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5.1 Introduction

In view of rapid development in computer communication, transport sectors, a pressing demand has recently been felt globally for efficient and reliable power sources. After the energy crisis of early 1970s and then later due to possible threat to exhaust the available conventional energy sources viz., petroleum, coal etc., tremendous efforts has been made to look for new, economical and pollution-free non-conventional sources of power to cope with the energy requirements. Among the various non-conventional energy sources such as solar, fossil, tidal, wind etc., power sources based on solid state electrochemical batteries show great promises to fulfil the demands of various sectors. The power generation in the solid state electrochemical devices is akin to those of conventional liquid/aqueous electrolyte batteries. ‘Superionic Solids’ or ‘Fast Ion Conductors’ are used as solid electrolytes with appropriate cathode and anode electrodes. Many of the major discrepancies of liquid/aqueous electrolyte batteries viz.,

- limited temperature range of operation;
- device failure due to electrode corrosion by electrolyte solution;
- bulky in size;
- less rugged etc.

could be easily overcome in the solid state devices. Moreover, miniaturization of solid state power sources has become a reality. In fact, several miniaturized solid state devices such as heart pace-makers, mini/micro-batteries etc. are already available commercially. In addition to this, a large numbers of batteries have been developed for vehicular traction as well as electrical transport. The efficiency and reliability of the solid state battery systems depends on the appropriate choice of the battery constituents viz., electrolyte, cathode, anode. The characteristic properties of these constituents are discussed below. Considerable attempts have been made in the past and are still ‘on’, to develop solid state batteries using various kinds of fast ion conducting solids described in Chapter 1. Several excellent review articles and papers have already been published on solid state batteries using fast ion conductors [Chandra and Agrawal 1980; Sequeira and Hooper 1985; Munshi and Owens 1989; Megahed and Scrosati 1995; Agrawal 1999]. The present study mainly aimed at to fabricate solid state batteries using the two new fast Ag⁺ ion conducting 2-phase composite electrolyte systems, reported in Chapters 3 & 4 and to study their
discharge behaviour/cell performance at the laboratory scale. In the section below results of various experimental studies on solid state batteries fabricated with these two new fast Ag⁺ ion conducting composite electrolytes have been discussed. Prior to this a general discussion on solid state battery fabrication, principle of emf generation and the characteristic requirements of the battery constituents have been given along with a brief overview on the fast silver ion conducting battery reported in the past.

5.2 Solid State Battery : Fabrication and Principle of EMF Generation

As mentioned, the solid state batteries are fabricated akin to liquid/aqueous electrolyte batteries. The solid electrolyte is sandwiched between appropriate anode and cathode material. The electrode materials can either be a solid (S) or a liquid (L) or a gaseous (G), hence, the solid electrolyte battery may have following possible cell configurations:

- Anode (S) | Solid Electrolyte | Cathode (S)
- Anode (S) | Solid Electrolyte | Cathode (L)
- Anode (L) | Solid Electrolyte | Cathode (S)
- Anode (L) | Solid Electrolyte | Cathode (L)
- Anode (S) | Solid Electrolyte | Cathode (G)
- Anode (G) | Solid Electrolyte | Cathode (G)

The first cell is a all solid state (S | S | S) configuration and has the possibility of miniaturization. This battery may be a primary (use and throw battery) or a secondary (rechargeable) type. On the basis of the energy drain, it can be divided into following two main sub-categories:

(i) Low energy density battery : The energy density < 0.1 W.h.cm⁻³. The solid state battery based on Ag⁺ and Cu⁺ ion conductors fall into this category because of the low decomposition potential of the electrolyte materials. Generally, majority of the batteries in this category are primary type.

(ii) High energy density battery : The energy density > 0.1 Wh.cm⁻³. The solid state batteries fabricated with Li⁺, Na⁺, H⁺, O²⁻, conducting polymer electrolytes deliver high energy density of
this magnitude. They are rechargeable type batteries with rechargeable cycles in the range of 100-1000 cycles.

