

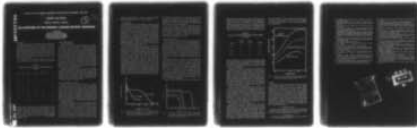
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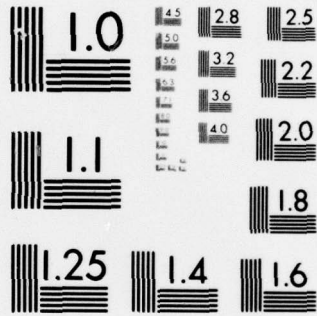
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PRIMARY BATTERIES

Lithium Battery Session

AN OVERVIEW OF THE PRIMARY LITHIUM BATTERY PROGRAM

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Introduction

In a paper presented at the 25th Power Sources Symposium, N. Wilburn¹ noted that a primary lithium cell of long wet stand life and high discharge rate capability had finally emerged after more than a decade of activity in this area of high energy battery technology. That cell utilized sulfur dioxide as the cathode reactant. Promising results with other lithium cell systems had begun to appear even prior to the time of the last symposium, and some of these will be highlighted in this overview.

It is convenient to categorize a lithium cell according to the cathode reactant being used. Table I lists examples of

Solid Cathode Reactants

Heavy Metal Halides

Cathode reactants can be categorized broadly as to whether solid (down to $(CF)_n$ in Table I) or liquid (the remainder of the entries in Table I). The use of a solid insoluble cathode reactant is the most obvious way to effect maximum isolation from the lithium anode. Amongst the solid reactants, the heavy metal halides received earliest attention^{2,3} probably due to their potentiality for electrical recharge. In line with their electrochemical reversibility, cells made with halide cathodes tend to have open circuit voltages falling close to the EMF values (see first three entries of Table I) and these cells are often capable of high rates of discharge. Unfortunately, high solubility⁴ of the halides results in cells of short wet-stand life^{3,5} tending to make them presently attractive mainly for cells in the reserve configuration^{5,6}.

Although a number of attractive alternatives to the halides now exist for primary cells (see below), this class of cathode reactants is worthy of continued attention for secondary cells where the choice is much more limited. The observation by Salomon⁷, that certain covalent inorganic solvents depress the solubility of the silver halides in organic solvents, may serve as a point of departure for future work.

Heavy Metal Sulfides and Oxides

Based on experience with common solvents, it was intuitive for battery scientists to turn to the heavy metal sulfides and oxides which are more insoluble than the halides. As a class, these substances often afford cells of long wet stand life, but tend to provide only marginal high energy output at only very low drain rates. Cells based on Ni_3S_2 ⁸ and CuS ⁵ exhibited flat voltage-time discharge characteristics for discharge rates of the order of hundreds of hours. Sealed D cells made with CuS reportedly⁵ provided only 88 Wh/lb at the 58 hour rate and lost over $\frac{2}{3}$ of that energy when discharged at a fourfold greater rate.

Examples of transition metal oxides proposed as cathode reactants include MnO_2 ,^{9,10,11} V_2O_5 ,¹² and MoO_3 .^{11,12,13,14} The EMF values of Table I were calculated on the assumption that one lower-valent oxide product is formed by reduction in each case. The fact that these values are lower than the experimental open circuit voltages, is evidence of unexplained complexity in the cathodic reduction process. Manganese dioxide reportedly¹² reacts directly with common organic electrolyte solvents. Both V_2O_5 and MoO_3 are more

