CHAPTER 5

SOLID STATE BATTERIES

5.1. Introduction

Electrochemical systems such as batteries using aqueous electrolytes were not suitable for their use in the biomedical devices, electronic devices needing memory backup and other consumer oriented applications [1]. As early as the turn of this century, it was recognized that certain compounds in the solid state could function as electrolytes and several studies have been done using these solid electrolytes in the electro chemical cell. In recent years, considerable progress has been made in the development of practical solid state batteries as energy sources. The historical development and some recent advances in this field of solid state battery research have been reviewed by various authors [2-10].

One of the areas of research currently under great interest has been in the application of solid electrolytes to solid state batteries. A solid state battery will be defined as one in which anode, electrolyte and cathode are solids. Solid State Batteries offer some attractive advantages over their liquid counterparts. They are inherently robust, spill proof and usually non-corrosive. They are compact and well suited to miniaturization and the ability of the component to stay in position can do obviate the need for separators, membranes and/or diaphragms which add to the mass and volume of liquid systems without producing concomitant increase in energy and power. Thin film configuration can be used and sometimes these can be formed into unusual shapes that fit them for specialized applications. They can perform adequately over wide temperature ranges which are highly desirable for military and other uses [11].

The magnitude of the required current density depends upon the application ranging from few micro ampere cm^{-2} for heart pace makers to several tenth of ampere cm^{-2} for traction batteries [12]. The current flow leads to potential drop due to ohmic effects and interfacial polarization. Thus, it is in battery applications that the electrolyte resistivity and the electrode- electrolyte interface phenomena assume real significance. In general, an inherent disadvantage of solid state batteries is that interfacial contact may be poor. The solid-solid interface will not accommodate readily volume changes when a current flow through the interface. These volume changes produce stresses in the interface and eventually a loss of contact between the electrode and the electrolyte occurs. So, when a solid electrode is employed in conjunction with a solid electrolyte, electrode polarization is almost inevitable at high current densities.

A significant development in the solid state battery field was the discovery of highly conductive electrolyte material MAg_4I_5 ($M=NH_4$, Rb and K) by Bradley and Greene [13] and Owens and Argue [14] having a conductivity of about 0.2S/cm. The commercialization of silver solid state batteries was directed towards practical application, where reliability and long shelf- life are desired. Their use is limited to specialized devices only and in all probability, the low voltage, limited rechargeability and high cost are major factors for pursuing other solid state batteries based on lithium solid electrolyte. However, the research effort in analyzing their electrochemical behavior and fabrication process was helpful in developing the present day rechargeable, lithium ion and lithium polymer batteries [5].

5.2. Different types of solid State Batteries

The batteries can be divided into two main groups depending on their applications. (1) Cells for low energy purpose, with low current density (2) Cells for high energy purpose, with greater current densities.

In certain applications, a very long shelf life, a small size and low weight are the main requirements for a cell while the attainable power and low costs are of less importance. These types of cells are applied in pacemakers, electronic watches, automatic exposure cameras etc. In this case, the self discharge of the cell must be as low as possible. Different types of solid state batteries are discussed here.

5.2.1. Lithium primary cells

The solid state battery which has had the greatest commercial success is the primary lithium based cell, because this metal is strongly electropositive, high thermal stability, low rate of self-discharge (shelf life of 5-10 years), the ability to operate over a wide range of environmental condition (temperature, pressure and acceleration), high value of emf and energy densities (0.3-0.7Whcm^{-3}). Limitation associated with this solid state battery includes low power capability due to high impedance of most of the lithium solid electrolytes. Many of the lithium based cells have been reviewed [15-18].

Commercially available lithium/iodide batteries have a solid anode of lithium and a poly phase cathode (poly-2-vinyl.pyridine) which is having 90% by weight of iodine. The discharge reaction is

$$2Li + P2VP.nI_2 \rightarrow P2VP.(n-1)I_2 + 2LiI$$

This cell has an open circuit voltage of 2.8V and electrolyte conductivity of 6.5×10^{-7} S/cm at 25°C and an energy density of 100-200 Whkg^{-1}. Such batteries are used in cardiac pacemakers, operating at 37°C, have an extended battery lives up to 10 years for 120-250 mAh capacities.

The cells of the type $Li/LiI\text{-}Al_2O_3/PbI_2$ are recommended for low rate operations and particularly suited for applications requiring long life under low drain or open circuit conditions. A mixture of PbI_2+Pb or $PbI_2+PbS+Pb$ has been used and a new system under development utilizes a mixture of TiS_2+S or As_2S_3 which increases the energy density. The solid electrolyte is a dispersion of LiI and LiOH with alumina have a high conductivity of 10^{-4} S/cm at 25°C [15]. The discharge properties of these solid state batteries are characterized by an OCV of 1.9 V and an energy density of 75-150Wh/kg used in pacemaker power sources (manufactured by Duracell International) and CMOS memory applications. The cell of the type $LiI/LiI\text{-}Li_4P_2S_7/TiS_2$ have an ionic conductivity of 2×10^{-3} S/cm at 25°C have an OCV of 2.5Vand energy density of 150-200 Wh/kg. Its application is mainly in power sources for electronic computers, such as CMOS memory back-up and are commercially available are design by XR2025HT by the Eveready Battery Company [19]. The $Li/LiI(SiO_2,H_2O)/Me_4NI_5+C$ cells are use in cardiac pulse generators and exhibited a voltage of 2.75V and an energy density of $0.4Whcm^{-3}$. The cathode is a mixture of carbon and tetra methyl ammonium pentaiodide (Me_4NI_5) [20].