The electromotive force (EMF) generation in these batteries depends on the choice of the electrode materials, as mentioned. In general, the solid electrolyte (MX) is sandwiched between the cathode and anode materials of different electrochemical potentials (\(\mu_1\) & \(\mu_2\)). Fig. 5.1 schematically shows the basic cell configuration of a solid state battery. Thermodynamically, the emf generation in a solid state battery in this cell configuration: \(M \mid MX \mid X\), involves following chemical reaction:

At the anode:

\[
M - e = M^+ \text{ (dissolved in MX)} \tag{5.1}
\]

At the cathode:

\[
X + e = X' \text{ (dissolved in MX or remains at the cathode/MX interface)} \tag{5.2}
\]

The \(M^+\) and \(X^+\) ions come together in the solid electrolyte by ion transport to form additional MX at either or both the electrolyte/electrode interfaces. Hence, the total cell reaction would be:

\[
M^+ + X^- \leftrightarrow MX \tag{5.3}
\]

If a constant supply of mobile ions could be maintained, the above chemical cell reaction leads to the emf generation which is governed by following expression [Kiukkola and Wagner 1957]:

\[
E = \frac{|Z|}{F} \int t_{\text{ion}} \, \text{d}\mu \tag{5.4}
\]

\[
E = (\mu_2 - \mu_1) \, t_{\text{ion}} \, |Z| / F
\]

\[
E = -\Delta G \, t_{\text{ion}} / |Z| \, F \tag{5.5}
\]

where \(\Delta G = (\mu_2 - \mu_1)\) is the Gibb's free energy involved in the above chemical reaction, \(t_{\text{ion}}\) is the ionic transference number, \(|Z|\) is the absolute magnitude of the valency of mobile ion, \(F\) is the Faraday's constant. When the battery is connected to an external load, it delivers a current from cathode to anode. In case of pure Ag\(^+\) ion conductors, the magnitude of both \(t_{\text{ion}}\) & \(|Z|\) are unity, hence, the emf is theoretically expressed as:

\[
E = \Delta G / F \tag{5.6}
\]
Fig. 5.1 A typical electrochemical cell with M and X electrodes of chemical potentials $\mu_1$ and $\mu_2$ respectively separated by an electrolyte MX.
'E' is also termed as open circuit voltage (OCV), which is theoretically equal to 0.687 V for the cell : Ag | Ag' ion solid electrolytes | I2. The ratio of theoretical (E) and measured (E') values of open circuit voltage gives rise to the ionic transference number 't_{ion}':
\[ t_{ion} = \frac{E'}{E} \]  
(5.7)

This electrochemical cell voltage measurement method is an experimental procedure used extensively to measure 't_{ion}' instantaneously for the Ag' ion conducting solids. The other method used is the Wagner's method, as mentioned earlier.

5.3 Solid State Battery Constituents : Characteristic Requirements

The effective and efficient performance of solid state batteries strongly depend on how close the characteristic properties of the solid electrolyte are to the ideal electrolyte as well as on the selection of the appropriate electrode materials compatible to the solid electrolyte. Hence, for the reliable operation, the solid state electrochemical battery constituents should possess following characteristic properties [Agrawal 1999] :

Solid Electrolyte : This is the key component of the device. Ideally, a solid electrolyte should have following properties :

- The ionic conductivity should be very high (~1 S.cm\(^{-1}\)). However, solids exhibiting \( \sigma \sim 10^{-1} - 10^{-3} \text{ S.cm}^{-1} \) are also considered as good electrolytes.
- Electronic conductivity must be as low as <10\(^{-8}\) S.cm\(^{-1}\). In other words, the ionic transference number \( t_{ion} \leq 1 \) and electronic transference number \( t_{e,h} \leq 0 \). Larger is the electronic contribution higher is the risk of internal short circuiting in the device, thus, shorter will be the shelf-life.
- The activation energy 'E\(_a\)' must be as low as possible (\( \leq 0.1 \) eV), ensuring an easy mobile ion transport through the bulk.
- Solid electrolyte materials should be of a low specific gravity and the mobile ion equivalent weight should be low.
• Decomposition potentials of the electrolyte material should be high and should have wide temperature range of stability.
• The materials should be thermodynamically stable with respect to dissociation type reaction, it should also withstand mechanical stress and thermal/electrical cycles.
• The solid electrolyte should be compatible with the electrode materials and inert as regards to its ambient environment/surroundings.

Electrode Materials: The magnitude of emf generation, shelf-life of the device, output power etc. of the solid state batteries are significantly affected by electrode/electrolyte kinematics. Hence, a careful selection of electrode materials is highly desirable. Ideally, the electrode materials should exhibit following characteristics:
• Both the anode and cathode materials should be electronic materials. Anode should supply the mobile ion species. Cathode is generally mixed with the solid electrolyte in order to avoid the cell polarization effect at the cathode/electrolyte interface.
• In order to obtain high OCV values, anode should be highly electropositive while cathode should be electronegative.
• Physical processes like inter-diffusion, formation of voids & dendritic growth, local overheating, pressure build-up etc. should be low.
• The equivalent weight and equivalent volume of electrode materials should be small to ensure a practical value of specific power.
• It is desirable that electrode materials must be reversible in order to construct a secondary rechargeable battery.

