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ECOM-2844

STATUS REPORT ON ORGANIC ELECTROLYTE
HIGH-ENERGY DENSITY BATTERIES

by

Klaus H.M. Braeuer
Jay A. Harvey

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TECHNICAL REPORT ECOM-2844

STATUS REPORT ON ORGANIC ELECTROLYTE

HIGH-ENERGY DENSITY BATTERIES

by

Klaus H. M. Braeuer

Jay A. Harvey

Power Sources Division

Electronic Components Laboratory

May 1967

DA TASK 1CO 14501 A 34A-00-01

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US ARMY ELECTRONICS COMMAND

FORT MONMOUTH, N. J.

Abstract

[The state of the art of high-energy density, organic electrolyte batteries has been summarized and reviewed] to present the data which has been published in a more convenient, condensed form, and to pinpoint the problem areas on which future work should be concentrated. [The report encompasses work which was published during the period 1962 to October 1966, and which was sponsored either by the US Government or by industrial companies and made available to the public. The material in this report is organized as follows: (1) selection of anode-cathode couples, (2) selection of battery components including electrolytes, half-cell systems, and separators, (3) design and performance of experimental cells, and (4) problem areas and areas of future work.]

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STATUS REPORT ON ORGANIC ELECTROLYTE HIGH-ENERGY DENSITY BATTERIES

INTRODUCTION

In recent years the United States Government has expended considerable effort to develop power sources which would provide energy densities greater than those presently available. The needs of the military and of the field of space exploration, with their increasing demands for electrical power sources for applications where weight and volume are costly commodities, have provided the impetus for this development.

This status report has been written for the US Army Electronics Command in an attempt to collect, summarize, and review the state of the art of high-energy density, organic electrolyte batteries. Its primary objectives are to present the data, which has been published in a large number of reports, in a more convenient, condensed form, and to pinpoint the problem areas on which future work should be concentrated.

In order to cover the subject with sufficient depth, the scope of this report has been limited to organic electrolyte batteries only. This was necessary because of the large body of data which has accumulated during the period beginning with early 1962 and ending with October 1966 during which time the Government has spent more than \$3,000,000 on organic electrolyte batteries. This limitation of scope is practical for several other reasons:

1. Most of the research has been directed toward the study of topics which are peculiar to these systems. Therefore, this research can not be discussed in context with similar efforts in other areas. For example, studies of the compatibilities of organic electrolytes with reactive electrode materials such as lithium and cupric fluoride have no counterpart in other areas of current battery development.
2. Much of the current work has been concerned with collecting basic data similar to that which has been available for aqueous electrolytes for decades: For example, conductivity measurements and studies of ionic equilibria. Therefore, this work is not comparable with the work in other areas of contemporary battery research.
3. No practical organic electrolyte battery has yet been developed, so that it would be premature to compare their performance with that of other power sources such as silver-zinc cells, ammonia batteries, metal-air batteries, or fuel cells, all of which have been further developed and actually used as power sources for special applications.

The data presented in the Tables and in the text of this report is included only for the purpose of the discussions and does not represent a complete compilation of the data available. However, references are indicated in the text to serve as a guide for the reader who desires more detailed information on any particular topic. The list of references at the end of this report has been made as complete as possible.

THE SELECTION OF ANODE-CATHODE COUPLES

The thermodynamic properties of electrode couples have served as the basic criterion for the selection of electrode systems for possible use in high-energy density batteries. Of primary importance in the consideration of a given electrode couple are the free energy change, ΔF° , for the postulated electrode reaction, and the equivalent weight of the electrode material. The free energy change can be defined by the equation,

$$\Delta F^\circ = \Delta F_p^\circ - \Delta F_r^\circ$$

where ΔF_p° and ΔF_r° are the standard free energies of formation for the products and reactants of the electrode reaction. These free energies are available in tables of thermodynamic data.

The standard electrode potential, E° , for a given couple can be calculated from the equation,

$$E^\circ = \frac{-\Delta F^\circ \text{ Kcal}}{(23 \text{ Kcal volt}^{-1} \text{ Faraday}^{-1})(n \text{ Faraday})}$$

where n is the number of electrons involved in the electrode reaction.

The theoretical capacity (amp-hr) of an electrode is given by the equation,

$$\text{Capacity} = \frac{(\text{wt. electrode})(n \text{ Faraday})(26.8 \text{ amp-hr Faraday}^{-1})}{(\text{mole wt. electrode material})}$$

and the theoretical energy density (whr/lb) of an electrode couple by

$$\text{Energy density} = \frac{(-\Delta F^\circ \text{ Kcal})(453.6 \text{ gr/lb})}{(\text{mole wt. reactants gr})(0.86 \text{ Kcal/whr})}$$

The above equations hold only for complete, reversible, electrochemical reactions, and represent the maximum values which would be obtained under ideal conditions. In practical electrochemical cells, where the conditions are not ideal, these values can never be realized; however, the calculated values do provide a convenient means of selecting potentially useful electrode couples. A collection of calculated parameters for electrode couples which have been proposed for high-energy density batteries is presented in Table I.

Lithium, magnesium, and calcium have been proposed as anode materials, while metal halides, metal oxides, oxygen and several organic compounds have been suggested as cathode materials. Most of these substances could, theoretically, provide cell voltages on the order of 3.0 volts and energy densities in excess of 500 whr/lb. When compared with the figures for the silver-zinc battery, one of the highest energy density aqueous systems,

TABLE I
HIGH-ENERGY DENSITY ELECTRODE COUPLES

Reaction	Equiv. Weight (g/ equiv)	Capacity ($\frac{\text{Amp-Hr}}{\text{gr}}$)	$-\Delta F^\circ$ of Reaction (Kcal/ mole)	E° (volts)	Energy Density (Whr/lb)
$2\text{Li} + \text{CuF}_2 \longrightarrow 2\text{LiF} + \text{Cu}$	57.6	0.465	163.2	3.55	749
$2\text{Li} + \text{CuCl}_2 \longrightarrow 2\text{LiCl} + \text{Cu}$	74.2	0.362	141.4	3.07	503
$2\text{Li} + \text{NiF}_2 \longrightarrow 2\text{LiF} + \text{Ni}$	55.5	0.483	130.4	2.83	620
$2\text{Li} + \text{NiCl}_2 \longrightarrow 2\text{LiCl} + \text{Ni}$	71.5	0.375	118.3	2.57	437
$2\text{Li} + \text{AgF}_2 \longrightarrow 2\text{LiF} + \text{Ag}$	79.9	0.336	238	5.16	786
$\text{Li} + \text{AgF} \longrightarrow \text{LiF} + \text{Ag}$	133.8	0.200	95.3	4.14	375
$\text{Li} + \text{AgCl} \longrightarrow \text{LiCl} + \text{Ag}$	150	0.178	65.5	2.84	229
$2\text{Li} + \frac{1}{2}\text{O}_2 \longrightarrow \text{Li}_2\text{O}$	15.0	1.78	133.9	2.91	2365
$\text{Ca} + \text{CuF}_2 \longrightarrow \text{CaF}_2 + \text{Cu}$	70.7	0.38	161.7	3.51	604
$\text{Mg} + \text{CuF}_2 \longrightarrow \text{MgF}_2 + \text{Cu}$	62.7	0.427	134.8	2.92	566

which has a theoretical voltage of 1.96 volts and maximum energy density of only 254 whr/lb, the reason for the interest in these reactive electrode couples becomes obvious.

Whether an electrode couple which has the requisite thermodynamic properties will be useful in a practical high-energy density battery depends on several non-thermodynamic considerations:

1. Can this couple be incorporated into a battery system which is capable of delivering electrical energy without suffering appreciable losses due to polarization, incomplete reaction, or parasitic side reactions? The research which has been done on this subject is extensive, and will be reviewed in the next chapter.

2. Can this couple be incorporated into a complete battery package without requiring extra weights for "dead weight" components such as electrolyte, casing, leads, or separator? If extra dead weight is required for the battery design it may negate the gains in energy density made by the use of high-energy density couples.

A figure of merit expression which provides a method of analyzing battery performance in terms of the three factors which determine its energy

density, namely, the thermodynamic properties of the electrode couple, the electrochemical behavior, and the design requirements, has recently been developed.¹ This system of analysis will be described in the chapter on Cell Studies of this report and will be used, in so far as the data allow, to compare the battery systems which have so far been tested.

SELECTION OF BATTERY COMPONENTS

A large portion of the research effort on organic electrolyte systems has been directed toward finding components which are suitable for use in high-energy density batteries. Investigations have been conducted to find the following:

1. Electrolytes which are compatible with the highly reactive electrode materials and which have acceptably high electrolytic conductivities.
2. Half cell systems which exhibit acceptable electrochemical reversibility.
3. Separators which are compatible with the high-energy systems and which are mechanically strong enough to prevent short-circuiting of the cells.

Selection of Solvents

The solvents to be utilized in electrolytes for high-energy density batteries must have the following properties:

1. They must be aprotic and unreactive toward the active metal anodes used in batteries of this type (for example, lithium).
2. They must be capable of forming solutions which have reasonably high conductivities. Solvents with high dielectric constants and low viscosities were considered chief candidates.
3. They must have a wide liquid range.

Many solvents have been tested; however, only a few have shown any promise of being acceptable. These acceptable solvents, their dielectric constants, viscosities, and melting and boiling points are summarized in Table II.

Selection of Solutes

Solutes for use in high-energy density batteries should have the following properties:

1. Form stable electrolytes which do not chemically react with the electrode materials.
2. Have high solubilities in organic solvents.

TABLE II
SOLVENT PROPERTIES

Solvent	Dielectric Constant	Viscosity (Centipoise)	Melting Point °C	Boiling Point °C
Propylene Carbonate (PC)	64.4	2.2	-49	242
γ -Butyrolactone (BL)	39	1.67	-4	206
Dimethylsulfoxide (DMSO)	48	1.93	6	189
Nitromethane (NM)	39.4	0.619	-29	101
Acetonitrile (AN)	38.8	0.36	-42	82
N,N-Dimethylformamide (DMF)	36.7	0.633	-61	153
Methylformate (MF)	8.5	0.330	-99	+31
N-Nitrosodimethylamine (NDA)	53.0	0.865	—	153
Ethylene Carbonate (EC)	89	1.9	36	248
Dimethyl Carbonate (DMC)	15	0.60	1	90
Formamide (FM)	111.5	3.76	3	211
2-Pentanone	22	0.47	-78	102
Cyclohexanone	18	2.8	-16	156
Methyl Acetate	7.2	0.41	-98	57

3. Dissociate in organic solvents to form conducting solutions.

The salts which have been found to have these properties include lithium perchlorate (LiClO_4), lithium aluminum chloride (LiAlCl_4), and the hexafluorophosphates of sodium, ammonium, and tetra alkyl ammonium (NaPF_6 , NH_4PF_6 , NR_4PF_6).

Electrolyte-Electrode Material Compatibilities

The highly reactive electrode materials used in high-energy density batteries cause special compatibility problems. Therefore, a considerable number of studies have been conducted to determine which electrolytes are compatible with the electrodes.

The stability of lithium metal, which appears to be the most promising anode material, has been determined by storing this metal in the electrolytes for a period of time. Corrosion of the lithium has been detected by visual observation¹⁷ and by measuring the amount of hydrogen evolved as a function of time.⁴⁹ Lithium has been found to be compatible with electrolytes which contain LiClO_4 , LiAlCl_4 , KPF_6 , or NaPF_6 dissolved in PC, BL, NM, or DMC, provided that these materials are sufficiently pure and that water, especially, has been excluded. Additional data on the compatibility of lithium with various electrolytes has been reported.^{4,5,6,9,16,17,21,28,49}

Cathode materials should have a very low solubility in electrolytes, especially for secondary batteries and for non-reserve primary batteries. The dissolution of the cathode material causes decreased battery capacity, not only because of loss of active material at the cathode, but also because of diffusion of the dissolved material to the anode where it discharges.

The solubilities of cathode materials such as cupric fluoride (CuF_2), cupric chloride (CuCl_2), cobalt fluoride (CoF_3), and silver chloride (AgCl), have been studied qualitatively by observation of the color of solutions formed when various electrolytes were allowed to equilibrate with the solid electrode material.^{17,21,24,49} More exact investigations of solubility have been carried out by quantitative measurements such as conductivity measurements,²⁴ titrations,^{7,9,14,41} and spectrophotometry.⁴¹ Solubility data of the following cathode materials have been published: CuF_2 ;^{4,7,9,13,16,17,21,24,49} CuCl_2 ;^{4,41} CoF_3 ;^{13,16,17,21,24,49} AgCl .^{12,14} CuF_2 has been found to be less soluble than CuCl_2 in a number of electrolytes which contain LiCl , LiClO_4 , LiAlCl_4 or LiBF_4 as solute and PC or BL as solvent. (Table III.)

