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The search for the better polymer electrolyte

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1. Introduction

The Department of Energy has been developing advanced batteries for over 20 years. Work started in the 1970s emphasized the development of high-energy batteries for electric vehicles. More recently, emphasis has shifted to high power batteries for hybrid vehicles. During the same time period, the concept of a lithium-based battery utilizing an ionically conducting polymer electrolyte was proposed. The Department of Energy, under its cooperative program with the United States Advanced Battery Consortium, began working on the development of lithium polymer batteries in the early 1990s.

A number of presentations at the joint workshop on Solid State Battery Technology were concerned with the physical phenomena associated with ionically conducting polymers and the technical alternatives for polymer electrolytes in advanced batteries. This paper presents some of the results of those presentations as well as the Department of Energy's view of the critical barriers to be overcome in developing an advanced battery for use in electric and hybrid electric vehicles.

Information on the science of polymer electrolytes in lithium batteries can be found Refs. [1–6]. These papers describe the advantages and characteristics of employing polymer electrolytes in lithium batteries. Problems such as compositional compatibility and stability, mechanical strength, and interfacial stability are discussed.

This paper addresses the requirements for the ionically conducting polymer needed to support advanced battery technology for vehicle applications. Towards that end, this paper is based on work done by the United States Advanced Battery Consortium and their principal lithium polymer development team of 3M/Hydro-Quebec. This paper also draws on the work being done by the Exploratory Technology Research program of the Office of Transportation Technologies and programs supported by the Office of Basic Energy Sciences.

In order to define the requirements for an advanced ionically conducting polymer, one has to define the requirements for the advanced battery itself. The battery needs help to define the needs for the polymer electrolyte. This includes both the electrochemical and mechanical properties needed to realize effective cells, modules, and battery packs. Underlying assumptions about polymer properties, as well as interface properties with the electrodes, are discussed. Finally, certain information about the current state of the art is presented from the 3M/Hydro-Quebec development program [7–12].

At this time, not all of the requirements are completely well defined. It is also not always clear how these properties can be obtained in alternative manufacturing processes that are being used to make prototype lithium polymer batteries at this time. The reader should study all of the papers in this proceedings to best understand the search for a better polymer electrolyte.

2. Advanced battery goals

Goals for advanced batteries have been developed and refined over an extended period of time. Originally, goals were developed for electric vehicle batteries. More recently, new goals were developed for high power batteries to be used in hybrid vehicles [13–15] [1]. These goals are interrelated. Both power and energy must be specified in a manner that relates to the desired operation of the vehicle. Appropriate cycling goals must also be set, related to how

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the battery exchanges energy with the vehicle's propulsion and charging systems. It is expected that the battery will last the life of the vehicle, thus, establishing a calendar life goal. The battery must exhibit these characteristics over the range of temperatures expected in vehicle operation. Finally, cost goals are established in order to make electric and hybrid vehicles competitive in the marketplace against conventional vehicles manufactured today. The cost goals represent the most significant barrier to the commercialization of advanced battery technology in vehicles and other energy system applications.

Table 1 provides the key goals for the energy storage battery to be used in electric vehicles. These goals were established in 1996 by the United States Advanced Battery Consortium. They reflect work by the Consortium and others on nickel metal hydride batteries. The energy and power performances were developed to assure competitive electric vehicle operation. The Consortium realized that lithium battery technology in general could offer a range of performance levels. These goals reflected the desire to set challenging, but achievable goals. These goals were set to be significantly beyond the range that could be realized by nickel metal hydride vehicle batteries. Quite similar goals have been set by the Lithium Battery Energy Storage Research Association in Japan. The Consortium and the Society of Automotive Engineers have defined the recommended practices to be used for measuring these parameters. These test procedures apply to testing of cells, modules, and full battery packs [9,14,15].

Table 2 provides the key goals for the high power energy storage needed for hybrid electric vehicles. The development of goals for hybrid vehicles is made more complex by the wide range of possible variations in the overall propulsion system. These goals were developed by the Consortium for the Partnership for a New Generation of Vehicles. They reflected the minimum needs of a power assist type hybrid vehicle. The Toyota Prius and the Honda Insight are typical power assist hybrid vehicles. It should be noted that the power levels are many times that of an electric vehicle battery. The requirements for cycling are also quite different, in that the battery is subjected to a large number of small cycles representing a small fraction of the total energy stored. The battery is operated in the middle of its charge–discharge range, where both forward and reverse reactions can occur at high rates without problem.

