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ON THE SELECTION OF ELECTROLYTES FOR HIGH ENERGY DENSITY STORAG--ETC(U)
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ON THE SELECTION OF ELECTROLYTES FOR HIGH ENERGY DENSITY STORAGE BATTERIES

by

M.A. Klochko and E.J. Casey

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by

M.A. Klochko and E.J. Casey

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ABSTRACT

The use of nonaqueous, molten salt and solid electrolytes for high energy density storage batteries (SB's) with anodes of Li, Na, Ca, Mg, Al and Ti, is discussed. Means to overcome the shortcomings of these systems, viz. low conductivity of the electrolyte, poor quality of the anodic metal deposited during recharging of the nonaqueous systems, high operating temperatures, of the molten salts and instability of solid-state electrolytes, are considered.

Electrolytes with compositions in the transition region between the pure electrolyte and its solutions in the solvent, are suggested for examination in secondary battery systems with each of the six light anodes mentioned above.

RÉSUMÉ

On discute de l'utilisation d'électrolytes solides et de sels fondus non aqueux dans les accumulateurs à haute densité d'énergie dont l'anode est constituée de Li, Na, Ca, Mg, Al ou Ti. On discute également des méthodes permettant de réduire ou d'éliminer les inconvénients que présentent ces systèmes, comme faible conductivité électrolytique, mauvaise qualité du métal redéposé sur l'anode lors de la recharge des systèmes non aqueux, températures opérationnelles élevées des sels fondus et, enfin, instabilité des électrolytes solides.

De plus, on propose de considérer l'utilisation de certains électrolytes, présentant une composition comprise dans la zone de transition entre l'électrolyte pur et l'électrolyte dissous dans un solvant, dans les accumulateurs secondaires dont l'anode est constituée de l'un des six éléments mentionnés plus haut.

TABLE OF CONTENTS

	Page
ABSTRACT/RESUME	iii
INTRODUCTION	1
"NON AQUEOUS" ELECTROLYTES	3
INORGANIC SOLVENTS	4
ORGANIC SOLVENTS FOR PRIMARY BATTERIES	6
SECONDARY BATTERIES WITH NONAQUEOUS ELECTROLYTES	10
CONCLUSIONS ABOUT SBs BASED ON "NONAQUEOUS" ELECTROLYTES	13
MOLTEN SALT ELECTROLYTES	15
Li AND Li-ALLOYS SBs	18
THE OTHER FIVE CANDIDATES	21
CONCLUSIONS ABOUT SBs BASED ON MOLTEN SALT ELECTROLYTES	22
SOLID ELECTROLYTES	27
COMPLEX COMPOUNDS OF AgI	27
BETA-ALUMINA SB	29
THE PROSPECTS FOR SOLID ELECTROLYTE SBs	30
AQUEOUS AND MIXED ELECTROLYTES FOR HED SBs	31
AQUEOUS ALKALI METAL BATTERIES	32
THE TRANSITION REGION OF COMPOSITIONS IN BINARY SYSTEMS	34
THE ACTIVE METALS: Li, Na AND Ca	36
THE PASSIVE METALS: Mg, Al AND Ti	38
PROSPECTS FOR THE USE OF TR ELECTROLYTES	41
SUMMARY	41
REFERENCES	42

INTRODUCTION

In considering the selection of anodes for high energy density (HED) storage (or secondary) batteries (SB), we note that there are some 19 metals whose free-energy density (ED) of reaction with oxidants such as O_2, Cl_2, and F_2 are higher than those of Zn with the same oxidants. Most of these metals react violently with water. The remainder are passivated by water. Therefore other electrolytes must be considered for these metals, based on non-aqueous, molten salt, or solid-state ionic conductors. Much experimental work has been carried out during the last two decades on primary and secondary batteries based on anhydrous electrolytes.

Six of the above mentioned 19 active metals can be singled out as the most promising ones for HED SB's: Li, Na, Ca, Mg, Al and Ti. Being located in the upper left-hand corner of the periodic table (even Ti is close) these metals possess HED's in their reactions with many other substances and have high potentials and low equivalent weights. Four of them, viz. Li, Na, Mg and Al, have been repeatedly studied electrochemically. The other two, Ca and Ti, have begun to attract attention of the researchers during the last decade. (At present, Mg and Al are finding their way into practical primary cells with aqueous electrolytes.) The main obstacle for the introduction of Mg, Al and Ti into SB's is their behaviour connected with passivation. By constrast, the use of the other 3 metals, Li, Na and Ca, is hindered by the rate of their reaction with water. However, the high energy of the reactions of all these six metals with the common oxidants, and their abundance in the earth's crust are facts which stimulate interest in their possible use. Some of the properties of these metals are given in Table I. They can be compared with zinc, which is currently the most widely used metal in primary batteries and is also the working anode in the Ni-Zn and Ag-Zn SB's.

Little practical success has been achieved up to now in the design and construction of SB's based on light metals with nonaqueous or fused salt electrolytes, despite extensive work done in that direction. The only new type of SB which is now under trial for practical large-scale use is based on the cell Na-S, with a solid electrolyte of the type $Na_2O(Al_2O_3)_{11}$, although molten salt SB's based on Li-FeS_x are nearing prototype stage, and other systems show some promise.

In this report short reviews of the literature related to each class of electrolytes will be presented, accompanied by some suggestions of the ways and methods of improving the SB's of each class. We treat first those inorganic and organic solvents whose solutions with salts form the class commonly but equivocally called non-aqueous electrolytes. Then we treat the

TABLE I

Some Properties of Some Active Anodic Metals

Metal	Atomic No.	g.-Equivalent	Abundance ppm	E° 25°	ED, Wh/kg		
					M+O_2	M+Cl_2	M+S
Li	3	6.94	65	-3.04	5536	2680	3020
Na	11	22.99	28300	-2.71	1873	1954	1329
Ca	20	20.05	36300	-2.87	3148	1991	1850
Mg	12	12.15	20900	-2.37	4158	1874	1712
Al	13	9.00	81300	-1.66	4609	1450	1320
Ti	22	23.95	4400	-1.61	2305	1116	1070
Zn	30	32.68	132	-0.76	1211	848	579

class of molten salt electrolytes, and finally the class of solid electrolytes. For each class we consider the prospects of finding rechargeable systems which can be formed with the light metals. A "transition region" (TR) is defined as the region of solution composition in which mole fraction (n_2) of solvent 2 in solvent 1 is $\lesssim 0.2$. This concept is particularly useful in the discussion on moist molten salt cells.

Unfortunately, a theoretical basis for choice of electrolyte systems based on molecular and cluster theories is not well enough advanced to permit a priori selection of electrolytes for high-performance battery systems with the light, active anodes. The void spaces in pure and in two-component solvents do seem to correlate with reasonably high conductivity and low freezing point. Further, the curious complexing which occurs in molten salts seems inextricably related to the morphology of the redeposited metallic anode, and therefore to its reversibility in a SB. Finally the nature of the structural metastability of the solid electrolyte superconductors seems to be germane to the recycling ability of solid electrolyte batteries; the open lattice must not collapse.

These are all topics which are relevant to the subject being treated, but they are not discussed in this review because we have been unable so far to show how the fundamental theoretical models can be used to formulate improved practical SB systems. Perhaps others will help us apply these models to SB science in a meaningful way.

"NONAQUEOUS" ELECTROLYTES

Many organic and inorganic compounds which are liquid at ambient temperatures have been considered as solvents for light metal salts, to determine whether the solutions so formed could be used as electrolytes in electrochemical cells. Among the requirements of these solvents are:

(a) A sufficiently large temperature-range of liquid state between the melting and the boiling points, (at least of the same order as that of water), under atmospheric pressure;

(b) Solubility of some salts of the anode metal to a minimum of 1 gram equivalent per liter;

(c) Conductivity of the solution (< 1 ωcm) sufficient that the IR losses during the battery's performance will be low;

(d) Low reaction rate of electrolyte with the anode;

(e) No passivation at anodic current densities < 1 amp cm^{-2};

(f) Reversibility of both electrochemical processes, required of electrodes in cells intended for secondary batteries.

The last condition is a difficult one. Only solvents can be used from which the anode metal can be electrochemically deposited. These conditions are discussed in a book [1] and in a review [2] published by R. Jasinski ten years ago, which contain references to the literature available up to that time. Many articles and patents have been published since then (1968) on electrochemical cells with non-aqueous molten salt and solid electrolytes. We mention or discuss here only those which are related to SBs or which are related to some features connected with reversibility.

On account of the rapid or even violent reaction between the alkali metals and water, other solvents, mostly aprotic, have been sought as the basis for electrolytes for power cells using these metals as anodes. However, the salts of these metals, especially of the MX type, where M is the metal and X the halogen, are generally not soluble in aprotic liquids. A method which may be called "complex solubilization" can be employed here, however. In the presence of Al halides the MX salts are fairly soluble in many aprotic solvents because of complex formation, according to the equation:

$$MX + AlX_3 \rightarrow MAlX_4 \rightarrow M^+ + AlX_4^-$$

Applying this method for the preparation of solutions of alkali metal salts in nitrobenzene, for example, one of the present authors many years ago succeeded in depositing Li, Na, K, Rb and Cs on the cathode at ambient temperature [3]. Very recently Tobias used this method again and described some results in [4].

INORGANIC SOLVENTS

A series of publications on Li-inorganic solvent batteries, the work of Auborn and co-workers for example, appeared during 1972-76. In one of his first reports Auborn stated that the use of covalent inorganic liquids as the basis of battery electrolytes had been overlooked by most workers, despite the fact that such compounds can be rendered ionically conductive and they are thermodynamically more stable than many organic solvents [5]. Phosphorous oxychloride, $POCl_3$, is cited as an example, and the OCV and the ED of cells based on it are given:

	V	ED - Wh/lb
$Li \mid LiPF_6 \mid CuF_2$ in $POCl_3$	4.0	149.3
$Li \mid LiBCl_4 \mid CuF_2$ in $POCl_3$	3.63	316

More details on Li cells based on three inorganic solvents -- $POCl_3$, $SOCl_2$ (thionylchloride) and SO_2Cl_2 (sulfurylchloride) -- are given in [6]. A table of the properties of the three solvents is also presented, showing the liquid range (+1.25° to +105.8°, -104.5° to +77°, and +59.1° to +69.4° for $POCl_3$, $SOCl_2$ and SO_2Cl_2 respectively; their dielectric constants (DC) 13.7, 9.05 and 9.15; and several other data. The conductivities of several Li complex compounds in these solvents, mostly at 1.0 mole concentrations, vary between 1.1×10^{-3} and 19.6×10^{-3} ohm^{-1} cm^{-1}. The properties of several cells, for example:

$$Li|POCl_3:LiBCl_4|Cl_2$$

and some others with metallic salt cathodes, were studied.

With some cathodes of conductive materials ($(C_4F)_n$, polytetracarbon monofluoride, for example) the solvent becomes the depolarizer. Batteries with $SOCl_2$ and SO_2Cl_2, carbon cathodes and Li anodes show EDs of 250 and 300 Wh/kg and OCV of 2.6 and 2.9V respectively [7]. In a later paper [8] cells of the type

$$Li|SOCl_2, LiAlCl_4|C$$

with E = 3.90V and ED theor. = 1875 Wh/kg, which were selected for development as primary batteries, were described. Two U.S. patents on electrochemical cells with inorganic oxyhalide or thiohalide solvents were granted to Auborn [9].

