High-Rate Nonaqueous Lithium Battery

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The theoretical basis of high-energy-density nonaqueous batteries is discussed with particular attention to the merits of lithium as an anode material. The development of a high-rate, high-energy nonaqueous battery is described. The electrochemical system employs lithium metal anodes and cupric chloride cathodes with an organic aprotic solvent electrolyte. The system has a theoretical energy density of 503 w-hr/lb compared to 208 for the silver-zinc system, one of the highest energy-density systems employed. Developmental efforts have gone primarily into the establishment of high rate capabilities with efficient performance over the range of rates from 10 to 60 min. Over this range of rates, for small 5 amp-hr cells, the energy-density (in w-hr/lb) improvement over the silver-zinc system ranges from 40% to almost 100%. Energy densities of 30–62 w-hr/lb have been demonstrated at discharge rates of 10–60 min employing small size 4–6 amp-hr cells. Some implications for future design of high-energy reserve-type batteries are discussed.

I. Introduction

ABOUT 1960, in response to almost sudden expansion of demands for electrochemical power sources, it became obvious to some that high-energy electrochemical couples will be required to meet energy-density demands in excess of those permitted by aqueous systems. The approach taken at Electrochimica Corporation since early 1962 has been to employ organic electrolytes in nonaqueous-type batteries with lithium anodes. On thermodynamic considerations it was easy to predict that large energy densities would be available from systems employing metal halide cathodes with lithium anodes. The major problems were, however, the achievement of compatibility of electrode reactions, the development of practical materials of construction, and the achievement of reasonably high rate capabilities. The latter aspect was a particularly challenging problem in view of the inherent lower specific conductivity of organic electrolytes in comparison with well-known aqueous systems.

II. Theoretical Considerations

Classical thermodynamic considerations make it clear that with certain magnesium and zinc-containing batteries we have reached the energy-density capability limits for aqueous electrochemical systems. In order to obtain still higher gravimetric and volumetric energy-density ratios, the employment of more active electrode materials, particularly anodes, becomes necessary. It is possible, for instance, to arrange currently used and potentially useful anode materials for galvanic cells according to merit figures expressing an individual electrode weight contribution towards the generation of a unit of energy (W_a, pounds per watt-hour) or expressing the individual volumetric contribution per unit of energy (S_a, cubic inches per watt-hour). Table 1 gives parameters W_a and S_a arranged in increasing order of W_a. According to this simple arrangement, lithium, obviously due to its low equivalent weight and high emf, is the most meritorious from a weight point of view, whereas beryllium would be from a point of view of volume. It is clear from Table 1 that the most desirable anode materials are obviously of the types that would not be stable towards an aqueous electrolyte and, therefore, a nonaqueous media should be considered.

Of the three possible basic approaches, fused salt electrolytes, nonaqueous inorganic solvent systems, and nonaqueous organic solvent systems, this laboratory selected to work on the basis of the latter approach in order to provide a convenient system with a broad electrolyte liquidity range centered around room temperature.

The far-reaching significance of employment of a lithium anode, even when coupled with relatively conventional cathode materials, can best be realized by comparison of nonaqueous high-energy battery systems with conventional aqueous batteries shown in Table 2. As can be seen, the silver-zinc system involved the highest theoretical energy density among the aqueous batteries. This system is already thermodynamically somewhat unstable in respect to water decomposition. Any efforts to achieve higher energy densities would result in the decomposition of water as the electrolyte solvent. On the other hand, systems employing metal halide cathodes and lithium anodes permit theoretical energy densities in excess of 500 w-hr/lb. Although there is no fixed ratio between the practical energy density and the theoretical energy density one can hope to achieve (because the latter is very much a function of the rate of discharge, size, and type of construction), it is reasonable to expect energy-density levels exceeding silver-zinc by 50–150% depending on cell size and rate of discharge.

