

SOLID ELECTROLYTE SYSTEMS — RECENT TRENDS

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ABSTRACT

Solid electrolytes, which possess high ionic conductivities comparable with those of aqueous electrolytes, have received much attention in the last decade, as they play a major role in the field of miniaturisation particularly as power sources. Recent developments in the field from the point of view of materials, development of proper electrodes for battery applications, the process of intercalation are highlighted. An account of the important electrochemical device applications is dealt with.

Key Words: Solid electrolytes, Power sources.

INTRODUCTION

The discovery of superior conductors possessing high ionic conductivities comparable to aqueous electrolytes, opened up a new field of active research in view of their numerous applications such as solid state batteries due to high conductivity and reduction in the power requirements of many electronic devices [1], oxygen sensors, fuel cells and water electrolyzers, electrochemical capacitors and coulometers (timers), memory devices, display panels, military and space technology. Practical applications of these materials involve a number of factors and a better understanding of the structural aspects is essential in discovering newer systems aiming at a breakthrough. In order to obtain network of conducting paths, for example, in the case of Ag^+ conductors, a number of cations and anions are introduced in $\alpha\text{-AgI}$ which forms the basis of most of the Ag^+ conductors. RbAg_4I_5 exhibits the highest conductivity but suffers from a low decomposition potential (0.66 V) and instability against iodine and moisture. Anion substituted systems like $\text{AgI-Ag}_3\text{PO}_4$ are found to be more stable than cation substituted ones. Low impedance cells with Ag^+ electrolytes are limited due to low cell voltage ($\sim 0.7\text{V}$) and low energy densities. Though about 50 Wh/kg has been predicted with RbAg_4I_5 cells, only 22 Wh/kg has been obtained. Performance of other materials is affected by the interface between the negative electrode and the electrolyte. Copper ion conductors suffer from polarisation at the anode due to oxidation of cuprous to cupric state and due to electronic conduction. Sodium ion conductors operating at room temperature are not available and suffer from anode polarisation. The problems with beta-alumina in Na-S batteries are: (i) high temperature of operation (ii) sealing as the electrodes are in liquid state and (iii) development of cracks due to formation of dendrites. Though high voltages and energy density can be achieved with Li anodes in lithium cells, difficulties due to an internal shorting (because of diffusion of other ions also) are encountered.

It is found [2] that long range order is not necessary for the preservation of high conductivity in ionic solids. Large number of cation incorporated Ag^+ conductors as well as AgI-Ag oxysalt materials have been investigated. Some of them (e.g. $\text{AgI-Ag}_3\text{AsO}_4$, $\text{AgI-Sb}_2\text{S}_3$) possess a glasslike structure and are more stable and useful for preparing transparent conducting glasses [3-5]. Boron containing compounds (e.g. Ag borates), in which the formation of glass with good thermal stability is easy, have been investigated for use in advanced electrochemical devices [6]. Rapidly quenched glasses containing Li halides show higher ionic conductivity (LiPO_3 and $\text{Li}_2\text{W}_2\text{O}_7$) [7]. Cu^+ conducting glasses (CuI-

$\text{Cu}_2\text{O-2O}_5$) and Na^+ conducting sodium borosilicate glasses [8] containing Sb_2O_3 have also been studied. AgI- quaternary amine iodide systems [9] possessing a conductivity of $3 \times 10^{-2} \text{ohm}^{-1} \text{cm}^{-1}$ have been used in Ag/Zeolite 4A-I_2 cell.

Li^+ — conductors

As for Li cells are concerned, attempts are being made to reduce the internal resistance and to improve performance for long duration small current discharge conditions. Li_3N is being widely studied [10, 11] due to its high conductivity at room temperature which can be increased by one order [10c]. Dopants like Al, Mg and Cu have a negative effect on conductivity. Li_3N cells suffer from high rate of self-discharge [10b]. This is overcome by (i) optimising the H_2 impurity (ii) using anodes with lower activity and (iii) applying a layer of electronically blocking but ionically conducting material (Li_2O or LiI).