The nature and concentration of the solute in the various electrolytes has a pronounced effect on the solubilities of CuF_2 and CuCl_2 .^{7,41,49} These effects may be attributed to the formation of soluble complex ions, to changes in the activity coefficients of the dissolved species or to precipitation reactions between solute and copper halide; however, little quantitative data is available. Attempts to reduce the solubility of CuCl_2 through the use of the common ion effect and mixed solvents have had insignificant results.⁴¹

The addition of small amounts of water to BL was found to increase the solubility of CuF_2 .^{7,9}

Decomposition Potentials of Solvents and Electrolytes

Another approach to the determination of electrolyte and solvent stabilities has been to measure decomposition potentials for the various systems. This method of analysis is based on the premise that electrolytes must not undergo electrochemical reaction at potentials below that at which a battery will operate.^{2,4,6,49,67,68,69} To carry out decomposition potential measurements the solution of interest is placed in an electrolysis cell equipped with a pair of Pt electrodes and the current is then measured as the voltage applied to the cell is increased. A sharp increase in current indicates that the decomposition potential has been reached.

TABLE III

SOLUBILITY OF CUPRIC HALIDES IN ORGANIC ELECTROLYTES

Cathode Material	Electrolyte	Solubility (Total Copper; Mole/Lit)	Reference
CuF ₂	LiAlCl ₄ -PC*	0.013	41
	LiBF ₄ -PC	0.022	41
	LiClO ₄ -PC	0.027	41
	LiClO ₄ -PC**	0.0047	49
	LiAlCl ₄ -BL	0.010	41
	LiBF ₄ -BL	0.000	41
	LiClO ₄ -BL	0.002	41
	LiClO ₄ -NM**	0.015	49
	LiClO ₄ -AN**	0.003	49
	LiClO ₄ -DMSO**	0.010	49
CuCl ₂	LiAlCl ₄ -PC	0.023	41
	LiBF ₄ -PC	0.049	41
	LiClO ₄ -PC	0.048	41
	LiAlCl ₄ -BL	0.046	41
	LiBF ₄ -BL	0.006	41
	LiClO ₄ -BL	0.008	41
*All concentrations are 0.1F except as noted.			
**1.0F concentration.			

Decomposition potentials determined in this fashion appear to be of questionable significance. Solvent decomposition is an irreversible process, the decomposition potentials are therefore dependent on such experimental conditions as type of electrode and the mode of potential increase.

Organic Electrolyte Conductivities

Electrolytes for batteries must be sufficiently conductive in order to make the ohmic losses as low as possible. Therefore, many organic electrolytes have been prepared and their conductivities measured.^{4,5,6,12,13,16,17,21,24,28,36,37,44,46,49} The effects of electrolyte composition, concentration, and temperature on the specific conductivities have been investigated. A compilation of some of the specific conductivity data is presented in Table IV. Only those data are shown which serve as examples for the present discussion, or which refer to electrolytes which have been actually

TABLE IV

THE SPECIFIC CONDUCTIVITIES OF ORGANIC ELECTROLYTES

A. The Effect of Solvent on the Specific Conductivities of 1.0F LiClO_4 Solutions. Temperature = 25⁰₄₉

Solvent	AN	DMF	DMSO	BL	NM	PC
Solvent Viscosity (centipoise)	0.36	0.63	1.9	1.7	0.62	2.2
Solvent Dielectric Constant	38.8	36.7	48	39	39.4	64.4
Electrolyte Conductivity ($\Omega^{-1}\text{cm}^{-1}$) $\times 10^3$	35.5	23.1	13.7	10.7	9.3	7.3

B. The Effect of Solute on the Specific Conductivities of 1.0F DMF Solutions. Concentration = 1.0F; Temperature = 27-29⁰₂₄

Solute	LiCl	NaBF_4	NaPF_6	KPF_6	CsPF_6	Morpholinium PF_6
Conductivity ($\Omega^{-1}\text{cm}^{-1}$) $\times 10^3$	8	20	21.5	23.6	25.5	25.7

C. The Effect of Solute Concentration on the Specific Conductivity of LiClO_4 -PC Electrolytes⁴⁹

Concentration (Formal)	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6
Electrolyte Viscosity (Centipoise)	2.64	3.15	3.86	4.85	6.19			
Electrolyte Conductivity ($\Omega^{-1}\text{cm}^{-1}$) $\times 10^3$	3.15	4.90	6.40	7.15	7.25	6.85	6.25	5.50

incorporated into experimental batteries. The following general conclusions can be drawn:

1. The specific conductivities of organic electrolytes are about one order of magnitude lower than those for corresponding aqueous solutions.

2. The nature of the solvent has a pronounced effect on the conductivity of the solutions. Generally, increasing the dielectric constant of the solvent increases the conductivity while increasing the viscosity of the solvent has the opposite effect.*

3. The specific conductivity of electrolytes increases as the size of the solute ions increases.

4. The specific conductivity is a maximum for most electrolytes when the concentration of solute is about one formal. The decrease in conductivity above this concentration has been attributed to increased viscosity.²⁴

Binary mixtures containing a solvent with a high dielectric constant and a solvent with a low viscosity have been utilized to obtain electrolytes with improved conductivities.^{6,14} 0.63 F LiAlCl₄ in a 1:1 mixture of PC and diethylether exhibited a higher conductivity ($1 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$) than equivalent solutions in either of the solvents alone (PC- $6 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$; Ether- $2.7 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$).

Attempts have been made to increase electrolyte conductivities by dissolving gases such as NH₃, SO₂ and CO₂ in the solutions.^{2,5,6} It was anticipated that the dissolved gas molecules would arrange themselves around the solute ions thus increasing the degree of dissociation of the solute and also, increasing the mobility of the solute ions. The results of these experiments were inconclusive since no significant improvement of the electrolyte conductivities was obtained.

HALF CELL STUDIES

Half cell studies have been conducted to determine whether the couples, which have been selected because of their high free energies of reaction and low equivalent weights, can serve as anodes and cathodes in a battery. Several electrochemical requirements must be met to achieve high-energy densities and trouble-free operation of the battery:

1. The electrode potentials at open circuit should be close to the potentials calculated from the thermodynamic values.

2. The electrodes should polarize little when current is applied.

3. The electrode potential should not appreciably change during the discharge or charge.

4. The coulombic efficiencies of the electrode reactions should be high.

*The data presented in Table IV-A are not truly representative of this trend, since the viscosities shown are those for the solvents and not the solutions, the viscosities of which may be several times larger than those for the pure solvents.

5. The electrode reactions must be reversible in order to be useful for application in secondary batteries.

Electrochemical Techniques

Half cell measurements have been used to study the electrochemical behavior of anode and cathode separately which is not possible when these electrodes are combined in a complete cell.

The techniques commonly employed in half cell investigations have included the following:

1. Potentiometric measurements. The relationship between the electrode potential, E , and the concentrations of potential determining species, C_o and C_r , is studied. Conformity to the Nernst equation,

$$E = E^o - \frac{RT}{nF} \ln \frac{C_r}{C_o}$$

is assumed to indicate that the electrode reaction is reversible.

2. Steady-state current-voltage measurements. The electrode potential, E , is measured as a function of the current density, i . From the intercept and slope of a Tafel plot of the data ($\ln i$ vs E) the exchange current density, i_o , and transfer coefficient, a , which are characteristic of the kinetics of the electrode reaction, can be determined. The limiting current, i_l , which is a measure of the maximum obtainable rate of an electrode reaction, under a given set of conditions, is another parameter which is commonly measured under steady-state conditions.

3. Cyclic and linear voltammetry. The current is measured while the electrode potential is scanned in either the cathodic or anodic direction. Peak currents, i_p , and peak potentials, E_p , which are characteristic of the electrode reaction, are observed. By varying the rate and direction of the potential scan, information about the reversibility of the reaction, and number of electrons and number of steps involved in the reaction can be gained.

4. Chronopotentiometry. A constant current pulse is applied to a working electrode, and the electrode potential measured as a function of time. Depletion of the electroreactive species at the surface of the electrode is marked by a sharp change in the electrode potential, and the time elapsed from the start of the pulse to the change in potential is designated the transition time, τ . For a diffusion controlled reaction, the current density, i , bulk concentration of electroactive species, C , and transition time are related by the equation,

$$\frac{i \tau^{\frac{1}{2}}}{C} = \text{constant.}$$

Deviation from this behavior indicates that the electrode process is not diffusion controlled.

5. Coulometric techniques. An electrode containing a known amount of active material is discharged, and the number of coulombs delivered during the discharge measured. The theoretical capacity of the electrode is given by the equation,

$$\text{capacity (coulombs)} = \frac{F M}{A}$$

where F is the Faraday (96.5×10^3 coulombs), M is the weight of active electrode material, and A is the equivalent weight of the electrode material. The coulombic efficiency is then calculated using the equation,

$$\text{efficiency (\%)} = \frac{\text{coulombs observed}}{\text{theoretical coulombs}} \times 100.$$

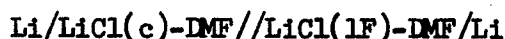
The cycling efficiency for a secondary system is calculated using a similar expression,

$$\text{cycling eff. (\%)} = \frac{\text{coulombs discharged}}{\text{coulombs charged}} \times 100.$$

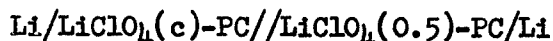
6. Discharge measurements. Electrodes are discharged either at constant current or constant load, and the electrode potentials measured as a function of time. The electrode polarization and the coulombic efficiency can be directly evaluated.

The Lithium Electrode in Primary Systems

The lithium electrode has been found to be reversible in several electrolytes. Illustrative of these findings are potentiometric studies conducted on the system

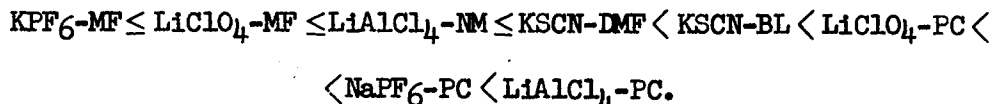


the potential of which was found to obey the Nernst equation over the LiCl concentration range $10^{-4} < c < 1F$,⁴¹ and the system



which obeys the Nernst equation over the LiClO_4 concentration range $0.1F < c < 1.0F$.⁴⁹

The relationship between current and potential for lithium electrodes has been measured under steady-state conditions in a number of electrolytes.^{12,13,14,62} In general, it has been found that the polarization of this electrode is small. The following sequence is observed when the electrolytes (1F) are arranged in the order of increasing polarization:



The effect of solvent appears to be more pronounced than that of the solute.

The exchange current density for the lithium electrode has been found to be on the order of 1 ma/cm^2 in electrolytes containing PC, BL, DMF, DMSO,⁴¹ and PC-NM⁵² mixtures. This high exchange current indicates that the lithium electrode is fairly reversible.

The coulombic efficiencies of lithium anodes vary between 70% and 100% depending on the electrolyte used. Further, the efficiencies are relatively independent of the current density as long as the current is below its limiting value. These observations are illustrated in Table V where representative coulombic efficiencies are listed for various electrolytes and current densities.

TABLE V
COULOMBIC EFFICIENCY OF LITHIUM ANODES

Electrolyte	Current Density (ma/cm ²)	Coulombic Efficiency (%)	Reference
0.5F LiBF ₄ -PC	23.5	81	41
	11.8	78	41
1.0F LiBF ₄ -BL	35.3	92	41
	17.7	98	41
	1.8	83	41
1.0F LiClO ₄ -PC	10.0	70	49
	5.0	73	49
	1.5	73	49
2.0F LiClO ₄ -DMC	2.0	90	49
1.0F LiClO ₄ -Cyclohexanone	2.0	70	49

The effect of electrode composition and fabrication on the coulombic efficiency of lithium anodes has also been investigated. The methods of electrode preparation have included the following:

1. Pressing or rolling lithium ribbon onto metal screen made of copper, silver, nickel, or aluminum.^{2,6,9,12,14,21,30,49}
2. Pressing lithium powder with or without conducting additives onto metal screens.^{21,36,49}
3. Dipping nickel screen into molten lithium.^{12,37}

The method of preparation which is simplest and which appears to give the best results in terms of least polarization and highest efficiency is that

of pressing or rolling the lithium onto screens. Dipping of nickel screen into molten lithium gave the least satisfactory results due to uneven distribution and poor adherence of the metal.

