

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

II. Cells with small temperature variation and low overvoltage

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A mixture of about 50 wt% Ag₂Se and 50 wt% Ag₂Te as the storage phase in analogue storage cells reduces the effect of temperature variations in the cells to negligible values. A fine dispersion of the above storage phase in the solid electrolyte 50 wt% RbAg_{4+y}I_{5-y}Se_y + 50 wt% RbAg_{4+y}I_{5-y}Te_y also reduces the overvoltage of the cell to values under 3 mV. Several cells with capacitances up to 140 mF, current densities up to 20 mA and potential variations in the charged state smaller than 1 mV in 120 mV over 6 months, have been constructed and tested.

1. Introduction

The aim of this work is to develop an analogue storage cell, based on a coulometer with a solid electrolyte, which is suitable for use in electronics. A reliable analogue storage cell should fulfil the following conditions:

- (a) good storage capability (> 100 mF),
- (b) high accuracy,
- (c) low overvoltage (< 3 mV),
- (d) small temperature variation ($\Delta U/\Delta T < 0.1$ mV K⁻¹),
- (e) small time constant (< 1 s) or rapid charging rate,
- (f) long charge storage capability.

All the above conditions, except (c) and (d), are fulfilled by the symmetric cell with Ag₂Se as the storage phase [1]. It is therefore of great importance to find a way of improving these two properties of the symmetric galvanic cells described in [1]. Any solution to the problem of temperature variations in diffusion cells with ionic compounds as the storage phase must necessarily consider the properties of the ionic compounds. The range of existence as homogeneous phases of almost all the ionic compounds shows a temperature dependence according to the equation

$$(M/A)_{\text{ion}} = \frac{a \pm \delta}{b} + kT \quad (1)$$

where $(M/A)_{\text{ion}}$ is the metal/nonmetal ratio of the ionic compound $M_{a \pm \delta}A_b$, k is a constant factor specific for each compound and T is the temperature. On the other hand, the redox potential of a nonstoichiometric ionic compound depends on the thermodynamic activity of the mobile ions, which in turn is a function of the deviation δ from the ideal stoichiometry of the ionic compound.

In most ionic compounds the effect of temperature on the range of existence as a homogeneous phase is positive (increased range of metal to nonmetal ratio with rise in temperature). In some cases, however, the effect of temperature on the range of existence of the compound is negative. It is conceivable to use, as the storage phase in solid-state galvanic cells, a mixture of two ionic compounds, one with a positive and the other with a negative temperature effect. Under these circumstances the resulting cell would show no temperature effect or at most a very small one.

Cells with β -Ag₂Se as the storage phase clearly show a positive temperature variation [1]. In contrast, there are reasons to believe that cells with β -Ag₂Te as the storage phase may have nega-

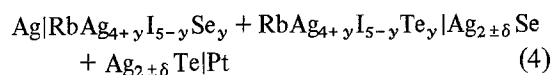
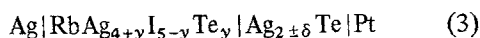
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tive temperature variations [2]. The use of $\beta\text{-Ag}_2\text{Te}$ as the storage phase (alone or mixed with $\beta\text{-Ag}_2\text{Se}$) may introduce notable advantages over cells with only $\beta\text{-Ag}_2\text{Se}$ as the storage phase, namely (a) a wider range of existence as a homogeneous phase; (b) an almost linear variation of the redox potential of the cell with the value of δ in $\beta\text{-Ag}_2\text{Te}$ [2]; and (c) values of the self-diffusion coefficient D_{Ag}^* , as well as of the diffusion coefficient D_{Ag} , of the silver ions in $\beta\text{-Ag}_2\text{Te}$ larger than in $\beta\text{-Ag}_2\text{Se}$ [3, 4].

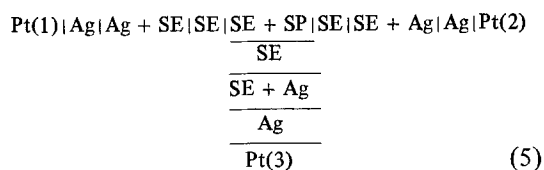
One way of reducing the overvoltage of galvanic cells, based on a diffusion process of the charge-bearing particles, is to minimize the path of mobility of the charge-bearing ions inside the storage phase. This effect may be obtained by producing a fine dispersion of the storage phase inside the solid electrolyte [5, 6].

