

AD-A212 177

4

DBT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY SEP 08 1988			3. DISTRIBUTION/AVAILABILITY OF REPORT Unclassified/Unlimited		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			4. PERFORMING ORGANIZATION REPORT NUMBER ONR Technical Report 12		
5a. NAME OF PERFORMING ORGANIZATION Dept. of Chem. Eng. & Mat. Sci. Corrosion Research Center			5b. OFFICE SYMBOL (If applicable) Code 1113		5c. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. ADDRESS (City, State, and ZIP Code) University of Minnesota Minneapolis, MN 55455			6b. ADDRESS (City, State, and ZIP Code) Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000		
7a. NAME OF FUNDING/SPONSORING ORGANIZATION DARPA/ONR			7b. OFFICE SYMBOL (If applicable) Code 1113		7c. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract No. N00014-88-K-0360
8a. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000			9. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
			WORK UNIT ACCESSION NO.		
10. TITLE (Include Security Classification) Flat Polymer Electrolytes Promise Thin-Film Power					
11. PERSONAL AUTHOR(S) M. Zafar A. Munshi and Boone B. Owens					
12a. TYPE OF REPORT Technical		12b. TIME COVERED FROM 7/88 TO 6/89		12c. DATE OF REPORT (Year, Month, Day) 89/06/15	
13. PAGE COUNT 12					
14. SUPPLEMENTARY NOTATION Published in IEEE Spectrum, August 1989					
15. COSATI CODES			16. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP			
			polymer electrolyte cell; lithium battery; rechargeable cell. (D.S.)		
17. ABSTRACT (Continue on reverse if necessary and identify by block number) In laboratories all around the world, scientists and engineers are working on a new solid-state battery that could be fabricated much thinner than 100 micrometers. The battery uses a solid polymer electrolyte as the ionically conducting medium, instead of a liquid electrolyte. Flat cells have been available for several years and have been incorporated into devices such as the Polaroid instant-film pack. However, these have been modifications of conventional liquid-electrolyte cell designs. Recent innovations in solid-state batteries that use lithium anodes, solid cathodes, and a solid polymer electrolyte that both separates and provides the ionic pathway between the anode and cathode. Ultimately, researchers expect the energy capacity of a typical packaged battery, based on a lithium anode and vanadium oxide (V ₆ O ₁₃) cathode, to rise as high as 150 Wh/kg, with a sustained power density of 200 W/kg and a peak power of 900 W/kg at half charge.					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ OTC 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

FLAT POLYMER ELECTROLYTES PROMISE THIN-FILM POWER

Emerging solid-state batteries thinner than this page combine high energy density with mechanical ruggedness for applications ranging from smart cards to space.

Even by today's standards, it is hard to imagine a practical battery thinner than the thickness of the paper on which this article is printed. But in laboratories all around the world, scientists and engineers are working on a new solid-state battery that could be fabricated much thinner than 100 micrometers. The battery uses a solid polymer electrolyte as the ionically conducting medium, instead of a liquid electrolyte.

Flat cells have been available for several years and have been incorporated into devices such as the Polaroid instant-film pack. However, these have been modifications of conventional liquid-electrolyte cell designs. Recent innovations in solid-state polymeric electrolytes point to the development of entirely new solid-state batteries that use lithium anodes, solid cathodes, and a solid polymer electrolyte that both separates and provides the ionic pathway between the anode and cathode.

The concept of a wholly solid-state battery is not new, but practical designs based on it may have far-reaching effects. Such batteries behave far better than those containing liquid electrolytes, which may suffer from high rates of self-discharge, leak electrolyte through battery seals, and operate poorly at both extremes of temperature.

In contrast, the slower rate of ion diffusion in batteries containing a solid polymer electrolyte reduces the rate of self-discharge; the absence of liquid eliminates leaks; and solid electrolytes function at temperatures as high as 140°C, whereas some organic liquid electrolytes may vaporize at 100°C or more.