An important problem in batteries with inorganic liquids as electrolytes is the corrosion and the compatibility of materials. The stability of Li in boiling oxyhalides and thiohalides was studied, and the corrosion rate of various casing and conducting materials, such as glasses, ceramics and metals, in Li $SOCl_2$ or $SO_2Cl_2|C$ batteries, was determined [10].

Marincic has studied the performance of primary Li battery with SO_2Cl_2, comparing it with conventional batteries (Zn/MnO_2, Zn-AgO and others). The theoretical ED of the Li/SO_2Cl_2 battery (1845 Wh/kg) is much higher [11a]. Studying the conditions of the optimization of that primary battery, he deduced a formula connecting the maximum capacity of the cell with various values of its elements, such as the density and the porosity of the anode, the atomic weight of its metal and so on [11b]. Two types of wafer cells for electronic watch application were designed [11c], and a patent for an electrochemical cell of a button type was granted. It is based on the cell:

$$Li/LiAlCl_4\text{-oxyhalide/C black}$$

which delivers about 50% more energy than the conventional AgO-Zn battery [12].

W.K. Behl and co-workers published a paper on cells:

$$Li/LiBCl_4\text{-}POCl_3/C$$

$$Li/LiAlCl_4\text{-}SOCl_2/C$$

They underlined the fact that during the discharge of these cells the solvents (i.e. $POCl_3$ and $SOCl_2$), are electrochemically reduced and behave as soluble cathodes. The ED, based on the cell's total weight, is 244 Wh/lb (537 Wh/kg). Details on the construction and the performance of these cells are given [13]. There is some evidence that such cells are rechargeable, at least partly.

Of the three inorganic solvents mentioned above, $SOCl_2$ has been chosen by several workers as the most promising for ambient-temperature high ED primary batteries. It was confirmed that $SOCl_2$ serves both as solvent and depolarizer for the cell. However, the proposed equations for the reactions between Li and $SOCl_2$ have not been confirmed by the analysis of the discharge products [14], and the stoichiometry remains uncertain. Experimental optimization of the $Li/SOCl_2$ primary cells with respect to the electrolyte and the cathode composition was discussed in [15].

Some other inorganic solvents were tried with Li anodes as well. Thus, for example, the decomposition reaction of concentrated $Li\text{-}NH_3$ solutions was reported in [16]. It is stated that, due to the energy theoretically available from the $Li/Li(NH_3)_n$ couple, it could serve as electrochemical fuel of exceptional interest for fuel cells or batteries. Application of this concept is not clear, however. A long-life multi-cell ammonia reserve battery, with a temperature operation range between -70° to +60°C was proposed in [17].

A mixture of $HF + N_2O_4$ was tested as an electrolyte and a cathodic reactant in cells with heavy metal anodes:

$$Cd/HF + N_2O_4/Ni$$

A suitable anode material should have a low direct corrosion rate, but should be able to undergo anodic oxidation at a reasonable rate. Of the tested metals Ta, Nb and Sn react too rapidly with the solution, and Zn, Ni, Fe, Cr are passivated by the application of anodic currents. Actually Cd exhibits the best anodic behaviour, and has an OCV of 1.19V at -40°C and 1.66V at +60°C [18]. The behaviour of light metals in such solutions would be of interest.

ORGANIC SOLVENTS FOR PRIMARY BATTERIES

A great many publications, articles, reports and patents on the use of organic solvents for HED cells have appeared during the last 15 years.

Most of these publications (perhaps over 90% of them) are concerned with Li cells and were recently reviewed in a paper which includes in its 169 references the literature up to 1974 [19]. We will, therefore, mention here only several of the more important works published during the last 2-3 years, and will start with those in which the work was related to primary batteries.

Many organic compounds which are liquid at ambient temperatures have been tried as solvents for electrochemical cells, the main criterion for their choice being the formation of conductive solutions with compounds of the anode metal. It was supposed that a sufficiently high value of the dielectric constant (DC) of the solvent is needed for the conductivity of solutions in it, although the dipole moment would seem to offer a more reliable basis for selection (See Table II).

The conductivities (K) in the nonaqueous solutions are about one order of magnitude lower than in aqueous solutions and about 2 orders lower than in molten salts. The K's of the solutions used in the conventional batteries, of H_2SO_4 in the lead-acid and of KOH in the Ni or silver alkaline SBs, are from 30 to 40 times higher than the K's of the best conducting nonaqueous solutions at the same temperature. This is an important fact at high rates of charge or discharge, but the IR loss in the electrolyte becomes small in any case at low power density.

The work on electrochemical properties of nonaqueous solutions, which started in the beginning of this century and has occupied the attention of many researchers, has produced valuable information for the design and construction of experimental primary batteries based on nonaqueous solutions. Some data from this preliminary work can be found in [1-4] and in [19-21], and in the publications cited in those references. As a result of the efforts spent during the last decade on primary nonaqueous batteries, at least some of these systems are now achieving the commercial stage.

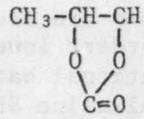
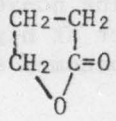
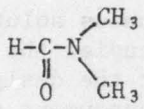
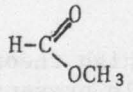
The attractive feature of such batteries is the high theoretical ED of their redox couples, accompanied by high OCV. In a table presented in Gilman's overview of the primary Li battery program, which is based mostly on propylene carbonate (PC) solutions, with a Li anode and various cathodes, the OCV for a $(C_4F)_n$ cathode was given as 5.23V, the theoretical ED being 918 Wh/lb and the experimental ED = 558 Wh/lb. For the $(CF)_n$ cathode the figures are even higher: ED = 1491 and 1000 Wh/lb. A critical discussion of the primary Li-nonaqueous batteries, as well as the recent literature references, can be found in [22].

Several researchers have carried out experimental work to determine the factors which influence the performance of Li-organic cells. The swelling of the cathode $(CF_x)_n$ influences the discharge through the formation of a LiF precipitate [23]. A film of LiCl is formed on the Li anode by its reaction with the depolarizer $SOCl_2$; this causes the voltage delay during discharge [24]. Traces of water are thought to cause the formation of a film on the anode in the Li/dimethyl sulfite system [25]. By 1973 there were advertisements that primary Li-organic (Li/SO_2) cells were commercially available [26].

A D-size Li-CuS cell with a mixed nonaqueous solvent is superior to the aqueous Leclanche cell of the same size, according to the authors of [27].

TABLE II

Properties of Solvents

Solvent	Formula	M.P. °C	B.P. °C	D.C. 25°	Maximum K of $LiClO_4$ Solution ~1M at 25°C
Propylene Carbonate PC		-49.2	241	64.4	0.0073
Butyro-lactone BL		-42	206	39	0.015
Dimethyl Formamide DMF		-61	153	36.6	0.021
Aceto-nitrile AN	$CH_3-C\equiv N$	-45.7	81	36	0.029
Methyl formate MF		-99	32	8.5	0.032
Thionyl-chloride TC		-104	77	9	0.015 ($LiAlCl_4$)(1M) 0.020 ($LiAlCl_4$)(2M)
Water		0	100	78	0.09 ($LiClO_3$) (1M)
H_2SO_4 25%					0.82 (25°)
KOH, 20%					0.60 (25°)
Molten Salts:					
KCl					2.42 (800°)
KOH					2.5 (400°)
NaOH					2.4 (350°)
KOH+NaOH eut.					0.75 (200°)

The performance characteristics of Li-SO_2 and Li-CF batteries were discussed. These showed excellent results at low temperatures. However, some unsafe features associated with leakage of SO_2 and/or internal shorting became apparent, and further efforts are needed before the Li-organic electrolyte battery can be considered fit for general use [28].

A long-life, wide-temperature-range organic electrolyte battery:

$$Li/PC{\cdot}THF,\ LiAsF_6/AgCl$$

where THF is tetrahydrofuran, was proposed in [29]. Further, a battery based on the cell:

$$Li/LiAsF_6 \text{ and } LiBF_4 \text{ in methyl formate}/V_2O_5 + C$$

with ED from 96 to 117 Wh/lb, and which works between -10° to +75°F, was discussed in [30]. A battery:

$$Li/LiClO_4, \text{ org. solv.}/CuO$$

was reported in [31]. Its reaction is:

$$2Li + CuO \rightarrow Li_2O + Cu$$

and 2.4V is expected. Asked about the nature of the solvent in that battery, the reporter said: "We are not yet prepared to discuss it" [31].

The discharge characteristics of the Li-SO_2 battery system are discussed in [32a], and these were compared with other systems in [32b]. With a practical ED of 290 Wh/kg at room temperature, it can operate down to -53°C with ED = 55 Wh/kg. The SO_2 is dissolved in acetonitrile + PC. The cell is:

$$Li/SO_2 + Ac.Nit. + PC/C.$$

Japanese workers have studied primary batteries with carbon-fluoride cathodes in the cell:

$$Li/LiBF_4 - BL/(CF_x)_n.$$

The K of the electrolyte at 45° shows a maximum of 9×10^{-3} ohm^{-1} cm^{-1}. The preparation of $(CF_x)_n$ and the ED dependence on the value of x in $(CF_x)_n$ are

reported [33]. Patents were granted for batteries of that type [34]. During the discharge of a cell:

Li/Li salt in PC/M

where M = Al, Zn, Mg or some other metals, Li forms with them intermetallic compounds [35]. The cathodic Li-Mg alloy prepared in this manner was used as an anode in the cell:

$LiMg/LiClO_4$ - PC/M

The presence of 0.1M H_2O does not affect the performance of the cell [36]. Li or Mg anodes in a solution of $(C_2H_5)_4NClO_4$ in PC was offered in a Japanese patent [37]. In another Japanese patent Mg or a Mg alloy is used as anode in the cell:

Mg/LiCl in BL & DMSO/$(CF_x)_n$

where DMSO is dimethyl sulfoxide. It is claimed that this battery has higher discharge capacity than a battery with $LiClO_4$-PC [38]. The authors of [38] were granted two more patents on nonaqueous batteries with Mg anodes [39].

From a review of the recent Russian electrochemical literature it can be concluded that intensive research of nonaqueous batteries is carried out in the U.S.S.R. Although no results of the performance of such batteries are published, papers on properties of Li solutions in solvents used in Li cells, and on the behaviour of metallic Li in nonaqueous solutions, which have appeared recently in Russian literature, can be considered as the tip of the iceberge of research in that field. The electrodeposition of Li from dimethylformamide solutions of its salts [40], or the behaviour of Li in aprotic solutions [41a] and the solubility and conductivity of its salts in these solutions [41b] are connected with the work of an unnamed Institute in Moscow; only the city, not the institute, is mentioned in these articles.

SECONDARY BATTERIES WITH NONAQUEOUS ELECTROLYTES

The fact that an alkali metal can be electrodeposited from a non-aqueous solution of its salts at ambient temperatures [3,4] suggests the possibility of designing a SB based on that system with an alkali metal as anode. If the metal can be regenerated by charging, it will work again as anode. Many attempts have been made to materialize this possibility.