2. Experimental

The preparation of samples of the storage phase with a well-defined deviation from the ideal stoichiometric composition, and the assemblage of the different phases of each cell in a single pellet, have been described in detail in Part 1 of this series [1]. For the investigation of the reduction of temperature variation, we have used the following auxiliary cells:



The solid electrolytes $\text{RbAg}_{4+y}\text{I}_{5-y}\text{Se}_y$ and $\text{RbAg}_{4+y}\text{I}_{5-y}\text{Te}_y$ used in these cells are the thermodynamically stabilized forms of RbAg_4I_5 resulting from a partial substitution of I by Se or Te, respectively [7]. The cell used for the study of the overvoltage effect was



where SE represents the solid electrolyte (50 wt% $\text{RbAg}_{4+y}\text{I}_{5-y}\text{Se}_y$ + 50 wt% $\text{RbAg}_{4+y}\text{I}_{5-y}\text{Te}_y$) and SP is the storage phase ($\text{Ag}_2\text{Se} + \text{Ag}_2\text{Te}$). Pt (1) is

Table 1. Variation of the e.m.f. of Cell 3 with temperature

T (°C)	E_3 (V)	ΔT (°C)	ΔE_3 (V)	$\Delta E_3/\Delta T$ ($\mu\text{V K}^{-1}$)
0	0.1054			
22	0.0998	+ 22	- 0.0056	- 254
38	0.0956	+ 16	- 0.0042	- 262
60	0.0898	+ 22	- 0.0058	- 264

the working electrode, Pt(2) is the counter electrode and Pt(3) is the reference electrode. This arrangement of the cell was used so as to eliminate simultaneously the polarization at both electrodes. All the experiments were conducted under the same conditions and precautions described in the previous paper [1].

3. Results and discussion

3.1. Reduction of the temperature effect

For Cell 2 a temperature variation of $\Delta E_2/\Delta T = + 240 \mu\text{V K}^{-1}$ has been calculated (see [1], especially Table 1). The variation of the e.m.f. of Cell 3 (E_3) with temperature, in the temperature range 0–60° C, is listed in Table 1. The temperature variation for this cell shows a negative value of $\Delta E_3/\Delta T = - 260 \mu\text{V K}^{-1}$.

Initially, the solid electrolyte of Cell 4 consisted of 50 wt% $\text{RbAg}_{4+y}\text{I}_{5-y}\text{Se}_y$ + 50 wt% $\text{RbAg}_{4+y}\text{I}_{5-y}\text{Te}_y$ and the storage phase of Cell 4 consisted of 50 wt% Ag_2Se + 50 wt% Ag_2Te . The data of Table 2 for the variation of the e.m.f. of Cell 4 have been obtained with a cell with such a composition. From these data a temperature variation of $\Delta E_4/\Delta T = + 50 \mu\text{V K}^{-1}$ has been calculated. This value is about five times smaller than the values obtained for Cells 2 and 3 with pure Ag_2Se or pure Ag_2Te , respectively.

Table 2. Variation of the e.m.f. of Cell 4 with temperature

T (°C)	E_4 (V)	ΔT (°C)	ΔE_4 (V)	$\Delta E_4/\Delta T$ ($\mu\text{V K}^{-1}$)
24	0.0987			
53	0.1000	+ 29	+ 0.0013	+ 45
24	0.0987	- 29	- 0.0013	+ 45
3	0.0974	- 21	- 0.0013	+ 62
53	0.0999	+ 50	+ 0.0025	+ 50

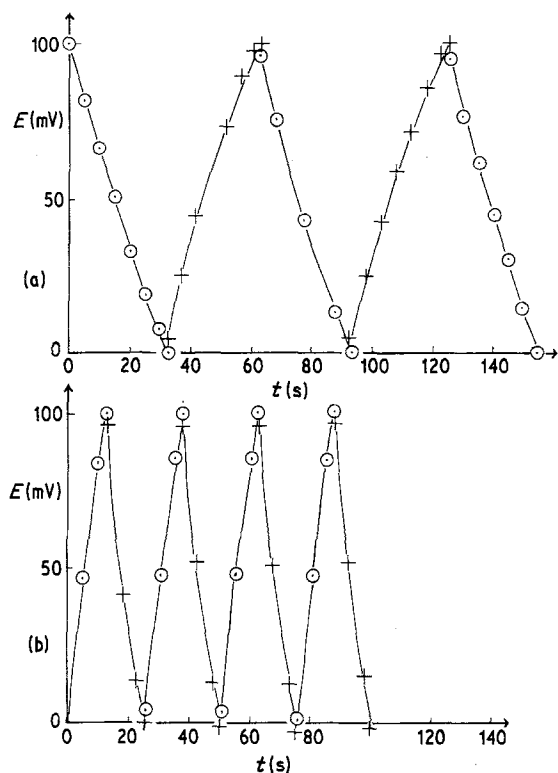


Fig. 1. Charge-discharge curves for Cell 5 with 65 mF capacitance at 22°C. (a) Current density = 0.4 mA cm⁻², (b) current density = 1.0 mA cm⁻².

