

*Substitution of silver by various metal ions in modified AgI solid electrolytes**

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The substitution process of silver by various metals in RbAg_4I_5 and other solid electrolytes of the AgI-modified type has been investigated. This process is of technological interest since it permits the use of copper, zinc or cadmium instead of silver as anode materials in solid state batteries which utilize these electrolytes.

1. Introduction

A previous paper reported the possibility of replacing silver by copper in RbAg_4I_5 solid electrolyte [1]. This substitution is of practical interest since it allows the use of copper instead of silver as anode material in RbAg_4I_5 solid state batteries with consequent advantages to their overall cost. In the present work the study of the substitution process has been extended to other metal ions and to other silver ion conducting electrolytes, also of the AgI-modified type. Among these we have considered the recently discovered alkylammonium iodide-silver iodide double salts.

These electrolytes may be subdivided into two classes. One is formed by the tetraalkylammonium iodide-silver iodide double salts, studied in detail by Owens [2, 3] and by Smyth and others [4]. The tetramethylammonium iodide-silver iodide, $(\text{CH}_3)_4\text{NI}\cdot 6\text{AgI}$, salt has been selected for study as being representative of these electrolytes. The other class, described by Berardelli and others [5], consists of the poly-

methonium iodide-silver iodide compounds. Among these we have examined the hexamethonium iodide-silver iodide, $(\text{CH}_3)_3\text{N}(\text{CH}_2)_6\text{N}(\text{CH}_3)_3\text{I}_2\cdot 12\text{AgI}$, salt ($\text{HexI}_2\cdot 12\text{AgI}$).

2. Experimental

The preparation of rubidium silver iodide, RbAg_4I_5 , and of the iodine-perylene ($\text{I}_2\text{-P}$) charge transfer complex have already been described [6, 7].

The tetramethylammonium iodide-silver iodide electrolyte was prepared as described by Smyth and others [4]. An intimate mixture of $(\text{CH}_3)_4\text{NI}$ and AgI (1:6 molar ratio) was melted in a sealed tube, quenched and the product powdered and annealed at 170°C for 20 h. The conductivity of pressed pellets of the electrolyte so prepared was $0.04\text{ ohm}^{-1}\text{ cm}^{-1}$ at room temperature. This was determined with an AC Bridge at 1000 Hz using as electrodes pressed mixtures of silver and electrolyte. This value agrees with those reported by Owens [2] and Smyth [4]. A similar procedure was used to synthesize the hexamethonium iodide(HexI_2)-silver iodide electrolyte. Following the method described by Berardelli and others [5], an inti-

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mate mixture of HexI_2 and AgI (1:12 molar ratio) was melted and quenched. The product was powdered and annealed for 20 h at 165°C . The conductivity was measured as before and found to be $0.003 \text{ ohm}^{-1} \text{ cm}^{-1}$ at room temperature, approximately one order of magnitude less than that reported [5].

The RbI-CuI double salts were obtained by crystallization from a solution in dry acetone mixtures of the two iodides, following the procedure already described [8]. The cuprous iodide was dried under vacuum at 80°C for several days. The salts were pressed into pellets for the resistivity measurements. The cells used for the polarization tests were prepared by pressing into a single pellet a mixture of copper or, alternately, zinc, cadmium, iron and nickel, and the electrolyte (1:3 weight ratio), the electrolyte and a mixture of silver and the electrolyte (1:3 weight ratio). The cells were encapsulated in plastic containers with gold-plated terminals.

Batteries were assembled by pressing the mixture of metal and electrolyte and the electrolyte into a single pellet. This pellet was placed in the plastic container to which the iodine electrode was added as a pressed pellet. The electrode surface and the electrolyte thickness were 1.25 cm^2 and about 0.15 cm , respectively. The cells were stored in a dry atmosphere.

The polarization and discharge curves were obtained and recorded using standard equipment.