5.2.2. Silver based cells

The first commercial solid state battery was manufactured at the end of 1960s by Gould Ionics using $RbAg_4I_5$ electrolyte, $Ag/RbAg_4I_5/I_2+C$. An essential constraint of any cell system is that the active component must not react with the electrolyte either directly or by electrolytic action. Free elemental iodine reacts with $RbAg_4I_5$, degrading it to poorly conducting phases. To avoid this process, a cell was assembled with another iodine based

RbI_3. (Ag/ $RbAg_4I_5$/RbI_3+C), which has an emf of 0.66V at 25°C and a theoretical energy density of 48Whkg^{-1} [9]. Takahashi and Yamamoto [9] proposed the solid state battery in a thin film configuration Ag/Ag_3SI/I_2,C. The open circuit voltage at 25°C was 0.687V with a reported ionic conductivity of 98.9 percent. Currents of about 1mA/cm^2 were obtained at 29°C. The performance of the cell was limited by the decomposition potential of the electrolyte which resulted in the electrolyte being thermodynamically incompatible with I_2 as cathode [19]. The high conductivity of the electrolyte 0.26 S/cm at 25°C permits the cell discharge at much higher current drains than those available with LiI based cells. Another type of silver solid state battery is based on AgI_4AsO_4 electrolyte and iodine–phenothiazine complex cathode (Ag/$Ag_7I_4AsO_4$/ I_2-Ph) performs well in terms of stability and performance [21]. The cell of the type Ag/$RbAg_4I_5$/Me_4NIn,C have shown promise in terms of discharge capabilities at temperatures between -40°C to +71°C have higher energy density and rate capability [22].

5.2.3. Copper based cells

Only a few promising types have been reported based on Cu^+ ion conductors. The cell $Cu_{(s)}$/Cu^+ conductors$_{(s)}$ / $Cu_xS_{(s)}$ with x=1.8 was introduced by Lazzari et. al., (1975) [23]. The use of iodine or an iodine based cathode was impossible because of the deterioration of the electrolyte. Takahashi and Yamamoto (1977) reported the following cell Cu/ $7CuBr.C_6H_{12}N_4CH_3Br$/S (or Se or Te) has an open circuit voltage of 0.373V using Se as the cathode and energy density of 4.5Whkg^{-1} at current densities of 60-150μAcm^{-2}. The feasibility and reversibility was demonstrated for the cell of the type $Cu_{.4}TiS_2$/$7CuBr.C_6H_{12}N_4CH_3Br$/$Cu_{8}TiS_2$ [9] with an emf of 0.5V and well over a hundred cycles were demonstrated. Another cell utilized NN′-dimethyltriethylenediamine dibromide-copper (I) bromide double salt as the copper ion conductor. The cell $Cu/47CuBr.3C_6H_{12}N_22CH_3Br/Cu_{1\,8}S$ had an emf of 0.47V. Similar OCV has been achieved using TiS_2 as the cathode [24]. The cell based on TiS_2 cathode of the type showed very promising results. The rechargeable cell (Cu,X/X/TiS2,C,X) where X= $Rb_4Cu_{16}I_7Cl_{13}$ was reported to have emf of 0.57V and yielded a current of several tens of microamperes without severe polarization, with one hundred cycles have been achieved without appreciable deterioration [25]. The Cu^+ based cells also suffer from low cell voltage and energy density and have a great cost advantage over expensive silver salts.

5.2.4. Sodium Sulphur Batteries

The sodium sulphur systems operate at elevated temperatures, using sodium cation crystalline electrolyte (Na β-alumina or NASICON) [26,27]. The cell can be depicted as follows Na_{liquid}/ Na β-alumina/S_{liquid} and C. The electrochemical half cell reaction taking place at the anode and the cathode during discharge are respectively:

$$2Na \rightarrow 2Na^+ + 2e^-$$

$$xS + 2Na^+ + 2e^- \rightarrow Na_2S_x$$

The chemical reaction is generally confined to the formation of polysulfide of composition which varies from Na_2S_5 to Na_2S_3. The working temperature is usually 350°C and energy density of about 200Wh/kg, with an OCV of about 2V, an available current density of about 5-10mA/cm^2 and a life time of several thousand hours over more than 1000 cycles.

5.2.5. Polymeric Batteries

Polymer electrolyte batteries operate at elevated temperatures (60-140°C) and its application as storage batteries for all electric vehicles and operate over several hundred cycles with energy efficiencies of 80%-90%. It uses a thin electrolyte film made of polyethylene oxide (PEO) to separate the lithium electrode from an ion- insertion type electrode such as V_6O_{13}, TiS_2 and V_3O_8 [28]. In many cells, the cathode is a composite and consists of small particles of insertion compound bound together with polymer electrolyte and carbon which improves its electronic conductivity. A cell of this type has a potential of about 2.8V and energy density is in the order of 200Wh/kg and the power density reaching 0.1 W/g. The polymer salt phases transform to resistive phases at lower temperatures and consequently little development has been reported at normal ambient temperatures. Cells have been reported operating at 26°C with MnO_2 cathodes with energy densities in the range 0.1-0.2Whcm^{-3} may be achieved [7].

5.3. Fundamental material properties

It is necessary to understand the fundamental properties of the materials used for fabricating a cell. The important parameter for the electrode material is electronic and ionic conductivity and electromotive force (emf) as a function of the electrode material. The most important parameter for the electrolyte is the ionic conductivity. The chemical and physical compatibility with respect to each other and the interfacial contact properties are also of utmost importance. All these properties will be a function of temperature. This is important especially in solid state batteries, since ionic conductivity increases strongly with temperature compared with liquid electrolytes. The ease of transferring ions between solid phases is also strongly enhanced by raising the temperature.

