JOURNAL OF APPLIED ELECTROCHEMISTRY 12 (1982) 213–218

# *Solid electrolyte cell using the electrolyte of the CuCl-CuI-RbCl system*

T. TAKAHASHI, K. KUWABARA, M. MIURA, M. NAKANISHI

*Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan*

Received 27 April 1981

The electrochemical behaviour of a solid electrolyte cell Cu, X/X/$Cu_{1.75}Se$ (X = $Rb_4Cu_{16}I_7Cl_{13}$) has been examined. The open circuit voltage was 0.2680 V at 25° C. The cell yielded a current of several microamperes at ambient temperature. Some charge–discharge cycles were possible. The failure of the cell was ascribed to the anode, owing to a decrease of the activity of metallic copper as well as a low rate of the charge transfer reaction, copper/copper ion.

## 1. Introduction

Solid electrolyte galvanic cells have two excellent characteristics. One is that they are 'leakage-free', because they contain no liquid electrolyte or liquid active materials, and another is the possibility of the cell being miniaturized, which meets recent needs in the electronic fields.

Most of the solid electrolytes used to date for cells working at ambient temperature are silver, lithium, and protonic compounds; for instance, $Ag_3SI$ [1], $RbAg_4I_5$ [1], $KAg_4I_4CN$ [2], LiI [3], LiI–$Al_2O_3$ [4] or PWA ($H_3W_{12}PO_{40} \cdot 29H_2O$) and PMoA ($H_3Mo_{12}PO_{40} \cdot 29H_2O$) [5]. However, silver containing electrolyte is expensive, the conductivity of lithium ion conductors is relatively low at room temperature, and PWA and PMoA are somewhat unstable. Therefore, other inexpensive, conductive and stable electrolytes are of interest.

An example of such solid electrolytes is a group of copper ion conductors; for example, N-alkylhexamethylenetetramine halide–cuprous halide and N,N′-dimethyltriethylenediaminedibromide–cuprous bromide, which were found by Takahashi and coworkers [6, 7]. A new solid electrolyte in the system CuCl–CuI–RbCl has been found recently to have high copper ion conductivity and very low electronic conductivity [8, 9].

Solid electrolyte cells using copper ion conductors have scarcely been described, except in reports by Lazzari *et al.* [10], Sammells *et al.* [11], and Takahashi and Yamamoto [12]. The present investigation was carried out to examine the open circuit voltage, the electrode polarizations and the charge–discharge performance of a cell with a copper ion conductor developed in the CuCl–CuI–RbCl system.

## 2. Experimental procedure

The electrolyte was prepared from cuprous choride, cuprous iodide and rubidium chloride by the procedure described in previous papers [8, 9]. The ionic conductivity of the electrolyte was of the order of $10^{-1}\ \Omega^{-1}\ cm^{-1}$ at 25° C. The anode material was a mixture of copper powder and the electrolyte, where the weight ratio of these powders was varied to obtain the best cell performance. The cathode material was copper selenide, $Cu_{1.75}Se$, which was obtained from a solid state reaction between copper powder and selenium powder. The selenide is a mixed conductor with electronic and ionic conductivities of ~ 10 and $2.1 \times 10^{-1}\ \Omega^{-1}\ cm^{-1}$ at room temperature, respectively.

The galvanic cell Cu, X/X/$Cu_{1.75}Se$, where X is the solid electrolyte, was assembled. The Cu, X anode of the cell (13 mm diameter) was divided into two parts (3 :10 in area) to measure the anode and cathode polarizations. The smaller part acted as a convenient reference electrode. The polarization was also measured using a copper wire in-