The couple $Li/CuSO_4$, with ED = 1060 Wh/kg and emf of 3.41V, has been studied with the aim of designing a SB with electrolyte based on the sulfates and perchlorates of tetraammonium complexes in PC and methyl sulfate. However, Li reduces the solvent [42], and other more stable solutions are needed.

Attempts were made to utilize transition-metal sulfides as cathodes in SBs. These sulfides, and especially those of Ti, are electrochemically active and reversible in cells:

$$Li/1M\text{-}LiAlCl_4 \text{ or } LiBF_4\text{-}PC/MS_x$$

More than 80 cycles were performed with TiS_3, it was reported [43a]. Eleven hundred shallow (4%) cycles were reported later [43b].

The chemistry of $NbSe_3$ and TiS_2 and their behaviour as cathodes in reversible cells with Li and non-aqueous electrolytes were studied at the Bell Laboratories. The reversibility of the MX_3 cathode system is explained by the formation of intercalation compounds between Li and the sulfide [44a]. For example, in the cell:

$$Li/1M\text{-}LiClO_4\text{-}PC/MS_3, \text{ where } M = Nb, Ti$$

Li_3MS_3 is formed, and the cathodic reaction was found to be completely reversible [44b]. Scanning electron-microscopic studies of the cycle behaviour of this cell were made in Bell Laboratories with $NbSe_3$, NbS_3, $TaSe_3$ and TiS_3. Although all these systems show rechargeability, cell failures are related to Li-anode morphology changes, accompanied by the formation of a relatively non-adherent deposit of Li [45a]. The discussion in reference [45a] is of substantial interest, since workers in the same field from other laboratories pointed out causes of delay in the achievement of practical results with Li-nonaqueous SBs. Thus the first crucial problem seems to be unfavorable morphology of the Li deposits, since Li is intrinsically reactive in all the solvents that are of interest for Li-organic electrolyte SBs. This reactivity does not appear with bars or foils of metallic Li, but only with a cycled Li electrode. If rechargeable Li SBs are to be practical, a means to control the morphology of Li must be found [45b]. The second critical problem is the chemical stability of the Li which deposits during the cycling of secondary cells. Electrodeposited Li has such a high surface area that it is not stable in many solutions in which flat Li foil is stable [45c]. However, the pessimistic opinions of [45b and c] have not held back the authors of [45a] from claiming a patent for a nonaqueous battery using chalcogenide electrodes, the specific structure of which is the main feature of the SB [46].

The reversibility problem of transition metal chalcogenides in Li non-aqueous batteries has attracted the attention of other researchers who have studied the structure of these compounds and the complexes they form with Li [47]. The relations between the structure of the ternary phases formed at the cathode of a Li-transition metal sulfide, or oxide, and the reversibility of the cell are discussed in [48]. The reversibility of the discharge

reaction is maximized when no chemical bonds are broken during discharge (intercalation reaction) and it is minimized when all the chemical bonds are broken, such as in the case of CuS or CuF_2. When only some, but not all, of the chemical bonds are broken and the structure is distorted as in TiS_3 and V_2O_5, partial rechargeability is found. Thus

Cells of the type:

$$Li/LiClO_4\text{-organic solvent}/V_2O_5$$

have been studied with various solvents. PC supports the greatest number of cycles. After about 400 cycles failure occurred, due to the swelling of the Li electrode as a result of its low density after being deposited at the negative electrode [49]. A reversible cell with a Li_2S_n dissolved cathode and electrolyte based on dimethyl sulfoxide and tetrahydrofuran as a mixed solvent,

$$Li/DMSO \text{ or } THF + LiClO_4/Li_2S_n$$

was studied in [50].

A nonaqueous Li-Br secondary cell:

$$Li/LiBr\text{-}PC/Br_2$$

was studied in [51]. At an OCV of 3.82V it has an ED of 320 Wh/lb. More than 1700 cycles were achieved. The Br_2 electrode was still completely serviceable but the Li electrode had partly disintegrated.

The authors of [49] were granted a U.S.A. patent on a rechargeable battery described above. The electrodes are enclosed in special wrappings to prevent the passage of large Li particles [52]. A patent was granted to the authors of [45a], who claim that the addition of certain dopants to their battery will improve its performance, especially the cycling [53].

Although most of the publications on nonaqueous SBs are concerned with Li anodes, there are several articles and patents on secondary cells with other light metals.

A cell

$$Na/PC + NaI/Na_xTiS_2$$

was described in [54]. A German patent was taken out for a nonaqueous rechargeable Na-halogen battery [55], and a series of Japanese patents has

been granted for nonaqueous batteries with Li, Mg or Al anodes. Nothing is said about cycle life, but good capacity is indicated [56].

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CONCLUSIONS ABOUT SBs BASED ON "NONAQUEOUS" ELECTROLYTES

Despite the availability of several articles and patents on nonaqueous secondary batteries [42-56], there is no evidence that these batteries have achieved the commercial stage. The reasons for this are given in various experimental works and reviews. However, the fact known long ago that light metals of high energy density can be electrodeposited from their nonaqueous solutions at ambient temperatures [3,4,21], and the successful completion of several primary nonaqueous batteries to the commercial stage, has raised hopes of the possible construction of secondary HED batteries, based on the same solutions. So far, considerable difficulties and obstacles have been met during the work on these batteries. One obstacle, which is common to both primary and secondary batteries, was mentioned above: it is the low conductivity of nonaqueous solutions, which in the best cases is less than 0.025 $ohm^{-1}cm^{-1}$. However, this difficulty can be circumvented by using electrodes of large surfaces with close distances between them. (A layer of 10 x 10 x 0.1 cm^3 will expose a resistance one thousand times less than the resistance of a cube with sides of 1 cm^2.) The second difficulty, which is specific for the secondary battery, limiting its cycle life, is the state of the anode after recharging. The brittle, crumbling, regenerated anode, impregnated with a gum-like substance must have electrochemical properties far different from the metallic bar or foil of the uncycled, fresh anode. Pointing to the changing morphology of the Li anode during cycling, the author of a 1976 review stated that on the whole the practical secondary Li-electrode in organic electrolytes will probably remain an unachieved ambition, at least for the near future, whereas several types of primary Li-batteries are already commercially available [19, p. 14]. The problems of preservation of Li-nonaqueous batteries, and of their recharging have not yet been solved according to A. Caiola, who has been working on such batteries for several years and has tested, with his co-workers, several inorganic and organic esters in search of new solvents for primary and secondary batteries with Li anodes [57].

It is of interest to note that despite these and some other pessimistic appraisals of the Li-nonaqueous SBs for the future, the well-known Soviet electrochemist, A.N. Frumkin, in his last public appearance at the XIth Mendeleev Congress in Alma-Ata (Kazakhstan) in the presence of many hundreds of chemists (September 22-27, 1975)) several months before his death, pointed out that among the most optimistic opportunities in applied electrochemistry are the creation of fuel cells for continuous power, and of HED SBs based on aprotic solvents and alkali metals [58]. And there are many North American enthusiasts who agree, as the references attests.

There are at least two ways to overcome the difficulties connected with the reversibility of SBs based on nonaqueous electrolytes:

(a) To increase the number of solvents and their mixtures in the design of electrolytes for SBs.

(b) To create conditions at which the changes in the active metals morphology during recharge would not influence the cycle life of the cell.

The ten or so organic solvents and the 4 or 5 inorganic ones tested in experiments with nonaqueous SBs represent only a small fraction of the liquid compounds which may prove to be useful as a basis for electrolytes in these batteries. The problem of nonaqueous solvents for electrochemical use is discussed in [59], where nine groups of organic and inorganic liquids -- nitriles, amides, amines and so on -- were considered. They include also such compounds as alcohols and acids which have not been tested for SBs, being not aprotic. In any event such compounds, especially in mixtures with aprotic ones, should be examined; this may turn out to be useful. Special attention must be given to inorganic compounds, which can play a double role, both as solvent for the conducting species and as oxidizer, i.e. an active cathode material. Hydrazine (H_2N-NH_2) and its mixtures with other compounds (NH_3, acetone) may show useable properties as solvents in SBs.

Hydrazine has many remarkable properties. Its liquid range (+10 to 105°) is slightly larger than that of water; it dissolves many inorganic salts and is miscible in any ratio with water and many other liquids. Its remarkable ability to dissolve more than 50 mole % of sulfur at ambient temperature [60] may be of importance in designing SBs, but on account of some of its properties it must be treated with care.

Acetamide (CH_3CONH_2) may also be useful as a solvent in SBs. Although its melting point is comparatively high, (81°C), its eutectic point with NH_4NO_3 is +36° and with $LiNO_3$ it is +27°; the ternary eutectic is still lower (+22°). The K of these systems at 75° is between 0.01 and 0.02 $ohm^{-1}cm^{-1}$ and suitable compositions of higher K can be found by dissolving salts of alkali metal [61]. Both hydrazine and acetamide are but examples of those many solvents which have not yet been tried in cells with light metals intended to be reversible. Various systems of solvents (some of them containing even several percent of water) are often more suitable than their components in revealing values of properties beyond those of the components.

During recharging, Li deposits, as well as those of other alkali metals, become crumbly and loose, which is a handicap to their complete use as anode during discharge. For example, during electrodeposition of Li from LiCl solutions in formamide, the metal becomes more crumbly as the electrolysis continues [62]. There are 3 methods which should be tried to circumvent this difficulty: (a) the use of alloys of the light metals with one another (Li-Al, Na-Mg) or with other elements; (b) the use of porous materials (felts of stable metals) to absorb the deposited metal; and (c) deposition of the metal on the cathode in the liquid state, in which case the morphology does not alter if the anode before discharge is also liquid.

The exclusive attention of Li as the anode in HED nonaqueous SBs at the expanse of the other five light metals cannot really be justified. Although its reactions have higher theoretical EDs, the difference between the ED available with it and with Na, Ca, Mg and Al, when the weight of the whole cell with its accessories (electrolyte, conductors, separators and casing), is taken to account, becomes quite small. These metals, and even Ti, may show such advantages in their electrochemical behaviour (especially in cycle life), which may counter-balance their comparatively lower EDs, which still remain sufficiently high.

MOLTEN SALT ELECTROLYTES

The theoretical and experimental work on electrochemical properties of molten salts done up to the 1910's was summarized in the monographs of Richard Lorenz, who made important contributions in that field [63]. Further developments in molten salt electrochemistry occurred in the 1930's in connection with the electrochemistry of light metals, Na, Mg and especially Al. Many books, papers and reviews on this topic have appeared, especially in the USSR from that time on (see, for example, [64,65]. The development of nuclear power in the 1950's and the 1960's stimulated a series of experimental works in molten salts which have been suggested as coolants and heat-transferring media in atomic reactors. The papers from the US Bureau of Mines and from the Atomic Energy Commission are legion. Several books and reviews which have appeared recently contain chapters on electrochemistry of molten salts [66]. A review of galvanic cells in molten salts with 351 references was published in 1968. Most of the works cited there deal with the potentials of various electrodes in fused salt media [67]. A review of molten salt batteries and fuel cells was published in 1971 [68].

