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HIGH ENERGY SULFURYL CHLORIDE BATTERIES

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INTRODUCTION

There is no practical alternative to the use of primary batteries to power man-portable electronic equipment for communications, surveillance, target acquisition, and Night Vision applications. For an increasing percentage of such newly-developed equipments, power and energy density requirements are so high that only the most energetic electrochemical couples can be considered for the purpose. Cells utilizing sulfuryl chloride as the cathode reactant are the latest and most energetic of the "liquid cathode cells" resulting from research initiated at the Electronics Technology and Devices Laboratory in the early 1970s.

Table I lists "full-cell" reactions and other electrochemical information for 5 different primary cell systems.

TABLE I - ELECTROCHEMICAL CELL REACTIONS

SYSTEM	CELL REACTION	Theoretical Potential E°(V)	Experimental OCV(V)	Theoretical Energy Density Wh/lb
Mg/MnO_2	$Mg + 2MnO_2 + H_2O \rightarrow Mn_2O_3 + Mg(OH)_2$	2.83	2.0	324
Li/SO_2	$2Li + 2SO_2 \rightarrow Li_2S_2O_4$	----	2.95	611*
$Li/SOCl_2$	$4Li + 2SOCl_2 \rightarrow 4LiCl + S + SO_2$	----	3.65	668*
Li/SO_2Cl_2	$2Li + SO_2Cl_2 \rightarrow 2LiCl + SO_2$	3.909	3.91	639
Ca/SO_2Cl_2	$Ca + SO_2Cl_2 \rightarrow CaCl_2 + SO_2$	3.818	3.30	584

*Based on open-circuit voltage.

The first system is the Army's present aqueous magnesium cell which follows conventional electrochemical practice in that the anode and cathode reactants are both solids and mechanically separated to interact only through an external electrical conductor. The other table entries are for "liquid cathode" cells which successfully violate the rule of separation of reactants. Although the anode and the cathode reactants are in direct contact (as the latter are liquids), their direct chemical reaction is kinetically hindered by a thin and protective layer of salt on the anode.

The relatively low theoretical energy density of the aqueous magnesium cell translates into a practical energy density of approximately 45 Wh/lb at moderate rates of discharge. In the nonaqueous systems it is possible to utilize much more reactive anodes and cathodes than in the aqueous magnesium system; therefore, higher electrode potentials, experimental voltages, and energy densities are feasible. For instance, the Li/SO_2 cell field-tested by our Laboratory actually provides an energy density of 100 Wh/lb at moderate rates of discharge. The $Li/SOCl_2$ cell is our first "oxychloride" system; it is already undergoing 6.3 stage development for target acquisition applications. It can deliver approximately 150 Wh/lb at moderate discharge rates. The Li/SO_2Cl_2 cell system, which will be discussed more extensively in this paper, has a theoretical energy density slightly lower than that of the $Li/SOCl_2$ cell. However, the higher terminal voltage and larger practical cathode capacities, which we have been able to obtain, allow us to project densities greater than 200 Wh/lb for a practical cell.

Several years ago, it was taken for granted that energy densities greater than 100 Wh/lb could be obtained only with cells utilizing lithium anodes. The last entry on Table I reveals that a Ca/SO_2Cl_2 cell system has the potentiality for performance in the same range as that of the lithium cells. Encouraging preliminary results on that system will also be reported here.

EXPERIMENTAL PROCEDURES

Preparation of Cells: Preparation of the electrolyte, electrodes, and assembly of the cell is discussed elsewhere (1). All steps and procedures involving the exposure of either the clean anodes or of the electrolyte were performed either in a glove box (argon atmosphere) or in a dry room. The preliminary "screening" of several different carbon black powders was performed on "uncompressed" electrodes made by a "standard" (1,2) technique, while the optimized United carbon electrodes were made using a cold-compression step in the fabrication process (1).

The cells were assembled using one 2 cm X 2.5 cm cathode sandwiched between two anodes of the same size with fiberglass filter papers providing mechanical saturation between the electrodes. A small lithium electrode was incorporated into the cell to serve as a reference electrode. All current densities are based on the total current divided by 5 cm^2. The cells were horizontally oriented on the bottom of an open teflon container with 5 cm^3 of electrolyte. The teflon container was, in turn, placed in a gas-tight glass outer container with electric feed-throughs.

