CHAPTER V

SOLID STATE BATTERY
5.1 Introduction:

Development of electronic and space science needed the incorporation of energy within the system with miniaturized size. Batteries or cells using liquid electrolytes are the earliest sources of electrical power but they are not much useful due to following limitations.\(^1\)

(a) Limited temperature range of operation i.e. these batteries failed to deliver power below freezing point and above bioling point of the liquid electrolytes.

(b) Large size.

(c) Less rugged.

(d) Limited shelf life due to corrosion of electrodes by liquid electrolyte.

These limitations can be overcome if solid electrolytes having high ionic conductivity are used instead of liquid electrolytes. The earlier workers attempted to produce solid electrolyte cells\(^2-4\) but they were unable to produce solid electrolyte cells because the electrolytes used by them had either poor ionic conductivity or high electronic conductivity. Takahashi and Yamamoto\(^5-8\) had given a solid state cell with Ag\(_3\)SI as electrolyte. A current density of 100 \(\mu A/\text{cm}^2\) at 25\(^\circ\)C is maintained without appreciable variation of cell voltage. Discovery of high conductivity solid electrolytes MAg\(_4\)I\(_5\) (where \(M = \text{Rb, K, NH}_4\)) by Bradley and Greene\(^9,10\) and Owens and Argue\(^11\)
independently contributed to the solution of the problem in this direction. The properties of MAq₄I₅ have been studied by a large number of workers.¹¹-¹⁷ It is found that MAq₄I₅ electrolytes have very high electrical (ionic) conductivity and very low electronic conductivity. The ionic conductivity is mainly due to movement of Ag⁺ ions. These electrolytes were found suitable for development of solid state cells because they were fulfilling the following conditions of ideal battery electrolyte to some extent.

1. Conductivity must be high and stable over the temperature range of application.
2. The electrolyte must not degrade by reaction with either electrode materials or environmental contaminants.
3. Its electronic conductivity must be low.
4. Its decomposition potential must be high.

Some of the solid state cells made earlier are given in brief. Argue et al.¹⁸ reported a solid state cell:

\[
\text{Ag} / \text{RbAg₄I₅} / \text{RbI₃} + \text{C}
\]

having 0.65 V open circuit voltage (OCV) and operated at constant current density of 0.41 mA/cm² for sufficient time. Scrosati et al.¹⁹ had given the following solid state cell:

\[
\text{Ag(Hg)} / \text{RbAg₄I₅} / \text{I₂} + \text{C}
\]

The OCV of this cell was 0.98V and internal resistance and volume were 300 ohms and 2 cm³ respectively. De Rossi et al.²⁰ made a
solid state cell having 0.56 OCV at 25℃ and short circuited current about 15 mA/cm² given below.

\[ \text{Ag} / \text{RbAg₄I₅} / I₂ + C + \text{I.B.A.I.} \]

Use of amalgamated silver disc as anode and a mixture of iodine, graphite powder and tetrabutyl ammonium iodide as cathode decreased the polarization effect. Takahashi and Yamamoto²¹ reported the following cells.

\[ \text{Ag} / \text{RbAg₄I₅} / \text{Te} \]
\[ \text{Ag} / \text{RbAg₄I₅} / \text{Se} \]

The OCV of these cells were 0.217 V and 0.250 V respectively. Chandra et al.²² reported a cell of the following structure.

\[ \text{Ag} / \text{KAg₄I₅} / I₂ + C \]

The cell had an OCV of 0.58 V at 40℃. The cell voltage remained constant for a long time when it was allowed to discharge at a current density of 0.3 mA/cm².

A large number of good solid electrolytes have been reported with Ag⁺ ion, Cu⁺ ion, alkali metal ions, O²⁻ ion and F⁻ ion conduction. Owens ²³,²⁴ searched a series of solid electrolytes AgI - Q₄Nₓ (where \( Q = \text{CH}_3\text{CH}_2\text{H}_3, (\text{CH}_3)_1/2, (\text{C}_2\text{H}_5)_1/2 \) etc.). Mellors and Louzovs ²⁵ found the solid electrolytes Ag₄MI₄CN ²⁶,²⁷ (M = K, Rb). Copper ion conductor were found by Takahashi et al., Lazzari and Scrosati ²⁸ and Takahashi.²⁹ Takahashi discovered a
solid electrolyte copper (I) rubidium chloro iodide having very high ionic conductivity ($\sigma = 0.34 \text{ ohm}^{-1}\text{cm}^{-1}$) at 25°C. This proved to be a suitable solid electrolyte for solid state cell.