If the negative electrode material is a metallic compound such as lithium, sodium or silver, the electronic conductivity will usually be more than sufficient for the current densities expected in solid state batteries [1]. The electronic conductivities of the positive electrode materials are not always large enough to be used in electrodes without requiring the addition of carbon. The critical electronic conductivity depends on the thickness and current densities envisage in practical batteries.

It is reported [29] that for the cells having Ag^+ ion conducting electrolytes, a silver anode and an iodine cathode, have highlighted the stability with respect to moisture and iodine diffusion. Many Ag^+ based fast ion conducting glassy solid electrolyte with binary [30-32], ternary [33-35] and quaternary [36-38] systems have been investigated. Although reasonably high capacities have been reported with out any significant polarization effects at low current drains, serious polarization at the cathode-electrolyte interface has been observed at high current drains. The latter lowers the cell capacity and eventually shortens the shelf life. It has been considered that this is due to the electrode- electrolyte polarization effects and the formation of compounds with poor ionic conductivity at the cathode electrolyte interface during the discharge process. In order to reduce these effects and to achieve better cell efficiencies at high current drains, different compositional ratios of cathode, anode and electrolyte have been investigated [29]. It is proposed that through the use of organic semiconductors commonly known as charge transfer complexes (CTC) or organo mineral complexes (OMC), the electronic and ionic conductivity components of the transport process in the cell system at equilibrium can be engineered so that maximum discharge efficiency at high current drain is attained [39]

5.4. Preparation of the cell materials

The battery performance is very sensitive to the chemical compositions of the constituents of the cathode material [29,40,41]. Hence various set of solid state primary batteries have been fabricated using the solid materials prepared with different cathode compositions.

The following solid state primary batteries, with different cathode compositions, have been fabricated and studied systematically in order to estimate the performance of the cells.

[Anode (Ag + SE) / solid electrolyte / Cathode (I_2 + C + SE)+ TAAI]

where Ag is the silver powder, SE is the solid electrolyte, I_2 the iodide, C the graphite and TAAI is the tetra alkyl ammonium iodide (alkyl= ethyl and butyl).

5.4.1. Electrolyte

The electrolyte materials were prepared from analar grade chemicals CdI_2, Ag_2O, V_2O_5 and H_3BO_3 chemicals by the melt quenching technique. Further details of the preparation of the electrolyte are given in chapter 2.

5.4.2. Anode

The choice of the anode for a solid state battery is dependent on the nature of the conducting ion in the electrolyte. In the present investigation, only silver could be used as the anode materials. It is prepared by mixing the silver powder and finely ground powders of electrolyte in 2:1 ratio by weight. The solid electrolyte is added to the silver powder to improve the interfacial contacts. Since silver is readily oxidized, the anode serves as an electron reservoir and hence is the negative terminal of the battery.

5.4.3. Cathode

The different compositions of the cathode compounds are made by varying the weight ratios of the iodide, graphite, solid electrolyte. Cathode materials of the type tetra alkyl ammonium iodide, iodine, graphite and solid electrolyte were also employed. Addition of carbon to the cathode mixture increases the electronic conductivity. The cathode receives electrons from the external circuit and hence is the positive terminal of the electro chemical cell. The addition of SE improves the interfacial effects and the added TAAI will react with AgI and form a better conducting layer or compound to reduce the activity of the iodide at the interface [40,42,43]. The TAAI added cathode compositions were mixed and taken in a crucible and heated to 50-60°C for half an hour and allowed to come to the room temperature before using.

5.4.4. Cell formation

The finely mixed anode material (Ag powder + electrolyte) was first poured into the die and has given a small pressure to make it a layer. On the top of that, the electrolyte material was added and has been given a small pressure. After this the cathode mixture (I_2+C+ electrolyte) was then poured over the electrolyte layer in the die and the three layers were pressed at a pressure of 5 tons/cm^2 to obtain a pellet of a solid state cell of the type Anode/electrolyte/cathode. A set of cells were fabricated with different cathode composition of the type,

(1) Ag/SE/I_2+C+SE (I_2:C= 7:3)

(2) Ag+SE/SE/I_2+C+SE (I_2+C+SE=1:5:1)

(3) Ag+SE/SE/ I_2+C+SE (I_2+C+SE=3:2:2)

(4) Ag+SE/SE/ I_2+C+SE+TAAI) (I_2+C+SE=3:2:2:1)

The typical discharge process of the silver ion conducting, solid state electrolyte cell is shown in Fig.5.1 and the circuit diagram for measuring the polarization and discharge characteristics is shown in Fig.5.2.

5.5. Open-circuit voltage

The first characteristic parameter of the battery is the open-circuit voltage. The electrochemical cell prepared by pressing anode, electrolyte and cathode materials

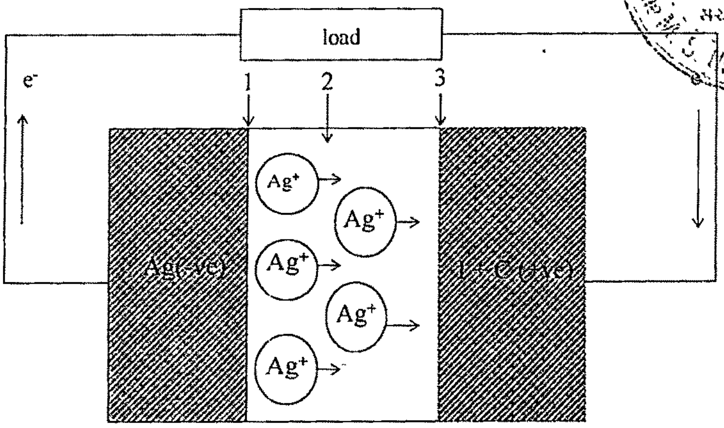

Fig.5.1. Discharge process of silver ion conducting, solid state electrolyte cell.
(1) anode-electrolyte interface (2) silver ion conducting solid electrolyte
(3) cathode-electrolyte interface.