The right stuff

The major problem in developing useful solid-state batteries has been identifying solid materials with sufficient ionic conductivity to serve as the electrolyte. In 1973, researchers at the University of Sheffield in England, led by Peter V. Wright, discovered that polyethylene oxide forms a natural compound, or complex, with a potassium salt, resulting in a material with relatively high ionic conductivity.

It wasn't until 1979 that Michel Armand, director of research at Centre National de la Recherche Scientifique, Saint-Martin d'Heres Cedex, France, proposed using the polymer as a solid electrolyte in lithium solid-state batteries. Subsequently, a large number of research groups have investigated a variety of polymer electrolytes.

At 10^{-4} (ohm cm) $^{-1}$ at 100°C, the ionic conductivities of these solvent-free polymer electrolytes are comparable to those of the room temperature solid electrolytes lithium iodide (LiI) and silver iodide (AgI). However, these values are still far smaller than the 1 (ohm cm) $^{-1}$ exhibited by aqueous-based electrolytes used in, for example, lead-acid car batteries.

If the polymer electrolytes can be formed in very thin sheets, then cell resistance falls to a useful level. Such a device is entirely solid-state, with no liquid or gas involved. The feasibility of this type of battery has been tested in a variety of research cells, and in some prototypes of practical size (Figs. 1 and 2).

The first such batteries had to operate near 100°C, because of the poor conductivity of the polymer electrolytes at room temperature. But recent technical articles from MHB Inc., Dayton, Ohio; Institut de Recherche d'Hydro-Quebec (IREQ), Varennes, Quebec, Canada; and others describe batteries using modified polymer electrolytes that can operate throughout a temperature range of -20°C to +140°C at voltages as high as 3.5 volts.

Performance data in a number of laboratories, including the United Kingdom Atomic Energy Authority's Harwell Laboratory, Didcot, England, and the University of

Minnesota, Minneapolis, indicate that if polymer electrolyte batteries can be successfully scaled up, they should provide up to five times the energy density of a lead-acid car battery.

Experimental studies on small laboratory cells - from one to six square centimeters in area - show that such batteries now provide an energy capacity of up to 200 watt-hours per kilogram. Sustained power density has reached 1000 W/kg, with a peak power of 800 W/kg at half-charge.

Ultimately, researchers expect the energy capacity of a typical packaged battery, based on a lithium anode and a vanadium oxide (V_6O_{13}) cathode, to rise as high as 150 Wh/kg, with a sustained power density of 200 W/kg and a peak power of 900 W/kg at half charge.

Batteries for Mars?

The potential applications of polymer electrolyte batteries span the entire range of battery products, from smart credit cards to standby power in telecommunications (see table), with their combination of high energy density and mechanical ruggedness making them particularly attractive for space applications.

The rapid growth in consumer electronics has produced a need for micropower sources that can be placed directly on integrated circuits. A typical application might be an on-chip power source to drive CMOS memory elements. Here, thin-film technology is useful since the power source must be constructed on the same substrate as the electronic circuitry. The fully integrated system must be compatible with the power output of the cells. Size may impose an upper bound on power capacity in this case, however, for cells that are both small and thin.

The first applications of such batteries are likely to take advantage of their small size. Likely candidates are smart credit cards, batteries for instant-film packs, and perhaps batteries built into printed-circuit boards in laptop personal computers.

Interest in commercializing this technology has directed much effort toward finding polymer compositions that provide adequate conductivity at room temperatures. Cells using such polymers are now being demonstrated in several R&D laboratories around the world. While mass-produced polymer electrolyte batteries are not presently available, industry experts expect them to arrive within the next three to five years.

The pluses for polymers

Inherent in thin-film technologies is a large surface area, which means that batteries can be configured into almost any shape that can be assembled and packaged by automated techniques. The anode is generally lithium, which can be obtained as a very thin film. It is light, soft, malleable, and highly electropositive, and its low equivalent weight results in a high specific energy.

