

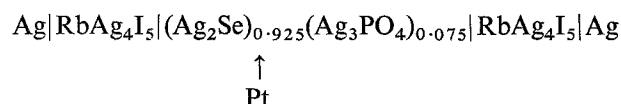
Solid state ionics—the electrochemical analog memory cell with solid electrolyte

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A new type analog memory cell with variable output voltage has been proposed and its performance examined. The cell construction is



in which $(\text{Ag}_2\text{Se})_{0.925}(\text{Ag}_3\text{PO}_4)_{0.075}$ is a mixed conductor exhibiting high ionic and electronic conductivity at room temperature. The potential difference between the silver electrode and the platinum electrode depends on the silver activity in the mixed conductor, and it is changed by passing the current between one silver electrode and the platinum electrode. The output voltage of the cell is changed in the range of 150 to 0 mV. At open circuit, the memorized cell voltage decreased by only 1% over several hours.

1. Introduction

Up to the present time, various types of silver-ion conductor which exhibit high conductivity in the solid state at room temperature have been found [1, 2, 3, 4, 5], and electrochemical devices using these electrolytes have been reported, for example, galvanic cells [6, 7] and coulometers [8, 9]. These devices have the advantages of achieving appreciable miniaturization and operating over a wide temperature range. The object of the present paper is to propose a new type analog memory cell with solid electrolytes.

A prototype cell was proposed by the present authors in a previous paper [10]. It was constructed with a silver electrode, solid electrolyte RbAg_4I_5 , and mixed conductor $\beta\text{-Ag}_2\text{Te}$. But, it had the disadvantage that the memorized cell voltage decreased with time on open circuit, because of the low ionic conductivity of $\beta\text{-Ag}_2\text{Te}$ at ambient temperature. The most effective way of improving this system is to find mixed conductors exhibiting high ionic conductivity at room temperature.

The ionic conductivities of the typical mixed

conductors, known so far, are summarized in Table 1. The ionic conductivities are relatively low at room temperature except with the last three solid solutions, which have recently been discovered in our laboratory [11, 12]. Of these solid solutions, which have high ionic and electronic conductivities at room temperature, $(\text{Ag}_2\text{Se})_{0.925}(\text{Ag}_3\text{PO}_4)_{0.075}$ exhibits the largest silver activity change. In this paper, the performance of the cell, employing $(\text{Ag}_2\text{Se})_{0.925}(\text{Ag}_3\text{PO}_4)_{0.075}$ as an electrode material is described. In the $\text{Ag}_2\text{Se}\text{-Ag}_3\text{PO}_4$ system, the solid solution containing 5 to 10 mole percent Ag_3PO_4 has a similar structure to $\alpha\text{-Ag}_2\text{Se}$, and a high ionic conductivity, comparable with that of RbAg_4I_5 . The electronic conductivity of this solid solution equilibrated with pure silver is about $2 \times 10^3 (\Omega \text{ cm})^{-1}$ at room temperature and varies with the change of the cation-to-anion ratio.

2. Experimental

2.1. Preparation of the samples

Silver selenide was prepared from the elements.

Table 1. Ionic conductivity of mixed conductors

Substance	Temperature °C	Ionic conductivity ($\Omega \text{ cm}$) ⁻¹
Cu ₂ S	400	2×10^{-1}
α -Ag ₂ S	200	3
β -Ag ₂ S	150	8×10^{-3} to 2×10^{-2}
	25	6×10^{-6} to 1×10^{-4}
α -Ag ₂ Se	150	2.7
β -Ag ₂ Se	105	5×10^{-5} to 1×10^{-3}
	25	1×10^{-6} to 2×10^{-5}
α -Ag ₂ Te	160	7×10^{-1}
β -Ag ₂ Te	97	1×10^{-3}
	25	1×10^{-4}
(Ag ₂ Se) _{0.925} (Ag ₃ PO ₄) _{0.075}	25	1×10^{-1}
(Ag ₂ S) _{0.69} (Ag _{1.7} Te) _{0.285} (Ag ₄ P ₂ O ₇) _{0.025}	25	1.6×10^{-1}
(Ag ₂ S) _{0.50} (Ag _{1.7} Te) _{0.45} (Ag ₃ PO ₄) _{0.05}	25	2.5×10^{-1}