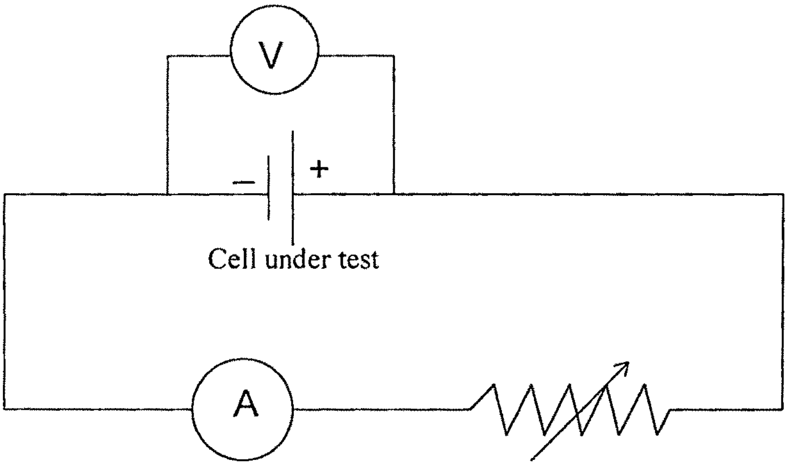

Fig.5.2. The circuit diagram for measuring the polarization and discharge characteristics of a cell.

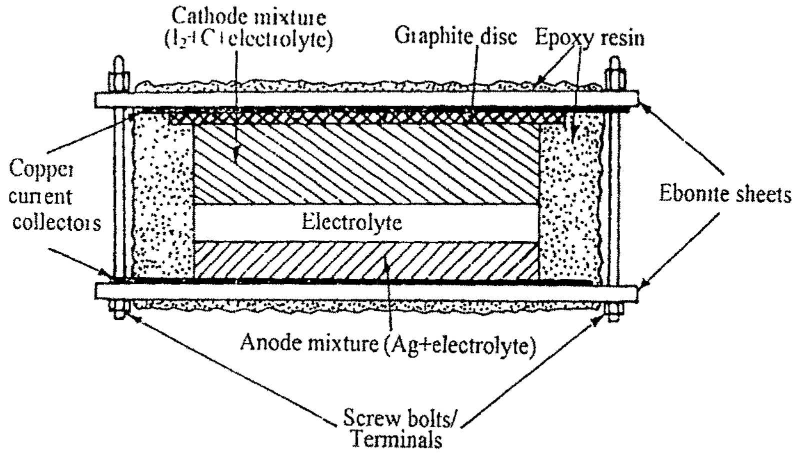

Fig. 5.3. Structure of a solid state battery, ref. [41].

together and on activation the open-circuit voltage (OCV) is measured. The measured OCV of the cell was comparable to the thermodynamically calculated theoretical voltage for the pure AgI and the transport number was determined and is discussed in Chapter 3.

Many workers [5,41] have reported that the solid state cell prepared in the laboratory level were sandwiched between graphite disc and copper foils were used over these two graphite discs as leads. The cell assembly was tightened together immediately after fabrication and sealed with epoxy resin to provide isolation from atmosphere effects as in Fig 5.3. It was reported that the potential of the cell measured remained constant for a period of 6 months. However we are not able to cover and preserve the cell. It is reported that this may be due to very low electronic conductivity of the electrolyte and lack of iodine diffusion into the electrolyte when the cell is inoperative.

Fig.5.4 shows the variation of OCV with temperature. Cell 1 exhibits a large variation of OCV which is due to the high vapor pressure at high temperatures. Thus liberated iodine diffuses into the electrolyte and reduces the stability of the cells at high temperatures. Figure shows the variation of OCV is less with temperature for the cells with TAAI added cathode materials. The low open circuit voltage indicates the reduced activity of iodine in the presence of alkyl group, which leads to longer shelf life of the batteries.

5.6. Polarization studies

The plot of cell voltage against current are usually referred as polarization or performance curve. A typical polarization curve has three regions. Initially there is a rapid fall in cell voltage at low current drain due to electrode polarization. Second is almost linear region,

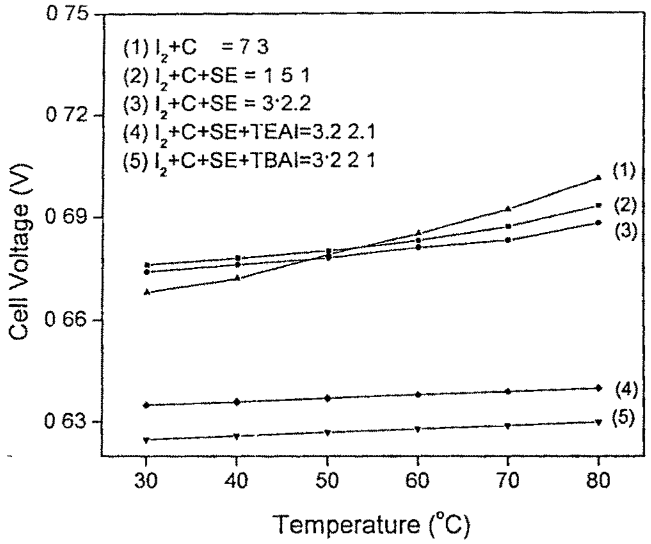

Fig.5.4. Temperature dependence of open circuit voltage of cells made up of different cathode materials.

