

CHAPTER 16

Solid Electrolytic Materials

16.1 Introduction

Also known as *superionic conductors*, *solid electrolytes* are ionic materials which exhibit high electrical conductivity (in comparison with liquid electrolytes) above a certain critical temperature. They are also termed as *fast-ion conductors*. A solid electrolyte has the following characteristics:

- It is crystalline with ionic bonding.
- Its electrical conductivity (over a specified temperature) is high ($10\text{-}10^{-2}$ siemen/meter).
- Its principal charge carriers are ions. Hence, the fractional contribution of the ionic conductivity to the total conductivity (termed as *ionic transference number*) is almost equal to one.
- Its electronic conductivity is small. The corresponding *electronic transference number* is less than 10^{-4} .

Examples of typical superionic conductors and their temperature *versus* electrical conductivities are presented in Figure 16.1.

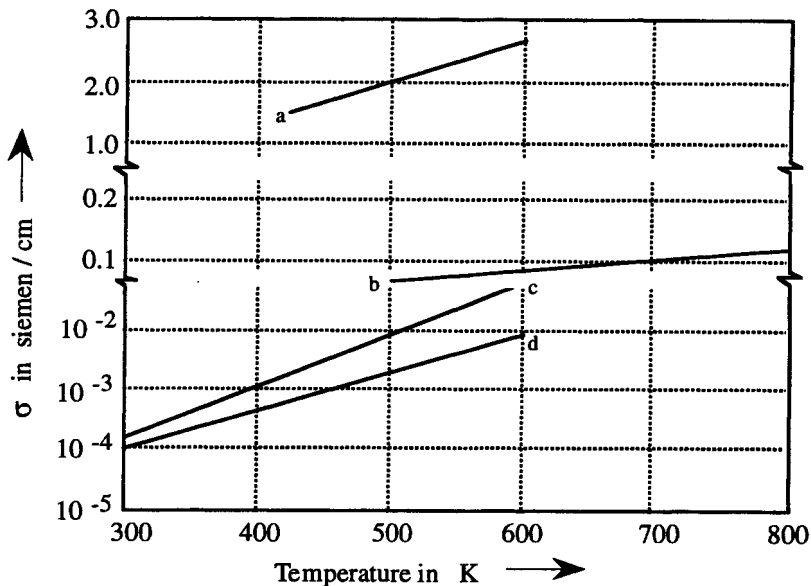


Figure 16.1 Electrical conductivity *versus* temperature of typical solid electrolytes: (a) β -AgI; (b) $\text{LiZr}_2(\text{PO}_4)$; (c) Li_3N ; and (d) $\text{Li}_3\text{B}_7\text{O}_{12}\text{S}$.

16.2 β -Phase to α -Phase Transition

Superionic materials exhibit high electrical conductivity above a certain critical temperature. This temperature is well defined in some cases and in some other materials the transitions are not abrupt (Figure 16.1). The temperature-dependent increase in the electrical conductivity is known as the *β -phase to α -phase transition*.

16.3 Structure of Fast-Ion Crystals

The ionic crystalline materials which permit fast-ion transport in general may have:

- Disordered structures
- Channeled structures
- Layered structures

The crystalline structure determines the dominance of electronic or ionic conduction. It is directly related to the *band-gap energy* of the materials. For solid electrolytes, the electronic band-gap energy is always in excess of $(T/300)$ eV (*Heyne's condition*) where T is the temperature in Kelvin. This is only a necessary condition, but need not be sufficient. The high conductivity of solid electrolytes is attributed to ion-ion interactions. Further, defects and disorders are eventually needed in the crystalline structure to sustain a significant ionic transport.

16.4 Types of Defects and Disorders in Solid Electrolytes

Essentially, there are two possible *crystalline defects* pertinent to solid electrolytes. They are:

- Point defects
- Molten sublattice defects

Point defects allow ionic transport through *Frankel (or Schottky) defect pairs*, induced thermally. Hence, the number of defects and the proportionate charge carriers are functions of temperature with the *activation energy* in excess of 1 eV. Examples of solid electrolytes with point defects are:

- Solid electrolytes with dilute defect density: AgCl, B-AgI, NaCl, KCl, etc.
- Solid electrolytes with concentrated defect density: Stabilized zirconia, (*hafia*), CaF₂, etc.

Molten sublattice defects correspond to insufficient sites in the sublattice region for the available ions to occupy them. This results in *ionic hopping on free-ion movement* from one available site to the other. This process allows all the ions to participate in the conduction phenomenon with the result the activation energy is rather low. In view of the fact that the defect infestation and the conduction of ions are decided by a statistical average, the solid electrolytes are termed as *average structures* rather than as *rigid structures*.

