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AgI-Ag_2S-Ag_2Se SOLID ELECTROLYTE SYSTEM

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In this study, results are presented with the incorporation of Se^{2-} either partly or fully in the S^{2-} in Ag_2S. The impedance studies are presented and analysed.

Key words: AgI-Ag_2S-Ag_2Se, solid electrolyte, impedance measurement

INTRODUCTION

Large number of silver ion conductors based on AgI have been reported[1]. AgI has high conductivity above 420K only, due to the transformation of the low temperature β-phase to the high temperature α- phase. Efforts have been taken to stabilise the average structure like α-AgI at room temperature by introducing stabilizer ions into the lactice. These stabiliser ions may be anions, cations or both. Alkali metal, ammonium and substituted ammonium ions were found to be effective in this process. The most well known system in $RbAg_4I_5$. This is not stable below 300K and also in moist and iodine atmosphere.

The first successful material with high ionic conductivity at room temperature was achieved by introducing s^{2-} ions in AgI. The compound Ag_3SI [2-5] has conductivity of 0.01 ohm^{-1}, cm^{-1} at 298K. But it decomposes in the presence of iodine resulting in a decrease in conductivity. Systems like Ag_2S-$Ag_{1.7}Te$-AgX [6], (where X = PO_4^{3-}, PO_3^-, $P_2O_7^{4-}$), Ag_2Se-Ag_3PO_4 [7], and other silver chalcogenides [8] have been reported and found to be mixed conductors.

In the present study, it is aimed to investigate the behaviour of a partial replacement of S^{2-} ions by Se^{2-} in the system Ag_3SI. The radius of S^{2-} is 1.84 Å while that of Se^{-2} is 1.98 Å.

EXPERIMENTAL

Preparation

AgI was prepared by the reaction of KI with $AgNO_3$. Ag_2S was precipitated by a reaction of thiourea with ammoniacal silver nitrate solution. Ag_2Se was obtained by the reaction of ammonical silver nitrate solution with sodium selenosulphate solution.

All samples, AgI-Ag S-Ag Se were prepared in such a way that the ration of Ag_2 S and Ag_2 Se was varied in the composition Ag SI (AgI: Ag_2S = 1:1) as AgI – $(Ag_2S)_x$– $(Ag_2Se)_{1-x}$ (where x = 0.2, 0.5, 0.8). All the necessary ingredients were mixed, vacuum sealed and heated at 823K for 10 hours. They were powdered and used for subsequent measurements.

Impedance measurement

Impedance was measured at room temperature using PAR-AC Impedance System (Model 368–1) in the range 5 Hz to 100 KHz. Pellets of 0.1 – 0.2cm thick and 2cm diameter with gold coated faces were employed.

RESULTS AND DISCUSSION

It is interesting to note that, with compositions x = 0.5 and 0.2 (increase in Se content), the impedance could not be measured due to very low resistance of the samples. This is due to the formation of metallic silver during heating of the samples with larger Se content, as evidenced by the appearance of white silver particles on the molten mass inside the glass ampoules. However, the sample AgI $-(Ag_2S)_{0.8}$ – $(Ag_2Se)_{0.2}$ which did not show any silver formation, had a conductivity of 3.6 × 10^{-3} $mho.cm^{-1}$ at room temperature. This did not show any semicircle in the impedance behaviour in the range of frequency examined (Fig. 1). The XRD indicated presence of a mixed pattern.

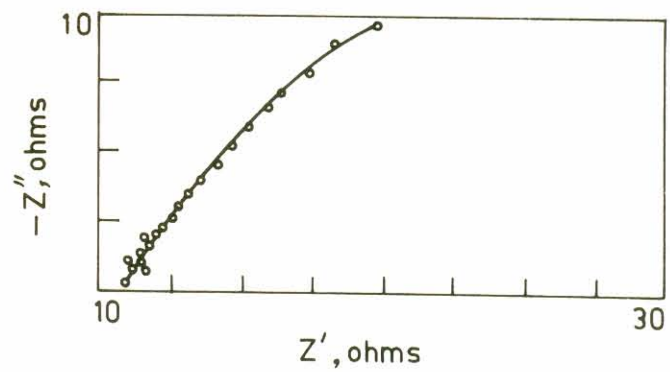

Fig. 1: Impedance of AgI - $(Ag_2S)_{0.8}$ - $(Ag_2Se)_{0.2}$

Cell performance

The following cell was constructed using AgI-$(Ag_2S)_{0.8}$– $(Ag_2Se)_{0.2}$ as electrolyte and the discharge characteristics were studied.

Ag + electrolyte	AgI:$(Ag_2S)_{0.8}$-$(Ag_2Se)_{0.2}$	$(I_2$ + C) + C
	3.2 g	0.3 + 0.5 g

Total weight = 5g

This gave an OCV of 460mV and SCC of about 2mA. Such systems with low OCV have been reported by earlier workers [9].

The above cell was discharged at 20μA and the discharge characteristics are shown in Fig. 2. From the figure, it is clear that the cell voltage is stable upto 500 hrs and thereafter falls sharply. Another interesting observation is upto about 300 hrs, the applied load is constant and thereafter the change in load is within a few tenths of ohms.

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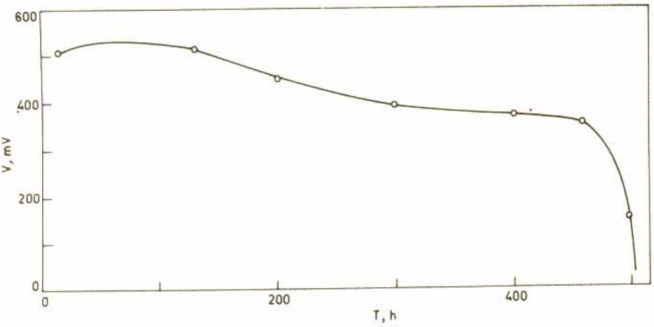

Fig. 2: Discharge at 20μA

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