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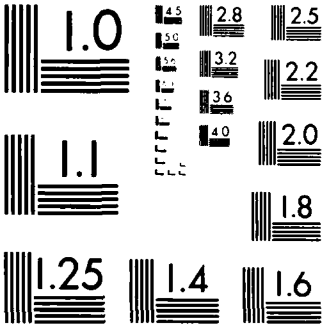

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ECO
Energy Conversion
225 NEEDHAM STREET
NEWTON, MA 02164, U.S.A.
TELEPHONE (617) 964-7010

A SAFE, HIGH-POWER-DENSITY LITHIUM BATTERY

Fraser Walsh

ECO Energy Conversion
225 Needham Street
Newton, MA 02164

March, 1985

Final Report for Period September, 1984 to February, 1985

Prepared for:

Office of Naval Research
Defense Advanced Research Projects Agency
1400 Wilson Boulevard
Arlington, VA 22209

Attn: Dr. R.A. Reynolds

under:

ONR Contract No. N00014-84-C-0724

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PROJECT SUMMARY

ONR Contract No. N00014-84-C-0724

"A Safe, High-Power-Density Lithium Battery"

Fraser Walsh
ECO Energy Conversion
225 Needham Street
Newton, MA 02164

The $Li/SOCl_2$ battery has received attention because of its high theoretical energy/power density. However, practical $Li/SOCl_2$ cells have not provided the desired power density and have suffered from concerns with cell safety on discharge. In previous work, ECO has shown that the use of a TAA-type catalyst significantly improves the safety of the $Li/SOCl_2$ cell at high rate. The objective of this Phase I program was to determine whether a stacked disk electrode configuration with TAA-catalyzed cathodes was feasible and whether the performance of this stack would meet a high power-density design goal.

Under the program, the effects of cathode thickness, preparation pressure, electrolyte gap and solute concentration on stacked-electrode cell performance and capacity were measured.

The results of the Phase I program included the demonstration of stacked-electrode cell performance and capacity at levels suitable to meet a design goal of 400 W/kg with high energy density. Further work in a Phase II program will be required to demonstrate in laser-sealed fully-packaged cells that the results of Phase I can be practically applied to provide a safe high-rate, energy-dense power source for military applications.

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EXECUTIVE SUMMARY

The performance and capacity of multi-electrode cells with TAA-catalyzed disk-type cathodes was determined. Cathode capacity in excess of 400 mA-hr/cm^3 with discharge voltages at 40 mA/cm^2 of over 3.25 V were obtained. The effects on cell performance and capacity of cathode thickness and fabrication pressure, as well as electrolyte gap and solute concentration were determined. The CSX 213 carbon used in the program was demonstrated to provide high performance and capacity; these levels were observed to increase on TAA catalysis.

The performance and capacity values of the stacked electrode cells tested in Phase I are sufficient to be used to provide a reliable forecast that a fully packaged cell can be made which will meet the desired power density goal of 400 W/kg with high energy density.

1.0 PROGRAM OBJECTIVE

1.1 Problem Addressed

The major program objective was to demonstrate that TAA-catalysis of cathodes in Li/$SOCl_2$ cells improves the power density of such cells sufficiently so that a 400 W/kg (fully packaged) battery can be obtained. It is this power density of 400 W/kg in a fully packaged power source, combined with high discharge capacity, which is the ultimate goal of the Phase I/II/III program.

Work on developing a high energy density Li/$SOCl_2$ cell useful in military applications has been carried out by a number of battery producers. These cells vary in configuration and reactive components; a summary of exemplar cell types is provided in Table 1. More recent work has centered on methods to improve cathode capacity or performance through the use of organometallic catalysts (5), of improved carbons (6,7), or cathode additives (8). All of these approaches are reported to improve cathode capacity and performance especially at reduced temperatures (-30° to -40°C). However, except for an organometallic catalyst, the cathode discharge mechanism has not been affected, and thus the safety of the resulting Li/$SOCl_2$ cell, especially under forced over-discharge or resistive load over-discharge conditions, has not been affected.

In recently reported work, ECO has determined that Li/$SOCl_2$ cells with TAA-catalyzed cathodes have improved safety (9). The basis for this improved safety appears to be a change in the cathode reaction based on observed changes in reaction products and in cathode energy density (10). The program approach was to determine whether disk-type cathode structures, when catalyzed with a TAA, provide the program-required power density while maintaining high cathode energy density.