16.5 Free-Ion-Like Theory

The movement of ions seeking the defects has been modeled as free-ionic motion. Accordingly, fast-ion conductors are classified into three categories:

- Type I: Ionic solids with mobile defects of low concentration ($\approx 10^{18}/\text{cm}^3$). These are the same as dilute point-defect versions indicated before.
- Type II: Conglomerated high-density defects extending over the substructure at microscopic dimensions. The corresponding defect concentration is on the order of $10^{20}/\text{cm}^3$. These solids are known as *concentrated point-defect versions*.
- Type III: This refers to the participation of all the ions in the conduction process. The mobile ions as charge carriers amount to nearly $10^{23}/\text{cm}^3$. The material is *liquid-like molten sublattice* often realized *via* channeled or layered structures.

In practice, Types II and III are commonly useful as fast-ion conductors.

16.6 Ionic Bonding

In some materials, the atoms are bound such that the transference of electrons from one atom to another is feasible and renders the atoms as ions. These ions have closed-shell electronic structure as illustrated in Figure 16.2. The formation of the pair of ions or the *ionic bond* is sustained due to the binding coulombic force of attraction between the *anion* (the atom that accessed extra electrons) and the *cation* (the atom that lost electrons becoming positively charged).

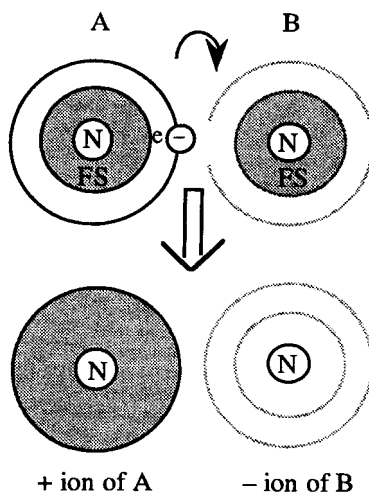


Figure 16.2 Ionic bond formation between two atoms (A and B).

N: Nucleus. FS: Filled shells. e: Electrons.

Atom A: Almost unfilled outershell with loosely bound one electron.

Atom B: Almost totally filled outershell with one deficiency to accommodate an electron.

16.7 Ionic Conductivity Based Classification of Solid Electrolytes

Both cations and anions participate in the electric conduction process in a solid lattice. However, the extent of mobility of these ions could be quite different. Alkali metal ions contribute a high conductivity in solid phase, as first observed in sodium β -alumina. Since then different alkali ion compositions have been synthesized and evaluated as superionic conductors. Typically, a large number of lithium ion conductors have emerged as such superionic materials. This is mainly due to the small ionic radii of Li_i^+ offering greater carrier mobility. A few examples of good lithium ionic conductors are lithium β -alumina, LiI doped with CaF_2 or Al_2O_3 , LiAlCl_4 , $\text{Li}_4\text{B}_7\text{O}_{12}$, $\text{Li}_4\text{SiO}_4 + 43 \text{ mol\% Li}_3\text{PO}_4$, $\text{Li}_{0.80}\text{Zr}_{11.80}\text{Ta}_{0.20}(\text{PO}_4)_3$, $\text{LiHF}_2(\text{PO}_4)_3$, and lithium-enriched Li_3N .

Structurally such compounds possess a high degree of disorder or channelled arrangement constituting Type III superionic conductors.

Further, the lithium compounds exhibiting superionic conduction contain tetrahedral anions like SO_4 , SiO_4 , PO_4 , GeO_4 , AlO_4 , ZnO_4 , TiO_4 , and GaO_4 .

Apart from lithium-based monophase compounds, binary solid solutions of LiSO_4 also show high conductivity. Examples are $(\text{LiSO}_4 + \text{M}_2^{\text{mo}}\text{SO}_4)$ and $(\text{LiSO}_4 + \text{M}^{\text{di}}\text{SO}_4)$ where M_2^{mo} are monovalent atoms like Na, K, Rb, Cs, Ag, and M^{di} are divalent atoms like Be, Mg, Zn, Mn, Cd, Ca, and Sr.

Ternary solid solutions of LiSO_4 which are superionic are: $(\text{Li}_2\text{SO}_4 + \text{ZnSO}_4 + \text{Na}_2\text{SO}_4)$ and $(\text{Li}_2\text{SO}_4 + \text{Ag}_2\text{SO}_4 + \text{AgI})$.