Electrochemical Measurements: Discharge and polarization curves were measured at 22° ±2°C using a constant current power supply. The polarization curves were measured by applying pre-determined constant currents starting from 0.04 mA/cm^2 and allowing 3 minutes before recording each closed circuit potential. All potentials were measured against the lithium "reference" electrode.

Cathode Porosity Determinations: The percent porosity is defined as the percent of wet cathode volume available for absorption of SO_2Cl_2. The volume of SO_2Cl_2 was determined by weighing a cathode before and after immersion in SO_2Cl_2 and "blotting" on a glass surface. The wet volume of the cathode was determined by measuring its linear dimensions with calipers.

Determination of "True" Surface Areas: The surface area of carbon black powders and of complete electrodes was measured by the Brunauer, Emmett, Teller (BET) method using an Orr Model 2100 Surface Analyzer.

Electrolyte Conductivities: Conductivities were measured using an AC bridge and a thermostatted glass-stoppered cell with a cell constant of 0.200 cm^{-1}.

RESULTS AND DISCUSSION

Sulfuryl Chloride Electrolyte Solution: Of the salts with known solubility in SO_2Cl_2, $LiAlCl_4$ has long-term chemical stability in solution, has a solubility upwards of 2 moles/liter and does not undergo noticeable direct chemical reaction with lithium. Conductivities of a 1.5 molar solution of $LiAlCl_4$ in SO_2Cl_2 are plotted for a wide temperature range in Figure 1.

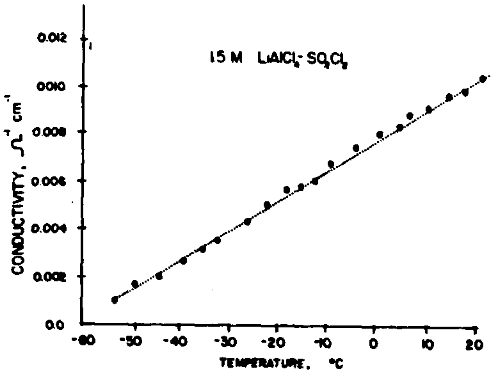

Figure 1. Conductivities of 1.5 M $LiAlCl_4$ - SO_2Cl_2.

No precipitation of the solute was noted down to -54°C (the freezing period of pure SO_2Cl_2 is -54.1°C). At room temperature, the specific conductivity of approximately 0.01Ω^{-1} cm^{-1} is of the same order as that encountered for the electrolyte used with other high energy battery systems. When using such electrolytes, internal voltage drops in cells are kept small by restricting separator and cathode thickness to less than a millimeter. The low conductivities encountered at -20°C or lower do affect performance significantly and improved electrolytes are being sought in our continuing in-house program.

Lithium Anode in Sulfuryl Chloride Cells: A lithium electrode with a freshly prepared (by mechanical abrasion) surface shows little voltage polarization for anodic current densities up to 40 mA/cm. On current reversal, dissolved Li^+ is reduced to metallic lithium and deposited on the surface of the lithium electrode in a highly dendritic form. Although precise thermodynamic measurements have not been performed, one may conclude that a fresh lithium electrode is close to reversible in a solution of $LiAlCl_4$ in SO_2Cl_2. The stability of the lithium electrode in SO_2Cl_2 is due to the formation of a self-limiting thin coating of LiCl, formed spontaneously according to the reaction in Table I. On long-term storage, that film apparently thickens and would introduce a "voltage delay" problem in a battery cell. This potential storage problem is presently under investigation by a contractor (3).

Teflon-Bonded Cathode in the Li/SO_2Cl_2 Cell: Electrodes for lithium thionyl chloride cells are normally formulated with Shawinigan carbon black and Teflon emulsion (normally 5-10% TFE in the dry electrode). Prior results for sulfuryl chloride cells, using similar electrodes, produced rather discouraging results (4). In the present work, we experimented with several different types of carbon black powders and with the process of electrode fabrication. Table II lists the carbons studied along with properties of the original powders and of completed electrodes fabricated using 16% TFE and a standard fabrication technique.