5.4 Silver Ion Conductor Battery: A Brief Overview

As mentioned earlier, silver iodide was probably the first solid exhibiting exceptionally high Ag⁺ ion conduction after β→α transition at ~ 147 °C [Faraday 1834; Tubandt and Lorentz 1914]. This remarkable characteristic property of AgI attracted widespread interest to develop Ag⁺ ion conducting superionic solids by way of solid solution of two or more ionic solids or arresting/freezing the superionic α-AgI in a glass network and/or dispersing the submicron size
second phase dispersoid particles into first phase host matrix salt of AgI etc. As mentioned earlier, the first room temperature fast Ag⁺ ion conductor: MAg₄I₅ (where M = Rb, K, NH₄) was reported independently by two groups of scientists: Owens and Argue [1967] and Bradley and Greene [1967]. In fact, the year 1967 has been marked as the beginning a new branch of science named afterwards as 'Solid State Ionics'. An extensive review, on the superionic solids in general and fast Ag⁺ ion conductor in particular, has been presented in the Chapter 1. Some important fast Ag⁺ ion conductor in different phases are listed in Tables 1.2, 1.3, 1.4, 1.5, 1.6 and 1.7. Solid state batteries have been fabricated using these Ag⁺ ion conducting systems. In the earlier attempts, pure silver halide (AgI, AgCl) were used. However, due to low room temperature conductivity these cells exhibited very high internal resistance, hence, their applications were limited to a very low current density of the order of few µA.cm² [Chandran and Agrawal 1980]. After the discovery of room temperature fast Ag⁺ ion conductors, the first solid state battery using fast Ag⁺ ion conductor, reported by Takahashi and Yamamoto [Takahashi and Yamamoto 1966a,b], has the following cell configuration:

\[ \text{Ag} \mid \text{Ag₃SI} \mid \text{C+I₂} \]

where Ag is the metal anode and (C+I₂) is the cathode with electronically conducting graphite. The solid electrolyte Ag₃SI exhibits a substantial electronic contribution, hence, the battery did not show a longer shelf-life. Owens and coworkers [Owens 1971, 1977] reported solid state battery using MAg₄I₅ in which they mixed solid electrolyte with the cathode material to have better electrode/electrolyte contact and to avoid the polarization effect. Table 5.1 lists some basic features of the solid state battery fabricated by Owens [Owens 1971]. Miniaturisation of the battery has also been attempted using the thin film of solid electrolytes [Kennedy 1977] Chandra and coworkers [Chandra and Mohabey 1979; Chandra et al. 1980a; Chandra and Agrawal 1980] developed a new technique of thin film formation of MAg₄I₅, [(CH₃)₄N]₂ Ag₃I₁; and Ag₇I₄PO₄ solids using electrodeposition method and studied the solid state battery characteristics. However, these battery systems have several limitations. The first major limitation is they are primary batteries with low open circuit voltage (OCV) due to low decomposition potential of the electrolyte material. The highest open circuit voltage attainable in these batteries is ~0.687 V (theoretically) when iodine (I₂) is used as cathode. The element iodine is a highly volatile and has a tarnishing action towards the electrolytes and electrodes.
Table 5.1: Some Important properties of Ag | RbAg| RbI solid state battery at 25 °C [Owens 1971].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCV</td>
<td>0.66 Volt</td>
</tr>
<tr>
<td>Theoretical specific energy</td>
<td>48 Wh/Kg</td>
</tr>
<tr>
<td>Practical specific energy</td>
<td>4.8 Wh/Kg</td>
</tr>
<tr>
<td>(at 25 μm/cm² discharge current)</td>
<td></td>
</tr>
<tr>
<td>Energy density</td>
<td>0.015 Wh/cm³</td>
</tr>
<tr>
<td>(at 25 μm/cm²)</td>
<td></td>
</tr>
<tr>
<td>Shelf-life</td>
<td>10 years</td>
</tr>
<tr>
<td>(predicted)</td>
<td></td>
</tr>
<tr>
<td>Shelf-life</td>
<td>5 years</td>
</tr>
<tr>
<td>(ascertained with (CH₃)₄NI₃ chelated)</td>
<td></td>
</tr>
</tbody>
</table>