Other compounds which are of interest as solid electrolytes are:

- Lithium orthosilicate (Li_4SiO_4) (polyhedra structure)
- Li_4SiO_4 with partial substitution of Si with Ge, P, Ti
- Li_4SiO_4 with partial substitution of Li with Zn and Al
- (Li_4SiO_4) modified by substituting SiO_4 with PO_4 , GeO_4
- $\text{LiZr}_2(\text{PO}_4)_3$, $\text{LiHf}_2(\text{PO}_4)_3$, $\text{LiZr}_2(\text{PO}_4)_3$ (Distorted rhombohedral symmetry)
- Li_5AlO_4 , Li_3GaO_4 , Li_6ZnO_4 , Li_2S , Li_2O , Li_3AlN_2 , $\text{Li}_{8+4x}\text{Sn}_{1-x}\text{P}_4$ anion polyhedra structure)
- Lithium nitride (Li_3N)
- Boracites of lithium ($\text{Li}_4\text{B}_7\text{O}_{12}\text{X}$, X: Cl, Br, S)
- Sodium and potassium based compounds:
 NaTaWO_6 , $\text{NaTa}_2\text{O}_5\text{F}$, NaSbO_3 , $2\text{M}_2\text{O} \cdot 3\text{Nb}_2\text{O}_5$ (M: Na, K)
 $\text{K}_{0.72}\text{L}_{0.72}\text{M}_{0.28}\text{O}_2$ (L: Se, In, M: Hf, Zr, Sn)
 $\text{Na}_{0.5}\text{In}_{0.5}\text{Zr}_{0.5}\text{S}_2$
 $\text{Na}_{0.8}\text{Zr}_{0.2}\text{S}_2$
- β -alumina-type gallates

16.8 β -Alumina

This represents a class of materials having structures similar to the following composition: $\text{M}_2\text{O} \cdot x\text{Al}_2\text{O}_3$ (M: Na, K, Rb, NH_4 , Tl, Ag and $x = 5$ to 11). Aluminum could also be replaced by Fe or Ga. Also, Al_2O_3 could be substituted with $\text{Al}(\text{OH})_3$, NaAlO_2 , or $\text{Al}(\text{NO}_3)_3$ in the sodium β -alumina ($\text{Na}_2\text{O} \cdot x\text{Al}_2\text{O}_3$). Again, the Na_2O radical can also be substituted with sodium nitrate, oxalate, carbonate or hydroxide.

16.9 Silver-Ion Conductors

The following silver-ion compounds are also usable as solid electrolytes:

- Ag_2S , Ag_2Se , Ag_2Te
- AgI
- Solid solution of AgI : $\text{MI} + 4\text{AgI}$ (M: K, Rb, NH_4)
- MAg_4I_5

16.10 Copper-Ion Conductors

Cu^+ superionic conductors commonly used are: CuI , KCu_4I_5 , $\text{RbCu}_x\text{Ag}_{4-x}\text{I}_5$, CuRbClI , Cu_2S , and Cu_2Se .

16.11 Oxygen-Ion Conductors

ZrO_2 , HfO_2 or CeO_2 forming various solid solutions with other oxides of Ca, Sr, Nd, Sm, Eu, Gd, Dy, Ho, Yb, or Tb.

16.12 Halide-Ion Conductors

- MF_2 (M: Pb, Ca, Ba, Sx)
- MF_3 (M: La, Y, Lu, Ce)
- $\text{La}_x\text{Sr}_y\text{F}_z$, $\text{Ca}_x\text{Y}_y\text{F}_z$
- $(\text{CeF}_3)_x(\text{MF})_y$, (M: Ca, Sr, Ba, Th)
- $\text{Pb}_{1-x}\text{Bi}_2\text{F}_{2+x}$

- MBiF_4 (M: K, Rb, Ti)
- BiO_xF_y
- BaCl_2
- SrBr

16.13 Activation Energy of Superionic Compounds

Ionic movement in a crystal refers, in general, to (1) normal ions into an adjacent interstitial site; (2) interstitial site into an empty normal site; (3) normal ions into adjacent empty normal sites; and (4) interstitial ions into adjacent empty interstitial sites. Accordingly, the free energy required for the transfer of an ion into an interstitial site and the free energy of activation for the mobility out of an interstitial site govern the fast and high ionic conduction. Both these free-energies should be low for such a conduction.

In addition to ionic conduction mode solid electrolytes, there are also fast-ion conductors based on *proton conduction* and *electronic conduction* with ionic transport.

16.14 Engineering Applications of Solid Electrolytes

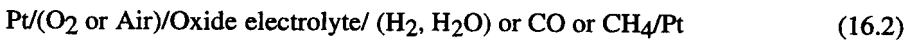
Fuel-cells: *Fuel-cells* refer to devices in which the embedded electrochemical species are constantly consumed and a continuous electrical energy is made available as the output. The type of solid electrolytes that the fuel cells use are oxide electrolytes.

The solid electrolyte is interposed between a gaseous phase (oxygen) on either side. Depending on the pressure difference of the oxygen in the sides (or the concentration gradient of the oxygen), the O_2^- ions will flow through the solid electrolyte generating an electromotive force given by:

$$V = [RT/|Z|F] \ln(P_2/P_1) \quad (\text{Gibbs-Duhem relation}) \quad (16.1)$$

where, P_1 and P_2 are the gas pressures, F is the *Faraday constant*, $|Z|$ is the absolute value of the valency, R is the gas constant, and T is the temperature.