TABLE II. Teflon-Bonded Carbon Cathodes (16% TFE)

Type of Carbon	Derivation	Carbon loading* (g/cm^2)	Per gram of carbon powder	Per cm^2 of electrode geometric area*	% electrode porosity
Shawinigan—50% compressed	Decomposition of acetylene	0.0194	66	1.28	87
Darco-G60	Steam-activation of charcoal	0.0048	301	14.4	64
United XC-6310-4	Decomposition of oil	0.0145	1000	14.6	81
Columbia HR 1670	Decomposition of oil	0.0104	1200	12.5	75

* Based on (length x width) area of electrode, one side.

The resulting electrodes have "true" (BET) areas spanning more than an order of magnitude and electrode porosities ranging from 64 to 87%. Figure 2 presents polarization curves for such electrodes, with current densities based on the "superficial" area of the electrodes. From the figure, it is clear that very significant differences exist between the electrodes, with "United" carbon black affording the best initial voltage over most of the current range. The results are replotted in Figure 3 after basing the current density on the "true" (BET) rather than on the "superficial" surface areas. On that basis, it may be concluded that almost identical results are obtained for all of the carbons in the lower range of current densities where mass transport effects may be expected not to play a dominant role. This is consistent with the surface-chemical mechanistic sequence to be discussed below.

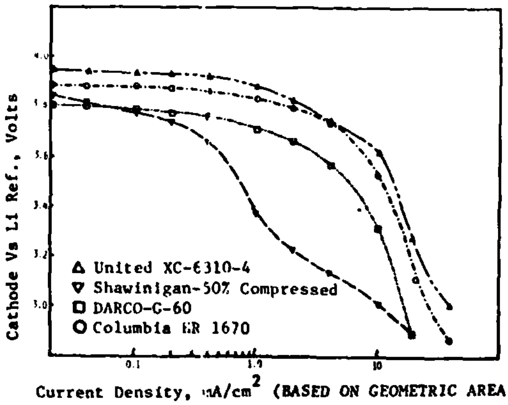

Figure 2. Polarization curves for Teflon-bonded carbon cathodes in lithium-sulfuryl chloride cells. Current densities based on "superficial" cathode areas.

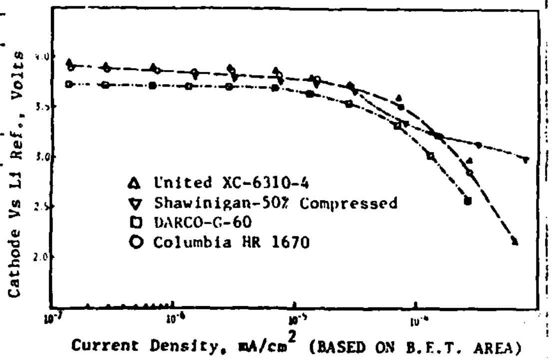

Figure 3. Polarization curves for Teflon-bonded carbon cathodes in lithium-sulfuryl chloride cells. Current densities based on "true" (BET) surface areas.

Figure 4 shows that the capacity of the test cathodes depends directly on the gross electrode porosity as measured by solvent absorption. The porosities are determined, to some extent, by the inherent microscopic "structure" of the carbon powders. Shawinigan black, for example, is noted for its highly developed acetylenic structure, carried over from the molecule from which it is originally derived.

From Figures 1-4 one can conclude that the "best" cathode would combine both high BET area and high porosity. Attempts were made to accomplish these conditions, simultaneously, by formulating cathodes with mixtures of Shawinigan black and the higher area carbons with unsatisfactory results. Success was achieved by varying the fabrication process in order to increase the porosity of United carbon electrodes. Figure 5 presents representative discharge curves for different formulations. The use of United Carbon and a "cold-compression" process (Trace 5, Figure 5) was adopted as standard for the balance of this work. The electrode was further optimized with respect to teflon content (at 11% TFE). A typical electrode had a porosity of 87% and a carbon loading of 0.024 gm/cm^2.

