

Thermoelectric power and electrochemical studies on $\text{CdI}_2\text{-Ag}_2\text{O-V}_2\text{O}_5\text{-B}_2\text{O}_3$ system

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Abstract A quaternary super-ion-conducting system, $20\text{CdI}_2-80[x\text{Ag}_2\text{O}-y(0.7\text{V}_2\text{O}_5-0.3\text{B}_2\text{O}_3)]$ where $1 \leq x/y \leq 3$, has been prepared by melt quenching technique. The electrical conductivity measured was the order of 10^{-4} S/cm at room temperature. The values of silver-ion transport number obtained by electromotive force technique are nearly unity. The thermoelectric power and electrochemical studies were done on the $\text{CdI}_2\text{-Ag}_2\text{O-V}_2\text{O}_5\text{-B}_2\text{O}_3$ system. The discharge and polarization characteristics were examined for different cathodes to evaluate the utility of these cells as power sources for low energy applications.

Keywords Glass · Silver-ion conductors · Thermo electric power · Solid state cells

Introduction

Super-ion-conducting glassy solid electrolytes have been studied extensively because of their technological importance in many electrochemical applications [1–5]. The advantages like long shelf life, no cell leakage, wide temperature range of operation, miniaturization etc. make the solid electrolytes interesting compared with the liquid electrolyte system. A number of high-ionic-conducting glasses have been examined widely, and progress has been

made towards understanding the transport properties of their highly disordered structures. Among them, Ag^+ -ion-conducting systems are the most widely investigated, and many AgI-doped oxide glasses have shown excellent cation-conducting properties [6]. For silver-based cells, which consist of silver anode and iodine cathode, reports have highlighted the stability with respect to moisture and iodine diffusion [7]. In battery applications, it is critically important to establish anode/glass and glass/cathode interfaces, which will remain intact during discharge, because ion transport within solid state occurs only in particle to particle contact, and hence, maximum contact must be achieved [7]. Some of the earlier works shows the high Ag^+ -ion conductivity even if the silver oxysalt system is doped with PbI_2 , CuI , etc. instead of AgI for electrolyte application in solid state batteries [8–9]. This leads us to study whether the silver oxysalt system $\text{Ag}_2\text{O-V}_2\text{O}_5\text{-B}_2\text{O}_3$ can serve as a host for the bivalent halide CdI_2 . The earlier study shows that conductivity increases with the addition of CdI_2 in the system $\text{CdI}_2\text{-Ag}_2\text{O-V}_2\text{O}_5\text{-B}_2\text{O}_3$ [10], and 20 mol% CdI_2 -doped system shows the better glass-forming ability. In the previous paper [11], we have reported the electrical conductivity of the glass system $20\text{CdI}_2-80[x\text{Ag}_2\text{O}-y(0.7\text{V}_2\text{O}_5-0.3\text{B}_2\text{O}_3)]$, where $1 \leq x/y \leq 3$, and the sample with $x/y=1.75$ shows the highest conductivity, 5.25×10^{-4} S/cm at room temperature. The purpose of this paper is to present the thermo electric power and electrochemical studies of the system $20\text{CdI}_2-80[x\text{Ag}_2\text{O}-y(0.7\text{V}_2\text{O}_5-0.3\text{B}_2\text{O}_3)]$, where $1 \leq x/y \leq 3$ for application in solid state batteries.

Experimental

Solid electrolytes were synthesized from analar grade CdI_2 , Ag_2O , V_2O_5 , B_2O_3 compounds by melt quenching tech-

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nique and is discussed elsewhere [10]. The glassy nature at room temperature was checked by X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The electromotive force (emf) method was employed for the evaluation of transport number of silver ions in these electrolyte materials [10]. A cell was constructed of a configuration (–) Ag+electrolyte/electrolyte/I₂+C+electrolyte (+) in the form of a pellet by pressing the cell components of the assembly under a pelletizing pressure of 5 tons/cm². The silver-ion transport number t_{Ag^+} in the case of individual composition was estimated from the measured values of open-circuit voltage (OCV) at room temperature.