This type of a cell is known as the *concentration cell*. Typically, the material dispositions in a fuel-cell arrangement are as follows:



The transported oxygen across the electrolyte is consumed continuously by burning it with a combustible fuel such as H_2 , CO or CH_4 . Thus, a continuous electromotive force (EMF) is generated.

Use of manganese-doped covalent cobalt chromite, nickel or cobalt-zirconia cermets as the solid electrolyte in fuel cells has also been recommended. Thin film fuel cell structures with stabilized zirconia electrolyte have been developed. Limitations of solid electrolyte-based fuel cells (as compared to molten salt fuel cells) are: (1) Higher temperature operation; (2) lower power delivery; and (3) use of expensive electrodes such as platinum. However, use of solid electrolyte fuel cells in conjunction with fluidized bed coal reactors have a promising future.

Solid-state batteries: Conventional batteries such as Volta or Leclanche cells use aqueous electrolytes. They have limited performance at excessive or high temperatures and limited shelf-life. They are also bulky and less rugged.

Substitution of aqueous electrolytes with solid electrolytes has led to *solid-state batteries*. Electrochemical EMF develops in a solid-state battery across a pair of electrodes between which a solid electrolyte is sandwiched and if a continuous flow of charge is

maintained through the electrolyte, it would constitute an electrical current between the electrodes externally. For example, the cell $M/MX/X$ can be used as an electrochemical cell with M ions moving across the electrolyte with the following set of reactions.



Corresponding EMF developed is given by:

$$V = \Delta G / (|Z_x|F) \quad (16.4)$$

where ΔG is the *Gibbs free energy* involved in the reaction, $|Z_x|$ is the valency of the moving ion and ΔG depends on temperature. It should be negative and large for a conceivable EMF; and the ionic conductivity due to the ions participating in the electrochemical reaction must be high in the electrolyte to obtain a low internal cell resistance and a high current delivery.

Further, electronic conductivity must be negligible lest internal battery "short circuit" may prevail, reducing the shelf-life of the battery. Electrode-electrolyte combination, must be physically and chemically compatible in terms of interfacial effects, interdiffusion, pitting, dendritic growth, etc. Typical electrode-electrolyte assemblies for solid-state batteries and their characteristics are presented in Table 16.1.

Coulometer: A solid-electrolyte coulometer is useful in estimating the electric charge and in RC time-constant networks (known as electrochemic timers marketed by Sanyo, Japan and Gould Ionics, USA).

Constructionwise, a coulometer has a solid electrolyte sandwiched between two electrodes. One electrode is made of the same material as the mobile ion species of the solid electrolyte. The other electrode is nonreactive (or insoluble to the mobile ion). For example, referring to Figure 16.3, the electrolyte is a silver ion conductor such as AgBr or RbAg_4I_5 . One of the electrodes is, therefore, made of silver and the other electrode is either gold or graphite.

When the device is charged across the terminals on the electrodes (of gold or graphite being at a negative or lower potential), the mobile silver ions flowing through the electrolyte accumulate at the gold (or graphite) electrode. When the device is discharged, these accumulated silver ions flow back to the silver electrode. As long as the silver is present on the gold (or graphite) electrode, the voltage across the device is a simple ohmic drop between the silver-to-silver couple. As the accumulated silver ions on the gold (or graphite) electrode deplete, the voltage across the device surges suddenly to an open-circuit voltage. The step or impulsive change of the voltage across the device can be used as a trigger in timing circuits. The Gould Ionics (USA) product is termed as the Coulister TimerTM. A typical structure of the device is illustrated in Figure 16.3.

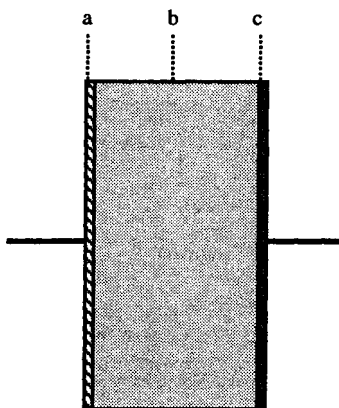


Figure 16.3 A typical solid-electrolyte-based coulometer.
(a) Silver film; (b) Solid electrolyte such as RbAg_4I_5 ; (c) Gold or graphite film.

Electrochemical capacitor: The commonly used liquid/gel-based electrolytic capacitors have limited operating temperature range ($0\text{--}100^\circ\text{C}$). They have also limited shelf-life due to the possibility of ionic leakage-current arising from aging and drying of the electrolyte. Further, to prevent electrolyte oozing, hermetical sealing is required which hampers any miniaturization feasibilities. These capacitors require the formation of nonconduction anodic film to function as a capacitor.

