CHAPTER VI

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CHAPTER VI

SOLID STATE BATTERY APPLICATIONS

6.1 BASIC BATTERY CONCEPTS AND PRINCIPLES OF OPERATION

Battery is a device that converts the chemical energy, contained in its active materials, directly into electrical energy by means of electrochemical oxidation-reduction (redox) reactions. The basic electrochemical unit of the battery system is called a galvanic cell. A cell consists of three major parts (1) Anode, (2) Cathode and (3) Electrolyte. The anode gives up the electron during electrochemical reaction, while the cathode accepts it. The electrolyte is an ion conductor, which provides the medium for transfer of ions inside the cell between cathode and anode. The basic cell scheme is shown in Figure 6.1(a). On connecting the external load (L), the electrochemical reaction takes place and the current begins to flow in one direction. The electron leaves the anode and flows through the load to the cathode. The ions migrate through the electrolyte to complete the cell reaction. In Figure 6.1(b), the cell reaction in Mercad battery system is shown as an example.
Fig. 6.1(a) Sketch of conventional liquid electrolyte cell.

MERCAD BATTERY SYSTEM

Anode : Cd
Cathode : HgO

Cell reaction : Cd + HgO + H2O → Cd(OH)2 + Hg

Fig. 6.1(b) Cell reaction in Mercad battery system.
The basic criteria for the selection of anode, cathode and electrolyte are as follows:

Anode:

The anode should have high efficiency as a reducing agent. Anode should also have very good conductivity, stability and ease in fabrication.

Cathode:

The cathode must have high efficient oxidising properties and should be stable, when it is in contact with electrolyte. The cathode should also provide a useful working voltage.

Electrolyte:

The electrolyte must have very high ionic conductivity and should have negligible electronic conductivity to avoid internal short circuit. The electrolyte should be non reactive with the electrode materials. The change in electrolyte properties with temperature must be low.

6.1.1 Battery Parameters

Some of the battery parameters, which are used to scale
the performance of the battery systems, are defined here.

**Open-Circuit Voltage (OCV):** The potential difference between the terminals of cell or battery, when the circuit is open (no-load condition).

**Current Density:** Current per unit area of the surface of the electrode.

**Discharge Rate:** The rate, usually expressed in milli amperes, at which electrical current is taken from the cell or battery.

**Discharge Capacity:** The product of discharge current and discharge time taken for a particular drop in cell voltage (usually 60% of OCV) and is expressed in milli-ampere-hour (mAh).

**Energy Density:** The ratio of the energy available from a cell or battery to its volume (expressed in Wh/L) or weight (expressed in Whr/kg).

6.1.2 Cell Classification

Electrochemical cells are generally identified as primary (non-rechargeable) or secondary (rechargeable) cells. Within this classification, other classifications are used to identify particular structures or designs. Based on
this, the battery systems are classified into four major types. Table 6.1 gives some examples of different class of batteries with its parameters. An excellent text on principles of battery operation, fabrication and performance is found in the literature [1]. The classification of different types of electrochemical cells are described below

(1) Primary Batteries: These batteries are once discharged and discarded.

(2) Secondary Batteries: These batteries can be recharged and reused for several cycles. These are also known as storage batteries or accumulators.

(3) Reserve Batteries: In these batteries, a key component is separated from the rest of the battery prior to activation. The reserve battery design is used to meet extremely long or environmentally severe storage requirements.

(4) Fuel cells: In these battery systems, the main electrochemical reactants are fed into the system and cell functions as long as the reactants are supplied. The fuel is usually gaseous or aqueous.