The solid polymer electrolyte has a large surface-to-thickness ratio. The main criteria for the polymer is that it must have high ionic conductivity with good mechanical integrity. Polymers with high molecular weight, or those whose molecules form complex networked structures -- known as crosslinking -- are strongest.

The composite cathode generally consists of the electroactive solid insertion compound, usually vanadium oxide (V_6O_{13}) or titanium disulfide (TiS_2), plus carbon and a small amount of electrolyte. The carbon enhances the electrode's electronic conductivity, while the electrolyte enhances the ionic conductivity of the insertion compound, as well as binding together the entire cathode. The cathode's large effective surface area results in high power capabilities.

During discharge, lithium is oxidized at the interface between the lithium anode and the polymer electrolyte, and the positive lithium ion is transported across the electrolyte. Simultaneously, lithium ions from the electrolyte pass into the positive electrode at the interface between it and the polymer. When the battery charges, these processes are

reversed. Experimental batteries are able to sustain several hundred charge-discharge cycles to the theoretical maximum capacity of the cathode without a loss in energy capacity.

Conducting flexibly

Unlike hard, inorganic electrolytes based on ceramic or glassy materials, polymer electrolytes can deform under stress when battery volume changes during charging or discharging. Thus, they solve a major problem encountered during development of previous solid-state batteries: the need for a flexible solid electrolyte that can accommodate expansion and contraction from dimensional changes in the electrodes during battery cycling.

Typically, when a lithium battery discharges, oxidation of the anode gradually depletes the metal at the metal-electrolyte interface. Likewise, the insertion of lithium ions in a host structure such as vanadium oxide (V_6O_{13}) results in a swelling of the cathode.

If the electrolyte cannot deform, then the interfacial contact degrades, producing nonuniform current distributions, localized high current densities, and ultimately battery failure. Interfacial resistance is measured using ac impedance techniques; depending on system load, that resistance drop can rise from five millivolts to as much as 100 mV. Deformable polymer electrolytes offer the promise of maintaining excellent electrode interfacial contact during cell operation.

Polyethylene oxide (PEO) is the most widely studied of the polymers proposed as battery electrolytes. It belongs to the class of solvating materials -- those that form chemical bonds with the lithium and other salts -- in this case, because oxygen atoms in the polymer backbone are acting as localized electron donors.

The flexibility of the polymer chain, and the spacing of the donor atoms, allow ions from the electrodes to move easily through the electrolyte. Continuing studies of the factors that govern formation of polymer-salt complexes and the mechanisms of ion

transport are expected to result in new polymer formulations for electrolytes with improved conductivity at and below 25°C.

Polymer waves

The mechanisms by which ions are transported through polymers are not well understood, but recent studies in more than a dozen laboratories have shown that the amorphous phase of the polymer is primarily responsible for the conductivity. This suggests that the motion of cations and anions through the polymer occurs by a liquid or wave-like mechanism, known as polymer segmented motion.

Many new polymer electrolytes can be synthesized by varying the salt's anion and cation, or by using other polymers with solvating powers that may be suitable hosts for the salt. Polymers with other so-called hetero atoms (those that easily form compounds with salts), such as nitrogen in amines or sulfur in sulfides, could also be used. Typical examples include nylon-6, polyethylene imine, polyvinylidene fluoride, polyethylene sulfide, polyethylene succinate, and polypropylene oxide.

Polyorganophosphazene -- another polymer structure, based on nitrogen linkage -- has been reported to form polymer electrolytes with high conductivity at room temperature. These polymers have not been studied as intensively as polyethylene oxides; they appear to form even more flexible films, but are also more difficult to cast. They have been synthesized by Peter Blonsky and Duward Shriver at Northwestern University, Evanston, Illinois, in collaboration with Paul Austin and Harry Allcock at Pennsylvania State University, College Park, Pennsylvania.

Such materials can form a number of complexes with a wide variety of salts; the resultant conductivity is more than three orders of magnitude higher than polyethylene oxide (PEO) complexes at 25°C. Most studies have been directed toward rechargeable batteries with lithium anodes and solid insertion cathodes. The insertion materials form a new family of cathodes now being used for battery construction.

