3.08</td>
<td>21</td>
</tr>
<tr>
<td>12**</td>
<td>--</td>
<td>--</td>
<td>4.60</td>
<td>59</td>
<td>0.93</td>
<td>3.13</td>
<td>20</td>
</tr>
<tr>
<td>5*</td>
<td>+35</td>
<td>1</td>
<td>3.92</td>
<td>( \frac{1}{2} )</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>6*</td>
<td>+35</td>
<td>1</td>
<td>4.10</td>
<td>( \frac{1}{2} )</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>13**</td>
<td>+35</td>
<td>1</td>
<td>4.82</td>
<td>( \frac{1}{2} )</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>14**</td>
<td>+35</td>
<td>1</td>
<td>4.58</td>
<td>(&lt;1)</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>7*</td>
<td>-15</td>
<td>2</td>
<td>4.26</td>
<td>118</td>
<td>1.80</td>
<td>3.05</td>
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</tr>
<tr>
<td>8*</td>
<td>-15</td>
<td>2</td>
<td>4.12</td>
<td>90</td>
<td>1.36</td>
<td>3.03</td>
<td>33</td>
</tr>
<tr>
<td>15**</td>
<td>-15</td>
<td>2</td>
<td>4.62</td>
<td>95</td>
<td>1.45</td>
<td>3.06</td>
<td>31</td>
</tr>
<tr>
<td>16**</td>
<td>-15</td>
<td>2</td>
<td>4.71</td>
<td>97</td>
<td>1.45</td>
<td>3.00</td>
<td>31</td>
</tr>
</tbody>
</table>

1 Open Circuit Voltage <1V after stand
* CuF₂: Dried in argon for 16 hours at 130°C
** CuF₂: Dried in argon for 113 hours at 130°C
Electrolyte: 15 gm LiClO₄/100ml BL.
CuF₂: Dried 16 hours at 130°C in Argon
No open circuit stand

Cell 1

Cell 2

Theoretical CuF₂ Capacity: 1 - 3.71 AH
2 - 4.18 AH

Theoretical CuF₂ Capacity: 3 - 3.59 AH
4 - 3.44 AH

TIME, HOURS

0 50 100 150 200 250

Cell Potential Volts

0 1 2 3

Performance of CuF₂-Li Cells

FIGURE 10
Electrolyte: 15 gm LiClO$_4$/100 ml BL

CuF$_2$: Dried 113 hours at 130°C in Argon

No open circuit stand

**THEORETICAL CuF$_2$ CAPACITY:**
- Cell 9: $\frac{10}{3} = 3.33$ AH
- Cell 10: $\frac{11}{3} = 3.67$ AH
- Cell 11: $\frac{12}{3} = 4.00$ AH

**TIME HOURS**

**PERFORMANCE OF CuF$_2$-Li CELLS**
PERFORMANCE OF CuF₂-Li CELLS

FIGURE 12

LTA #540-10

Stand Conditions: 2 weeks; -15°C
Discharge Conditions: 200 Ohms; 435°C

Theoretical CuF₂ Capacity:

- Cell 7: 7.25 AH
- Cell 8: 4.12 AH
- Cell 15: 4.52 AH
- Cell 16: 4.71 AH

Time, Hours
4. **APPENDIX**

4.1 **X-RAY ANALYSIS OF CuF$_2$**

**A. Preparation of Sample**

About 10 g of the material to be analyzed is delivered under argon into a "Hi-speed" micronizer blender and ground for ca. 20 seconds. The material is then transferred to a polyethylene envelope, and the latter is heat sealed.

Prior to mounting on the diffractometer, the powder is pressed by hand into a 1/16 inch thick aluminum die which has been taped to a microscope slide. A second slide is then taped to the opposite side of the die, and the original slide is removed leaving a smooth plane of compacted material.

**B. Analysis**

A Phillips Model 12045B/3 X-ray generator is used in conjunction with Phillips No. 12096 Control Panel and No. 52090 Minneapolis-Honeywell Strip Chart Recorder. The sample is rotated from 80° to 10° Bragg angle at the rate of 1 degree/minute under monochromatic CuK$_\alpha$ radiation ($\lambda = 1.5418\AA$).

**C. Calculation**

1. **CuF$_2$·2H$_2$O**

   The highest amplitude on chart between the limits of 18.4 and 18.6 degrees is selected, and percent CuF$_2$·2H$_2$O is calculated

   $\%$CuF$_2$·2H$_2$O = 0.0227 x amplitude x scale factor.

2. **CuO**

   The highest amplitude between the limits of 38.6 and 38.8 degrees is selected, and percent CuO is calculated

   $\%$CuO = 0.0417 x amplitude x scale factor.
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