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Analogue storage cells based on a coulometer with solid electrolyte and stoichiometric variation of the storage phase.
I. Cells with symmetric electrodes

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Symmetric solid-electrolyte galvanic cells such as $Pt/Ag_{2\pm\delta}Se/RbAg_{4+y}I_{5-y}Se_y/Ag_{2\pm\delta}Se/Pt$, based on a continuous variation of the redox potential of the 'storage phase' $Ag_{2\pm\delta}Se$ with its composition, show considerable advantages over other types of cells, e.g. high accuracy, long charge-storage capability, effectively a double range of potential variation, and suppression of anodic polarization at the metal–electrolyte interface. The temperature characteristics as well as the overvoltage of this cell have been quantitatively determined and analysed. This cell can discharge in the temperature range −30 to 130° C with a current density up to $10\,mA\,cm^{-2}$.

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1. Introduction

Besides the use of solid-electrolyte galvanic cells for thermodynamic measurements and other basic studies (dating from the mid 1950s) the use of galvanic cells for more utilitarian purposes such as batteries and coulometers first started at the beginning of the 1960s with the discovery of compounds with exceptionally high ionic conductivity at room temperature, e.g. Ag_3SI and Ag_3SBr [1, 2] and especially $RbAg_4I_5$ [3, 4]. The great hopes for these galvanic cells were not fully met, mainly because of the following limitations:

(a) The cells are not cheap. Until now only ionic compounds of silver have been shown to have sufficiently high ionic conductivity at room temperature.

(b) Solid-state galvanic cells are easily polarized.

(c) The solid electrolyte shows quite significant variations in properties with temperature.

In spite of the above limitations the use of solid electrolyte galvanic cells as batteries or coulometers has some advantages over other types of cells or devices, namely: (a) a very small volume and consequently a very light weight, (b) a wide range of working temperatures, and (c) exact thermodynamic correlation between electrode potential and the number of coulombs passed through the cell at any current density. It is therefore well worth while to continue the investigation of solid electrolyte cells. In this, the first of two papers, we shall report the results of our investigation on two types of solid-state galvanic cells.

2. Theoretical considerations

Most solid electrolyte cells reported in the past 14 years [5–10] have been used either as condensers at room temperature or as coulometers for integrating and timing circuits (memory cells and timers). A feature common to these solid electrolyte cells is the use of a silver anode, the silver ions being the positive charge carriers. Two disadvantages may result from this arrangement, namely, anodic polarization and growth of silver needles during the cathodic deposition of silver in the discharge process. To reduce anodic polarization several measures have been adopted, e.g., using an amalgamated silver electrode [6], using as anode a pressed pellet of a mixture of silver powder and solid electrolyte [7] or using as anode a pressed tablet of finely divided silver, graphite and solid

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electrolyte [10]. The cell of Kennedy *et al.* [5] also suffers from an incomplete anodic dissolution of the silver deposited on the Au electrode.

The two main requirements in solid electrolyte coulometers are high accuracy and long charge-storage capability. In the cells already mentioned, based on the variation of the redox potential at the cathode, these requirements are not satisfactorily fulfilled because of the variation of the vapour partial pressure of the non-metallic phase with temperature, especially in cells with I_2 or Se at moderate temperatures. This disadvantage may be avoided by using a compound with the capability of varying the metal/non-metal ratio in the 'storage phase' so that the redox potential varies continuously with the composition of the storage phase. The cell reported by Takahashi and Yamamoto [11, 12]

$$\mathrm{Ag/RbAg_4I_5/Ag_2Se\,(or\ Ag_2Te)\,(+\ 7.5\ mol\%\ Ag_3PO_4)} \qquad (1)$$

is based on this principle. This cell has nevertheless a silver working electrode. To avoid the subsequent anodic polarization and the growth of silver needles in this cell the following cell with symmetric disposition has been conceived:

$$\mathrm{C\,(or\ Pt)/Ag_{2\pm\delta}Se/RbAg_{4+y}I_{5-y}Se_y/Ag_{2\pm\delta}Se/C\,(or\ Pt)} \qquad (2)$$