Lithium batteries were reported by Liang, Rao, Schneider et al., and Faster et al. They used LiI (pure and doped) as electrolyte and different cathodes in their electrochemical batteries. Design, engineering and construction of commercial Li/I$_2$ cells have been discussed by Schneider et al. and Liang and Holms. These cells are useful to power as a source for cardiac pace makers, for watches and microelectronic applications.

It is concluded that silver ion and copper ion batteries give low voltage and low current drain while the Li ion batteries give high voltage and low current drain.

To reduce resistance of electrolyte, electrolyte-films were used instead of electrolyte pellets. Sato was first to make a solid state cell of PbCl$_2$ using vacuum deposition method. Weininger, Kennedy et al., and Kennedy also used vacuum deposition techniques for making thin films for solid state cells. Chandra et al. used electrolytic method for preparing thin films of MAg$_4$I$_3$ on silver substrate. Some of them are 

Ag / Film KAg$_4$I$_3$ / I$_2$ + C cell having OCV 0.61 V and
Ag / Film NH$_4$Ag$_4$I$_3$ / I$_2$ + C cell having OCV 0.644 V. It has
also been reported that the film made by electrolytic method is not pure. Therefore pellets of NH$_4$Ag$_4$I$_5$ are used to make electrochemical cell.

5.2 Mechanism of Electrochemical Cell:

Configuration of the electrochemical cell is shown in Fig. 5.1.

Thermodynamically an electrochemical e.m.f. would be generated when electrolyte is pressed between two electrode materials with different chemical potentials. If a constant supply of ions could be maintained and transported through the electrolyte, it would deliver current connected across the load resistance. As NH$_4$Ag$_4$I$_5$ solid electrolyte is predominantly ionic, the main mobile charge carriers are Ag$^+$ ions. The reaction occurring at different regions of the cell is given below.

Anode  $\quad$ Ag $\rightarrow$ Ag$^+$ + e$^-$  \hspace{1cm} (5.1)

Electrolyte $\quad$ Ag$^+$ ion produced at anode moves towards cathode through the electrolyte

\[ \text{Ag}^+ \quad + \quad \text{e}^- \quad = \quad \text{Ag} \] \hspace{1cm} (5.2)

Cathode  $\quad$ Ag (solid) + $\frac{1}{2}$ I$_2$ $\rightarrow$ AgI (solid)  \hspace{1cm} (5.3)

Thus the net reaction is the formation of AgI(solid) from solid Ag and I$_2$ in vapour phase. The cell reaction at the cathode represented by (5.3) is reversible, and the process is isothermal and isochoric. Hence the external work obtainable should be equal
to the change in free energy and the e.m.f. of the above cell at a particular temperature and constant pressure can be calculated by the well known expression:

$$E = \frac{-\Delta G}{F} + \frac{RT \ln P_{I_2}}{2F}$$  \hspace{1cm} (5.4)

where $\Delta G$ is the free energy increase in the reaction (5.3), $P_{I_2}$ is the vapour pressure of $I_2$, $R$ is the gas constant, $F$ is Faraday's constant and $T$ is the absolute temperature. The vapour pressure of iodine, $P_{I_2}$ can be calculated by:

$$\ln P_{I_2} = \frac{-\Delta G_{I_2}}{RT}$$  \hspace{1cm} (5.5)

where $\Delta G_{I_2}$ is the free energy increase of the reaction $I_2(s) \rightarrow I_2(g)$. A combination of Equ.(5.4) and Equ. (5.5) leads to the following expression for e.m.f $(E)$ of the cell.

$$E = \frac{-\Delta G}{F} - \frac{\Delta G_{I_2}}{2F}$$  \hspace{1cm} (5.6)

where $\Delta G + 1/2 \Delta G_{I_2}$ is the free energy increase of the reaction $Ag(s) + 1/2 I_2 \rightarrow AgI(s)$. $\Delta G + 1/2 \Delta G_{I_2}$ can be calculated from the available thermodynamic data\textsuperscript{45,46} as:

$$\Delta G + 1/2 \Delta G_{I_2} = -14,400 + 8.27 \ T \log T -6.3 \times 10^{-3} T^2 - 23.4 T$$  \hspace{1cm} (5.7)

The Equ. (5.6) together with Equ. (5.7) yields the following expression for e.m.f of a silver iodine battery as a function of temperature.

$$E(mV) = \frac{14,400 -8.27 \ T \log T + 6.3 \times 10^{-3} \ T^2 + 23.4 \ T}{23.04}$$  \hspace{1cm} (5.8)
5.3 Properties of Electrodes:

Cells or batteries have three components:
an anode, a cathode and an electrolyte (solid or liquid).
As electrolyte is kept between anode and cathode, it is also
called separator. The role of electrode systems in the
performance of batteries is as important as that of electrolyte.