6.1.3 Problems with Liquid Electrolyte Cells

A large variety of liquid electrolyte battery systems
<table>
<thead>
<tr>
<th>Cell Class and example:</th>
<th>Anode</th>
<th>Cathode</th>
<th>Cell reaction</th>
<th>Voltage Volts</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1. Primary Battery - Leclanche Cell:</strong></td>
<td>Zn</td>
<td>MnO₂</td>
<td>Zn + 2MnO₂ → ZnO + MnO₂</td>
<td>1.6</td>
</tr>
<tr>
<td><strong>2. Secondary Battery - Lead Acid Cell:</strong></td>
<td>Pb</td>
<td>PbO₂</td>
<td>Pb + PbO₂ + 2H₂SO₄ → 2PbSO₄ + 2H₂O</td>
<td>2.1</td>
</tr>
<tr>
<td><strong>3. Reserve Battery - Cuprous Chloride Cell:</strong></td>
<td>Mg</td>
<td>CuCl</td>
<td>Mg + Cu₂Cl₂ → MgCl₂ + 2Cu</td>
<td>1.6</td>
</tr>
<tr>
<td><strong>4. Fuel Cell - Hz/O₂ Cell:</strong></td>
<td>Hz</td>
<td>O₂ (air)</td>
<td>Hz + 1/2 O₂ → H₂O</td>
<td>1.23</td>
</tr>
</tbody>
</table>
are being used today and all these battery systems have the following disadvantages to a greater or lesser amount.

(1) Short shelf life due to corrosion of electrode materials.
(2) Leakage.
(3) Limited temperature range of operation.
(4) No miniaturisation possible.
(5) Less rugged.

6.2 SOLID STATE BATTERIES

In conventional battery system, the ion transport medium (or) electrolyte is a liquid. Recently, availability of fast ionic conducting solids stimulated the development of Solid Electrolyte Batteries [2]. These Solid State Cells have the following advantages over the conventional liquid electrolyte cells.

6.2.1 Advantages of Solid State Batteries

(1) Absence of leakage or gassing.
(2) Low self discharge and a very long shelf life.
(3) High thermal stability.
(4) Ability to operate over a wide range of conditions of temperature, pressure, acceleration, etc.
(5) High energy density.
(6) Excellent packaging efficiency (without the use of separators).

(7) Miniaturisation.

However, solid state battery systems have the following limitations, which restricts their practical utility.

6.2.2 Limitations

(1) Low power capacity.

(2) High impedance of Solid Electrolyte at ambient temperature.

(3) Mechanical stress due to volume changes associated with discharge reactions.

(4) Reduced electrode efficiency at high discharge rates.

(5) Formation of high resistance discharge product.

6.2.3 Criteria for the Design of Solid State Batteries

A cell or battery system consists of electrolyte and electrode (cathode and anode) materials. Different types of solid electrolyte materials of different ion conducting species have been synthesised. Variety of electrode materials have been synthesised and studied so far. Excellent reviews and research articles about solid electrolyte materials and electrode materials are available in literature [3-10]. The following are the important
criteria for the design of solid state batteries.

Solid Electrolyte

The ionic conductivity of the solid electrolyte should be as high as possible at ambient temperatures, so that, the internal resistance of the fabricated cell is as minimum as possible to avoid lowering of potential of the cell. The activation energy of the migrating ion should be as minimum as possible. The electronic conductivity of the solid electrolyte acts as an internal short circuit of the cells and leads to the fast degradation of the cell. Hence, the electronic conductivity must be negligible. The solid electrolyte should be stable under ambient conditions such as temperature, pressure, humidity and atmosphere to facilitate mass production. The Gibbs free energy of the total electrochemical reactions must be negative and large to get a meaningful voltage.

Electrodes

The electrodes, both anode and cathode, should be good electronic conductors to support the flow of current through the load. The electrodes must have a good mechanical stability and able to withstand electrochemical potential gradients. The anode should be highly electronagative and
cathode should be highly electropositive.

Electrode / Electrolyte Interface

The electrode and electrolyte must be chemically and physically compatible with each other. They should be inert to avoid damage of interface region by processes like interdiffusion, formation of voids and dendritic growth. The interfacial integrity between the electrode and electrolyte must be maintained.