Ag
Reference electrode

The working principle of Cell 2 as a coulometer is based on the continuous variation of the redox potential in the solid phase $Ag_{2\pm\delta}Se$ with its composition. The range of existence of β-$Ag_{2\pm\delta}Se$ as a homogeneous phase at 100° C varies between $\delta = +6 \times 10^{-4}$ (silver excess; Ag_2Se in equilibrium with silver metal) and $\delta = -2 \times 10^{-4}$ (silver deficit; Ag_2Se in equilibrium with selenium) [13]. We may consider the symmetric Cell 2 as an integration of two single cells:

Left: $\mathrm{C/Ag_{2\pm\delta}Se/RbAg_{4+y}I_{5-y}Se_y/Ag}$ (2a)

Right: $\mathrm{Ag/RbAg_{4+y}I_{5-y}Se_y/Ag_{2\pm\delta}Se/C.}$ (2b)

The electromotive force (e.m.f.) E of each of the single cells in the rest state is given by

$$E = -(RT/F)\ln a_{\mathrm{Ag}} \qquad (3)$$

where a_{Ag} is the thermodynamic silver activity in the storage phase $Ag_{2\pm\delta}Se$.

For the assemblage of Cell 2 care should be taken that the masses of Ag_2Se on both sides of the cell are approximately the same. Furthermore, it is very important that the silver activities in both Ag_2Se pellets are quite different. One may, for instance, obtain first the pellet of the left side in equilibrium with silver metal while the pellet of the right side has been previously prepared in equilibrium with selenium. Accordingly the thermodynamic state of Cell 2 at time $t = 0$ is:

Left half-cell:
$a'_{\mathrm{Ag}} \gtrsim 1$, δ positive (metal excess)

Right half-cell:
$a''_{\mathrm{Ag}} \ll 1$, δ negative (metal deficit).

By passing a current in Cell 2 from left to right, silver ions move from the left-side Ag_2Se pellet to the right-side one. Accordingly the value of δ decreases in the left-side Ag_2Se pellet and increases in the right-side one. Simultaneously the redox state of each of the two Ag_2Se pellets will change. Using a Ag reference electrode, combined with each of the two C (or Pt) electrodes, the diagrams of Figs. 1a and b for the variation of the e.m.f.s E_{2a} and E_{2b} of the two half-cells will be obtained. Once the e.m.f. E_{2b} of the half-cell on the right side has reached the value of $E_{2b} = 0$, i.e., once the value of the e.m.f. E_{2a} of the half-cell on the left has reached a maximum value, the polarity of the cell will be changed and the silver ions will move in the opposite direction. By combining the two diagrams of Figs. 1a and b one may obtain diagrams for the variation of $E_2 = E_{2a} + E_{2b}$ and of I (the electric current), represented in Fig. 2 after several cycles have been completed.

It is possible to replace the compound $Ag_{2\pm\delta}Se$ as the storage phase in Cell 2 by the compound $Ag_{2\pm\delta}Te$, which exists in the range $\delta = -11.3 \times 10^{-4}$ to $\delta = +1.8 \times 10^{-4}$ [13] as a homogeneous phase at 100° C.

The use of the Ag reference electrode in Cell 2 is restricted to the preliminary work of obtaining the E–t curves of Fig. 2 and will no longer be used when the cell works as a coulometer.