The properties of ideal electrodes are discussed below:

(1) Equivalent weight, equivalent volume and electrochemical
class.

Equivalent weights and equivalent volumes of both
anode and cathode must be low. A combination of a highly
electropositive anode, a highly electronegative cathode and a
high specific capacity leads to a high energy density for the
cell. Silver and copper anode do not satisfy these conditions.

(2) Stability against the electrolyte.

The electrolyte must be compatible with the
electrodes (anode and cathode). The cell Ag / Ag₃SI / I₂ + C
was found to exhibit lower OCV because Ag₃SI reacts with I₂
and forms more resistive AgI.

(3) Electronic and ionic conductivities.

In order to support the flow of current to applied
load, both electrodes must be good electronic conductors. Most
of the anode materials are metals or metal alloys (e.g., Ag, Li, LiAl, LiSi etc.) so they satisfy this condition. The cathode materials (e.g., I₂) do not exhibit a good electronic conduction. To increase electronic conductivity of cathode material, electrically conductive powder (e.g., graphite powder) is dispersed in active cathode material (I₂) or by its (cathode) reaction with certain organic materials.

The ionic conductivity of the electrodes needs individual consideration. Apparently anode structures need not necessarily incorporate an ionic conductor. A small ionic conductivity in some cathode materials may be desired. The need for ionic conductivity within the electrode structure depends upon volume changes that accompany the discharge at each electrode, the ionic charge carriers within the electrolyte layer and the electrical conductivity of discharge product.

5.4 Selection of Anode and Cathode Materials:

In these solid state cells, all the current is carried by silver ions. For electrolyte \( \text{NH}_4\text{Ag}_4\text{I}_5 \), \( \text{Ag}^+ \) therefore silver metal is a suitable choice for anode. In this work pressed silver powder pellet is used as anode. For cathode the following points are to be kept in view: (i) The cathode reversible potential must be less positive than the decomposition potential of the electrolyte, (ii) The half cell reaction must be electrically compatible with the mobile ion. The best cathode
materials are the elements of group VI and VII of the periodic table (i.e., halogens and chalcogens). The suitable chalcogens are Te, Se and S. In halogens only iodine is available in solid state while chlorine and bromine are in gaseous and liquid state respectively at room temperature. Therefore iodine is the most suitable cathode. To satisfy the condition of high electronic conductivity of cathode, iodine is mixed in graphite powder and their pellets are used as cathode in present work.

5.5 Experimental Arrangement for investigating cell

Characteristics:

Solid electrolyte $\text{NH}_4\text{Ag}_4\text{I}_5$ is prepared as described in Chapter II. 0.7 gm of this material is weighed and pelletized at a pressure of 2.5 tons/1.33 cm$^2$. Cylindrical pellets of 1 mm thickness and 1.33 cm$^2$ cross-section area are prepared. At this pressure and mass, the electrical (ionic) conductivity of pellets are found to be maximum.

Electrochemical Cell — Fine silver powder is pelletized at a pressure of 5 tons/1.33 cm$^2$ for anode. Iodine and graphite powder are grounded in agate mortar in the ratio of 1 : 3 and 1 : 5 separately and this mixture is pelletized at 5 tons/1.33 cm$^2$ for cathode. The cells are designed using silver pellets as anode, $\text{NH}_4\text{Ag}_4\text{I}_5$ pellets as electrolyte and pellets of iodine and graphite mixture as cathode.
Fig. 5.1- Schematic diagram of electrochemical cell.
as shown in Fig. 5.1. The cell voltage is measured by D.C. microvoltmeter PP 9004 Philips and temperature is recorded by iron-constantan thermocouple.

5.6 Characteristics of Electrochemical Cell:

The following characteristics are studied:

(1) Open Circuit Voltage — The cell is kept in a furnace for measurements above room temperature. The open circuit voltage is measured from 40° to 120°C.

(2) Discharge Characteristics with Time — The experimental arrangement is shown in Fig. 5.2. The cell is allowed to discharge at a fixed load current. At different load currents, cell voltage is measured as a function of time. This characteristic is studied with cathodes having iodine and graphite ratio 1:3 and 1:5 at different temperatures from 40° to 120°C.

(3) Discharge Characteristics with loads — The cell is allowed to discharge at fixed temperature, the cell voltage and current are measured as a function of load. The experiment is repeated with cathodes having different \( (I_2 + C) \) ratio and at temperatures from 40° to 150°C.