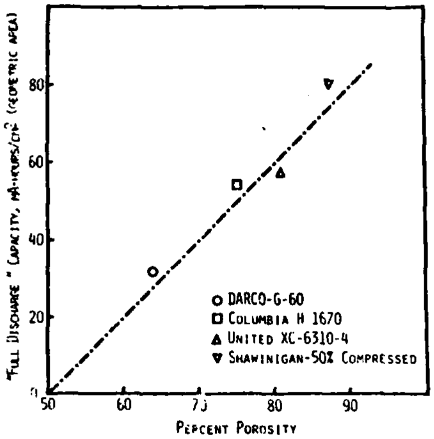

Figure 4. Capacity-porosity relationship for Teflon-bonded carbon cathodes (standard, "uncompressed" fabrication).

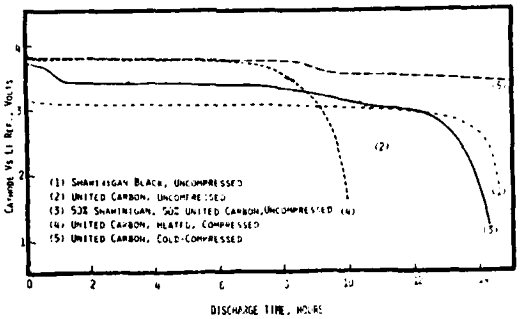

Figure 5. Discharge curves at current drains of 5 mA/cm^2 for differently-formulated cathodes in lithium-sulfuryl chloride cells.

Figures 6 and 7 compare performance of the cathodes of our Li/SO_2Cl_2 cell with that of the older Li/$SOCl_2$ system, which was previously the most energetic ambient temperature primary cell system known. Because anode polarizations are small, the voltages are essentially those of a complete practical cell. Although the performance illustrated in Figure 6 and 7 is excellent, there is still the possibility for significant improvements at high currents and low temperatures and that is one thrust of our continuing battery research program.

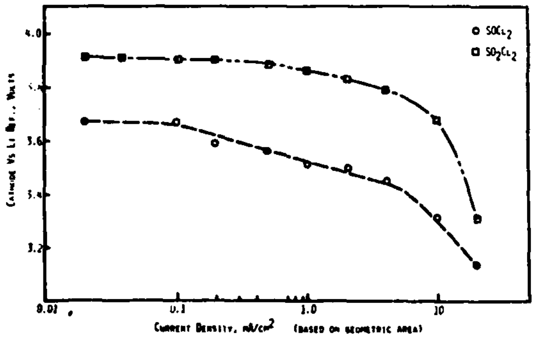

Figure 6. Comparison of cathodic polarization curves for lithium-sulfuryl chloride and lithium-thionyl chloride cells.

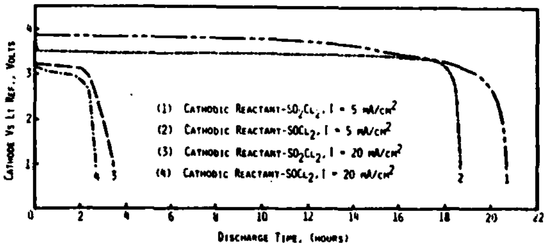

Figure 7. Comparison of cathodic discharge curves for lithium-sulfuryl chloride and lithium-thionyl chloride cells.

Electrode Discharge Products in the Li/$SOCl_2$ Cell: The overall discharge reaction listed for the Li/SO_2Cl_2 cell in Table I was deduced through x-ray diffraction, gravimetric chloride determinations and volumetric determinations of SO_2 gas release. First, it was determined that LiCl is, practically speaking, insoluble in the electrolyte solution employed here. Hence, discharged cathodes could be exhaustively washed with pure SO_2Cl_2 to eliminate entrained $LiAlCl_4$, without solubilizing LiCl formed as a product in the cathode. Diffraction patterns for cathodes which were carefully washed, dried and crushed revealed only cubic LiCl. Two cells made with United carbon cathodes were discharged at a current density of 5 mA/cm^2 to a cutoff voltage of 2 Volts. The cathodes were washed with SO_2Cl_2, dried and quantitatively extracted with water. Aliquots of the aqueous solutions were potentiometrically titrated for Cl^- using a standardized $AgNO_3$ solution. A small correction for occluded $AlCl_4^-$ was made by determining Al^{+3} colorimetrically and subtracting four times that number of equivalents. The corrected equivalents of Cl^- were found equivalent to the coulombs of electricity passed, to within a 2% tolerance. This establishes that LiCl is the only ionic product of cell discharge and also that the LiCl is quantitatively precipitated in the pores of the cathode.