6.3 EARLIER WORK ON SILVER SOLID STATE BATTERIES

The first silver based solid state cell

\[ \text{Ag} / \text{AgI} / \text{I}_2 \]

was reported by Weininger [11] in 1959. This cell has an Open Circuit Voltage (OCV) of 687 mV at 25°C. Though the OCV is high for this battery, the internal resistance of the cell is very high due to the low conductivity of the of AgI at 25°C. Later, high ionic conductivity of the order of \(10^{-2} \text{ S cm}^{-1}\) in Ag$_x$Si$_{1-x}$ was reported by Takahashi and Yamamoto in 1969 [12]. The solid state cell using Ag$_x$Si$_{1-x}$ has been studied with the following configuration

\[ \text{Ag} / \text{Ag}_x\text{Si}_{1-x} / \text{I}_2 \]

\[ \text{Ag(s)} + 1/2 \text{I}_2(s) \rightarrow \text{AgI(s)} \]
The OCV of the above cell was 675 mV as compared with the theoretical thermodynamical value of 687 mV. The internal resistance of the cell was about 10 ohms and it could withstand current-density of 100 μA/cm². Owens and Argue [13] have shown that the reaction

\[ \text{I}_2 + \text{Ag}_3\text{SI} \rightarrow 3\text{AgI} + \text{S} \]

may increase the internal resistance of the cell and therefore the iodine cathode is not chemically compatible. Later, sulfur was tried in the place of iodine, but the cell gave very low OCV of 230 mV only. Cells based on other silver halides like, AgBr, AgCl were also studied, but all these efforts had a very little success and only limited application of these systems resulted. The historical review about these systems was given by Mugudich 1964 and Foley, 1969 [14,15].

A dramatic development has taken place after the discovery of high ionic conduction in MAg₄I₅ (M = K, Rb, NH₄) at room temperature, by Owens and Argue in 1967 [16] and Bradley and Greene in 1966 [17]. Owens and co-workers have fabricated the solid state batteries

\[ \text{Ag / RbAg}_4\text{I}_5 / \text{I}_2, \text{C} \]

which exhibited OCV of 687 mV. These cells delivered higher current but, they had thermodynamic instability. The iodine
reacts with the electrolyte to form RbI9 as

\[ \text{I}_2 + \text{RbAgI}_5 \rightarrow \text{RbI}_9 + 4\text{AgI} \]

which again resulted in an increased cell resistance. Later, the cells with RbI9 cathode were tried [18]. Although these cells exhibited greater stability, the discharge products were highly resistive. Besides these cells, many other cathode materials, such as Ag2Se-Se, etc. [19] have also been investigated. These cells were found to exhibit lower potentials and lower discharge capacities compared to other silver cells.

The use of tetra methyl poly-iodides like, Me4NIS and Me4NI0 (Me = methyl group) as cathodes resulted in stable cells. These cells discharged to form ionically conductive solid reaction products between silver iodide and tetra methyl ammonium iodide [20]. Batteries utilising these cathodes have exhibited better discharge properties.

Although the silver iodine based battery systems demonstrated efficient performance relative to their intrinsic capabilities, their commercial usage is still very limited. This is largely due to the low energy densities and the materials cost associated with the electrode and electrolyte. However, active research is still going on due to their specialised applications, possibility of making
micro batteries, high efficient performance, etc. [1,3-5].

6.4 PRESENT WORK

In the present work, the highest conducting compositions of the glass in Silver Molybdovanadate (SMV): AgI-Ag2O-(MoO3+V2O5) and Silver Molybdoarsenate (SMA): AgI-Ag2O-(MoO3+As2O5) systems are used as solid electrolytes for the application of solid state batteries. The transport properties of the highest conducting composition of the glass in these two systems are summarised in Table 6.2 [21,22]. From the Table 6.2, it is clear that these glasses have very high ionic conductivity and negligible electronic conductivity at ambient conditions. Moreover, their activation energy for the conducting species is also very less. Thus, SMV and SMA glassy systems are suitable for the application of solid state batteries.

