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ACTIVE ENERGY STORAGE MATERIALS FOR INTEGRATED CELL STACKS

INTERIM REPORT

BY

J. H. FISHWICK - C. E. DREMANN

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UNITED STATES ARMY ELECTRONICS COMMAND · FORT MONMOUTH, N.J.

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FOOTE MINERAL COMPANY
ROUTE 100, EXTON, PENNSYLVANIA 19341

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JULY 1, 1970 THROUGH JANUARY 15, 1971

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U. S. ARMY ELECTRONICS COMMAND, FORT MONMOUTH, NEW JERSEY

ABSTRACT

The objective of this program is to develop suitable inorganic separator materials capable of continuous and protracted operation in contact with molten lithium metal and a fused LiCl-KCl eutectic.

This interim report describes the preparation and properties of seven materials based on the cations Li and Ca and aluminate and zirconate anions. It also describes the manufacture of test pieces from the seven materials and the preliminary results of an exploratory test performed under vacuum at 590°C for 96 h. An extensive bibliography is included.

FOREWORD

This interim report presents the results obtained from July 1, 1970, to January 15, 1971 under Contract No. DAAB07-70-C-0173, "Active Energy Storage Materials for Integrated Cell Stacks".

The authors would like to recognize the contributions to this investigation by W. C. T. Yeh and R. W. Talley.

CONTENTS

TABLES

1. INTRODUCTION AND PRIOR ART

Requirements for the development of inorganic separators suitable for use in a high temperature lithium battery have been previously discussed in some detail[1-5] and need little clarification in this report. It will suffice to mention that, as pointed out by Lander[5], separators have two primary functions: to physically separate the positive and negative plates so that electronic current will flow outside the cell; and to permit flow of ionic current in the electrolyte between the plates. In the case of a lithium battery, the separator must be capable of continuous and protracted operation in contact with molten lithium metal and a fused salt such as the LiCl-KCl eutectic. The separator must also be porous to permit ionic transport, and the pores must be wettable by the electrolyte. In addition, the separator must be mechanically strong and must be able to withstand thermal cycling.

Arrance and Plizga[1] studied the compatibility of several materials with lithium metal and found MgO, ThO_2, $Mg_2Al_2O_4$, $CaZrO_3$, and AlN to be highly resistant at 500°C for as long as 500 hours. Alumina, zirconia, and silicates did not possess sufficient chemical resistance to lithium to warrant further study. Samples of lithium zirconate and lithium metaaluminate were also tested at 500°C for 190 hours. These materials were found to exhibit intermediate and good compatibility respectively with lithium metal at this temperature.

Beals and Mapes[3] studied several ceramic materials as potential anode-cathode separators for a lithium-chlorine battery. They studied the solubility of the materials in LiCl-KCl at 500°C and the compatibility with molten lithium at 500°C. Apart from several binder-free nitride materials, which appeared to be the most promising, Beals and Mapes also obtained fairly good results with $CaZrO_3$, $LiAlO_2$, $LiZrO_3$, $MgAl_2O_4$, $Na_2O \cdot 11Al_2O_3$, and ThO_2. CaO showed less than 5% weight loss after 186 hours in molten lithium at 500°C, but it was "relatively soluble" in LiCl-KCl. MgO showed less than 5% weight change in molten lithium for 500 hours, but it was soluble in the fused salt.

Shimotake, Fischer, and Cairns[4] studied paste electrolytes and found the filler materials $LiAlO_2$, MgO, and Y_2O_3 to have the best compatibility with the cell materials studied.

Poluboyarinov et al[6] tested refractory insulating materials in lithium vapors at high temperatures in vacuum. They concluded that refractories made of pure alumina and pure zirconia, and also zircon, calcium zirconate, and silicon nitride cannot be used for service in lithium vapors owing to their poor chemical resistance. Boron nitride, calcium oxide, and magnesium oxide were found to be suitable materials for use as insulators. Also, silicon carbide bonded with a siliceous bond exhibited a satisfactory resistance to lithium vapors and also had the necessary electric-insulating properties.