To evaluate non-ionic discharge products, it was first determined quantitatively that gaseous SO_2 is released during cell discharge. A cell was then assembled with electrolyte which was pre-saturated with SO_2. The cell was attached to a gas buret (using fluorocarbon oil as the displacement liquid), and discharged at 5 mA/cm^2 while monitoring the volume of gas released. In duplicate experiments, it was established that one mole of gas was produced for every two equivalents of electricity passed.

The overall reaction listed in Table I is the simplest one consistent with the analytical results reported above. The following individual electrode reactions are consistent with the overall reaction:

anode: $2[Li \rightarrow Li^+ + e^-]$ (1a)

cathode: $2Li^+ + SO_2Cl_2 + 2e^- \rightarrow 2LiCl + SO_2$ (1b)

overall: $2Li + SO_2Cl_2 \rightarrow 2LiCl + SO_2$ (2)

$$E° = 3.909 \text{ V } (30°C)$$

As already discussed above, the capacity of the cathode is proportional to its porosity. As is apparent from these findings, the porosity is required in order to accommodate the LiCl precipitate while allowing continued good transport of the cathode reactant and of conducting ions.

The analytical results reported above contradict earlier reports (5) that Li_2SO_4 and molecular sulfur are major products of cell discharge. It is felt that the earlier results may have resulted from a failure to avoid water contamination early in the analytical procedure. The present results are particularly significant for their relevance to battery safety, inasmuch as molten sulfur can react vigorously with lithium under conditions of cell malfunction. This is potentially a very significant advantage of the Li/SO_2Cl_2 over the older $Li/SOCl_2$ system (see Table I).

Cathode Mechanism in the Li/SO_2Cl_2 Cell: Sulfuryl chloride is known (6) to dissociate into SO_2Cl_2 according to the following reaction:

$$SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2 \qquad (3)$$

Both gases are appreciably soluble in our electrolyte (1.09 and 0.62 molal for SO_2 and Cl_2, respectively, at 24°C as determined in this laboratory). Furthermore, as determined by W. Behl (7), of this laboratory, molecular Cl_2 is more reactive than undissociated SO_2Cl_2. Figure 8 shows that saturation of the electrolyte with either SO_2 or Cl_2 produces a noticeable shift in the cathode polarization curve. The particularly marked effect of SO_2 implies that the latter is acting by removing Cl_2 as cathode reactant and shifting the equilibrium of reaction (3) to the left. A complete cathode mechanism, consistent with our observations, would involve the production of Cl_2 by reaction (3) followed by the cathodic reduction of Cl_2:

$$Cl_2 + 2e^- + 2Li^+ \longrightarrow 2LiCl \qquad (4)$$

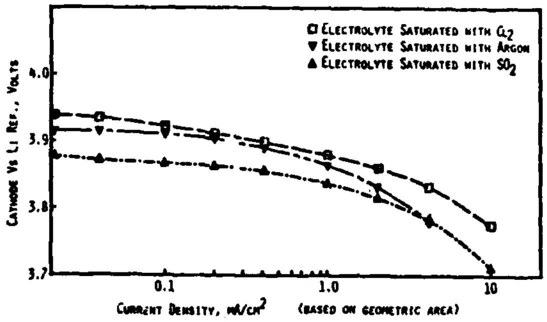

Figure 8. Cathodic polarization curves of lithium-sulfuryl chloride cells containing gas-saturated electrolyte.

Carbon is a known catalyst for reaction (3) and that would explain the importance of high electrode surface area to good electrode performance. Quantitative information on reaction (3), in the condensed phase, is desired for confirmation of the proposed cathode mechanism and as a basis for future cathode improvements. Preliminary studies have been performed using ultraviolet spectrophotometry. Figure 9 shows that "aged" sulfuryl chloride absorbs light with wavelengths less than 460 mμ (the liquid appears yellow). The absorbance is diminished by freshly-saturating with argon, and further diminished by saturating with SO_2 (the latter does not absorb light in this region of the spectrum). The absorbance is intensified by adding Cl_2. Comparison of the results suggests that the "aged" solution has undergone decomposition. Estimates of the rate of decomposition can be made by recording the absorbance (e.g., at 400 mμ) vs time relationship for freshly degassed samples. Preliminary results reveal that, at 30°C, the homogeneous rate for the "neat" solvent is equivalent to less than 0.2 mA/cm² (exact rates depend on solvent purity) and, hence, would not support good cathode performance at high current densities. In the presence of carbon, however, the estimated heterogeneous rate of decomposition is sufficiently large to account for the full range of current densities covered in Figure 8.