3. Results and discussion

3.1. Substitution of silver by copper in RbAg_4I_5

Preliminary results, indicating that silver may be substituted by copper in RbAg_4I_5 , have been reported [1]. Applying to the cell $\text{Ag}|\text{RbAg}_4\text{I}_5|\text{Cu}$ (I) polarizing potential less than 0.68 V (RbAg_4I_5 decomposition potential at 25°C [9, 6]) with the copper electrode as positive, relatively high currents result (Fig. 1, curve a). When electrolyte is mixed with the metals, thus reducing interfacial electrode-electrolyte polariza-

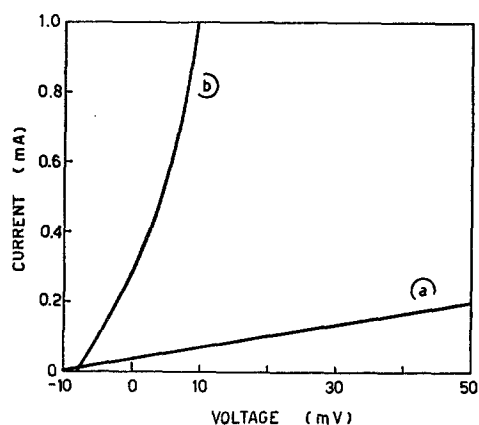


Fig. 1. Polarization curves of cell (I) at room temperature. Curve a: pure Ag and Cu electrodes. Curve b: Ag-electrolyte and Cu-electrolyte mixed electrodes.

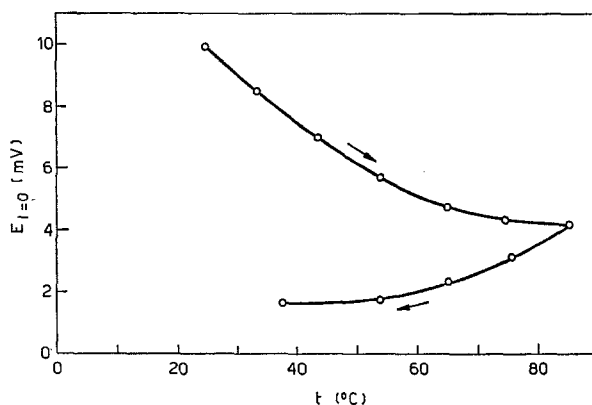


Fig. 2. Variation of the e.m.f. of cell (I) with temperature. (Ag-electrolyte and Cu-electrolyte mixed electrodes.)

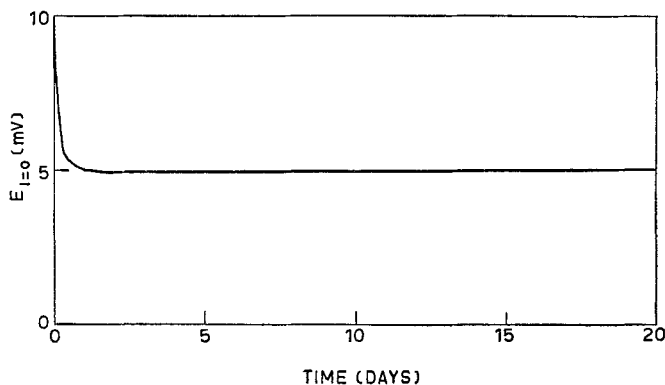


Fig. 3. Time dependence of the e.m.f. of cell (I) at room temperature. (Ag-electrolyte and Cu-electrolyte mixed electrodes.)

zations [9, 6], the currents for comparable applied voltages, are higher, as shown in Fig. 1, curve b. Since the electronic conductivity of RbAg_4I_5 is very low (about $10^{-11} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°C [9, 6]) the substantial currents passed through cell (I), with voltages well below the decomposition potential of the electrolyte, may be attributed to copper dissolution at the positive electrode and silver deposition at the negative electrode. This indicates that silver may be, at least partially, substituted by copper in RbAg_4I_5 .

The electromotive force (e.m.f.) of cell (I) is 9.8 mV at 25°C , with the silver electrode positive. The variation of the e.m.f. with temperature in both directions is shown in Fig. 2. The e.m.f. decreases as the temperature increases and, on cooling, it initially decreases to stabilize around 2 mV . The time dependence of the e.m.f. at 25°C is shown in Fig. 3. The e.m.f. initially decreases and then remains constant at about 5 mV . This tendency to decrease with time increases at higher temperatures, as indicated in Fig. 4.

These results show that the substitution process, which may be tentatively indicated as



is spontaneous and irreversible.