Tables of the open circuit voltage (OCV) and of theoretical EDs are presented in [68] for hypothetical cells formed by light metals with halogens, oxygen and sulfur at 500°C. We have combined these two into one, Table III.

TABLE III

OCV and ED (KWh/kg) of Cells at 500°C

	F		Cl		Br		I		O		S	
	V	ED	V	ED	V	ED	V	ED	V	ED	V	ED
Li	5.56	5.74	3.65	2.31	3.21	0.99	2.57	0.57	2.14	3.84		
Na	5.12	3.27	3.52	1.61	3.16	0.82	2.59	0.50	1.62	1.40	1.82	1.25
K	5.02	2.32	3.76	1.35	3.48	0.78	2.98	0.52	1.27	0.72		
Mg	5.01	4.31	2.68	3.57	2.26	0.66	1.61	0.34	2.68	3.56		
Ca	5.60	3.84	3.53	1.70	3.06	0.82	2.48	0.49	2.88	2.75	2.33	1.71
Al	3.87	3.71							2.48	3.91		

The voltages of Ca and its EDs are remarkable: they are higher than or close to those of Na. As to Mg and Al, they too present values of V and ED close to those of Na. The ED for the chloride, for example, of Mg is even higher than that of Li. And as the V's and ED's of practical cells are lower than those of the hypothetical ones because of the IR losses (for V) and the weight of the whole cell (for ED), the practical figures for these light metals are even closer. However, as is shown in Table IV, also taken from [68], the cell voltages, the power capacities, and the EDs of the molten salt experimental SBs are much higher than those of the conventional ones.

Two reviews were published on high temperature cells and batteries based on molten salt and solid electrolytes. The first one describes the cells

$$Li/LiCl/Cl_2(C)$$

and $$LiAl/LiCl\text{-}KCl/Cl_2(C)$$

with gaseous Cl_2. Li cells with chalcogenides as cathode materials are also mentioned as well as some details of their construction. This review, and the 26 references attached to it, reflects the state of the Li molten salt batteries to the end of 1970 [69].

The second review [70], prepared two years later is more comprehensive. It discusses in detail some theoretical problems, the thermodynamics and rate processes in electrochemical cells, and presents tables and graphs characterizing the high-temperature secondary cells. Five such cells, with molten salt electrolytes and Li anodes, are presented in Table 7 of the review and the cycle-life and the state of development, with the literature references, are indicated.

The operating temperature of these cells is from 340° to 650°C and the cycle-life is quite different: 100 cycles for the cell

$$Li(Al)/LiCl\text{-}KCl/TeCl_4(C) \quad (1)$$

to >220 for the cell:

$$Li(Al)/LiCl\text{-}KCl/Cl(C) \quad (2)$$

These two cells are in the laboratory development state, being evaluated as cells and batteries. The other three, viz.

$$Li/LiX\text{-}MX/S \quad (3)$$

$$Li/LiX\text{-}MX/Se \quad (4)$$

$$Li/LiCl/Cl_2 \quad (5)$$

TABLE IV

Comparison of Properties of Conventional And New Types of SBs [68]

Battery	t°	Cell Voltage	Power Capacity W/kg	ED Wh/kg	Cycle Life
Pb-acid	ambient	2.1-1.5	6-30	20-30	100-400
Ni-Fe	"	1.3-0.8	7-40	30-35	100-3000
Ni-Cd	"	1.3-0.8	7-45	36-40	100-2000
Ag-Zn	"	1.35-1.1	25-150	80-100	100-300
Zn-air	"	1.4-1.0	40-60	100-150	
Na-air	130°	2.6-1.8	80-100	180-273	
Li-S	340°	2.3-1.2	550-800	250-360	
Na-Bi	350°	0.8-0.4	80	40	
Na-S	300°	2.1-1.2	200-350	180-330	
Li-Cl (G.M.)	650°	3.5-3.0	200-400	300-400	
LiCl (Sohio)	450°	3.4-1.0	330-440	100-180	225
Li-Te	470°	1.8-1.0	550-800	185-265	
Li-Se	375°	2.2-1.2	600-1000	220-330	

are still in the early experimental stage, as single cells. The number of charge-discharge cycles of the secondary cell depends, for the same system, upon the current density (current per unit of electrode area) and on the depth of discharge (the fraction of the stored energy that is removed). Generally, molten salt cells withstand deep discharge cycles better than aqueous or non-aqueous cells, it seems.

The problems connected with the cells (1) and (2) are low capacity and parasitic currents, and of the cells (3-5) corrosion of the seals and insulators. All these cells were (in 1973) in the early stages of development. The cells (2-5) have ED of 200 Wh/kg [70].

We will now consider some publications on molten salt SBs which have appeared since 1973.

Li AND Li-ALLOYS SBs

Of all the light metals, Li shows the least tendency to dissolve rapidly and easily its molten salts, a favorable fact for Li cells. Li dissolves in LiCl at 640° up to 0.2-0.5 mole %, whereas the solubility of Na in NaCl at 811° is 2.8 mole % and of Ca in $CaCl_2$ at 1000° is 5.4 mole % [70a].

The two Li-Cl cells shown in Table IV, which operate at 650° and 450° respectively, have required substantial improvements directed to their possible practical use. The first one, studied in the G.M. laboratories, has had its operation temperature lowered from 650° to 425° by the utilization of the ternary salt mixture LiF-LiCl-KCl. The cell:

Li(liq.)/LiF + LiCl + KCl/Cl on C (porous graphite)

gave 232 cycles and about 350 Wh/kg ED (1.26 Mj/kg), has been described as one of the most promising high-temperature SBs for vehicular propulsion [71].

However, more publications have appeared on Li SBs with S or sulfide cathodes. Thus, a cell:

Li/LiCl-KCl eutec./S-As

was tested. It operated at 380°C. Arsenic was added to retain S in the electrode, inside a molybdenum-mesh support. Discharge and charge cycling was carried out [72]. The same cell, with LiF-LiCl-KCl as electrolyte, was developed in the Argonne Labs for application to electric automobiles. Its ED was > 200 Wh/kg and specific power > 200 Wh/kg, when operated at 380 to 425° [73].

The S cathode was, evidently, not always perfect, and several workers have preferred to use sulfides instead, mostly FeS and FeS_2. Pure S is unsuitable because the operating temperature of these cells is so high (about 400°) that S dissolves in the LiCl-KCl electrolyte and reacts with Li at the anode, leading to self-discharge. However, in the Li-FeS_2 cell, these problems have been circumvented [74]. Attempts were also made by other workers to replace S by sulfides of Fe, Ni, Co and Cu; several disclosures were issued on this topic [75].

Various sulfides have been tested as cathodes for Li cells with LiCl (58.8 mole %) + KCl (41.2 mole %) as electrolyte. In Table V the OCV and the theoretical ED for such SBs, are given, as well as the formulas of the cathode material before and after discharge. Up to 300 cycles, (for Cu_2S up to 912) have been achieved [76]. At the temperatures of the electrolytes (350°-400°), Li is liquid and highly corrosive. Therefore many attempts have been made to use Li alloys which are solid at those temperatures. The compound LiAl melts at 718°, i.e. it is solid at the operating temperature of the SB, which is usually below 450°. Experiments have been carried out on the anodic dissolution of this alloy. It shows a voltage between -1.95 to -2.0V at a Li content of 14.7 to 48 atom. % [77]. The Argonne Labs are developing SB cells of more than 120 Wh/kg ED, intended for off-peak energy storage and for car propulsion. Higher energy-density cells have been constructed using FeS_2:

$$\underset{\text{eut.}}{\text{LiAl/LiCl-KCl}}/FeS_2$$

However, the electrochemically formed Li-Al alloys, used as anode, presents difficulties during cycling. It is proposed that pyrometallurgically prepared alloys might show better results [78].

In the cell of the SB:

Li-Al/KCl-LiCl/Te

With a BN separator, the failure mechanism and capacity loss, due to the disintegration of the Al-Li alloy during cycling, were studied by X-ray radiography [79].

Li-Al anodes have been combined in cells with Cl_2 in the Sohio Carb-Tek battery, operating with a molten salt electrolyte in the range of 400-500°C. A porous carbon cathode and a BN separator were used. The $TeCl_4$ additive to the positive electrode is used to enhance the capacity in the 3.25-2.5V range. The battery presented many problems with the materials of the electrode, the casing and the seal. Corrosion by Cl_2 is especially troublesome. It was found that in an O_2-free electrolyte vanadium may serve as a stable current carrier [80].

Li-Al and Li-Si alloys were used in [illegible]

Li-Si or Li-Al/LiC[illegible]S_x

TABLE V

$Li-MS_n$ SB
Theoretical ED's, OCV, and the Composition of the Cathodes Before and After Discharge

Sulfides	Fe-S	Cr-S	Ni-S	Cu-S
Probable composition of the cathode before the discharge	$FeS_{1.5}$	CrS	Ni_3S_2	Cu_2S
Discharged Cathode	Fe	Cr	Ni	Cu
Theoret. ED Wh/kg (Li-MS)	1153 (968 for FeS_2)	693	678	518
OCV	1.62	1.27	1.70	1.68

for high ED pre-prototype cells and comparison was made [81]. There are advantages and disadvantages to each.

The structure and anodic discharge behaviour of Li-boron alloys in the LiCl-KCl eutectic melt are discussed in detail in more recent articles. In one study, from the shape of the discharge curves the existence of a compound Li_2B in the Li-B system was surmised. The experiments have shown that Li-B alloys promise good results if used in the high-energy-and high-power-density molten salt SBs now being used with other light metal anodes [82].

The data in some very recent publications indicate that long life may very well be achievable in some Li-molten salt systems. Particularly encouraging is the work reported in Proc. IECEC in 1977 by the teams from Argonne National Laboratory, General Motors Research Laboratory and Atomics International, under the stimlous of the U.S. Government's Energy Research and Development Administration. In the earlier symposium, at Argonne National Laboratories in 1976, more detailed reviews of the several approaches being made by these groups were given. At this rate of effort and progress the capability for industrialization of molten salt HED battery systems indeed seems feasible by 1983, as ERDA (now Dept. of the Energy) intends.

THE OTHER FIVE CANDIDATES

All the molten salt SBs reviewed above have either a Li anode or a Li-Al one in which Li prevails quantitatively. As to the other 5 light metals (Table III) they are seldom mentioned in the literature as candidates for anodes in these SBs, except Al which has been offered for that purpose in a few publications. In [82] it is stated that molten salt batteries with Ca or Mg anodes yield only a small proportion of their theoretical energy because Ca anodes react chemically with the electrolyte and both Ca and Mg anodes are passivated at high current drains, becoming coated with resistive films of solid salts. In a melt containing Li salts, Ca replaces Li^+ ions:

$$Ca + 2LiCl \rightarrow CaCl_2 + 2Li \qquad (1)$$

The Li metal so produced will form a liquid alloy with Ca (m.p. 231°). The fact is observed in thermal batteries [83a]. The reaction (1) occurs in the thermal battery

$$Ca/LiCl\text{-}KCl\text{-}CaCrO_4/Fe,$$

to which heat for the electrolyte melting is provided by $Fe + KClO_3$ pellets [83b]. More recently a rechargeable battery based on calcium was described:

$$Ca\text{-}Al/CaCl_2 + NaCl/FeS$$

Although its OCV is only about 1.86V, the cell was shown to be capable of sustaining some tens of cycles, and shows promise [84]. See the several other excellent papers as well in the same Proceedings of the Symposium at Argonne.