3. Experimental procedures

Before assembling the different phases of Cell 2

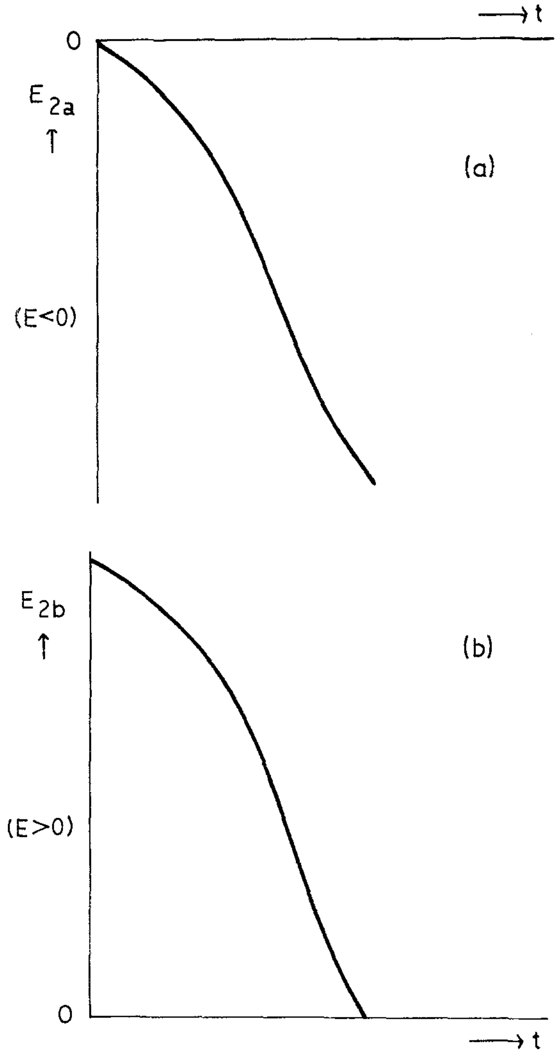

Fig. 1. Schematic variation of E_{2a} and E_{2b} with time of the two half-cells in Cell 2 with the change of metal/non-metal ratio in each storage phase.

in a single pellet, the two samples of Ag_2Se on the left and right sides were prepared separately with a well-defined state of deviation from the ideal stoichiometric composition. Two Ag_2Se pellets of exactly the same weight were maintained in evacuated Pyrex tubes at 130° C for 5 days, one in contact with metallic silver and the other in equilibrium with selenium vapour at a vapour pressure corresponding to that temperature. The cooled pellets were separately crushed in a mortar to a very fine powder.

In a 0.8 cm diameter die we put successively powders of each of the five different phases that make up Cell 2, after the previously laid phase had been pressed at about 4.9 MN m^{-2}. Finally all the phases were pressed together at a pressure of about 14.7 MN m^{-2}. After the pellet was removed from the press, the edges were carefully polished with fine sandpaper to remove any possible contamination with particles of the adjacent phase which could lead to an electrical short.

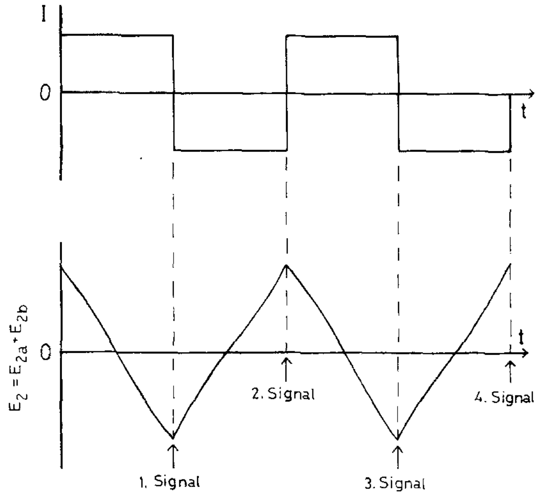

Fig. 2. Schematic diagrams of $E_2 = E_{2a} + E_{2b}$) versus t and I versus t for the charge–discharge process of Cell 2.

As the solid electrolyte for Cell 2 we have used the thermodynamically stabilized compound $RbAg_{4+y}I_{5-y}Se_y$, resulting from a partial substitution of the iodine ions by Se ions in the compound $RbAg_4I_5$ [14]. The Ag reference electrode consisted of a silver wire wound firm around the $Ag_{4+y}I_{5-y}Se_y$ pellet in the middle of the symmetric Cell 2.

Two other symmetric cells were investigated besides Cell 2, namely Cells 4 and 5 overleaf. The solid solution 92.5 mol% Ag_2Se + 7.5 mol% Ag_3PO_4, used as storage phase in Cell 4, has, according to Takahashi [15], an ionic conductivity of 0.13 Ω^{-1} cm^{-1} at 25° C.

As solid electrolyte for Cell 5 we used the solid solution 85 mol% $C_6H_{12}N_4CH_3I$ + 15 mol% CuI, obtained as by Takahashi *et al.* [16]. We have measured an ionic conductivity for this compound of 1.3×10^{-3} Ω^{-1} cm^{-1} at room temperature, in good agreement with the value reported by Takahashi [16].