In the present work, solid state batteries have been fabricated using the highest conducting compositions of the glass in SMV and SMA systems (listed in Table 6.2) as solid electrolytes. The cells are fabricated with different cathode materials and battery performance is studied. In this chapter, the laboratory scale study of the primary batteries are presented and the battery performance is analysed.
Table 6.2  Highest conducting composition and transport parameters of SMV and SMA systems

<table>
<thead>
<tr>
<th>System: High $\sigma$ composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity at activation (S cm$^{-1}$)</td>
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<td>-----------------------------------</td>
</tr>
</tbody>
</table>

For SMV: 60% AgI - 24% Ag2O - 16% (0.1 MoO3 + 0.9 V2O5)

| 1.91 x 10$^{-2}$ | 0.33 | 0.34 | 0.999 |

For SMA: 60%AgI - 25.5% Ag2O - 14.5% (0.6 MoO3 + 0.4 As2O3)

| 1.65 x 10$^{-2}$ | 0.35 | 0.37 | 0.999 |
6.5 EXPERIMENTAL

6.5.1 Fabrication of Solid State Batteries

The solid state cells are fabricated according to the scheme,

\[
\text{Anode} / \text{Solid Electrolyte (SE)} / \text{Cathode} \\
\text{Ag+SE} / \text{SMV (or) SMA} / [(I+C)SE]+TAAI
\]

where, I - Iodine, C - Graphite and TAAI - Tetra Alkyl Ammonium Iodide.

Solid Electrolyte: Finely ground powders of SMV (or) SMA glasses, compositions listed in Table 6.2, have been chosen as solid electrolytes for the fabrication of batteries.

Anode: Mixer of silver powder and solid electrolyte in the weight ratio 1:1 is used as anode material. Analar grade silver powder (mesh size 400) and the solid electrolyte (SMV or SMA glass) are mixed in required proportion and finely grounded. Pressed pellets of the above mixture is used as an anode. The addition of solid electrolyte to silver provides more anode / electrolyte interfacial contact area and hence better interfacial properties.

Cathode: Analar grade chemicals are used for the preparation of cathodes. Different cathode materials, (1) Iodine and (2) Mixer of iodine and Tetra Alkyl Ammonium
Iodide, have been used for the fabrication of solid state batteries. Graphite powder and solid electrolyte materials are also added to the above cathode materials in required proportions. Graphite powder is added to the cathode to increase its electronic conductivity and solid electrolyte is added to have better electrolyte/cathode interfacial properties and hence battery performance.

The cell performance is very sensitive to the chemical compositions of the cathode constituents. To select the best cathode composition, the cells are fabricated with various compositions of the cathode constituents and the battery performance is studied. The compositions of the cathode ingredients are varied according to the following scheme.

(i) In the first step, the mixture of I+C is chosen as cathode material and the cells are fabricated for various I:C ratios (10:0, 9:1, 8:2, etc.). The battery performance of these cells are studied and the best I:C cathode composition is chosen.

(ii) To this best I:C composition, solid electrolyte is added in various weight ratios as (I+C):SE and batteries are fabricated and studied.

(iii) Finally, Tetra Alkyl Ammonium Iodide (TAAI), (Alkyl =
Methyl (or) Ethyl (or) Butyl is added in various ratios as [(I+C)+SE]:TAAI.

Cell Construction

The anode and electrolyte layers were pressed at a pressure of 5000 kg/cm² to form a pellet of 10 mm in dia. and about 1 mm to 1.5 mm in thickness. Cathode pellets are prepared separately by grinding its constituents thoroughly and pressing to form a pellet of 15 mm in dia. and 1 mm to 1.5 mm in thickness. The cell is assembled by sandwiching the Anode/Electrolyte and cathode pellets between graphite discs and copper foils, as shown in Figure 6.2. The cells are then immediately sealed by Epoxy resin and stored at ambient conditions. Set of similar cells are fabricated and the Open Circuit Voltage (OCV), polarisation and discharge studies are carried out.

6.3.2 Setup for Polarisation and Discharge Characteristics

Polarisation characteristics are the plots of the variation of the terminal voltage as a function of current drawn from the cell. The circuit shown in Figure 6.3 is used to study the polarisation and discharge characteristics of the fabricated batteries. In the polarisation studies, the cell voltage is measured as a function of current drawn.
Fig. 6.2 Cross sectional view of cell assembly. (1) Hylem holder, (2) Screw, (3) Copper foils, (4) Graphite discs, (5) Anode, (6) Solid electrolyte, (7) Cathode and (8) Epoxy sealing.