5.7 Results and Discussion:

The e.m.f of the cell \( Ag / NH_4AgI_5 / I_2 + C \) can be
FIG. 5.2 - EXPERIMENTAL ARRANGEMENT FOR MEASUREMENTS.
calculated from Equ. (5.8). The measured OCV and calculated OCV are given in Table 5.1.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Open circuit voltage (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
</tr>
<tr>
<td>40</td>
<td>680</td>
</tr>
<tr>
<td>50</td>
<td>685</td>
</tr>
<tr>
<td>60</td>
<td>685</td>
</tr>
<tr>
<td>70</td>
<td>690</td>
</tr>
<tr>
<td>80</td>
<td>695</td>
</tr>
<tr>
<td>90</td>
<td>695</td>
</tr>
<tr>
<td>100</td>
<td>690</td>
</tr>
<tr>
<td>110</td>
<td>690</td>
</tr>
<tr>
<td>120</td>
<td>690</td>
</tr>
</tbody>
</table>

The measured values of OCV are in fair agreement with the calculated values. At higher and lower temperatures, they differ slightly. This may be due to following reasons.

(i) Polarization of cell.
(ii) More electronic conduction.

Due to above agreement in measured and calculated values of OCV, it appears that the electrolyte is purely ionic and the charge
FIG. 5.3 - DISCHARGE CHARACTERISTIC OF

$\text{Ag/AgCl}_5 / \text{I}_2 + \text{C}$ CELL AT 40°C.
FIG. 5·4 - DISCHARGE CHARACTERISTIC OF CELL
Ag/NH₄Ag₄I₅/I₂+C AT 60°C.

CATHODE (I₂ + C = 1:3)

CELL VOLTAGE (VOLTS)

DISCHARGE TIME (HOURS)

0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1
2
3
4
5
6
7
8
9
10

500 µA
150 µA
50 µA
Cathode (I_2 + C = 1:3.)

50 μA.

150 μA.

500 μA.

Fig. 5.5 - Discharge characteristic of cell

Ag/NH_4AgI_5/I_2 + C at 80°C.
CATHODE \((12^+C=1:3)\)

50μA

150μA

500μA

FIG. 5·6 - DISCHARGE CHARACTERISTIC OF CELL

\[ \text{Ag/NH}_4\text{Ag}_4\text{I}_5/12^+C \] AT 100°C.
CATHODE \((I_2 + C = 1:3)\)

**FIG. 5.7 - DISCHARGE CHARACTERISTIC OF CELL**

Ag/NH$_4$Ag$_4$I$_5$/I$_2$ + C AT 120°C.
FIG. 5.8 - DISCHARGE CHARACTERISTIC OF CELL

Ag/NH₄Ag₄I₅/I₂+C AT 40°C.
FIG. 5.9 - DISCHARGE CHARACTERISTIC OF CELL

Ag/NH₄Ag₄I₅/I₂+C AT 80°C.
FIG. 5.10—DISCHARGE CHARACTERISTIC OF
CELL Ag/NH₄Ag₄I₅/I₂+C AT 120°C.
transport is wholly by Ag⁺ ions.

The cell is allowed to discharge at fixed temperature and cell voltage is measured as a function of time. Voltage Vs. time curves at temperatures 40°, 60°, 80°, 100° and 120°C with cathode \( (I_2 + C = 1 : 3) \) are shown in Figs. 5.3 to 5.7 respectively and with cathode \( (I_2 + C = 1 : 5) \) are shown in Figs. 5.8 to 5.10. It is observed that cell voltage remains nearly constant for 50 μA current drain up to 100°C for sufficiently long time. Above 100°C it falls rapidly. This may be due to increase in electronic conductivity of electrolyte above 100°C. For 150 μA current drain, cell voltage remains constant for very long time between temperatures 50° to 90°C as shown in Figs. 5.3 to 5.6. Above 90°C and below 50°C it falls rapidly. Below 50°C the cell voltage falls due to following reason. At low temperature the electrochemical reaction is slow, therefore, iodine in the cathode must be complexed to reduce its activity because elemental iodine degrades the electrolyte via the reaction. \(^{49}\)

\[
I_2 + NH_4Ag_4I_5 \rightarrow NH_4I_3 + 4AgI
\]

The product AgI is more resistive, therefore, cell voltage falls rapidly. Above 90°C the cell voltage decreases due to increase in the electronic conductivity of the electrolyte. When higher current (500μA) is drawn, the cell voltage falls rapidly at all temperatures. This may be due to anodic and cathodic polarizations. \(^{22}\) Anodic polarization is due to oxidation of
anode/electrolyte ($\text{NH}_4\text{Ag}_4\text{I}_5$) interface as both are in solid state. As the interface area gets depleted of silver, the anode reaction will cease. The functioning of cell involves the migration of $\text{Ag}^+$ ions through the electrolyte to react with the cathode and forming the discharge product $\text{AgI}$. The $\text{AgI}$ layer which is produced at cathode, polarizes cathode. This $\text{AgI}$ layer produces hindrance for $\text{Ag}^+$ ions from reaching to cathode. This results in cathode polarization and increase in cell resistance. This will increase with the increase in current drain.

