

Solid-state ionics - solid electrolyte cells with copper ion conductors

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A solid electrolyte cell has been developed using a high copper ion conductivity solid electrolyte, $7\text{CuBr}\cdot\text{C}_6\text{H}_{12}\text{N}_4\text{CH}_3\text{Br}$, a copper anode, and a chalcogen cathode. The open-circuit voltages of the cells with sulphur, selenium, and tellurium as cathode materials were 0.448, 0.373, and 0.258 V, respectively, at 25°C. These cells yielded a current of several tens of microamperes at room temperature and several milliamperes at 114°C without appreciable polarization. An energy density of 4.5 Wh kg⁻¹ at room temperature was evaluated from the weights of the electrolyte and electrode materials for the cell using a selenium cathode in the discharge current density range 60-150 μA cm⁻².

1. Introduction

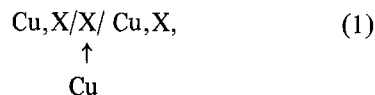
In recent years, a considerable amount of interest has been shown in the area of solid electrolyte galvanic cells which resulted from the discovery of a number of compounds exhibiting high ionic conductivity at ambient temperature; reviews were presented by Foley [1], Hull [2] and Owens [3]. Except in a few cases [4, 5], most of the solid electrolytes used for the cells reported previously were silver containing compounds such as Ag₃SI [3], RbAg₄I₅ [3], and KCN·4AgI [6], and their practical use has been limited because of the high price of these solid electrolytes. It is desirable, therefore, to use low price solid electrolytes such as copper compounds.

Quite recently, *N*-alkyl-hexamethylenetetramine halide-copper (I) halide double salts have been found by Takahashi *et al.*, [7] to have high copper ion conductivity and extremely low electron conductivity at room temperature. This paper describes the performance of the cell with a chalcogen cathode, copper anode, and solid copper ion conductor, *N*-methyl-hexamethylenetetramine bromide-copper (I) bromide double salt ($7\text{CuBr}\cdot\text{C}_6\text{H}_{12}\text{N}_4\text{CH}_3\text{Br}$), which has a conductivity of $1.7 \times 10^{-2} (\Omega\cdot\text{cm})^{-1}$ at 20°C.

2. Experimental

The solid electrolyte $7\text{CuBr}\cdot\text{C}_6\text{H}_{12}\text{N}_4\text{CH}_3\text{Br}$ was prepared by combining the hydrobromic acid solution of copper (I) bromide and the aqueous solution of *N*-methyl-hexamethylenetetramine bromide $\text{C}_6\text{H}_{12}\text{N}_4\text{CH}_3\text{Br}$. After copper (I) bromide (4.02 g) was dissolved in 10 ml of 47% hydrobromic acid, 10 ml of water was added to this solution. Then, the 10 ml aqueous solution of 0.846 g $\text{C}_6\text{H}_{12}\text{N}_4\text{CH}_3\text{Br}$ was added to this solution with stirring, which was followed by the addition of 300 ml of water. The precipitate was filtered, washed with methanol, and dried in vacuo on P₂O₅ before it was pressed to form a pellet at 4 000 kg cm⁻², and then heated in a sealed evacuated Pyrex vessel at 130-165°C for 17 h.

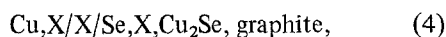
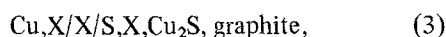
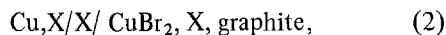
The anodic polarization was measured by the cell



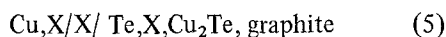
where X is the solid electrolyte $7\text{CuBr}\cdot\text{C}_6\text{H}_{12}\text{N}_4\text{CH}_3\text{Br}$, with the help of the copper wire reference electrode inserted into the electrolyte. A mixture of powdered copper (325 mesh) and the electrolyte (2:1 weight ratio) served as the

electrodes. About 0.8 g of the electrolyte were stacked between two electrodes, the copper wire ($\phi = 0.5$ mm) being placed in the middle of the electrolyte, and pressed at $4\,000\text{ kg cm}^{-2}$ to form a pellet of 13 mm in diameter. The potential difference between the anode and the reference electrode was measured by a digital voltmeter with an internal resistance of $1\,000\text{ m}\Omega$.