TABLE 1

Selected High Power Li Batteries

Producer	Couple	Configuration	Power Density, W/kg	Ref.
Eagle-Picher	Li/CF_x	jelly roll; DD-size	360	1
Honeywell	$Li/SOCl_2$	reserve; 112V; 5.5 A-hr	63-148	2
Altus	$Li/SOCl_2$	reserve; 88V; 2.8 A-hr	480	3
GTE	$Li/SOCl_2$	four-plate; D-size; 11 A-hr	33	4

1.2 Phase I Research Goals

The goal of the Phase I effort was to initially investigate the energy and power densitites of TAA-catalyzed carbon cathodes used in electrochemical reduction of $SOCl_2$. Of specific interest in this work was the measurement of the performance and capacity of $Li/SOCl_2$ cells with TAA-catalyzed disk electrodes.

The specific objective of the Phase I research program was to demonstrate, in a laboratory cell, that the performance of the $Li/SOCl_2$ couple with a cathode catalyzed with a metallated dibenzotetraaza-[14]-annulene (TAA) meets the design requirements for a fully-configured high energy/power density battery. ECO has recently been issued a patent which teaches the use of TAAs in such cells (11). A second objective of the Phase I research program was to initially characterize the performance of TAA-catalyzed disk-type cathodes.

The Phase I research attempted to answer the following questions:

1. What is the electrochemical activity of the ECO proprietary catalyst for $SOCl_2$ reduction in multielectrode disk-type cells?

2. What performance improvements are observed in multielectrode $Li/SOCl_2$ TAA-catalyzed cells?

3. What cell components are required to be used with TAA-catalyzed disk-type cathodes to meet military high-rate performance requirements?

2.0 PREVIOUS WORK

2.1 Improved Cathode Materials

A number of recent publications have centered on the advantages of the use of one carbon type over another: work from Japan describes a carbon, prepared by furnace treatment of an oil, which provides a 20% increase in discharge capacity and 100 mV performance improvement at 20 mA/cm^2 (7) compared to a standard acetylene black. Significantly larger capacity increases for a CSX carbon (CSX 174; Cabot Corp.) were reported by Klinedinst (6) with cathaode capacity values reported as high as 52 mA-hr/cm^3 at a rate of over 32 mA/cm^2. Load voltages were increased by over 250 mV at these rates compared to an acetylene black. These improvements alone (e.g., 250 mV performance to 3.26 V at 32 mA/cm^2 and from 28.5 mA-hr/cm^3 to 52 mA-hr/cm^3) are worthy of note because they represent a significant increase over the performance and capacity of the carbons of the type used in Li/SOCl$_2$ batteries of the type summarized in Table 1. Given that these batteries almost meet the program power density requirements, a simple substitution of carbons into the cathodes of such batteries should be sufficient to provide power sources capable of meeting program energy/power density goals. However, such a simple substitution will not result in a change in cathode reaction mechanism (and thus safety) nor in an optimization of battery performance or capacity available through the use of advanced materials.

2.2 Cathode Catalysts

One approach to improving the performance of the cathode in Li/SOCl$_2$ cells is the use of a cathode catalyst. Catalysts used have included copper (12), cupric chloride (13), platinum (14), and metallated organometallics (5,15). While the use of inorganic or metal catalysts does not affect the cathode reaction mechanism, the metallated organometallic catalysts are reported to change the cathode mechanism by further reducing the sulfur moiety in $SOCl_2$. For example, Doddapaneni, based on results using phthalocyanine catalysts (16), reported that the cathode reaction with such catalysts is changed to provide a product via a mechanism in which the presence of the organometallic inhibits the dimerization of SO while the sulfur is further reduced. This results in the following overall cell reaction:

$$5\ Li + 2\ SOCl_2 \longrightarrow 4\ LiCl + S + 1/2\ Li_2S_2O_4$$

with 2-1/2 e^- available per $SOCl_2$ reduced. This represents an increase of 25% in cathode gravimetric charge density, and a potential change in cell safety. Unfortunately, this type of organometallic, a phthalocyanine, is not stable, even when heat-polymerized, in the electrolyte, and so this improved cathode chemistry is available only for higher-cost reserve cells.