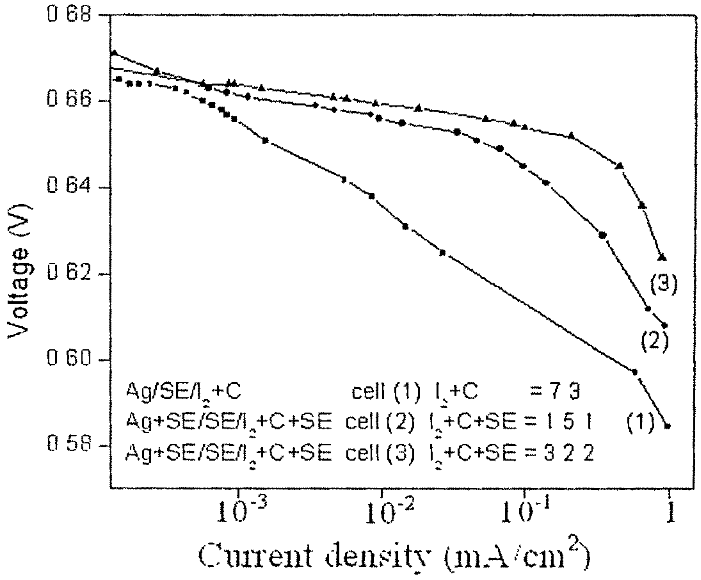

Fig.5.5. Polarizations measurements were made for different cathode composition in the system $xCdI_2$-(100-x) [$2Ag_2O$-($0.7V_2O_5$-$0.3B_2O_3$)] with x=20% CdI_2.

the internal resistance of the cell components causes a further voltage loss (the iR polarization). In the final region at relatively high current drain, the iR polarization is combined with, further electrode polarization caused by depletion of electro active materials at the electrode surfaces [3].

A set of batteries were fabricated with different cathode compositions and the polarizations are examined. The polarizations measurements were made for different cathode compositions in the electrolyte system $xCdI_2$-(100-x) [$2Ag_2O$-($0.7V_2O_5$-$0.3B_2O_3$)] with x=20% CdI_2 is shown in Fig.5.5. Here the variation of cell potential is noted for different current densities. The potentials were noted after 2 minute of connecting each load In the figure, for (cell(1)) the voltage drops suddenly. These polarization losses are mainly due to the bulk resistance and the nucleation at the electrode/electrolyte interface. The polarization characteristics can be improved by using the electrolyte with higher conductivity or reducing the interfacial resistance [43]. This can be seen from the polarization characteristics of cell (2) and cell (3) in which interfacial resistance has been reduced by adding small amount of electrolyte to the anode and cathode. The cell made with the cathode composition I_2+C+ SE= 3:2:2 show the better performance among the other two cells. Hence it is selected for other studies. Fig.5.6 (a) and (b) shows the polarization characterization obtained for other samples made of the electrolyte $20CdI_2$-80[xAg_2O-y ($0.7V_2O_5$-$0.3B_2O_3$)] with x/y ratio 1.75 and of the electrolyte $20CdI_2$-$53.4Ag_2O$-26.6[xB_2O_3-(1-x)V_2O_5] with x=0.8 of the cathode composition $3I_2$+2C+2SE. The polarization characteristics for the cells made with cathode compositions [I_2+C+SE+TAAI =3:2:2:1] are shown in Fig. 5.7. The current drain obtained from the cells is improved progressively by the addition of TEAI and TBAI to the cathode

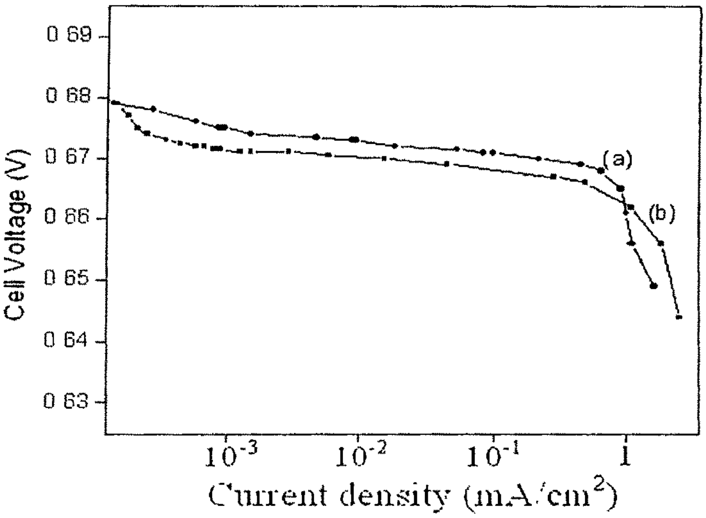

Fig.5.6. (a) Polarization characteristics of the cell using 20CdI$_2$-80[xAg$_2$O-y (0.7V$_2$O$_5$-0.3B$_2$O$_3$)] with x/y ratio 1.75 and (b) the electrolyte 20CdI2-53.4Ag$_2$O-26.6 [xB$_2$O$_3$-(1-x)V$_2$O$_5$] with x=0.8 of the cathode composition 3I$_2$+2C+2SE.