Belkov et al[7] studied the stability of boron nitride in lithium vapors at 1400-1500°C and concluded that the observed reaction was due to the presence of B_2O_3, Si, and Al which react with the Li to form Li_2O, Li_3BO_3, and α-$LiAl(SiO_3)_2$.

The free energies of formation of various metal oxides at 500° and 700°C were shown in reference 1. The oxides possessing more highly negative free energies than Li_2O, and, therefore, theoretically more stable, are MgO, BeO, ThO_2, and CaO. Y_2O_3, which has free energies of formation of -139.5 and -134.7 k cal/g. atm O at 500° and 700°C respectively, may also be added to this list. Aluminum oxide and zirconium oxide have less highly negative free energies than lithia, but may be suitable as separator materials if the kinetics of the reaction with lithium are favorable.

In this investigation, we are studying the manufacture and compatibility of oxidic compounds composed of the cations Li and Ca and aluminate and zirconate anions. The actual compounds selected for study are: lithium metaaluminate, lithium pentaaluminate, lithium zirconate, calcium metaaluminate, calcium hexaaluminate, calcium aluminate (CA-25 from Alcoa), and calcium zirconate.

2. EXPERIMENTAL STUDY

The investigation performed under this contract has been broken down into ten phases. This report presents the results obtained on the first four phases, which have been completed, and on a portion of the fifth phase, which is still in progress.

The work carried out under each phase will be discussed separately below.

2.1 Phase 1: Literature Search

A search was made in Chemical Abstracts from 1960 to the present, Proceedings of the Annual Power Source Conference, Abstracts of the Electrochemical Society Meetings, and in various selected Patent, Ceramic, and Metallurgical literature. The literature search was made to collect data and general information of the following subjects:

(a) The preparation and properties of the various oxidic materials being studied in this investigation. This included the kinetic and thermodynamic properties of the materials and the manufacture of shapes.

(b) The preparation of porous ceramic separators and a characterization of the pore distribution with regard to ionic conductivity; and fused salt batteries in general.

(c) The preparation and properties of fused salt electrolytes with particular emphasis on the LiCl-KCl system.

Classification of the literature into the above three groups is somewhat arbitrary because certain references present data concerned with more than one group. Nevertheless, it will be convenient to discuss the references in the order listed above.

(a) Powder Preparation and Properties

(i) Calcium Aluminates

Three compounds in the calcium oxide-aluminum oxide system are being studied in this investigation. They are: calcium metaaluminate($CaO \cdot Al_2O_3$), calcium hexaaluminate ($CaO \cdot 6Al_2O_3$), and a calcium aluminate cement identified as CA-25. The latter is a product purchased from Alcoa and corresponds to the empirical molar formula $CaO \cdot 2.5Al_2O_3$.

Information on the preparation and properties of the calcium aluminates was derived from references 8-20.

(ii) Calcium Zirconate

One compound in the calcium oxide-zirconium oxide system is being studied - calcium metazirconate ($CaO \cdot ZrO_2$). Data on the preparation and properties of this compound may be found in references 21-34. Calcium oxide is a well-known additive for stabilizing the cubic structure of zirconium dioxide, and hence promoting the thermal shock resistance of zirconia-based ceramics.

(iii) Lithium Zirconate

One compound in the lithium oxide-zirconium oxide system is being studied-lithium metazirconate ($Li_2O\cdot ZrO_2$). There is a paucity of data on this compound. All of the references that were found are Russian.[35,36]

(iv) Lithium Aluminates

Two compounds in the lithium oxide-aluminum oxide system are being studied-lithium metaaluminate ($Li_2O\cdot Al_2O_3$) and lithium pentaaluminate ($Li_2O\cdot 5Al_2O_3$). References 21 and 37-48 give pertinent data on the preparation or properties of these compounds.