Thermo electric power (TEP) measurements were carried out on thermocells of the configuration Ag(T)/electrolyte/Ag(T+ΔT). For TEP measurements, the thermocells were constructed in the form of circular pellets of 1-cm diameter at a pelletizing pressure of 5,000 kg cm⁻², and silver paste was applied on both faces of 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 range 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 ±5 °C, which was obtained between the sample holders by using auxiliary heaters wounded on each of the sample holder shafts. The average of sample temperature was taken as (T₁+T₂)/2. The temperature at the two faces was recorded by means of Cr–Al thermocouples and a high impedance digital micro-voltmeter. Thermoelectric power (θ) values were calculated using the relation $\theta = \Delta V / \Delta T$, where ΔV is the thermo emf developed across the sample, and ΔT , the temperature difference across the two faces of the sample.

The highest conducting composition of the series 20CdI₂–80[xAg₂O–y(0.7V₂O₅–0.3B₂O₃)] with x/y=1.75 is used as the solid electrolyte for the fabrication of solid state primary cells. It is observed that cell performance is very sensitive to the chemical composition of the constituents of cathode materials [12]. Cathode materials play a major role in improving the life time of the cell [7]. Hence, different solid state cells of the configuration (–) Ag, electrolyte/electrolyte/I₂, C, electrolyte (+) have been fabricated using the solid electrolyte with x/y ratio equal to 1.75 with different cathode compositions to evaluate the performance of the cells.

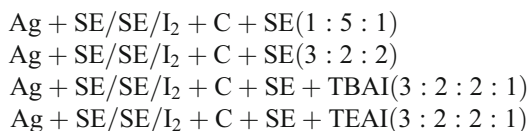
Anode Because Ag⁺ ions are the current carrying species in the electrolyte, anodes were prepared by mixing the powders of silver and the solid electrolyte (SE) in 2:1 weight ratio. They were finely mixed in an agate mortar and

were poured in a steel die of 1.0 cm in diameter, and a small pressure was applied to form a layer. Because silver is readily oxidized, the anode serves as an electron reservoir and hence, the negative terminal of the battery. Then the SE powder was poured on the top of the anode powder, and a small pressure was applied.

Cathode The following three types of cathodes were used in the present study: iodine (I₂)+carbon+SE, (1:5:1); I₂+carbon+SE, (3:2:2); I₂+carbon+SE+TAAI, (3:2:2:1). Carbon in the cathode mixture serves as an electron conductor, and the solid electrolyte improves the interfacial properties. Cathode materials of the type tetra alkyl ammonium iodide (TAAI)+iodine+graphite+solid electrolyte were also employed. The TAAI-added cathode compositions were mixed and taken in a crucible and heated to 323–333 K for half an hour and allowed to come to room temperature before using it. The cathode receives electron from the external circuit and hence, the positive terminal of the electrochemical cell.

The cathode mixture was then poured over the electrolyte layer in the die, and the three layers were pressed at a pressure of 5 tons/cm².

So, cells of the following type were constructed.



The open-circuit voltage was measured by means of a Keithley electrometer Model 614. The polarization and discharge characteristics were examined systematically to estimate the performance of each cell.

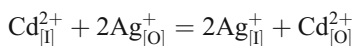
Results and discussion

The glassy nature of the samples was confirmed by XRD and DSC analysis. The transport number of the silver ions t_{Ag^+} can be found out by the relation $t_{\text{Ag}^+} = E/E_0$, where E the emf measured the open-circuit voltage at room temperature and E_0 is the standard emf corresponding to the cell reaction obtained from thermo dynamical calculations for Ag/I₂ couple. The measured open-circuit voltage of the galvanic cell constructed using these samples as the solid electrolyte phase is comparable to the corresponding theoretical value for the Ag/I₂ couple, i.e., 687 mV. The silver-ion transport number (t_{Ag^+}) of these CdI₂ doped samples was evaluated from the emf method and is found out to be nearly unity (Table 1). Thus, it is evident that silver ion would be the majority of charge carriers in this CdI₂-doped silver oxysalt system. The high silver-ion