Four types of galvanic cells,



and



were examined. The anode of these cells was a mixture of 0.2 g of the electrolyte and 0.4 g of copper powder. The electrolyte (0.8 g) and the anode layers were pressed at $4\,000\text{ kg cm}^{-2}$ to form a pellet of 13 mm in diameter. The cathode of cell 2 was a mixture of 0.3 g of CuBr_2 , 0.1 g of the electrolyte, and 0.07 g of graphite, and the cathode of cells 3–5 was a mixture of 0.2 g of chalcogen, 0.3 g of the electrolyte, 0.07 g of copper chalcogenide, and 0.07 g of graphite, and these electrode materials were each pressed at $4\,000\text{ kg cm}^{-2}$ to form a pellet of 13 mm in diameter. In order to measure the anodic and cathodic polarizations, the anode was divided into two parts, one part serving as reference electrode, of which the area ratio to the anode was 3:10. The cell was sealed up with polyester resin.

3. Results and discussion

3.1. The characteristics of the solid electrolyte $7\text{CuBr}\cdot\text{C}_6\text{H}_{12}\text{N}_4\text{CH}_3\text{Br}$

In order to obtain a high performance solid electrolyte cell, a small polarization at the boundary between the electrolyte and the electrode must be obtained in addition to the electrolyte having high ionic and low electronic conductivities. In the previous investigation [7], the electrolyte $7\text{CuBr}\cdot\text{C}_6\text{H}_{12}\text{N}_4\text{CH}_3\text{Br}$ was prepared by grinding together CuBr and $\text{C}_6\text{H}_{12}\text{N}_4\text{CH}_3\text{Br}$ and heating the mixture. The grinding and heating process had to be repeated to obtain an electrolyte showing a small anodic polarization. Therefore, in this study, the electrolyte was synthesized by the precipitation

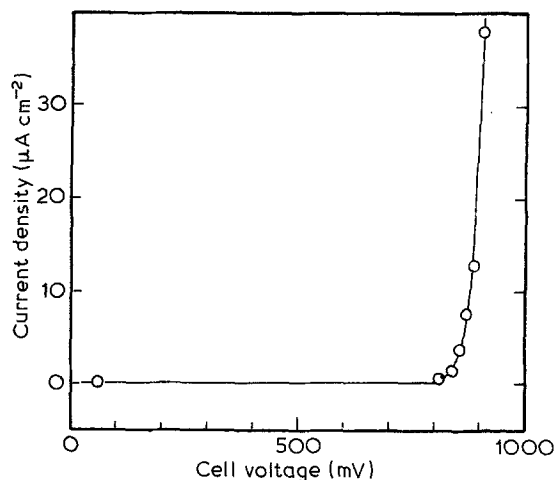
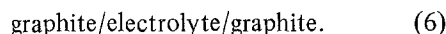


Fig. 1. Current–voltage curve of cell 6 at 25°C .

method as described in the previous section. By this method, the electrolyte $7\text{CuBr}\cdot\text{C}_6\text{H}_{12}\text{N}_4\text{CH}_3\text{Br}$ showing a small anodic polarization was easily prepared.

The content of the constituent elements in the samples obtained by the present method was determined by elementary analysis and the results were in good agreement with the calculated values of the formula $7\text{CuBr}\cdot\text{C}_6\text{H}_{12}\text{N}_4\text{CH}_3\text{Br}$ (found; C, 6.75%; H, 1.24%; N, 4.44%; calc.: C, 6.78%; H, 1.21%; N, 4.52%). The X-ray diffraction investigation indicated that the diffraction pattern of the sample was almost the same as that of the solid state reaction product which was reported previously [7].