Lithium has been selected as the basic anode material and copper chloride as the active cathode. The selection of a metal halide as a cathode was necessitated by the aprotic nature of the solvent, which precludes the use of metal oxides or hydroxides as cathode materials, simply because there are no stable H^+ and OH^- ions in organic electrolytes of this type for the migrational transport of current. Thus, a compatible lithium anode, organic electrolyte nonaqueous battery system must be based on the combination of two electrode couples into a galvanic system in accordance with the scheme

$$\mathrm{M/MX_n/M'X_m\ (or\ LiM'X_m)/LiX/Li} \qquad (1)$$

where X is a halide, M is a relatively noble metal, and M′ is a metal effectively not more noble than lithium.

The choice of cathode material, the metal halide, is quite significant from the point of view of the theoretical watt-hours per pound one computes for a system of this type.

This gravimetric energy density (GED) can be computed from thermodynamic data for the over-all reaction and the

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Table 1 Individual weight-to-energy and volume-to-energy merit figures for selected anode materials

Material	Density, g/cc	lb/amp-hr × 10^{-4}	in.^{3}/amp-hr	Half-cell potential[a] E^0, v	W_a[b] lb/w-hr × 10^{-4}	S_a[c] in.^{3}/w-hr × 10^{-3}
Lithium	0.53	5.7	0.0298	3.02	1.89	9.86
Beryllium	1.82	3.7	0.0056	1.70	2.175	3.29
Magnesium	1.7	10.0	0.0163	2.34	4.27	6.96
Aluminum	2.7	7.4	0.0076	1.67	4.43	4.55
Calcium	1.5	16.4	0.0303	2.87	5.71	10.5
Sodium	1.0	19.0	0.0526	2.71	7.01	19.4
Strontium	2.6	36.0	0.0384	2.89	12.4	13.3
Zinc	7.14	26.8	0.0104	0.76	35.3	13.7
Cadmium	8.65	46.2	0.0148	0.402	111.5	36.8

[a] For simplicity of comparison, the standard potential values in aqueous systems, in reference to the standard hydrogen electrode, are taken.
[b] As an individual electrode contribution, W_a is defined as W_a = lb/amp-hr × E^0.
[c] As an individual electrode contribution, S_a is defined as S_a = in.^{3}/amp-hr × E^0.

faradaic equivalence of participating electrode materials, by the following relation:

$$\mathrm{GED} = \frac{-\Delta F}{n \cdot 23.06} \times 12{,}156 \frac{n}{\Sigma MW} = 527.1 \frac{(-\Delta F)}{\Sigma MW} \text{ w-hr/lb)} \quad (2)$$

where ΔF = free energy change, Kcal/mole, and MW = the sum of molecular weights of both cathodic and anodic reactants.

Substitution of the corresponding value for the system $Cu/CuCl_2 - Li^+/Li$ results in a theoretical GED value of 503 w-hr/lb.

Although other metal halides may theoretically offer higher energy densities (e.g., 746 w-hr/lb for CuF_2), cupric chloride has shown itself to offer definite kinetic advantages resulting in reasonably lower polarizaton for high current density discharges. For this reason, the work discussed here has been concentrated on the $CuCl_2/Li$ system for which the over-all cell reaction is

$$CuCl_2 + 2Li = Cu^0 + 2LiCl \quad (3)$$

In order for a selected electrochemical system (couple) to provide the basis for a useable galvanic cell, certain criteria of stability and compatibility must be met, particularly to achieve a high rate capability of a lithium-organic electrolyte cell. The following factors are desirable. 1) Both electrodes should have reasonably low polarization at practical levels of current density. 2) The conductivity of the electrolyte should be reasonably high, preferably in excess of 5 × 10^{-3} mhos-cm. 3) The effect of resistivity of the separators should be reasonably low. 4) Cell and battery design should provide for adequate heat transfer to the surroundings.