Different proportions of the mixture Ag₂Se + Ag₂Te in the storage phase cause different values of the temperature variation of the cell. It is therefore possible to create a mixture of the two compounds for which the temperature characteristic of Cell 4 becomes practically zero. The composition of this ideal mixture must be found experimentally since no equation is known to relate all the parameters involved.

3.2. Reduction of the overvoltage of cells with diffusion of the charge-bearing ions in the storage phase

In the first part of this work [1] we discussed the causes of the overvoltage in diffusion cells with several different phases and concluded that interface polarization played the minor role and diffusion polarization the major role in the overall polarization. The diffusion polarization may be considerably diminished by reducing the path for the mobile Ag⁺ ions between the Ag electrode and

the storage phase (or, in the case of symmetric cells [1], inside the storage phase). This reduction may be achieved in two ways, either by diminishing the thickness of the storage phase, which implies a diminution of the cell capacitance, or by obtaining an adequate dispersion of the storage phase inside the solid electrolyte. We have chosen the second way.

The storage phase of Cell 5 consists of a homogeneous mixture of the two silver chalcogenides (50 wt% Ag₂Se + 50 wt% Ag₂Te) and the solid electrolyte (50 wt% RbAg_{4+y}I_{5-y}Se_y + 50 wt% RbAg_{4+y}I_{5-y}Te_y). The most effective mixture was that corresponding to the ratio of about 1 part (volume) of the silver chalcogenides to 2.5 parts (volume) of the solid electrolyte. Using mixtures of this composition as the storage phase it was possible to reduce the overvoltage of Cell 5 to less than 3 mV. The overvoltage was measured by the same procedure described in [1]. Fig. 1 illustrates the charge-discharge process of Cell 5 for a cell of about 65 mF capacitance at 22°C and two different current densities.

3.3. Development of operative cells with different storage capacitances

Once the efficiency of Cell 5 was experimentally tested, the second and last step consisted of developing operative cells with different storage capacitances for practical purposes, such as in coulometers and timers. The design of such cells is shown in Fig. 2.

In the first trial the cell was encapsulated in a Teflon case. However, this material was not firm enough to resist the elevated pressures (≥ 14.7 MN m⁻²) necessary to ensure good contact between the different phases. The Teflon case had to be replaced by a ceramic one. The cell was assembled by successively putting each constituent phase inside the capsule and applying gentle pressure after each phase had been laid. At the end, all the phases were pressed together at a higher pressure. The storage phase was prepared separately prior to assembling the different components of the cell, in the form of a pellet of smaller diameter with a coil of platinum wire inside. One of the two ends of the coil was pointing out of the pellet to be used as a counter electrode. The storage-phase pellet was located in the cell in such a way that it