The decomposition voltage of the electrolyte was measured with cell 6,



From the current–voltage curve of cell 6 shown in Fig. 1, the decomposition voltage is estimated to be about 0.83 V at 25°C . Thus, the voltage of the cell using this electrolyte was found to be limited to 0.83 V.

The anodic polarization curves for the electrolytes obtained at various annealing temperatures were measured at room temperatures with the help of cell 1 and are shown in Fig. 2. In this measurement, all the potentials were recorded within one minute. At higher current densities, however, as the anode potentials became rapidly too positive with time they are indicated by the dotted lines in Fig. 2. These curves indicate that an optimum

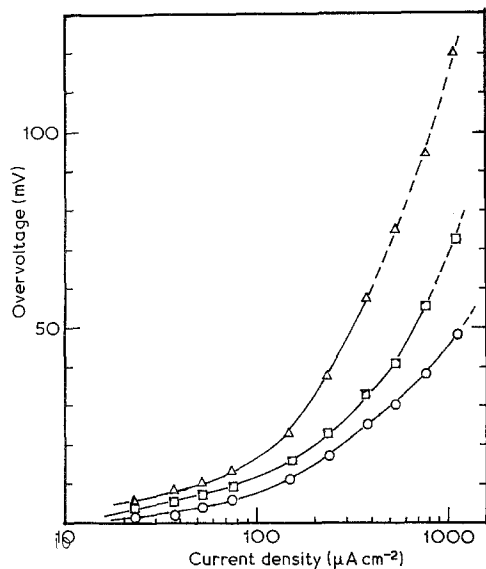


Fig. 2. Anodic polarization curves of cell 1 at 20° C using the electrolyte $7\text{CuBr}\cdot\text{C}_6\text{H}_{12}\text{N}_4\text{CH}_3\text{Br}$ annealed at 140° C (Δ); 158° C (\circ) and 165° C (\square).

annealing temperature will be found to obtain the electrolyte which shows the smallest anodic polarization. The electrolyte prepared at 165° C decomposed slightly which was suggested by the sample turning pale brown. In the sample prepared at 140° C, free copper (I) bromide was found by X-ray diffraction investigations. All samples have almost the same electrical conductivity of $1.2 \times 10^{-2} (\Omega \text{ cm})^{-1}$ at room temperature, so that the anodic polarization may be supposed to be affected by the presence of free copper bromide or some thermal decomposition product in the electrolyte.

Table 1. Open-circuit voltage at 25° C

Cell	Observed OCV (V)	Cell reaction	ΔF_{298}^0 (kJ mol ⁻¹)	Calculated e.m.f (V)	Reference
3	0.448	$2\text{Cu} + \text{S} = \text{Cu}_2\text{S}$	-86.6	0.449	10
		$1.965\text{Cu} + \text{S} = \text{Cu}_{1.965}\text{S}$	-81.2	0.428	11
		$1.9\text{Cu} + \text{S} = \text{Cu}_{1.9}\text{S}$	-76.8	0.419	12
		$1.8\text{Cu} + \text{S} = \text{Cu}_{1.8}\text{S}$	-73.9	0.425	12
		$\text{Cu} + \text{S} = \text{CuS}$	-52.7	0.546	10
			-48.5	0.502	12
4	0.373	$2\text{Cu} + \text{Se} = \text{Cu}_2\text{Se}$	-71.8	0.372	10
		$\text{Cu} + \text{Se} = \text{CuSe}$	-45.2	0.468	10
5	0.258	$2\text{Cu} + \text{Te} = \text{Cu}_2\text{Te}$	-47.7	0.247	10
		$1.41\text{Cu} + \text{Te} = \text{Cu}_{1.41}\text{Te}$	-32.3	0.237	10
		$\text{Cu} + \text{Te} = \text{CuTe}$	-26.16	0.271	10