ECO recently completed work showing that a new class of organometallics, the dibenzo-[14]-tetraazaannulenes (TAAs) are active cathode catalysts for $Li/SOCl_2$ cells (9,10). The advantage of this catalyst type is its demonstrated stability in $Li/SOCl_2$ cells and its significant effect on reaction mechanism. Based on data obtained to date, overall cell reaction with the ECO TAA catalyst is:

$$4\ Li + SOCl_2 \longrightarrow 2\ LiCl + Li_2O\ (solv.) + S$$

with [illegible]$^-$ available per $SOCl_2$ reduced. This represents a doubling in cathode gravimetric charge density, and a significant change in cell safety due to the change in the cathode mechanism. ECO has already proven this TAA catalyst to be stable in $Li/SOCl_2$ cells, even when the cells are stored for weeks at 160°F (10).

2.3 Safety Considerations

Dey (16) first proposed the following reaction mechanism for applications. The results obtained in Phase I showed that it is technically feasible to use a TAA-catalyzed cathode to provide a cell capable of providing 400 W/kg. Further work in a Phase II program will center on developing this cathode structure into a practical, laser-sealed cell, and proving that the packaged system meets the requirements of advanced high-power-density power source.

6.0 ACKNOWLEDGEMENT

The author wishes to express thanks to Mr. M. Yaniv and Mr. F. Kulik for their technical support.

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a CSX carbon; this capacity was even further improved through the use of the TAA catalyst.

5.2 Future Directions

The Phase I objective was met of demonstrating that TAA-catalyzed disk-electrode cathodes can meet the performance requirements of a cell designed to provide 400 W/kg and high energy density. Previous work (9,10) has shown that such cells should have improved safety compared to conventional high rate cells. There are a number of questions which remain before the Phase I research can be extended to the production and sale of a product of use to the military. These questions include:

1. What is the performance and capacity of Li/$SOCl_2$ sealed cells in configurations suitable to demonstrate utility in military applications?

2. Can the performance (capacity and discharge voltage) be improved by further modifications of the catalyst used or the electrode structure?

3. What is the performance (including safety) and capacity of sealed cells with such optimized components or structures?

4. What is a cost-effective design for production of such an optimized cell?

5. Is there a market demand (commercial, military) for such an optimized cell based on unit cost, safety, energy/power density and shelf life?

Answers to these types of practical and research questions will further clarify the feasibility of the use TAA-catalyzed electrodes to provide sealeld cells capable of meeting the performance goals for high-rate batteries in military at approximately 0.04 cm thick using a 1.8 M $Li/AlCl_4/SOCl_2$ electrolyte. An electrode pair, including a 0.05 cm electrolyte gap thus has a thickness of less than 0.15 cm, or only 60% of the maximum allowable (0.25 cm as described in Section 2.4) to meet the 400 W/kg goal. If stacks are made up on these dimensions, the current density requirement is reduced to 40 mA/cm^2 at 3V. At this current density, the performance of CoTAA-catalyzed cells was observed to be over 3.25 V or well over the performance required to meet the 400 W/kg goal. The expected volumetric energy density of the design cell, when fully packaged, is approximately 0.34 $W\text{-}hr/cm^3$ which compares favorably with published values for high rate reserve batteries (21).

5.0 TECHNICAL FEASIBILITY

5.1 Program Accomplishments

The Phase I research provided the following answers to the questions identified in Section 1.2:

1. The ECO TAA-catalyzed carbons have been shown to provide improved performance over high-performance carbons in $SOCl_2$ reductions in multi-electrode disk-type cells.

2. Cathode volumetric capacity and discharge performance were observed to be improved in multi-electrode $Li/SOCl_2$ TAA-catalyzed cells.

3. A thin disk (0.04 cm) cathode configuration with a 0.05 mm electrolyte gap using 1.8 M $LiAlCl_3$ solute concentration was shown to provide cells which meet the military high-rate goal (400 W/kg) while maintaining high volumetric energy density.