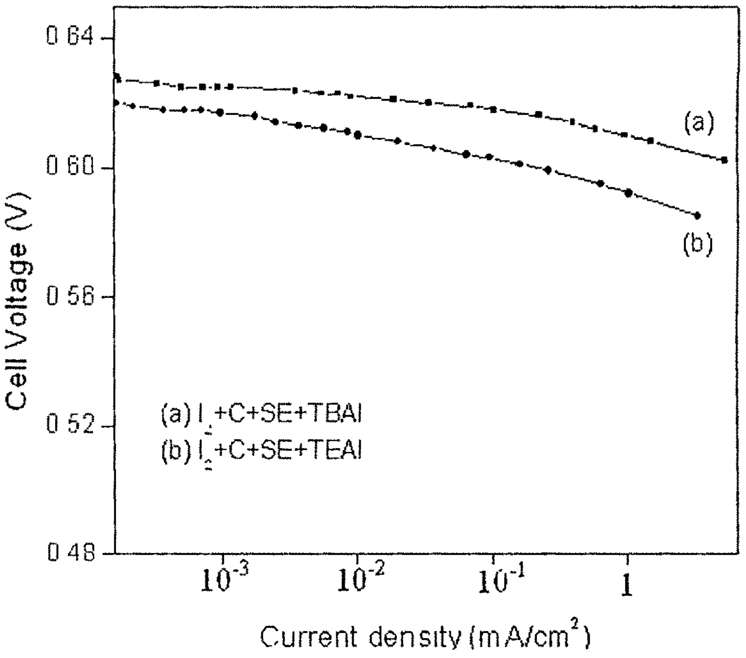

Fig.5.7. Polarization characteristics for the cells made with cathode compositions [I+C+SE+TAAI =3:2:2:1]

composition $3I_2$+2C+2SE.

It is found that the addition of TAAI to the cathode reduces the iodine activity at the electrode/electrolyte interface [41]. At the interface, the TAAI reduces the iodine activity by forming a strong complex $(CH_3)_4NI$, which avoids the tarnishing actions of molecular iodine with the electrolyte and hence increases the specific energy. Also, the iodine activity of the reaction product $[(CH_3)_4N]_2Ag_{13}I_{15}$ is highly conducting and offers good charge transfer continuity [44]. Hence, the improvement in polarization characteristics of these cells is attributed to reduced internal resistance (iR) drop compared with the cell of (I_2+C+SE) cathodes. This is due to the formation of a complex with higher conductivity than AgI [44].

5.7. Discharge Characteristics

The discharge characteristics of a battery are represented by the terminal voltage versus time at a steady discharge current or at a fixed load. Fig.5.8 shows the discharge characteristics of the cells with different cathode composition with a current density of 100μAcm^{-2}. The cell made with the $xCdI_2$-(100-x) [$2Ag_2O$-($0.7V_2O_5$-$0.3B_2O_3$)] with x=20% of CdI_2 doped glassy electrolyte with the cathode composition I_2+C+SE= 3:2:2 displays the best shelf life. The initial drop in the cell potential in the discharge profile can be attributed to the formation of low conducting AgI layer at the cathode-electrolyte interface. Under identical conditions the time taken by the cells to drop to a particular value of the terminal voltage increases from cell (1) to cell (4). This was due to the decrease in the overall cell resistance with change in anodes and cathodes.

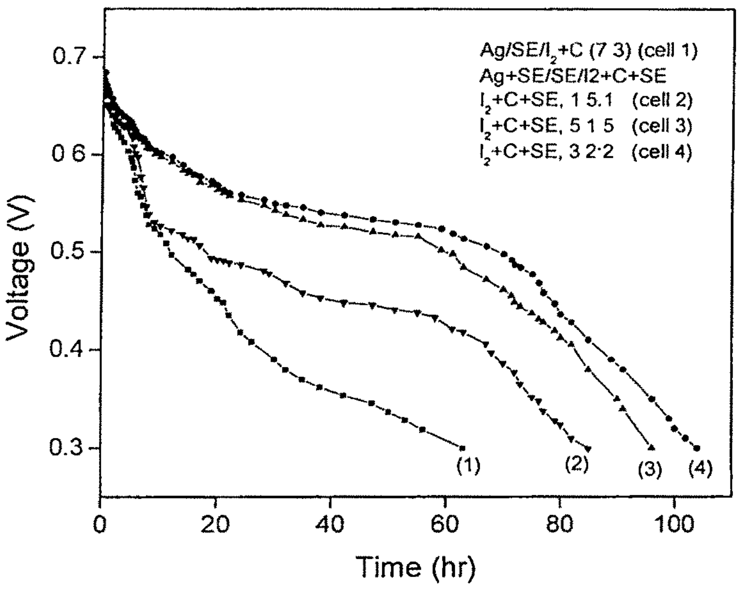

Fig.5.8. Discharge characteristics of the cell made with different cathode compositions of the electrolyte system xCdI$_2$-(100-x) [2Ag$_2$O-(0.7V$_2$O$_5$-0.3B$_2$O$_3$)] with x=20%