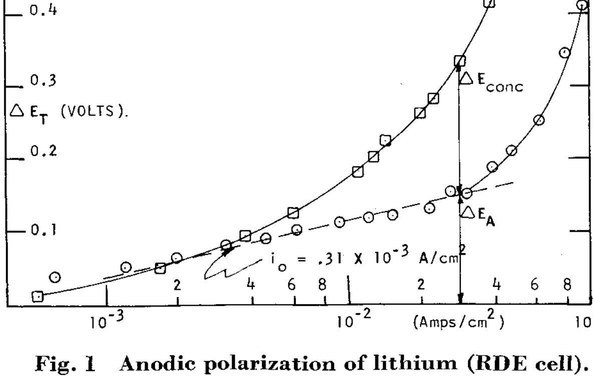

Fig. 1 Anodic polarization of lithium (RDE cell).

III. Performance Studies on High-Rate Lithium Cells

Studies to date have been confined to small cells with capacities in the range of 0.5–6 amp-hr. Primary efforts have been devoted to the study of those factors which would limit performance at high rates of discharge. The emphasis was on rates ranging from 15 to 60 min. The practical realization of high-energy-density yields would require the development of large-capacity cells, which is not the subject of the present paper. Some energy-density determinations in comparison with the silver-zinc system were made, however, using 4–6 amp-hr cells, the largest covered by this study.

Many factors affect and limit the high rate capability of any galvanic cell. The principal among these are the polarization of the cathode, the polarization of the anode, the specific conductivity of the electrolyte, and the resistivities offered by the separators employed. Concerning the latter aspect, it should be realized that since separator type and thickness employed have a pronounced effect on wet-stand life, i.e., the open circuit capacity retention of the battery in the activated state, there must be a tradeoff between the wet-stand capability and the discharge rate capability. This represents, thus, an area for design optimization for a given set of operational requirements.

Single electrode polarization studies for lithium anodes conducted early in the program have demonstrated the relatively good electrochemical reversibility of this electrode. An example of a study of the lithium anode using the rotating disc (RDE) method is shown in Fig. 1 for a solution containing lithium-chloroaluminate in propylene carbonate-nitromethane solvent. The plot shows total net polarization, which is the sum of activation polarization (related to charge transfer) and of concentration polarization (which is related to the

Table 2 Energy densities of electrochemical battery systems[1]

System	Theoretical w-hr/lb	Practical range[a] w-hr/lb
Conventional aqueous Batteries		
Pb-Acid (Sec)	115	7–12
Nickel-Cd (Sec)	107	8–17
Silver-Cd (Sec)	120	12–45
Silver-Zinc (Prim)	208	20–100
Silver-Zinc (Sec)	208	15–55
Nonaqueous high energy		
$CuCl_2$-Li (Prim)	503	28–(230)
$CuCl_2$-Li (Sec)	503	20-(160)
CuF_2-Li	746	

[a] Practical energy yield is a function of rate, size, and construction type.

Table 3 Effect of rate of discharge on efficiency and energy density (4–6 amp-hr cells—room temperature)

Rate of discharge, min	Voltage plateau V_p, V	Faradaic efficiency η_F, %	Energy density w-hr/lb
10	2.15	55–60	30–32
15	2.35	60–62	36–38
20	2.2–2.3	65–75	37–46
30	2.4	82–84	49–53
60	2.5	95–98	60–62

mass transfer between electrolyte and electrode). As can be seen, the concentration polarization becomes relatively more important at higher current densities when one compares the curves for low and high rotational speeds. In the region of current densities from 10^{-3} to 10^{-2} amps/cm^2, the net polarization for the case of the high rotational speed (which eliminates essentially all concentration effects due to the high rate of mass transport) follows a linear relationship in respect to the logarithm of current density. Since in this region concentration polarization is negligible, the data permit a calculation of an important parameter in electrode kinetics, known as exchange current density i_0. The resulting value is $i_0 = 0.31 \times 10^{-3}$ amps/cm^2. On the basis of this magnitude, the electrochemical reaction of dissolution of lithium can be judged as fairly reversible, i.e., capable of taking place at reasonable current densities without excessive polarization.