Table 1
Advanced battery goals (based on USABC EV interim commercialization criteria for high energy battery)

Parameter	Goal
Energy	150 W h/kg; 230 W h/l
Power	300 W/kg; 460 W/l at 80% DoD for 30-s pulse
Cycle life	1000 at 80% DoD on USABC Dynamic Stress Test
Calendar life	10 years
Cost	\$150/kW h
Operating temperature	−30°C to 65°C

Table 2
Advanced battery goals (Based PNGV/USABC — high power energy storage minimum requirements — fast response engine [power assist hybrid])

Parameter	Goal
Energy	75 W h/kg; 100 W h/l
Power	750 W/kg; 1000 W/l
Cycle life	200,000 cycles for 25 W h pulses; 50,000 cycles for 100 W h pulses
Calendar life	10 years
Cost	< \$150/kW h
Operating temperature	−40°C to 52°C

3. Developing goals for the electrolyte

Goals for the electrolyte in any battery have to reflect the goals for the battery itself. The electrolyte plays a key role in determining the characteristics of the battery. Achieving high power levels requires the electrolyte to have a high ionic conductivity, ($> 1 \times 10^{-3}$ S/cm). This can be partially achieved by increasing the total surface area of the electrodes. This eventually leads to diminishing returns as the increased inert materials are needed to enclose a physically larger cell. Then the cell's specific energy and energy density fall off rapidly. The electrolyte contributes nothing to the battery's energy, so the practical approach is to fabricate it as thinly as possible. Mechanical limitations in fabrication and the need to assure electrical isolation of the electrodes limit the practical thinness of the polymer electrolyte.

Understanding the relationship of polymer properties to the cell's cycle life is more complex. It is generally considered desirable for the polymer electrolyte to be strong and hard, as would a mechanical separator in a cell with a liquid electrolyte. In addition, the polymer material must remain in intimate electrochemical contact with the electrode materials. To this end, it must effectively 'wet' and adhere to the electrode materials. This complex property is often characterized as 'stickiness'.

The cell and its components must also be capable of exhibiting a long calendar life. This means that the cell's electrical properties, such as capacity, must remain stable for long periods of time regardless of any cycling activity. This requires the cell components, including the electrolyte, to be chemically stable and to not participate in any undesirable side reaction. At the same time, it is also desired that the cell properties be stable over a range of operating temperatures. In particular, the electrolyte's conductivity properties must not degrade significantly at lower temperatures.

Table 3
Desired electrochemical polymer properties (at 25°C) (based on assumption of a multiple ion conductor)

Parameter	Property
Electrochemical properties[a]	
Ionic conductivity	$>1\times10^{-3}$ S/cm
Electrical conductivity	$<1\times10^{-7}$ S/cm
Electrical breakdown	>5 V/μm
Lithium ion transference number, t_0^+	0.3 to 0.8
Stability	5 V vs. lithium metal

[a] These properties are assumed measured 25°C.

Cells based on polymer electrolytes are expected to be more tolerant of abuse than liquid electrolytes. The inherent stability of the polymer electrolyte and its tendency to not participate in side reactions are considered important assets with regard to abuse tolerance at the cell level. Finally, the cost of materials remains an important issue for all advanced batteries. Costs of base materials, complexity of synthesis processes, and the needs of the actual cell manufacturing process play an important role in determining the battery's overall cost.

4. Desired electrochemical properties

Table 3 summarizes the key electrochemical properties for a polymer electrolyte. These properties are based on a multiple ion conductor. These properties would support the engineering of the high performance cells sought for application in electric and hybrid vehicles. These specific properties are based on current experience and therefore serve as a reasonable set of development goals.

If the development goal is a single ion conductor, then another set of goals can be developed that are appropriate for a single ion conductor. In any case, adequate electrical resistance and electrochemical stability are also important.

Perhaps more important than the properties themselves, is how they are measured. After many inquiries, this author is led to conclude that there are a broad range of measurement techniques, as well as considerable variation in how samples are prepared for measurement. Research and development activities are currently being hampered by a lack of recognized standards for these measurements.

It is also important to understand the importance of many other factors when a given polymer electrolyte is used to engineer cells for evaluation. Considerable variation is introduced by the choice of electrode materials and electrode morphology. This not only includes the active electrode material, but the use of binders and electronic conductivity enhancers. The choice of current collectors, and the potential use of an inert porous separator with the polymer electrolyte further complicates that problem of isolating and understanding the electrolyte behavior. Without systematic and careful experimentation, full understanding of the electrolyte electrochemical properties is hard to achieve.