To characterize this process a standard Tubandt experiment was performed. This is usually employed to determine transport numbers in solid electrolytes [10, 11] and consists in passing charge through a cell composed of separable layers and determining the changes in weight of the various layers and comparing them with the faradaic variations. The experimental set-up used in the present case is shown in Fig. 5 and some typical results are presented in Table 1.

In the light of these results, the following remarks can be made:

- (a) The anodic process consists in the dissolution of both copper and silver. This is probably due to the fact that reaction 1 takes place spontaneously in the anodic layer

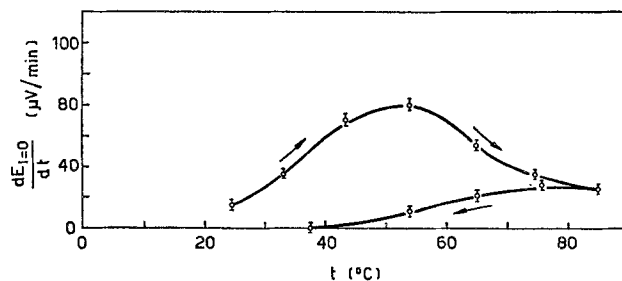


Fig. 4. Time dependence of the e.m.f. of cell (I) at various temperatures. (Ag-electrolyte and Cu-electrolyte mixed electrodes.)

Table 1. Typical results of the Tubandt experiment in the cell of Fig. 5 at 25°C

Current density ($\mu A\ cm^{-2}$)	Coulombs (C)	Change in mass (mg)			Theoretical mass change*	
		A	B	C	Cu mg	Ag mg
88.5	10.08	-7.9	-1.8	+9.5	-6.6	11.3
442.5	8.1	-6.7	-2.0	+8.8	-5.3	9.0

* Assuming that the electrode processes involve monovalent ions

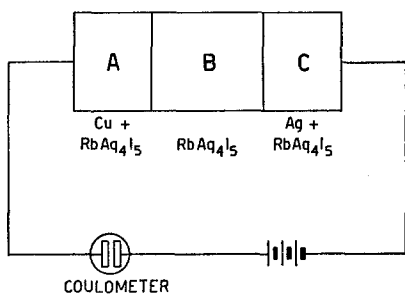


Fig. 5. Experimental cell to characterize copper dissolution in $RbAg_4I_5$.

(consisting of a mixture of copper and the electrolyte, $RbAg_4I_5$). Furthermore micro-cells of the type $Cu|RbAg_4I_5|Cu$ may also be active in this layer. This would explain the instability of the e.m.f. of cell (I).

- (b) Copper ions can migrate through the cell and contribute, to a small extent, to the transport of the current, as indicated by the observed mass changes in the B section of the cell shown in Fig. 5.
- (c) The substitution of silver by copper in $RbAg_4I_5$ does not appear to exceed 0.34% in weight (about 1.5 atoms of Cu for 100 atoms of Ag).

To further investigate points (b) and (c), constant current electrolyses were carried out at 25°C through freshly made cells similar to (I), with the copper electrode as positive. The results are shown in Fig. 6. A change in slope is noted after the passage of 7.2 C which corresponds, for the mass of electrolyte used,* to a dissolution of 0.32–0.34% in weight of copper. This confirms

* This mass includes both the electrolyte mixed with the anode and the electrolyte layer between the two electrodes.

the results of the Tubandt experiment and indicates that, after the solubility limit of copper is reached, the resistance of the cell increases.

The electrolyses were then continued until a sharp rise in voltage which indicates gross dendritic deposition at the negative electrode with consequent loss of contact between this and the electrolyte [12]. The cells were examined under the microscope and the negatives showed both silver and copper dendrites. The copper-content of the electrolytes were obtained by atomic absorption giving results of 0.36–0.38% by weight of copper confirming the solubility limit found in the Tubandt experiment.

A solubility limit of copper in $RbAg_4I_5$ was anticipated on the basis of the $CuI-RbI$ phase diagram [13]. A complete substitution is not possible because of the instability of the compound $RbCu_4I_5$. Furthermore, the compounds $RbCu_2I_3$ and Rb_2CuI_3 , which are compatible with the phase diagram, are not conductive the resistivity being of the order of $4\ M\ \Omega\ cm$, as measured in our laboratory.