TABLE I
CATHODE REACTANTS FOR LITHIUM PRIMARY CELLS

CATHODE REACTANT	CALCULATED CELL EMF, VOLTS	EXPERIMENTAL OCV, VOLTS	THEORETICAL ENERGY DENSITY OF REACTANTS, WH/LB	ENERGY DENSITY OF REACTANTS BASED ON EXP. OCV, WH/LB	ASSUMED ELECTRONS PER MOLECULE	LITERATURE REFERENCE
CuF_2	3.55	3.30	749	-	2	(3)
$CuCl_2$	3.07	3.1	503	-	2	(3)
$AgCl$	2.84	2.84	229	-	1	(3)
Ni_3S_2	-	1.8	-	388	4	(8)
CuS	-	2.15	-	436	2	(11)
YbO_2	2.69	3.48	349	-	1	(10)
MoO_3	1.93	3.3	197	-	2	(10), (12)
V_2O_5	2.34	3.5	217	-	4	(10)
$(C_6F_6)_4$	5.23	3.14	918	550	1	(10)
$(CF)_4$	4.66	3.14	1,491	1,000	1	(10)
SO_2	-	2.95	-	503	1	(20)
$POCl_3$	-	3.10	-	700	3	(26)
$SOCl_2$	-	3.65	-	701	2	(26)
$SOCl_2$	-	3.65	-	1,178	2 2/3	(29)
SO_2Cl_2	-	3.90	-	-	-	(30)

several classes of cathode reactants, along with their thermodynamic EMF's, experimental open-circuit voltages in a representative electrolyte (often with propylene carbonate as the solvent), energy densities based on the two different voltages, and a number of electrons transferred per molecule of cathode reactant consumed. The latter is either postulated or experimentally verified.

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stable according to Dampier¹¹ and Dey¹² and provide marginal high energy performance at low rates of discharge.

Carbon Fluorides

Cathode reactants with the insolubility of graphite may be obtained by treating that substance with fluorine.¹⁵ Depending on the experimental conditions, compounds with stoichiometry close to $(C_4F)_n$ or $(CF)_n$ may be obtained. Prior to 1970, K. Brauer in the U.S. began work on $(C_4F)_n$ (tetracarbon monofluoride) cathodes^{16,17} apparently basing his choice on the electronic conductivity of the cathode reactant. Watanabe and co-workers^{18,19} in Japan chose $(CF)_n$ (carbon monofluoride) for experimentation and found it could be utilized, in spite of its non-conductivity, by physically mixing with conducting graphite or carbon. Several U.S. companies with ECOM participation²⁰ have since engaged in the development of sealed cells utilizing $(CF)_n$.

As part of a fluorocarbon cathode program in our laboratory, known and novel fluorocarbon materials have been synthesized,^{21,22} their theoretical energy contents determined calorimetrically,²² and evaluations made of their electrochemical behavior²³. Theoretical energy densities,²¹ EMF,²¹ and typical open circuit voltages¹⁰ of lithium cells made with $(C_4F)_n$ and $(CF)_n$ appear in Table I. It can be seen from the table that both $(C_4F)_n$ and $(CF)_n$ are, theoretically, amongst the most energetic materials yet proposed for use as cathode materials for lithium batteries. The open circuit voltages fall far below the theoretical values, but even the energy densities, calculated on the basis of the open circuit voltages, are impressively high, particularly for $(CF)_n$. Figure 1 shows the discharge curves at a moderate discharge rate for lithium cells made with the two different graphite fluoride cathodes, revealing output voltages falling far below the theoretical values of Table I. However, with its high coulom-

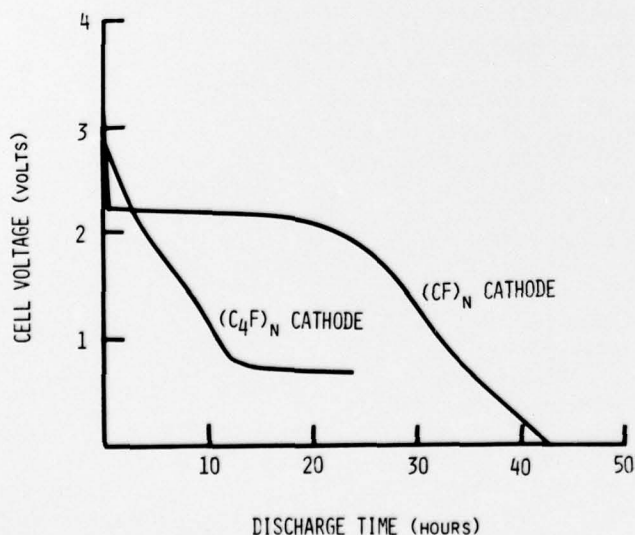


Figure 1. Comparative discharge curves for lithium cells with $(C_4F)_n$ and $(CF)_n$ cathodes and a propylene carbonate-lithium perchlorate electrolyte. Discharge current density of 1 mA/cm^2 . Data from References 16 and 27.

bic efficiency, the performance of the $(CF)_n$ cell is sufficiently good to qualify as the best solid cathode system now available. At moderate rates of discharge, the electrical performance of $(CF)_n$ cells rivals that of SO_2 cells, falling behind only at high rates and low temperatures.