The stoichiometric quantities of the silver (99.999% purity) and selenium powders (99.99% purity) were weighed before being thoroughly ground together. They were then sealed under vacuum in a Pyrex tube and heated at 350°C for 48 h. Silver phosphate was prepared by mixing aqueous solutions of AgNO₃ (reagent grade) and Na₂HPO₄ (reagent grade). The precipitate was washed by decantation and filtered. It was dried *in vacuo* over phosphorous pentoxide and then heated in nitrogen gas at 100°C.

The Ag₂Se-Ag₃PO₄ solid solution was made by heating the mixture of Ag₂Se and Ag₃PO₄ at 800°C for 17 h in a sealed, evacuated, silica tube. The solid electrolyte, RbAg₄I₅, was prepared by Owen's procedure [4].

2.2. Cell structure

The schematic diagram of the memory cell is shown in Fig. 1. The mixed conductor (Ag₂Se)_{0.925}(Ag₃PO₄)_{0.075} was pressed under a

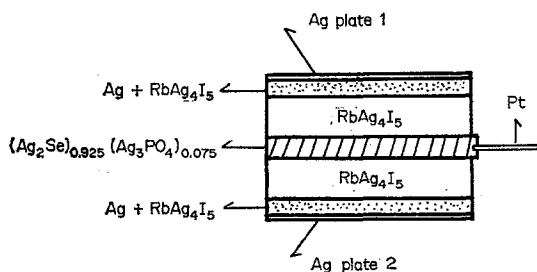


Fig. 1. Schematic diagram of the cell.

pressure of about 8000 kg cm⁻² to form a disk of about 0.5 mm in thickness and 13 mm in diameter, making a contact with a platinum wire on the edge. The disk was placed between two RbAg₄I₅ tablets. A mixture of powdered silver and RbAg₄I₅ was used for the silver electrode. A constant d.c. current was passed between the platinum electrode and the silver electrode 1 (working electrode), and the potential difference between the platinum electrode and the silver electrode 2 (reference electrode) was measured. This arrangement was employed to reduce the polarization on the silver working electrode. All measurements were carried out in a vacuum chamber.

3. Results and discussion

3.1. Principle of the cell

Upon passing a direct current from the platinum electrode to the silver electrode 1 in the cell shown in Fig. 1 (charging process), a definite amount of silver is transferred from the mixed conductor phase to the silver electrode, decreasing the cation-to-anion ratio in the mixed conductor. If the direction of the current is reversed (discharging process), the ratio increases. The chemical potential of silver, μ_{Ag} , in the mixed conductor is related to the potential difference, E , between the silver reference electrode 2 and the platinum electrode by

$$\mu_{\text{Ag}} - \mu_{\text{Ag}}^{\circ} = -EF \quad (1)$$

where μ_{Ag}° is the chemical potential of pure silver and F the Faraday constant. Denoting the chemical potentials of electron and silver ion in the mixed conductor by μ_e and μ_{Ag^+} , respectively, we have the general relation

$$\mu_{\text{Ag}^+} + \mu_e = \mu_{\text{Ag}} \quad (2)$$

For the mixed conductor equilibrated with pure silver,

$$\mu'_{\text{Ag}} - \mu_{\text{Ag}}^{\circ} = -\bar{E}F \quad (3)$$

$$\text{and} \quad \mu'_{\text{Ag}^+} + \mu'_e = \mu'_{\text{Ag}} \quad (4)$$

are established where μ'_{Ag} , μ'_{Ag^+} and μ'_e are the chemical potentials of each species in the mixed conductor equilibrated with pure silver and \bar{E} is the potential difference between the silver reference electrode 2 and the platinum electrode put in the mixed conductor which is equilibrated with pure silver. When the degree of disorder of the silver ions in the mixed conductor is high, the chemical potential of the silver ion is essentially independent of the small deviation of the cation-to-anion ratio, that is,