Solid-electrolyte-based capacitors have *double-layer capacity* at the ionic-solid-inert-metal electrode interface and could offer capacitance in the range $10\text{--}10^3$ microfarad/cm². Referring to Figure 16.4, the capacitor arrangement has a solid electrolyte with M^+ mobile ions, a reversible electrode of metal M and a polarization electrode of metal M' to which a negative voltage is applied. For example, if the electrolyte is AgBr in which Ag^+ interstitials and vacancies are mobile, the electrode M is Ag while M' could be platinum or graphite.

With the negative voltage applied to M' , the defect concentration near the electrode surfaces is illustrated in Figure 16.4. The concentration of positive interstitials, n_i increases towards the electrode while the vacancies (effective negative charges) decrease as per Poisson-Boltzmann distribution of charges in an electric field. This gives rise to a *diffuse space-charge layer* and a *diffuse layer capacity*. The resultant capacitance is decided by the series combination of two capacitors termed as the diffuse-layer capacitor (C_d) and an inner-layer capacitor (C_i). C_d is decided by the Faraday electrolytic chemistry and is a function of temperature. C_i is essentially a parallel-plate capacitance given by $\epsilon_0\epsilon_r/d_c$, where ϵ_0 is the absolute permittivity of free space, ϵ_r is the dielectric constant of the electrolyte, and d_c is a close separation from M' electrode as decided by the finite size of the ions. Effectively, the total capacitance $C = (C_i + C_d)$ depends on mobile ion or defect concentration. Existing developments largely refer to capacitors with Pt/AgBr , Pt/AgI , C/AgI , and $\text{Pt}/\text{RbAg}_4\text{I}_5$ electrode-electrolyte combinations.

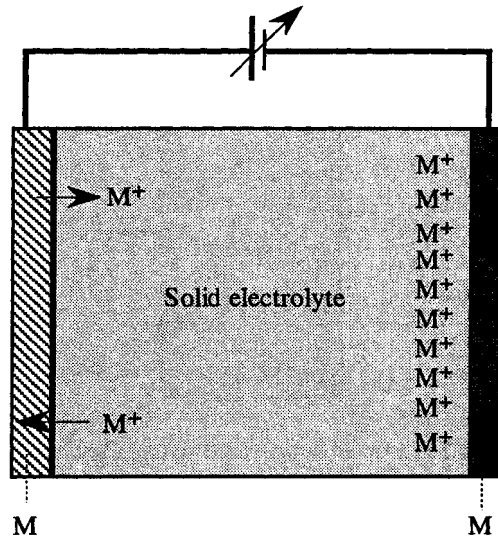


Figure 16.4 Solid-electrolyte-based capacitor. M: Reversible ion electrode (positive); M': Polarized metallic electrode (negative).

Solid-electrolyte electrochromic devices: *Electrochromic devices* are based on materials in which a color change is induced due to an applied electric field or current (see Chapter 18). The mechanisms considered as responsible for the electrochromic effects are:

- Creation of color centers to electron trapping induced by the electric field
- Electric field induced charge transference to an impurity center causing a growth of absorption band at that center
- Shift in absorption band (and hence color) due to tunneling process induced by the applied electric field (*Franz-Keldysh effect*)
- Electrochemical redox reactions in which ions or molecules can be reduced or oxidized (redox) electrochemically with a change in color

Solid-electrolyte-based electronic devices have, for example, the following cell geometry (Figure 16.5):



with WO_3 as the cathode. With the application of a potential (less than about 1 volt) across the cell, a blue coloration appears on the $RbAg_4I_5$ film. Upon voltage reversal, the coloration disappears. Other possible cell geometries are structured as follows:



The observed blue coloration is due to the formation of tungsten bronze A_xWO_3 , (A: H^+ , Li^+ , Ag^+ , etc.).

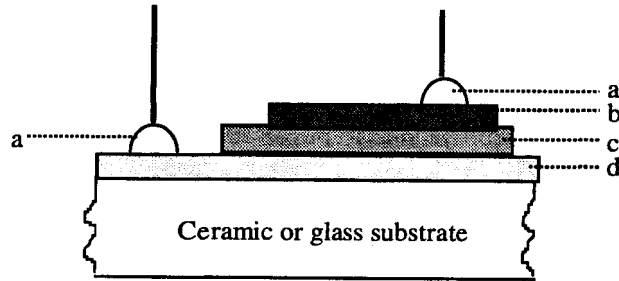


Figure 16.5 Construction of an electrochromic cell. (a) Silver-dag contact material. (b) RbAg_4I_5 . (c) WO_3 . (d) Transparent tin oxide electrode.

Oxygen sensor (Concentration Type): An oxide electrolyte (for example, calcium stabilized zirconia, CSZ) with oxygen on both sides with a pressure difference would allow oxygen ions to flow through the electrolyte developing a potential across it.