Table 1 The x/y ratio, silver-ion transport number t_{Ag^+} , activation energy E_a from conductivity measurements, and heat of transport obtained for the series $20CdI_2-80[xAg_2O-y(0.7V_2O_5-0.3B_2O_3)]$

x/y ratio	Silver-ion transport number t_{Ag^+}	Activation energy from conductivity measurements E_a (eV)	Heat of transport $q_{Ag^+}^*$
100	0.896	0.404	–
1.25	0.963	0.363	0.394
1.50	0.967	0.298	0.357
1.75	0.988	0.288	0.278
2.00	0.976	0.351	0.316
2.25	0.975	0.363	0.277
2.50	0.978	0.332	0.377
2.75	0.975	0.313	0.302
3.00	0.982	0.308	0.299

transport number obtained here can be attributed because of the change of the main environment of Cd and Ag ions and is explained on the basis of Pearson's theory of hard and soft acids and bases [HSAB] [13]. There seems to be an exchange reaction taking place in the glassy matrix as per the following equation



where the subscript [I] indicates the iodine environment and [O] indicates the oxygen environment. The HSAB theory indicates that a hard acid would prefer to bind with a hard base, and a soft acid would prefer to bind with a soft base. So the soft acid Ag^+ and soft base I^- prefer to form AgI clusters resulting in high silver-ion conductivity. The high silver-ion conduction in this system is similar to other PbI_2 , CuI-doped systems [8, 9].

In the presently studied systems, the predominant conducting species are Ag^+ ions, and hence, ionic conductivity takes place. When a temperature gradient is maintained across the pellet, a voltage appears across the pellet because of the flow of silver ions within the pellet. When the thermodynamical steady state is reached, the sign of the voltage across the pellet represents the sign of the electric charge on the mobile species [14]. Hence, thermoelectric power is an important tool for determining the nature of the charge carriers.

The expression for the thermoelectric power of a super ionic conductor can be represented as [15],

$$\theta = \theta_{hom} + \theta_{het} = -\frac{q_{Ag^+}^*}{eT} + \frac{1}{e} \times \left[k \ln \frac{n_{Ag^+}}{N} + S_{Ag^+}^{Ag} - S_{Ag^+} \right] \quad (1)$$

where $q_{Ag^+}^*$ is the heat of transport, N is the number of normal site per unit volume, $S_{Ag^+}^{Ag}$ is the partial entropy of Ag^+ ion in silver metal, n_{Ag^+} is the number of Ag^+ ions per

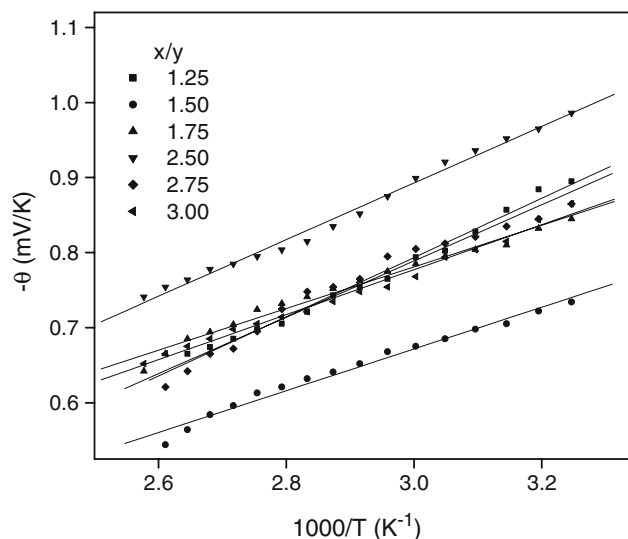


Fig. 1 Thermoemetric power plot obtained for the series $20CdI_2-80[xAg_2O-y(0.7V_2O_5-0.3B_2O_3)]$ with different x/y ratios

unit volume, and S_{Ag^+} is the transport entropy of the silver ion. The variation of thermopower with inverse of temperature follows a straight line, obeying the expression for homogeneous thermoelectric power,