All the measurements were carried out in purified N_2 atmosphere. The temperature of the cell

$$\mathrm{C/Ag_2Se(+\,Ag_3PO_4)/RbAg_{4+y}I_{5-y}Se_y/Ag_2Se(+\,Ag_3PO_4)/C} \tag{4}$$

Ag
Reference electrode

and

$$\mathrm{Pt/Cu_2Se/C_6H_{12}N_4CH_3I{\cdot}CuI/Cu_2Se/Pt} \tag{5}$$

Cu
Reference electrode

could be changed at will between 0 and 130 ± 0.5° C, The testing of Cells 2, 4 and 5 as coulometers was performed by fixing the current density i through the cell and following the variation of the potential E between each of the C (or Pt) electrodes and the Ag reference electrode or, in other cases, between the two C (or Pt) electrodes as a function of time. When the potential of the anode had reached a maximum value (in the case of Cell 2 about 265 mV), the polarity of the cell was changed mechanically by means of a switch. Current densities between 0.2 and 1.0 mA cm^{-2} were generally used. Occasionally current densities of 2, 5 and 10 mA cm^{-2} were also used.

4. Experimental results

Changes in the oxidation state of the two quasi-single cells of the symmetric Cell 2 have been brought about in three different ways:

(a) By short pulses of electric current through the cell, followed by waiting periods, until the new oxidation condition reached a uniform value in the whole mass of the storage phase. For these experiments the Ag reference electrode of the cell was used. The curves of Figs. 3 and 4 have been obtained in this way with a symmetric cell of storage masses $m'_{\mathrm{Ag_2Se}}(\mathrm{left}) = m''_{\mathrm{Ag_2Se}}(\mathrm{right}) = 0.431$ g at 101° C and 0° C respectively. The equality of both figures is only apparent, since the curves of Fig. 3 were obtained with a current density of 0.4 mA cm^{-2} while the curves of Fig. 4 were obtained with a current density of 0.2 mA cm^{-2}.

The broken line between the two extreme potential values represents approximately the variation of the potential E_2 between the two C electrodes of the symmetric cell. The peaks of the potential E_2 can be used as signals for changing the polarity of the cell.

(b) By changing the oxidation state of Cell 2 in a continuous manner. According to this procedure the current, as well as the value of the potential E_1 at which the polarity of the cell is to be automatically changed, are previously fixed and

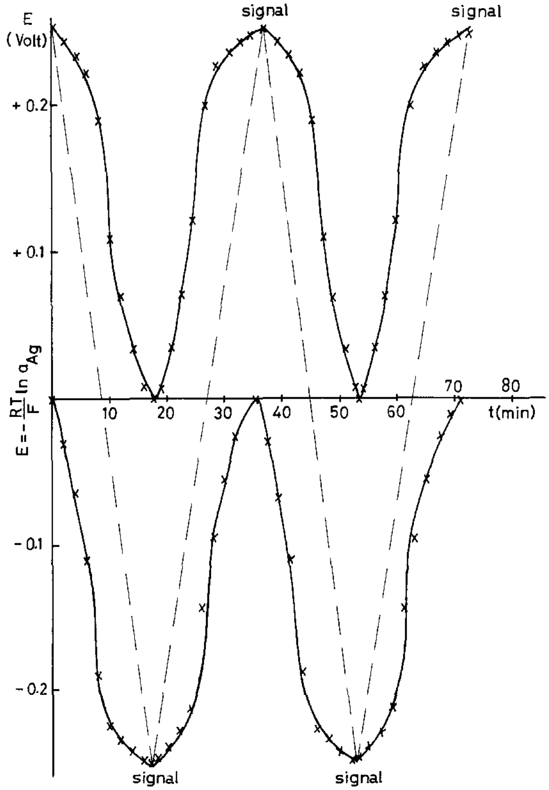

Fig. 3. E.m.f. versus t diagrams for the two half-cells of Cell 2, for a cell with $m'_{\mathrm{Ag_2Se}} = m''_{\mathrm{Ag_2Se}} = 0.431$ g, at $T = 101°$ C and $i = 0.4$ mA cm^{-2}.