It has been found that lithium electrodes can be stored in an argon atmosphere, in paraffin oil, or in LiClO_4 -PC electrolyte for several months without losing coulombic efficiency or showing increased polarization.⁴⁹ It has also been shown that etching lithium electrodes with methanol is deleterious since it results in electrodes which polarize severely at the beginning of their discharge. This may be due to film formation on the electrode surface during the etch procedure.

The Lithium Electrode in Secondary Systems

In secondary or storage battery applications it is necessary that the lithium electrode operates efficiently not only during discharge, but also during charge. Therefore, considerable work has been done in studying the electrodeposition of lithium.

One of the primary objectives of this work has been to obtain compact, adherent deposits on a variety of metal substrates. In pursuing this goal, many variables have been investigated including the effects of electrolyte composition and concentration, cathodic current density, and amount of lithium deposited.^{12,14,40,41,49} Best results have been obtained by depositing lithium from concentrated solutions of LiClO_4 or LiAlCl_4 in PC, LiAlCl_4 in NM, or LiAlCl_4 in an NM-PC mixture. 10 ma/cm² appears to be the optimum current density for deposition from these solutions. Under these conditions, grey, dendritic, fairly adherent deposits were obtained. The adherence of the deposit was slightly improved by the presence of 0.2% of the sodium salt of Rhodamine B or of disodium fluorescein in the LiAlCl_4 -PC solution. Coarser, more dendritic deposits were obtained when the current density and/or when the total amount of lithium deposit were increased.

When deposition of lithium was carried out from solutions containing AlCl_3 it was generally found that small amounts of aluminum were co-deposited with the metal. The amount of aluminum co-deposited depended on the composition of the electrolyte and the current density. When deposition was carried out at 2 ma/cm² from a solution which was 7.5F AlCl_3 , saturated with LiCl in PC, it was found that the co-deposit amounted to approximately 2% by weight.¹⁴ For a solution which was 0.35F AlCl_3 , 0.15F LiCl in PC, the following results were obtained when 8.6 coulomb/cm² were deposited on copper substrates:⁴⁰

current density (ma/cm ²)	5	9	15	21	30
weight % Al	40	9	38	50	72

The coulombic efficiency of anodic-cathodic cycling is of great significance in secondary battery applications of the lithium electrode. A summary of the results of measurements of cycling efficiencies is presented in Table VI.

TABLE VI

CYCLING EFFICIENCIES OF LITHIUM ELECTRODES

A. Effect of Electrolyte Composition on Cathodic and Anodic Efficiencies¹⁴Current density: 2 ma/cm² on charge and discharge

Conditions: 3 min. cathodic deposition; anodic stripping to cut-off of 2.0V vs lithium reference electrode

Substrate: Nickel

Electrolyte	Coulombic Efficiency	
	Cathodic	Anodic
0.64F LiClO ₄ -PC	95-100%	84%
0.63F LiAlCl ₄ -PC	95-100%	50%

B. Effect of Electrolyte Composition on Cycling Efficiencies⁴¹

Substrate: Polished platinum disc

Current density: Equal for both charge and discharge in all cases

Electrolyte	Amount Deposited (coul/cm ²)	Current Density (ma/cm ²)	Cycling Efficiency (%)
0.1F LiBF ₄ -BL	1	10	51
0.1F LiBF ₄ -AN	3	10	22-35
0.5F LiClO ₄ -BL	0.5	10	84
0.1F LiClO ₄ -DMSO	3	10	71
0.05F LiClO ₄ -PC	1	5	4
0.1F LiClO ₄ -PC	1	5	76-78
0.2F LiClO ₄ -PC	1	6	78
0.3F LiClO ₄ -PC	1	5	80

C. Effect of Current Density on Cycling Efficiency⁴¹Electrolyte: 0.3F LiClO₄-PC

Substrate: Polished platinum

Amount Deposited: 1 coul/cm²

Current density (ma/cm ²)	5	10	20
Cycling Efficiency (%)	80	81	75

TABLE VI (CONTD)

D. Effect of Amount Deposited on Cycling Efficiency⁴¹Electrolyte: 1.0F LiBF₄-PCCurrent density: 25 ma/cm² cathodic; 100 ma/cm² anodic

Substrate: Polished platinum disc

Amount deposited (coul/cm ²)	1.5	3.0	6.0	30.0
Cycling efficiency (%)	67	75	46	36

E. Effect of Substrate on Cycling Efficiency⁴¹Electrolyte: 0.5F LiAlCl₄-PCCurrent density: 10 ma/cm² both cathodic and anodicAmount deposited: 5 coulombs/cm²

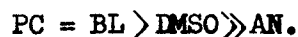
Electrode material	copper (flat)	copper (porous)	silver (flat)	platinum (flat)	beryllium (flat)
Cycling Efficiency (%)	75	86	95	98	63

F. Effect of Water on Cycling Efficiency⁴⁰Electrolytes: 0.2F LiClO₄-PCCurrent density: 5 ma/cm² both cathodic and anodicAmount deposited: 0.15 coul/cm²

Conditions: Anodically stripped until steep increase in voltage

Water added (mole/lit)	0.00	0.01	0.12	0.42	0.61
Cycling Efficiency (%)	50	45	33	18	5

Both the solvent and solute used in making up the electrolyte affect the efficiency of cycling. The data which are so far available on the effect of electrolyte composition on the cycling efficiency do not allow a quantitative comparison. However, a comparison may be made qualitatively. The solvents, given in order of decreasing cycling efficiency, are



The solutes, listed in order of decreasing cycling efficiency, are



The concentration of the solute has little effect on the cycling efficiency of the lithium electrode except in so far as the concentration affects the limiting current of the electrode reaction. The cycling

efficiency increases only slightly with increasing concentration of solute. When the limiting current is exceeded, the cycling efficiency is drastically reduced. This phenomenon is illustrated in Table VI-B.

The current density appears to have little effect on the cycling efficiency of the lithium electrode as long as the current does not exceed the limiting current for the system.⁴¹ There have been experiments conducted which tended to indicate that there was a dependence of the cycling efficiency on the current density; however, in these experiments the total amount of lithium deposited was not kept constant, and it has been shown that the amount of lithium does have an effect on the efficiency of the deposition.^{14,41} It was found that the greater the amount of lithium deposited the lower the efficiency. The effects of current density and amount of lithium deposited are illustrated in Tables VI-C and VI-D.

The metal substrate onto which lithium is deposited has some effect on the cycling efficiency. The highest efficiencies have been obtained with platinum, silver, and aluminum substrates. It appears the lithium forms alloys with these metals as is indicated by the fact that during anodic stripping of electrodeposited films of lithium, the potential shifts gradually toward more positive values. On nickel, stainless steel, and beryllium substrates, the efficiency is usually less. Anodic stripping of lithium deposits on these metals gives constant potentials until the deposits have been entirely consumed, at which time a sudden potential step occurs. This indicates that no alloys form between lithium and these substrates.^{12,41}

The efficiency of cycling for lithium electrodes tends to decrease as the number of cycles increases. At best, the cycling efficiency for lithium electrodes appears to be about 85%. The reasons for this low value are not entirely understood, however, the processes most likely responsible follow:

1. Loss of electrical contact during anodic discharge due to a preferential attack at the base of lithium dendrites. This idea is supported by the fact that higher efficiencies are obtained when alloy forming substrates are used. If the base of the dendrite were alloyed it would be less reactive than pure lithium.⁴¹
2. Mechanical loss of electrodeposited lithium. This is supported by the fact that efficiency is dependent on amount of lithium deposited which indicates that as more lithium is deposited the deposit becomes less adherent.^{14,41}
3. Alloy formation with substrate material. It has been shown in cases where alloying was suspected that not all of the lithium on the electrode was utilized during an apparently complete anodic discharge.^{14,41}
4. Occurrence of side reactions which consume lithium, but produce no electricity. The decrease of efficiency with increasing number of cycles indicates a buildup of deleterious impurities through side reactions.⁴¹

Mass Transport Limitations of the Lithium Electrode

Experimental evidence is available which indicates that both the cathodic and anodic reactions of the lithium electrode are diffusion controlled. The evidence which leads to this conclusion has been collected by measurements of limiting currents and by measurements of chronopotentiometric transition times. Limiting currents for both the anodic and cathodic reactions have been observed and are listed in Table VII-A.

TABLE VII

LIMITING CURRENT DENSITIES AND CHRONOPOTENTIOMETRIC CONSTANTS OF THE LITHIUM ELECTRODE

A. Limiting Current Densities, i_L .

Electrolyte	Agitation	Reaction	i_L (ma/cm ²)	Ref.
0.15F LiCl, 0.35F AlCl ₃ -PC	Stirred	Cathodic	15	40
0.32F LiAlCl ₄ , 0.64F AlCl ₃ -PC	Unstirred	Cathodic	0.55	14
		Anodic	13	14
0.63F LiAlCl ₄ -PC	Unstirred	Cathodic	14	14
		Anodic	13.8	14
0.05 LiClO ₄ -PC	Stirred	Anodic	4	41
0.10F LiClO ₄ -PC	Stirred	Anodic	11	41
0.2F LiClO ₄ -PC	Stirred	Anodic	21	41
0.30F LiClO ₄ -PC	Stirred	Anodic	26	41

B. Chronopotentiometric Constants, $i\tau^{1/2}/C$, for Cathodic Reactions⁴¹

Electrolyte	Concentration	$i\tau^{1/2}/C$
LiClO ₄ -PC	.05F < C < .3F	200 ± 15
LiClO ₄ -DMSO	0.1F	280 ± 20
LiBF ₄ -DMF	0.1F	395 ± 20
LiBF ₄ -AN	.05F; 0.1F	633
LiAlCl ₄ -BL	0.2F	285

Chronopotentiometric methods have been used to determine the characteristics of the cathodic reactions of the lithium electrode. If the quotient,

$i\tau^{1/2}/C$, where

i = current density of galvanostatic pulse

τ = chronopotentiometric transition time

C = electrolyte bulk concentration

is constant over a wide range of current densities and concentrations, this is assumed to be indicative of a diffusion controlled reaction. As illustrated in Table VI, this behavior has been observed in several cases.

Other Anodes

Magnesium, calcium, aluminum, and beryllium have all been investigated for possible use as high-energy density anodes. The results so far obtained have been unpromising.

The potentials at open circuit and during anodic discharge have been measured for each of these metals.^{24,28,44} The results were much less reproducible than for the lithium electrode. During discharge, voltage oscillations and transients were common, which indicates that these electrodes are not as reversible as the lithium electrode, and that under some conditions these electrodes tend to form passivating films.

The Copper Fluoride Electrode

Copper fluoride, CuF_2 , has been extensively studied for possible use as a cathode material in high-energy density, primary batteries. The characteristics which qualify it for this use are a low equivalent weight, high free energy of reaction and an ability to discharge with high coulombic efficiency and low polarization in organic electrolytes. No successful use of CuF_2 in secondary batteries has yet been accomplished since no system has been devised which will provide the fluoride ions necessary for recharging this electrode.

The discharge characteristics of CuF_2 electrodes are greatly affected by the solvent, solute, and solute concentration of the electrolyte. In some electrolytes a constant decrease in potential is observed during discharge, while in others the potential is found to remain fairly steady until the CuF_2 has been almost completely consumed. Systems which exhibited this latter behavior include solutions of LiClO_4 and NH_4SCN in 2-pentanone, 2,4-pentanedione, ethylacetate, PC, MF, and BL.^{6,9,21} Electrodes discharged in these electrolytes also gave better coulombic efficiencies than those discharged in systems in which no voltage plateau was observed. Generally speaking LiClO_4 electrolytes give the best results in terms of efficiencies and polarization while electrolytes containing hexafluorophosphates give the poorest results. The effect of electrolyte on the behavior of CuF_2 electrodes is summarized in Table VIII-A.

The effect of solute concentration on the efficiency of CuF_2 electrodes has been studied with LiClO_4 -PC electrolytes. The results show that the efficiency increases as the concentration increases up to a value of 1.25F, and then decreases as the concentration increases further (Table VIII-B).