A somewhat different picture emerges for the polarization of the cathode. Here, the over-all reaction is much more complex than that of lithium dissolution. It starts and ends with a solid state, in accordance with the reaction

$$CuCl_{2(s)} + 2e^- \rightarrow Cu^0_{(s)} + 2Cl^- \qquad (4)$$

which represents an electrode of the so-called "second kind," the kinetic treatment of which is very complex and still under investigation, since several charge transfer and chemical steps are involved in the over-all process. However, it is possible from an over-all point of view to determine an apparent current exchange value from similar polarization data, as illustrated in Fig. 2. As shown here, a much larger polarization is encountered for the cathode at the current density of 10 mamp/cm^2 than is for the anode. A corresponding calculation of the exchange current density i_0 results in values of 0.30–0.32 $\times$ 10^{-4} amps/cm^2. Thus, the exchange current density parameter for the cathode is almost exactly an order of magnitude lower than for the anode. The significance of this is that from a polarization point of view, the cathode limits over-all performance of a practical cell.

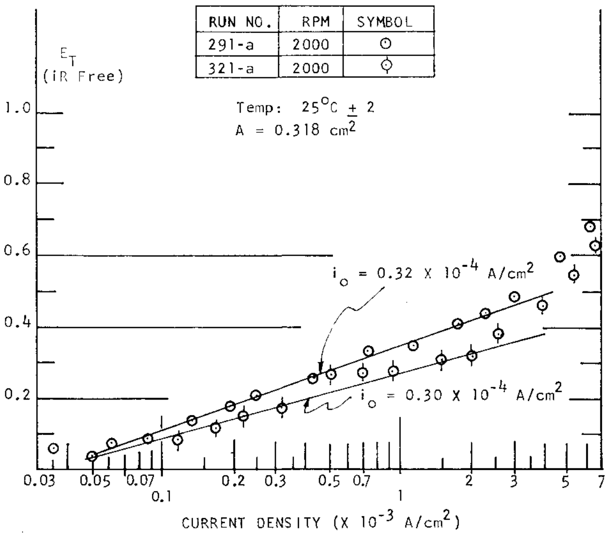

Fig. 2 Total polarization of Cu/CuCl₂ electroformed cathode in the RDE.

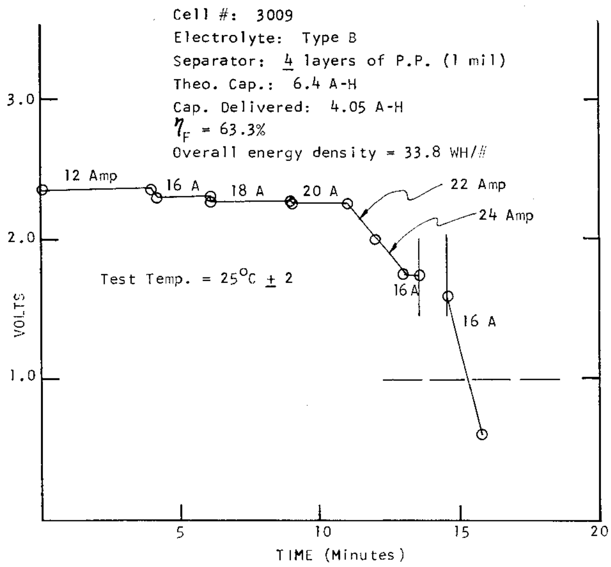

Fig. 3 Discharge rate capability study.