The potential difference so developed is a direct measure of the pressure difference ($p_2 - p_1$) of the oxygen. In other words, the cell voltage could implicitly measure the oxygen content on one side if the other side is kept at a standard oxygen pressure. Measurement of oxygen content is feasible down to 10^{-7} atm in oxygen containing inert gases, down to 10^{-15} atm in pure O_2 , and down to 10^{-25} atm in reducing atmospheres like CO/O_2 , CO/CO_2 , $\text{H}_2/\text{H}_2\text{O}$, etc. For oxygen ion mobility across the CSZ cell, the electrolyte warrants a temperature of operation as 1000°C . Lower temperature (700°C) measurements for oxygen pressures on the order of 10^{-10} atm is feasible with $\text{Cu}-\text{Cu}_2\text{O}$ cells. Variations of oxygen measurement cells include oxygen or sulfur sensors and are known as *formation-type cells*.

In concentration, cells with the electrolyte replaced by those carrying other types of mobile ions are useful as sensors for other ionic species. For example, using a sodium-ion conductor (sodium β -alumina), the relevant cell can be used for measuring sodium content in sodium-mercury amalgam.

Solid-electrolyte thermometer: This in principle, is similar to CSZ concentration cell ($\text{Pt} \mid \text{O}_2 \text{ at } p_1 \mid \text{CSZ} \mid \text{O}_2 \text{ at } p_2 \mid \text{Pt}$). The corresponding EMF developed across the cell is: $V = (RT/4F) \ln(p_1/p_2)$. Hence, the measurement of V directly yields the system temperature. This thermometer is useful for temperatures higher than 1000°C at which gas thermometers are limited due to lack of compatible materials. With modifications, such thermometers could also be deployed for the measurement of thermal gradients.

16.15 Solid-Electrolyte-Based Thermoelectric Generation

A solid electrolyte develops an EMF when its two faces are either at different temperatures or at different pressures due to the electrochemical activity of mobile ionic species in the conductor. In principle, this refers to *thermoelectric power generation*.

16.16 Solid-Electrolyte-Based Active Electromagnetic Surfaces

Controllable electromagnetic absorption and/or reflection by materials are of importance in the development of radar absorbing surfaces and in certain EMI/EMC problems [4,5]. Conventionally, microwave materials composed of a combination of metallic and/or nonmetallic (dielectric) absorbing constituents are used for this purpose (see Chapter 22). For discrete-tuned frequency applications magnetically and dielectrically lossy materials could be

blended to obtain moderate performance on absorption/reflection characteristics. The base materials for such applications include: Graphite/iron/aluminum particles (spherical/fibrous/flaky) dispersed in a host medium such as natural rubber-latex, polyisoprene, neoprene, silicone, urethane, etc. However, for better absorption the frequency-tuning is done by the principle of quarter-wave window(s) *via* multiple layers of lossy dielectrics.

An alternative approach suggested by Meyer et al. [7] consists of distributing a large number of magnetic dipoles on a conducting surface to achieve pronounced reflection/absorption characteristics depending on the orientation and distribution of the dipoles. A successful application of **this** principle has been reported by Chatterjee et al. [8]. Typically, a reflectivity reduction on the order of -20 to -30 dB could be accomplished at selective resonance frequencies by these passive surfaces. Uses of such single-frequency tuned-absorbers include narrowband RCS reduction, minimizing unwanted reflections inside aircraft romes and reducing reflections from shipborne structures, etc.

Modified versions known as graded absorbers designed for broadband applications have been developed for the purpose of broadband RCS reduction, EMI shielding, sidelobe absorption in antennas, and test screens used to prevent personnel radiation hazards in high power radar range applications.

The aforesaid materials are, in general, known as *passive absorbers* and are detailed in Chapter 22. In contrast, recently a class of electromagnetic materials/surfaces have been studied which can be manipulated electrically/electronically to alter their reflection characteristics, scattering pattern and frequency selectiveness. Such materials are known as active media with the surface made "actively" sensitive to incident microwaves. The design principle of such surfaces is the logical extension of smearing the surface with the dipoles (as described by Meyer et al. [7] and Chatterjee et al. [8]) except that the included dipoles at the resonant structures should be made electronically "active" or "tunable" so as to yield desired reflection/absorption characteristics.

The use of pyrosensitive solid electrolytes (such as AgI) has been suggested by the author [4] as active elements at the nodes of synaptic arrangement. On thermally energizing these nodes, the solid-electrolyte material would exhibit superionic electric conduction at elevated temperature(s). With the result the surface (at the nodal points) which is dielectric at cold conditions becomes conducting at hot conditions. Thus, the microwave reflection at this test surface can be effectively altered by the electrothermal synergism. The heating of the nodes can be performed by conductive line segments of heating elements joined (synapsed) at the nodes where the solid electrolytes are planted.