In sulphate based electrolytes [12, 13], many mono and divalent cations are found to have high mobility. The eutectic composition of Li_2SO_4 (60%), LiClO_4 (40%) with 10% of Na_2SO_4 gives a high conductivity. Such systems increase the possibility of developing newer anodes. Li-metal sulphide (FeS_2) molten salt batteries [14], lithium chlorate in the range $130\text{-}150^\circ\text{C}$, LiCl-KCl molten systems with FeS_2 , COS_2 , NiS_2 electrodes are being studied for vehicular traction [15]. $\text{LiI-Al}_2\text{O}_3$ ($\sigma = 10^{-1} \text{ohm}^{-1} \text{cm}^{-1}$ at 300°C) [16], $\text{LiI-(CH}_3)_6\text{N}_2(\text{RI})_2$ where R is H, CH_3 or C_2H_5 (eg. $\text{LiI-dimethyl triethylene diammonium di-iodide}$), $\text{LiI-styrene vinyl pyridine co-polymer double salts}$ [17] are being investigated. The system $\text{LiI-Li}_2\text{O-Al(PO)}_3$ is reported for high energy density (HED) batteries.

Another new class of Li^+ conductors, in which, polyion complexes [complexes of poly (sodium acrylate) as poly-anion salt and polybrene as poly cation salt] dispersed with LiClO_4 having a conductivity of 10^{-3} to $10^{-8} \text{ohm}^{-1} \text{cm}^{-1}$ at $100^\circ\text{-}200^\circ\text{C}$, have been discovered [18]. Among lithium oxo metallates of type Li_nMO_6 (where $n = 6, 7$ or 8 and M is IV, V, VI group element), Li_7TaO_6 is the best with a conductivity of $5 \times 10^{-4} \text{ohm}^{-1} \text{cm}^{-1}$ at 200°C [19].

Choice of electrodes

The choice of proper electrodes, particularly the cathode, plays an important role in the designing of solid state batteries. A general approach is to use a mixture of cation-conducting electrolyte and an electronic conductor like graphite. Iodine in the cathode must be complexed to reduce its activity as elemental iodine degrades the electrolyte. Me_4NI_5 , MeNI_9 , a number of charge transfer complexes [17, 20] have

been studied with some success. Selection of polyamide and RbI cathodes is based on their complexing ability. If the discharge product is an ionic conductor, then the electrode functions with low polarisation.

MnO₂ has offered scope [16,21-26] as cathode with LiI-Al₂O₃ system. Transition metal chalcogenides, MX₂ (M → Tl, Zr, Mo, W and X → S, Se, Te) with Li₉Cl₃N₂ are found to give high decomposition voltages and low electronic transference numbers. Recently Na_{0.1}CrS₂ is found to be a good cathode in Li secondary cells [27].

Intercalated electrodes

The electrode-electrolyte interface plays a limiting role in the cycling behaviour of these cells. Non-uniform contacts result in dendrites. This is overcome by the removal of the electroactive species from the interface during the reaction by using intercalated electrodes. Several classes of non-stoichiometric compounds, especially, the transition metal dichalcogenides in which Li and Na atoms can be inserted have drawn considerable attention. The layer chalcogenides (TiS₂), the 3-D network oxides (V₆O₁₃ and V₂O₅) [28] and layered mixed metal disulphides Cr_nV_{1-n}S₂ as rechargeable electrodes have been investigated.

Ag intercalated electrodes of TiS₂ (Ag_xTiS₂) [29], NbS₂ and TaS₂ have been investigated and NbS₂ offers scope in terms of prolonged cycling process. High energy density has been reported with AgCrSe₂ which is a p-type semiconductor with E_g = 0.5 eV at normal temperature and exhibits ionic conductivity above 473°K [30].

Intercalation of Li⁺ into transition metal chalcogenides [31] results in the formation of phases which are both electronic and ionic. MoO₃, Cr₂O₃ have shown promise as cathodes in secondary organic electrolyte Li batteries. Li can also be inserted in certain lamellar compounds in type M^{II}PX₃ like NiPS₃, FePSe₃ [32] which have large free energy of intercalation without any change in the host lattice parameters. Li intercalation in polyacetylene [33] is also proposed for HED batteries. (CH)_x is the simplest conjugated polymer which gives intercalation compounds either with cations (Li⁺, Na⁺, K⁺) or with anions (ClO₄⁻, PF₆⁻). The polymer solid electrolytes are emerging as a new tool in electrochemistry for precise study of intercalation [33].

Graphite intercalation compounds with AlF₃, MgF₂ or CuF₂ are being studied and C₁₆AsF₅ is found to be highly conducting [34].

The cell,

Li	/	LiBr	/	Br ₂
(−)				(+)
Anode				Cathode

with a theoretical OCV of 3.5 V and 1.25 Wh.cm⁻³ is under development [35].

