

Study of $x\text{CdI}_2-(100-x)[2\text{Ag}_2\text{O}-(0.7\text{V}_2\text{O}_5-0.3\text{B}_2\text{O}_3)]$ electrolyte system for application in solid-state primary cells

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Abstract

A new, glassy, solid electrolyte system $\text{CdI}_2\text{-Ag}_2\text{O-V}_2\text{O}_5\text{-B}_2\text{O}_3$ has been synthesized and the composition with high ionic conductivity is used as an electrolyte in a solid-state cell. The silver ion transport number of this electrolyte is nearly unity. The thermoelectric power varies inversely with absolute temperature. The discharge and current–voltage characteristics are examined for different negative and positive electrodes to evaluate the applicability of these cells as power sources for low-energy applications.

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1. Introduction

The search for a new, glassy, solid electrolyte system has increased given the technological need for lightweight, compact power sources that are capable of storing electrical energy. Considerable progress has been made in the development of practical solid-state batteries [1–5]. Such a battery is defined as one in which the negative electrode (anode), electrolyte and positive electrode (cathode) are all solids. The advantages of solid-state batteries over their liquid counterparts are that they are inherently robust, spill-proof, and usually non-corrosive. Moreover, they are compact and well suited to miniaturization and the ability of the component to stay in position can obviate the need for separators, membranes and/or diaphragms that add to the mass and volume of liquid systems without producing a concomitant increase in energy and power [6].

In battery applications, the electrolyte resistivity and electrode–electrolyte interface phenomena assume real significance. In general, an inherent disadvantage of solid-state batteries is that interfacial contact may be poor. So, when a

solid electrode is employed in conjunction with the solid electrolyte, electrode polarization is almost inevitable at high current densities.

Many solid electrolyte systems have been studied to achieve an ionic conductivity that is comparable with that of liquid electrolytes [4,6]. Among the solid electrolyte material studied to date, systems based on silver ions show high ionic conductivity and good stability towards temperature and moisture. The commercialization of silver solid-state batteries has been directed towards practical applications where reliability and long shelf-life are desired. It has been reported [7] that the characteristic parameters are very sensitive to the chemical composition of the cathode material. Many AgI-doped silver oxysalt systems have been studied [4,6] and recently there have been reports [8–10] of a silver oxysalt system with a different dopants other than AgI namely CuI and PbI_2 . The work has demonstrated the feasibility of obtaining high silver ion conductivity and a cost-effective suitable electrolyte system for electrochemical applications. The research discussed here examines the thermoelectric power and performance characteristics of cells prepared with different cathode materials from the system $x\text{CdI}_2-(100-x)[2\text{Ag}_2\text{O}-(0.7\text{V}_2\text{O}_5-0.3\text{B}_2\text{O}_3)]$ where $x=20$ and a modifier-to-former ratio of 2.

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2. Experimental procedure

Analar grade CdI_2 , Ag_2O , V_2O_5 and B_2O_3 chemicals were used for the preparation of the electrolyte system. The chemicals were weighed according to their molecular weight percentage and mixed thoroughly. The resulting mixtures were heated in the temperature range 800–1000 K for 4 h. Each melt was then quenched in liquid nitrogen to form a glass. The glassy nature of the samples was confirmed by X-ray diffraction and differential scanning calorimetry (DSC). The emf method was employed to evaluate the contribution of silver ions in the CdI_2 -doped system. A cell with the configuration Ag, electrolyte|electrolyte| I_2 , C, electrolyte, was used. The silver ion transport number is given by $t_{\text{Ag}^+} = E/E_0$, where E is the open-circuit voltage (OCV) at room temperature and E_0 is the standard emf corresponding to the cell reaction obtained from thermodynamical calculations for the Ag/ I_2 couple. The open-circuit voltage was measured by means of a Keithley Electrometer Model 614.

Thermoelectric power measurements were performed by measuring the potential difference developed between two faces of the sample across which a known temperature gradient was maintained in a cell of configuration Ag (T)|electrolyte|Ag ($T + \Delta T$). For this purpose, all the solid samples were made into circular pellets of 1 cm diameter at a palletizing pressure of 5000 kg cm^{-2} and silver paste was applied on both the faces of the pellet. The pellet was mounted in a sample holder of the thermoelectric power apparatus. The thermoelectric power of the present system was obtained by a differential method, in which the thermo emf across the glass sample was measured at different temperatures, in the 303–373 K, i.e. from room temperature to just below the glass transition temperature. Two matched heaters were mounted along the axis of the two sample holder shafts. The two heaters provide a controlled temperature gradient of $\pm 5^\circ\text{C}$, which was obtained between the sample holders by using auxiliary heaters wound on each of the sample holder shafts. The average of the sample temperature was taken as $(T_1 + T_2)/2$. The temperatures of the two main heaters were measured by means of Cr–Al thermocouples and a high-impedance digital micro voltmeter. The thermoelectric power (θ) values were calculated using the relation:

$$\theta = \frac{\Delta V}{\Delta T} \quad (1)$$

where ΔV is the thermo emf developed across the sample; and ΔT , the temperature difference across the two faces of the sample.