TABLE VIII

THE COPPER FLUORIDE CATHODE

A. Effect of Electrolyte on Voltage Plateau and Coulombic Efficiency⁴⁹

Cathode: 85% CuF_2 , 10% graphite, 5 % polyethylene powder, pressed
3 min at 90°C and 4000 lb/cm²

Discharge: 2 ma/cm² at room temperature to final voltage of 0 V
vs lithium reference electrode

Electrolyte	Coulombic Efficiency (%)	Plateau Voltage (V vs Li)
1.25F LiClO_4 -2-pentanone	60	3.4
1.25F LiClO_4 - 2,4-pentanedione	25; >80	3.0; 2.1 (2 plateaus)
1.0F LiClO_4 - cyclohexane	40	2.5
2.25F LiClO_4 - ethyl acetate	60; >80	3.4; 1.6 (2 plateaus)
2.0F LiClO_4 - dimethylcarbonate	65	3.5 → 0 (no plateau)
2.0F LiClO_4 - dimethylsulfite	30	3.0
1.0F LiClO_4 - PC	75	3.3
1.35F NH_4SCN - PC	>60	2.1
1.15F KSCN - PC	60	2.0 → 0 (no plateau)
1.15F AlCl_3 - PC	4	3.4 → 0 (no plateau)
1.0F KPF_6 - PC	2	2.2 → 0 (no plateau)

B. Effect of Solute Concentration on Coulombic Efficiency⁴⁹

Cathode: 85% CuF_2 , 10% graphite, 5% polyethylene powder, pressed
3 min at 90°C and 4000 lb/cm²

Electrolyte: LiClO_4 - PC

Discharge: 2 ma/cm² at room temperature to final voltage of 0 V
vs lithium reference electrode

LiClO_4 concentration (F)	0.25	0.50	0.75	1.00	1.25	1.50
Coulombic Efficiency (%)	15	37	65	75	77	72

TABLE VIII (CONTD)

C. Effect of Current Density on Voltage Plateau and Coulombic Efficiency⁴⁹

Cathode: 85% CuF₂, 10% graphite, 5% polyethylene powder pressed 3 min at 90°C and 4000 lb/cm²

Electrolyte: 1.0M LiClO₄ - PC

Discharge: Room temperature to final voltage of 0 V vs lithium reference

Cathodic current density	2	4	6
Coulombic Efficiency (%)	76	63	59
Plateau Voltage (volts vs Li)	3.3	3.25	2.9

D. Effect of Temperature on Voltage Plateau and Coulombic Efficiency⁴⁹

Cathode: 85% CuF₂, 10% graphite, 5% polyethylene powder pressed 3 min at 90°C and 4000 lb/cm²

Electrolyte: 1.0M LiClO₄ - PC

Discharge: 2 ma/cm² to final voltage of 0 V vs lithium reference electrode

Temperature (°C)	0	15	30	40	60
Coulombic Efficiency(%)	28	42	60	55	70
Plateau Voltage (volts vs Li)	3.3	3.3	3.4	3.4	3.5; 1.7*

*Two plateaus observed.

One of the chief factors which limits the application of the CuF₂ electrode is that its behavior is very sensitive to the current density at which it is operated. It has been found that as the current density increases, both the coulombic efficiency and the potential of the electrode decrease.^{13,29} This point is illustrated in Table VIII-C.

The behavior of CuF₂ electrodes is strongly influenced by the composition of the material and the technique used to fabricate the electrodes. The following methods of electrode preparation have been investigated:

1. Pasting a mixture of CuF₂, conductive additive, binder, and solvent onto a metal screen.^{6,8,13,21,49}

2. Preparing a filter cake of CuF₂, conductive additive, and fibrous material on a metal screen.^{5,7,21,36}

3. Pressing a dry mixture of CuF₂, conductive additive, and fibrous material onto a metal screen.^{6,13,29,30,49}

4. Hot pressing a mixture of CuF₂, conductive additive, and binder onto a metal screen.^{13,49}

5. Sintering CuF_2 onto a metal sheet.^{13,30}
6. Chemically reacting CuO with BrF_3 .⁴⁹
7. Anodic oxidation of copper electrodes in fluoride containing electrolytes.^{30,49}

Each method of electrode preparation has a unique set of variable parameters associated with it. These parameters may include, for example, particle size, amount and kind of conductive additive, amount and kind of binder, compacting pressure and temperature, or plate thickness. The situation is further complicated by the fact that many of these parameters are interrelated, so that, for example, the kind of binder chosen affects the compacting temperature, while the particle size would affect the optimum compacting pressure and plate thickness. This interrelation of the variables makes the job of evaluating a particular electrode quite complex, and causes considerable difficulty when attempts are made to compare the performance of electrodes prepared by different methods. However, it is felt that a discussion of the performance of electrodes prepared by the various methods enumerated in the preceding paragraph is of value, since it serves to indicate which methods of preparation may be found useful in the future, and also shows which methods have proved to be unsatisfactory. Therefore, a presentation of some of the test results for the various preparative methods is included below:

1. Pasted Electrodes:

A. A mixture of 70% CuF_2 and 30% silver flake, wetted with xylene, has been pasted onto an expanded silver mesh, placed in a vacuum to remove the solvent, and baked at 200°C. When discharged in $\text{NaPF}_6\text{-PC}$ or $\text{NaPF}_6\text{-BL}$ to 2.0 V cut-off (vs Li reference), this type of electrode yielded 72% coulombic efficiency.¹³

B. A mixture of 90% CuF_2 , 9% graphite, and 1% cellulose acetate + solvent (10% methanol, 90% ethyl acetate) was pasted on a metal screen so that it had a thickness of 0.025" after evaporation of solvent. Discharged in 4.7F $\text{LiClO}_4\text{-MF}$ at 10 ma/cm² these electrodes yielded 60-70% coulombic efficiency with an average voltage of 2.7 V. Electrodes of this type appear to be suitable for discharge at the 1-10 hour rate.⁸

2. Filter Cake Electrodes:

A. A mixture of 77-90% CuF_2 , 7-16% graphite, and 3-7% paper fiber was suspended in heptane, filtered in a paper sheet mold, pressed at 60-500 psi, and vacuum dried. The loading of electrodes prepared in this fashion was about 1.8 g of CuF_2/in^2 . These electrodes were discharged across constant loads of 200 Ω and 100 Ω with coulombic efficiencies of 81% and 65% respectively. The average voltage was greater than 2.5 V vs a lithium reference. Losses of efficiency were attributed to incomplete wetting of the electrodes, especially when the amount of graphite was high and the amount of paper fiber low.^{6,8} Coulombic efficiencies were not greatly affected by the thickness of the filter cake in the region 0.05-0.15".⁷

B. 80g of CuF_2 were ball-milled in PC, blended with 10g of graphite fiber, and 10g of powdered graphite, copper or silver. This mixture was filtered to form a cake which was sandwiched between expanded copper mesh. Discharged in 1.0M LiClO_4 -PC at 1 ma/cm² these electrodes yielded up to 58% coulombic efficiency.²¹

3. Dry Pressed Electrodes:

A. A mixture of 86% CuF_2 , 7% graphite, and 7% paper fiber was pressed onto metal screen at 5000 psi. This type of electrode had low coulombic efficiency due to slow and incomplete wetting by the electrolyte.⁶

B. A mixture of 78-92% CuF_2 , 5-11% fibrous material, and 3-11% acetylene black was pressed at 10,000-20,000 psi to form the electrode. When discharged at 1-10 ma/cm² in 1.0M $(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6$ -DMF or 1.0M LiClO_4 -PC this type of electrode polarized severely.²⁹

C. A mixture of 88% CuF_2 , 10% graphite, and 2% glass filter paper floc was pressed at 500 psi at room temperature. These electrodes had poor mechanical strength and yielded 61% efficiency when discharged at 2 ma/cm² in 1.0M LiClO_4 -PC. When fabricated with higher compacting pressures, these electrodes had greater mechanical strength, but yielded lower coulombic efficiency due to incomplete reaction.⁴⁹

4. Hot Pressed Electrodes:

A dry mixture of 85% CuF_2 , 10% graphite, and 5% thermoplastic binder (polyethylene, Teflon, PVC-PVA² copolymeres) was pressed onto expanded copper mesh at 3000-4000 psi and 90°C for 3 min. The loading was about 0.2g mix/cm². Discharged at 2 ma/cm² in 1.0M LiClO_4 -PC coulombic efficiencies of 65-80% at average voltages of 3.3 V were obtained.⁴⁹

5. Sintered Electrodes:

A. CuF_2 powder was pressed at 200°C onto copper, aluminum, or nickel screens. When discharged in $(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6$ -DMF electrodes of this type polarized severely.³⁰

B. A mixture of CuF_2 , conductive additive, and thermoplastic binder (acrylic dissolved in xylene) was pasted onto a metal screen, vacuum dried, and heated to 150°C where the binder sintered. Discharged in NaPF_6 -PC and NaPF_6 -BL, electrodes of this type showed low polarization and fair coulombic efficiency.¹³

C. A mixture of CuF_2 and silver or copper flakes, supported on a metal sheet without binder, was sintered. Discharged at 0.2 ma/cm² in NaPF_6 -PC electrodes of this type yielded 57% efficiencies at average voltages of 2.0-2.5 V vs a lithium reference.¹³

6. Electrodes Formed by Chemical Reaction:

An attempt was made to prepare CuF_2 electrodes by reacting porous CuO electrodes with BrF_3 . No CuF_2 was formed by this method.⁴⁹

7. Electrodes Prepared by Anodic Oxidation of Copper:

Attempts were made to form CuF_2 by anodic oxidation of copper electrodes in AsF_3 -PC solutions⁴⁹ and in aqueous HF solutions.³⁰ No success was attained.

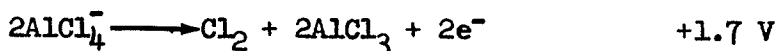
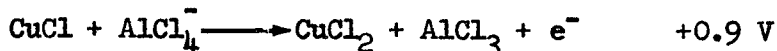
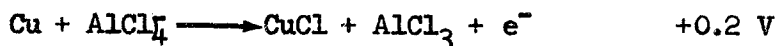
The temperature at which CuF_2 electrodes are discharged affects their behavior. It has been found that as the temperature is increased the efficiency of the electrode reaction increases. However, at higher temperatures there is an increasing tendency for the electrode to discharge in two steps rather than in one, as is most desirable. For example, at 60°C a second plateau at 1.7 V is observed when the cathode is discharged in 1F LiClO_4 -PC. (Table VIII.)

The Copper Chloride Electrode

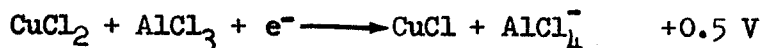
The copper chlorides, CuCl_2 and CuCl , have been investigated to a considerable extent for possible use as cathode materials in organic electrolyte batteries. These compounds have an advantage over CuF_2 in that systems can be constructed which give reversible electrode reactions. Therefore, they can be used in secondary batteries, whereas CuF_2 has primary battery applications only. CuCl_2 and CuCl have, however, the disadvantages that they provide lower energy densities and are more soluble than CuF_2 .

The behavior of CuCl_2 electrodes during charging is strongly dependent on the nature of the electrolyte. Pure copper electrodes can be anodically oxidized in 0.5F LiAlCl_4 solutions of PC, BL, DMSO, and AN to give CuCl with about 100% coulombic efficiency. In 0.5F LiAlCl_4 - DMF, however, CuCl_2 is formed with 100% efficiency.⁴¹

Copper powder mixed with graphite has been found to oxidize in steps, forming first CuCl and then CuCl_2 when electrolyzed in 1.0F LiAlCl_4 -PC. When all of the CuCl had been consumed, chlorine gas was formed on further anodization.⁴² Under steady-state conditions at 1-5 ma/cm² the following reactions were found to occur at the potentials indicated (vs Ag/AgCl reference electrode):

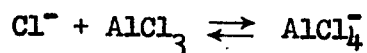


CuCl_2 undergoes stepwise reduction to CuCl and copper. At current densities of 1-5 ma/cm² the following reactions occur at the indicated potentials (vs Ag/AgCl reference electrode):



The coulombic efficiency of CuCl_2 reduction varies between 50% and 75% depending on the electrode structure, volume and composition of electrolyte,

and discharge rate. These low efficiencies are explainable in part by the formation of soluble copper species such as CuCl_3^- or CuCl_2^- which diffuse away from the electrode and are therefore lost to the reaction. The formation of these species is reduced if an excess of AlCl_3 is present, since the reaction,



consumes chloride ions, and thus prevents their reaction with the copper chlorides.⁴¹ This explanation for low coulombic efficiency is supported by the following experimental observations:⁴²

1. The coulombic efficiency for reduction is increased when excess AlCl_3 is added to the electrolyte. The efficiency increases from 50% in 1.0F LiAlCl_4 to 64% when a 0.5F excess of AlCl_3 is present in the same electrolyte.

2. Cathodic efficiency increases from 60% to 73% when the current density is increased from 5 to 10 ma/cm^2 with 1.0F LiAlCl_4 -PC electrolyte. In this case it is postulated that the copper chloride is reduced before the soluble complexes have a chance to form or to diffuse into the bulk electrolyte.

