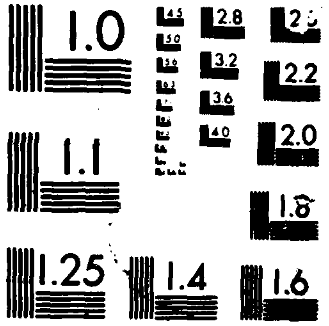
AD-A176 237 SOLID STATE BATTERIES(U) MINNESOTA UNIV MINNEAPOLIS DEPT OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE M Z MUNSHI ET AL JAN 87 N00014-85-K-0634 1/1

UNCLASSIFIED F/G 10/3 NL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Contract N00014-85-K-0634

R & T Code 413d019---01
Replaces Old
Task # 627-850

TECHNICAL REPORT NO. 1

Solid State Batteries

by

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To be Published in

Proceedings of the Symposium on Electrochemistry and
Solid-State Science Education at the Graduate and Undergraduate Level

169th Meeting of the Electrochemistry Society
Boston, Mass.
May, 1986

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
Unclassified

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

3. DISTRIBUTION / AVAILABILITY OF REPORT
Unclassified/Unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
ONR Technical Report #1

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
Corrosion Research Center

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
Office of Naval Research, Resident Rep.

6c. ADDRESS *(City, State, and ZIP Code)*
University of Minnesota
Minneapolis, MN 55455

7b. ADDRESS *(City, State, and ZIP Code)*
Federal Building, Room 286
536 South Clark Street
Chicago, IL 60605-1588

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
Office of Naval Research

8b. OFFICE SYMBOL *(If applicable)*
Code 1113

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
Contract No. N00014-85-K-0634

8c. ADDRESS *(City, State, and ZIP Code)*
800 North Qunicy Street
Arlington, VA 22217-5000

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO

11. TITLE *(Include Security Classification)*
Solid State Batteries

12. PERSONAL AUTHOR(S)
M.Z.A. Munshi and B.B. Owens

13a. TYPE OF REPORT
Technical

13b. TIME COVERED
FROM 7/15/85 TO 12/30/86

14. DATE OF REPORT *(Year, Month, Day)*
January 1987

15. PAGE COUNT
14 pages

16. SUPPLEMENTARY NOTATION
Presented at 169th National Meeting of the Electrochemical Society, May 1986

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
batteries, solid electrolytes, solid state battery

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

The all solid state battery has been an idealized technological goal because of the assumption that the problems of batteries containing liquid phases are, at least in part, due to the fluid properties which can lead to high rates of self discharge, leakage of electrolyte through battery seals, and poor performance at both extremes of temperatures due to phase transitions. The major problem in developing useful solid state batteries has been to identify solid state ionically conducting materials with adequate conductivity to serve as the battery electrolyte. Recent work on new glasses and new polymer electrolytes have stimulated this field of investigation.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL
Boone B. Owens

22b. TELEPHONE *(Include Area Code)*
(612) 625-1332

22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
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SOLID STATE BATTERIES

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ABSTRACT

The all solid state battery has been an idealized technological goal because of the assumption that the problems of batteries containing liquid phases are at least in part due to the fluid properties which can lead to high rates of self discharge, leakage of electrolyte through battery seals, and poor performance at both extremes of temperature due to phase transitions. The major problem in developing useful solid state batteries has been to identify solid state ionically conducting materials with adequate conductivity to serve as the battery electrolyte. Recent work on new glasses and new polymer electrolytes have stimulated this field of investigation.

1. INTRODUCTION

Batteries have been successfully used as the most convenient portable form of stored electricity. In spite of the extensive investigations on batteries during the past century, there continues to be a need for further improvements in these devices. One of the areas of research has been in the application of solid state electrolytes to solid state batteries. In common with most battery systems the solid state batteries have solid electrodes. The distinction is that whereas the majority of batteries utilize a liquid electrolyte, the solid state battery incorporates an ionically conducting solid electrolyte based on ceramics, glasses, polymers or just simple ionic salts. The major advantages and disadvantages of solid electrolyte cells are summarized in Table 1.