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

where $q_{Ag^+}^*$ is the heat of transport of silver ions, e is their charge, T is the absolute temperature, and H is a correction term because of electrode contact potential effects, which for thermo cells constructed with reversible electrodes is almost temperature independent and constant [15]. So, TEP should vary linearly with $1/T$, and the slope is equal to

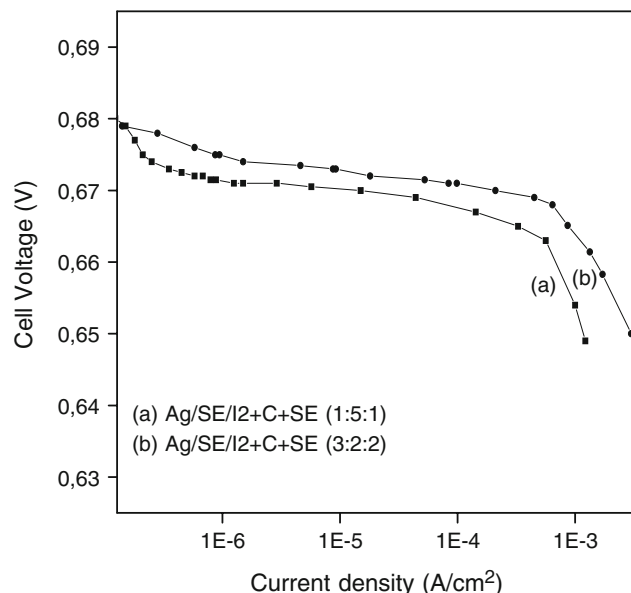


Fig. 2 The current–voltage plots for different cathode composition on the electrolyte system $20CdI_2-80[xAg_2O-y(0.7V_2O_5-0.3B_2O_3)]$ with $x/y=1.75$

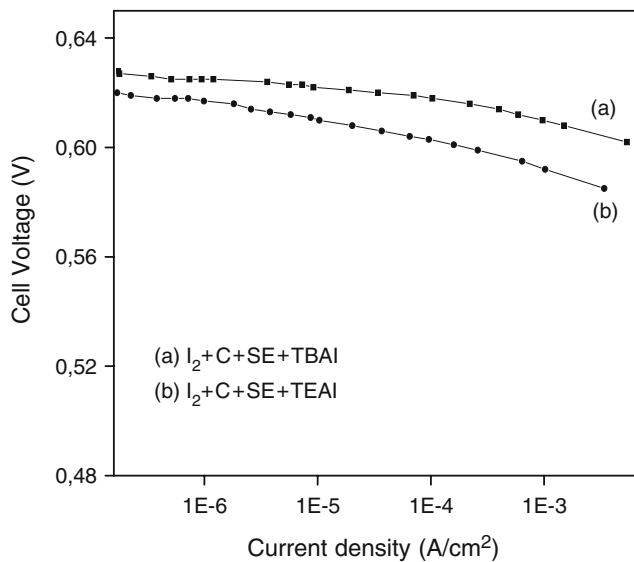


Fig. 3 Polarization characteristics for the cells made with cathode compositions [I+C+SE+TAAI=3:2:2:1]

$q_{Ag^+}^*$. The thermoelectric power ($-\theta$) versus $10^3/T$ for the present electrolyte system with different x/y values are given in Fig. 1. The heat of transport, $q_{Ag^+}^*$ of the mobile species is obtained from the slope of these curves and is shown in Table 1, which agrees closely with the activation energy for the migration of silver ions [11]. For materials possessing average structure, the mobile ions can jump from one site to another of equal energy [16]. The distinction between interstitial Ag^+ ions and Ag^+ ions at normal site is lost. Hence, the heat of transport, which is equal to the barrier height for ion hopping, is expected to approach the activation energy of Ag^+ ion migration (Table 1). This is in agreement with the theory of Rice and Roth [17] for disordered solids.