The results in Figure 1 reflect a marked difference in kinetics of cathodic reduction for two rather similar fluorocarbon materials and suggest that other carbon-fluorine compounds of greater reactivity might be identified, or synthesized. Such substances as oxygen-cross linked perfluoroanthracene already have been observed²³ to afford at least transitory higher-voltage performance than $(CF)_n$.

Liquid Cathode Reactants

The invention of the sulfur dioxide depolarized cell prior to 1971²⁴ constituted an ironic twist in the development of lithium battery technology, much of the previous effort having been directed at maximum separation of cell reactants. Although lithium is thermodynamically highly unstable in the solution of SO_2 in the organic electrolyte (a solution of LiBr in propylene carbonate and acetonitrile) which is commonly used, the anode is, in practice, protected against corrosion by the formation of a lithium dithionite film. The passivating film is more or less readily removed during cell discharge.

It develops that SO_2 is not unique as a lithium-passivating liquid cathode reactant. Auburn et al.^{25,26} observed that lithium is stable in a number of phosphorous and sulfur oxyhalides. Cells based on the use of several oxyhalides with Teflon-bonded carbon cathode electrodes were reported by Behl et al.^{27,28} and Auburn et al.²⁹ Unlike the SO_2 cell, the new "inorganic electrolyte" cells do not employ an organic co-solvent. A commonly suitable solute is $LiAlCl_4$. Several of the oxychloride solvents of interest are listed in Tables I and II. In Table I, the values of electrons/molecule and of energy density correspond to previously postulated products of reaction^{28,29} and require verification.

Figure 2 shows the discharge curves of lithium cells

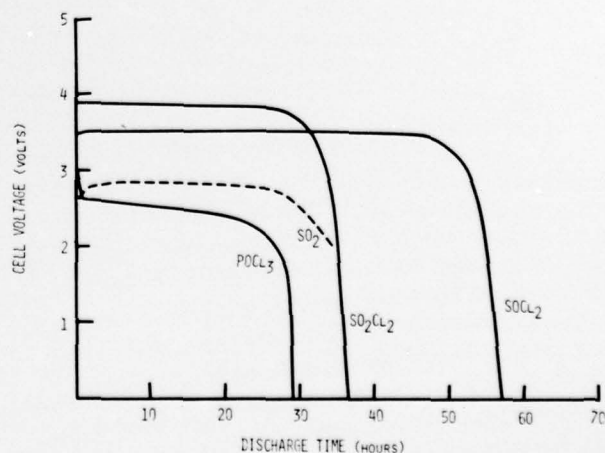


Figure 2. Comparison of discharge curves of lithium cells utilizing several different liquid cathode reactants. $POCl_3$ and $SOCl_2$ data from Reference 28. SO_2Cl_2 and SO_2 data from References 30 and 20, respectively.

fabricated with three different oxychloride electrolyte solvents/cathode reactants and Teflon-bonded carbon cathode electrodes.^{28,30} A curve for a commercial SO₂ cell is included for comparison. From the point of view of voltage output, the cell made with POCl₃ is the poorest of the group and that made with SO₂Cl₂ is the best. However, since SO₂Cl₂ has a relatively low boiling point (see Table II), SOCl₂ represents

TABLE II
PHYSICAL PROPERTIES OF SOME OXYCHLORIDE SOLVENTS

SOLVENT	FREEZING POINT (°F)	BOILING POINT (°F)	DENSITY (G/CM ³)
POCl ₃	34	226	1.675
SOCl ₂	-156	169	1.655
SO ₂ Cl ₂	-65	158	1.667

the best combination of a good liquidus temperature range with good electrochemical performance and has been selected for immediate further development on that basis. Future improved "inorganic electrolyte" cells may be based on other pure or mixed oxyhalides.