On the basis of the results obtained in this study the substitution process leads to a compound of approximate formula $RbAg_{3.94}Cu_{0.06}I_5$. Unfortunately this is too close to that of pure $RbAg_4I_5$ to allow the detection of any differences with techniques, such as X-ray powder diffraction or differential thermal analysis, as experimentally verified.

It is not clear what the conductivity mechanism is in a cell similar to (I) once the copper solubility limit is reached. The drastic change in resistance could indicate that the electrolyte, under the polarizing conditions of cell (I), passes from a silver to a copper ion conductor. In favour of this hypothesis are the results of the Tubandt experiment and the copper dendrites

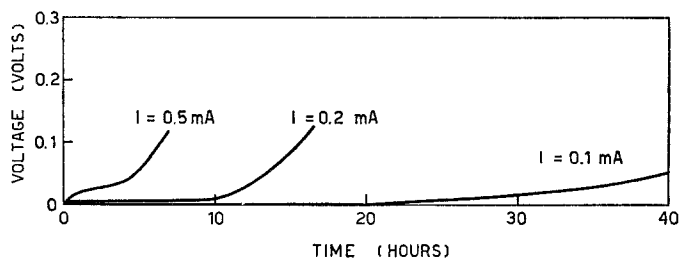
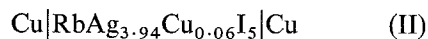
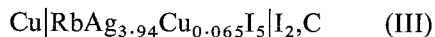


Fig. 6. Electrolyses of cells similar to (I) at various constant currents and at room temperature. (Ag-electrolyte and Cu-electrolyte mixed electrodes.)

observed at the negative pole of cells after the electrolyses which indicate that copper ions can migrate through the substituted electrolyte. On the other hand the micropolarization curves of the cell:



are neither linear nor reproducible, as shown in Fig. 7. Furthermore the open circuit voltage (OCV) of the cell:



is 0.68 V at 25°C. This value should be compared with 0.72 V, the thermodynamic value related to CuI formation at 25°C and which one would have expected if the electrolyte was a pure copper ion conductor. This disagreement could be explained if the expected OCV is greater than the decomposition potential of the electrolyte (which in effect should be close to that of pure RbAg_4I_5) or if the copper transport number is lower than 1. Unfortunately the resistance of the substituted electrolyte in cell (I) is too high to submit it to a Tubandt experiment. Attempts gave scattered results.

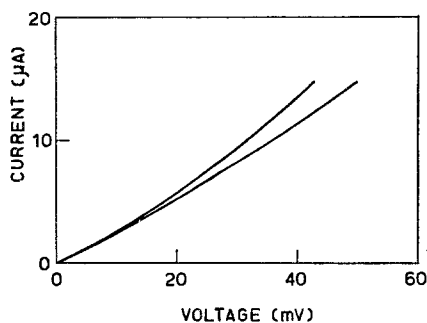
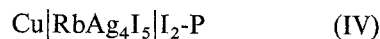


Fig. 7. Micropolarization curves of cell (II) at room temperature.

We have therefore restricted our attention to the substitution process which remains technologically interesting since it allows the use of copper instead of silver as anode material in RbAg_4I_5 solid state batteries with economical advantages. In fact a mixture of copper and electrolyte (RbAg_4I_5) may be used as electrode in the battery



where the iodine-perylene charge transfer complex acts as an iodine electrode with reduced iodine pressure [7]. The silver substitution by copper takes place spontaneously in the anodic mixture and, until the dissolution process reaches its maximum limit, the current through the electrolyte during discharge is mainly transported by silver ions. In fact the OCV of cell (IV) is 0.67 V at 25°C—very close to the thermodynamic value related to AgI formation (0.69 V at 25°C). The difference may be ascribed to the reduced iodine activity in the cathode (the free enthalpy change related to the substitution process is negligible, because of the low value of the e.m.f. of cell (I)). The initial discharge process of cell (IV) therefore appears to be the dissolution of copper at the anode and the formation of mainly silver iodide at the cathode. Cell (IV) nevertheless remains formally a copper-iodine solid state battery with all the related advantages (lower cost and weight) with respect to conventional RbAg_4I_5 batteries using silver as anode material. At the initial stage of the discharge, cell (IV) obviously displays behaviour comparable to that of conventional silver-based RbAg_4I_5 batteries, as shown by the typical discharge curve reported in Fig. 8. When the solubility limit of copper is reached, the con-