One of the major problems in this field is the absence of solid electrolytes that exhibit adequately high ionic conductivities for appropriate ionic species. Some solid electrolyte batteries have been designed for operation at elevated temperatures where the electrical conductivity permits reasonable power levels. The greater interest is for solid state batteries that would be operable at normal ambient temperatures and in this area the materials problems remain challenging. A large number of silver ion conducting solid electrolytes have been reported (1) in which the conductivities are equivalent to those of aqueous solutions. The batteries developed around these electrolytes must incorporate silver electrodes and are inherently limited by the thermodynamic properties of the electrolyte to low energy density devices.

There is a greater interest in alkali ion conducting solid state batteries that would have more energetic anodes and consequently higher levels of energy density. The last decade has witnessed the emergence of new batteries based on various lithium anode systems with significantly increased energy densities. However, these have been restricted to primary systems. The major areas of concern associated with primary batteries have been related to the presence of the liquid electrolyte phase. These include problems with cell leakage, internal self-discharge, case corrosion, drying out of the cell, loss of conductivity due to phase transitions at the extremes of temperatures, inability to withstand high levels of shock and severe restrictions on the capability for useful discharge at very low temperatures. The major interest in developing an all-solid-state battery with a solid electrolyte was to minimize these problems and design an active primary battery that was capable of storage or operation for up to ten years at uncontrolled temperatures ranging from -55° up to 70°C. In spite of extensive investigations on lithium solid state batteries, the major application for primary cells has been as a power source for cardiac pacemakers operating at low power levels (100 μω) and in a 37°C isothermal environment.

Lithium ion conducting solid electrolytes have received considerable attention and materials based on ceramics, glass compositions, ionic crystalline materials and polymeric materials have all been reported (4-8). Most recently, glasses and polymers have been designed into solid state batteries (9). The electrolytes are still fairly resistive, as shown in Table 2. Reasonable impedance batteries have resulted by designing cells with very thin electrolyte layers. The rechargeable lithium battery is not yet commercially available in consumer products, although primary cells have been sold for the past ten years. This difference arises in part from technical difficulties with liquid electrolyte systems and from a safety concept. A very high energy secondary rechargeable lithium battery is an attractive proposition, but the consumer market would be reluctant to accept a possibly unsafe product. A new family of cathode materials now being used for battery construction involves fast ionic transport (10). They are known as solid solution electrodes. The best solid solution electrode materials utilizing liquid electrolytes are conductors of lithium ions. A number of attempts have been made to develop solid state secondary lithium cells based on intercalation compounds such as TiS_2 or V_6O_{13} as the reversible cathode.

2. Battery Design

The lithium solid state batteries have received the most attention and it is possible to differentiate them in terms of the method in which their electrolyte element is formed. Table 3 also compares the properties of the silver-iodine solid state battery with three lithium solid state batteries. As indicated, the silver-iodine battery utilizes a silver ion conducting electrolyte with resistances ranging from 3 to 100 (Ω.cm). However the low energy density as well as the cost of materials and manufacturing processes restricted the commercial application of this battery system. Three of the batteries in Table 3 are fabricated with discrete layers of the solid electrolyte formed from powdered materials. The $Li/LiI/I_2$(2VP) system does not involve discrete layers of electrolyte but instead the electrolyte forms in-situ by the direct chemical reaction between the electrode materials. This advantage of forming a resistive electrolyte in a very thin film minimizes the overall effect on battery impedance besides providing a simplified method of cell manufacture. In contrast, discrete layers require the formation of disks compacted at high pressures which is an added step in the battery production.