$$\mu_{\text{Ag}^+} \simeq \text{constant} \quad (5)$$

Thus, from Equations (1)–(5), one obtains

$$\mu_e - \mu'_e = -(E - \bar{E})F = -\Delta EF \quad (6)$$

By assuming that the concentration of holes in the mixed conductor is negligibly small compared to that of excess electrons, the relation between the excess electron concentration, n_e , and the decrease of the cation-to-anion ratio of the sample from that equilibrated with pure silver, r , is given by

$$n_e = \bar{n}_e - r(N_0/V_m) \quad (7)$$

where \bar{n}_e is the excess electron concentration of the mixed conductor equilibrated with pure silver, V_m the molar volume and N_0 the Avogadro number. This assumption will be appropriate for the $\text{Ag}_2\text{Se}-\text{Ag}_3\text{PO}_4$ solid solution which has an $\alpha\text{-Ag}_2\text{Se}$ like structure [11]. When the concentration of excess electrons is high, as in this mixed conductor, n_e is given by Fermi statistics as

$$n_e = \frac{\pi(8m_e^*kT)^{3/2} f(\mu_e/RT)}{2h^3} \quad (8)$$

where m_e^* is the effective mass of an excess electron, k the Boltzmann constant, h the Planck constant, and f the Fermi-Dirac function. In the cell shown in Fig. 1, RbAg_4I_5 is essentially a silver ion conductor, and the decrease r , is given by

$$r = \frac{q}{xF} \quad (9)$$

where q is the amount of coulombs passed through the cell and x the number of moles of anion in the mixed conductor. By combining Equations (6), (7), (8), and (9), we have Equation (10) as the relation between q and ΔE ,

$$-\frac{q}{xF}(N_0/V_m) = \frac{\pi(8m_e^*kT)^{3/2}}{2h^3} f(-\Delta E/RT + \mu'_e/RT) - \frac{\pi(8\bar{m}_e^*kT)^{3/2}}{2h^3} f(\mu'_e/RT) \quad (10)$$

where \bar{m}_e^* is the effective mass of an excess electron in the mixed conductor equilibrated with pure silver.

3.2. The comparison of the theoretical equation with the experimental results

In order to obtain the numerical relation between ΔE and q using Equation (10), one must have the values of V_m , m_e^* , \bar{m}_e^* and μ'_e . These values in the $(\text{Ag}_2\text{Se})_{0.925}(\text{Ag}_3\text{PO}_4)_{0.075}$ solid solution have been reported by the present authors [11], and are shown in Table 2. The value of the effective

Table 2. Characteristics of $(\text{Ag}_2\text{Se})_{0.925}(\text{Ag}_3\text{PO}_4)_{0.075}$ equilibrated with pure silver at 20°C.

n_e^- (cm^{-3})	\bar{m}_e^*/m_e	V_m ($\text{cm}^3 \text{mole}^{-1}$)	μ'_e/RT
4.3×10^{19}	0.21	3.88	8.48

mass of an excess electron in the solid solution depends on the deviation from the composition equilibrated with pure silver, that is r . It may be assumed, however, to be a constant value in the range of a small change of ΔE . Under such condition, Equation (10) can be rewritten as Equation (11) using the numerical values at 20°C shown in Table 2,

$$q/x = 16.0[f(8.48) - f(-39.3 \Delta E + 8.48)] \quad (11)$$

Further, according to the tabulated values [13], the Fermi-Dirac function $f(\eta)$ may be reduced to a linear function of η in the range of a small deviation of η , and Equation (11) may be expressed by the following simple formula,

$$\begin{aligned} q/x &= 16.0 f'(8.48) \times (39.3 \Delta E) \\ &= 1810 \times \Delta E \end{aligned} \quad (12)$$

where $f'(8.48)$ is the differential coefficient of $f(\eta)$ at $\eta = 8.48$. This equation shows that ΔE increases linearly with the number of coulombs passed through the cell. The calculated isotherm and the experimental results for the cell with 0.484 g $(\text{Ag}_2\text{Se})_{0.925}(\text{Ag}_3\text{PO}_4)_{0.075}$ at 20°C are shown in Fig. 2, where the line and the circles