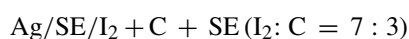
Electrolyte samples from the series $x\text{CdI}_2-(100-x)[2\text{Ag}_2\text{O}-(0.7\text{V}_2\text{O}_5-0.3\text{B}_2\text{O}_3)]$ with $x=20$ and a modifier-to-former ratio of 2 was used to fabricate the solid-state cells. Different cathode compositions were used to evaluate the performance of the cells.

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 for the anode material. It was prepared by mixing the silver powder and finely-ground powders of the electrolyte in a 2:1 ratio by weight. The solid electrolyte was added to silver powder to improve the inter-

facial contacts. Since silver is readily oxidized, the anode served as an electron reservoir.

Cathodes of different composition were made by varying the weight ratios of iodide, graphite, and solid electrolyte. The addition of carbon increases the electronic conductivity.

The finely-mixed anode material (Ag powder + electrolyte) was first poured into a die and a small pressure was applied to form a layer. The electrolyte material was added and a small pressure was applied. Finally, the cathode mixture ($\text{I}_2 + \text{C} + \text{electrolyte}$) was then poured over the electrolyte layer in the die and the three layers were pressed at 5 tons cm^{-2} to obtain a pellet for a solid-state cell of the type; anode|electrolyte|cathode. A series of cells were fabricated with different cathode compositions, namely:



The temperature dependence of the OCV and the polarization and discharge characteristics were examined systematically to estimate the performance of each cell.

3. Results and discussion

The glassy nature of the electrolytes was confirmed by XRD and DSC analysis. The X-ray spectrum for a 20 mol% CdI_2 -doped system and the DSC spectrum obtained for a 30 mol% CdI_2 -doped system are shown in Fig. 1(a) and (b) respectively. The occurrence of silver ion migration and the negligible electronic conductivity of this CdI_2 doped $\text{Ag}_2\text{O}-\text{V}_2\text{O}_5-\text{B}_2\text{O}_3$ system was confirmed by the emf method. The OCV of the cell made from 20 mol% CdI_2 is 0.671 V and is therefore lower than the thermodynamic value for the Ag/ I_2 couple, viz., 0.687 V. The 20 mol% CdI_2 system has a silver ionic transport number of 0.98. All the other samples have silver ion transport numbers close to unity, as shown in Table 1. The occurrence of silver

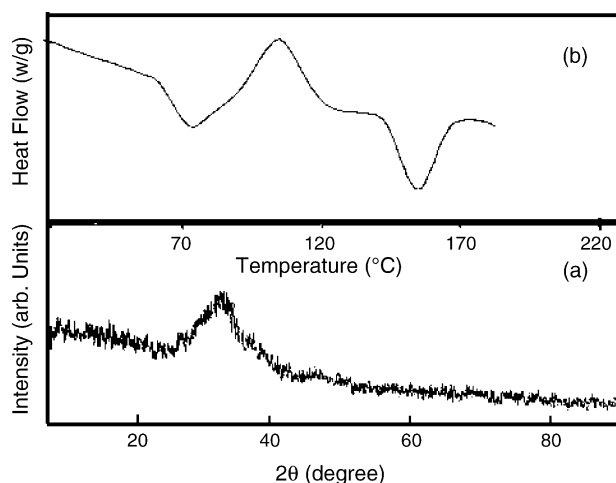


Fig. 1. (a) X-ray spectrum of 20 mol% of CdI_2 -doped system; (b) DSC spectrum of 30 mol% CdI_2 -doped system.