0021–891X/82/010213–06$02.60/0

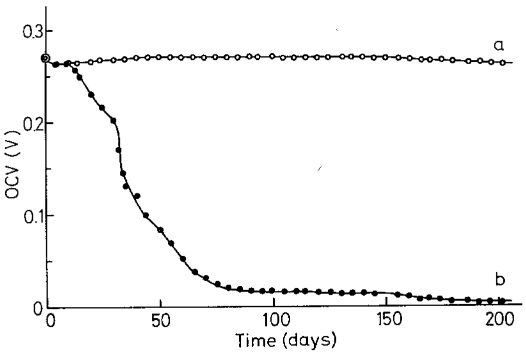

Fig. 1. Open circuit voltages of the cells (a) CK7 and (b) CK8. CK7: cell with the electrolyte $Rb_4Cu_{16}I_7Cl_{13}$. CK8: cell with $Rb_4Cu_{16}I_8Cl_{12}$.

serted into the electrolyte, which served as a reference electrode and showed almost the same results as in the above case. The anode and the electrolyte were pressed simultaneously at 400 MPa to reduce contact resistance at this electrode. The cathode and the electrolyte were pressed in a similar manner and these two tablet blocks were combined. The cell was sealed with polyester resin. The polarization was measured by passing a certain current in the direction of the cell discharge using a power supply. The cell was held at each current level for 30 s. The cell resistance at a.c. 100 kHz was examined while the cell was at the open circuit voltage for over 200 days.

## 3. Results and discussion

### 3.1. *Open circuit voltage*

The open circuit voltages (OCV) were examined using two kinds of cells, CK7 series and CK8 series; the former contained the electrolyte $Rb_4Cu_{16}I_7Cl_{13}$, developed by Takahashi *et al.* [9], and the latter contained the electrolyte $Rb_4Cu_{16}I_8Cl_{12}$, found by Geller *et al.* [8]. Fig. 1 shows the typical changes of OCV with the passage of time at room temperature. The OCV of the cell CK7 is very stable over six months, while the OCV of the cell CK8 begins to decrease after 10 days and rapidly falls after 30 days. Since conditions other than the electrolyte compositions in these cells were the same, the difference in OCV behaviours suggested that the electrolyte $Rb_4Cu_{16}I_7Cl_{13}$ is more stable than $Rb_4Cu_{16}I_8Cl_{12}$.

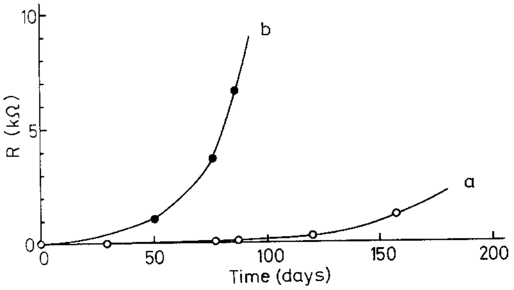

Fig. 2. Time dependence of the internal resistance of the cells (a) CK7 and (b) CK8.

The time dependence of the cell resistance is shown in Fig. 2. The resistance of CK8 increases more steeply than that of CK7, which also suggests the degradation of the electrolyte $Rb_4Cu_{16}I_8Cl_{12}$ in a comparatively short time. This was confirmed by X-ray diffraction. The diffraction pattern of $Rb_4Cu_{16}I_8Cl_{12}$ after several tens of days was different from the as-prepared sample, and the diffraction lines assigned to cuprous iodide and cuprous chloride could be observed. Accordingly, the electrolyte composition $Rb_4Cu_{16}I_7Cl_{13}$ was used in all the following experiments.

The cell had an initial OCV value of 0.2680 V, which differs from the emf of 0.3715 V calculated by the use of the free energy change [13] in the following reaction at 25° C:

$$2Cu + Se = Cu_2Se. \quad (1)$$

Since $Cu_{1.75}Se$ was used as the cathode-active material in the present cell, the emf should be based on the following reaction:

$$0.25Cu + Cu_{1.75}Se = Cu_2Se. \quad (2)$$

However, the thermodynamic data on $Cu_{1.75}Se$, a nonstoichiometric compound capable of accepting copper atoms to some extent, are absent in the literature such as the JANAF tables. The emf values relating to the following reactions were estimated from the known data in order to compare the observed OCV.