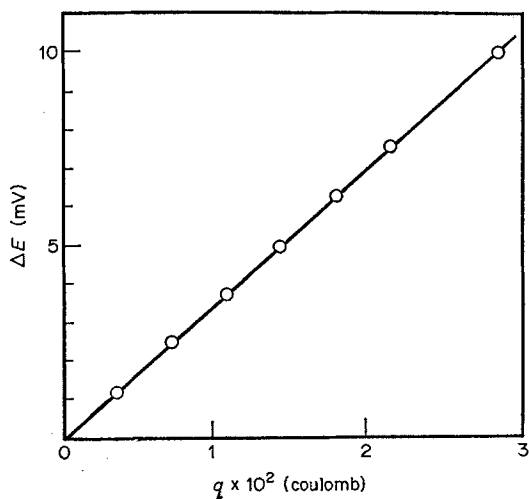


Fig. 2. ΔE versus q curve of the cell $\text{Ag}||\text{RbAg}_4\text{I}_5|(\text{Ag}_2\text{Se})_{0.925}(\text{Ag}_3\text{PO}_4)_{0.075}$ (0.484 g) at 20°C . The circles represent the experimental values and the line is the theoretical isotherm.

represent the calculated and experimental results, respectively. As the potential difference of the cell between the silver electrode and the mixed conductor electrode equilibrated with pure silver, \bar{E} , was nearly zero, the potential difference between the silver electrode and the mixed conductor electrode, E , is approximately equal to ΔE . It is found in Fig. 2 that the experimental values coincided with the calculated ones showing a good linear relationship when ΔE was between 0 and 10 mV. Above 10 mV, however, the experimental values deviated from the line, the deviation being increased with increasing ΔE . Above 20 mV, the experimental

and calculated values did not coincide, probably because the effective mass of an excess electron is not constant over this range of ΔE values.

3.3. Accuracy of the cell as a coulometer

For practical use, this type of memory cell should be capable of operation over a wide current range and for long and short operation times. In Fig. 3, the typical charge and discharge

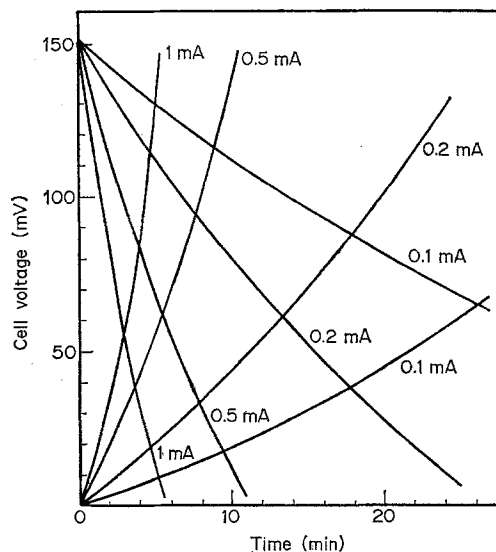


Fig. 3. The cell voltage versus time curves of the cell $\text{Ag}||\text{RbAg}_4\text{I}_5|(\text{Ag}_2\text{Se})_{0.925}(\text{Ag}_3\text{PO}_4)_{0.075}$ (0.484 g) at 20°C .

curves of the cell with 0.484 g $(\text{Ag}_2\text{Se})_{0.925}(\text{Ag}_3\text{PO}_4)_{0.075}$ at 20°C are shown under various current drains. The potential difference was measured while the current was passing through the cell. The good reproducible results were obtained in the voltage range of 0 to 150 mV, and the charging period from 0 to 150 mV agreed almost with the discharging periods from 150 to 0 mV in the current range of 0.1–10 mA. The measured amounts of coulombs passed through the cell within these periods of time is shown in Table 3. The difference in all cases is less than 1%.