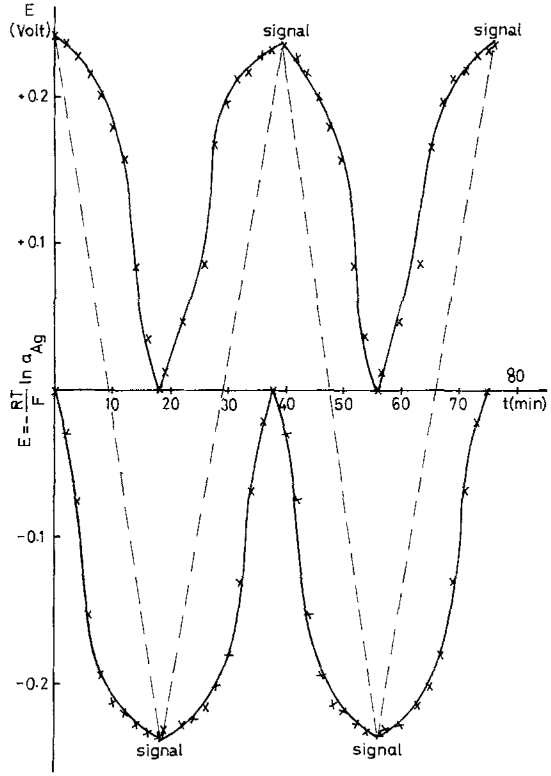

Fig. 4. E.m.f. versus t diagrams for the same cell of Fig. 3, at $T = 0°$ C and $i = 0.2$ mA cm^{-2}.

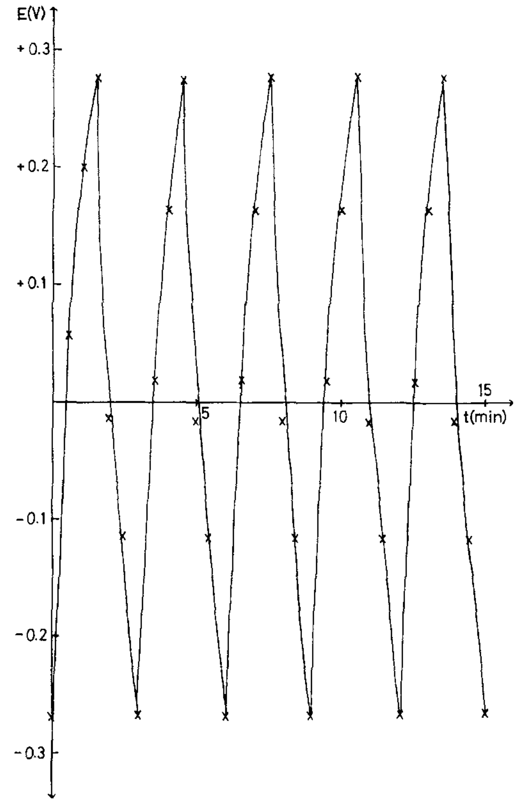

Fig. 5. Variation of E_2 with continuous flow of current through the cell and with changes of polarity at $E_2 = \pm 0.265$ V, for a cell with $m'_{Ag_2Se} = m''_{Ag_2Se} = 0.1$ g, at $T = 58°$ C and $i = 1.0$ mA cm^{-2}.

the current flows continuously through the cell in alternate directions. The silver reference electrode of Cell 2 was no longer used for these experiments. The variation of the potential E was recorded at equal time intervals. Fig. 5 shows an example of the curves obtained in this kind of experiment.

(c) By changing the oxidation state of Cell 2 in a continuous manner every half cycle. The current flows continuously through the cell, until the maximum predetermined value of the potential has been reached. At that point the current is cut off and a waiting period follows until the cell potential has dropped to a lower constant value. By changing the polarity of the cell at this point, the same procedure can be repeated for the next half cycle. Fig. 6 reproduces an example of the results obtained in this way.

The symmetric Cells 4 and 5 were investigated in the same way as Cell 2. The results obtained may be summarized as follows: additions of Ag_3PO_4 to the storage phase Ag_2Se did not bring about any improvement in the function of Cell 2. On the contrary the range of existence of the solid solution $Ag_2Se + Ag_3PO_4$ as a homogeneous single phase is narrower than that of the pure phase Ag_2Se. Accordingly the capacitance of Cell 4 is smaller than that of Cell 2. Furthermore, Cell 4 shows a very rapid self-discharge, probably due to an increase in the electronic conductivity of the storage phase.