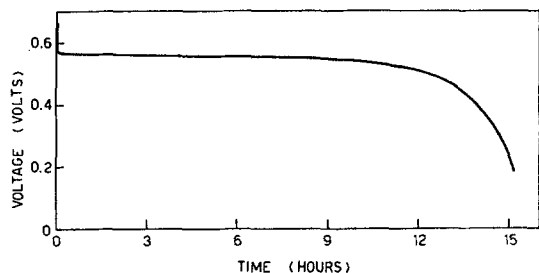


Fig. 8. Typical discharge curve of cell (IV) at 0.2 mA constant current and at room temperature. (Cu-electrolyte mixed electrode.)

ductivity mode of the electrolyte changes and the resistance of the battery increases. Consequently the performance becomes poorer. The best battery design, therefore, is that based on a cell with a life limited to the solubility of copper in RbAg_4I_5 . With the geometry of our cells, copper saturation occurs after the passage of 7.2 C (see Figs. 6 and 8). In this configuration the amounts of copper in the anode and iodine in the cathode may be reduced to 5.7 mg and 12 mg, respectively, assuming electrode utilization coefficients of 80%. This would result in a battery having a capacity of 2 mA h.

It has also to be considered that the substitution process proceeds spontaneously under open circuit conditions and this may affect the shelf life. The effect mentioned above is slow at low temperatures but becomes severe at high temperatures (see Fig. 4). Fig. 9 shows a constant current electrolysis ($I = 0.2$ mA) of a cell similar to (I) left in open circuit at room temperature for about 1 month. A degradation, with respect to the curve of a freshly made cell (also reported in Fig. 9) is noticed, indicating that the performances may degrade with time. Conse-

quently, it is necessary to store the batteries under a reserve-type configuration, where the anodic mixture is brought in contact with the other components just before use.

3.2. Substitution of silver by various metals in RbAg_4I_5

To extend the study of the substitution process in RbAg_4I_5 to other metals, technologically more interesting than copper, we have considered the cell



where M was zinc, cadmium, iron or nickel. Cell (V) was polarized under the same blocking conditions for silver used in cell (I). The polarization curves are reported in Fig. 10 where the polarization curve for copper is also shown. The substantial currents passed through the cell, under very low applied voltages when cadmium and zinc, respectively, were used as anodes, indicate that silver may also be partially replaced by these two metals in RbAg_4I_5 .

The e.m.f. of cell (V), when M is zinc or cadmium, at 25°C is about 10 mV with the silver electrode positive hence the substitution of silver by these metals is spontaneous at room temperature.

On the contrary, when M is iron or nickel, the e.m.f. of cell (V) acquires opposite polarity (a few millivolts). The related current-voltage curves show severe polarizations for currents greater than 10 μA , in the case of iron, and 50 μA in the case of nickel (Fig. 10). In Fig. 11 the polarization range is extended to the decomposition potential of the electrolyte. With

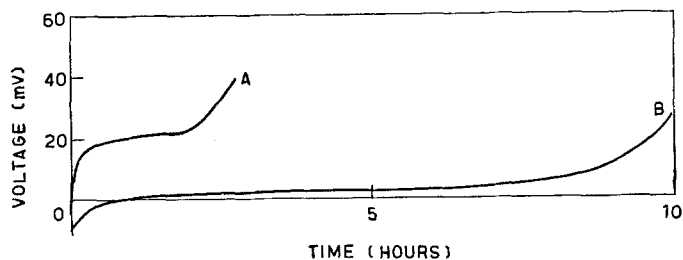


Fig. 9. Electrolyses of cells similar to (I) at 0.2 mA constant current and at room temperature. Curve A: cell left at open circuit for one month. Curve B: freshly made cell. (Ag-electrolyte and Cu-electrolyte mixed electrodes.)