Fig. 6.3 Circuit arrangement for measuring polarisation and discharge characteristics (C - cell under test).
from the cell. Different current drains are obtained by connecting different load resistances. The cell voltage is measured after 10 seconds of connecting the load. The variable load is provided by the resistance box RL. The current is measured using a Philips ammeter (accuracy of 0.1 nA) and the terminal voltage is measured using a microvoltmeter (accuracy 0.1 µV).

The variation of terminal voltage with time at a constant load or constant current density is known as the discharge characteristics of the solid state battery. For discharge studies, the circuit shown in Figure 6.3 is used. The current during the measurement is monitored by the ammeter. The discharge studies are carried out for different current densities (i.e. different discharge rates). For both polarisation and discharge studies, the cut off voltage was fixed at 400mV, which is approximately 60% of the OCV.

6.6 RESULTS AND DISCUSSION

In this section, the results for batteries (using SMV and SMA glasses as solid electrolytes) are presented and performance is discussed. Table 6.3 summarises the results for sets of batteries studied with different cathode materials. The open circuit voltage of the cells for the cathode I+C is found to be 687mV and is equal to the
Table 6.3 Cell parameters of SMV & SMA glassy electrolytes studied at room temperature (30°C)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Cathode</th>
<th>OCV</th>
<th>Current Drain for 0.4 Volts</th>
<th>Operating time for OCV to .4V</th>
<th>Discharge at 50μA/cm²</th>
<th>Capacity Density</th>
<th>1 year hrs.</th>
<th>1 year mAh</th>
<th>1 year Whr/Kg</th>
<th>OCV mV</th>
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<tr>
<td>Electrolyte: SMV</td>
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<td>I:C variation</td>
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<tr>
<td>10:0</td>
<td>687</td>
<td>0.01</td>
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<td>2</td>
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<td></td>
<td></td>
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<tr>
<td>9:1</td>
<td>687</td>
<td>2.0</td>
<td></td>
<td>80</td>
<td>3.1</td>
<td>1.42</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>8:2</td>
<td>687</td>
<td>4.0</td>
<td></td>
<td>90</td>
<td>3.5</td>
<td>1.6</td>
<td></td>
<td></td>
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<tr>
<td>7:3</td>
<td>687</td>
<td>5.0</td>
<td></td>
<td>130</td>
<td>5.1</td>
<td>2.3</td>
<td>610</td>
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<tr>
<td>6:4</td>
<td>687</td>
<td>5.0</td>
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<td>120</td>
<td>4.7</td>
<td>2.1</td>
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<td>(I+C):SE variation</td>
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<tr>
<td>9:1</td>
<td>687</td>
<td>3.5</td>
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<td>130</td>
<td>5.1</td>
<td>2.3</td>
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<tr>
<td>8:2</td>
<td>687</td>
<td>5.0</td>
<td></td>
<td>140</td>
<td>5.5</td>
<td>2.5</td>
<td></td>
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<tr>
<td>7:3</td>
<td>685</td>
<td>7.0</td>
<td></td>
<td>160</td>
<td>6.3</td>
<td>2.9</td>
<td>630</td>
<td></td>
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<tr>
<td>6:4</td>
<td>683</td>
<td>4.0</td>
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<td>80</td>
<td>3.1</td>
<td>1.4</td>
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<tr>
<td>Electrolyte: SMA</td>
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<tr>
<td>(I+C):SE=7:3</td>
<td>686</td>
<td>7.5</td>
<td></td>
<td>150</td>
<td>5.9</td>
<td>2.7</td>
<td>630</td>
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<td>(with I:C=7:3)</td>
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thermodynamically calculated theoretical voltage. The polarisation characteristics of various SMV based cells, differing in cathode composition I:C, are shown in Figure 6.4. The current drain for the drop in voltage of 0.4V is about 2 to 5 mA, with the composition I:C = 7:3 giving maximum current of 5 mA. The discharge characteristics with the current density of 50 μA/cm² for these cells are shown in Figure 6.5. From figure, it is clear that cathode of composition I:C = 7:3 gives higher discharge capacity and energy. The cathode of composition 6:4 also gives current and energy equal to that of 7:3, but this cathode pellet is highly brittle and is not suitable for practical use. Hence, the cathode I:C = 7:3 is found to be the best and it is fixed for further studies.

