The Road from Solid Polymer Electrolytes to Commercial Lithium Ion (Li-Ion) Polymer Batteries

Solid polymer electrolytes (SPEs) serve two principal roles in a Li battery. It is the separator that insulates the anode from the cathode in the battery and it is the medium through which ions are transported between the anode and cathode during discharge and charge. Consequently, the SPE should not only have high ionic conductivity, but it also should be an electronic insulator. In addition, it should have adequate mechanical strength to withstand the stack pressure changes and stresses of the electrodes during discharge/charge cycling of the battery. Preferably, the mechanical strength of the polymer electrolytes should be comparable to that of the porous polyolefin separators used in conventional Li batteries utilizing organic liquid electrolytes.

In general, conductivity and mechanical strength of a polymer electrolyte follow an inverse trend, i.e., mechanical strength decreases as conductivity increases. We recognized this behavior as early as 1988 when we attempted to fabricate rechargeable solid-state Li batteries with MEEP-based SPEs (1). Although these classical polymer electrolytes based on poly[bis((methoxy ethoxy) ethoxy)phosphazene] (MEEP) have room temperature ionic conductivities exceeding 10^{-5}S/cm, they are glutinous materials with a tendency to flow under mild pressure. Consequently, Li batteries could not be constructed with these electrolytes unless their mechanical strength was increased. We developed two approaches to prepare mechanically strong MEEP electrolytes.

In the first approach, mechanically strong electrolytes were prepared by forming interpenetrating polymer network (IPN) structures and composites with morphologically rigid polymers such as poly (ethylene glycol diacrylate) (PEGDA), poly (vinyl pyrrolidinone) (PVP), poly(ethylene oxide) (PEO), or poly(propylene oxide) (PPO) (2). In the second approach we encapsulated MEEP electrolytes in thin, highly porous, fiber glass separator mats (1). A Li cell of the configuration, Li/MEEP-(LiX)-fiberglass/TiS$_2$, was constructed and cycled at room temperature. This represents one of the early demonstrations of room temperature performance of conventional solid polymer electrolyte-based rechargeable Li batteries. Because of the relatively low conductivities, however, these solid polymer electrolytes, derived from Li salt complexes of long chain polymer hosts, are not suitable for the development of Li batteries capable of high power performance at and below room temperature

Solid Polymer electrolytes with conductivities exceeding 10^{-3} S/cm at room temperature have been prepared as gel electrolytes (3,4). They are formed by absorbing organic liquid electrolytes into polymer structures. Examples include gel electrolytes obtained by immobilizing LiPF$_6$ solutions in mixtures of ethylene carbonate (EC) and propylene carbonate(PC) in polymers such as polyacrylonitrile (PAN), poly(vinylidene fluoride) PVF), poly(methyl-methacrylate) (PMMA), poly(vinyl pyrrolidinone) (PVP) and poly(ethylene glycol diacrylate) (PEGDA)-based electrolytes(3,4). The mechanical strength of these gel electrolytes is usually adequate for use as separators in Li-ion batteries, but their soft morphology often is unsuitable for the high speed

processing employed in large volume manufacturing of batteries. The flow properties of some of these electrolytes can also lead to internal short-circuits and safety hazards.

In order to develop highly conductive polymer electrolytes which can be handled like conventional separators, we set out to prepare microporous membrane-bonded polymer electrolytes. As an example of this concept, we encapsulated PEGDA-based gel electrolytes into the pores of several types of Celgard® membranes(5). We found that ionic conductivities of these polymer electrolytes can be modulated by controlling the thickness and porosity of the separator. This was an extension of the work we had carried out previously with unsupported PEGDA-based electrolytes having the compositoin of PEGDA-EC/PC-LiX (LiX=LiClO$_4$, LiAsF$_6$) with a room temperature conductivity of about $3x10^{-3}$ S/cm (4).

Conductivities of a few of these separator-bonded electrolytes are shown in Table 1. The PEGDA-based electrolytes were formed by in-situ polymerizing the tetra-ethylene glycol diacrylate (TEGDA)-containing electrolyte solutions on Celgard membranes. The pores of the membranes were fully covered by the solid electrolytes. As expected, membranes with higher porosity gave electrolytes with higher conductivity. In addition to good mechanical strength, the resulting electrolyte showed excellent electrochemical stability with a voltage window spanning 0.0V to 4.3V versus Li$^+$/Li. Li/LiMn$_2$O$_4$ cells using these electrolytes as the separators showed excellent cycling behavior at room temperature (5).