Many promising new materials are chalcogenides of transition metals that undergo reversible topochemical reactions with lithium. They include compounds such as vanadium oxide (V_6O_{13}), titanium disulfide (TiS_2), molybdenum trioxide (MoO_3), and niobium disulfide (NbS_2).

One of the most widely described cell systems uses a lithium anode, a polyethylene oxide electrolyte, and a vanadium oxide (V_6O_{13}) cathode. Similar cells with titanium disulfide (TiS_2) as the cathode and with lithium perchlorate ($LiClO_4$) as the salt have shown promise.

But the reactivity of the anodes complicates the manufacturing process. A dry-room atmosphere is required to handle lithium, which is moisture sensitive. The packaged battery must then be hermetically sealed to prevent degradation during storage and operations.

Hot and cold

The package must also withstand the elevated temperatures that have been necessary to obtain adequate ionic mobility within the electrolyte component of the cell. This requirement also complicates the practical application of these batteries.

Very specialized high-energy batteries, conceived for electric vehicles or for maintaining power supplies at times of high demand, could incorporate appropriate insulation and thermal management for operation at constant elevated temperature.

Materials with adequate conductivities - 10^{-4} (ohm cm) $^{-1}$ at room temperature -- have been reported by IREQ and by Centre National de la Recherche Scientifique, Saint-Martin d'Heres, France, but their resistivity increases as operating temperature is reduced.

Presently, several organizations claim to have developed room-temperature polymer electrolytes, and plan to commercialize them in batteries. To judge by the few technical papers that have been published, often without complete details, the two front runners are probably MHB Inc. and IREQ.

Who's who

The impetus behind IREQ's research was to develop a battery for propulsion of electric vehicles. To produce the required sustainable power density for this application -- at least 80 W/kg -- operating temperature was fixed at 90-100°C for most of the test, which was performed in 1983 at IREQ laboratories by Michel Gauthier, group leader.

As a result of this work, a new family of polymer electrolytes with higher conductivities has emerged. Few details have been released, but the polymers are thought to be based on modified polyethylene oxide formed into complexes with plasticizer salts -- those that lower the melting point of the polymer.

Other technical issues as well must be addressed before polymer electrolyte battery technology can be commercialized. Experimental verification of thermal management and cell balances for large-scale series and parallel arrangements must be carefully scrutinized. Failure tests on overcharge and overdischarge need to be verified, and cell protection schemes devised if necessary.

The batteries must be abuse tested, lest misuse trigger rapid exothermic runaway. Battery disposal is a significant problem: are the materials toxic?

Finally, the manufacturing and material costs of the components must fall considerably to make them viable. Lower-cost reactants and polymers must be identified and introduced. Early polymer-electrolyte battery prototypes that used current collectors made of nickel were estimated to cost up to \$200 per kW-h, but newer versions with plastic collectors should cost no more than \$100 per kW-h -- competitive with the cost of lead-acid car batteries.

Other groups involved in fundamental studies on polymer electrolytes -- including polymer synthesis, electrochemical research, and complete cell testing and technology development -- include four in England (the Chloride Group in Manchester, London's Imperial College of Science, Technology, and Medicine, the University of Salford in Lancaster, and the United Kingdom Atomic Energy Authority's Harwell Laboratory in

Didcot); three in France (Alcatel CGE in Annecy, the University de Grenoble, and Centre National de la Recherche Scientifique at Saint-Martin d'Heres); one in Denmark (the Riso National Laboratory in Roskilde); five in the United States (Northwestern University in Evanston, Illinois, Detroit's General Motors Co., the University of Pennsylvania in Philadelphia, the Argonne National Laboratory in Illinois, and the University of Minnesota in Minneapolis); and two in Japan (Sophia University, and Hitachi Ltd., both of Tokyo).