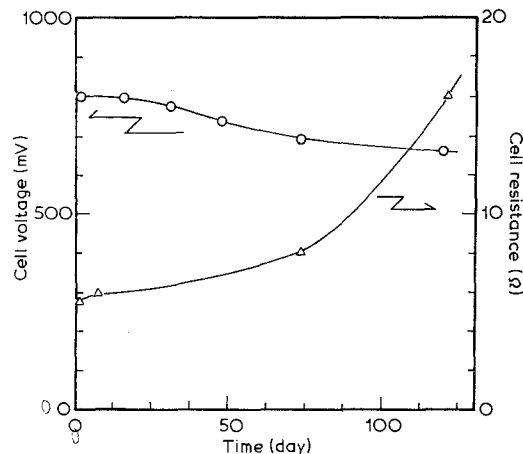
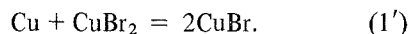


Fig. 3. Time dependence of the open-circuit voltage and the cell resistance of cell 2 at room temperature.

3.2. Open-circuit voltage

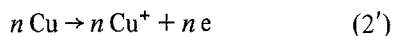
The time dependence of the open-circuit voltage (OCV) of cell 2 was measured and is shown in Fig. 3. The value in the initial stage, 0.8 V, is in good agreement with the e.m.f., 0.79 V at 25° C, calculated from the free energy change of the reaction 1' [8],



However, the OCV decreases gradually with time and the cell resistance increases with time as shown in this figure. This behaviour indicates that the solid electrolyte may react with CuBr_2 to give a poor conductivity solid. Recently, galvanic cells using high copper ion conductivity solid such as

N,N'-dimethyl-triethylenediamine dibromide-CuBr or hydro-hexamethylenetetramine chloride-CuCl as electrolyte and a bromine-perylene charge transfer complex or CuBr₂ as cathode were reported by Lazzari *et al.*, [4], and Sammells *et al.*, [5]; These cells showed a loss even upon standing on open circuit and finally stabilized at around 0.35 V, because of the deterioration of the halogen electrolyte. These results seem to exclude the possibility of using a halogen cathode. In this study, therefore, the chalcogen cathodes, which were proposed by Takahashi and Yamamoto, [9] as the cathode material of the cell using RbAg₄I₅ as electrolyte, have been examined.

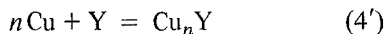
The open-circuit voltages of cells 3–5 kept a constant value at room temperature for a long period of time. The OCV at 25°C, measured under a vacuum to reduce the influence of oxygen, is shown in Table 1. It is well known that the copper chalcogenides have several phases such as Cu₂S, Cu₁₈S, CuS, Cu₂Se, CuSe, Cu₂Te, Cu_{1.4}Te and CuTe. Since 7CuBr·C₆H₁₂N₄CH₃Br is really the copper (I) ion conductor, the cell reactions at the anode and the cathode can be expressed as



and

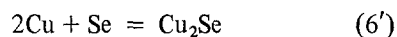
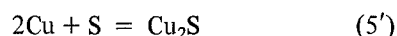


respectively. Then, the overall reaction is

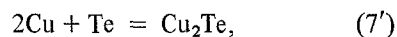


The values of e.m.f. of the cells at 25°C were calculated from the standard molar free energy change of Equation 4', ΔF_{298}^0 , and the calculated values are shown in Table 1. As seen in this Table,

the observed OCV of cells 3–5 are in fairly good agreement with the values calculated from the standard molar free energy changes of the reactions



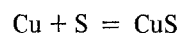
and



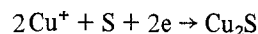
though ΔF_{298}^0 of reaction 7 is somewhat indefinite [10]. Recently, the OCV of the cell,



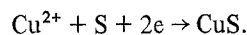
using aqueous electrolyte has been measured by Mathiess and Rickert [12] to be 0.251 V at 25°C. Here, the cell reaction



was proposed and the value of the standard molar free energy change of the reaction calculated from the observed OCV agreed well with the previously reported values. These results suggest that the cathode reaction of cell 3 using copper (I) ion conductor as the electrolyte is



and that of cell 7 using copper (II) ion conductor as the electrolyte is



The observed OCV and the e.m.f. calculated from the thermodynamic data [10] at various temperatures are shown in Table 2. From the temperature dependence of the observed OCV, the standard molar enthalpy change, ΔH_{298}^0 , and the standard entropies, S_{298}^0 , of Cu₂S, Cu₂Se, and Cu₂Te were evaluated and the values are shown in Table 3 together with those listed in Mills' book.