IV. Energy Density Studies

Cupric chloride-lithium cells with a 4–6 amp-hr capacity range in a case 3¼ × 2¼ × 3¼ in. were studied at high rates of discharge. In order to test the discharge rate capability, cells were subjected to increasing discharge currents to correspond to rates greater than 20 min. An example of the results is shown in Fig. 3. As can be seen, flat voltage characteristics were obtained for each current level from 12 amp to 20 amp, i.e., from the 20-min rate to the 12-min rate. The difference in voltages between these two rates was only 90 mv, i.e., from 2.35v to 2.26v. However, at still higher current levels, 22 amp and 24 amp, voltages declined gradually. This was to be expected since at this point most of the capacity of the cell was already consumed towards the end of the 20-amp period of discharge. These studies have led to the

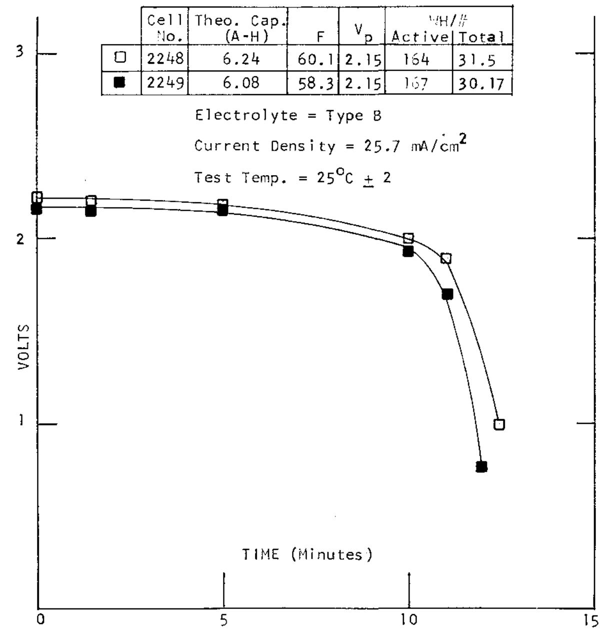

Fig. 4 Cells discharged at 10-min rate, expanded nickel grids.

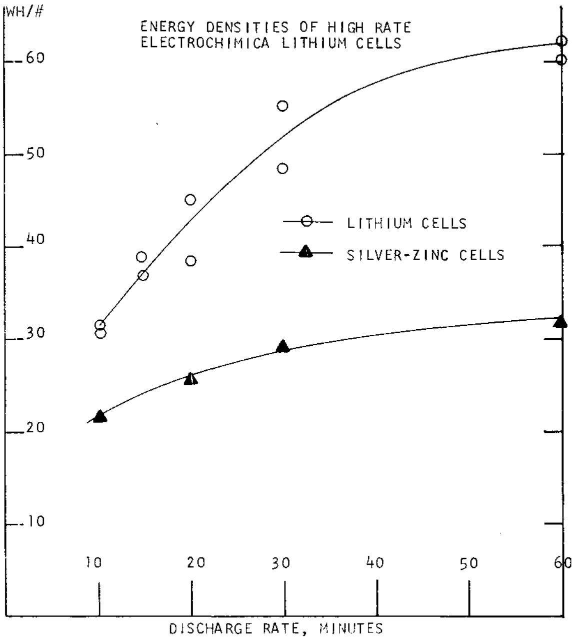

Fig. 5 Effect of rate of discharge on energy-density yields of 5 amp-hr Electrochimica lithium cells in comparison to silver-zinc cells.

conclusion that there should be no difficulty in achieving discharge rates as high as 10 min, provided cell designs can be developed to provide adequate heat transfer during discharge at these very high rates. Indeed, it was possible to achieve an efficient discharge at the 10-min rate in similar cells using the same electrolyte. This is illustrated in Fig. 4, which shows that the cells were capable of performing at a high emf of 2.15v with a faradaic efficiency of almost 60%.

As discussed previously, the rate of discharge has a profound effect upon energy density, simply since it affects both voltage plateau and the faradaic efficiency. A set of results illustrating this point for 4–6 amp-hr capacity cells is given in Table 3.