Both lithium metaaluminate and lithium pentaaluminate undergo phase transformations. According to Lehmann and Hesselbarth[40], lithium metaaluminate prepared at 600°C gives a low-temperature modification which transforms to a high-temperature modification above 600°C. Lejus and Collongues[39] found the $\alpha \rightarrow \gamma$ change to occur at 900° and to be accompanied by a 30% increase in volume. Hummel[38] showed that lithium pentaaluminate undergoes a solid phase inversion between 1200 and 1300°C. A similar phenomenon occurring at 1290°C was reported by Lejus and Collongues[39] for lithium pentaaluminate. Shimotake et al[4] prepared α - $LiAlO_2$ at or below 625°C to minimize formation of the γ - $LiAlO_2$. They also report that the compound $LiAl_5O_8$ exists in a number of polymorphs, one high-temperature form (>1295°C) being a lithium spinel.

(b) Porous Ceramic Separators and Fused Salt Batteries

As mentioned earlier in this report, the ceramic separators must be porous to permit ionic transport and the pores must be wettable by the electrolyte. Several investigators[1-5,49-75] have discussed these problems in varying detail. In addition to references 1-5, which were discussed previously, some of the other references should be specifically mentioned. Joglekar and Batra[49] studied the porosity, pore size, and permeability of three types of commercial battery separators and found no correlation between the measured properties and battery performance. Guillot et al[50] made a container out of alumina containing $LiAlO_2$ to reduce the high-temperature corrosion of fuel cells operating at 550-800°C. Selover and Benak[56] used fused salt as an electrolyte and a porous separator consisting of BN, Si_3N_4, BeO, ThO_2, MgO, $LiAlO_2$, AlN and their mixtures. Swinkles[58] used an electrode consisting of an electric nonconductive layer more wettable by the electrolyte than an electric conductive layer; the contact angle difference with respect to the electrolyte was 30-90°. For the Li/LiCl/Cl_2 system, the anode may consist of an electric conductive porous material, such as stainless steel in contact with Li, and of electric nonconductive materials such as AlN and Cerac-4 in contact with the LiCl.

Rightmire et al[61] examined some of the Engineering aspects and operating characteristics of a fused salt secondary battery. The battery, which operates above 350°C used carbon plate cathodes, solid Al-Li anodes, and a fused LiCl-KCl electrolyte. Wilcox[63] described a lithium-chlorine cell containing molten LiCl as the electrolyte that operated at 1200°F. Weaver[53] found that BeO is a suitable insulator for use at 640°C in a lithium-chlorine battery.

(c) Fused Salt Electrolytes

The literature was searched for fused salt electrolytes in general and for the LiCl-KCl system in particular. References 76-97 are pertinent.

2.2 Phase 2: Preparation and Properties of Ceramic Powders

The oxidic materials studied in this investigation (with the exception of CA-25) were made by reacting the appropriate stoichiometric mixtures in the solid state. X-ray diffraction analysis was used to determine the completeness of the reactions.

A list of the raw materials used to prepare the powders is given in Table I, which also shows the source of the materials and their particle size.

The raw materials were weighed in the appropriate stoichiometric amounts on a torsion balance to give approximately 500 g of product. The combined materials were thoroughly mixed in a V-blender using an intensifier bar for 1/2 hour, and calcined (with the exception of $Li_2O \cdot Al_2O_3$) in platinum crucibles in a silicon carbide resistance furnace in air. The calcium hexaaluminate was mixed in a paste with water prior to calcination; this was found to promote better mixing and was found to be necessary only for this product. Because of an apparent reaction with platinum, the lithium metaaluminate was calcined in porcelain crucibles. To obtain satisfactory correlation of x-ray diffraction data with standard patterns, it was necessary to calcine, mill, and recalcine the calcium zirconate and lithium zirconate materials. Finally, all powders were milled to >99% -325 mesh to provide satisfactory material for making shapes for compatibility testing and property measurements.

The temperatures at which the powders were calcined, the color and density (air pycnometer) of the powders, and the principal x-ray diffraction peaks are given in Table II. While correlation with the standard x-ray patterns was good, in several instances there were minor deviations in intensity. Also, a few small extraneous unidentified peaks were found in some of the patterns.