The range of existence of the storage phase of Cell 5 (β-Cu_2Se) is not so well determined as that of α-Cu_2Se [17–19]. It seems in any case that the range of existence of β-Cu_2Se depends very strongly on the temperature. Furthermore, we have observed that Cell 5 undergoes a very rapid self-discharge, probably due to the fact that the solid solution 85 mol% $C_6H_{12}N_4CH_3I$ + 15 mol% CuI, used as solid electrolyte in this cell, is predominantly an electronic conductor.

5. Discussion

The efficiency of Cell 2 as a reliable analogue

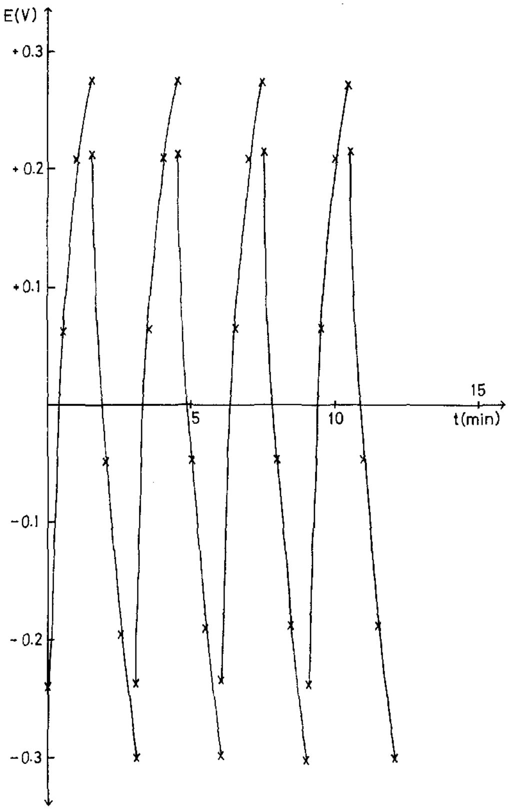

Fig. 6. Variation of E_2 with continuous flow of current through the cell every half cycle. Data obtained with the cell of Fig. 5 under the same conditions.

storage device depends mainly on two limiting factors. One is the temperature dependence of the potential E of the cell. This effect is referred to in electronics as the 'temperature characteristic of the cell'. The second limiting factor is the difference in potential values between the dynamic state and the equilibrium state of the cell. This second factor is called the 'overpotential of the cell' and is defined as the change in cell voltage when the current is switched off. Since the reasons for the two effects are different, we shall discuss each factor separately.

5.1. *Temperature characteristics of Cell 2*

It has already been pointed out that the similarity of the curves in Figs. 3 and 4 is only apparent because both groups of curves were obtained with different current densities. The amount of coulombs transferred through Cell 2 in each full semi-cycle is proportional to the number of silver ions transferred from one storage phase to the other. This corresponds exactly to the total deviation from the stoichiometric composition suffered by each of the two $Ag_{2\pm\delta}Se$ pellets during a full semi-cycle. This value can be calculated by means of the equation

$$\Delta\delta = It/n_{Ag_2Se}F \qquad (6)$$

where I is the electric current, t is the time of current flow between two consecutive extreme oxidation potentials, n_{Ag_2Se} is the number of moles of Ag_2Se in each Ag_2Se pellet and F is the Faraday constant. For the experimental conditions of Figs. 3 and 4 with $I = 2 \times 10^{-4}$ A and $I = 10^{-4}$ A respectively and with $n_{Ag_2Se} = 1.46 \times 10^{-3}$ mol and $t = 1.05 \times 10^3$ s, one obtains the following values of $\Delta\delta$ at 0°C and 101°C:

$$\Delta\delta_0 = 7.45 \times 10^{-4}\,\text{mol}^{-1}$$

$$\Delta\delta_{101} = 1.59 \times 10^{-3}\,\text{mol}^{-1}.$$

Accordingly, the range of existence of β-Ag_2Se as a homogeneous phase at 101°C is approximately double that at 0° C.