Table 2. Open-circuit voltage

Cell 3			Cell 4			Cell 5		
Temperature (°C)	Experimental (V)	Calculated (V)	Temperature (°C)	Experimental (V)	Calculated (V)	Temperature (°C)	Experimental (V)	Calculated (V)
0	0.443	0.446	0	0.370	0.370	0	0.253	0.244
16	0.445	0.447	22	0.373	0.372	15	0.256	0.245
26	0.448	0.449	31	0.374	0.373	20	0.257	0.246
35	0.449	0.450	43	0.375	0.375	29	0.259	0.247
46	0.450	0.451	50	0.376	0.376	58	0.264	0.250

Table 3. Thermodynamic data of copper (I) chalcogenides

	ΔH_{293}° (kJ mol ⁻¹)	Reference	S_{298}° (J mol ⁻¹ K ⁻¹)	Reference
Cu ₂ S	-79.9	Beilen (1965)	121	Kelley (1961)
	-79.7	Wagner (1957)	126	This paper
	-78.7	Richardson (1955)		
Cu ₂ Se	-76.6	This paper		
	-59.4	Gattow (1956)	128	Rau (1969)
	-69.9	Valverde (1968)	124	This paper
Cu ₂ Te	-61.9	This paper		
	-59.8	Fabre (1888)	148	This paper
	-16.7	Kochnew (1954)	137	Mills (1974)
	-41.8	Mills (1972)		
	-38.1	This paper		

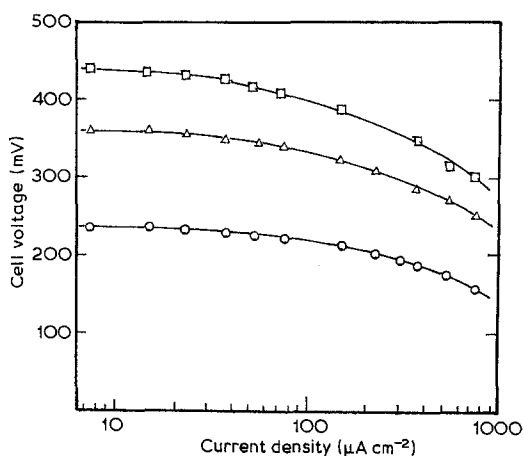


Fig. 4. Current-voltage curves of cell 3 (□), cell 4 (Δ), and cell 5 (○) at 22°C.

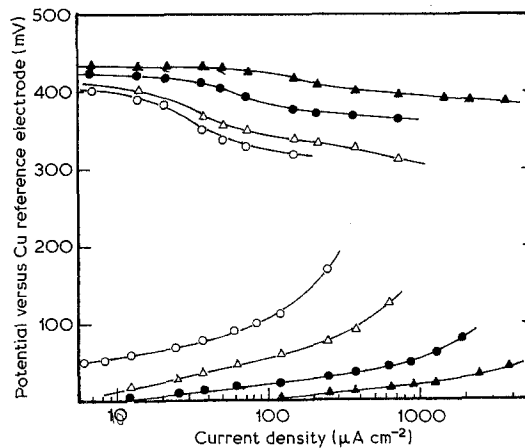


Fig. 5. Polarization curves of cell 3 at various temperatures (○) -20°C; (Δ) 0°C; (●) 22.5°C; (▲) 52°C.