$$1.5Cu + 0.5CuSe_2 = Cu_2Se \quad (3)$$

$$Cu + CuSe = Cu_2Se \quad (4)$$

$$0.5Cu + 0.5Cu_3Se_2 = Cu_2Se. \quad (5)$$

The emfs are 0.3387, 0.2993 and 0.3279V for Reactions 3, 4 and 5, respectively. These values

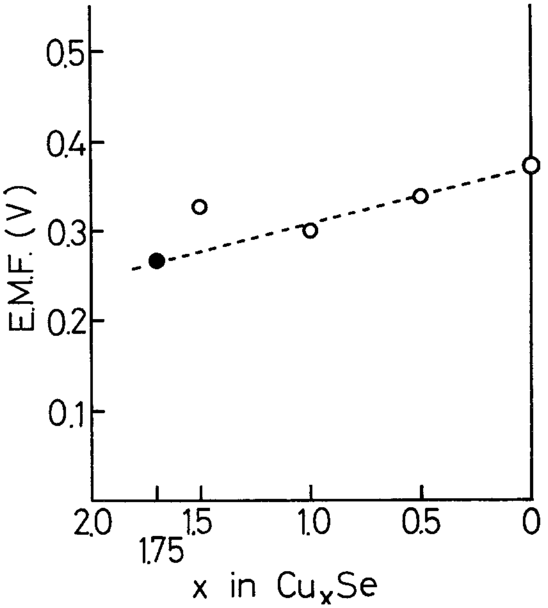

Fig. 3. Emfs (○) calculated from thermodynamic data for the reaction, aCu + bCu$_x$Se = Cu$_2$Se and the observed OCV (●).

and the observed OCV are indicated in Fig. 3. The emf decreases as the value of $x$ increases in the reaction, aCu + bCu$_x$Se = Cu$_2$Se (a, b: stoichiometric coefficient), and four values except the emf for Reaction 5 are situated on a straight line. Accordingly, Reaction 2 can be regarded as a reasonable cell reaction.

### 3.2. *Polarization and discharge*

Figure 4 shows the anode and cathode polarizations for cells in which the anode compositions contain various weight ratios of copper powder to electrolyte. The anode polarization was larger than the cathodic one and was minimized when the weight ratio of the components was 1:1. In the following cells, anodes with a mixing ratio of 1:1 were used.

The discharge was repeated daily for ten days for a single cell and the polarization curves were obtained as shown in Fig. 5. These results include the *iR* drops. The resistance of the electrolyte is very low and the *iR* drop was negligibly small, being only 1.0 mV even when the thickness of the electrolyte tablet was 3 mm and the current passed was 1.0 mA.

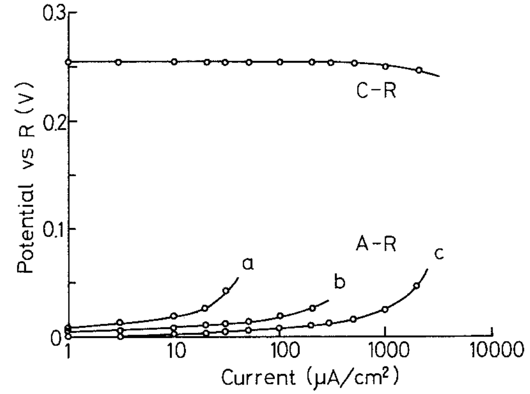

Fig. 4. Polarization curves at the various anodes. Mixing ratios of copper to the electrolyte are (a) 1:0, (b) 2:1 and (c) 1:1 by weight.

The cathode polarization is comparatively low but increases slightly. The copper selenide, Cu$_{1.75}$Se, is capable of copper atom acceptance up to the composition Cu$_2$Se. However, when the copper ions are transported from the electrolyte to the selenide surface more rapidly than their migration rate in the bulk of the selenide, copper in the selenide will accumulate in the neighbourhood of the interface. This process continues with the charge and leads to a decrease of the cathode potential.