Unlike the situation for solid cathode reactants, the coulombic capacities of the cells of Figure 2 reflect the relative ability of the carbon cathode electrodes to accommodate products of reaction before passivation, rather than the coulombic capacities of the cathode reactants. The capacities are, therefore, dependent on physical electrode structural characteristics which are process-variable and not yet fully evaluated. The cathode passivating agent is known to be Li₂S₂O₄ for the SO₂ cell.³¹ From studies on carbon rods in our laboratory, LiCl has been identified as the cathode passivating agent in the SOCl₂ cell at room temperature.

Figure 3 compares energy densities of SO₂ and SOCl₂ cells at the nominal thirty-hour rate of discharge. The results for the SO₂ cell were obtained from commercial D cells in a spiral configuration. Similar good performance can be obtained at much higher rates of discharge and during periodic pulse applications. Since the SO₂ system is presently the most advanced, it has been selected by the Army for field evaluation and test for high energy battery applications. Several thousand 10-cell (D-size) batteries are presently in the process of procurement for that purpose.

The projected curve for a sealed SOCl₂ C cell (spiral configuration) was obtained by de-rating the results for prototype cells by 25%. The room temperature results for sealed cells have already been realized in our laboratory. On the basis of the projection, the SOCl₂ cell promises a 50% improvement over the SO₂ cell. The present most significant problem in the further development of the SOCl₂ cell is the occurrence of a "voltage-delay" after high temperature storage. This appears to result from further thickening of the film

normally protecting the lithium anode from direct attack by the solvent. Internal efforts at ECOM and contractual efforts at GTE Laboratories, Mallory, and EIC are presently focussing upon that problem.

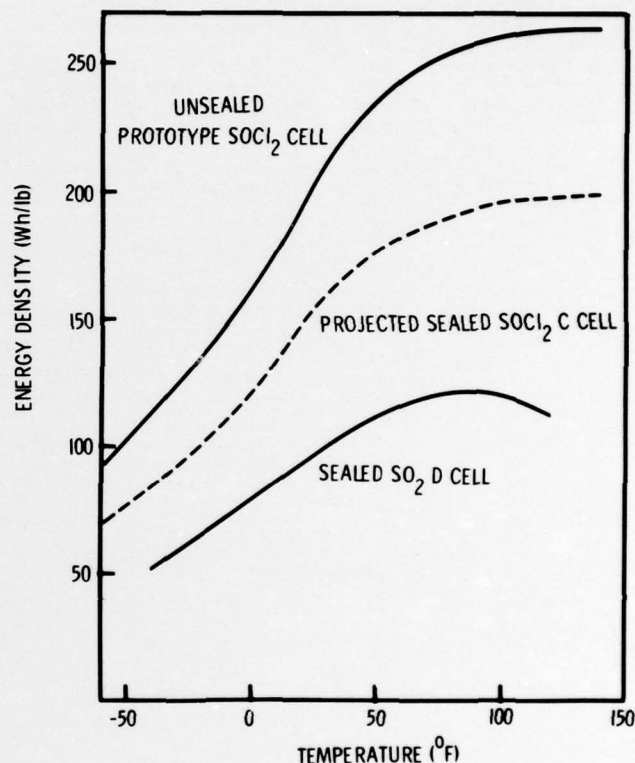


Figure 3. Comparison of energy densities of lithium-organic and inorganic electrolyte cells. SOCl₂ data from Reference 28. SO₂ and (CF)_n data from Reference 20.

Summary

Advances have been made recently in the area of both solid and liquid cathode reactants for non-reserve lithium primary cells. Amongst the solid cathode reactants, carbon monofluoride has already served as the basis for a successful sealed low-rate cell. Improvements appear quite possible through the utilization of modified (CF)_n formulations and of other carbon-fluorine compounds. Amongst the liquid cathode reactants, sulfur dioxide has served as the basis for the most successful lithium cell yet fully developed. Providing engineering and stability problems are solved, thionyl chloride and other oxyhalides of phosphorous and sulfur may provide the basis for cells of much better performance than that of the Li-SO₂ system.

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