3.3. Anode and cathode polarizations for the cell Cu/7CuBr · C₆H₁₂N₄CH₃Br/chalcogen

The current-voltage curves for cells 3-5 at room temperature are shown in Fig. 4. The voltage plateaux extending to a current density of 50 μA cm⁻² were seen when the voltages were recorded within 1 min. As the internal resistance of these cells is not so high (< 20 Ω), the decrease of the cell voltage at a current density above 50 μA cm⁻² is attributed not to resistance polarization: but probably to anodic and cathodic polarizations. The cathode and anode potentials with respect to the copper reference electrode for cells 3-5 at various temperatures are shown in Figs. 5-7, respectively. At lower current densities, both the anodic and cathodic polarizations must be considered and

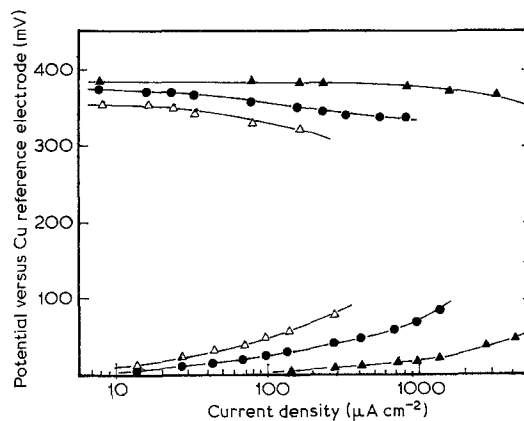


Fig. 6. Polarization curves of cell 4 at various temperatures (Δ) 0°C; (●) 21.5°C; (▲) 52.5°C.

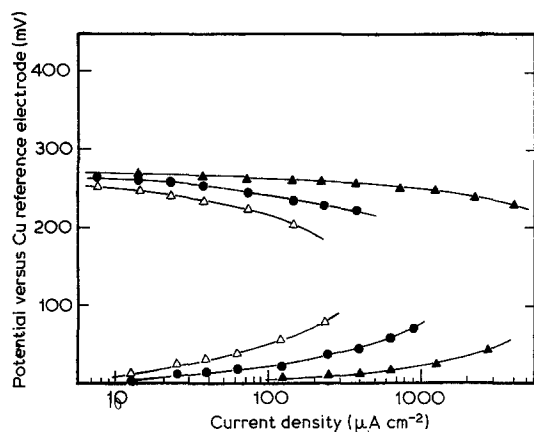


Fig. 7. Polarization curves of cell 5 at various temperatures (Δ) 0°C ; (\bullet) 23.5°C ; (\blacktriangle) 53°C .

they decrease with increasing temperature. At higher current densities, the cathode potential remained constant with time, while the anode potential became more positive with time, thus the anodic polarization played a more important role than the cathodic polarization.

3.4. Discharge curve

The constant load ($5\text{ k}\Omega$) discharge curves at room temperature for cells 3–5 are shown in Fig. 8. The anode capacity of these cells was 17 mA h , and the cathode capacities 340 , 130 and 84 mA h , respectively. Of these cells, cell 3 presented the highest cell voltage at the initial stage of discharge but after 50 h , the cell voltage decreased quickly. The average current was $70\text{ }\mu\text{A}$ ($54\text{ }\mu\text{A cm}^{-2}$) and the capacity was 4 mA h to the cut-off voltage of 300 mV . The cathode efficiency was only 1.2% . This low efficiency may be due to the high resistivity of sulphur; that is, the cathode reaction zone is the three phase boundary of sulphur, electrolyte, and graphite, and after discharge the surface of sulphur will be coated with the reaction product of copper sulphide, thus reducing the area of the three phase reaction boundary.

On the other hand, the cell voltage of cells 4 and 5 decreased gradually with discharge time. For cell 4, the average current was $65\text{ }\mu\text{A}$ ($50\text{ }\mu\text{A cm}^{-2}$) and a capacity of 26 mA h was obtained to the cut-off voltage of 260 mV , corresponding to a cathode efficiency of 18% . For cell 5, the average current was $50\text{ }\mu\text{A}$ ($38\text{ }\mu\text{A cm}^{-2}$), the capacity was 17 mA h to the cut-off voltage of 180 mV , and the cathode

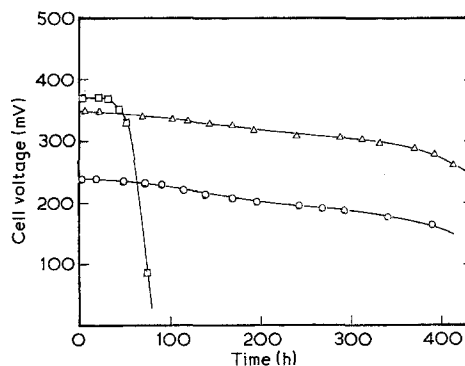


Fig. 8. Constant load ($5\text{ k}\Omega$) discharge curves of cell 3 (\square), cell 4 (Δ), and cell 5 (\circ) at room temperature.