In the second step, the cells differing in cathode compositions (I+C):SE are studied with I:C = 7:3 and SE = SMV. The parameters of these cells are listed in Table 6.3. The OCV of the cell with (I+C):SE = 7:3 is found to be 687mV and that of 7:3 is 685mV. In Figures 6.6 and 6.7, the polarisation and discharge characteristics of these cells are shown. All these cells exhibit almost similar polarisation characteristics and gives around 5mA current. The cell with cathode composition (I+C):SE = 7:3 exhibits excellent discharge characteristics with the energy density of 2.9 Whr/kg (refer Table 6.3). Thus, the addition of SE
Fig. 6.4 Polarisation characteristics for the cells with IC cathodes in SMV system.
Fig. 6.5 Discharge characteristics for the cells with I+C cathodes in SMV system.
Fig. 6.6 Polarisation characteristics for cells of (I+C)+SE cathodes in SMV system.
Fig. 6.7 Discharge characteristics for cells with \((I+C) + SE\) cathodes in SMV at a discharge rate of 50 \(\mu\text{A/cm}^2\).
Improves the performance of the battery appreciably and energy density of this cell is high compared to the cells of other cathodes.

From these studies, it can be seen that the cathode of composition 7:3 is the best. Similar cells of cathode composition $(I+C):SE = 7:3$ are fabricated and their discharge characteristics at different discharge rates are studied. The discharge profiles of these cells are shown in Figure 6.8. The discharge capacity of the cell at different discharge rates are almost equal, which shows that the present battery is stable for variations in current drains in the studied range.

With the best cathode composition, $(I+C):SE = 7:3$, the study of cells of SMA glass as solid electrolytes are undertaken. Similar cells with SMA glass as solid electrolyte are fabricated and their performance is studied. The results of these studies are summarised in Table 6.3. The OCV of the SMA based cell is found to be 683mV, which is almost equal to the OCV obtained for the SMV based cells. In Figures 6.9 and 6.10, the polarisation and discharge characteristics (at different discharge rates) are shown respectively. The current drain for the drop in voltage of 0.4V for the present SMA based cell is 7.5mA. The SMA based cell also exhibits discharge profiles similar to SMV based
Fig. 6.8 Discharge curves for different current drains in SMV based cells for \((I+C) : SE = 7:3\) cathode.
Fig. 6.9 Polarisation characteristics for cell of (I+C):SE = 7:3 cathode in SMA based cell.
Fig. 6.10  Discharge characteristics at different current drains for (I+C):SE = 7:3 cathode in SMA based cell.
cells, proving its stability for the different current drains in the studied range. The energy density of the cell is about 2.7 Whr/kg.

6.6.1 Cell Performance

In the above section, the results for the set of primary cells were presented. In this section, the battery performance is analysed based on results of polarisation and discharge characteristics, temperature and time dependence of OCV of the cells.

Polarisation Characteristics

In the polarisation characteristics of the above cells, initially, the voltage is independent up to a certain drain current and thereafter it starts decreasing. The drop in voltage of the cell is due to polarisation by the following factors, (1) Ohmic or iR drop in electrolytes and electrodes and (2) Nucleation and crystallisation process at the electrode/electrolyte interface. During low current drain these factors are insignificant and the terminal voltage is almost constant. At high current drains, the ohmic drop is of the order of the terminal voltage. Further, high current drain depletes electroactive material at electrode/electrolyte interfacial area and increases the cell resistance.
Hence, voltage of the cell decreases at high current drain.

The cells were able to provide high voltages up to a current drain of nearly 1mA and after that voltage falls off due to the above mentioned factors. This is mainly due to the iR drop, nucleation at the electrode / electrolyte interface and depletion of electroactive materials.

Discharge Characteristics

The discharge characteristics of the cells exhibit a sudden drop in terminal voltage, then a gradual decrease in the voltage and finally a steep fall in the voltage. The initial fall is due to the electrode process mentioned earlier. In the second region, during discharge, the cell reaction results in the formation of AgI layer at the cathode/electrolyte interface. At ambient temperature, the resistance of AgI is high when compared to the internal resistance of the cell. Hence, the iR drop across the layer is more and therefore the formation of AgI layer decreases the terminal voltage. As the discharge proceeds, the thickness of the AgI layer increases, which results in the progressive voltage drop across the terminals.