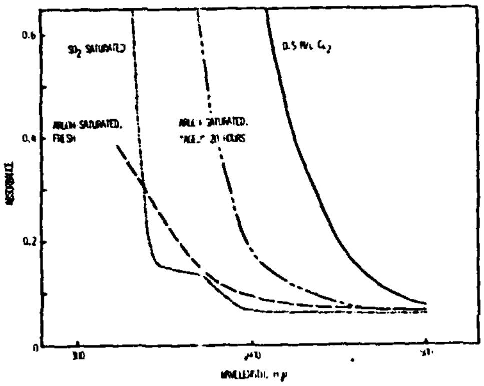

Figure 9. Ultraviolet spectra of sulfuryl chloride samples.

Performance of Electrodes in the Ca/SO$_2$Cl$_2$ Cell: The overall discharge reaction listed for this cell in Table I is based on analogy to the Li/SO$_2$Cl$_2$ cell. For that assumed reaction, the thermodynamic cell potential is only 91 millivolts less than that for the analogous lithium system. From Figure 10, it can be seen that experimental cell voltages are always at least ½ Volt less than the thermodynamic value of 3.818 Volts. Furthermore, most of the low current density polarization occurs at the calcium anode, which might otherwise be expected to assume a potential approximately 90 millivolts positive to the lithium reference electrode. However, it is highly encouraging that the calcium anode shows little tendency to undergo additional polarization at high current densities (i.e., it holds promise for good "high-rate performance). The cell polarization at high current densities is almost entirely attributable to the cathode, similar to the situation for the Li/SO$_2$Cl$_2$ cell.

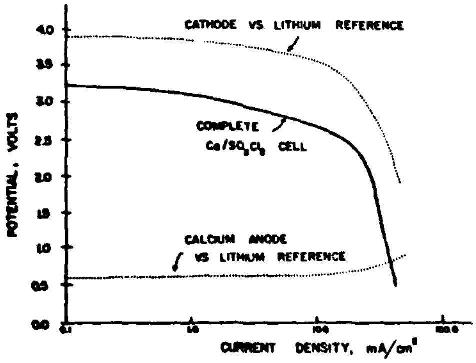

Figure 10. Polarization curves for a calcium-sulfuryl chloride cell.

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Figure 11 compares cell polarizations for our Ca/SO_2Cl_2 cell with those for our Li/SO_2Cl_2 cell and with a commercial Li/SO_2 cell of the type presently being used in Army radio sets. From the figure, it is clear that the new calcium cell, while still inferior to our best lithium technology, has the potentiality for displacing the Army's present lithium-sulfur dioxide cell for at least some applications. This may apply particularly where the greater chemical stability of calcium outweighs the superior electrochemical performance of lithium.

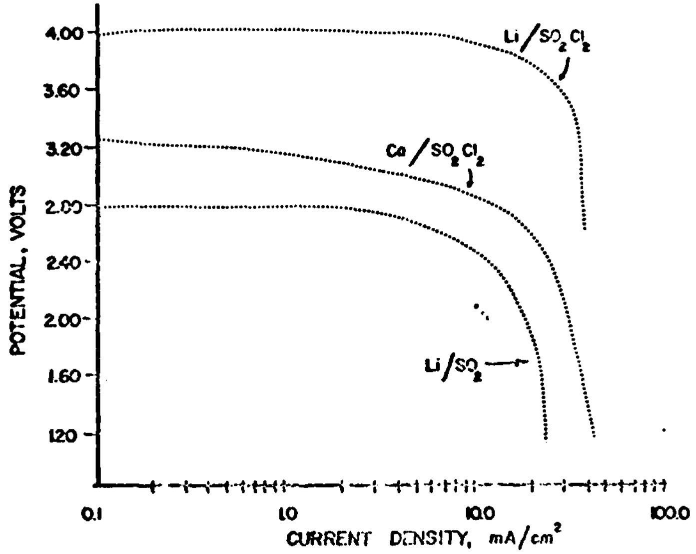

Figure 11. Polarization curves for three different high energy cells.