5. Desired polymer mechanical properties

Table 4 summarizes the desired mechanical properties for the polymer electrolyte. An understanding of mechanical properties is more difficult to obtain because of its proprietary nature. Organizations doing actual manufacturing of lithium polymer cells have developed their understanding based on their particular manufacturing methods. Since manufacturing methods vary, so do mechanical properties.

Some mechanical strength is desired just to assure that the thin film layers of active material can be wound into cells. Hardness is considered desirable to resist formation of dendrites, while 'stickiness' affects stable electrochemical performance. A high melting point assures that the material is electrochemically stable. A low glass transition temperature assures that there will be no crystallization and formation of high resistance grain boundaries. A high average molecular weight for the final polymer also assures chemical stability.

Current manufacturing processes for making lithium polymer cells or cell materials vary. Thin layers of the electrolyte and electrode material can be manufactured in a variety of methods. One option is to mix the electrolyte or electrode materials with a solvent or carrier fluid. This is then mechanically coated and dried to form the electrolyte or electrode layer. Alternatively, electrode and electrolyte layers can be extruded onto a manufacturing base. The manufacturing base for either process can be the current collector or an inert material. In either case, the mechanical properties of the polymer electrolyte layer are largely determined by the manufacturing process.

Supplemental processes, such as radiation cross-linking or thermal treatments may also affect the final properties of the polymer electrolyte.

This intimate linking of the manufacturing processes and final polymer properties complicates their understanding by the research community at large. The few organizations doing pilot manufacturing tend to want to protect certain aspects of their processes from public disclosure. Their data relating the polymer electrolyte properties back to their manufacturing processes are closely held informa-

Table 4
Desired mechanical polymer properties (properties will depend on manufacturing process)

Parameter	Property
Tensile strength	2 MPa ($\sim$ 300 psi)
Melting point	>250°C
Glass transition temperature	<-70°C
Molecular weight	$\sim 1\times105$

tion. Work done by hand in a laboratory environment often bears little relationship to the development work being carried out in these pilot production facilities.

6. Interface properties

Interface properties could be the subject of a whole separate paper. Some of the most important properties are the ionic conductivity and the diffusion rate at the interface itself. If the interface is a significant barrier to conductivity and diffusion, then the most ideal electrolyte properties are meaningless. Interface properties relate back to the electrochemical and mechanical properties of the electrodes. The electrodes are often a composite material, with the electrochemically active material only one component of the mix. The electrode is often compounded with an electronic conductor to lower the local resistance to the current collector. A second compound is polymer electrolyte, to provide good ionic conduction to the bulk electrolyte layer. Additional layers may be added in the fabrication process to address known issues in controlling the interface during cell operation. The number of possible electrolytes and electrode material, plus the possible combinations, precludes any organized discussion at this time.

7. Real world systems

There are a number of lithium polymer technology systems emerging in the battery market today. The Department of Energy's cooperative program with the United States Advanced Battery Consortium has sponsored the team of 3M/Hydro-Quebec to build large lithium polymer cells and modules to address the needs of the electric vehicle market. This technology uses an ultra thin lithium foil as the anode, and a composite cathode utilizing vanadium oxide. The vanadium oxide is blended with carbon and the polymer electrolyte and bonded to a metal foil current collector.

The system is based on $Li(CFSO_2)_2$ in solvating aprotic polymer (polyethylene oxide copolymer). This system operates well in a temperature range of 60–80°C. (It is considered a warm battery.) The total thickness of a cell is on the order of 100 μm.

Other lithium polymer systems are rapidly emerging in response to the demand for compact and lightweight batteries for the consumer electronics market. The emphasis is on fabricating small flat prismatic cells. Many are based on well-known gel electrolyte technology that appears to be well suited for this purpose. This technology is emerging as the de facto baseline against which all other technology will be measured. At this time, the ability of gel electrolyte technology to meet the criteria previously outlined for automotive applications remains to be determined.

8. Where do go from here

The possibilities for lithium polymer technology are many and diverse. The organizations that are rapidly moving into production have real needs to improve their product for broader applications. The research community continues to create new possibilities and options. Hopefully, both sides will continue to share their views in open forums and learn from each other. The Department of Energy and the United States Advanced Battery Consortium are continuing to afford all parties an opportunity to speak to the technical and programmatic issues of concern. The July 1999 Solid State Battery Technology workshop in Towson, MD was seen as an opportunity to bring the relevant parties together to study these questions. The search for the better polymer electrolyte is continuing.

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