Several advantages have been cited for solid state batteries. However, there are also problems inherent with the design. These include:

(1) low ionic conductivities of the electrolyte relative to that of the similar liquid electrolyte systems,
(2) dimensional changes occurring during the discharge of a battery,
(3) discharge product impedance
(4) poor interfacial contact between the electrolyte and electrodes and current collector.

Another problem in an all-solid-state lithium battery is the question of safety. If the application could cause melting of the lithium metal, then lithium alloys with much higher melting points should be investigated. These have thus far been restricted to Li-Al or Li-Si alloys. As pointed out by Taylor (11), "The performance penalty that you suffer when using these alloys is quite substantial. There may be problems with the manufacturability of the product. One distinct advantage of lithium is that you can bend it, twist it, roll it, form it into thin foils and shape it into whatever you want, but whenever you start to alloy it with different materials, I'm not sure all that is possible".

3. Li-Ion Conducting Material

In recent years the solid electrolyte research in many laboratories has been directed to lithium ion conducting materials with the main emphasis being placed on an all-solid-state lithium batteries. Some of the highest room temperature lithium ion conductivities have been found in glasses based on ternary compositions containing LiI, Li_2S and either B_2S_3, GeS_2 or P_2S_5. Values reported have been as high as $2 \times 10^{-3} (\Omega.cm)^{-1}$ at 25°C (6,7). The activation energy has been reported as 0.30 eV with t_+ for the lithium cation as being close to 1. Cells were fabricated using these glasses as either pressed powders or vacuum deposited thin films, with Li or Li-Al anodes and various cathodes (12,13). The stability of the electrolyte with electrode materials was investigated by calorimetric measurements of the heat flow from electrode/electrolyte mixtures that were pelletized and stored at 37°C. Only one $\mu\omega$ was observed over a 6 month storage interval for the glass mixed individually with LiAl, $Bi_2Pb_2O_5$ or TiS_2. The performance of $Li/Bi_4B_2O_9$ cells was reported for current densities of $150\mu A/cm^2$ at 110°C with an open-circuit cell voltage of 2V. These new glasses appear feasible for small low power cells and possibly higher power cells operating near 100°C. However the interfacial properties between electrodes and electrolyte appear to restrict the rate capability.

Single crystal lithium nitride has also shown higher ionic conductivity due to the highly mobile lithium vacancies in this material. The development of new preparative techniques related to hydrogen-doped Li_3N has led to conductivity values as high as $6 \times 10^{-3}(\Omega.cm)^{-1}$ (14). Polycrystalline material has been manufactured with good mechanical and electrical properties ($\sigma \approx 3 \times 10^{-3}(\Omega.cm)^{-1}$ at room temperature). The application of this material as an electrolyte in rechargeable batteries depends on the ability to fabricate thin ceramic films. However, because the decomposition potential is low, (~ 0.4V) the stability and practical energy density of any cell may be severely limited.

4. Polymer Electrolytes

The work of Fenton et al. (15) showing high ionic conductivity on solid polymer electrolytes based on polyethylene oxides (PEO) doped with an alkali metal salt, followed by Armand's (16) proposal for the use of such polymer electrolytes in an all-solid-state electrochemical battery has stimulated the development activities for all-solid-state lithium batteries. The attractive mechanical properties of this material resulted in further investigations on ionically conducting polymers. Conductivity values of 10^{-4} to 10^{-3} $(\Omega.cm)^{-1}$ at 100°-140°C for PEO doped with lithium salts such as lithium-trifluoromethane sulphonate ($LiCF_3SO_3$) show that about eight PEO per Li are required to give a high value for ionic conduction. Materials that are more dilute with respect to the salt content yield higher conductivities. However the material is too soft to be used at higher temperatures and a ratio of 8 or 9 PEO/Li is generally regarded as the optimum composition, representing a quasi-solid material.

Differential scanning calorimetry experiments have shown the presence of both crystalline and amorphous phases and the general view (17) is that the highest conductivity occurs in the amorphous phase. Complex impedance studies using lithium reversible electrodes suggest the lithium transport number is about 0.5, and efforts are underway to increase this value in order to avoid limiting current effects.