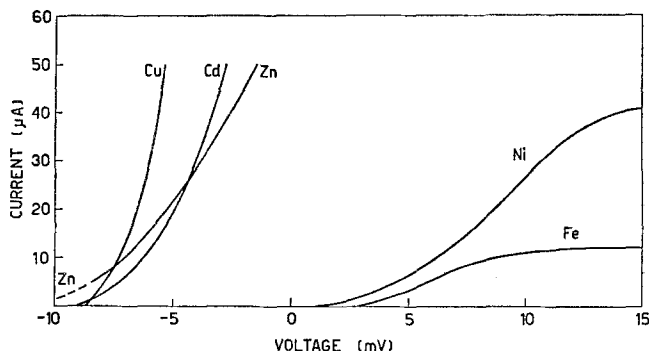


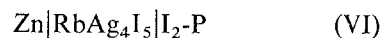
Fig. 10. Polarization curves of cell (V) at room temperature. (Ag-electrolyte and M-electrolyte mixed electrodes.)

iron, an anodic process, different from the initial dissolution of the metal in the electrolyte, seems to occur at a potential of about 170 mV. We have not attempted to clarify this process since this study was limited to the investigation of the effective substitution of silver by other metals in RbAg_4I_5 .

The polarization results indicate that this substitution takes place, other than with copper, mainly for zinc and cadmium. Therefore these metals may also be used as anode materials instead of silver in RbAg_4I_5 solid state batteries

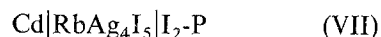
with substantial practical advantages since they cost much less than silver.

The battery:



presents, at room temperature, an OCV of 0.67 V and performances similar to that of cell (IV), as shown by the typical discharge curve reported in Fig. 12, curve A.

The battery:



also has at room temperature an OCV of 0.67 V, but shows a lower capacity than cell (IV) (see Fig. 12, curve B). This probably implies that the solubility of cadmium is lower than that of copper in RbAg_4I_5 .*

3.3. Substitution of silver by copper in alkylammonium iodides-silver iodide solid electrolytes

Recently the alkylammonium iodides-silver iodide double salts have been proposed as new classes of silver conducting electrolytes as alternatives to RbAg_4I_5 in solid state batteries [3, 4, 14]. In order to test the substitution process also in these electrolytes, we have assembled the cells:



and

* It should be noted in this connection that all batteries were assembled with the same amount of electrolyte.

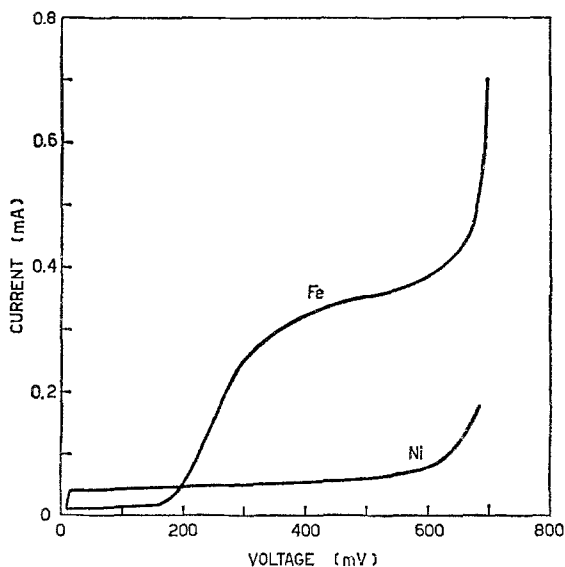


Fig. 11. Polarization curves of cell (V) at room temperature extended to the decomposition potential of the electrolyte. (Ag-electrolyte and M-electrolyte mixed electrodes.)

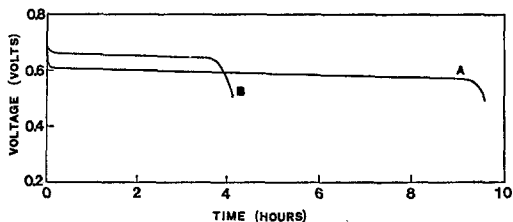


Fig. 12. Typical discharge curves of cell (VI) (curve A) and of cell (VII) (curve B) at 0.2 mA constant current and at room temperature. (Zn-electrolyte and Cd-electrolyte mixed electrodes.)