To demonstrate the feasibility of realizing an active surface of the type under discussion, a test surface shown in Figure 16.6 has been developed and tested by the author as reported in [4]. It consists of a heat-resistant dielectric such as ceramic plate with two-dimensional array of holes made to accommodate the pellets of a solid electrolyte. There are a number of solid electrolytes which exhibit high electric conductivity (on the order of 10^{-1} to 10^{-4} siemen/cm) at characteristic temperatures. For example, RbAg_4I_5 has a high conductivity (0.27 siemen/cm) even at room temperature; other materials like β -alumina and β -AgI show increasing conductivity with increasing temperature. The compound β -AgI exhibits superionic conductivity with an abrupt transition at a temperature close to 147°C . This transition as mentioned earlier is known as the β - to α -phase transition.

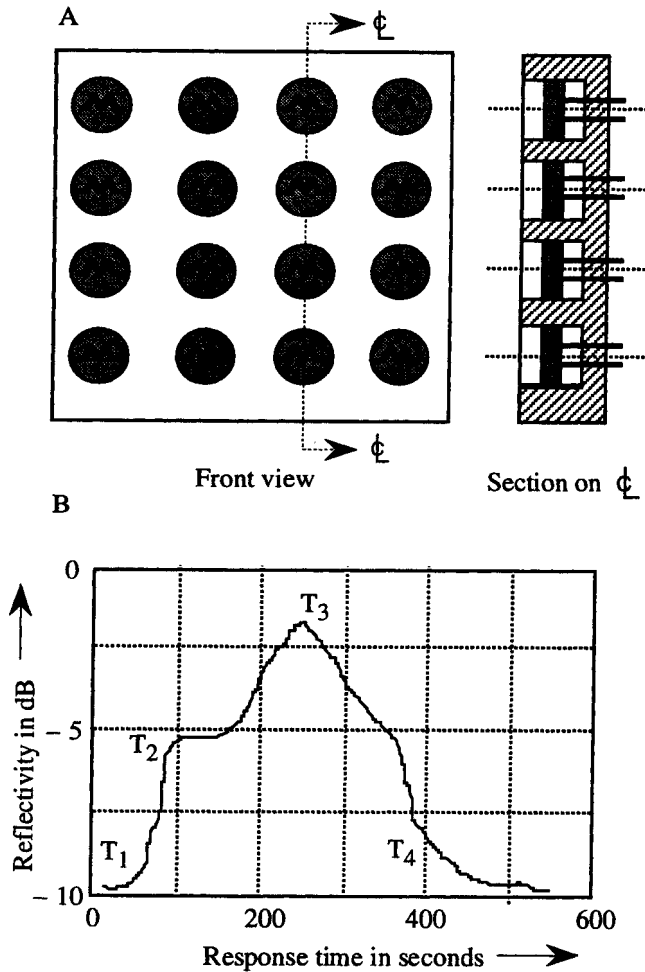


Figure 16.6 (A) An active electromagnetic reflective surface constituted by pellets of AgI embedded in a passive substrate. (B) Reflectivity response of the active surface.

(a) Heat resistant substrate. (b) AgI pellet. (c) Nichrome filament.

$T_1 = 45^\circ\text{C}$; $T_2 = 150^\circ\text{C}$; $T_3 = 180^\circ\text{C}$, and $T_4 = 80^\circ\text{C}$.

(Dimensional details of a typical active test surface is given in [4].)

In the construction of the active test surface of Figure 16.6, the silver iodide (AgI) powder was pelleted as tables and used in the nodes of the ceramic plate. These nodal points were connected by constantan wire on the rear side of the ceramic plate. By properly energizing the matrix of heating elements from a direct current source, the solid-electrolyte pellets in the two-dimensional array could be chosen for heating selectively.

Upon energization those pellets which receive the heat energy would switch to α -phase posing thereby a high conductivity zone. Microwave energy falling on these zones would therefore suffer intense reflection. Hence, with the proper choice of nodes selected for heating, the reflection/transmission pattern of the overall surface can be controlled and configured as desired.

16.17 Kondo Insulators

A class of materials which can be regarded as the duals of solid electrolytes refers to *Kondo insulators* [9]. They exhibit Kondo lattice behavior near room temperature, but step

into semiconducting properties with very small energy gaps as the temperature is lowered. In other words, such materials exhibit higher conductivity at low temperatures and become insulators at higher temperatures.

Certain metallic rare-earth and actinide compounds exhibit Kondo insulation characteristics. Specifically, cerium compounds such as $\text{Ce}_3\text{D}_{14}\text{Pt}_4$ have a resistance rising some two orders of magnitude on cooling from 300 to 4 K.

16.18 Conclusions

Fast-ion conductors have creditable performance characteristics which set them at the brink of massive industrial application potentials in the near future. Their applications involve their use mostly in bulk form. This offers their usability with large power handling capabilities.