Other polymer systems under current investigation include nylon-6, polyethylene imine, polyvinylidene fluoride, and polyethylene sulphide. The conductivities of some of these are shown in Table 4. A limited number of actual cell tests have been carried out on the above mentioned polymers and the only one with any published degree of success is the lithium salt doped polyethylene oxide.

5. Polymer Electrolyte Batteries

During the past decade, extensive research has been made in the development of cells employing polymeric electrolytes. The principal thrust has been in Europe and Canada. The aims of the Anglo-Danish and Canadian-French programme have been to develop a secondary rechargeable all-solid-state lithium battery for a variety of applications including vehicular traction application and this has resulted in the emergence of a polymer electrolyte-based system (Figure 1). In its simplest form, the anode consists of lithium metal or a lithium alloy and the cathode consists of a composite structure containing the electrolyte phase together with V_6O_{13} and acetylene black. The polymeric solid electrolyte is sandwiched between the two electrodes. By fabricating the individual cell components as thin films, to compensate for the low conductivity of the electrolyte, reasonable impedance batteries have resulted. Typical dimensions used are:

25 - 30 μm electrolyte

25 - 50 μm Li electrode

100 - 150 μm V_6O_{13} cathode

The operating temperature of the cell is 100 - 140°C and current densities of 0.1 - 1.5mA/cm^2 with PEO-$LiCF_3SO_3$ electrolytes are reported to give energy efficiencies and specific powers of 70-80% and 100-300 ω/dm^3 respectively, (13,30). The initial open circuit voltage of the system is over 3V. Further extensive research is now underway in developing the polymer electrolyte materials for battery applications.

Conclusions

Although the primary lithium solid state batteries are used as power sources for very low power devices such as cardiac pacemakers and electronic memory circuits, the possibility of a high (or medium) power all-solid-state rechargeable system continues to stimulate interest worldwide. The recent new developments in polymer and glass based electrolytes for battery applications, operating at elevated temperatures of 100-150°C, has opened up the possibility of practical high energy, high power cells. However considerable work must be done to establish feasibility of a scaled-up battery.

Acknowledgement

This work was supported in part by the Office of Naval Research.

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Table 1: MAJOR ADVANTAGES AND DISADVANTAGES OF LITHIUM SOLID-ELECTROLYTE CELLS (REF. 2)

Excellent storage stability--shelf life of 10 y or better	Low current drains (micro-amperes)
High energy densities	Power output reduced at low temperatures
Hermetically sealed-no gassing or leakage	Care must be exercised to prevent shorting or shunting of cell (which could be a relatively high drain on cell)
Wide operating temperature range, up to 200°C	
Shock- and vibration-resistant	

Table 2: Resistivity R of Electrolytes for Solid State Batteries at Ambient Temperature. (Ref. 3)

Electrolyte	Log of R
-Li I	6 to 7
-Li I-Dispersed Phase e.g. $LiI(Al_2O_3)$	4 to 5
-Li Polymers e.g. PEO[A], $LiClO_4$	4 to 5
-Li Glasses e.g. Li_2S, P_2S_5, LiI	3 to 4
-Li-β-Alumina	3 to 4
-Li_3N	3 to 4
-Ag or Cu Electrolyte Salts e.g. $RbAg_4I_5$, $Rb_4Cu_{16}I_7Cl_{13}$, Ag_3SI	1 to 2

[A] PEO is Polyethylene oxide.