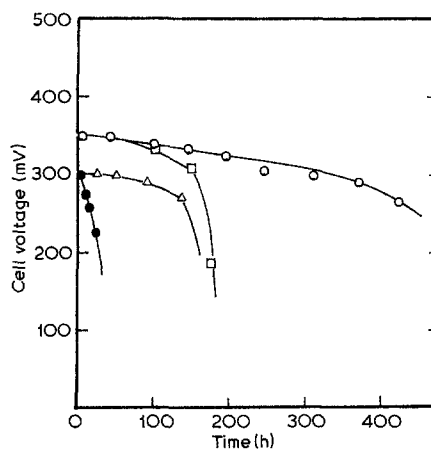


Fig. 9. Discharge curves at various loads of cell 4 at room temperature (\circ) $5\text{ k}\Omega$; (\square) $2\text{ k}\Omega$; (Δ) $1\text{ k}\Omega$; (\bullet) $0.7\text{ k}\Omega$.

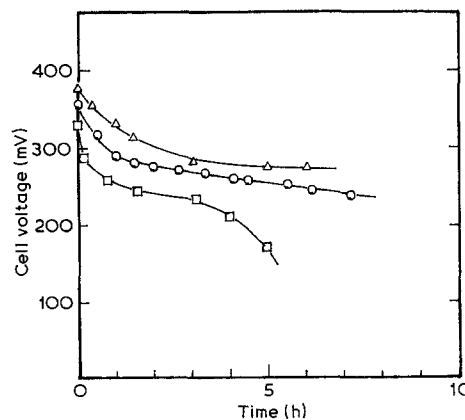


Fig. 10. Steady current discharge curves of cell 4 at 114°C (Δ) 4 mA cm^{-2} ; (\circ) 8 mA cm^{-2} ; (\square) 11.5 mA cm^{-2} .

efficiency was 20%. The discharge curves under constant loads of 0.7 k Ω , 1 k Ω and 2 k Ω at room temperature for cell 4 are shown in Fig. 9, where the average discharge currents are 350 μ A, 280 μ A, and 160 μ A. As shown in this figure, almost the same capacities were obtained at currents of 160 and 280 μ A. At a higher current intensity, such as 350 μ A, the capacity dropped considerably. The energy density of cell 4 calculated from the total weight (2 g) was 4.2 Wh kg⁻¹, the value of which is comparable to the solid silver compound electrolyte cells reported previously [3].

The solid electrolyte cells containing selenium and tellurium in the cathode possess an advantage of operational capability at higher temperature because the vapour pressures of these elements are very low and their contaminating reactions on the electrolyte are negligible even at high temperature when the cell is not in operation. The typical discharge curves under constant current drain at 114°C are shown in Fig. 10. The plateaux of cell voltage can be seen against discharge time at relatively high current density such as 8 mA cm⁻². Therefore, this type of solid electrolyte cell can be used at high temperatures up to 150°C, above which the electrolyte decomposes.

4. Conclusion

The solid electrolyte cell, Cu/7CuBr·C₆H₁₂N₄CH₃Br/X (X = S, Se, Te), was found to have the following characteristics:

(1) The cell was capable of achieving a current

density of several tens of microampere ranges at room temperature.

(2) The energy density of the cell with a selenium cathode was about 4 Wh kg⁻¹.

(3) The cell can be operated at temperatures up to 150°C. These characteristics are not so good as those of the cells using silver ion conducting solid electrolytes, but the cells with copper compounds as electrolyte and chalcogens as cathode have the significant advantages of low cost and a long shelf-life.

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