All of the technical goals planned for the Phase I program were achieved. High gravimetric cathode capacity was observed for

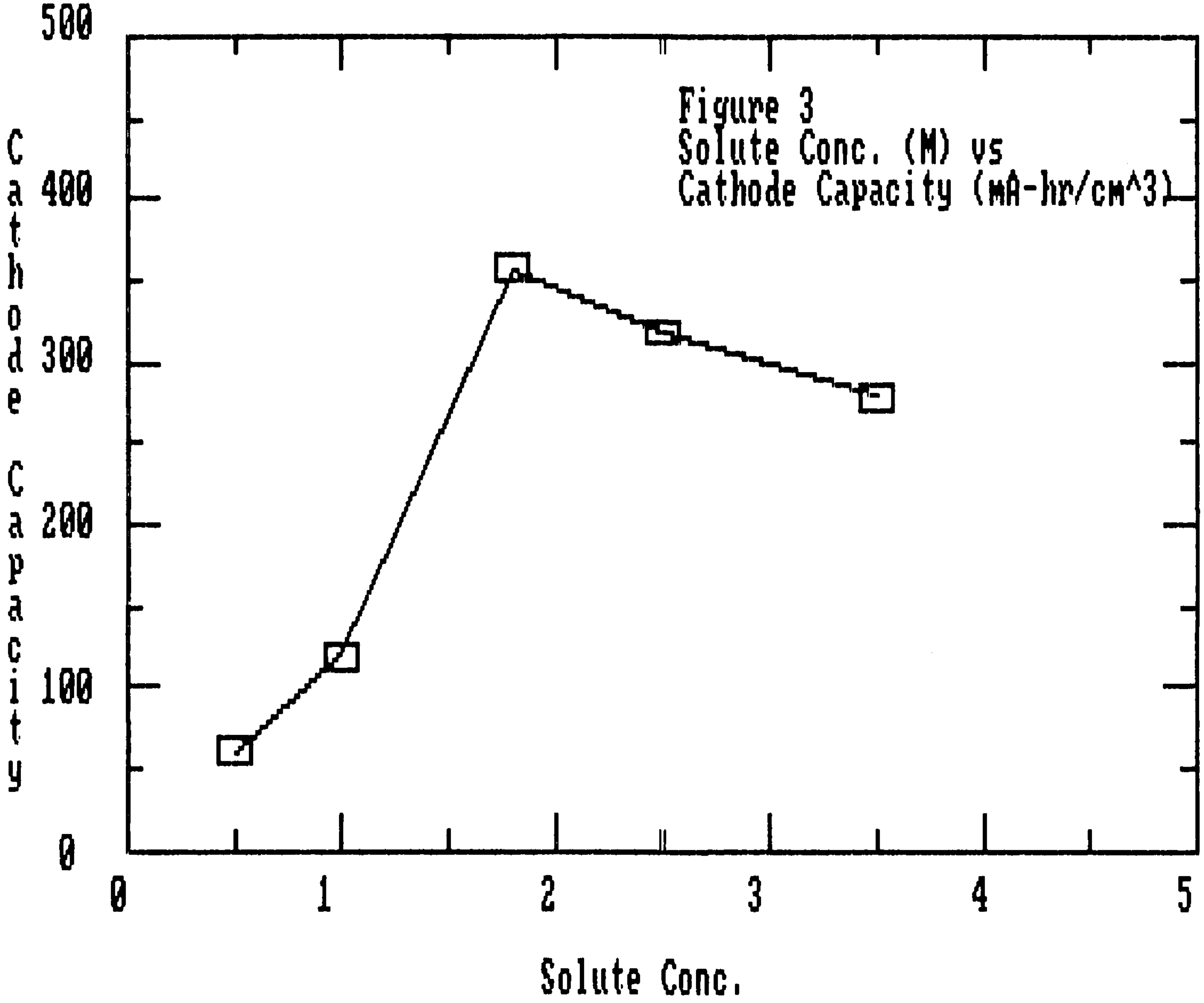

Figure 3
Solute Conc. (M) vs
Cathode Capacity (mA-hr/cm^3)

4.3 Effect of Electrolyte Gap

Three different electrolyte gap widths were evaluated (0.25, 0.50 and 0.75 mm) with four cells run per gap width. The cathodes contained 5% CoTAA-catalyzed carbon. The discharge capacity of these cells did not change significantly because all cells were flooded (cathode not catholyte limited). As shown in Table 3, the effect of increasing gap, as expected, is one of increased cell resistance and is related to gap width. For a 0.50 mm gap, and an 80% porosity, 0.040 cc volume of electrolyte is available per cm^2 of surface area. This volume will provide over 65 mA-hr/cm^2 capacity (assuming 90% utilization and a $4e^-/SOCl_2$ reduction mechanism).