The cell voltage of the cell having cathode ($I_2+C=1:3$) remains more stable than the cell having cathode ($I_2+C=1:5$) when constant current is drawn as shown in Figs. 5.3 to 5.10. This may be due to presence of more free iodine in cathode (1:3).

The cell is allowed to discharge at constant temperature. The instantaneous cell voltage and current is measured as a function of loads. The experiment is repeated at different temperatures from $40^\circ$ to $160^\circ$C and with cathodes of different ($I_2+C$) ratio. Cell voltage Vs. load curves are shown in Figs. 5.11 and 5.12. Cell current Vs. load curves are shown in Figs. 5.13 and 5.14. It is observed that the instantaneous cell voltage is stable at higher loads while it varies at lower loads. At lower loads, higher current is drawn from the cell so it gets polarized and variation in cell voltage results but at higher loads, low current is drawn so there is no polarization
Fig. 5.11 - Cell Voltage vs Load Characteristics of Cell Ag/NH$_4$Ag$_4$I$_5$/I$_2$ + C.

Cathode (I$_2$ + C = 1:3)
FIG. 5-12 - CELL VOLTAGE VS LOAD CHARACTERISTIC OF CELL Ag/NH$_4$Ag$_4$I$_5$/I$_2$ + C.
FIG. 5.13—CURRENT VS LOAD CHARACTERISTIC OF CELL

\[ \text{Ag/NH}_4 \text{Ag}_4 \text{I}_5/\text{I}_2 + \text{C} \]

CATHODE \( (\text{I}_2 + \text{C} = 1:3) \)

- \( \square - 80^\circ \text{C} \)
- \( \nabla - 90, 100^\circ \text{C} \)
- \( \Delta - 70, 110, 120^\circ \text{C} \)
- \( \bullet - 60^\circ \text{C} \)
- \( \circ - 50, 40^\circ \text{C} \)
FIG. 5.14—CURRENT VS LOAD CHARACTERISTIC OF CELL Ag/NH$_4$Ag$_{4}^{1.5}$/I$_2$ + C.

CATHODE (I$_2$ + C = 1:5)

1st - 80°C
2nd - 90, 100°C
3rd - 70, 110, 120, 130, 140°C
4th - 40, 50, 60°C
5th - 150, 160°C
and cell voltage is stable. At temperatures from 70° to 120°C cell reaction is very fast so it does not polarize at lower loads also. Therefore, at these temperatures instantaneous cell voltage remains stable at all loads. Due to above reason higher cell current is obtained also between 70° to 120°C temperature range as shown in Figs. 5.13 and 5.14.

5.8 Storage Characteristics :

The storage capability of a battery is referred to as its shelf life or shelf life is the length of time that a battery may be stored and still deliver adequate power for a specific applications. There are following limitations for degradation of cell.

(1) Atmospheric degradation due to diffusion of H₂O and O₂ into the cell.
(2) Electrolyte disproportionation to resistive phase at low temperature.
(3) Diffusion of iodine to the anode through the electrolyte during storage. This diffusion rate increases with increase of temperature. This decreases shelf life of cell.

The cells fabricated in this work suffer with above limitations, therefore, their shelf life is not very long. Some modifications are necessary to overcome these limitations.

(1) Cell should be kept in an enclosure so that atmospheric degradation is checked.
(ii) Iodine should be in some compound form (i.e., KI₃) instead of elemental form so that its diffusion through electrolyte is reduced.

After modifications the shelf life of the cell may be improved.

The solid state cell $\text{Ag} / \text{NH}_4\text{AgI}_3 / \text{I}_2 + \text{C}$ shows $580 \text{ mV OCV at } 40^\circ\text{C}$. It discharges rapidly at high current drain (500 $\mu\text{A}$) but up to 150 $\mu\text{A}$ current drain it is stable for fairly long time between the temperatures $50^\circ\text{ to } 90^\circ\text{C}$. The cell is useful to power as a source of higher loads.
REFERENCES


37 -------- Ibid., p. 27.

38 Sato, A., Compt. rend 234, 2283 (1952).