3. The formation of CuCl_2^- and CuCl_3^- has been observed in conductometric titrations of CuCl and CuCl_2 solutions with LiCl-PC .⁴¹

The Silver Chloride Electrode

Silver chloride, AgCl , has been found to undergo reversible, efficient electrode reactions in a number of organic electrolytes, and is therefore an attractive cathode material for secondary battery applications. The major disadvantages of AgCl are its high equivalent weight and the low free energy of its reaction with lithium. These factors combine to make the theoretical energy density of a lithium - silver chloride battery (229 whr/lb) less than half that of a lithium - copper fluoride battery (749 whr/lb).

TABLE IX

THE SILVER CHLORIDE ELECTRODE

A. Effect of Electrolyte on Efficiency of Cathodic Reduction⁴¹

Electrode: 10 parts AgCl , and 1 part Ag powder pressed at 1500 lbs into recessed Pt electrode. Theoretical capacity 8.5 ma hr/cm^2

Conditions: Discharged at 4.2 ma/cm^2 at room temperature until steep decrease in potential

Solvent	PC	PC	PC	PC	BL	DMF	BL
Solute	0.5F LiAlCl_4	0.25F Morpholinium- PF_6	1.0F LiBF_4	0.5F KPF_6	1.0F KPF_6	1.0F LiBF_4	1.0F LiBF_4
Coul. Eff.	27%	10%	27%	0%	0%	56%	60%

TABLE IX (CONTD)

B. Effect of Current Density on Efficiency of Cathodic Reduction¹⁴

Electrode: 90% AgCl and 10% acetylene black pasted on silver screen and dried at 120°C

Electrolyte: 0.63F LiAlCl₄-PC

Conditions: Discharged at room temperature until steep decrease in potential

Current Density (ma/cm ²)	0.7	1.0	2.0	3.0	4.0	5.0
Coul. Eff.	100%	96%	84%	66%	47%	28%

C. Effect of Electrode Composition on Efficiency of Cathodic Reduction¹⁴

Electrode: 75% AgCl plus 25% additive wet pasted on Ag screen, dried, and sintered at 400°C

Electrolyte: 0.63F LiAlCl₄-PC

Conditions: Discharged at 2.9 ma/cm² at room temperature until steep potential decrease

25% Additive	Ag ₂ O	Ag Flake	Graphite	Carbon	Acetylene Black
Coul. Eff.	5-10%	8-10%	20-30%	25-36%	42%

D. Effect of Mix Weight on Efficiency of Cathodic Reduction¹⁴

Electrode: 75% AgCl, 10% Ag flake, 10% graphite, 4% acetylene black, and 1% polyvinylalcohol (in H₂O), wet pasted, pressed at 500 psi, and dried at 120°C

Electrolyte: 0.63F LiAlCl₄-PC

Conditions: Discharged at 2.9 ma/cm² at room temperature until steep decrease in potential

Mix Weight (g mix/cm ²)	0.025	0.05	0.1	0.15
Coul. Eff.	97%	82%	49%	19%

E. Effect of Temperature on Cathodic Polarization of Electrodes¹⁴

Electrode: 90% AgCl and 10% acetylene black

Electrolyte: 0.63F LiAlCl₄-PC

Conditions: Steady-state measurements of polarization in millivolts vs a Ag/AgCl reference. Values include ohmic drop in separator and electrolyte.

Temp.	ma/cm ²	1	3	6	10
-30°C		350	-	-	-
-20°C		120	230	360	-
19°C		80	180	270	300
65°C		50	120	150	180

The cathodic discharge of silver chloride electrodes has been investigated in a number of electrolytes. As can be seen in Table IX the nature of the solvent and solute has a pronounced influence on the discharge characteristics. One observation is that AgCl electrodes can not be discharged in electrolytes which contain KPF₆. A possible explanation of this phenomenon may be that potassium chloride, KCl, which is highly insoluble in most organic electrolytes, forms an insulating film on the surface of the electrode or perhaps precipitates in the pores of the electrode and inhibits the cathodic reduction.

Another factor which influences the discharge characteristics of AgCl electrodes is the current density. Table IX-B illustrates the decrease of coulombic efficiency from 100% to 28% as the cathodic current density increases from 0.7 to 5.0 ma/cm² for a AgCl-acetylene black electrode.

The method used to prepare AgCl electrodes has an effect on their behavior. The preparative methods investigated have included pasting, pressing, and sintering mixtures of AgCl with additives such as silver oxide, silver flakes, graphite, and acetylene black onto platinum or silver grids. The highest discharge efficiencies were obtained with electrodes containing 90% AgCl and 10% acetylene black; pasted or pressed electrodes performed better than electrodes which were sintered at 400°C.¹⁴

The amount of material used or mix weight (expressed in grams mix/cm² of electrode) has an inverse effect on the efficiency of cathodic utilization. Table IX-D shows that as the mix weight increases from 0.025 to 0.15 g/cm² the efficiency drops from 97% to 19% for a AgCl, Ag flake, graphite electrode. The effect of temperature, as illustrated in Table IX-E, is that as the temperature increases the electrode polarization at any given current density decreases.

The cycling behavior of Ag-AgCl electrodes which contained solid LiCl as part of the electrode mix has been investigated. The LiCl was incorporated into these electrodes to provide a source of chloride ion for the charging cycle of the battery. This concept offers the advantages that electrolytes containing chloride ion are not required, and mass transport problems are reduced. To test this concept a mixture of 29 mg of silver powder and 11.4 mg of LiCl (stoichiometric ratio) was pressed at 1500 pounds pressure into a recessed platinum electrode, and cycled to 25% depth at 8.5 and 4.2 ma/cm² in 0.5F LiClO₄-PC electrolyte. Cycling efficiencies of 93-100% were achieved.⁴¹

Other Metal Halide Electrodes

The electrochemical behavior of several other transition metal halides has been investigated. The materials studied have included cobalt fluoride (CoF₃), chromium fluoride (CrF₃), nickel fluoride (NiF₂), nickel chloride (NiCl₂), silver fluoride (AgF), silver difluoride (AgF₂), manganese fluoride (MnF₃) and antimony fluoride (SbF₃). In general, the cathodic reduction of these compounds is characterized by higher polarization and lower coulombic efficiency than is found with silver and copper halides. So far, the cathode-electrolyte systems utilizing these metal halides have

not shown much promise under test conditions. The results of the tests which have been performed are as follow:

Cobalt Fluoride - CoF_3 electrodes have been prepared by pasting,²¹ hot pressing,⁴⁹ dry pressing,²⁸ and filter cake,^{6,21} techniques. Cathode mixtures of 70-95% CoF_3 and 5-30% conductive and binding additives have been utilized. These electrodes were discharged in 1.0F $\text{LiClO}_4\text{-PC}$,^{21,49} 1.0F $\text{NaPF}_6\text{-PC}$,²¹ 2.4F $\text{LiClO}_4\text{-MF}$,⁶ and 1.0F $(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6\text{-AN}$ ²⁸ at current densities of 0.04 - 2.0 ma/cm^2 . The highest coulombic efficiencies, which were about 30%, were obtained in $\text{LiClO}_4\text{-PC}$ electrolyte.^{6,49} At low current densities (0.05 ma/cm^2) two voltage plateaus were observed; one at 3.1-3.25 V and one at 2.3-2.6 V vs a lithium electrode. At the higher current densities the voltage decreased steadily from 2.3 V to 0 V, and no voltage plateaus were found. Ferromagnetic measurements on the discharged electrodes indicated that metallic cobalt was present.

Chromium Fluoride - Electrodes containing 85% CrF_3 , 10% graphite, and 5% polyethylene powder have been prepared by the hot pressing technique. When discharged at 1.8 ma/cm^2 in 1.0F $\text{LiClO}_4\text{-PC}$ the potential of these electrodes decreased steadily from 1.3 V to 0 V vs a lithium reference electrode. The coulombic efficiency under these conditions was 8%.⁴⁹

Nickel Fluoride and Nickel Chloride^{6,30,36,37} - NiF_2 and NiCl_2 electrodes have been prepared from mixtures containing graphite, and asbestos fibers pressed onto metal screens, and also by incorporating the NiF_2 and NiCl_2 into sintered nickel matrices. Both types of electrodes exhibited severe polarization and coulombic efficiencies of less than 30% when discharged in 1.0F $\text{LiClO}_4\text{-PC}$ or 2.4F $\text{LiClO}_4\text{-MF}$ electrolytes. Attempts to improve performance by doping the NiCl_2 electrodes with sulfur and MgCl_2 and the NiF_2 electrodes with MgF_2 have yielded inconclusive results.³⁷

Electrodes containing AgF and AgF_2 ,^{5,6,10,29,44,56} MnF_3 ,⁵ SbF_3 ,³⁰ and CaF_2 ⁵⁷ have been examined in half-cell studies. However, the results of these studies are still preliminary and shall not be summarized in this report.

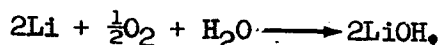
Metal Oxide Electrodes

Of the several metal oxides which have been investigated to date only silver oxide can be electrochemically reduced in organic electrolytes.^{5,9,29,30,50} Other oxides which have been studied include manganese dioxide (MnO_2),^{2,6,28,29,44} chromium oxide (CrO_3),^{5,44} vanadium oxide (V_2O_5),^{2,6,30,44} stannic oxide (SnO_2),² cupric oxide (CuO),² iron oxide (Fe_3O_4),³⁰ nickel oxide (NiO),³⁰ and lead oxide (PbO_2).²⁸ These compounds were found to be either electrochemically inert, or reduced with such low efficiency and high polarization that they appeared to be useless.

Silver Oxide - Electrodes prepared by pressing a mixture of 3.0 g Ag_2O , 1.5 g graphite, and 0.5 g asbestos fiber onto silver screen have been discharged in 2.4F $\text{LiClO}_4\text{-MF}$ at -15° and 1.5F $\text{LiClO}_4\text{-PC}$ at 25° . At current densities of 0.5 to 0.7 ma/cm^2 the voltage of these electrodes ranged from 3.66 V to the cut-off of 1.9 V; coulombic efficiencies of up to 40% were obtained.⁶

Air Electrodes

The cathodic reduction of oxygen in organic electrolytes has been studied³⁵ to determine the feasibility of a lithium-moist air battery with the proposed cell reaction,



Pure oxygen has been reduced at a platinum electrode immersed in 1.0*M* LiClO_4 -*N*-nitrosodimethylamine and in 1.0*M* $(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6$ -*N*-nitrosodimethylamine. From voltammetric sweep data it was concluded that the reduction occurs in two steps; the first step at -0.6 V and the second at -1.75 V vs a Ag/AgCl reference electrode. The peak currents from the voltammetric sweep data were found to increase as the time of hold at open circuit potential was increased indicating that the reduction was limited by the rate of diffusion or adsorption of oxygen at the electrode.

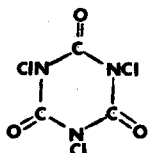
Under galvanostatic conditions (1 ma/cm²) the polarization of the oxygen electrode was found to increase with time. This observation has been interpreted as indicating a buildup of insoluble reaction products at the electrode.

Organic Cathode Materials

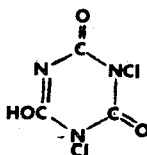
Several organic halogen and nitro compounds have been tested as possible cathode materials for primary, organic electrolyte batteries. Included in these tested have been hexachloromelamine, trichloroisocyanuric acid and its derivatives, *N*-chlorosuccinimide, aromatic nitro- and nitroso-compounds, and dichlorobenzquinonediimine. Many of these compounds offer higher theoretical energy densities than, for example, the metal halides, provided that complete reduction of the organic compounds can be achieved.

Electrochemical studies of these compounds have revealed that some of them are reduced in organic electrolytes at potentials of greater than +3 V vs a lithium anode at current densities on the order of 10 ma/cm². These compounds are, therefore, electrochemically as reactive as the copper halides. However, the coulombic efficiencies achieved with the organic cathodes have been either not reported or they have been based on a hypothetical reaction. This has been done because neither the reaction mechanisms nor the reaction products of the cathodic reduction of organic compounds in aprotic electrolytes have been identified experimentally. This general lack of basic data makes it impossible to estimate the chances of success of organic cathode materials in organic electrolyte primary batteries.

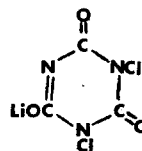
Tri-chloroisocyanuric acid and its derivatives: The cathodic reduction of the following compounds has been investigated:^{6,30,65}



Trichloroisocyanuric acid



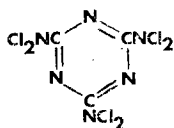
Dichloroisocyanuric acid



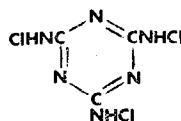
Lithium (or potassium) di-chloroisocyanurate

The highest voltages (vs lithium) and coulombic efficiencies were obtained for di-chloroisocyanuric acid (see Table X-A). The data indicated that for none of these compounds was more than one chlorine functional group readily available for reaction at potentials greater than +2 V vs lithium anode.