Temperature Dependence of OCV of the Cells

The variation of OCV with temperature for the cells
with different cathode materials are shown in Figure 6.11. The OCV of the cells increases with temperature. The variation of OCV with temperature decreases progressively for cells made up of Iodine, I+C, and (I+C)+SE cathodes. Thus, the addition of graphite and solid electrolyte not only improves the polarisation and discharge characteristics of the batteries but also stabilises the cells to possess uninterrupted constant voltage source in the tested temperature range 30°C-70°C.

Time Dependence of OCV of the Cells

The fabricated batteries are stored in dry ambient condition (at 30°C) and the OCV of the cells is measured at regular intervals. The time dependence of the OCV of the cell up to one year is given in Figure 6.12. The shelf life of the battery with iodine alone as cathode is very poor. The tarnishing action of iodine molecule with the electrolyte and other parts of the cells lead to the decrease in shelf-life of the battery. The addition of graphite (C) and solid electrolyte (SE) to the cathode reduces the above mentioned effects and stabilises the cells. But, still there is a non-negligible drop in the OCV of the cell, reducing its shelf-life.
Fig. 6.11 Temperature dependence of OCV of the cells for different cathode composition. (1) I+C, (2) I+C+SE (3) I+C+SE+TMAI and (4) I+C+SE+TBAI.
Fig. 6.12 Time dependence of OCV of the cells for different cathode composition. (1) I, (2) I+C, (3) I+C+SE (4) I+C+SE+TMAI and (5) I+C+SE+TBAI.
6.6.2 Cells with Alkyl Ammonium Iodide Cathodes

In order to improve the performance of these cells, the other cathode materials are experimented. B.B. Owens et al. [20] have suggested that some alkyl ammonium iodides may react with AgI to form conductive compounds at ambient conditions and reduce the activity of the iodine. On the similar grounds, in order to improve the stability of the present cells under study, the addition of Tetra Alkyl Ammonium Iodides (TAAIs) to the (I+C):SE cathode is considered. The battery configuration of these cells are given below

\[
\text{Ag+SE} / \ 	ext{Solid Electrolyte} / \ [(I+C)+SE]+TAAI \quad 1:1 / \ 	ext{SMV or SMA} / \]

where, Alkyl (A) = Methyl (M) or Ethyl (E) or Butyl (B). With \((I+C):SE = 7:3\) and \(I:C = 7:3\). Set of similar cells were fabricated with various alkyl ammonium iodides in the weight ratio, \([(I+C)+SE]:TAAI = 9:1\).

**OCV: Temperature and Time Dependence**

Table 6.4 summarises the results for cells of SMV and SMA solid electrolyte systems respectively. The OCV of the SMV based cells are found to be 675mV, 673mV and 660mV respectively for batteries with TAAI = TMAI, TEAI and TBAI.
<table>
<thead>
<tr>
<th>Electrolyte: SMV</th>
<th>Electrolyte: SMA</th>
<th>[(I+C)+SE]</th>
<th>[I+C] variation</th>
<th>[I+C] variation</th>
<th>[I+C] variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMAI-9:1</td>
<td>TMAI-9:1</td>
<td>TMAI-9:1</td>
<td>TMAI-9:1</td>
<td>TMAI-9:1</td>
<td>TMAI-9:1</td>
</tr>
<tr>
<td>TBAI-9:1</td>
<td>TBAI-9:1</td>
<td>TBAI-9:1</td>
<td>TBAI-9:1</td>
<td>TBAI-9:1</td>
<td>TBAI-9:1</td>
</tr>
<tr>
<td>675</td>
<td>675</td>
<td>673</td>
<td>660</td>
<td>660</td>
<td>657</td>
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<tr>
<td>652</td>
<td>656</td>
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<td>650</td>
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</tr>
<tr>
<td>1.8</td>
<td>1.8</td>
<td>0.9</td>
<td>0.7</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>4.0</td>
<td>4.2</td>
<td>2.0</td>
<td>1.6</td>
<td>2.4</td>
<td>1.9</td>
</tr>
<tr>
<td>102</td>
<td>106</td>
<td>50</td>
<td>40</td>
<td>60</td>
<td>47</td>
</tr>
<tr>
<td>9.0</td>
<td>10.0</td>
<td>50</td>
<td>37.0</td>
<td>60</td>
<td>42.0</td>
</tr>
</tbody>
</table>