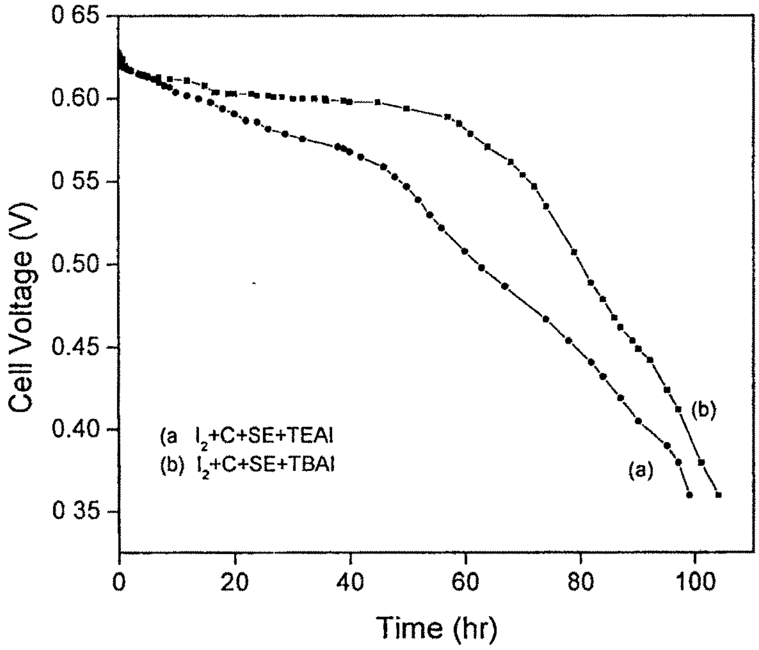

Fig. 5.9. Discharge characteristics of the cell with TAAI added cathode of the electrolyte system xCdI$_2$-(100-x) [2Ag$_2$O-(0.7V$_2$O$_5$-0.3B$_2$O$_3$)] with x=20% CdI$_2$.

Ideally, the internal resistance of a cell should be contributed by the electrolyte impedance only since the materials used in anodes (eg., silver) and in cathode (eg., carbon) are all good conductors and possess negligible resistance. The internal resistance (r) of a cell is defined as the drop in potential (i.e., open circuit voltage minus voltage upon current drawn divided by the current drawn from the cell, $r = \frac{E-V}{I}$, where E is the voltage at zero current drain (OCV), V is the voltmeter reading and I is the current in the circuit.

In cells employing solid electrolytes, the contacts between anode/electrolyte and cathode/electrolyte are not as good as the contacts in cells using liquid electrolytes. As silver is consumed during discharge, contact between silver and electrolyte will decrease and hence internal resistance will increase. This in turn will lead to fast drop in cell voltage. The cell in which the anode is purely silver (Fig.5.8 (cell (1)) the voltage decreases faster with time compared to the other cells. Consequently, upon consumption of the silver atoms, the anode electrolyte contact decreases, and there by increases the internal resistance of the cell.

The interface between a solid anode and a solid electrolyte during discharge has been examined by Jow and Liang [45,46] for a $Li/LiI(Al_2O_3)/PbI_2,Pb$ solid state galvanic cell. It was found that one of the failure modes during discharge of the cell was attributable to the loss of interface contact between the lithium anode and the $LiI(Al_2O_3)$ solid electrolyte. The loss was the result of void formation at the interface during discharge. In the present series, it has been shown that the anode composition can influence the anode/electrolyte interface and therefore contribute to the high internal resistance of the cell.

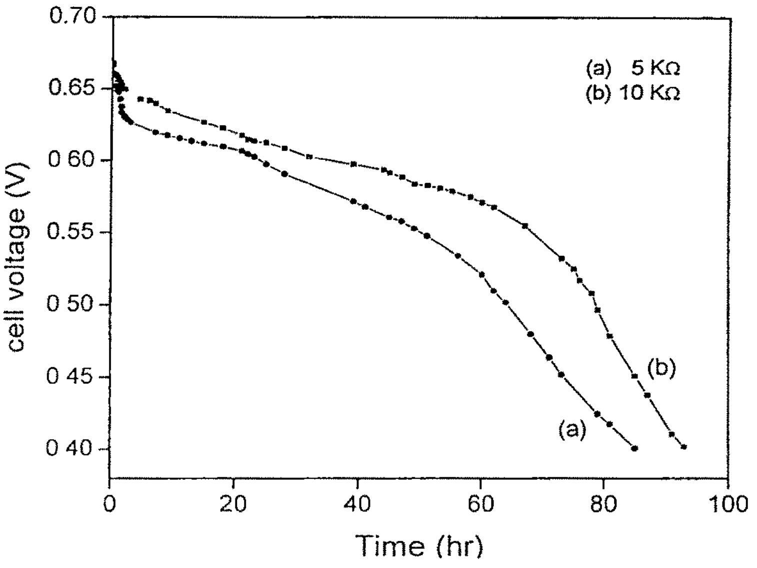

Fig.5.10. Discharge curves under different load conditions for the electrolyte system $20CdI_2$-80[xAg_2O-y ($0.7V_2O_5$-$0.3B_2O_3$)] with x/y ratio 1.75.