Rechargeable systems

Japan is marketing a low capacity rechargeable battery
Ag Complex of AgI / Ag₂Se-Ag₃PO₄
 and tungstate

under the name 'memoriode' [35]. This is used for timing and memory devices. Rechargeability of cells based on Ag⁺ conductors is limited by the build up of high resistance at potentials above 0.66 V as well as dendrite growth and poor utilisation of Ag electrode.

Rechargeable cells with Cu⁺ conduction of Rb₄Cu₁₆I₇₋₈Cl₁₃₊₈ and intercalated TiS₂ cathodes gives OCV of 0.59 V and a few tens of μA at room temperature [36] without appreciable polarisation and more than hundred charge-discharge cycles without much deterioration.

Thin film configurations

To avoid problems of low conductivity, another approach is the study of thin film configurations. Thin films of AgI and AgBr are found to give open circuit voltage (OCV) of 0.65 V and 0.36 V. R.F. Sputtered thin films of Li₁₄Zn(GeO₄)₄, LISICON [37], are used for HED batteries. Hybrid films of Li/LiClO₄, polyacrylonitrile, plasticiser/MnO₂ showed a stable e.m.f. of 3 V for 70 hr at a discharge c.d. of 90 μA.cm⁻² [38]. Bet-

ter discharge characteristics are observed with a deposition of a solid solution of a cathode (CdI₂ or HgI₂) and one or more elements selected from In, Ga, Ta, Cu, Ag, S, Se, Te, the electrolyte and anode being Li₃N and Li respectively [39, 40].

Beta-alumina and mixed crystals

Considerable research is being carried out on beta-alumina which finds application in the production of caustic soda-chlorine through molten salt electrolysis, where β-alumina is employed as diaphragm. This has reduced the energy consumption from 3000 kWh/ton to 2350 kWh/ton with equal current efficiencies compared to other methods [41]. Mixed crystals of type Na_{1+x} M_{2-1/3x+y} Si_x Zr_{3-x} O_{12-2/3x+2y} where, M→Zr, Ti or Hf; Z→P, Sb, Bi, V, Nb or Ta and with x = 0.01 to 3 and y = 0 to 0.5 have also been developed [42]. A capacity of 5.77 Ah has been obtained with Na_{3.2} Zr_{1.45} Si_{2.2} P_{0.78} O_{10.89} as electrolyte in Na-S battery.

The compounds Na_{1+x} Zr₂ Si_x P_{3-x} O₁₂ (sodium zirconium phosphosilicate) known as NASICON is found to have a 3-D conductivity unlike β-alumina (which has a 2-D conductivity) and does not hydrate [43]. Sodium β-alumina is used to form a high temperature regenerative concentration cell for elemental sodium. The feasibility of the alkali metal thermoelectric converter (AMTEC) for direct conversion of heat to electricity has been demonstrated. A wide range of aerospace power is possible. Much interest has been shown on ammonium β-alumina, (NH₄)₁₊₄ Al₁₁ O_{17+4/2} because it supports proton mobility and affords a route to materials closer to ideal β-alumina stoichiometry [44].

There is a technological need for high temperature Cu⁺ conductors. Most of the Cu compounds decompose at 500°-600°K. A new class of compounds known as copper chevral compounds, Cu_xMo₆S_{8-y} where y = 0 to 0.4 have been found as potential Cu⁺ conductors [45]. Copper β-alumina possesses high ionic conductivity upto 1600°K. But it is not possible to get it directly from the oxides. This is obtained by electrochemical transfer of Cu⁺ from a fused chloride into sodium β-alumina and is a time consuming process. CuCl is volatile and tends to coat the interior of the cell.

It is now possible to exchange the Na⁺ in NASICON with Li⁺, K⁺ or Ag⁺, and also divalent cations in Li₂O stabilised Naβ⁺-alumina since divalent cations are found to be more mobile in β⁺ structure than in the β-form [46,47]. Sr, Ba and Cd β⁺-alumina show highest conductivity at moderate temperatures. β and β⁺ alumina containing polyatomic cations (eg. NO⁺) are of interest because the intramolecular modes of the cations provide a method of probing the potential energy environment of the conduction planes in the crystals.