Attempts have been made to reduce this activity by way of chelating the elemental iodine in the various forms such as: KI₃, RbI₃, (CH₃)₄NI₃, (C₂H₅)₄NI₃ etc., but this reduces the value of open circuit voltage. Some charge transfer complexes (like I₂-Ph) [Pampallona et al. 1976] and non-stoichiometric solid solution electrodes [Steele 1976] have also been attempted. These batteries demonstrated some successful rechargeable behaviour. Recently, Takada et al. [1990] reported rechargeable battery using silver ion conducting solids. Agrawal and coworkers have fabricated several primary type solid state batteries using fast Ag⁺ ion conducting solids in the glassy/composite electrolyte phases and studied their discharge performance under different load conditions and with several cathode materials [Agrawal and Kumar 1994, 1996; Agrawal and Gupta 1995; Agrawal, 1999; present investigation]. The emf generation in these batteries is akin to that discussed earlier in Section 5.2. The chemical reaction involved in the silver ion conducting battery in the cell configuration: Ag (Anode) | Ag⁺ ion conducting solid electrolyte | C+I₂ (Cathode), can be visualised as follows:

At the anode:

\[ \text{Ag} - e^- = \text{Ag}^+ \] (dissolved in electrolyte and moves towards the cathode in the bulk)
At the cathode:

\[ I + e = I^- \text{ (remains at the electrolyte/cathode interface)} \]

\[ \text{Ag}^+ + \frac{1}{2} I_2 \rightarrow \text{AgI} \]

The overall cell reaction is:

\[ \text{Ag}^+ + \frac{1}{2} I_2 \rightarrow \text{AgI} \]

The theoretical value of OCV involved in this chemical cell reaction is 0.687 V, as mentioned earlier. When chelated iodine is used as cathode, OCV reduces to ~0.66 V [Owens 1971].

As mentioned earlier, in the present work, solid state batteries with the two newly synthesized fast \(	ext{Ag}^+\) ion conducting 2-phase composite electrolyte systems: 0.9[0.75\text{AgI} : 0.25\text{AgCl}] : 0.1 \text{SiO}_2\) and 0.9[0.75\text{AgI} : 0.25\text{AgCl}] : 0.1 \text{ZrO}_2\) have been fabricated and their discharge characteristics have been studied under different load conditions and cathode preparations. The results of these experimental measurements are discussed below in Section 5.5.

### 5.5 Results and Discussion

The solid state batteries fabricated in the following (S | S | S) cell configuration:

- **Cell-(A):** \( \text{Ag} | 0.9[0.75\text{AgI} : 0.25\text{AgCl}] : 0.1 \text{SiO}_2 | (C + I_2) \)
- **Cell-(B):** \( \text{Ag} | 0.9[0.75\text{AgI} : 0.25\text{AgCl}] : 0.1 \text{ZrO}_2 | (C + I_2) \)

Ag metal has been used as anode while cathode is a pressed pellet of mixture of elemental iodine and conducting graphite in the 1:1 weight ratio. As mentioned, the elemental iodine is a very volatile and attacks the electrolyte as well as the metal electrodes. The tarnishing action of the elemental iodine has been reduced by way of chelating the iodine in the following forms viz., \( \text{Kl}_3\), \( \text{RbI}_3\), \( (\text{CH}_3)_4\text{NI}_3\), \( (\text{C}_2\text{H}_5)_4\text{NI}_3\), etc., as mentioned. The method of chelation has already been discussed earlier in Chapter 2. Thus, in order to study the influence of different cathode materials with reduced iodine activity, following additional solid state batteries have been fabricated:

- **Cell-(C):** \( \text{Ag} | 0.9[0.75\text{AgI} : 0.25\text{AgCl}] : 0.1 \text{SiO}_2 | \text{C + KI}_3 \)
- \( \text{Ag} | 0.9[0.75\text{AgI} : 0.25\text{AgCl}] : 0.1 \text{SiO}_2 | \text{C + (CH}_3)_4\text{NI}_3 \)
- \( \text{Ag} | 0.9[0.75\text{AgI} : 0.25\text{AgCl}] : 0.1 \text{SiO}_2 | \text{C + (C}_2\text{H}_5)_4\text{NI}_3 \)