4.4 Effect of Electrolyte Concentration

Cells were prepared with stacked electrodes and with varying electrolyte solute concentrations (0.5 to 3.5 M $LiAlCl_4$). The cathodes contained 5 w/o CoTAA-CSX carbon, were pressed at 500 psi, and had an approximate thickness of 11 mils (0.03 cm). Provided in Figure 3 are the average data obtained (up to six cells run per electrolyte concentration) on cathode capacity as a function of electrolyte solute concentration. Cathode capacity is shown to be directly related to electrolyte solute content with a maximum near 1.8 M $LiAlCl_4$.

4.5 Summary of Results

The effects of cathode thickness, cathode fabrication pressure, electrolyte gap and electrolyte solute concentration on TAA-catalyzed cathode capacity and performance were investigated. Over eighty laboratory cells were discharged in these tests: a stacked electrode configuration was used with two cathodes/three anodes. The results obtained showed that TAA-catalyzed cathode capacity in excess of 400 mA-hr/cm^3 can be obtained with cathodes

TABLE 3

Effect of Increasing Electrolyte Gap on Cell Performance

Gap, mm	0.50	0.75
Current Density, mA/cm^2	Performance Loss, mV	
0	0	0
2	0	0
5	10	40
20	20	120
50	80	220

NOTE:

1. Performance loss measured vs difference in load voltage versus performance at 0.25 mm gap.

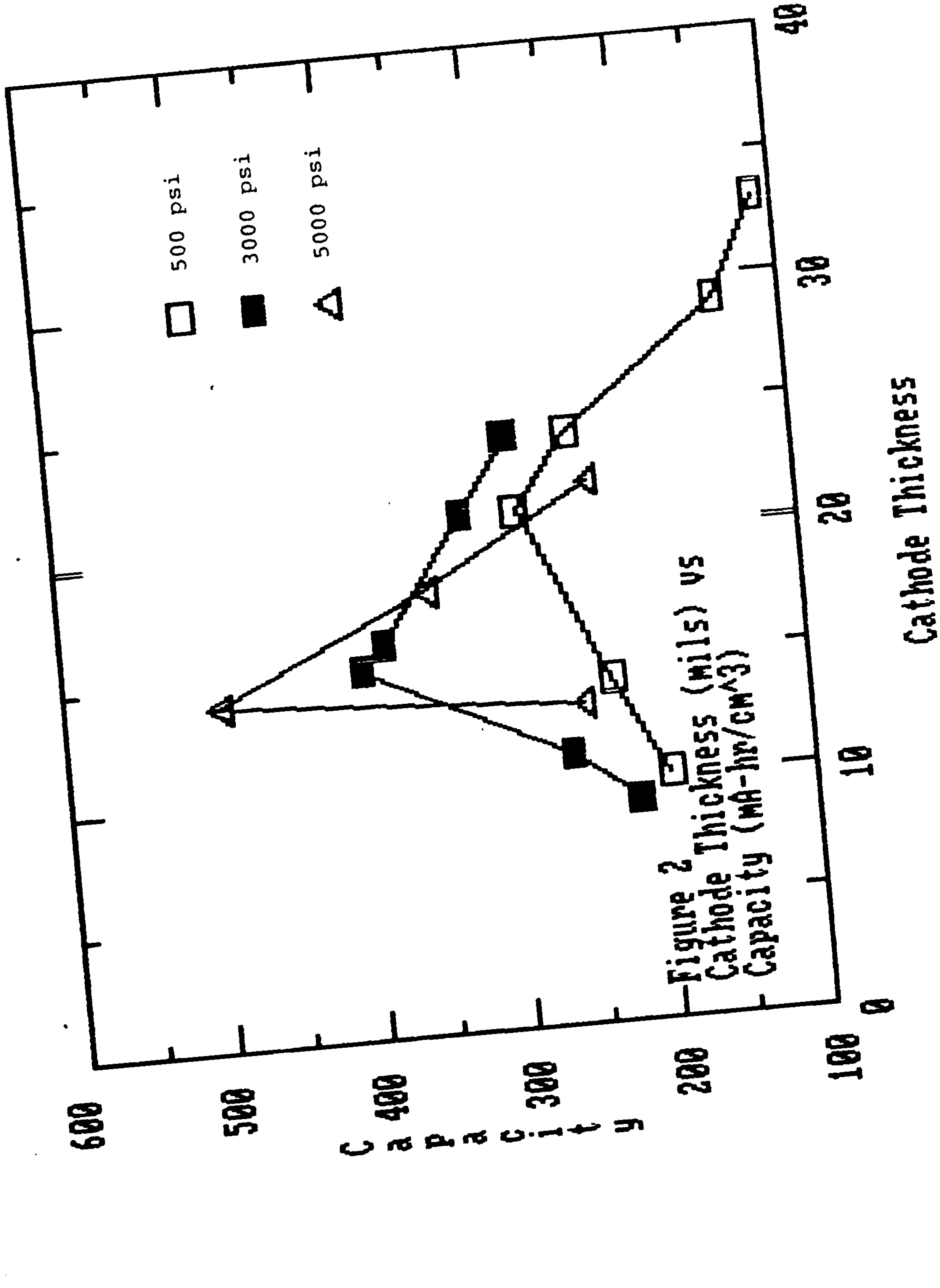

Figure 2
Cathode Thickness (mils) vs
Capacity (mA-hr/cm^3)

TABLE 2

Comparison of Performance and Capacity of Carbons

Carbon	CSX	BP	SAB	Vulcan
Current Density, mA/cm^2		Performance (V vs Li Reference)		
0	3.65	3.65	3.65	3.65
2	3.65	3.64	3.63	3.65
5	3.61	3.60	3.45	3.59
20	3.28	3.33	3.09	3.15
50	2.97	2.94	2.72	2.80
		Cathode Capacity (mA-hr/cm^3 to 2.0 V)		
20	230	260	255	170
		Cathode Capacity (A-hr/g to 20 V)		
20	1.45	1.10	1.05	0.65
No. of cells	6	2	2	2

4.0 RESULTS

4.1 Comparison of Carbons

A comparison of performance and capacity was made of cells containing a single cathode-anode pair. The cathodes were prepared at 3000 psi to a thickness of 20 to 25 mil using 67 to 113 g of carbon. The electrolyte was 1.8 M $LiAlCl_4/SOCl_2$. Provided in Table 2 are average performance and capacity (at 20 mA/cm^2) data for the cells tested. The cathode capacities obtained ranged from 170 to 260 mA-hr/cm^3 (0.65 to 1.45 A-hr/g) which is significantly better than those recently reported by Klinedinst (6) for various carbon cathodes at 30 mA/cm^2 (23 to 52 mA-hr/cm^3) or by Dey (all less than 1 A-hr/g at 20 mA/cm^2). Based on its highest observed gravimetric energy density and power density, the CSX carbon was chosen for further study.

4.2 Effect of Cathode Thickness

A series of cells (16) were run (in duplicate) each containing an electrode stack (3 anodes/2 cathodes). The cathodes were prepared to contain varying weights of CSX (15 to 80 mg) applied to a 4.5 cm^2 surface and formed under varying pressures (500 to 5000 psi). Provided in Figure 2 are the data obtained displayed as cathode thickness (mils) versus cathode capacity (mA-hr/cm^3) at three different forming pressures (500, 3000 and 5000 psi). A cathode thickness of approximately 15 mils (0.04 cm) is shown to be optimal.

An identical series of cells (16) were run (in duplicate) each containing an electrode stack with the cathode containing 5 w/o CoTAA-catalyzed CSX. Again, an optimal thickness of approximately 0.04 cm was observed although the capacity values were observed to be increased from 37 to 95% over the range tested.