Incorporation of polymer electrolytes into porous separator membranes lowers their conductivity to a degree determined by the solid fraction of the membrane. However, mechanically strong thin electrolyte films can be prepared which are useful to the construction of rugged batteries. The conductivity loss of the electrolyte due to the porous membrane is compensated for by its smaller thickness. It should be noted that in this work we used commercially available separator membranes to demonstrate the concept. By suitably optimizing the thickness and porosity of the porous membrane, it should be possible to prepare solid polymer electrolytes with conductivities comparable to that of unsupported polymer electrolytes, (i.e., without the membranes). It is not necessary to fully cover the pores of the membrane with the polymer electrolyte. A fraction of the pore may be left open to store liquid electrolytes to provide high ionic conductivity in the cell. The polymer electrolyte layer can be used to bond the separator to the electrodes to achieve a monolithic cell package suitable for the construction of thin prismatic batteries with dimensional stability.

Various modifications of this concept have been adopted to fabricate practical batteries which are being introduced commercially. Das Gupta and Jacob (6) reported on Li-ion batteries with bonded electrolytes in which a microporous separator and electrodes were coated with a liquid electrolyte solution and a layer of a polymer adhesive plasticized with a liquid electrolyte solution. The separator and the electrodes were then bonded. Another variant is a process in which an adhesive layer (e.g. PVdF) is applied to the separator and used to bond the electrode and separator films (7,8). Sony described liquid electrolyte plasticized polyacrylonitrile layer directly applied either to the electrode or the separator (9). Note that practical utility of polyacrylonitrile-based electrolytes for Li and Li-ion batteries were reported by us in many publications since 1990 (3,4,10). In Sanyo's work (11) on separator bonded electrolytes, they added polymer precursor solutions to spirally-

wound liquid electrolyte-based Li-ion cells and solidified the cell package by thermal polymerization. Researchers from Telecordia technologies (12) described a process wherein propylene carbonate-plasticized electrodes were permanently bonded to several different untreated microporous polyolefin separators. Batteries fabricated using this process reportedly exhibited excellent performance: 3 C rates with 75-80% capacity utilization at room temperature and 50% capacity at C/2 at –20°C, very low internal impedance and high specific energy (>180 Wh/kg).

In conclusion our work to improve the mechanical strength of gel polymer electrolytes by bonding them to micro-porous membranes has been transitioned into a successful technology for the fabrication of commercial Li-ion polymer batteries.

References:
1. M. Alamgir, R. K. Reynolds and **K. M. Abraham** in "Materials and Processes for Lithium Batteries," The Electrochemical Society, PV 89-4, K. M. Abraham and B. B. Owens, Editors, The Electrochemical Society, Pennington New Jersey, (1989), pp. 321.
2. **K. M. Abraham** and M. Alamgir, Chem. Mater. 3, 339 (1991).
3. **K. M. Abraham** and M. Alamgir, J. Power Sources, 43-44, 195 (1993).
4. **K. M. Abraham** and M. Alamgir, J. Electrochem. Soc. 136, 1657 (1990) (See also U. S. Patent 5,252,413 (1993).
5. **K. M. Abraham**, M. Alamgir and D. K. Hoffman, J. Electrochem. Soc. 142, 683 (1995).
6. U. S. Patents 5,437,692 (1995); 5,498,489 (1996) and 5,512,389 (1966).
7. G. Venugopal, J. Moore, J. Howard and S. Pendalwar. J. Power Sources, 77, 34 (1999).
8. U. S. Patent, 5,981,107 (1999), 6,024,773 (2000) and 6,051,342 (2000).
9. K. Kezuka, T. Hatazawa and K. Nakajima in Proceedings of the 10th IMLB, Como, Italy, May, 2000 (Abstract # 4).
10. **K. M. Abraham**, H. S. Choe and D. M. Pasquariello, Electrochim Acta. 43, 2399 (1998)
11. T. Fujii, Proceedings of the 17th International Seminar and Exhibit on Primary and Secondary Batteries, Boca Raton, Fl, March, 2000.
12. 12. A.S. Gozdz, I. Plitz, A. DuPasquier and T. Zhang. In Rechargeable Lithium Batteries, The Electrocheical Society Proceedings Volume, PV 2000-21, pp 336, 2001

Table1. Conductivities of Porous Membrane-based Solid Electrolytes at 25°C

Membrane Porosity(%)	Thickness (micron)	Electrolyte	Thickness (micron)	Conductivity (ohm^{-1} cm^{-1})
70	25	30(m/o)EC-30 PC tetraglyme-2 PEGDA-8LiAsF$_6$	37.5	1.1 x 10^{-4}
55	25	74(m/o) EC-16 PC-2 PEGDA-8 LiAsF$_6$	40.0	1.7 x 10^{-4}
35	25	74 (m/o) EC-16 PC-2 PEGDA-8 LiAsF$_6$	40.0	3.0 x 10^{-5}
34	25	30 (m/o) EC-30 PC-30 tetraglyme-2 PEGDA-8LiAsF$_6$	37.5	1.2 x 10^{-5}
42	25	30 (m/o) EC-30 PC-30 tetraglyme-2 PEGDA-8LiAsF$_6$	37.5	1.7 x 10^{-5}
Unsupported Electrolyte		3(m/o) PEGDA-68 EC/15 PC-14 LiPF$_6$	100	3 x 10^{-3}