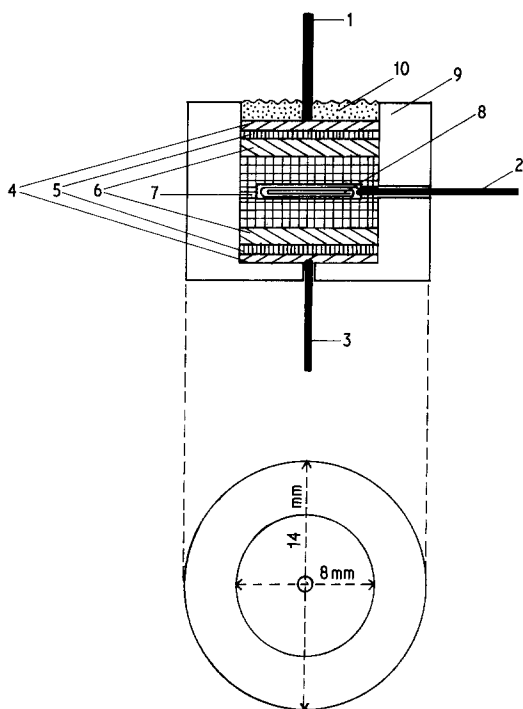


Fig. 2. Schematic representation of an analogue storage cell with 50 wt% Ag_2Se + 50 wt% Ag_2Te as the storage phase. 1, Working electrode; 2, counter electrode; 3, reference electrode; 4, Ag foil; 5, Ag pellet; 6, Ag + solid electrolyte; 7, solid electrolyte (50 wt% $\text{RbAg}_{4+y}\text{I}_{5-y}\text{Se}_y$ + 50 wt% $\text{RbAg}_{4+y}\text{I}_{5-y}\text{Te}_y$); 8, storage phase + solid electrolyte; 9, ceramic case; 10, plastic seal.

was completely surrounded by the solid electrolyte (see Fig. 2).

In order to test the electrochemical behaviour of such cells as a function of their storage capability, cells of different sizes were constructed. The principal specific electronic properties of three cells, with capacitances of 65 mF, 100 mF and 140 mF, are given in Table 3.

Fig. 3 demonstrates the method of calculating the time constant of the cells at different current densities. It is clear that solid-state galvanic cells based on the diffusion of charge-bearing ions through the storage phase have a relatively large time constant and this depends markedly on the mass of the storage phase and on the current density. In other words, these cells are more appropriate for rather slow charge-discharge processes. This apparent limitation is nevertheless largely compensated for by very high accuracy and very long charge storage capability, which in the cells studied has been proved to be better than 1 mV over 6 months.

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Table 3. Specific electronic properties of three different analogue storage cells, with storage phase 50 mol % Ag_2Se + 50 mol % Ag_2Te , after the disposition of Cell 5 (see Fig. 2)

Specification	Type		
	I	II	III
Capacitance (mF)	65	100	140
Maximum output voltage (mV)	~ 160	~ 160	~ 160
Output voltage (mV)	0 - 120	0 - 120	0 - 120
Maximum input current (mA)	10	15	20
Overvoltage (mV)	< 3 (at $I = 0.5$ mA)	< 4 (at $I = 0.5$ mA)	< 4 (at $I = 1$ mA)
Polarization resistance (Ω)	< 6 (at $I = 0.5$ mA)	< 6 (at $I = 0.5$ mA)	< 4 (at $I = 1$ mA)
Working temperature range ($^{\circ}\text{C}$)	- 30, + 100	- 30, + 100	- 30, + 100
Temperature characteristics ($\mu\text{V K}^{-1}$)	~ 50	~ 50	~ 50
Time constant (s) (at $I = 10$ mA) (see Fig. 3)	0.6	1	1.8
Potential variation over 6 months of the cell at loaded state (120 mV) (mV)	< 1	< 1	< 1

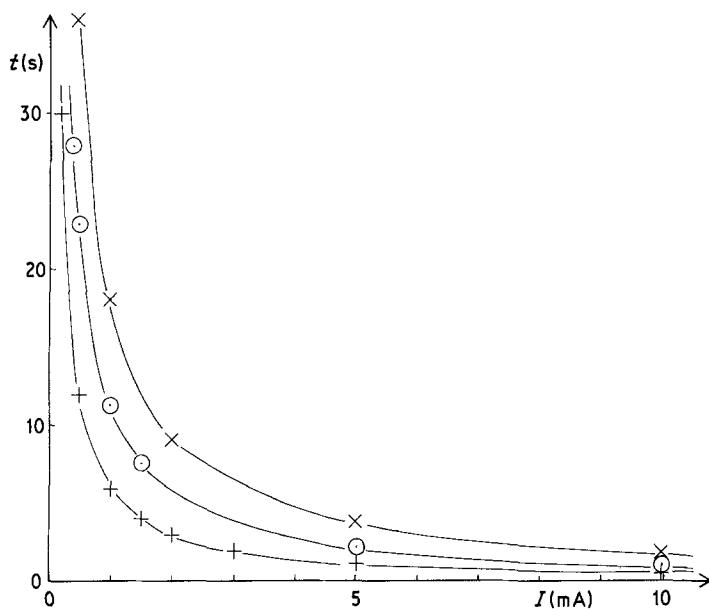


Fig. 3. Loading velocity curves as a function of current density for three cells with different capacitances. +, Cell of 65 mF; o, cell of 100 mF; x, cell of 140 mF.

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