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History of Solid State Batteries

by

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<p>Historically, batteries have combined liquid electrolytes with solid electrodes because solid electrolytes were too resistive and could not accommodate the volumetric changes associated with the cell reactions. Solid materials utilized as battery electrolytes include: (1) simple ionic salts - AgI; (2) double salt compounds - RbAg_4I_5; (3) dispersed phase solid electrolytes - $\text{KII}(\text{Al})_3$; (4) ceramic compounds - $\text{Na}-\text{g}^{\text{th}}-\text{Al}_2$; (5) in-situ formed electrolytes - LiI; (6) glasses - $\text{LiI}-\text{Li}_2\text{S}-\text{P}_2\text{S}_5$; (7) polymer electrolytes - $(\text{PEO})_8\text{LiClO}_4$. Commercialization has been limited because of performance and cost factors.</p>			
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HISTORY OF SOLID STATE BATTERIES

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Solid electrolytes have been of considerable interest because of the possibility for fabricating batteries that would exhibit enhanced stability and operate over a wide temperature range. The scientific activity devoted to this field has been a function of the availability of solid electrolyte materials. Prior to 1965 there were limited materials that exhibited ionic conductivities of sufficient magnitude for a practical battery (1,2). Whereas liquid electrolytes exhibited conductivities of nominally one S/cm solid electrolytes exhibited conductivities of less than 10^{-6} S/cm. It was known that certain solid electrolytes exhibited "liquid like" conductivity values of one S/cm at elevated temperatures. The high temperature phases of the silver halides and some cuprous halides exhibited this characteristic. However, at ambient temperatures, the stable crystal structures exhibit very limited ionic mobility.

Early investigators of solid state batteries developed several electrochemical systems for low power ordinance applications during the late 1950s, as shown in Table 1 (3,4). These cells had very high internal resistances and were limited to current densities of a few microamps/cm². Since most of these cells were based on silver ion conducting electrolytes it was necessary to use silver as the anode; therefore the cell voltages and the energy densities were quite low. Nonetheless, these batteries did exhibit long shelf-life and good mechanical stability.

The major limitations of low specific energy and power were due to the solid state of the electrolyte material. Consequently, battery scientists interested in improved solid state batteries had to develop more conductive solid electrolyte elements. This could be achieved by finding new structures in which the ionic transport occurred more readily, or by developing techniques for fabricating the electrolyte in a very thin configuration with high surface area. Both of these approaches were followed during the subsequent twenty years. The discovery of highly conducting double salts of silver compounds led to the development of solid state cells in which the internal resistance was proportionately reduced. Ag₃SI had an ionic conductivity of 0.01 S/cm at ambient temperature and RbAg₄I₅ had a value of 0.27 S/cm. These salts were combined with silver anodes and the resulting cells were capable of current drains in excess of 100 mA/cm².

The use of polyiodide cathodes resulted in cells, of the types Ag/RbAg₄I₅/Me₄NI₃ capable of efficient discharge over a wide temperature range. Because of the absence of phase transitions stable performance was observed between -40 and +70°C. Further, these solid state cells could be stored as active primary cells for over 10 years (5). Although the system performed relatively efficiently, inherent limitations of cost and energy content restricted their application. Nonetheless, it did illustrate the feasibility of totally solid-state batteries that could accommodate the volume changes associated with cell discharge reaction and give efficient performance over an extended period of time and a wide range of temperature.

The development of more energetic solid-state batteries focused on the use of lithium-ion conducting materials with lithium anodes. Lithium iodide is the

most conductive of the alkali metal halides, 10^{-7} S/cm at ambient temperature. Liang (6) discovered the addition of a dispersed phase, such as Al₂O₃, increased the conductivity by about 2 orders of magnitude. Liang and colleagues developed a commercial lithium solid state battery using various polyvalent metal salts as the cathode. The internal resistance of the cell was reduced by fabricating the electrolyte as a very thin layer, but the cells were limited to fairly modest current drains. The cells did exhibit excellent storage life at high temperatures such as 100°C.

The development of the in-situ electrolyte battery based upon the use of a lithium anode with an iodine-complex cathode resulted in a cell that found widespread use in cardiac pacemakers. These cells are fabricated by contacting the anode with the cathode so that the electrolyte LiI forms in-situ as a very thin layer.

Other techniques for obtaining more conducting electrolyte elements in solid-state cells have included the development of both glass and polymeric electrolytes. Solid electrolyte batteries for ambient temperatures have evolved through the following stages,

1. Crystalline ionic solid electrolytes - (AgI)
2. Double salts - (RbAg₄I₅)
3. Dispersed phase electrolytes - (LiI-Al₂O₃)
4. Ceramic compounds - (Na-S⁻-Al₂O₃)
5. In-situ formed electrolyte - (LiI)
6. Glass electrolytes - (LiI-Li₂S-P₂S₅)
7. Polymer electrolytes - (PEOG-LiClO₄)

Little commercialization has occurred, but in the specialty areas the solid state batteries may be quite useful for highly stable, long-life, low power applications.

TABLE 1

Early Solid Electrolyte Battery Systems (3,4)

Systems	Cell potential (volts)
Ag/AgI/V ₂ O ₅	0.46
Ag/AgBr/CuBr ₂	0.74
Ag/AgBr-Te/CuBr ₂	0.80
Ag/AgCl/KICl ₄	1.04
Ni-Cr/SnSO ₄ /PbO ₂	1.2-1.5

Acknowledgement

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