In a U.S.S.R. patent, Na anodes in molten salts (NaOH + NaBr) were offered as a source of electric power at high temperatures, but no cycling data were presented [85a]. A secondary battery operating at 150° with high ED and output is offered in a German patent. The cell:

$$Na/NaAlCl_4/C$$

has a beta-Al_2O_3 separator [85b].

There are several publications on molten salt SBs with Al anodes. $AlBr_3$, the Al halide with the lowest m.p. (97.5°), mixed with one or more alkali metal halides, was offered as an electrolyte in a battery $Al/AlBr_3$ + MX/C, operating at a low temperature range, 50-250°, but nothing is said in the patent abstract about cycling [86].

Low-melting electrolytes based on chloraluminates, $AlCl_3 \cdot MCl$, where M is Li, Na, K, were considered in [87]. Cells with Al anode and various cathodes, both inorganic and organic, were tested. The sulfur cathodes seem to be the most suitable, although complex chlorides, fluorides and sulfides show possibilities. An experimental Al-S cell is described in detail in [88]. The overall reaction: $2Al + 3S \rightarrow Al_2S_3$, provides a ED of 1275 Wh/kg at 200°. It is a primary battery, however.

The potentialities of the use of titanium in rechargeable SBs has been the principal topic of a recent report prepared by the authors. The situation can be summarized as follows. Although Ti can be dissolved in molten salts and deposited from these solutions by electrochemical reduction [89], the present authors have not found any publications in which Ti is offered as the rechargeable negative plate in molten salt SBs. Perhaps no serious attempts have been made to investigate the possibility of using cells with Ti as negative plate, either in nonaqueous or molten salt electrolytes; at least, nothing of such attempts has been published. There are however, several publications discussing the use of Ti as cathodic material, or in supports, casing and conductors. In Table I of [90a], titanium is listed as an anode among other candidate metal-oxygen systems. Its voltage and EDs in such systems are among the highest and the cost per KWh the lowest, but no indications of its use were claimed in [90a]. The detailed review of possibilities is given in [90b].

CONCLUSIONS ABOUT SBs BASED ON MOLTEN SALT ELECTROLYTES

The main advantage of molten salt electrolytes for HED SBs is the fact that each of the selected six most active light metals -- Li, Na, Ca, Mg, Al and Ti -- can work reversibly in molten electrolytes, i.e. they can be

anodically oxidized during discharge, and cathodically reduced by recharging. This can also be done somewhat in non-aqueous solutions but the deposition stage has not yet been achieved, for any of the pure metals, except Ti, in aqueous solutions. Another advantage of the molten salt electrolytes is their good conductivity, which is by two orders higher for the same salt than in non-aqueous solutions and from 5 to 10 times higher than in aqueous systems. At high conductivities, i.e. at low resistances (R) of the electrolyte, the IR losses can be very small. There are, however, two intrinsic shortcomings connected with the high temperatures of operation (300° to 450°C) of most of the SBs incorporating molten salt electrolytes. The first is the high rate of corrosion of materials -- the electrodes, supports, conductors, seals, casings and even the separators if not carefully chosen. The second shortcoming is the energy loss through radiation, which takes place in any device the temperature of which is higher than that of the environment. Since both these effects are more intensive the higher the operating temperature, alleviation of both these problems can be accomplished by lowering the m.p. of the electrolyte, and the temperature of the battery's operation. There have been several attempts to achieve this goal; thus three cases [85,86,87] are cited above, of which two [85 and 87] are based on $AlCl_3$ compounds and one, [86], on the low-melting $AlBr_3$. In [88], the $AlCl_3$-containing electrolyte melts below 100°, but the operating temperature is given as 200-300°.

To form a clear idea of the possibilities of the lowering of the temperature of the electrolyte, one must scan the following Tables of some low-melting salts and systems. Tables VI-VIII, have been drawn up from various sources, the most important of which are indicated on each Table.

There are many molten salt electrolytes which are liquid in the range from 60° to 125°C. Among the low-melting systems there are many which contain cations of Li^+, Na^+, K^+ and Al^{+++} and anions of Cl^-, Br^-, and NO_3^-. The Tables cover only a fraction of all the low melting systems: studies on some others have been published in the literature, and still many more possible combinations have not yet been investigated. The latter contain Ca^{++}, Mg^{++}, and Ti^{++} cations, as well as HSO_4^-, HSO_3^-, HCO_3^- and some other anions. The compatibility of each light metal cation with any low-melting molten salt electrolyte must be tested experimentally. It can be anticipated that at least some such combinations will have useable properties.

We have already discussed the useful and interesting combinations of low-melting electrolytes which can be found among systems formed by alumohalogenides (or haloaluminates). Similar compounds and systems are formed by $FeCl_3$, two complexes of which are presented in Table VI ($NaFeCl_4$ and $KFeCl_4$), and by other salts of polyvalent metals (Sb, As, Bi, Ti, Nb). Salts of organic acids, and systems formed by them, may also find useful applications as electrolytes for HED SBs. By choosing the suitable low-melting electrolyte for each redox couple containing a light metal, the problem of designing HED SBs, operating at temperatures between 50 and 100°C, can be systematically addressed.

The availability of low-melting salt combinations opens up potentialities for all the light metals. As we have seen above, almost all the research work on HED SBs with molten salt electrolytes is carried out with Li as an anode to which, in one case, Al is added. Such a limited

TABLE VI

Low-Melting Inorganic Compounds and Systems [91]

A. Compounds

Compound	M.P., °C	Compound	M.P., °C
$TeCl_2$	175	BiI_3	43
$MoCl_3$	194	SbI_3	170
InCl	225		
$InCl_2$	235	NH_4CNS	87.7
		KCNS	171
$LiClO_3$	127.6		
$LiClO_4$	236	NH_4NO_3	169
		$NaFeCl_4$	163
$SbBr_3$	96.6	$KFeCl_4$	250
$GaBr_3$	124.5	$NaNH_2$	208
$SnBr_2$	232		

B. Systems

A	B	C	M.P., °C	Mole %: B	C
$LiNO_3$	- NH_4NO_3		97	75	
TlCl	- CuCl		122	60	
KCNS	- NaCNS		123.5	70	
$LiNO_3$	- KNO_3		125	44	
KCl	- $SnCl_2$		180	62	
NaOH	- KOH		187	40	
$LiNO_3$	- NH_4NO_3	- NH_4Cl	86	66.7	7.5
$NaClO_3$	- $LiClO_3$	- $LiNO_3$	92.6	(50)	(40)
$LiNO_3$	- KNO_3	- $NaNO_3$	120	53	17

TABLE VII

Organic Salts and Systems [92]

A. Compounds

Compound	M.P., °C
$TlCOOH$	100.8
$KCOOH$	167.5
$TlCOOCH_3$	130

B. Systems

System	M.P., °C	Mole % B	C	D
$KCNS-KHCO_2$	78.5	54		
$Ca(HCO_2)_2-2TlHCO_2$	94.2	91.2		
$Sr(HCO_2)_2-2TlHCO_2$	96.8	94.9		
$KCNS-KHCO_2-KNO_3$	55.5	48.3	16.8	
$(Cs,K,Li)CH_3CO_2$	73	27	20	
$KBr-KCNS-KHCO_2$	75	43	55	
$KCl-KCNS-KHCO_2$	70	43.5	55	
$K,Li-HCO_2-CNS$	53	50	45	5

C. Systems with Acetamide (AcAm) [61]

Acetamide CH_3CONH_2	81			
$LiNO_3$-AcAm	86	84		
NH_4NO_3-AcAm	37	70		
$LiNO_3-NH_4NO_3$-AcAm	22	20	71	

TABLE VIII

Alumohalides and Their Systems [93]

A. Individual Alumohalides

Compound	M.P., °C	Boiling P. °C
AlF_3	445	1272
$AlCl_3$	192.4	187
$AlBr_3$	97.5	253
AlI_3	191	380

B. Systems

A	B	C	M.P., °C	Mole % B	Mole % C
LiCl	- $AlCl_3$		105	58	
NaCl	- $AlCl_3$		110	61	
KCl	- $AlCl_3$		128	67	
NaCl	· $AlCl_3$		150	50	
LiBr	- $AlBr_3$		105	(75)	
LiBr	$AlBr_3$		195	50	
NaBr	- $AlBr_3$		95	76	
KBr	- $AlBr_3$		88	74	
KBr	· $AlBr_3$		191	50	
NaI	- AlI_3		123	70	
KI	- AlI_3		105	67	
NaCl	· $AlCl_3$	- $NaI \cdot AlI_3$	80		
$AlCl_3$	- NaI	- AlI_3	65		
NaCl	- KCl	- $AlCl_3$	88	16.5	63.5

approach cannot be justified either from the theoretical point of view nor from practical considerations. Although the first impression left by scanning the data of Table III is that the ED of Li in combinations with oxidizers is much larger than the EDs of other light metals, there are other good possibilities. Thus the ED of the Mg-Cl couple is higher than that of the Li-Cl couple; that of the Mg-O couple is very close to that of Li-O, and that of the Al-O couple is even higher. As for Na and Ca, although their EDs are lower than those of Li, the differences become much smaller if they refer to the battery as a whole, since the weight of the redox couple is only a fraction of the total. If the availability and the price of Li is compared with those of the other 5 light metals being considered (Na, Ca, Mg, Al and Ti), the advantages of the HED of Li redox couples will almost disappear. The possibility exists that each of them in some electrolyte might offer better performance than Li. It would seem that more research effort should be applied to the other 5 metals, each of which possibly could show substantial advantages over Li under certain conditions. Titanium, for example, could some day emerge as one of the most useful anodes for HED SBs. Almost the same could be stated about Ca, the peculiar behavior of which in molten phosphate (the electrochemical reduction of such a compound as $Ni_{12}P_5$) shows its potentialities there [94].

SOLID ELECTROLYTES

Appreciable ionic conductance of several solid salts was known from the start of this century, and the emf's of cells with such compounds were measured then. However, attempts to use these compounds as electrolytes in batteries mushroomed only during the last decade. Some practical results have been achieved for two kinds of solid electrolytes, namely, for those based on AgI and its complexes and for compounds based on β-Al_2O_3. Some conclusions will be drawn concerning the prospects of solid electrolyte batteries based mostly on derivatives of these materials as solid electrolytes.

COMPLEX COMPOUNDS OF AgI

The most important property which has permitted the use of these compounds as electrolytes is their high electrolytic conductivity in the solid state, even at ambient temperatures. For some the values are between 1×10^{-4} and 2×10^{-2} ohm^{-1} cm^{-1}, which are not far from those of aqueous salts.

A historical review of the conductance studies of these compounds and the emf's of cells based on these solid electrolytes, was published in 1969 [95]. Another review, which discusses the conductance and the structure of various solid electrolytes (AgI and its derivatives, Ag_2S, Li_2SO_4, $Na_2O \cdot 11Al_2O_3$) was published in 1972 [96]. There have been several papers published since, especially by Italian & Japanese workers.