The accuracy of this type of coulometer was checked with a current of 0–5 mA for a period of 0–120 min, using a triangular wave current. The relation between the cell voltage, E , and the amount of coulombs, q , passed through the cell was preliminarily examined by the constant

Table 3. Measured coulombs in the charging and discharging period at various currents

Current μA	Charging period from 0 to 150 mV (min)	Coulombs	Discharging period from 150 mV to 0 (min)	Coulombs
10000	0.527	0.316	0.529	0.318
4000	1.34	0.316	1.34	0.316
2000	2.66	0.319	2.66	0.319
1000	5.32	0.319	5.31	0.319
500	10.67	0.320	10.61	0.318
200	26.54	0.319	26.85	0.322
100	52.99	0.318	52.99	0.318

current drain of 1 mA to draw a calibration curve, and the initial and final cell voltages were applied to E on the calibration curve to determine q passed through the cell. The error, ε , was calculated by the following equation

$$\varepsilon = \frac{q - q_s}{q} \quad (13)$$

where q_s is the coulombs calculated by the calibration curve of E against q . The error is less than 1% in all cases as shown in Table 4.

Table 4. Accuracy of the electrochemical cell

Current, mA	Coulombs	Error %
0.0.1	0.293	± 0.7
0.0.5	0.300	± 0.0
0.1.4	0.294	-0.7
0.5.0	0.250	± 0.2

According to Equation (10), the amount of coulombs passed to charge the cell to a certain voltage should be changed linearly with the amount of the electrode material, x . In Fig. 4, the amount of coulombs passed to charge the cell from 0 to 130 mV is shown against the amount of the mixed conductor used for the electrode material. It gives a straight line.

3.4. Change of the open-circuit voltage

If the open-circuit voltage (OCV) of this type of electrochemical cell is kept constant for a certain period of time after the cell is charged to a certain cell voltage, the cell may be used for an

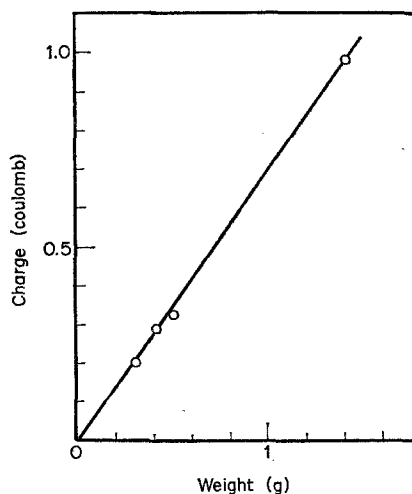


Fig. 4. The amount of the electrode material versus the quantity of electricity to charge the cell from 0 to 130 mV.

analog memory device. In general, electrochemical cells with solid electrolytes show an appreciable polarization at the electrolyte-electrode interface. This is possibly eliminated in this study by using a silver reference electrode to measure the OCV of the cell. The time dependence of the OCV at 20°C is shown in Fig. 5 after the cell is charged from 0 to 150 mV at various charging currents. At a low current charge of 0.2 mA, the change of the OCV is less than 1% for at least 3 h. At higher current, however, the OCV decreases slightly with time. For example, at 4 mA, the OCV changes from 150 mV to 147 mV over 5 h. But, the change is very much smaller than that of the cell using β -Ag₂Te as the mixed conductor electrode [11]. In the cell investigated in this study, as the silver reference electrode was used, the polarization at the silver

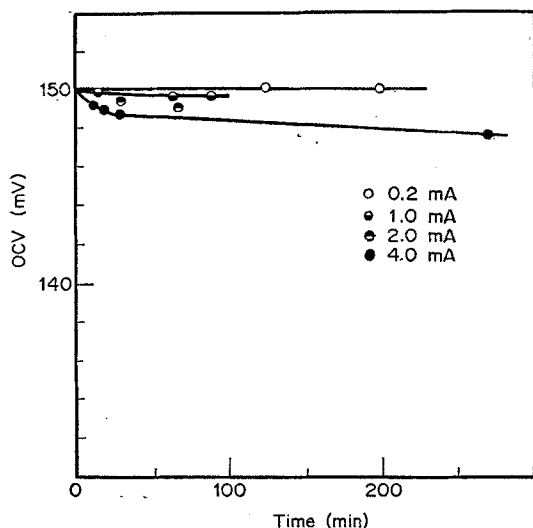


Fig. 5. Time dependence of the OCV of the cell $\text{Ag} | \text{RbAg}_4\text{I}_5 | (\text{Ag}_2\text{Se})_{0.925} (\text{Ag}_3\text{PO}_4)_{0.075}$ (0.484 g) after being charged by various currents at 20°C .