Hexachloromelamine and derivatives: The compounds in this category which have been studied include



Hexachloromelamine



Trichloromelamine

The electrochemical behavior of solutions of these compounds has been investigated by potentiostatic, steady-state techniques. The results of some of these studies are outlined in Table X-B. At 1.0 V cathodic polarization hexachloromelamine is reduced at a carbon electrode with current densities of up to 80 ma/cm². This indicates that its electrochemical activity is higher than that of trichloromelamine or trichloroisocyanuric acid.

N-chlorosuccinimide; m-Dinitrobenzene; 2,4-Dinitrophenol; Picric Acid; 4-Nitrosophenol; p-Quinonedioxime: These compounds have been studied using the technique of linear potential sweeps. Peak voltages and currents for the cathodic reduction of these compounds, dissolved in electrolyte solutions, are shown in Table X-C. 4-nitrosophenol and p-quinonedioxime were not reduced in the voltage range studied,²⁹ while 2,4-dinitrophenol exhibited a reduction peak which was unaffected by increases in the concentration of the material.³⁰ The peak currents for the reduction of N-dichlorosuccinimide were found to increase with increasing concentration.³⁰ m-Dinitrobenzene and picric acid have been discharged as pasted electrodes which contained equal weights of active material and carbon. The results of these discharges, shown in Table X-D, reveal that both of these compounds are discharged with high coulombic efficiencies, and that m-dinitrobenzene exhibited two voltage plateaus (at +2.7 V and +1.2 V vs lithium), while picric acid exhibited only a gradual voltage decrease from about 3 V to zero volts.

Dichlorobenzquinonedimine: When this compound was reduced at 15.5 ma/cm² in LiClO₄-MF and LiClO₄-DMF a single voltage plateau at 1.8-2.2 V was observed.⁶⁴

TABLE X

ELECTROCHEMICAL BEHAVIOR OF ORGANIC CATHODE MATERIALS

A. Discharge of Trichloroisocyanuric Acid and its Derivatives in
1.0F LiClO₄-MF⁶₅Electrodes: 0.65g active material, 0.35g carbon, 0.05g carbon
fiber

Counter Electrode: lithium

Conditions: 15 ma/cm² to 2.0 V cut-off

Compound	Cell Voltage	Coul. Eff.
Dichloroisocyanuric acid	3.4-2.0	49%
Li-dichloroisocyanurate	3.0-2.0	37%
Trichloroisocyanuric acid	3.0-2.0	31%

B. Steady-State Current for Cathodic Reduction of Compounds

Dissolved in 1.0F LiPF₆-DMF³⁰Working Electrode: Speer HP-10 carbon, 1 cm²Counter Electrode: 1 cm² lithium

Reference Electrode: Ag/AgCl

Conditions: Potentiostatic; 1.0 V cathodic polarization

Compound	Current (ma/cm ²)
0.1F Trichloroisocyanuric acid	10
1.0F " "	10
1.0F Trichloromelamine	10
0.1F Hexachloromelamine	40
1.0F " "	80

C. Linearly Varying Potential Scans of Organic Compounds²⁹Electrodes: Working and counter electrodes are Speer HP-10
carbon; 1 cm²

Reference Electrode: Ag/AgCl

Conditions: Organic compounds dissolved in electrolyte; 0.1F
concentration; 50 mv/sec scan rate

Compound	Peak Voltage and Current	
	1.0F LiPF ₆ -DMF	1.0F LiPF ₆ -NDA
N-Chlorosuccinimide	+0.5V; 7 ma	+0.1V; 9 ma
m-Dinitrobenzene	-0.5V; 7 ma	-0.4V; 6 ma
2,4-Dinitrophenol	-0.3V; 7 ma	
Picric Acid	+0.1V; 6 ma	

TABLE X (CONT'D)

- D. Discharge of m-Dinitrobenzene and Picric Acid⁵⁰
 Cathodes: 0.25g organic material, 0.25g carbon, wet pasted onto
 15.2 cm² expanded copper
 Anodes: Two lithium electrodes, 15.2 cm²
 Separator: Two layers of 15 mil glass fiber filter paper
 Conditions: Galvanostatic; 2 ma/cm² at room temperature

Compound	Electrolyte	Coul. Eff.	Plateau Voltage (vs Li)
m-Dinitrobenzene	1.0F LiClO ₄ -PC	20%	2.4 - 2.0
m-Dinitrobenzene	2.0F LiClO ₄ -DMC	94%	2.7; 1.2
Picric acid	2.0F LiClO ₄ -DMC	70%	3.0 → 0

SEPARATORS

Separators for use in organic electrolyte batteries should have the following properties:

1. Compatibility with organic electrolytes and highly reactive electrode materials.
2. Sufficient mechanical strength to prevent short circuiting of the cell during discharge and prolonged activated storage.
3. Low ohmic resistance to reduce IR loss during discharge.
4. High permeability for ions participating in the electrochemical reaction to minimize concentration polarization.
5. Low permeability for dissolved electrode materials to assure long shelf life on activated stand.

The materials which have so far shown the best overall performance include non-woven porous materials such as asbestos filter paper, glass fiber filter paper, polyolefin mats, and microporous rubber. However, no materials have as yet been found which will prevent or reduce the diffusion of dissolved cathode materials from the catholyte to the anode.

Methods of Experimental Evaluation of Separators

Compatibility Tests: The separator materials were immersed in various electrolytes for extended periods of time. The separator-electrolyte compatibility was then judged by visual observation of the samples.²

Separator Swelling: The amount of swelling which the separator materials underwent when exposed to electrolyte was measured by comparing

the thickness of the material before and after it had been immersed in the electrolyte for a period of time sufficient for equilibrium to be reached.⁴⁹

Electrolyte Absorption: A sample of separator material was weighed before and after equilibration with the electrolyte. The percentage absorption was then calculated using the equation,^{21, 49}

$$\text{Absorption (\%)} = \frac{\text{wet wt.} - \text{dry wt.}}{\text{dry wt.}} \times 100 .$$

Electrolyte Retention: A weighed sample of separator material was equilibrated with electrolyte, and then either drained for 30 minutes on a glass plate inclined at 45°, or centrifuged for 2 minutes at 25g²¹ before reweighing. The percentage of electrolyte retention was then calculated from

$$\text{Retention (\%)} = \frac{\text{drained wt.} - \text{dry wt.}}{\text{wet wt.} - \text{dry wt.}} \times 100 ,$$

or

$$\text{Retention (\%)} = \frac{\text{centrifuged wt.} - \text{dry wt.}}{\text{wet wt.} - \text{dry wt.}} \times 100 .$$

Separator Resistance:⁴⁹ Resistance measurements were made using an AC impedance bridge and a cell equipped with platinized platinum electrodes. The resistance of the separator was calculated using the relation, $R_s = R_t - R_o$, where R_s is the separator resistance, R_t is the resistance of the cell with the separator interposed midway between the platinized electrodes, and R_o is the resistance of the cell with only the electrolyte present. The specific resistance of the separator, ρ , was defined by the equation

$$\rho = \frac{R_s \times A}{L}$$

where A is the area (cm²) and L (cm) the thickness of the separator.

Separator Cell Tests:⁴⁹ The cell utilized in testing the separator materials consisted of one cathode flanked by two lithium anodes with separators being interposed between the cathode and each anode. The cathode, which had a theoretical capacity of 0.8 AH, was prepared by hot pressing a mixture of 85% CuF₂, 10% carbon, and 5% binder onto a metal grid. The anodes had a theoretical capacity of 1.0 AH each. 1.0M LiClO₄-PC was employed as the electrolyte. The AC impedance of each cell was measured before the discharge was started. The discharge was carried out at a constant current density of 2.0 ma/cm² until a potential of 0 V was reached. The coulombic efficiencies were calculated, and a post mortem inspection of the cell components conducted.

TABLE XI
SEPARATOR PROPERTIES⁴⁹

Electrolyte: 1.0F LiClO₄-PC
Cell: Two lithium anodes; one copper fluoride cathode
Discharge: 2 ma/cm² to final potential of 0 V

Separator Material	Thickness (mils)		Electrolyte		Specific Resistance (ohm cm)	Cell Tests		
	dry	wet	Absorption	Retention		Separator Thickness	Cell Resistance (Ohm)	Cathodic Coul. Eff.
Asbestos Filter Paper	15	19	945%	94%	90	2x15 mil*	—	84%
Non-Woven Polypropylene (Kendall Mills, H-612)	50	100	1920%	97%	434	1x50 mil	10.1	70%
Glass Filter Paper (Hurlbut, 934-AH)	15	15	710%	98%	110	2x15 mil	7.4	69%
Glass Mat, Styrene Bound (Hydromatic packing)	30	32	1130%	97%	100	1x30 mil	1.3	68%
Polypropylene Mat (Pellon FT-2140)	10	10	345%	76%	415	1x10 mil	3.8	64%
Polypropylene Mat (Pellon 34-235)	15	15	620%	93%	208	2x15 mil	—	64%
Porcus Polyethylene (ESB, Porothene)	2	2	368%	27%	1611	1x2 mil	3.0	63%
Kimwipes #900-S (Kimberly-Clark)	5	6	735%	50%	281	3x5 mil	4.4	63%
Filter Paper (S&S #589)	8	8	162%	88%	710	2x8 mil	4.7	49%
Asbestos Fuel Cell Paper (Johns Mansville)	15	35	448%	96%	88	1x15 mil	8.6	16%
Lexan Film (GE)	1	2	199%	43%	>35000	1x1 mil	4.7	16%
Cas Ion Exchanger (ESB, #1021)	8	13	29%	69%	>5500	1x12 mil	7.2	7%

*First number here refers to number of layers; the second number indicates the thickness of each layer

Cell Storage Tests: Test cells were stored after activation for various lengths of time under controlled conditions. They were then discharged to determine their coulombic efficiency and energy density,^{6,9,49} or opened, without being discharged, and the amount of copper which had precipitated at the anode and in the separator analytically determined.⁵³

Results of Separator Evaluation

The results of the evaluation of a number of separator materials are collected in Table XI. These results reveal that the best performance is obtained with non-woven fibrous materials such as asbestos and glass-fiber filter paper, which exhibit low resistances and high electrolyte absorbence and retention. Materials which have high resistance and low electrolyte absorbence and retention such as Lexan Film and cadmium sulfide ion exchanger gave the lowest coulombic efficiencies in the cell tests. It was noted that the loss of efficiency was not caused by short-circuiting due to dendrite formation, but instead appeared to be caused by excessive polarization due to the low permeability of the separator material.

Separators made from asbestos, polypropylene fiber, and glass-fiber have been shown to be compatible with PC electrolytes and lithium and copper halide electrodes. However, they have proved to be ineffective in reducing self-discharge in these cells. Also, their high electrolyte absorption is undesirable since the extra electrolyte required adds to the dead weight of the cell.

Storage tests have been carried out with lithium-copper fluoride cells. These cells were discharged through a constant 200-ohm load after various periods of storage at room temperature. The results of these storage tests are summarized in Table XII.

TABLE XII

EFFECT OF STORAGE TIME ON Li/CuF₂ CELLS⁶

Electrodes: Two lithium electrodes (5.5-6.0 amp-hr capacity);
one CuF₂ electrode; (4.0 amp-hr capacity)
Electrolyte: 1.4F LiClO₄-PC
Separator: 1.1 mm microporous rubber
Conditions: Discharged across 200 ohm load until potential
of 0 V reached

Time of Storage	Length of Discharge
0 weeks	150 - 225 hours
1 week	90 - 105 hours
2 weeks	20 - 50 hours

The activated storage capability of cells similar to the ones mentioned above has been investigated at two different temperatures. The capacity of cells stored at -15°C did not noticeably change over a period of six weeks. Cells stored at 35°C had completely lost their charge after only two weeks.

The rate of self discharge of lithium-copper chloride cells has also been determined.⁵³ Cells consisting of one lithium anode and two copper chloride cathodes, separated by two layers of Pellon 2517 or Pellon 405B, were utilized. The electrolyte was 0.3F LiCl, 3.0F AlCl_3 -PC, 55% NM. After two weeks activated storage at room temperature, these cells were disassembled, and the copper deposited on the anode and in the separator analytically determined. The rate of self-discharge for these cells was calculated as being $5-7 \times 10^{-3} \text{ mg Cu/cm}^2\text{-day}$.