As can be seen, at a 15-min rate, cells were capable of operating at an emf of 2.35v and a faradiac efficiency of 61%, resulting in energy densities of 36–38 w-hr/lb. Despite the small size of these cells, which is unfavorable for the purpose of demonstration of energy density, it is interesting to point out that equivalent capacity silver-zinc cells yield only 22–25 w-hr/lb. An interesting comparison of the effect of rate of discharge on energy density yields of small 5 amp-hr cells in both chemical systems is given in Fig. 5. Although the cells being compared were small, it can be seen that the lithium cells offer an energy-density advantage ranging from 40% at the 10-min rate to almost 100% at the 60-min rate.

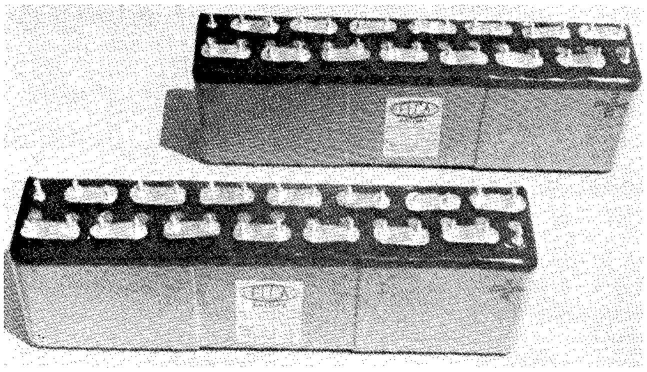

Fig. 6 30-v high-rate nonaqueous batteries.

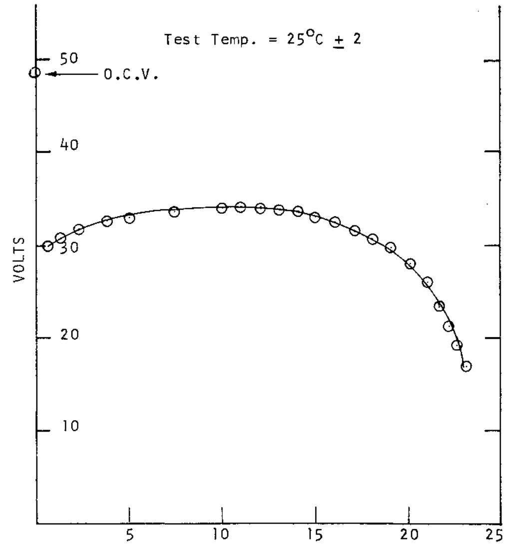

Fig. 7 Discharge of 28-v battery at 8-amps–20-min rate of discharge (room temperature).

Some initial work has been done on construction of complete batteries using 4 amp-hr cells. Although these batteries were not optimized in design, and simply packaged by encapsulation as illustrated in Fig. 6, they have shown a capability of operating at a 20-min rate. The discharge of a 28 v battery of this type is illustrated in Fig. 7. As can be seen, the voltage of the battery rises somewhat, initially, as the internal heat developed during the discharge improves the conductivity of the electrolyte.

V. Concluding Remarks

The cupric chloride-lithium system, with an organic electrolyte, has demonstrated its capability of delivering high energy densities with rate capabilities as high as a 10-min rate. To demonstrate the full energy-density capabilities of this system requires the design and construction of large capacity cells in which the weight of packaging materials will decrease in proportion to total cell weight. However, scaleup to large size cells requires, at the same time, more careful considerations of the amount of heat generated within the cells and of the modes of heat transfer which must be designed into the cell itself and into its surroundings.[2] Although this area is common to all batteries, it is significantly more important in the field of high-energy lithium batteries since the amounts of irreversible heat to be rejected, particularly at high rates of discharge, become significant. With proper thermal design of the cells and heat-transfer means, high-rate lithium reserve-type batteries should become a reality in the foreseeable future. Such batteries can be expected to have important Naval applications.

References

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