Cells (VIII) and (IX) were polarized with the copper electrode as positive under applied voltages lower than the decomposition potential of the electrolytes, which is approximately 0.68 V at room temperature for $\text{HexI}_2 \cdot 12\text{AgI}$ [14] and probably similar for the other electrolyte. Also in these cases the electronic conductivity is very low (reported as $10^{-11} \text{ohm}^{-1} \text{cm}^{-1}$ for $(\text{CH}_3)_4\text{NI} \cdot 6\text{AgI}$ at room temperature [4] and apparently of the same order of magnitude for $\text{HexI}_2 \cdot 12\text{AgI}$ [14]). Therefore the substantial currents actually passed through cells (VIII) and (IX) under voltages well below the decomposition potential of the electrolytes (Fig. 13) indicate that, as in RbAg_4I_5 , silver ions may be partially replaced by copper ions in the two electrolytes examined. The different position of the two curves in Fig. 13 is accounted by the lower conductivity of $\text{HexI}_2 \cdot 12\text{AgI}$.

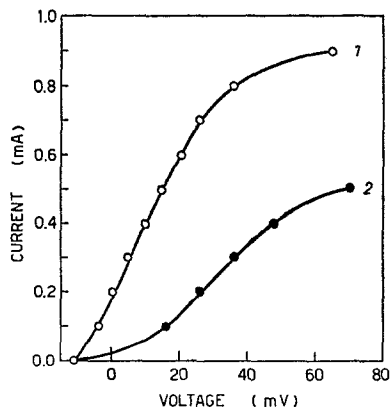
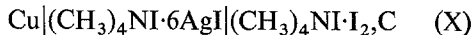


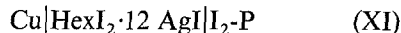
Fig. 13. Polarization curves of cell (VIII) (curve 1) and of cell (IX) (curve 2) at room temperature. (Ag-electrolyte and Cu-electrolyte mixed electrodes.)

These results indicate that in batteries based on the alkylammonium and polymethonium iodides-silver iodide salts as electrolytes, copper may be used instead of silver as anode material. The battery:



has an OCV of 0.66 V at room temperature and shows good discharge capabilities, as indicated by the typical discharge curve shown in Fig. 14, curve A.

Similar behaviour is presented by the battery:



which shows at room temperature an OCV of 0.67 V and the performances indicated by the typical discharge curve of Fig. 14, curve B.

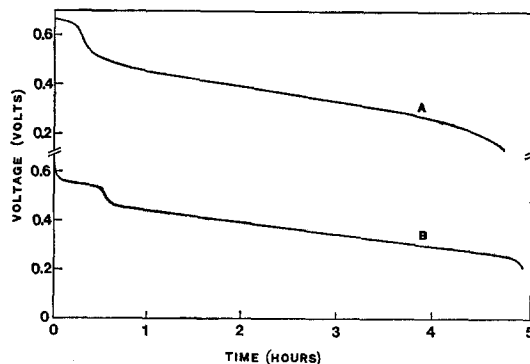


Fig. 14. Typical discharge curves of cell (X) (curve A) and cell (XI) (curve B) at 0.2 mA constant current and at room temperature. (Cu-electrolyte mixed electrode.)

As in the case of the batteries using RbAg_4I_5 as electrolyte, the initial discharge process of cells (X) and (XI) is probably the dissolution of copper at the anode and the formation of mainly AgI at the cathode, with the current predominantly transported by Ag^+ ions through the electrolyte. This hypothesis is supported by the fact that the e.m.f. of the cell;



where the electrolyte may be the alkylammonium iodide-silver iodide or the polymethonium iodide-silver iodide salt, is of the order of 10 mV at 25°C. Therefore the substitution process is also spontaneous in these electrolytes. Further-

more the OCV of batteries (X) and (XI) is 0.67 V at 25°C, equal to that shown by cell (IV) and close to that for AgI formation.

Batteries (X) and (XI) furnish less capacity than battery (IV) and this probably indicates that the copper solubility is lower in these electrolytes than in RbAg_4I_5 . The discharge curves show an initial step which is absent from the curves of batteries (IV), (VI) and (VII). The reason for this difference is not clear. Further studies are in progress to fully characterize the substitution mechanism and the discharge processes.

Additional work is also needed to reduce the self-degradation of the batteries due to the spontaneity of the substitution processes. This effect greatly reduces the performances of the batteries, especially above 25°C. The reserve-type configuration proposed must be considered only as a partial solution since it limits the range of applicability of the batteries. On the other hand, the possibility of using copper, zinc or cadmium instead of silver as anode material in solid state batteries with AgI-modified electrolytes is technologically so interesting that it was considered important to report this work even at a preliminary stage.

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