Although the polarization characteristics of the electrodes in a calcium-sulfuryl chloride cell are highly encouraging, we are presently faced with the serious problem of reduced cathode capacity (i.e., life) in any electrolyte containing dissolved calcium ions. Presently, cathode life is one-half or less of that for the analogous lithium cell. Micrographs of spent cathodes from the two types of cells (Figure 12) provide a clue to the origin of the problem. In the lithium cell, the LiCl which forms in the cathode during discharge, is deposited as multiple discrete clusters of cubic crystals which allow relatively easy passage of ions, reactants and products from the liquid electrolyte phase. By contrast, the solid product phase in the cathode from the calcium cell appears continuous and "glassy" and would be expected to interfere with transport and conduction processes in the electrolyte phase. Studies are currently in progress to evaluate and overcome this problem.

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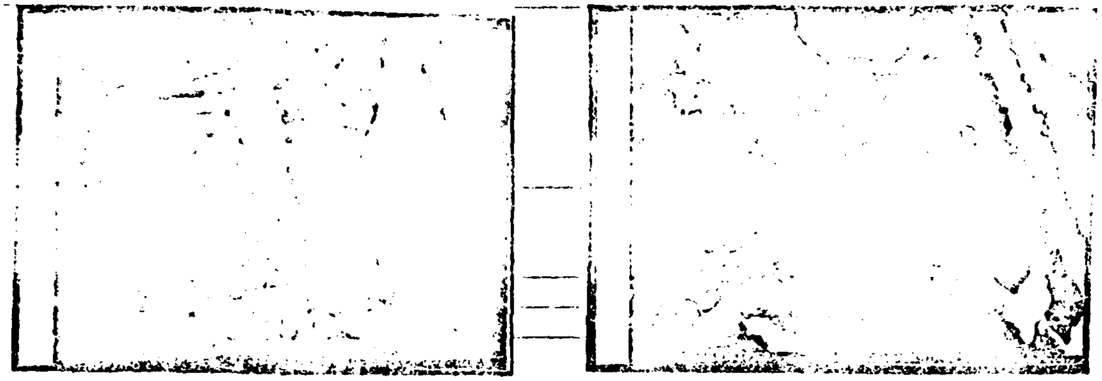

a. Lithium anode

b. Calcium anode

Figure 12. Scanning electron micrographs for fully discharged cathodes in SO_2Cl_2 (3200 X magnification).

Finally it may be noted that on thermodynamic grounds, approximately 500 millivolts of terminal voltage can be "recaptured" if the calcium electrode can be made to operate more reversibly. The present performance, similar to that observed in the lower-potential $Ca/SOCl_2$ system (8,9) can be attributed to "film polarization" in the protective coating (probably $CaCl_2$, according to the reaction in Table I) formed by limited spontaneous reaction of the anode with the solvent. Improved terminal voltage can be expected if it is discovered how to minimize the latter coating while still retaining its protective properties.

REFERENCES

1. S. Gilman and W. Wade, Jr., Electrochem Soc., 127, 1427 (1980).
2. W. K. Behl, J. A. Christopulos, M. Ramirez and S. Gilman, J. Electrochem Soc., 120, 1619 (1973).
3. F. Marakar, "High Rate Lithium-Sulfuryl Chloride Battery Technology," First Quarterly Report, Contract DAAK20-81-C-0420 (ERADCOM), Gould Labs, March 1982.
4. J. J. Auborn and N. Marincic, "Power Sources 5," D. H. Collins, Editor, p. 683, Academic Press, London (1975).
5. J. J. Auborn, R. D. Bezman, K. W. French, A. Heller and S. F. Lieberman in Proceedings of 26th Power Sources Symposium, p. 45 (1974).
6. "Encyclopedia of Chemical Technology," Vol. 14, K. Othmen, Editor, p. 45 (1969).
7. W. K. Behl, J. Electrochem Soc., 127, 1444 (1980).
8. R. L. Higgins, Proceedings of the 29th Power Sources Conference, p. 147 (1980).
9. R. J. Staniewicz, J. Electrochem Soc., 127, 782 (1980).

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