Table 6.4: Cell parameters of SMV and SMA glassy electrolytes studied at room temperature (30°C) with TAI cathodes.
While, the OCV of the SMA based cells are found to be 670mV, 660mV and 657 mV respectively. The OCV is reduced compared to the cells of [(I+C)+SE] cathodes in both the systems. The temperature dependence of OCV of these cells is shown in Figure 6.11. From figure, it is clear that the variation of OCV, for cells with TMAI and TBAI, is very less compared to the other cells. The above observations are promising for these batteries to possess high temperature shelf life and also an uninterrupted constant voltage source in the tested temperature range 30°C - 70°C. The OCV verses time for these batteries are shown in Figure 6.12. For a storage period of one year, the OCV values drops only by 15 mV and this shows that these cells have excellent stability and long shelf life.

Polarisation Characteristics

Figures 6.13 and 6.14 show the polarisation characteristics of the cells with TAAI cathodes in SMV and SMA systems respectively. The current drain that could be obtained from these cells progressively improves by the addition of TMAI, TEAI and TBAI to the cathode in the same order. These cells can be used up to 1-5 mA without any serious polarisation. The drain current for the drop in OCV of up to 400mV are 9mA, 16mA and 37mA respectively for cathodes of TMAI, TEAI and TBAI in SMV cells and 10mA, 20mA
Fig. 6.13 Polarisation characteristics for [(I+C)+SE]+TAAI cathodes in SMV based cells.
Fig. 6.14 Polaronisation characteristics for [(I+C)+SE]+TAII cathodes in GmF based cells.
and 47mA respectively in SMA cells. The improvement in polarisation characteristics of these cells are attributed to less iR drops even at higher current densities compared to cells of (I+C)+SE cathodes which may be due to the formation of less resistive complexes than AgI [20].

Discharge Characteristics

The discharge profiles of cells with TAAI at constant current density of 50μA/cm² is shown in Figures 6.15 and 6.16 for SMV and SMA solid electrolytes respectively. The discharge characteristics of these cells show less discharge capacity when compared to the cells without TAAI in both SMV and SMA solid electrolytes cells. The use of alkyl ammonium poly iodides may yield better discharge profiles. Taking into consideration of the long shelf life, polarisation and discharge characteristics, only these cells provide us a reliable battery performance of longer stability.

6.7 SUMMARY AND CONCLUSIONS

The highest conducting composition of the glass in SMV and SMA glassy systems are used as solid electrolytes for the fabrication of solid state batteries. The primary cells of varying cathode compositions have been fabricated and studied. High OCV of around 687 mV to 650mV are obtained
Fig. 6.15 Discharge characteristics for the \([(I+C)+SE]+TAAI\) cathodes in SMV based cells at 50 \(\mu\)A/cm\(^2\).
Fig. 6.16 Discharge characteristics for the [(I+C)+SE]+TAAI cathodes in SMA based cells at 50 μA/cm².
for these cells, which suggests that the fabricated batteries are suitable for electrochemical applications of commercial interest. Our results on the cells of varying cathode composition indicates that the battery performance is very sensitive to the composition of the cathode and the present study is very helpful to choose proper composition of the cathode constituents. The set of battery systems, studied, provides current drain of about 5 to 8 mA and energy density of about 0.5 to 3.0 Whr/kg. The stability of these cells are improved appreciably by the addition of alkyl ammonium iodides to the cathode structure. Further, the polarisation characteristics of these cells are also improved by the addition of TAAI to the cathodes.

The present study indicates that the batteries based on SMV and SMA solid electrolytes are suitable for low power device applications. The parameters of the production type batteries are expected to be still better, in view of the fact that the present results are obtained from the hand made laboratory cells.
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