As a rule, one solid phase of these electrolytes is a fairly good conductor, its open structure allowing the cation (Ag^+, Na^+, Li^+) to move fairly freely inside the lattice. In the case of AgI the conductivity, K, increases by two orders of magnitude at 147°C, as the beta-modification is transformed into a more open alpha-structure. At ambient temperature the conductivity of AgI itself is very small, but it is much higher in some complexes, such as $RbAg_4I_5$, in which K = 0.2 ohm^{-1} cm^{-1} at 20°C, for example. Since the discovery of the high ionic conductivity of $RbAg_4I_5$ [97a] much work has been done on solid electrolytes. Takahashi and coworkers have studied the conductance and the crystal structure of AgI complexes as well as their behavior in electrochemical cells [97b].

Values of K as high as 6 X 10^{-2} ohm^{-1} cm^{-1} have been found in combinations of AgI with substituted ammonium iodides [98]. These studies were extended and the results used in the development of primary solid-state batteries, for operation at ambient temperatures, based on cells such as:

$$Li/LiI\text{-}CaI_2/AgI \quad (C)$$

[99a], and with Ag_2CrO_4, Ag_3PO_4 and the superlattices formed with AgI [99b].

The properties of the AgI-based solid electrolytes have been studied also in the U.S.S.R. and several publications have appeared. The research was directed towards the use of solid electrolytes in batteries and in information devices [108,a]. A thin-film glavanic battery with solid $RbAg_4I_5$,

$$Ag/RbAg_4I_5/Te$$

was studied [108,b]. Several publications describe the construction and properties of that cell [109], the method of symthesizing the compound $RbAg_4I_5$ by precipitation in acetone [110], and so on.

Although primary batteries of various types based on AgI complexes are at present available commercially, no substantial success has been achieved with rechargeable SBs with Ag compounds conducting at ambient temperature (although Ag/complex/Ag coulometers capable of being cycled many thousands of times are readily available). After a decade of studies, cells based on AgI complexes have not yet been made which are rechargeable to any extent: the complex tends to break down.

BETA-ALUMINA SB

The beta-alumina cell from the very beginning was considered to be a SB. The first detailed publications on it appeared in 1967 [100], and since that time scores of open publications and patents and several reviews on this SB have been issued. In the reviews cited above on high temperature cells [69,70] substantial portions are devoted to this SB; the structure and properties of its solid electrolyte, $Na_2O.11Al_2O_3$, are discussed in [96]. The cell has a Na anode and a S cathode:

$$Na/Na_2O.11Al_2O_3/S$$

and its performance is based on the fact that the electrolyte is specifically accessible to the Na^+, which reacts with S at the cathode as follows:

$$2Na + S \rightarrow Na_2S.$$

During the charging process Na^+ ions are carried back through the beta-alumina electrolyte to the anode where they are reconverted to Na metal. In practice polysulfides of Na are formed at the cathode. The high operating temperature of the Na/S battery is due to the high m.p. of the Na polysulfides formed at the cathode. The conductivity of the beta-alumina is better the higher the temperature. Attempts have been made to decrease the operation temperature by incorporating MgO or FeO into the electrolyte [101]. Many patents have been granted to workers who claimed that the SB can be improved by other suggestions (see for example [102]).

The history of the beta-alumina SB development and the state of the problem in 1974, is presented in Ref. [103], which includes references to the most important literature up to that time. The processes at the cathode are complicated. The Na-S phase diagram has been investigated: two eutectics (at 235° and 257°) were found and the region of the two liquid layers was bracketed at 78 - 100% S [103]. The paper seems to be one of the most comprehensive and substantial articles yet to be issued on that topic. The article relates the technological uses of the SB which started at the Ford Company in the U.S.A. In 1967 British companies started to work on this SB, and in 1972 the World's first demonstration of a Na-S SB powered vehicle - a 18 cwt van. A British consortium which was set up to exploit Na-S SBs, was expected to produce a prototype vehicle during the 1975-1978 period and to be marketing the SB by 1980. It is believed that the Na-S SB has a potential saving of a factor of nine over the lead-acid battery and could have a range of more than 100 miles in electric cars. Electric buses with a 40 mile operational range have already been built [104]. Although the time-table has slipped somewhat as materials problems have been uncovered and resolved, it is very probable that the united efforts of the U.K. and the U.S.A. scientists and others world-wide, on the Na-S SB, may yet be crowned with success.

The shortcomings of solid electrolytes -- the sensitivity of the beta-alumina batteries to vibration and shock, and the low conductivity and high cost and low cyclability of the AgI based cells -- have stimulated the search for new types of these electrolytes. In the 1972 review [105a] of the advances in Li solid-state batteries, most of the cells discussed contained Ag compounds. However some cells without these compounds, as for example, the cells:

$$Li/LiI/I_2 \quad \text{or} \quad Li/LiI/I_2\text{-benzidine}$$

are also discussed [105a]. The iodine-benzidine cell is discussed in some detail in [105b], and the iodine cell in [106]. The properties of the high-temperature phase of Li_2SO_4 as a solid electrolyte is considered in [107]. So far, such cells have found only limited practical applications, and these as primary batteries with very small currents and long shelf life, for pace-makers for heart patients, for example. Little success has crowned attempts to make mini-SBs based on solid electrolytes.

Considerable activities in the field of solid electrolyte batteries have been reported from the U.S.S.R. during recent years. It is unusual that the review of the solid electrolyte problem made by Russian workers [96] should be published not in the review magazine "Advances in Chemistry", as would be expected, but in the electrochemical journal "Elektrokhimia", which usually does not issue reviews. However, the authors of [96] are working in the "Institute of New Chemical Problems" - the leading institute of the Academy in the field of electrochemical sources of power, and the Soviet Academy, as well as the government, are paying considerable attention to this field as a part of their research on energy-conservation.

In the Institute of New Chemical Problems, the resistance at the boundaries between Na and $Na_2O.MgO.10Al_2O_3$ was studied [111a] and a patent for a solid electrolyte containing NaF and Al_2O_3 was granted [111b]. These solid electrolytes were synthesized by a gas-flame method. Those with the composition $M_2O{\cdot}nAl_2O_3$ (n = 5 to 12) possess ionic conduction at ambient temperatures, $\sim$ 0.1; this value decreases when Na_2O is partially replaced by Li_2O or MgO [112].

Some amounts of Sb_2O_3, added to the sulfide cathode of the solid Al_2O_3 battery, decrease the melting point of the sulfide, while not impairing the work of the cell [111].

THE PROSPECTS FOR SOLID ELECTROLYTE SBs

For reasons discussed above, the AgI-based cells, being useful for some special types of primary batteries, are not very promising for secondary ones. The beta-alumina cells, on the contrary, have already been developed to the pilot-plant stage and their prospects are fairly good to become commercialized. They are the most advanced among the candidate batteries for traction. The main problem here is connected with the high operating

temperature, which could be easily lowered or even brought to ambient conditions, if a solid electrolyte with K values of about 0.1-0.3 ohm^{-1} cm^{-1} could be found. Since the anode metal ion (Na^+,Li^+) must move through the interstitial vacancies, the structure of crystals with such vacancies must be studied and analogous compounds synthesized. Such compounds might be found among silicates; thus even at present some Li-containing silicates, Li_4SiO_4, for example, are known for which K = 9.0×10^{-4} at 25°C and $2.2 \cdot 10^{-3}$ at 400°C. $LiAlSiO_4$ has a K-value of 5.6×10^{-5} [114]. Among the great variety of silicates, perhaps other, better-conducting complexes can be found. Dehydrated zeolites of special structure might be found which can act as a ion-exchanger electrolyte, containing ions of any light metal in the series from lithium to titanium. In some special cases perhaps even ion-exchanger resins might be applicable as separators, being impregnated with the cations of the chosen anode metal.

Cells with Se complexes, such as

$$Mg/Ba_xMg_{6-x}Se_6/NbSe$$

are examples of how the electrolyte can adjust to accommodate the anode-metal cations [115]. Similar complexes which can in principle be synthesized for Al, Ca and Ti. But Na and K complexes, such as Na_2SbO_3, $NaTaWO_6$, $2K_2O \cdot 3Nb_2O_6$, and some others with K = n x 10^{-5} ohm^{-1} cm^{-1} [116], may also serve as solid electrolytes. Perhaps some with higher conductances will be found. Recent advances in synthetic inorganic chemistry raise the hopes of achieving some success in this direction. United efforts of electrochemists, crystallographers and inorganic chemists in the field of solid ionic conductors may increase the chances of creating HED SBs based on solid electrolytes.

AQUEOUS AND MIXED ELECTROLYTES FOR HED SBs

Unlike the conventional SBs of today - the Pb-acid, the Ni- and Ag-alkaline - which are based on aqueous electrolytes, there are new types of HED SBs which are in various stages of completion and which incorporate non-aqueous, molten-salt or solid electrolytes. The reason for avoiding water as an electrolyte solvent is its incompatibility with the HED light metal anodes, which either react violently with it (Li, Na, Ca) or are passivated by it (Mg, Al, Ti). However, properties of the electrolytes used in the new SBs -- the low conductivity of the non-aqueous and the solid electrolytes, the high temperatures of operation often necessary in the latter, and also in molten salt electrolytes -- as well as the unsatisfactory morphology of the regenerated anode metal in most of these batteries -- are hampering their development. Aqueous solutions per se are free of these particular shortcomings. It is quite natural to consider the possibilities

of the use of some water as a component in mixed aqueous-nonaqueous, or aqueous-molten salt electrolytes. In this Section we deal with the possible use of the six light, active metals in SBs based on "moist" or "transition region" electrolytes.

The main reason for avoiding water as a solvent is the fact that the electrolysis of aqueous solutions of alkali and alkaline-earth metal salts commences at 1.7-2.0 volts (depending on the electrode material) and results in the evolution of O_2 and H_2. If the cell itself has a higher voltage, "internal electrolysis" can, but not always does, proceed during its operation, accompanied by the evolution of H_2 and O_2 and by self-discharge [117]. However, this fact does not preclude attempts to create moist primary batteries with Li, Na or Ca, provided that their reaction with the water can be decelerated.

Minor admixtures of water to nonaqueous electrolytes are often harmful, for example in batteries with inorganic solvents such as $POCl_3$, $SOCl_2$, SO_2Cl_2 where it is important that the electrolyte be free of water contamination because of the possible formation of oxychloride cements:

$$MOCl_n + H_2O \rightarrow MO(OH)Cl_{n-1} + HCl$$

where M = P or S [118]. Special "water scavengers" (synthetic zeolites) have been proposed [119] to maintain the H_2O level in the electrolyte below that which interferes with the optimal performance of the cell Li or $Na/POCl_3/(CF)_n$.

In some cases the introduction of water into nonaqueous and molten salt batteries is desirable and helpful. We now consider some such cases.