The theoretical oxide compositions of the calcined powders are presented in Table III.

TABLE I STARTING MATERIALS FOR MAKING POWDERS

Material	Source	Particle Size (U. S. Sieve)
Lithium carbonate (Technical Grade)	Foote Mineral Co.	86.6% -325 mesh
Aluminum oxide (A-2)	Aluminum Co. of America	98.0% -325 mesh
Calcium carbonate (Non-Fer-Al)	Diamond Alkali Co.	100.0% -325 mesh
Zirconium dioxide (TAM-CP Grade)	National Lead Co.	100.0% -325 mesh
Calcium aluminate cement (CA-25)	Aluminum Co. of America	90.0% -325 mesh

TABLE II <u>CALCINATION TEMPERATURE AND PROPERTIES OF POWDERS</u>

Oxide	Calcination Temp. (°F)	Color	X-Ray Reference	X-Ray Data		Density (g/cc)
				d	I	
$CaO \cdot Al_2O_3$	2600 for 6 h	white	ASTM #1-0888	2.97	1.00	2.90
				2.52	0.39	
				2.41	0.26	
$CaO \cdot 6Al_2O_3$	2900 for 8 h	white	ASTM #7-85	2.63	1.00	3.68
				2.48	0.87	
				1.53	0.75	
$CaO \cdot 2.5Al_2O_3$ (CA-25)	---	off-white	---	2.99	1.00	3.32
				2.56	0.87	
				2.09	0.75	
$CaO \cdot ZrO_2$	2900 for 6 h	gray-white	ASTM #9-364	4.02	0.55	4.64
				2.84	1.00	
				2.00	0.44	
$Li_2O \cdot ZrO_2$	2850 for 6 h	white	Reference 36	4.37	1.00	4.19
				2.56	0.40	
				3.35	0.33	
$Li_2O \cdot Al_2O_3$	2200 for 2 h	white	Reference 38	4.00	1.00	2.72
				2.68	0.71	
				2.58	0.69	
$Li_2O \cdot 5Al_2O_3$	2550 for 3 h	white	Reference 38	2.40	1.00	3.59
				1.98	0.51	
				1.40	0.67	

TABLE III THEORETICAL OXIDE COMPOSITIONS OF POWDERS

Powder	Oxide			
	CaO	Al_2O_3	Li_2O	ZrO_2
$CaO \cdot Al_2O_3$	35.49	64.51	-	-
$CaO \cdot 6Al_2O_3$	8.40	91.60	-	-
$CaO \cdot 2.5Al_2O_3$(CA-25)*	18.0	79.0	-	-
$CaO \cdot ZrO_2$	31.28	-	-	68.72
$Li_2O \cdot ZrO_2$	-	-	19.52	80.48
$Li_2O \cdot Al_2O_3$	-	77.33	22.67	-
$Li_2O \cdot 5Al_2O_3$	-	94.46	5.54	-

*From reference 18

2.3 Phase 3: Fabrication of Shapes from the Ceramic Powders

To determine the physical properties of shapes made from the different powders, bars were pressed in a steel die and fired at various temperatures. The porosity of the fired bars made in this phase was not controlled and resulted solely from the natural microstructure of the fired powder.

A temporary binder (50% solution of Mobilcer C*) was used in all powders to provide green strength. Bars were pressed at 7630 psi in a steel die having the dimensions 1/2 x 1/2 x 5 1/4". The bars were dried and then fired in silicon carbide resistance furnaces at various temperatures. The firing schedule for bars heated to 2750°F or below consisted of heating at 100°F /h to temperature, soaking for 2 h at the maximum temperature, followed by an overnight cooling. Bars fired above 2750°F, were heated in one furnace at 100°F/h up to 2350°F, transferred to a high-temperature furnace at this temperature, further heated at 125°F/h to the maximum temperature, soaked at this temperature for 2 h, cooled to 2350°F at 300°F/h, transferred to the original furnace, and cooled overnight. All bars were fired on alumina sand precalcined at 3000°F.