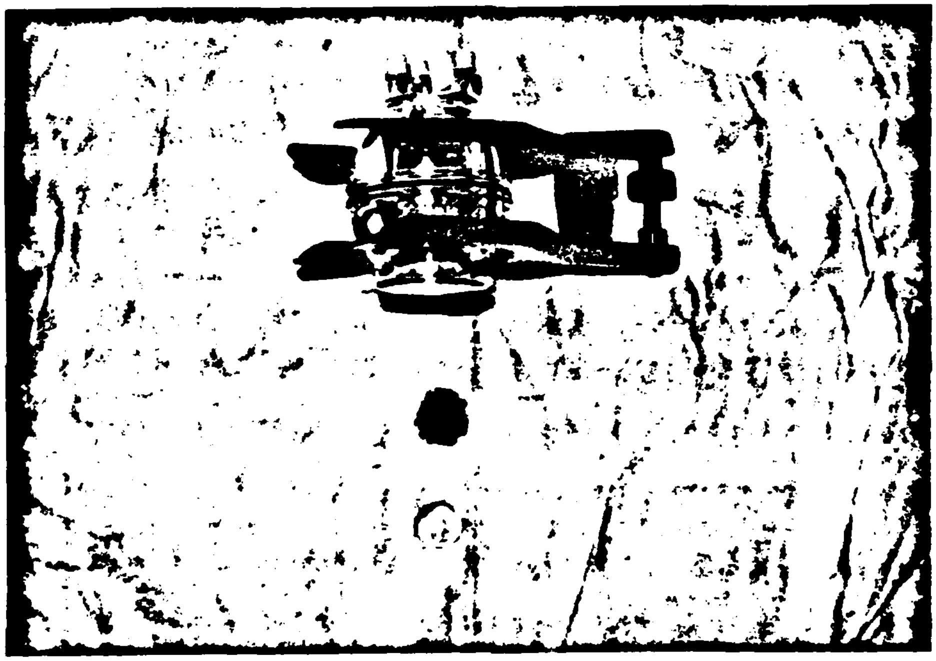

Figure 1

ECO Cell with Electrode

stoichiometric amount of $AlCl_3$ in $SOCl_2$, while stirring, with slow addition of a 5% stoichiometric excess of LiCl; during addition, the $SOCl_2$ temperature was kept below 40°C. The electrolyte was purified by adding small, fresh Li chips until the chips appeared not to blacken. The electrolyte was then filtered through fluted filter paper into a storage bottle, where a few more small Li chips were added.

3.3 Cell Performamce Data

The ECO laboratory cell (Figure 1) was used. This is a two-piece glass cell with a Viton O-ring seal. The top piece has three septum-sealed ports through which pass the current collector tabs. The bottom piece (i.d. 4 cm) holds the electrode stack and electrolyte (5 ml). The electrode stack is held under compression by a glass weight (50 g). Preliminary tests were done with an anode/cathode/reference electrode stack. Initial performance under cathode-limiting conditions (anode and catholyte in excess) is done over the load range of 1 to 50 mA/cm^2 (load based on one-side cathode SA). Discharge capacity at a 20 mA/cm^2 load was measured (to a cut-off voltage of 2.0 V cathode vs reference). Stacked-electrode cell tests were carried out with a 3 anode/2 cathode electrode stack. Initial performance data under cathode-limiting conditions were obtained over the load range of 1 to 50 mA/cm^2 (load based on both-side cathode SA). Discharge capacity at a 20 mA/cm^2 load was measured to a cut-off voltage of 2.0 V cathode vs anode.

Variations in cathode thickness (10 to 35 mil) were obtained by either varying the carbon load or the pressure used in cathode preparation. Variations in electrolyte gap were obtained by varying the number of separators used.

solvent depositing the CoTAA from a 1.5 mg/ml solution in DMF; the DMF was removed by heating at 80°C under vacuum (20 mm Hg) until a constant carbon weight was obtained. Other than this carbon catalysis, no other carbon pre-treatment was carried out.

The electrolyte was prepared from $SOCl_2$ (Kodak), $AlCl_3$ (Mallincrodt) and LiCl (Fluka) using the materials as received.

The anode and reference electrodes were prepared from lithium foil (0.5 mm; Foote Mineral).

3.2 Test Cell Components

Cathodes (4.5 cm^2 single side SA) were prepared from TAA-catalyzed or uncatalyzed carbon. A weighed aliquot of carbon was mixed with an aqueous dispersion of PTFE (10 w/o) and then applied as a slurry to an expanded nickel screen (Exmet 5 Ni 7) with spot-welded nickel wire current collector. The cathode was then pressed (500 to 5000 psi); excess water was removed by drying overnight at 100°C. The cathode was then heated for 5 minutes at 320°C under Ar to sinter the PTFE. Final cathode thickness was then measured with a precision micrometer.