ANION CONDUCTORS

F⁻conductors

F⁻ion conductors are most important halide ion conductors for practical applications. β-PbF₂ (σ = 10⁻⁶ ohm⁻¹ cm⁻¹), β-PbSnF₄ (σ = 10⁻² ohm⁻¹ cm⁻¹), NH₄Sn₂F₅ (σ = 10⁻¹ ohm⁻¹ cm⁻¹), La_{1-x} Ba_x F_{3-x}, BaSnF₄ are a few F⁻ conductors having high ionic conductivity [48,49]. A thin film cell, Bi, BiF₃/PbF₂/Pb gives an OCV of 0.4 V and a c.d. of 345 μA.cm⁻²

O²⁻ conductors:

Among the anion conductors, oxygen ion conductors form a major class of compounds due to variety of applications. Materials like Y₂O₃ stabilised ZrO₂ are used for measuring the equilibrium potential of O₂ in minerals and this has become a powerful tool for determining numerous thermochemical data concerning the field of geoscience [50]. Recent applications include electrolysis of steam at high temperature to generate H₂ and as electrocatalyst for various chemical reactions in the gaseous phase like decomposition of nitric oxide, synthesis of methane and oxidation of ammonia to nitric oxide [51]. Another interesting application of oxygen ion conductors is the control of oxygen content in a flowing inert gas. This is known as electrochemical pump which

requires the application of an external voltage across the wall of the solid electrolyte tube through which the gas is allowed to flow. This is used to remove oxygen from liquid metals.

Most of the existing oxygen ion conductors include oxides of quadrivalent cations and crystallise with the fluoride structure [51,52]. Materials with other structures like the perovskite structure are found to exhibit ionic conduction, whose conductivity is enhanced by doping with aliovalent impurities. Doped tantalum pentoxide also exhibits oxygen ion conduction. Doping in some of the oxides like Bi_2O_3 is to stabilise the fluorite phase at room temperature. Due to their high electrolyte polarisation, the oxygen ion conductors are unsuitable for room temperature applications and their ionic conductivities are comparable with RbAg_4I_5 only at 1000°C (eg. ZrO_2 -9m% Y_2O_3).

Another class of oxides, known as mullites, e.g. aluminosilicate of variable compositions, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ to $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ have been investigated [52]. Ionic conductivity in hollandite type phases with different single-charge cations have been investigated [53]. Since mullite is stable from room temperature to its melting point (1830°C) and has good thermal shock resistance with relatively simpler procedures for its preparation coupled with low cost, mullite solid solutions appear to be promising materials for use as oxygen sensors in elevated temperature systems.

Ion conducting poly (ethylene) oxide (PEO) has been used as solid electrolyte. Complexes between PEO and various alkali metal salts have been developed as 'Solid Polymer Electrolytes' high energy density battery systems [54]. Polymeric electrolytes based on complexes of PEO with Li salts (e.g. $\text{PEO}_{4.5}\text{LiCF}_3\text{SO}_3$ and PEO LiClO_4) have been investigated [55].

Other systems

Crystals with fluorite structure have attracted much attention because of high ionic conductivity at elevated temperatures. Attention has been devoted to CaF_2 , SrF_2 , BaF_2 and $\beta\text{-PbF}_2$. Nitrates of Sr, Ba, and Pb having similar structure have recently been investigated and transport is attributed mainly to the anion Frenkel defects [56].

Though iodine is insulator, when doped with H1, it exhibits proton conductivity [57]. Some sintered oxides based on SrCeO_3 (eg. $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-x}$ where x is the number of O_2 deficiencies per perovskite type oxide unit cell) hydrated antimonite oxide, hydrated α -zirconium hydrogen phosphate exhibit protonic conductivity [58], especially the first class of compounds in H_2 atmosphere, [59]. These are being used for high temperature steam electrolysis and fuel cells. Using such proton conductors for gas cells [60], much information on electrode reactions or thermal equilibrium in H_2 containing gases has been obtained.

Another family of $\text{M}_5\text{RE Si}_4\text{O}_{12}$ where M is Ag, Na and RE is rare earths Sm to Lu, Y and Sc have been found to have high ionic conductivity. These are characterised by the dependence of ionic conductivity and activation energy on the kind of RE ion and the first ionisation potential of rare earths on the radius of RE [61].

Acknowledgement: The authors express their sincere thanks to Prof Dr K I Vasu, Director, Central Electrochemical Research Institute, Karaikudi, for his kind encouragement and permission to publish this paper.

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