*Mobil Oil Company

2.4 Phase 4: Physical Property Measurement

The physical properties of the bars fired at various temperatures are presented in Table IV. Modulus of rupture (MOR) was measured by three point loading on a 20,000 pound Budd Tensile Tester according to ASTM method C 328-56. The linear shrinkage was measured using ASTM method C 326-56. The percent absorption and apparent porosity were measured according to ASTM method C 373-56. The measured density was obtained by recording the dimensions of the bars and weighing them. The last column of Table IV shows the percent of voids calculated from the densities of the calcined powders and the measured density of the fired bars.

The results given in Table IV more or less follow the expected trend: as the firing temperature was increased, the shrinkage and strength were increased and absorption was decreased. These changes are a reflection of the sintering process that takes place between the grains on firing. Most of the bars exhibited a moderate to good strength when fired at the higher temperatures. Lithium zirconate, however, could be considered an exception.

It is interesting to compare the apparent porosity as measured by a water absorption method with the percent of voids calculated as described above. When these two values correspond, the pores are probably continuous. When the values are much different, the pores are probably isolated or discontinuous. Proceeding on this assumption, both $CaO \cdot 6Al_2O_3$ and $Li_2O \cdot 5Al_2O_3$ should have continuous porosity. $CaO \cdot ZrO_2$ has pores that are continuous for all firing temperatures except 2900°F, at which temperature they are only partially continuous. For $Li_2O \cdot Al_2O_3$, only about 60% of the pores are continuous. The pores in $CaO \cdot Al_2O_3$ and $CaO \cdot 2.5Al_2O_3$ are presumably largely discontinuous. It is recognized, however, that very small pores of Angstrom size may be continuous, but impermeable to water

The results presented in Table IV were carefully evaluated before making the test pieces for the compatibility testing described in the next section. In general, the test pieces were fired at that temperature which provided warp-free bodies having the greatest strength.

The test pieces were made in a manner similar to that used for making the bars (see Phase 3). A 50% solution of Mobilcer C was used as a temporary binder and the powders were pressed in a steel die at 7630 psi. The pressed pieces (1/2 x 0.050 x 5 1/4") were cut to form pieces having the dimensions 1/2 x 0.050 x 2 1/8". A hole 1/16" in diameter was drilled in one end of each piece to permit the piece to be suspended by stainless steel wire in molten lithium and fused salt eutectic. All pieces were fired under a layer of alumina sand to prevent warping. Firing was accomplished in silicon carbide resistance furnaces using the same schedule as described for the bars in phase 3.

TABLE IV PHYSICAL PROPERTIES OF FIRED BARS

Material	Firing Temp. (°F)	MOR (psi)	Shrinkage (%)	Absorption(%)	Apparent Porosity(%)	Measured Density (g/cc)	Voids (%)
$CaO \cdot Al_2O_3$	2950	Fused on Firing					
	2900	6770	14.35	0.27	0.73	2.63	9.31
	2750	2328	10.78	0.58	1.47	2.42	16.55
	2500	933	1.27	0.61	1.52	1.75	39.66
	2250	1329	0.19	0.76	1.72	1.70	41.38
$CaO \cdot 6Al_2O_3$	3000	10950	12.11	6.93	20.42	2.92	20.65
	2750	6838	7.33	12.01	30.40	2.53	31.25
	2500	2254	3.01	17.20	38.72	2.21	39.95
	2250	519	0.52	20.85	43.25	2.04	44.57
$CaO \cdot 2.5Al_2O_3$	3000	6674	9.63	0.39	1.11	2.79	15.96
(CA-25)	2750	4487	6.27	0.75	2.04	2.44	26.51
	2500	4432	3.84	0.58	1.52	2.26	31.93
	2250	2216	-0.35	1.44	3.57	1.94	41.57
$CaO \cdot ZrO_2$	3000	2394	9.82	4.63	17.30	3.70	20.26
	2900	2814	9.29	3.59	13.92	3.63	21.76
	2750	2229	8.54	5.61	20.30	3.58	22.84
	2500	1563	1.96	12.47	35.79	2.93	36.85
$Li_2O \cdot ZrO_2$	2900	510	3.84	Disintegrated		2.90	30.79
	2750	1172	4.55	in boiling H_2O		2.88	31.26
	2500	225	4.22	Disintegrated in boiling H_2O		2.86	31.74
$Li_2O \cdot Al_2O_3$	3000	5303	12.82	5.37	11.95	2.14	21.32
	2900	5884	9.44	7.04	15.58	2.06	24.26
	2750	3932	7.50	9.86	19.55	1.83	32.72
	2500	1027	2.26	14.02	24.88	1.60	41.18
$Li_2O \cdot 5Al_2O_3$	3000	2117	4.20	19.85	41.42	2.04	43.18
	2900	2490	3.76	21.18	42.35	2.02	43.73
	2750	1915	2.59	22.91	45.19	1.94	45.96
	2500	447	0.29	26.21	48.41	1.82	49.30