Table 1

Heat of transport $q_{\text{Ag}^+}^*$ obtained from thermoelectric power studies and silver ion transport number obtained from emf method for series, $x\text{CdI}_2-(100-x)[2\text{Ag}_2\text{O}-(0.7\text{V}_2\text{O}_5-0.3\text{B}_2\text{O}_3)]$ with different x values

Composition x	Heat of transport $q_{\text{Ag}^+}^*$	Silver ion transport number t_{Ag^+}
10	0.320	0.96
15	0.345	0.97
20	0.316	0.98
25	0.315	0.98
30	0.314	0.98

ionic conduction in the mixed system $\text{CdI}_2\text{-Ag}_2\text{O-V}_2\text{O}_5\text{-B}_2\text{O}_3$ is quite similar to that in CuI- and PbI_2 -doped systems [8–10]. The silver ion conductivity of the present CdI_2 -doped systems is due to the exchange reaction between CdI_2 and Ag_2O and can be explained on the basis of the Pearson theory of hard and soft acids and bases [11], as discussed elsewhere [12,13].

The thermoelectric power of a super ionic conductor can be represented as

$$\theta = \theta_{\text{hom}} + \theta_{\text{het}} = -\frac{q_{\text{Ag}^+}^*}{eT} + H \quad (2)$$

and

$$H = \frac{1}{e} \left[-S_{\text{Ag}^+} + k \ln \frac{n_{\text{Ag}^+}}{N} + S_{\text{Ag}^+}^{\text{Ag}} \right] \quad (3)$$

where $q_{\text{Ag}^+}^*$ is the heat of transport; N , the number of normal sites per unit volume; $S_{\text{Ag}^+}^{\text{Ag}}$, the partial entropy of Ag^+ ion in silver metal; n_{Ag^+} , the number of Ag^+ ions per unit volume; S_{Ag^+} , the transport entropy of the silver ion; H , the correction term due to the electrode contact potential. In the thermo cells with reversible electrodes, such as the ones studied here, H is assumed to be temperature independent [14,15]. The thermo emf values observed during the thermoelectric power studies of all the samples are found to be negative when the hot end is connected to the positive polarity of the voltmeter. This means that the charge on the mobile species is positive. The variation of thermoelectric power ($-\theta$) versus $10^3/T$ for the present electrolyte system with different x values is given in Fig. 2. The heat of transport ($q_{\text{Ag}^+}^*$) of the mobile species is obtained from the slopes of these curves and is shown in the Table 1. The activation energy for Ag^+ ion migration (calculated from conductivity studies) [12] is comparable with the heat of transport estimated from the thermoelectric power. The heat of transport, which is equal to the static barrier height for ion hopping [16], is therefore expected to approach the activation energy of Ag^+ ion migration. This is in agreement with the theory of Rice and Roth [17] that allows the theoretical estimation of activation energy and thermoelectric power. The formula proposed by these authors is based on the assumption that the ions contained in highly-disordered solids may be considered to be in free-ion state. Thus:

$$-\theta_{\text{hom}} = \frac{\Delta h}{eT} \quad (4)$$

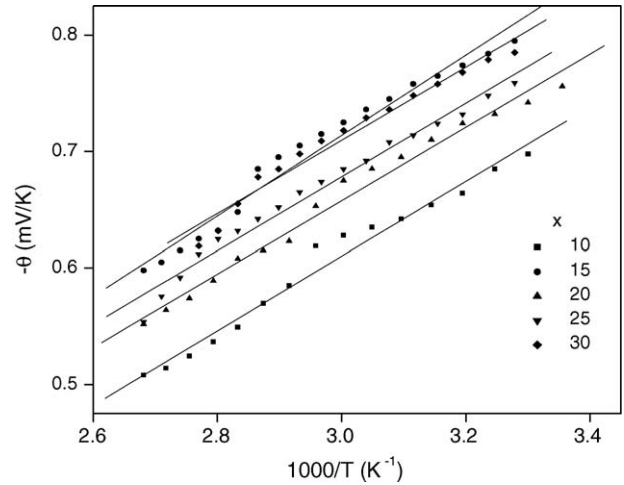


Fig. 2. Thermoelectric power versus inverse of temperature for system $x\text{CdI}_2-(100-x)[2\text{Ag}_2\text{O}-(0.7\text{V}_2\text{O}_5-0.3\text{B}_2\text{O}_3)]$ with different x values.

where Δh is the activation energy of mobile ions,

$$-\theta_{\text{hom}} = \frac{q_{\text{Ag}^+}^*}{eT} \quad (\text{in terms of heat of transport}) \quad (5)$$

$$\Delta h = q_{\text{Ag}^+}^* \quad (6)$$

Eq. (6) leads to the conclusion that in the case of highly-disordered solids, the ionic heat of transport tends to be equal to its activation energy. Thus, it can be concluded that the present system is highly disordered and that the results seem to support the theory of Rice and Roth [17,18].