COMPLETE ORGANIC ELECTROLYTE BATTERIES

Several of the components which exhibited acceptable performance in the individual tests described in the preceding chapter of this report have been incorporated into complete, experimental batteries. These batteries have been tested under various conditions of discharge and cycling to determine their voltages of operation, capacities, energy densities, cycle lives, and shelf lives. The results of these tests along with the details of construction and test procedures will be discussed below.

Before the test results are described it should be pointed out that no attempts have yet been made to optimize the design of battery packages for organic electrolyte systems. In the case of the cells described below the packages have been designed for ease of fabrication using simple laboratory procedures, and do not represent the design optimum, which may be achieved in the future.

It was found in preparing this summary of the test results that the methods of reporting test data are as numerous as are the people making the reports. This inconsistency in reporting makes it difficult in some cases to compare the work of the various investigators. Therefore, the last part of this chapter has been devoted to a discussion of a method of data analysis which may help to alleviate this problem. The utility of this method of analysis will be demonstrated by applying it to some of the data summarized below.

Flat Plate Primary Batteries

Battery System:	$\text{Li/LiClO}_4\text{-MF/CuF}_2$
Source:	Livingston Electronics Corporation ^{6,7}
Construction:	<u>Anodes:</u> Two lithium anodes of 5.18 amp-hr capacity with 30 cm^2 electrode area, made by pressing lithium metal onto expanded silver mesh. <u>Cathodes:</u> One CuF_2 cathode of 3.85 amp-hr capacity and 30 cm^2 electrode area, made by pressing mixture of 82.6% CuF_2, 11.6% graphite,

and 5.8% paper pulp onto expanded silver mesh.

Separator: 0.03-inch-thick microporous rubber.

Electrolyte: 6.0 ml of 4.68F LiClO_4 -methyl-formate.

Casing: Polyethylene envelope; total cell weight 21 grams.

Performance:

This battery yielded 124 whr/lb when discharged to 2.0 V cut-off across constant load of 100Ω (70 hr. rate) at -15°C . Average voltage was 2.72 V; at the 30-hour rate under these conditions the energy density was 94 whr/lb; at 35°C 83 whr/lb at the 20-hr. rate; shelf life is poor and is probably limited by attack of electrolyte on lithium anode.

Battery System:

$\text{Li/LiClO}_4\text{-PC/CuF}_2$

Source:

Livingston Electronics Corporation^{6,7,9}

Construction:

Anode: Two Li anodes of 5.10 amp-hr capacity and 30 cm^2 electrode area.

Cathode: 82.6% CuF_2 , 11.6% graphite, and 5.8% paper pulp; 4.97 amp-hr capacity and 30 cm^2 area.

Separator: 0.03 inch microporous rubber.

Electrolyte: 7.0 ml of 1.4F LiClO_4 - propylene carbonate.

Casing: Polyethylene envelope; total cell weight 25 grams.

Component Weight (in grams and % of total battery weight):

cathode, CuF_2	9.4 (37.6%)
graphite	1.3 (5.2%)
paper pulp	0.7 (2.8%)
Ag mesh	0.3 (1.2%)
anodes, lithium	1.3 (5.2%)
Ag mesh	0.6 (2.4%)
electrolyte	9.3 (37.2%)
separators	1.3 (5.2%)
PE envelope	0.8 (3.2%)
total	25.0 (100%)

Performance:

When discharged across 200Ω load (265 hr. rate) at 35°C this cell yielded 223 whr/lb with an average voltage of 3.05 V (3.3 V to 2.0 V cut-off); when stored at 35°C cells underwent

complete self-discharge within a few days, but were stable for six weeks at -15°C ; dissolution of CuF_2 caused self-discharge.

Battery System:

$\text{Li/LiClO}_4\text{-PC/CuF}_2$

Source:

The Electric Storage Battery Company⁴⁹

Construction:

Anode: Five lithium anodes made by pressing Li ribbon onto copper screen; 120 cm^2 total area.

Cathode: 85% CuF_2 , 10% graphite, and 5% polyethylene powder pressed onto copper screen; four cathodes used in each cell had total capacity of 7 amp-hr.

Separator: 0.015 inch glass fiber filter paper.

Electrolyte: 15 ml of 1.0M LiClO_4 -propylene carbonate.

Casing: Vacuum formed polyethylene

Component weights (in grams and % of total battery weight):

cathode, mixture	15.45 (33.7%)
copper screen	2.43 (5.3%)
anodes, Li metal	2.23 (4.6%)
copper screen	1.27 (2.8%)
separators	1.41 (3.1%)
electrolyte	18.00 (39.5%)
PE casing	5.04 (11.0%)
total	45.83 (100%)

Performance:

Discharged at constant current and room temperature from about 3.3 V open circuit to 0 V. Obtained voltage plateau at approximately 3 V with energy densities and coulombic efficiencies as follow:

current density (ma/cm ²)	0.5	1.0	2.0	3.0
energy* density (whr/lb)	52	117	120	99
coulombic efficiency (%)	27	60	57	53

*Energy densities based on final voltage of 0 V.

The low energy density at 0.5 ma/cm² discharge has been attributed to self-discharge. Higher and lower temperatures also caused decreased performance when batteries were discharged at 2 ma/cm². At 0°C these batteries yielded 27 whr/lb and 19% efficiency while at 40°C they yielded 105 whr/lb and 56% efficiency. Lower performance at 0°C explained by concentration polarization, and at 40°C by increased rate of self-discharge.

Battery System:

Li/LiAlCl₄, AlCl₃-PC, NM/CuCl₂

Source:

Electrochimica Corporation^{52,53}

Construction:

Anode: Li metal pressed onto metal grid.

Cathode: 85.0% CuCl₂, 7.5% silver powder, and 7.5% carbon black pressed onto copper grid; 0.38 mm thick with capacity of 0.8 to 1.0 amp-hr.

Separator: Two layers of polypropylene mat.

Electrolyte: 3.0F AlCl₃, 0.3F LiCl - propylene carbonate containing 55% nitromethane.

Performance:

Open circuit voltage 3.1 V. When discharged at room temperature the following results were obtained:

discharge rate (min)	60	30	15
current (ma)	700	2000	4000
current dens (ma/cm ²)	7.2	19.4	38.8
voltage range	2.3-1.6	2.2-1.9	2.0-1.5
energy dens (whr/lb)	27	29	25
current eff. (%)	82	100	84.5

Rate capability was outstanding. Self-discharge due to CuCl₂ dissolution is main problem with this battery.

Battery System:

Li/proprietary electrolyte/CuCl₂

Source:

Electrochimica Corporation⁵⁴

Construction:

Anode: Li metal pressed onto metal grid.

Cathode: CuCl₂ mixture with capacity of 0.8 to 1.0 amp-hr.

Separator and Electrolyte: Not reported.

Casing: A standard metal casing used by this company on other types of commercial batteries.

Performance:

This battery system is claimed to operate satisfactorily over a wide range of temperatures. When discharged at 100 ma (10-hr rate) the following results were obtained:

Temperature, °C	-54	-40	27	71
Plateau voltage	1.4-0.8	2.0	2.5	2.5
Coul. Eff.	24%	77-95%	100%	70-80%
Energy dens (whr/lb)	5	28	38	28

At 71°C self-discharge becomes appreciable in this system. Outstanding performance at low temperatures down to -40°C.

Battery System:

Li/LiClO₄-MF/ACL-70*

Source:

Monsanto Research Corporation⁶⁵

Construction:

Anode: Li metal pressed onto one side of polypropylene separator tape.

Cathode: Mixture of 81% dichlorotriazinetrione (ACL-70), 13% Shawinigan acetylene black, and 6% carbon fiber pressed onto separator.

Separator: 0.003-inch polypropylene tape.

Electrolyte: 1.9 ml of 1.0M LiClO₄ - methyl formate.

Casing: This system has been investigated for possible use in tape batteries currently under study at Monsanto; in these experiments the active electrode materials were supported on either side of a polypropylene tape in the normal tape battery configuration; however, for test purposes the tapes were pressed at 4 lb/in² between metal current collectors and discharged under static conditions.

Component weights (in grams and % of total component weight):

anode, Li metal	0.30 (7.5%)
cathode, ACL-70	1.30 (32.7%)
carbon black	0.20 (5.0%)
carbon fiber	0.10 (2.5%)
separator	0.05 (1.3%)
electrolyte	2.02 (51.0%)
total	3.97 (100%)

*ACL-70 - Monsanto's Tradename for Dichlorotriazinetrione

Performance: When discharged at 7.8 ma/cm^2 (158 min.) these tapes had a voltage range of 3.7 to 2.0 V with an average voltage of 3.18 V. They delivered 144 whr/lb (to 2.0 V cut-off) with a coulombic efficiency of 58% (assuming both chlorine atoms in ACL-70 are active). The tests were performed at room temperature.

Flat Plate Secondary Batteries

Battery System: Li/LiAlCl₄-PC/AgCl

Source: Lockheed Missiles and Space Company^{12,14}

Construction: Anode: Li metal anodes prepared by pressing Li onto silver screen; 10 anodes/battery.
Cathode: Mixture of 75% AgCl, 15% Ag₂O, and 10% graphite pressed onto silver screen; 9 cathodes/battery with 5 amp-hr capacity and 300 cm² area.
Separator: Glass-fiber mat.
Electrolyte: 0.6F LiAlCl₄ in propylene carbonate.
Casing: Sealed aluminum cans; total cell weight 275 grams.

Performance: For single discharge at 1.4 ma/cm^2 from open circuit potential of 2.85 V to 1.90 V obtained 28 whr/lb with 80% cathode utilization. Cells had average voltage of 2.5 V and a cycle life of 30-50 cycles when cycled at a current density of 1 ma/cm^2 and depths of discharge varying between 9% and 78%. With 100% depth of discharge cells failed after 7 cycles. Lifetime limited by poorly adherent Li formed during charge. Appears to be promising system for low rate, long life operation.

Battery System: Li/KPF₆-PC/NiX₂

Source: Gulton Industries^{37,39}

Construction: Anode: Mixture of 90% Li powder and 10% graphite.
Cathode: 50% NiX₂ and 50% graphite; composition of NiX₂ unknown, but preparation was by treating NiF₂ with thionyl chloride, and thus partially converting the fluoride to the chloride.

Electrolyte: KPF_6 dissolved in either propylene carbonate or dimethylsulfoxide.

Performance:

The following results were obtained for single discharges:

current density (ma/cm^2)	2	100
voltage range (V)	3.0-1.0	1.6-0.6
coulombic efficiency (%)	66	33
energy density (whr/lb)	60	6

This system has been cycled 20 times at $2 \text{ ma}/\text{cm}^2$ for both charge and discharge with a 10% depth of discharge. It delivered an average voltage of 2.0 V under these conditions.

Battery System:

$\text{Li}/\text{KPF}_6\text{-BL}/\text{AgF}_2$

Source:

Whittaker Corporation^{56,57}

Construction:

Anode: Li metal pressed onto silver grid; two anodes/battery.

Cathode: Mixture of AgF_2 , carbon, and polyethylene binder pressed onto silver grid; one/battery.

Separator: Non-woven nylon.

Electrolyte: Saturated solution of KPF_6 in butyrolactone.

Casing: Heat-sealed polyethylene bag.

Performance:

Open circuit potential 3.7 V; voltage plateau on discharge at $1 \text{ ma}/\text{cm}^2$ was 3.0 V-3.4 V. When charged and discharged at this current density to a low voltage cut-off of 1.0 V, a depth of discharge of 90% was obtained. During first 10 cycles of operation, the charge-discharge efficiency was 99%, but this dropped to 70% after 40 cycles. Lead breakage was chief failure which limited cycle life in this battery.

Analysis of Results With the Figure of Merit Expression

As can be seen from the foregoing presentation of the performance data for a variety of cell tests, there is a lack of consistency in the methods chosen for reporting the results. This lack of consistency makes it difficult in some cases to adequately compare the work of different

investigators, and may even lead to a misinterpretation of the results. It is therefore suggested that a standard method of reporting the results of discharge tests, based on the figure of merit expression, described below, be adopted.¹

The figure of merit expression takes into account the three main factors which determine the energy density of a given battery under a given set of conditions. These factors are the thermodynamic properties of the electrode couple, the electrochemical behavior of the cell, and the design of the battery package.