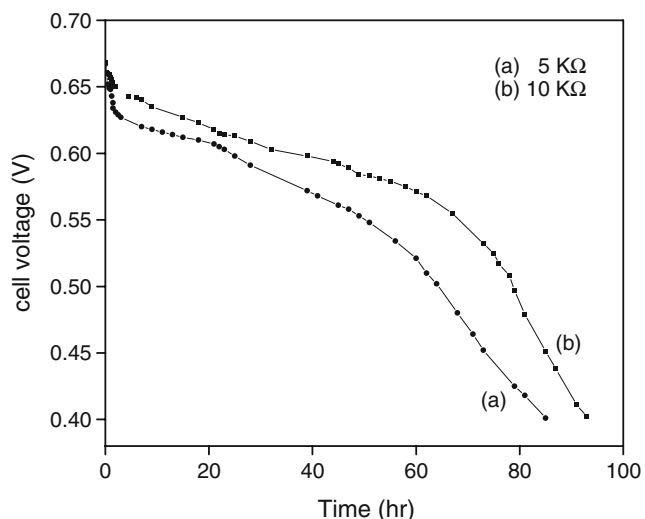


Fig. 4 The discharge characteristics under different load conditions for the cells with the cathode composition $I_2+C+SE=3:2:2$

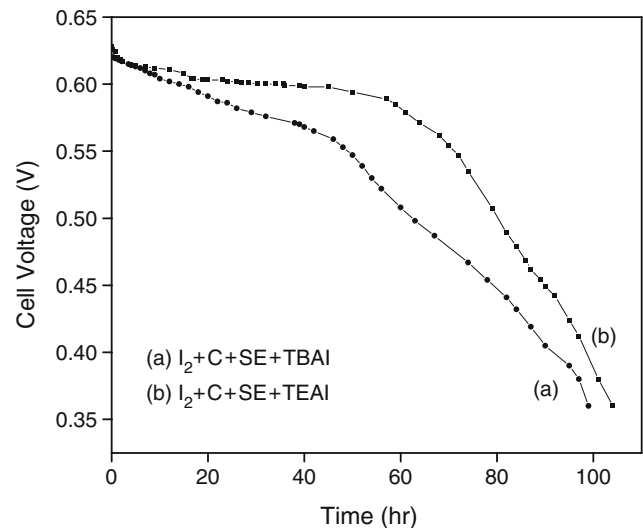
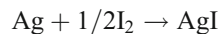
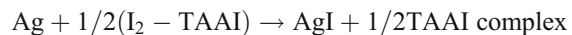


Fig. 5 Discharge characteristics of the cell with TAAI-added cathode for the electrolyte system $xCdI_2-(100-x)[2Ag_2O-(0.7V_2O_5-0.3B_2O_3)]$

The electrochemical cells were activated by pressing together the anode/electrolyte/cathode materials. The OCV is measured immediately after the construction of the cells discussed earlier, and the measured OCV is found to be around 680 mV. The low OCV (621 and 628 mV) obtained for TAAI-added cells is because of the reduced activity of iodine in the presence of alkyl group; this enhances battery shelf life [18]. The low open-circuit voltages for cells using organic cathodes, when compared to the cells with I_2 cathodes, were because of the different energy of formation of cell reactions [19]. In the pure I_2 cathode cells, the cell reaction is



where as in organic cathode cells, it is considered as



The plot of cell potential against current is usually referred as polarization curve. Polarization measurements were made for different cathode compositions by applying different loads. Figure 2 shows the current–voltage plots for

Table 2 Cell parameters measured at room temperature for cells made up of different cathodes