Table 3: Characteristics of Solid-Electrolyte Cells (Ref. 1)

System	Cell voltage, V	Energy density at 1-Y rate Wh/L	Energy density at 1-Y rate Wh/kg
$Ag/RbAg_4I_5/Me_4NI_5$, C	0.66	40-80	15-25
$Li/LiI(Al_2O_3)/PbI_2$, PbS,Pb	1.9	300-600	75-150
$Li/LiI/I_2$(P2VP)	2.8	350-700	120-200
$Li/LiI(SiO_2)/Me_4NI_5$	2.75	400	125

Table 4: Conductivity of Polymer Electrolytes

Solid Electrolyte	$\sigma(\Omega cm)^{-1}/T^{o}C$	Ref.
$(PEO)_x$ $LiCF_3SO_3$ (monomer-salt = 8:1)	10^{-3}-10^{-4}/100-140°C	(14)
Nafion^R Li^+ PC	2 x 10^{-3}/R.T.	(18)
Ion exchange membranes with attached ionophoretic groups	10^{-12}-10^{-15}/R.T.	(19)
Viton^R cross-linked with diamine and gelled with 1M PC-$LiClO_4$	6 x 10^{-3}/100	(19)(20)(21)(22)
Poly(vinylidene fluoride) gelled with PC-$LiClO_4$	2 x 10^{-3}/100^a	(19)(20)(21)(22)
PEO-$LiClO_4$, 12:1	2 x 10^{-3}/100	(23)
xlinked PEO-$LiClO_4$, 8:1	6 x 10^{-4}/100	(24)
PEO-$LiCF_3SO_3$, 9:1	2 x 10^{-4}/100	(25)
Polyethylene adipate $LiCF_3SO_3$, 4:1	7 x 10^{-5}/100	(26)
Polyethylene succinate $LiBF_4$, 6:1	5 x 10^{-5}/100	(27)
Polybis (methoxy-ethoxy-ethoxy phosphogene)-$LiCFSO_3$, 4:1	7 x 10^{-4}/100	(28)
Poly(N-methyl aziridine) $LiClO_4$, 8:1	10^{-5}/100	(19)
PPO - LiI 8:1	~3 x 10^{-4}/100	(29)
PPO - $LiCF_3SO_3$, 9:1	1.5 x 10^{-4}/100	(29)

a - extrapolated value

PEO = polyethylene oxide

PC = propylene carbonate

PPO = polypropylene oxide

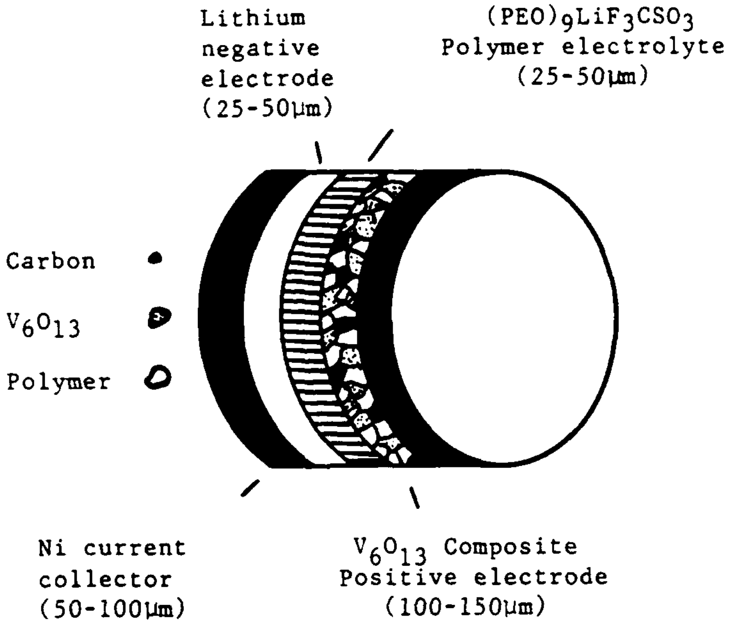

Figure 1: Solid-State Cell

Key words:

batteries, lithium - page 1
intercalation, design - page 2
conductivity, glasses - page 3
polymer, impedance - page 4
salt, electrolyte - page 5

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