- **Cell-(D):** \( \text{Ag} | 0.9[0.75\text{AgI} : 0.25\text{AgCl}] : 0.1 \text{ZrO}_2 | \text{C + KI}_3 \)
- \( \text{Ag} | 0.9[0.75\text{AgI} : 0.25\text{AgCl}] : 0.1 \text{ZrO}_2 | \text{C + (CH}_3)_4\text{NI}_2 \)
The open circuit voltage (OCV) measurements and cell potential discharge characteristic studies under different load conditions on the above batteries were carried out with the help of digital multimeter. To avoid the influence of humidity on the cell performance all the measurements were done by placing the battery inside a desiccator. Figs. 5.2 and 5.3 shows the potential discharge profile for the cells [A] & [B] under two different loads viz. ~1 MΩ and 100 KΩ. The OCVs ~0.675 & 0.68 V, obtained for the cells [A] & [B] respectively, are very close to the theoretically OCV (~ 0.687 volts). It can be obviously noted from both the discharge profiles that the cell voltage remained practically constant ~ 0.66 volts, for more than 120 -150 hours under 1 MΩ load conditions, except for a very little initial drop. However, for 100 KΩ load, larger initial voltage drops were observed and the cell potential remained constant at ~ 0.325 V for cell [A] & 0.18 V for cell [B] afterwards for more than 50-100 hours. The initial drop in the cell potential can be attributed as usual cell polarization effect and the formation of low conducting AgI at the electrode/electrolyte interface, which is very fast when the cell is discharged under low load or high current drain conditions. Table 5.2 lists some important cell parameters calculated in the plateau regions (indicated by vertical dotted bars) of the discharge profiles of Figs 5.2 & 5.3. The effect of various chelated iodine cathode materials on the performance of group of cells [C] & [D] were tested under 1 MΩ load only. Figs 5.4 and 5.5 show the discharge profiles for the two group of cells. The discharge profile of cell of group [A] & [B] from Figs 1.2, 1.3, tested under 1 MΩ, is redrawn in these figures, for the direct comparison of cell performance. Normally it is expected that the use of chelated iodine as cathode improves the performance of the cell as well as increase the shelf-life of the battery. However, on comparing these discharge curves one can obviously note that the batteries fabricated with chelated iodine cathodes discharged more rapidly than those with elemental iodine as cathode. The ionic transference number (t_ion) obtained by electrochemical cell potential measurement on cells (A) & (B) clearly indicates that 't_ion' is very close to unity for both the electrolyte systems. This is excellent agreement with result reported earlier by Wagner’s method.
Fig. 5.2. Variation of cell potential with time. Dotted vertical bars indicates the plateau region.
Fig. 5.3. Variation of cell potential with time. dotted vertical bars indicates the plateau region.
Table 5.2: Typical cell parameters calculated in the plateau region of the discharge curves for the solid state batteries: Cell-(A), Ag | 0.9[0.75AgI : 0.25AgCl : 0.1SiO₂ | (C+I₂), Cell-B, Ag | 0.9[0.75AgI : 0.25AgCl : 0.1ZrO₂ | (C+I₂).

<table>
<thead>
<tr>
<th>Cell</th>
<th>Load (KΩ)</th>
<th>Working Voltage (mV)</th>
<th>Current Density (μA.cm⁻²)</th>
<th>Discharge capacity (μA.h)</th>
<th>Power Density (mW.Kg⁻¹)</th>
<th>Energy Density (mW.h.Kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1000</td>
<td>660</td>
<td>3.3</td>
<td>79.2</td>
<td>0.38</td>
<td>45.4</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>325</td>
<td>16.2</td>
<td>260</td>
<td>0.92</td>
<td>73.5</td>
</tr>
<tr>
<td>B</td>
<td>1000</td>
<td>656</td>
<td>3.3</td>
<td>101</td>
<td>0.43</td>
<td>66.3</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>178</td>
<td>8.9</td>
<td>91.3</td>
<td>0.32</td>
<td>16.25</td>
</tr>
</tbody>
</table>
Fig. 5.4 Variation of cell potential with time (in hours).
Fig. 5.5 Variation of cell potential with time (in hours).
5.6 Conclusion

On the basis of the experimental studies on the discharge characteristics of the solid state batteries fabricated with the two new fast Ag⁺ ion conducting 2-phase composite electrolyte systems: 0.9[0.75AgI:0.25AgCl]:0.1SiO₂, 0.9[0.75AgI:0.25AgCl]:0.1ZrO₂ as electrolyte, under different load conditions and cathode preparations, it can be concluded that the batteries using (C+I₂) as cathode performed relatively more satisfactorily. These batteries are suitable for a low current drain applications and are of primary type.