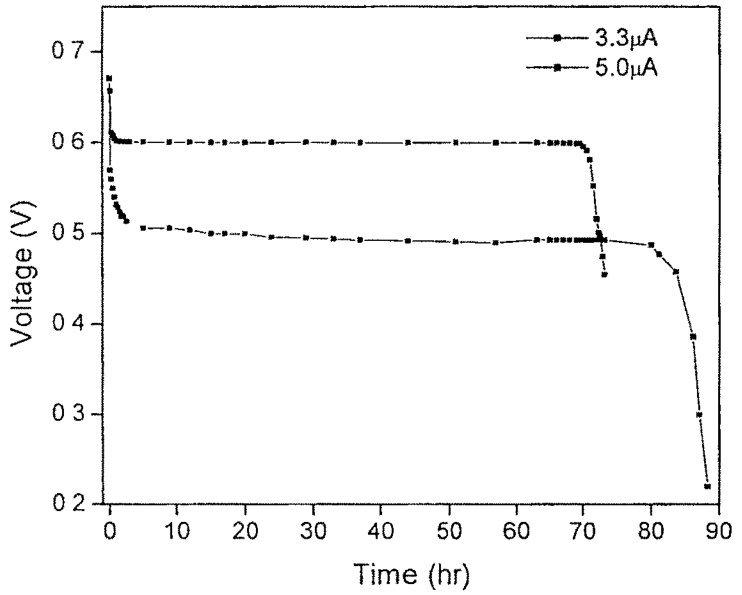

Fig. 5.11. Discharge plot for different values of discharge currents is seen for the cell system with electrolyte composition $20CdI_2$-$53.4Ag_2O$-26.6[xB_2O_3-(1-x)V_2O_5] with x=0.8

Table 5.1

Cell parameters measured at room temperature for batteries made up of CdI_2-Ag_2O-V_2O_5-B_2O_3 glassy electrolyte compound studied with different cathode materials.

1. Different load and different drain currents

Parameters	Load (kΩ)		Current drain (μA)	
	10	5	3.3	5.0
Open Circuit voltage (V)	0.683	0.681	0.682	0.684
Cell weight (g)	1.1	1.1	1.0	1.0
Electrolyte diameter (cm)	1.0	1.0	1.2	1.2
Discharge time from OCV to 0.4V (h)	93	85	89	72
Discharge capacity (mAh)	9.3	8.5	0.45	0.24
Energy density (Wh/kg)	5.41	4.79	0.23	0.15

2. Different cathodes

Parameters	I_2+C (7:3)	I_2+C+SE (5:1:5)	I_2+C+SE (1:5:1)	I_2+C+SE (3:2:2)
Open circuit voltage (V)	0.679	0.682	0.684	0.684
Cell Weight (g)	1.0	1.0	1.0	1.0
Electrolyte diameter (cm)	1.2	1.2	1.2	1.2
Discharge time from OCV to 0.3V (h)	63	85	96	104
Discharge capacity (mAh)	6.3	8.5	9.6	10.4
Energy density (Wh/kg)	2.71	4.1	5.6	6.24

3. Cathodes with TAAI

Parameters	TEAI	TBAI
Open Circuit voltage (V)	0.675	0.681
Cell weight (g)	1.1	1.1
Electrolyte diameter (cm)	1.0	1.0
Discharge time from OCV to 0.36V(h)	104	99
Discharge capacity (mAh)	10.4	9.9
Energy density (Wh/kg)	6.45	5.84

The cell parameters measured for all the cells made with this glassy electrolyte and different cathode materials are summarized in the Table.5.1. Another way of improving the discharge characteristics was to avoid the formation of AgI at the cathode electrolyte interface (which was not possible since it was the product of the reaction) or to convert the reaction product into a high conducting compound. The polarization point of the cells with TAAI added cathode increases and the open circuit voltage decreases. The decrease in OCV was due to the reduced iodine activity and the increase in the polarization point was due to the fact that as soon as AgI was formed it reacts with TAAI to form high conducting compound. The discharge characteristics of the cell with TAAI added cathode materials exhibit better discharge performance and is shown in Fig.5.9. The discharge curves under different load conditions are shown in Fig.5.10 for the electrolyte system $20CdI_2$-$80[xAg_2O$-$y\ (0.7V_2O_5$-$0.3B_2O_3)]$ with x/y ratio 1.75. The discharge plot for different values of discharge currents is seen for the cell system with electrolyte composition $20CdI_2$-$53.4Ag_2O$-$26.6\ [xB_2O_3$-$(1-x)V_2O_5]$ with x=0.8, Fig.5.11.

When a cell is discharging continuously, the AgI content formed at the cathode-electrolyte interface, progressively increases, and at the anode, silver is consumed continuously, resulting the contact between silver and the electrolyte will decrease thereby increasing the internal resistance of the cell and causing an internal voltage drop. The internal resistance of the cell is found to increase with time during discharge. This can be explained on the basis of the direct cell reaction.

At anode: $Ag \rightarrow Ag^+ + e^-$

At cathode: $I_2 + 2e^-$(from load circuit) $\rightarrow 2I^-$

$2Ag^+$ (through electrolyte) $+ 2I^- \rightarrow 2AgI$ (at cathode)

5.8. Summary

The glasses of high conducting compound of the electrolyte system CdI_2-Ag_2O-V_2O_5-B_2O_3 is used for the fabrication of solid state cells. The primary cells are fabricated using the electrolyte system CdI_2-Ag_2O-V_2O_5-B_2O_3 with varying cathode compositions. The high open circuit voltage in the range 0.68 V is obtained for cells made up of CdI_2-Ag_2O-V_2O_5-B_2O_3 electrolyte material suggests that the fabricated batteries are suitable for electrochemical applications. The battery performance is very sensitive to the composition of the cathode and the present study assists the choice of the best composition for the cathode constituents. The stability of these cells is improved appreciably by the addition of TAAI to the cathode. Further the polarization characteristics of these cells are also improved by the addition of TAAI to the cathode. A set of solid state cells exhibit OCVs between 0.679 and 0.684 mV, discharge capacity of 0.234 to 10.4 mAh and energy densities between 0.15 to 6.45 Wh/kg. These results suggest that the cells fabricated with this present electrolyte material are suitable for low power ionic device applications that require long shelf life.

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