working electrode-electrolyte interface is not included in the OCV and the OCV change with time may be due mainly to the polarization in the electrolyte-mixed conductor interface and to the slow diffusion of silver in the mixed conductor. If the latter is the main reason of the OCV change, some period of time will be necessary to obtain a homogeneous activity of silver in the mixed conductor phase and the OCV change may depend on the thickness of the mixed conductor electrode. It was found that the thinner the mixed conductor phase, the smaller the change of the OCV of the cell. For example, the OCV change of the cell, with mixed conductor electrodes 0.5 mm or 1.0 mm thick changed from 150 mV to 149.2 mV or from 150 mV to 147.9 mV during 1 h, respectively.

For the OCV change in a long period of time, the electronic conductivity of the solid electrolyte RbAg_4I_5 may play a role. That is, the cell undergoes self-discharge by electronic current in the electrolyte during long-term storage. In Fig. 6, the time dependence of the OCV at room temperature is shown after the cell is charged to 150 mV. The OCV decreases gradually with time. Assuming that the OCV change is due to the electronic conductivity of RbAg_4I_5 , the electronic conductivity was calculated as less than $4 \times 10^{-9} (\Omega \text{ cm})^{-1}$ at room temperature.

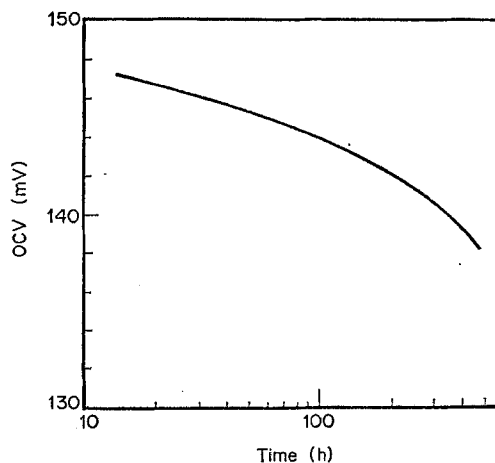


Fig. 6. Time dependence of the OCV of the cell $\text{Ag} | \text{RbAg}_4\text{I}_5 | (\text{Ag}_2\text{Se})_{0.925} (\text{Ag}_3\text{PO}_4)_{0.075}$ (0.30 g) at room temperature.

This calculation was done using the OCV change of 5.8 mV for 360 h, the slope of E versus q curve, and the dimensions of the RbAg_4I_5 . The values for the electronic conductivity reported so far show a certain discordance. The electronic conductivity of RbAg_4I_5 has been evaluated to be less than $10^{-11} (\Omega \text{ cm})^{-1}$ by Owens [7]. De Rossi and Scrosati [14] and Takahashi *et al.* [15] have found the values of $1 \times 10^{-8} (\Omega \text{ cm})^{-1}$ and $1 \times 10^{-9} (\Omega \text{ cm})^{-1}$ respectively. The electronic conductivity of RbAg_4I_5 can be said, therefore, to be less than $10^{-8} (\Omega \text{ cm})^{-1}$, and the contribution of the electronic conductivity to the OCV in a short period of time can be considered negligible.

4. Conclusion

A new type memory cell with a solid electrolyte and a mixed conductor of the $\text{Ag}_2\text{Se}-\text{Ag}_3\text{PO}_4$ system has been proposed. This type of cell has many unique properties. Firstly, it exhibits the output voltage, and secondly, it maintains its OCV constant for a long period of time. Further, it has a good linear relation between the cell voltage and the number of coulombs passed through the cell in the cell voltage range of at least 0 to 10 mV, and it is able to integrate the current when this is in the micro ampere range. Therefore, this cell must have a wide application as a coulometer and an analog memory.

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