The variation in cell OCV with temperature is presented in Fig. 3. Cell 1 exhibits a large variation in OCV, which is due to the high vapour pressure at high temperatures. Thus, liberated iodine diffuses into the electrolyte and reduces the stability of the cells at high temperature [19].

The plot of cell voltage against current is usually referred as the polarization or performance curve. A typical polarization curve has three regions: (i) a rapid fall in cell voltage at low current drain due to electrometric effects' (electrode

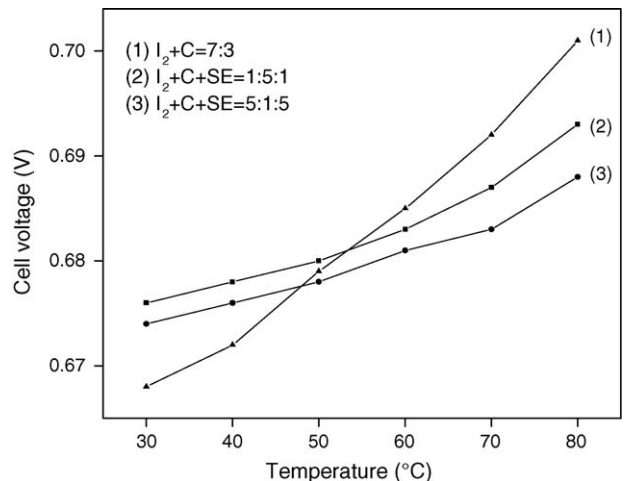


Fig. 3. Variation in OCV with temperature for cell made up of 20 mol% CdI_2 -doped system with different cathode compositions.

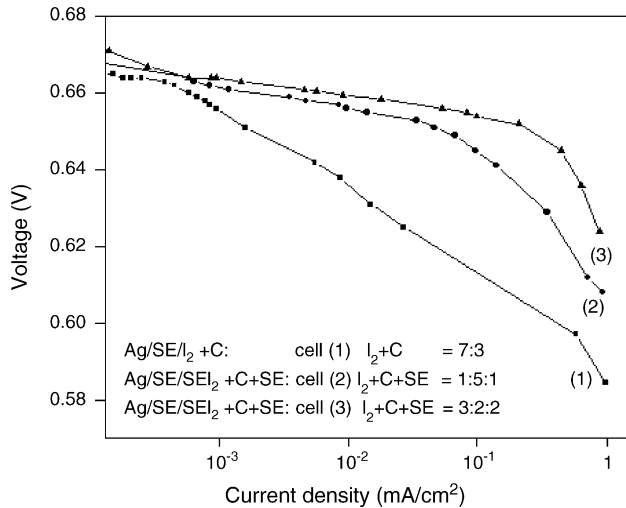


Fig. 4. Polarization characteristics of cells made up of different cathode compositions.

‘polarization’); (ii) an almost linear region during which the internal resistance of the cell components causes a further voltage loss (so-called ‘iR polarization’); (iii) a combination of iR polarization and further electrode polarization (caused by depletion of electroactive materials at the electrode surfaces at high current drain [3]). Current–voltage plots for different cathode compositions in the electrolyte system $x\text{CdI}_2-(100-x)[2\text{Ag}_2\text{O}-(0.7\text{V}_2\text{O}_5-0.3\text{B}_2\text{O}_3)]$ with $x=20\%$ CdI_2 are shown in Fig. 4. Here, the variation in cell potential was recorded of 2-minute intervals for different current densities. The voltage of cell (1) 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 an electrolyte with higher conductivity or by reducing the interfacial resistance [20]. This can be seen from the polarization characteristics of cells (2) and (3), in which the interfacial resistance has been reduced by adding a small amount of electrolyte to both the anode and the cathode. The cell made with the cathode composition $\text{I}_2 + \text{C} + \text{SE} = 3:2:2$ provides the better performance.

The discharge characteristics of cells with different cathode compositions at a current density of $100 \mu\text{A cm}^{-2}$ are given in Fig. 5. The best shelf-life is obtained from the cell made from the $x\text{CdI}_2-(100-x)[2\text{Ag}_2\text{O}-(0.7\text{V}_2\text{O}_5-0.3\text{B}_2\text{O}_3)]$ with $x=20\%$ CdI_2 -doped glassy electrolyte and a cathode composition of $\text{I}_2 + \text{C} + \text{SE} = 3:2:2$. The initial drop in cell potential can be attributed to the formation of a low-conducting AgI layer at the cathode|electrolyte interface. Under identical conditions, the time taken for the thermal voltage to drop to a particular value increases from cell (1) to cell (4). This is due to the decrease in overall cell resistance with change in the composition of anodes and cathodes [21].