The temperature used for firing each composition and the appearance of the piece after firing are shown in Table V.

TABLE V FIRING CONDITIONS AND APPEARANCE OF TEST PIECES

Material	Firing Temperature (°F)	Color	Appearance
$CaO \cdot Al_2O_3$	2750	white	slight bowing
$CaO \cdot 6Al_2O_3$	3000	white	good
$CaO \cdot 2.5Al_2O_3$ (CA-25)	3000	pink-white	good
$CaO \cdot ZrO_2$	2900	yellow-white	slightly rough surface
$Li_2O \cdot ZrO_2$	2750	off-white	good
$Li_2O \cdot Al_2O_3$	2900	white	good
$Li_2O \cdot 5Al_2O_3$	2900	white	good

2.5 Phase 5: Compatibility Testing in Li and LiCl-KCl

The fired ceramic shapes made in Phase 4 will be tested for stability in both molten lithium and fused LiCl-KCl eutectic at various temperatures up to and including 650°C under an inert atmosphere. Stability of the ceramic pieces will be evaluated by observing color change and appearance, and by measuring the weight and electrical resistance before and after testing. Care will be exercised to avoid thermally shocking the pieces during this phase of the work.

A preliminary test has been run at 590°C for 96 hours under a constant vacuum of 5-10 microns. Details of this test will not be given at this time because of the exploratory nature of the test. Also, the conclusions resulting from this test are regarded as highly tentative.

In general, the test indicated that all of the ceramic shapes exhibited good resistance to the LiCl-KCl eutectic as far as the weight change was concerned. Calcium metaaluminate showed the greatest weight change (a 4.61% loss) and lithium zirconate showed the least change (a 0.11% gain). The electrical resistance of the pieces after testing differed markedly. All of the aluminates possessed high resistances ($>10^{7}$ ohms), but both of the zirconates became conductive. All materials were perfect insulators prior to the exposure to Li or LiCl-KCl.

None of the ceramic pieces showed a good resistance to lithium metal under the test conditions adopted. Calcium zirconate exhibited the lowest weight change (a loss of 0.02%) but became conductive (3×10^{2} ohms) after the test. Lithium pentaaluminate showed the greatest weight change (a loss of 73.2%). The weight changes of lithium metaaluminate and lithium metazirconate are not known because the test pieces disintegrated on cleaning in methanol and water.

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13. ABSTRACT

The objective of this program is to develop suitable inorganic separator materials capable of continuous and protracted operation in contact with molten lithium metal and a fused LiCl-KCl eutectic.

This interim report describes the preparation and properties of seven materials based on the cations Li and Ca and aluminate and zirconate anions. It also describes the manufacture of test pieces from the seven materials and the preliminary results of an exploratory test performed under vacuum at 590°C for 96 h. An extensive bibliography is included.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Electrochemical cells						
Oxidic materials compatible with molten Li and fused LiCl-KCl						
Lithium aluminates						
Calcium aluminates						
Lithium zirconate						
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