'Smartening up credit cards

One particularly obvious application for polymer-electrolyte batteries is as the power source driving the microprocessor contained in smart credit cards. These smart cards, which look just like any other credit card, have been tested extensively in France and Japan, and are currently being marketed there. In the United State, trials are just beginning. [For more on the technology of these cards, see "The very smart card: a plastic pocket bank," by Hiro Shogase, IEEE Spectrum, October 1988, pp. 35-39.]

Such cards are used in retail stores just as existing credit and debit cards are. The card maintains information on funds levels, credit ratings, bank-account access, medical history, security clearance, college transcript records, and various other sorts of data. The microprocessor automatically shuts itself off if attempts at unauthorized access are made.

Currently available cards have a touch-sensitive keyboard on the back side, a built-in microprocessor, a digital display, and a nonrechargeable lithium battery with a life of two years. Their microprocessor is driven by a nonrechargeable, nonaqueous organic electrolyte battery 1-2 millimeters thick.

Rechargeable solid-state lithium polymer electrolyte batteries offer great promise for smart card applications, especially as thin films are so easily configured. One possibility might be to use solar cells, recessed contacts, or piezoelectric devices -- along with appropriate circuitry -- as charging sources [Fig. 3].

A solar cell could easily be mounted on the back of the card. A high-intensity light source directed at the solar cells could recharge the battery while the card is inserted into the computer that reads and processes information from the microprocessor.

Much research and applications engineering remains to be done before such visions are realized, but the latest research shows increasing promise for practical polymer-electrolyte flat cells within five years -- and perhaps significantly less.

To probe further

The last three international Solid State Ionics Conferences (held in July 1983 in Grenoble, France; in August 1985 in Lake Tahoe, California; and in September 1987 in Garmisch-Partenkirchen, West Germany) produced a number of papers on the development of polymer electrolytes. Their proceedings are available from Elsevier Science Publishers BV, Journals Department, Box 211, 1000 AE, Amsterdam, the Netherlands; or Elsevier Science Publishers, 655 Avenue of the Americas, New York, NY 10010; 212-633-3750.

Proceedings from the Second, Third and Fourth International meetings on Lithium Batteries (held respectively in April 1984 in Paris, in May 1986 in Kyoto, Japan, and in May 1988 in Vancouver, B.C., Canada) contains a number of articles on polymer electrolyte battery development. The volumes are available from Elsevier Sequoia S.A., Lausanne, Switzerland.

The monthly journal Solid State Ionics (North-Holland, Amsterdam) is a good source of recent developments in this field. Further information on solid ionic conductors can be found in "Solid Ionic Conductors," by Duward F. Shriver and Gregory C. Farrington, in the May 20, 1985, issue of Chemical & Engineering News.

Periodically, papers on ionically conducting polymers appear in the monthlies Journal of Polymer Science (Interscience Publishers, New York City); Polymer Journal (Society of Polymer Science, Tokyo); and Macromolecules (American Chemical Society,

Washington, D.C.). Pertinent articles also appear in the bimonthly Journal of Applied Electrochemistry (Chapman & Hall, London).

The Journal of the Electrochemical Society and the national meetings sponsored by that society provide good sources on polymer electrolytes and polymer electrolyte batteries. Society conferences are held twice a year; the next two are scheduled for Hollywood, Florida, October 15-20, 1989, and Montreal, Quebec, Canada, May 6-11, 1990. Contact the Electrochemical Society, 60 South Main Street, Pennington, New Jersey 08534; 609-737-1902.

Several recent books include articles on polymer electrolytes and solid-state batteries. Polymer Electrolyte Review (Vol. I), edited by J.R. MacCallum and C.A. Vincent (Elsevier Applied Science, London, 1987) is a comprehensive coverage of polymer electrolytes, polymerization, and developments. Electrochemical Science and Technology of Polymers (Vol. I), edited by Roger G. Linford (Elsevier Applied Science, London, 1987), deals with the electrical and thermodynamic properties of both ionically and electrically conducting polymers.

Acknowledgement

The authors wish to acknowledge the financial support of the Office of Naval Research. **and Defense Advanced Research Projects Agency.**