Ideally, the contribution of the internal resistance of a cell is due only to the electrolyte impedance since the materials used in anodes (e.g., silver) and in cathodes (e.g., 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.

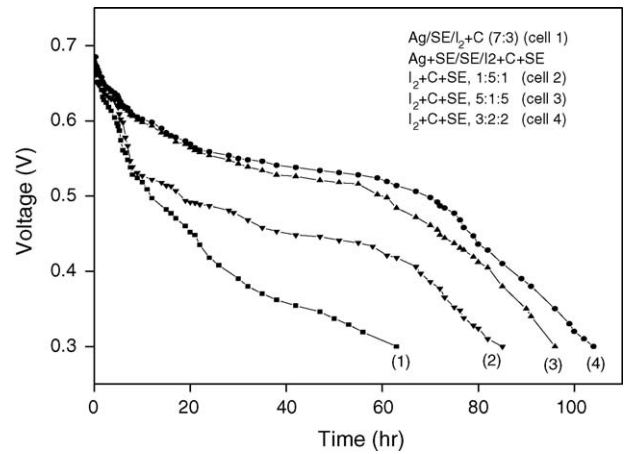


Fig. 5. Discharge characteristics of cells made up of different cathode compositions.

the OCV minus the voltage under load) divided by the current drawn from the cell, namely:

$$r = \frac{E - V}{I}$$

where E is the OCV; V , the voltmeter reading when the cell is under load; and I , the current in the circuit.

In cells employing solid electrolytes, the contacts between the anode|electrolyte and cathode|electrolyte interfaces are not as good as the contacts in cells using liquid electrolytes. As silver is consumed during discharge, the contact between silver and electrolyte will decrease, and hence internal resistance will increase. This, in turn, will lead to a rapid fall in cell voltage. The cell in which the anode is purely silver (cell (1), Fig. 4) and the voltage decreases faster with time compared with the other cells. Consequently, upon consumption of the silver atoms, the anode electrolyte contact decreases and this increases the internal resistance of the cell.

Jow and Liang [22,23] have examined the interface between a solid anode and a solid electrolyte during discharge of a $\text{Li/Li}(\text{Al}_2\text{O}_3)/\text{PbI}_2/\text{Pb}$ solid-state cell. A loss of interface contact between the lithium anode and the $\text{Li}(\text{Al}_2\text{O}_3)$ solid electrolyte was observed and was the result of void formation at the interface during discharge. For the present series, of compounds, the anode composition is found to influence the anode|electrolyte interface and therefore contributes to the high internal resistance of the cell. The cell parameters measured for all the cells made with the glassy electrolyte and different cathode materials are summarized in the Table 2. When a cell is discharging continuously, the AgI content formed at the cathode|electrolyte interface progressively increases. By contrast, silver is consumed continuously at the anode and causes a decrease in the contact between silver and the electrolyte. Thus, increases the internal resistance of the cell and causes an internal fall in voltage. The internal resistance of the cell increases with time during discharge. This can be explained on the basis of the cell reactions, namely:

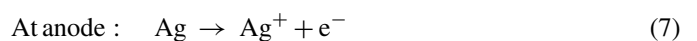
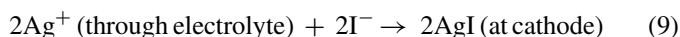


Table 2
Cell parameters measured at room temperature for cells with the electrolyte system and different cathodes

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 0.3 V (h)	63	85	96	104
Discharge capacity (mAh)	6.3	8.5	9.6	10.4
Energy density (Wh kg ⁻¹)	2.71	4.1	5.6	6.24



4. Conclusions

The present investigation of the electrolyte system CdI₂–Ag₂O–V₂O₅–B₂O₃, confirms that it supports the stable conduction of silver ions. The thermoelectric power confirms the nature of the positive charge on the mobile species and the heat of transport, is comparable with the activation energy of ion transport. The latter confirms the highly-disordered nature of the present glass samples. Primary cells are fabricated with a 20 mol% CdI₂-doped sample as the electrolyte material and with cathodes of variable composition. The polarization and discharge characteristics show that cell performance is very sensitive to the composition of the cathode materials. The high OCV obtained from these cells suggests that they are suitable for device applications. The results suggest that cells fabricated with the electrolyte system of the present study are suitable for low-power ionic devices, which require long shelf-lives.

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