The anode polarization at low current densities is initially quite small, but increases remarkably with repeated discharge cycles. When the cell was assembled using copper powder which had not been treated by hydrogen gas, the anode polarization was larger than that shown in Fig. 5. This suggests that the increase of the polarization with repetition of the discharge may arise from the consumption of the fresh copper powder or the decrease of the copper activity due to oxidation by trace amounts of air initially enclosed in the anode tablet.

Two constant load discharge curves at room temperature are shown in Fig. 6. The anode and cathode capacities calculated from the amounts of anode and cathode materials were 42 and 56 mAh, respectively. During the discharge with 100 kΩ, the average current was 2.5 μA (1.9 μAcm$^{-2}$) and the accumulated capacity to the cut-off voltage at 0.230 V was 2.5 mAh, corresponding to a cathode efficiency of 4.5%. With the 50 kΩ load, the average current was

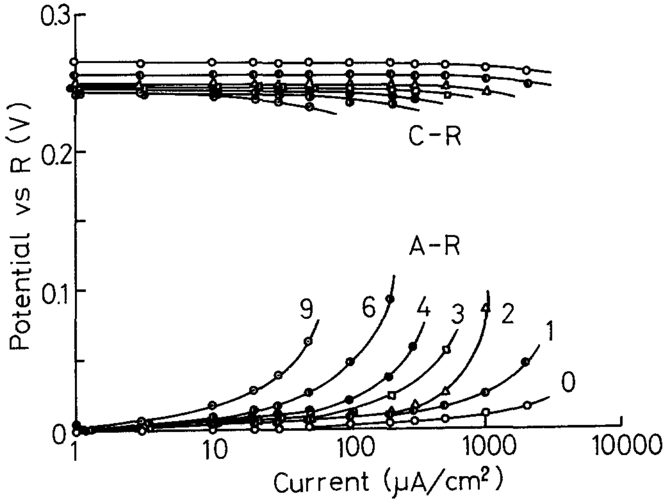

Fig. 5. Anode and cathode polarizations. The numbers refer to daily repeated measurements after preparation of a fresh cell.

4.5 μA (3.4 $\mu\text{Acm}^{-2}$) and a capacity of 4.5 mAh was obtained to the cut-off voltage at 0.185 V, corresponding to a cathode efficiency of 8.0%.

### 3.3. *Charge–discharge cycles*

If, after a discharge, the current is reversed, the copper content in the copper selenide will decrease and fresh metallic copper will deposit on the anode side. In other words, some recharging will occur.

Relatively little performance degradation was observed when 10–15 charge–discharge cycles were carried out, using a period of 20 min at current densities of 100–200 $\mu\text{Acm}^{-2}$. Figure 7 shows the voltage–time cycles obtained with a 60 min interval at 100 $\mu\text{Acm}^{-2}$, after an initial discharge for 30 min. A detectable breakdown could not be observed, but the potential decreased gradually with repeating cycles. This decrease seems to correspond to the slight lowering of the potential in the anode polarization, described in the above section.

Figure 8(a) shows the curves obtained from the first few cycles in which a charge–discharge current of 500 $\mu\text{Acm}^{-2}$ was applied for 30 s, followed by 60 s at open circuit. The cell voltage decreased rapidly in the initial discharge, but the cell recovered the starting OCV value after opening the circuit for 60 s. The cell was then charged for 30 s and the circuit was opened again for 60 s to complete the first cycle. Starting with the

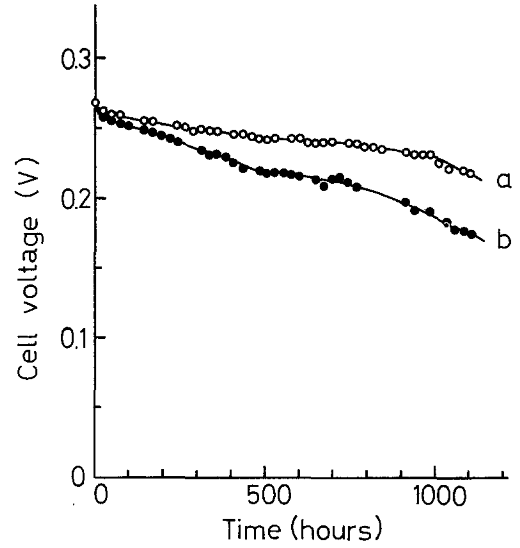

Fig. 6. Discharge curves with constant loads, (a) 100 kΩ and (b) 50 kΩ.