Parameters	5 kΩ	10 kΩ	TEAI	TBAI
Open-circuit voltage (V)	0.681	0.683	0.621	0.628
Cell weight (g)	1.1	1.1	1.1	1.1
Electrolyte diameter (cm)	1.0	1.0	1.0	1.0
Discharge time (h)	85	93	104	99
Discharge capacity (mA h)	8.5	9.3	10.4	9.9
Energy density (W h/kg)	4.79	5.41	6.45	5.84

different cathode composition of the electrolyte system $20\text{CdI}_2-80[x\text{Ag}_2\text{O}-y(0.7\text{V}_2\text{O}_5-0.3\text{B}_2\text{O}_3)]$ with $x/y=1.75$. The cell potentials were recorded 120 s after connecting the load for various discharge currents. The voltage of cell “a” drops suddenly. These polarization losses are mainly because of the bulk resistance and the nucleation at the electrode/electrolyte interface. The cathode mixture with 3:2:2 (cell “b”) gives the better performance compared to cell a (cathode mixture, 1:5:1). So the other two cells made with tetra-ethyl ammonium iodide (TEAI) and tetra-butyl ammonium iodide (TBAI) of the cathode mixture, 3:2:2:1.

Figure 3 shows the polarization characteristics of the cells made with cathode compositions [I+C+SE+TAAI=3:2:2:1]. The polarization characteristics for the cells with TEAI and TBAI show the better performance. The current drain obtained is improved progressively by the addition of TEAI and TBAI to the cathode. It has been reported that the addition of TAAI to the cathode reduces the iodine activity at the electrode/electrolyte interface [20]. At the interface, the TAAI reduces the iodine activity by forming a strong complex $(\text{CH}_3)_4\text{NI}$, which avoids the tarnishing actions of molecular iodine with the electrolyte and hence, increases the specific energy. This is because of the formation of a complex with higher conductivity than AgI. The ionic conductivity of the reaction product $[(\text{CH}_3)_4\text{N}]_2\text{Ag}_{13}\text{I}_{15}$ is highly conducting and offers high charge transfer continuity [12]. Hence, the improvement in polarization characteristics of these TAAI-added cells is attributed to reduced internal resistance drop compared with the cells of (I+C+SE) cathodes.

The discharge characteristics of a cell is represented by the terminal voltage versus time at a steady discharge current or fixed load. Figure 4 shows the discharge characteristics under different load conditions for the cells with the cathode composition $\text{I}_2+\text{C}+\text{SE}=3:2:2$. The initial drop in cell potential in the first few hours can be attributed to the formation of a low-conducting AgI layer at the cathode/electrolyte interface. In solid electrolyte cells, the contact between the anode/electrolyte and cathode/electrolyte interfaces is not good compared with the 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 leads to the rapid fall in cell voltage. When a cell is discharging continuously, the AgI content formed at the cathode/electrolyte interface progressively increases, and silver is continuously consumed at the anode, which leads to the decrease in the contact between silver and electrolyte. So, the internal resistance of the cell increases with time during discharge. The discharge characteristics for the cells made of TAAI-added cathode compositions shows better performance (Fig. 5). Table 2 shows the cell parameters measured at room temperature (303 K) for cells made up of different cathodes.

Various cell parameters for the cell with 5 and $10\text{k}\Omega$ load resistance in the plateau region are listed in Table 2. These investigations indicate that the cells prepared with this new fast Ag^+ -ion-conducting glass is suitable for low-current drain applications.

Conclusions

A CdI_2 -doped silver-ion-conducting system with composition yielding the highest conductivity has been used as electrolyte in the fabrication of solid state cells. The polarization and discharge characteristics show that the cell performance is very sensitive to the composition of the cathode materials. The thermo electric 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 transport number measurements by emf technique shows that the silver-ion transport number is almost unity, and this CdI_2 -doped system behaves as silver-ion-conducting fast ionic glasses.

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