One way to determine quantitatively the temperature characteristics of Cell 2 is to follow the changes in the equilibrium potential of the cell as the temperature varies. This procedure will be most conveniently performed by following simultaneously the variation of the potentials E_{2a} and E_{2b} of the two half-cells. The results of this investigation are reported in Table 1. The observed negative values of E''_{2a} at the half-cell of the left side, when the temperature drops from t' to t'', mean that a certain amount of silver has segregated from Ag_2Se and is first deposited at the interface $Ag_2Se/RbAg_{4+y}I_{5-y}Se_y$. After a while this silver migrates to the Ag reference electrode and the value of E''_{2a} turns gradually to 0. Using the data of Table 1 the temperature characteristics of Cell 2 can be calculated as $\Delta E/\Delta t = 240\,\mu$V K^{-1} in the temperature range between 100 and 0°C. This value is about ten times higher than the value reported for practical memory devices [20]. Methods for reducing this value drastically in diffusion coulometric cells are reported in the second paper of this series [21].

5.2. *Overvoltage of Cell 2*

The overvoltage of Cell 2 with graphite electrodes

Table 1. Variation of the potentials of the two half-cells of Cell 2 with temperature

Temperature variation from t' to t'' (°C)			*Potential variation*							
			Left half-cell (2a)				*Right half-cell* (2b)			
t'	t''	Δt	E'_{2a} (V)	E''_{2a} (V)	ΔE_{2a} (V)	$\Delta E_{2a}/\Delta t$ (V K^{-1})	E'_{2b} (V)	E''_{2b} (V)	ΔE_{2b} (V)	$\Delta E_{2b}/\Delta t$ (V K^{-1})
100	60	40	0.0001	−0.0089	0.0090	0.00022	0.2610	0.2496	0.0114	0.00029
80	40	40	0.0002	−0.0200	0.0202	0.0005	0.2548	0.2475	0.0073	0.00018
40	15	25	−0.0012	−0.0228	0.0216	0.00086	0.2462	0.2393	0.0069	0.00028
15	0	15	0.0003	−0.0069	0.0072	0.0005	0.2422	0.2398	0.0024	0.00016

and with m_{Ag_2Se}(left) = m_{Ag_2Se}(right) = 0.1 g is about 65 mV at $I = 1.0$ mA cm^{-2} and $T = 58$°C (Fig. 6). The overvoltage for the same cell at 20° C is about 145 mV. A systematic variation of the three fundamental factors affecting the overpotential of Cell 2, namely, mass of the storage phase Ag_2Se, current density and temperature, has led to the following results:

(a) The influence of the mass of Ag_2Se and of the current density on the value of the overvoltage is noticeable but relatively small. On the other hand the effect of the temperature is unusually high, especially at low temperatures. This effect cannot be explained solely by an increase in the resistance to the mobility of the ions with a decrease in temperature.

(b) By substitution of the graphite electrodes by Pt electrodes in Cell 2 the overvoltage of the cell drops to values between 25 mV and 15 mV. One possible explanation to the high overvoltage of cells with graphite electrodes may be the anisotropic conductivity of the graphite employed.

(c) A cell overvoltage of 15 mV is for practical purpose too high [20]. Two different causes are probably responsible for the high overvoltage of Cell 2, namely, interface polarization and diffusion polarization. The contribution of the interface polarization to the overall polarization of the cell is probably minor.

Hence the diffusion polarization presumably plays a major role in the observed overall polarization of the cell. In the steady state, the potential E_2 of Cell 2 is given by the sum

$$E_2 = E_{2a} + E_{2b} \tag{7}$$

of the potentials of the two half-cells and reflects the oxidation state of the two storage phases Ag_2Se in the cell. During the flow of current across the cell, a gradient concentration of these ions across the two Ag_2Se pellets is created due to the time-dependent mobility of the Ag ions. Accordingly, the potential shown between the two electrodes during the flow of current does not correspond exactly to the real oxidation state of the Ag_2Se pellets. After the current has been switched off, the concentration of the silver ions becomes uniform in the whole mass of the Ag_2Se pellets and the potential of the cell drops to a constant value.

The observed overpotential effect of Cell 2 can be reduced to some extent by reducing the mass of the two Ag_2Se pellets in the cell, but this reduction takes place at the expense of a considerable diminution of the capacitance of the cell. A method for reducing the overpotential of cells with stoichiometric variation of the storage phase to values under 3 mV is reported in the second paper [21].

Acknowledgement

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