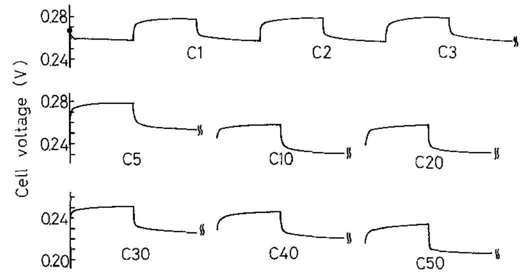

Fig. 7. Charge–discharge curves at 100 $\mu\text{Acm}^{-2}$ with a 60 min period. C*n* is the *n*th cycle.

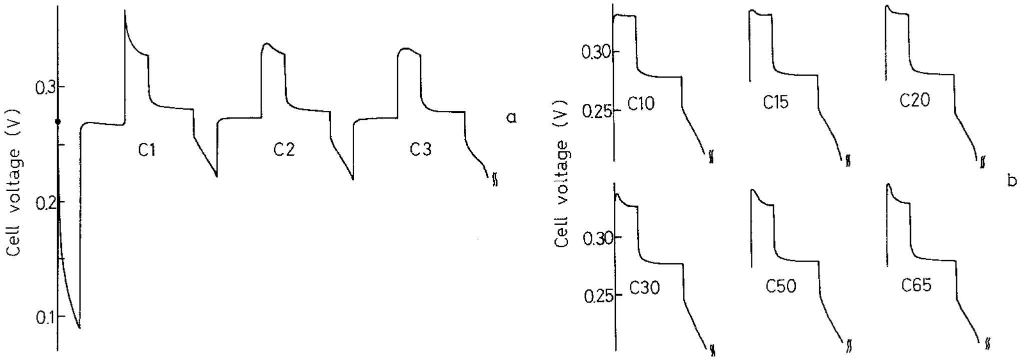

Fig. 8. Intermittent charge–discharge curves at (a) 500 $\mu$Acm$^{-2}$ and (b) the curves from the 10th to 65th cycles.

second discharge curve, the net polarization was about 50 mV, as seen in Fig. 8(a).

This type of intermittent charge and discharge was carried out continuously and typical curves are shown in Fig. 8(b). Breakdown began to appear after nearly the 70th cycle. The small peak on the charging curve could be considered to be caused by the migration lag of the copper ion at the cathode–electrolyte or anode–electrolyte boundaries. Armstrong *et al.* [14] pointed out that the charge transfer reaction at the metallic copper–copper ion electrode is slow.

Finally, the current was raised to 5 mAcm$^{-2}$ and charge–discharge cycles with a period of 3 min were carried out 20–30 times. Such treatment and the polarization measurement as described in the above section were alternated several times over a few days. Figure 9 shows the polarization curves thus obtained. The four curves for the anode polarization are almost identical. The polarizations as shown in Fig. 5 appear to be suppressed by the charge–discharge treatment. This result indicates that the polarization described in the previous section was not caused by the degradation of the electrolyte. In other words, such an anode polarization can arise not only from the slow charge transfer reaction of copper–copper ion, but also from the lowering of the activity of the copper powder. The interfacial contact between the tablets would be improved by the charge–discharge treatment and the copper in the anode would be replenished by the charging.