AQUEOUS ALKALI METAL BATTERIES

A short report was made on the Symposium on Batteries for Traction (see [90]) on the studies in the Lockheed Research Laboratory on electric power sources based on reactions of alkali metals with water, work which was started in 1969 by Littauer et al. These reactions produce very high ED's, are very efficient, ∿1400 Wh per pound of alkali metal. Two configurations have been developed, one described as a dynamic cell and the other a static one. Both are fed with an alkali metal and water, and produce H_2 and alkali metal hydroxide; the former can be used as a source of power. (In the dynamic cell it generates mechanical power which is transferred into an electric motor.) The MeOH (M = Li, Na) can be used for regenerating alkali metal [120]. Little was said about the cell reactions, and it could be understood, that the cells are a kind of a hybrid between a primary battery and a fuel cell.

More recent publications from Lockheed and by others, dealing with these batteries, have appeared. In a German patent a battery based on the cell:

M/3M-KOH/Fe or Ni

is described [121a]. A Li-H_2O primary battery for several minutes of discharge is described in [121b]. Amalgams, alloys, membranes, separators and noble metals are not required. Two designs of cell are mentioned, which operate in either fresh water or seawater at 16000 psi (about 1087 atmosph.) [121c]. The basic cell reaction:

$$Li + H_2O \rightarrow Li^+ (aq) + OH^- (aq) + \tfrac{1}{2}H_2$$

E = 2.2V. The Li + H_2O reaction is considered hazardous because of its high heat of reaction: (ΔH° = -53.3 Kcal/mole) (8400 Wh/kg of Li). However, the presence of OH^- ions in concentrations greater than about 1.5M causes the formation of a protective film which moderates or decelerates the reaction rate [122a]. X-ray analysis of the film has shown that it consists principally of LiOH + minor amounts of LiOH H_2O. It is porous and permits the reaction Li + H_2O to proceed, but only slowly, relative to the uninhibited reaction [122b]. A battery based on this cell can be used in marine devices, where seawater is the electrolyte [122c].

The passivation of the Li anode also depends on the concentration of LiOH. Passivation started at 2.8M of LiOH, but in 5M solution the anode requires more than 1 hour to recover to the active state. The anodic behaviour of Li in alkaline electrolytes may be unlike that of any other metal. Provided the hydroxyl ion concentration is sufficient, a film forms on the anode, which prevents violent direct reaction of Li with H_2O. At concentrations in the range 3.5-5M LiOH the anodic film acts as a barrier, insulating most of the Li surface. The reaction of the metal with the electrolyte occurs at the base of the pores which permeate the film. The passivation is transient, with the duration being from seconds to hours [123a]. The electrochemical behaviour of Li is determined by the formation of a film which is thicker than that formed by Zn or Cd when they are polarized anodically. The LiOH concentration influences the thickness of that film [123b]. A mathematical model of Li-H_2O cell is developed in [124].

The claim of the authors of [123] that the electrochemical behaviour of Li in aqueous solutions of its hydroxide is unique, needs further examination. It has not yet been proved experimentally that Na or Ca do not form films in concentrated solutions, of the hydroxyl ion (OH^-). NaOH solutions can be prepared in the so-called transition region between molten NaOH and its aqueous solutions, i.e. with compositions at which the mole fraction of water $<<$ 0.2. The physico-chemical properties of the compositions in the transition region are often quite different from those of dilute solutions of salts or hydroxides in water. These will be discussed in more detail, as they relate to the role of water in secondary batteries based on light metal anodes.

THE TRANSITION REGION OF COMPOSITIONS IN BINARY SYSTEMS

From the 1880's, when Van't Hoff's theory of osmotic pressure and that of electrolytic dissociation of Arrhenius appeared, the attention of researchers was diverted to the studies of dilute solutions of electrolytes. Fundamental properties of concentrated solutions, and especially those in which the concentration of ions is of the same order of, or higher than, that of the non-conducting species, received less attention than their practical importance attested. Concentrated solutions seemed to drift out of the field of vision of the researcher. The appearance of the new electrostatic theories of conductance of Debye and Huckel, Falkenhagen, Onsager and of other theorists, shifted the interest of workers in the field of electrolytes still towards more dilute solutions, to which the new theories could be applied with some precision. This report will not discuss the accomplishments, limitations and the failures of these theories.

Aside from some conceptual difficulties, one of the harmful effects of this theory was the diversion of research from the opposite end of the property vs composition diagram, where mole fraction of the salt is >> 0.9, i.e. a dilute solution of the non-conducting component dissolved in the conducting one - water in a molten salt, for example. The transition region (TR) between the pure electrolyte and its solutions in the non-electrolyte presents a theoretical challenge but is of considerable practical significance, in batteries and in power cells, in electro-winning and electrolysis cells as well.

The conductance of a binary system can be approached from the values of conductivity of the pure electrolyte; one follows the variation of conductance as one adds water or other second component to the pure electrolyte.

The same approach is useful for other electrochemical properties as well: the e.m.f. and the anodic behaviour of light, active metals, for instance. A very important fact must be taken into account: the structure of water in the TR, and therefore its reaction, can be expected to be quite different from its structure and reactions in dilute aqueous solutions. (The same is true in relation to other non-conducting solvents.) The molecular structure of any liquid can be assumed to be close to that of the crystals from which it is derived. The narrower is the temperature gap between the liquid and the solidus curve, the closer the structures of liquid and solid. In the composition regions between the pure water and a eutectic point the structure of the liquid is basically like that of water;

between eutectic and the pure salt or its hydrates the structure is basically that of these compounds. At the eutectic point, the conductance-isotherm runs through a maximum and the viscosity-isotherm breaks. Examples are shown in [125].

Hydrates can play an important role in electrolytes for batteries with active metals. The water, being involved in the hydrate structure, is less active than at the compositions on the "water" side of the diagram, i.e. between the eutectic and pure water. The rate of the anodic dissolution of the alkali and alkaline-earth metals can be made low enough, so that the anodic reaction can be harnessed. Hydrates of the halogens, like Cl_2 can be employed for storage of the Cl_2 in a rechargeable battery.

Let us now consider, what happens to a molten salt such as $LiClO_3$ when small amounts of water are gradually added to it. The ions of the salt melts, which are frozen in the lattice of the solid salt, can move when the salt melts, and the melt will conduct. The addition of a few percent of water lowers substantially the viscosity (η) of the salt, acting as a "lubricant" for the movement of the ions, increasing their mobility and the conductivity of the melt. Thus, for example, whereas the 100% $LiClO_3$ at 128°, $K = 0.107$ $ohm^{-1}cm^{-1}$ and $\eta = 66.1$ cp, the addition of only 1.1% by weight (5.28 mole %) of H_2O increases K to 0.138 and decreases η to 43.6. At 14.5 wt % of H_2O the conductivity is about 2 times that of pure $LiClO_3$ and η is about 10 times less [126]. The addition of small amounts of water may lower substantially the melting point. Thus 14.5% of water mentioned above decreases the m.p. of $LiClO_3$ from 127.6° to 20°C. For the binary system $LiNO_3$ (m.p. 260°) and NH_4NO_3 (m.p. 169°), the eutectic is at 97°. Other low-melting systems (see Tables VI-VIII) can be formed at ambient temperatures (-10°C to +50°C) by the addition of 5-10 wt % of H_2O to binary mixtures, but the composition of the system at these temperatures will still remain in the TR. If this composition can be controlled, electrodeposition may be possible for the light metals such as Na and Ca. In the case of molten salt electrolytes the addition of water would lower the operating temperature to ambient, decreasing simultaneously the viscosity of the electrolyte and increasing its conductivity.

In the case of non-aqueous (inorganic and organic) solvents, the addition of small amounts of H_2O will increase the usually poor conductivity, and permit the use of comparatively high-melting solvent (eg. acetamide, m.p. 81°). From such a binary electrolyte, water in acetamide, the morphology of the metal deposited during recharge might be quite acceptable.

THE ACTIVE METALS: Li, Na AND Ca

The processes in the primary Li batteries which were discussed in [120-124] cannot be reversed electrochemically, because they are accompanied by the evolution of H_2, which is removed from the cell. In the hypothetical cell

$$\text{Li} \;\Big|\; \begin{matrix}\text{LiCl} + \text{AlCl}_3 + \text{Cl}_2\cdot 6\text{H}_2\text{O} \\ + \text{KOH} + \text{H}_2\text{O} + \text{dioxane}\end{matrix} \;\Big|\; \text{Cl}_2\cdot 6\text{H}_2\text{O}$$

the anodic dissolution of Li may run with a controllable speed. The limiting current at the anode will decrease as the OH^- concentration is increased. LiOH is only sparingly soluble in water. KOH is added for conductivity; the concentration can be very high. Experiments in which Li, Na and K are dissolved in aqueous solutions of their hydroxides have shown a substantial decrease in the rate of the process as the OH^- -ions concentration is increased. Breaks in the curve, rate of dissolution vs OH^- concentration, occur at compositions corresponding to the formation of hydrates; corresponding breaks were also observed on the conductivity-and viscosity-composition curves. The decrease of the dissolution speed is substantial. Thus when the concentration of NaOH was increased from 7-m to 21-m, the speed decreased 200 times.

In the solution containing 1-m H_2O in 10-m dioxane, the speed of Na dissolution was reported to be a thousand times less than in pure water [122a]. If by regulating the composition of the electrolyte in the Li/Cl_2 described above, the deposition of metallic Li on the negative electrode during recharging can be achieved, then a SB on the basis of this cell, operating at ambient temperatures, could be realized. As to the $Cl\cdot 6H_2O$ hydrate, it can be isolated from the electrolyte by a separator, as it is done in a semi-aqueous Li-HgO primary battery [128], or replaced by another cathode material, like Br_2, or $CuCl_2$ or other. A Li-alloy might aid in achieving reversibility.

Let us consider some examples. A primary Li battery:

$$\text{Li} \;\Big|\; \begin{matrix}\text{LiNO}_3 \\ + \text{urea}\end{matrix} \;\Big|\; \text{C}$$

is patented in the U.S.S.R. [129a]. A secondary battery with an alkali metal or its alloy as anode, a strong oxidant (strong acids, molten nitrates or nitrites, chlorates or perchlorates) in an inert medium as electrolyte, and a cathode of steel, Mo or other alloy is offered in a German patent granted to the workers of the Moscow Energy Institute. It is claimed, that the violent reaction of the alkali metals with the oxidants subsides if the heat produced in the reaction is conducted away. H_2SO_4, $H_2S_2O_7$, HSO_3Cl and HSO_3F are among the possible oxidants listed.

A battery

$$Li/H_2SO_4/Fe \text{ or } Mo$$

has ED = 7.4 KWh/kg, and the products of the reaction:

$$H_2SO_4 + 12\ Li \rightarrow 2LiH + Li_2S + 4Li_2O$$

are mostly soluble in the liquid. The temperature of the anode is 40-50° and the cathode (which is heated) is at 250-400° [129b]. Could it be made reversible with judicious additions to the electrolyte?

The formation of an anodic film on alkali metal anodes is mentioned in [129b]. If the fact can be confirmed, that Li is not unique in its reaction with water (as it is claimed in [123-124]), then Na may also develop such a film in contact with H_2O or non-aqueous liquids and so be protected.

A primary Na-H_2O battery is offered in a U.S.A. patent. From the description, which is not very clear, it follows that the construction is similar to that of the Li battery [128]
aqueous solutions are separated [130]. A Na-H_2O primary cell with a rotating cathode has been constructed and studied [131a]. It is similar to a fuel cell; thus Na and H_2O are fed into the cell constantly, and the rate of the feed can be regulated. The electrolyte, a NaOH solution, is self-generated and removed, and H_2-gas is evolved. It is significant that
metal-water battery with Na or K anodes is offered in a U.S.A. patent by the authors of [130]. However, in the abstract no mention was made of the cathode material, the electrolyte composition and the cell reaction [132].