The equation which defines the figure of merit M_w , is

$$M_w = Q_0 K_1 K_2$$

where Q_0 = the calculated thermodynamic energy density of the electrode couple. K_1 = a proportionality factor which describes the electrochemical efficiency of the electrode reaction, taken as being equal to the product, voltage efficiency (e_v) times coulombic efficiency (e_c). The voltage efficiency is the average voltage of the battery during discharge divided by the standard potential of the electrode couple, and the coulombic efficiency is the coulombs delivered by the battery divided by the theoretical coulombic capacity of the electrodes. K_2 = a proportionality factor which describes the design efficiency of the battery package, taken as being equal to the weight of the active electrode material divided by the weight of the total battery package. This equation has been utilized to analyze some of the data presented in this chapter (Table XIII).

The agreement between the calculated energy densities shown in the Table and the experimentally determined energy densities indicates that the figure of merit expression gives a good representation of the results. Further, by comparing the individual values for the parameters, Q_0 , e_v , e_c , K_1 , and K_2 , it is possible to analyze the weakness of the various systems and to determine in what fashion varying the conditions of discharge and the battery design affects the battery performance.

As an example of how this system of evaluation might be used, the following analysis of the data presented in Table XIII is given:

1. Comparison of the e_c factors (coulombic efficiency) for Li/CuF₂ cells under a variety of conditions reveals that at low discharge rates, when glass-fiber separators are used, the lack of coulombic efficiency is the main cause of the low energy density; this may well be due to self-discharge. By changing the conditions of discharge, e.g., a slightly higher temperature and a microporous rubber separator, this problem is considerably reduced.

2. When LiClO₄-MF electrolyte and lower temperature, -15°C, are used both the voltage efficiency, e_v , and the coulombic efficiency, e_c , are reduced.

3. The lithium-silver chloride secondary system suffers from a low theoretical energy density, and, for the set of data illustrated here,

TABLE XII

THE FIGURE OF MERIT
EVALUATION OF DISCHARGE DATA

Electrode Couple	Li/CuF ₂	Li/CuF ₂	Li/CuF ₂	Li/CuF ₂	Li/CuF ₂	Li/CuF ₂	Li/AgCl
Electrolyte	LiClO ₄ -PC	LiClO ₄ -PC	LiClO ₄ -PC	LiClO ₄ -PC	LiClO ₄ -PC	LiClO ₄ -MF	LiAlCl ₄ -PC
Separator	glass fiber	glass fiber	glass fiber	glass fiber	micropor. rubber	micropor. rubber	glass fiber
Temperature	25°C	25°C	25°C	25°C	35°C	-15°C	25°C
Current Dens. (ma/cm ²)	0.5	1.0	2.0	3.0	0.5	0.9	1.4
Q ₀ (whr/lb)	749	749	749	749	749	749	229
e _v	0.85	0.85	0.85	0.85	0.86	0.77	0.88
e _c	0.27	0.60	0.57	0.53	0.81	0.49	0.80
K ₁	0.23	0.51	0.49	0.45	0.70	0.38	0.70
K ₂	0.34	0.34	0.34	0.34	0.43	0.41	0.10
M _v (Calcul.)	58	128	122	113	225	115	16
M _v (Exper.)	52	117	120	99	223	124	28

from a low weight efficiency. If the "dead weight" in the cell could be reduced to achieve a weight efficiency comparable to that obtained for the lithium-copper fluoride cells, the energy density might be increased by a factor of 3-4.

The above discussion serves to illustrate the utility of this method of analysis, and shows how easily different conditions and different systems can be compared. However, this type of evaluation should be used primarily as a method of summarizing the data, not as a substitute for a detailed discussion where all of the known facts are brought to bear.

PROBLEM AREAS AND AREAS OF FUTURE WORK

Organic electrolyte cells have been constructed which delivered higher energy densities than 200 wh/lb. However, these cells have exhibited several shortcomings which have so far frustrated attempts to develop a practical organic electrolyte battery. These shortcomings are as follow:

1. Lack of rate capability.
2. Lack of shelf life.
3. Lack of cycle life and cycling efficiency in secondary systems.

In order to overcome these limitations and to provide the additional data required for battery design, the following efforts are felt to be necessary.

To Improve the Rate Capability

1. Unambiguous experiments are needed to identify the factors which cause the rate limitation in organic electrolyte systems. The identification of these factors would then serve as a basis for a systematic approach to improve the rate capability.

2. Attempts should be made to find electrolytes with high conductivities, high solute solubilities, and low viscosities in order that higher rates of mass transfer can be achieved. Solvents with low dielectric constants, which usually do not strongly solvate ionic substances, should not be left out of these investigations, since solvation mechanisms other than ion-dipole interaction are known to exist.

3. Investigations must be conducted to find suitable separators which have high permeability for the ions involved in the electrode reactions. This work should include the measurement of diffusion coefficients, transference numbers, and membrane potentials as well as the other factors which affect the membrane performance such as electrolyte absorbence, membrane swelling, and perm-selectivity.

4. The buildup of reaction products such as LiF and LiCl in the cathode should be investigated to determine what effect it has on the rate capability of the electrode. An adverse effect might be corrected by choosing an electrolyte in which the reaction products are more soluble so

that the pores of the cathode would remain open during discharge. To effectively choose a new electrolyte system, however, would require an understanding of the ionic equilibria in organic electrolytes as well as a knowledge of the transference numbers of the soluble species. Another approach to the problem might be to attempt to find electrolytes which would provide for the formation of a porous precipitate of reaction products on the anode rather than the cathode.

5. Slightly soluble salts that can supply ions for the electrochemical reactions by means of a salt transformation cycle may be incorporated into the cathode mix, thus minimizing mass transport problems and providing higher rates in starved electrolyte configurations and in secondary systems.

6. The rate capability may be improved by increasing the rate of mass transport in the cathode. This might be accomplished by preparing electrodes with well-defined porosity and structure designed to provide natural convection during charge and discharge. Alternatively, the rate capability might be improved by shortening the path of diffusion of the cathode material to the reactive sites at the conductive additive. This may be accomplished by the use of small particle size metal halide-carbon mixtures in the electrode.

7. Another approach to overcome the rate limitation may be to make metal halides conductive by doping. Semiconductive or electronic conductive cathode materials might be reduced directly, rather than via a mechanism involving dissolved intermediates. Doping techniques for these materials must be developed, however, before this approach can be tested thoroughly.

8. Continuing searches for new cathode systems must be conducted. Organic compounds, especially, may offer higher rates in primary systems, and investigations of these compounds should be increased in both scope and depth.

To Improve the Shelf Life

1. Further research is necessary to determine the causes of self-discharge. This requires an in-depth study of the ionic equilibria between electrolyte and solid electrode materials and reaction products, the goal being the identification of the soluble species and the determination of the solubility products and stability constants for the solution constituents. These studies should also include the determination of the effect on the rate of self discharge of temperature, electrolyte composition, and open circuit storage. These studies of equilibria and the other parameters which affect dissolution and precipitation may also shed some light on how to solve the problem of dendrite formation.

2. The shelf life may be improved by the use of different solvents, solvent mixtures, or solutes in the electrolytes. Another approach might be to incorporate into the cathode mix a slightly soluble salt which would shift the equilibria in the vicinity of the cathode toward the insoluble cathode material.

3. The effects of impurities on the rate of self-discharge need further study. Harmful impurities should be identified and removed from the electrolytes and other battery components by proper purification techniques. Maximum permissible impurity levels should be determined in order that costly purification procedures, which do not improve the shelf life, can be avoided.

4. Separators should be found which prevent the migration of dissolved cathode materials to the anode, but which allow the transfer of the ions which participate in the electrode reactions. Materials which might conform to these specifications include plastic films, ion exchange membranes, or heterogeneous materials which are porous enough to allow the passage of ions such as lithium ion, but which contain particulate matter which adsorb or in some other fashion react with dissolved metal halide complexes so as to prevent their migration to the anode. The field of separators for organic electrolyte systems has been little explored, and there is great need for basic, systematic studies in this area. Separators might also be found which would minimize the problem of dendrite formation. This could be accomplished with materials of sufficient mechanical strength to prevent dendrite formation, or with materials which chemically react with the metal so that dendrites which do form are prevented from growing large enough to short-circuit the cell.

5. The problems associated with the formation of insulating films on lithium anodes should be investigated since these films consume reactive material, cause severe electrode polarization, and prevent complete reaction during discharge. This may be approached by finding practical ways to prevent the diffusion of moisture, oxygen, and nitrogen into the battery. Another approach might be the use of suitable electrolytes or of anodes made from lithium alloys. By the proper choice of these components it would be possible to prevent the reaction of the anode with impurities from the air, and would alleviate the problem of trying to prevent the diffusion of these impurities into the battery.

6. The search should continue for new cathode materials which are insoluble and have little tendency to form dendrites. Organic compounds with functional groups such as N-chloro, perhalide, quinone, or nitro-might be considered for investigation, especially in terms of attempting to control their solubility by polymerization, or polycondensation.

To Improve the Cycle Life and Cycling Efficiency

1. Little is known about the factors which limit the cycle life and cycling efficiency of organic electrolyte, secondary systems. Therefore, these factors must be identified and characterized before a systematic effort to solve the problem can be launched. An approach to eliminate the side reactions which cause the lack of cycle life and cycling efficiency might be to use other electrolytes or electrolytes of higher purity.

2. Practical answers to the problems of overcharge and of charging at too high a rate must be found. These operations cause solvent decomposition with the formation of sludges and insulating films on the electrodes.

3. Further work is necessary to improve the structure of electro-deposited lithium. The aim should be to obtain compact, non-dendritic deposits with good mechanical strength, so as to prevent mechanical loss of lithium. To achieve this, the effect of substrate, electrolyte composition, current density, temperature, and electrode configuration and separation must be investigated.

4. Optimization of the cathode composition and structure may improve cycling efficiency and cycle life. Also, the incorporation of slightly soluble salts which provide ions for reaction during charging or which combine to form stable compounds with the products of the discharge may prove fruitful. To extend this idea further, it should be pointed out that this area of cathode additives and pretreatment has been little explored, and might provide answers to several problems including cycle life, cycling efficiency and shelf life.

Additional Data Required for Battery Design

1. Optimum electrode configuration and spacing, and optimum electrolyte volume must be determined for each system which shows promise of being developed into a workable battery.

2. In order to properly design a battery package, the physical properties of the battery components must be known. For the electrolyte such properties as vapor pressure, freezing and boiling points, thermal expansion coefficient and heat capacity must be determined, while for the electrodes, heat capacities, heat conductivities, and electrode reaction temperature coefficients should be measured. It should be further pointed out that the inherently low conductivities of the organic electrolyte systems may cause serious heating problems, especially at high discharge rates, so that provision must be made for heat dissipation.

3. The mechanical strength of the electrode structures must be considered, and provision made for the loss of mechanical integrity during charge and discharge.

4. Safety precautions must be defined. The high reactivity of lithium may create problems in the handling, storage and disposal of this material, while the thermodynamic instability of the perchlorates, popular ingredients of electrolytes, should be characterized to insure that this material does not represent a potential hazard under the anhydrous conditions needed for lithium containing batteries.

5. Suitable concepts for overcharge control, pressure control, venting and battery activation must be developed.

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Unclassified

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)		2a. REPORT SECURITY CLASSIFICATION	
US Army Electronics Command Fort Monmouth, N.J. 07703		Unclassified	
3. REPORT TITLE		2b. GROUP	
STATUS REPORT ON ORGANIC ELECTROLYTE HIGH-ENERGY DENSITY BATTERIES			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)			
Technical Report			
5. AUTHOR(S) (Last name, first name, initial)			
Braeuer, Klaus H. M., & Harvey, Jay A.			
6. REPORT DATE		7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
May 1967		51	70
8a. CONTRACT OR GRANT NO.		9a. ORIGINATOR'S REPORT NUMBER(S)	
b. PROJECT NO. 100 14501 A 34A		ECOM-2844	
c. Task No. -00		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d. Subtask No. -01			
10. AVAILABILITY/LIMITATION NOTICES			
Distribution of this document is unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY	
		Commanding General US Army Electronics Command Fort Monmouth, N.J. AMSEL-KL-PB	
13. ABSTRACT			
The state of the art of high-energy density, organic electrolyte batteries has been summarized and reviewed to present the data which has been published in a more convenient, condensed form, and to pinpoint the problem areas on which future work should be concentrated. The report encompasses work which was published during the period 1962 to October 1966, and which was sponsored either by the US Government or by industrial companies and made available to the public. The material in this report is organized as follows: (1) selection of anode-cathode couples, (2) selection of battery components including electrolytes, half-cell systems, and separators, (3) design and performance of experimental cells, and (4) problem areas and areas of future work.			

Unclassified
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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
High-Energy Density Batteries Organic Electrolyte Batteries Anode Cathode Couples Electrolytes Separators Half-Cell Studies Complete Battery Performance						

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ESC-FM 3391-67