Anodes (3 cm^2) were prepared from Li foil pressed into a nickel screen (Exmet 5 Ni 7) with spot-welded nickel wire current collector. Reference electrodes, when used, were prepared by pressing Li foil into both sides of a .5 cm^2 nickel screen (Exmet 5 Ni 7) with spot-welded nickel wire current collector.

The separator used was a glass microfiber (Whatman GF/A) with a thickness of 0.25 mm (80% void volume); electrolyte gap was varied by changing the number (1 to 3) of separators between the anode and cathode.

The electrolyte used was 0.5 to 3.5 M $LiAlCl_4$ in $SOCl_2$. The electrolyte was prepared by dissolving the required

2.4 Performance Requirements

As provided in the SBIR Solicitation DOD 84.1, the program goal is the development of a cell which meets the power density requirement of 400 W/kg (fully packaged) and has one or more other unique properties (e.g.: minimum weight).

In developing a cell design to meet these goals, ECO has followed the disk-type electrode design of GTE (4) on the basis that this design type has cost advantages in manufacture. Such disk electrodes can be prepared as thin wafers and stacked with lithium anodes to provide a high surface area design. The required dimensions of packaged stacks in such cells can be defined assuming an average volume density of packaged Li/$SOCl_2$ cells of approximately 2 g/ cc. [e.g.: GTE D-size Continuum^{TM} cells with 0.34 W-hr/g and 0.68 W-hr/cm^3 or high-rate reserve cells reported by GTE at 0.72 W-hr/cm^3 and 0.33 W-hr/g]. On this basis, if only a 3 V discharge voltage is available at 65 mA/cm^2, then 4 electrode pairs must each be less than 0.25 cm (100 mils) thick to meet the design goal of 400 W/kg. One objective of the Phase I program was to demonstrate that electrode pairs (including electrolyte gap) can be made less than 0.25 cm thick, and to determine that the performance and capacity of such pairs meet the program goal of providing a high power/energy density power source.

3.0 METHODS

3.1 Materials

Under Phase I, four different carbons were examined (with and without TAA catalysis) as cathode material. The four carbons were: CSX 213 (Cabot), Vulcan XC-72 (Cabot), Black Pearls 2000 (Cabot) and SAB (50%; Gulf). The TAA-catalyzed carbons were prepared either by physically mixing the carbon with the desired weight of cobalt dibenzotetraaza-[14]-annulene (CoTAA) or by

$Li/SOCl_2$ batteries:

$$4\ Li + 2\ SOCl_2 \longrightarrow 4\ LiCl + SO_2 + S$$

with the cathode reaction involving formation of SO, an unstable bi-radical, which dimerizes and then decomposes to form S and SO_2:

$$SOCl_2 + 2e^- \longrightarrow SO + 2\ Cl^-$$
$$2\ SO \longrightarrow (SO)_2$$
$$(SO)_2 \longrightarrow S + SO_2$$

Dey further suggested that the SO dimerization reaction is likely to be the rate limiting reaction: pressure buildup [SO_2] from $(SO)_2$ decomposition is observed to be slow at first and to increase toward end of discharge as would be expected from this proposed reaction sequence (e.g.: second order reaction).

Other reaction intermediates have been proposed including S_2O (17), OClS (18) and SCl_2 (19). Inorganic cathode catalysts such as Pt, Cu or $CuCl_2$ have not been reported as specifically altering the production of one of these species as part of the $SOCl_2$ reduction mechanism. However, organometallic cathode catalysts have been reported to change the mechanism (5,10). In particular, Doddapaneni suggested that the metal center of metallated phthalocyanine interacts with the SO radical and prevents it from dimerization. In $SOCl_2$ reduction on TAAs, the mechanism includes initial abstraction of the oxygen followed by reduction of SCl_2. This change in mechanism was observed to result in an improvement in safety for AA-size cells overdischarged at high rate (9). One advantage of the use of the organometallic catalyst is thus to improve cell safety; an objective of the Phase I program was to demonstrate that this increase in safety was not accomplished through loss in cathode performance in high-rate disk electrodes.

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