In all publications on alkali metal-water batteries in which the cell reaction is disclosed, the following equation is proposed:

$$Me + H_2O \rightarrow MeOH + \tfrac{1}{2}H_2$$

No SB can be based on this reaction as long as H_2 is being lost. Perhaps it could be retained in the electrolyte under high pressure. A more fruitful approach might be to react the anode with an oxidant like Cl_2, Br_2 or oxygen in such a way that the product formed remains inside the cell and H_2O does not decompose but works only as a "lubricant" for decreasing the viscosity, increasing the conductance and lowering the operating temperature. Thus in the cell:

$$Me/MeAlCl_4/Cl_2 \cdot 6H_2O$$

MeCl is the discharge product and Me and Cl_2 the charged products. Cl_2 is captured by H_2O to form $Cl_2 \cdot 6H_2O$. The $Zn/Cl_2 \cdot H_2O$ storage system has been described [84].

If H_2 is evolved it could be captured by the simultaneously deposited metal to form a hydride, although such a process would require special conditions. Na reacts with molten NaOH forming NaH:

$$2Na + NaOH \rightleftharpoons Na_2O(s) + NaH$$

at 400° [133]. It would be worthwhile to study such reactions in cells at temperatures below 150°, using a NaOH + KOH eutectic to which a few percent of water has been added.

Mixtures of KOH, NaOH, LiOH and of their eutectics, with water, acetone, dioxane [134] and other solvents, may serve as suitable electrolytes for SBs with sodium or other alkali metals. There are interesting possibilities to be explored.

Ca is cheap, and its sources are practically inexhaustible. Its reactions with oxidants have high theoretical ED's. The study of its behaviour in reversible cells might be rewarded by success. Several publications on the use of Ca in primary thermal batteries can be found in the literature. In one cell, with a Ca-Ba alloy and a molten salt electrolyte, the presence of water has been shown to be harmful [90a]. However, detailed studies of the behaviour of a Ca anode in other mixed water-molten salt electrolytes have not been carried out. The reaction of Ba with water is slow, and alloying it in suitable proportion with Ca may be helpful in controlling the rate of the anodic dissolution of Ca. $Ca(OH)_2$ is very sparingly soluble in water, and film formation by it on the anodically polarized Ca surface is very probable. However, this film may dissolve rapidly enough in low-melting hydrates, such as $Ca(NO_3)_2 \cdot 4H_2O$ (m.p. 42.7°), $CaCl_2 \cdot 6H_2O$ (m.p. 30.2°, or $Mg(NO_3)_2 \cdot 6H_2O$ (m.p. 89.9°), to permit substantial anodic limiting current densities, and to offer prospects of rechargeability. A cell of the type:

$$Ca(Mg,Ba) \mid \begin{matrix} CaCl_2\text{-}AlCl_3 \\ OH^-, H_2O/(<5\%) \end{matrix} \mid Cl_2 \cdot 6H_2O \text{ or } CaCl_2$$

if studied in detail for example, might open the vistas for a useful SB based on an anode of Ca or one of its alloys.

THE PASSIVE METALS: Mg, Al AND Ti

Mg and Al are cheap and the ED of their couples with oxidants is high. A review of the performance of Mg and Al as primary cell anodes, published in 1959, indicated that Mg dry cells were already available for special purposes, and might achieve commercial significance, but that prospects for dry cells based on Al were poor [135]. Since 1960 several publications have been issued on the behaviour of Mg, such as in aqueous solutions of $MgCl_2$ [136], and on its use in aqueous primary batteries [1].

A comprehensive paper on the use of Mg alloys in aqueous power sources has appeared recently. The author recommends more extensive use of Mg in primary batteries because the price per gram-equivalent is 2.2 times smaller than that of Zn and the theoretical ED is more than 8 times higher than that of Zn in acid solution and about 6 times higher in basic solutions. Mg has the most negative electrode potential that in practice can be achieved in aqueous cells. The cell:

$Mg/NaClO_4/O_2$

is discussed [137a]. The metallurgy of the lithium-rich end of the Li-Mg system has recently been examined in some detail [137b]. The Mg dry cells commercially available are described in the new monograph on primary batteries [138]. A commercial sea-water-activated Mg battery is described in [139] and there are several patents on that topic.

There are no known SB systems with Mg in aqueous solutions. The Mg anode's irreversibility in aqueous solutions is thought to be due in part to the existence of monovalent Mg ions during the electrochemical discharge, in part to the self-corrosion and film formation, and in part caused by other factors [136,140]. All attempts to deposit this metal on the negative electrode from aqueous electrolytes have failed.

It is claimed that the Mg cell with molten salt electrolyte:

$$Mg/LiCl\text{-}KCl/Ni$$
$$\text{eut.}$$

is reversible [141]. It operates at temperatures above the eutectic melting point, i.e. about 400°C. Small amounts of water may decrease the operation temperature.

Studies of Mg cells with solutions of its salts in acetamide-H_2O mixtures may be of interest for Mg SBs. A cell:

$$Mg/LiCl\text{-acetamide}/V_2O_5$$

is mentioned in [1, p 100] but bromides of Cu or Co may be more effective than V_2O_5. Once formed on the surface, MgO is only slowly complexed away.

Since Al offers the possibility of a 2-to 3-fold reduction in anode weight and volume over Zn in alkaline primary batteries, many attempts have been made to use it. Cells of the type:

$$Al/3M\text{-}KOH/C$$

have been proposed for large Al-air or Al-O_2 batteries. Al alloys are also used with porous Ni as cathodes [142]. There are several articles and patents dealing with Leclanché type dry cells in which Zn is replaced by Al and various compounds are used as electrolytes. A cell:

$$Al/HClO_4 + HCl/MnO_2 \text{ or } PbO_2$$

is offered in [143]. Some organic compounds, like HCO_2NH_2, are added to increase the shelf-life of the cell [144]. Water-activated reserve batteries with Al anodes are described. The chlorine at the cathode is delivered by an organic compound, a commercially available chlorinating agent, which reacts according to equation (1) [145]

$$C_3N_3O_3Cl_3 + 2Al + 6H_2O \rightarrow C_3N_3O_3H_3 + 2Al(OH)_3 + 3HCl \qquad (1)$$

Despite these works, in the recent book on primary batteries it is stated that Al has not been utilized in a commercially important battery and its realization still has to be considered to be in the experimental stage. Wasteful anode corrosion is still a problem [138].

None of these facts generates much hope for the realization of rechargeable batteries with Al anodes in aqueous solutions. However, the oxide film on Al can be complexed away in alkali solutions. In very strong alkali, such as the low-melting eutectics of KOH and NaOH, Al might be rechargeable. The performance of Al in the TR of such a melt to which some water is added might be very interesting: the battery's operation temperature could be markedly decreased and the film formed on the Al rendered porous (an asset).

The possibilities for rechargeable Al systems based on other moist inorganic and organic nonaqueous electrolytes are simply not known.

The electrochemical properties of Ti were discussed in a previous report and some pure and mixed electrolytes considered [146]. The tight oxide film on Ti can be anodically dissolved in acidic aqueous solutions [147a-d], and electroplaters have found complexes from which it can be deposited [148]. However this oxide film militates against both anodic oxidation and cathodic reduction being accomplished in the same aqueous solution. No passivation occurs during anodic dissolution of Ti in $CH_3OH + HCl$ in the absence of H_2O [149]. Ti and Ti-alloy cathodes in aqueous alkaline solutions absorb H and render the system rechargeable [150-152]. Thus cells based on strong KOH

$$NiTi_2H_x/KOH + H_2O/Ni(OH)_2$$

have been constructed and cycled [150-152], but Ni in this case is just a carrier.

The utilization of Ti as a rechargeable negative rests on the attenuation of the effects of the passivating oxide film. In the review, several dry molten salt systems are proposed which would seem to have promise [146]. The effects of addition of moisture to decrease both the m.p. and operating temperature were not considered. Fluorides were preferred, but

the lower-melting system $MgCl_2$-$AlCl_3$-$NaCl_3$ was thought to offer promise too.

PROSPECTS FOR THE USE OF TR ELECTROLYTES

In view of the harmful effects often cited in the literature of even small traces of water on the operation of non-aqueous batteries with alkali metal anodes, it might be supposed that electrolytes of the TR composition cannot be applied to these batteries. This same idea may dominate when molten salt SBs are considered. Such a priori misgivings are not always justified. A dilute solution of water in a salt has the structure either of this salt proper or its adjacent hydrate, and the energy, properties and reactions of this water are quite different from those of pure water or of dilute solutions of various compounds in it. On the other hand, a small amount of water in the electrolyte system will decrease its melting point and increase its conductivity. Mixtures of water with such liquids as dioxane, some alcohols and other aprotic and even proton-forming substances, may open new prospects for non-aqueous SBs.

However, since the theoretical foundation of TR electrolytes is inapplicable at this stage to the process of selection of electrolytes for study, each new composition of such electrolytes must be tested and studied experimentally with the prospective electrode materials of the battery. We should not continue to reject a priori the transition region solutions as possible electrolytes for the active metals in SBs.

SUMMARY

The electrolytes offered at present for HED SBs with light metal anodes have serious shortcomings which hamper the construction of such batteries with long cycle life. The main defect of the non-aqueous electrolytes - their poor conductance and the unsatisfactory morphology of the anodic metal deposit during recharge - can be eliminated by the use of mixed solvents, some of which may contain some minor additions of water as one of the components.

The high temperature of the operation of molten salt batteries can be decreased by the use of low-melting salt systems.

Solid electrolytes of high conductivity ($K > 1.10^{-1} ohm^{-1} cm^{-1}$) may be found among non-stoichiometric compounds such as oxides, sulphides, silicates and zeolites, through which the cations of the light metals can move freely at ordinary temperatures.

Electrolytes with the composition in the transition region, i.e. in between the pure electrolyte the molten salt and its solutions with the non-conducting solvent, deserve more attention. Such electrolytes might improve the conductance of non-aqueous systems and the quality of the anodic metal deposits formed during recharging of the battery. In molten salt SBs, these electrolytes would allow lower operating temperature. A judicious choice of compositions of these TR electrolytes can lead to suppression of the chemical dissolution of the anode, attenuation if not elimination both its violent reaction with the electrolyte and its passivation.

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The use of nonaqueous, molten salt and solid electrolytes for high energy density storage batteries (SB's) with anodes of Li, Na, Ca, Mg, Al and Ti, is discussed. Means to overcome the shortcomings of these systems, viz. low conductivity of the electrolyte, poor quality of the anodic metal deposited during recharging of the nonaqueous systems, high operating temperatures, of the molten salts and instability of solid-state electrolytes, are considered.

Electrolytes with compositions in the transition region between the pure electrolyte and its solutions in the solvent, are suggested for examination in secondary battery systems with each of the six light anodes mentioned above.

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KEY WORDS

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BATTERIES, STORAGE

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MOLTEN SALT

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