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Defining Terms

Active electromagnetic surfaces: The surface which exhibits electromagnetic absorption or reflection of electromagnetic waves controllable by an external application of voltage or current.

Coulometer: A device to estimate electric charge in RC-type networks.

Electrochemical capacitor: A capacitor with an electrochemical material as the dielectric medium between the electrodes.

Electrochromic device: A device exhibiting a color change due to an applied electric field or current.

Electronic conduction: Electrical conductivity dictated by the flow of electrons.

Fuel cells: Devices which consume embedded electrochemical species and deliver electrical energy.

Fast-ionic conductor: Same as solid electrolyte.

Ionic bonding: The bonding between the atoms which permits transfer of electrons from one atom to the other, rendering the atoms as ions.

Ionic conduction: Electrical conductivity dictated by the flow of electrons *via* ionic hopping or free ion movement .

Ionic transport: Transport of ions in solid electrolytes constituting ionic conduction process. (Note: An interesting theory on ionic transport in solid electrolytes has been portrayed by Rice and Roth [10], a summary of which is presented in Appendix 16A.)

Table 16.1 Details on Typical Solid-Electrolyte-Based Batteries [1]

Materials*	Solid Electrolyte	Cathode Materials	Electrochemical Reaction	Approximate Open cell Voltage (V)	Current Density per cm ²	Approximate Energy Density	Remarks
							(W h kg ⁻¹)
							Theoretical
							Practical
(1) Silver or (Ag-Hg amalgam)	AgI-based solid electrolytes	(a) I ₂ solid, RbI ₃ , (C ₄ H ₉) ₄ NI-I ₂ complex + C (b) Ag ₂ Te-Te, C (c) Ag-Se-Se, C	Ag + 1/2I ₂ → AgI 2Ag + Te → Ag ₂ Te 2Ag + Se → Ag ₂ Se	0.69 0.22 0.27	~ 1mA ~ 1mA ~ 1mA	49 29 -	1-10 - - A(R) B(M) V(L) C(H) R(L)
(2) Lithium	LiI (pure & doped)	(a) I ₂ , C (b) AgI, Ag (c) CuI, Cu (d) PbI ₂ , Pb	Li + 1/2I ₂ → LiI Li + AgI → Li + Ag Li + CuI → LiI + Cu 2Li + PbI ₂ → 2LiI + Pb	3.0 2.11 2.08 1.9	~ 10 μA ~ 10 μA ~ 10 μA ~ 10 μA	- 560 -	A(R) B(VL) V(H) A(H)
	Lithium β-alumina or molten eutectics like LiCl-KCl	Molten sulfur impregnated graphite or (polysulfides)	2Li + xS → LiI ₂ S _x	2.3	~ 1 A	1400	B(H) R(R)
(3) Sodium	Sodium β-alumina	Sulfur-impregnated graphite or polysulfides C ₈ CrO ₃	2Na + xS → Na ₂ S _x	2.0 3.5	~ 1 A ~ 1 A	760 1100	A(H) B(H) R(R)

* Mobile cation type.

A(R): Room temperature operation; A(H): High temperature operation (~ 300 °C); B(M): Moderate current drain; B(L): Low current drain; B(VL): Very low current drain; B(H): High current drain; V(L): Low voltage; V(H): High voltage; C(H): High cost; R(L): Limited rechargeability; R(R): Rechargeable.

Appendix 16A: Theory of Ion Transport in Solid Electrolytes [10]

Ionic solids exhibiting exceptionally high levels of ionic conductivity are found among the cation disordered ionic compounds of the silver halide-chalcogenide type, the various substituted beta aluminas, and certain defect-stabilized ceramic oxides. A theoretical model for ionic transport phenomena in such "super" ionic conductors can be based on the hypothesis that there exists in the ionic conductor an energy gap E_o above which ions of mass M , belonging to the conducting species, can be thermally excited from localized ionic states to free-ion like states in which an ion propagates throughout the solid with a velocity v_m and energy $E_m = 1/2Mv_m^2$. On account of the interaction with the rest of the solid such an excited free-ion like state is supposed to have a finite life-time τ_m . On the basis of a postulated Boltzmann transport equation for the thermal occupations of the various free-ion like states, simple expressions can be derived for the ionic conductivity σ , thermal conductivity K_I , and thermoelectric power Q . The theoretical result for Q is well substantiated in [10] by available experimental data. The result for σ may be used to deduce empirical values for the characteristic "mean-free path", $\ell_o = v_o\tau_o$, of the free-ion like state excited at the gap entry E_o . The characteristic life-time τ_o could be deduced in principal from measurements of the frequency dependent ionic conductivity $\sigma(\omega)$ which, according to the model of [10], should be of the Drude type.