## 4. Conclusions

The OCV of the galvanic cell Cu, X/X/$Cu_{1.75}Se$ (X = $Rb_4Cu_{16}I_7Cl_{13}$) was 0.268 V at 25° C, which could be ascribed to the cell reaction, $0.25Cu + Cu_{1.75}Se = Cu_2Se$. The OCVs reported are, for example, 0.337–0.470 V [10], 0.378–0.710 V [11] or 0.257–0.448 V [12], depending on the cathode materials. Copper selenide ($Cu_{1.75}Se$) can be considered as one of the effective electrode materials (e.g. $TiS_2$ or $Cu_{1.8}S$ [10]). Work on the cathode material should be encouraged to raise the OCV value.

The anode polarization was more significant than the cathode one. Such behaviour was also described in earlier papers [10, 12] and was supposed to be a result of the poor reversibility of the copper electrode in the solid electrolyte. But, in this study, the anode polarization was considered to arise not only from the slow charge transfer reaction at the anode–electrolyte interface, but also from the decrease of the copper activity. The copper in the anode could be replenished by the charging and the cell performance was improved.

The OCV of the cell was almost constant over

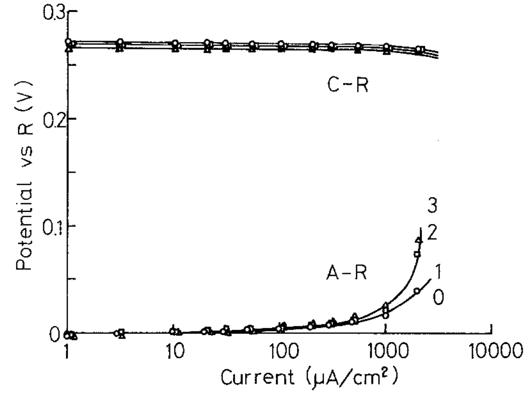

Fig. 9. Polarization curves after charge–discharge cycling at 5 mAcm$^{-2}$. The numbers are the experimental times (days) repeated.

six months and the cell was able to achieve cell currents in the range of several microamperes at room temperature. These results showed the availability of the conductor $Rb_4Cu_{16}I_7Cl_{13}$ as the electrolyte for the galvanic cell. It is possible that the cell may be used as a source of electricity for any devices working at low power.

## References

[1] B. B. Owens, 'Advances in Electrochemistry and Electrochemical Engineering', Vol. 8 (edited by P. Delahay and C. W. Tobias), Wiley-Interscience, New York (1971) p. 1.
[2] D. V. Louzas, W. G. Darland and G. W. Mellors, *J. Electrochem. Soc.* **120** (1973) 1151.
[3] B. B. Owens and K. R. Breenen, in 'Progress in Batteries and Solar Cells', Vol. 3 (edited by A. Kozawa) JEC Press, Cleveland (1980) p. 38.
[4] P. R. Mallory and Co. Inc., US Patent 464071.
[5] O. Nakamura, T. Kodama, I. Ogino and Y. Miyake, *Chem. Lett.* **1979,** 17.
[6] T. Takahashi, O. Yamamoto and S. Ikeda, *J. Electrochem. Soc.* **120** (1973) 1431.
[7] T. Takahashi and O. Yamamoto, *J. Electrochem. Soc.* **122** (1975) 83.
[8] S. Geller, J. R. Akridge and S. A. Wilber, *Phys. Rev. B.* **19** (1979) 5396.
[9] T. Takahashi, O. Yamamoto, S. Yamada and S. Hayashi, *J. Electrochem. Soc.* **126** (1979) 1654.
[10] M. Lazzari, G. Razzini and B. Scrosati, *J. Power Sources* **1** (1976/77) 57.
[11] A. F. Sammells, J. Z. Gougoutas and B. B. Owens, *J. Electrochem. Soc.* **122** (1975) 1291.
[12] T. Takahashi and O. Yamamoto, *J. Appl. Electrochem.* 7 (1977) 37.
[13] K. C. Mills, 'Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides', Butterworths, London (1974) p. 244.
[14] R. D. Armstrong, T. Dickinson and K. Taylor, *J. Electroanal. Chem.* 57 (1974) 157.