

Single and multi-layerbuilt solid electrolyte cells with a copper ion conductor

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The performances of two types of solid electrolyte cell were investigated. One was a single-layer cell $\text{Cu}_2\text{X}/\text{X}/\text{Cu}_2\text{Se}, \text{Se}$ ($\text{Se}/\text{Cu}_2\text{Se} = 3$ in weight) where X was a copper ion conductor $\text{Rb}_4\text{Cu}_{16}\text{I}_7\text{Cl}_{13}$. The open circuit voltage (OCV) of the cell was 385 mV at room temperature and was stable after 250 days. Appreciable polarization could not be observed up to about ten microamperes of discharge rate. The other was the multi-layerbuilt cell consisting of two, three or five single cells. As expected, the OCVs and the overpotentials of the layerbuilt cells were nearly proportional to the number of single cells assembled.

1. Introduction

Galvanic cells for use in fields such as electronic wrist-watches and electronic calculators must be reliable over long periods. Cells with solid electrolytes may be used for such applications because of their long flat voltage plateau on discharge, their leak-free characteristics after prolonged storage at ambient temperature and the possibility of miniaturizing them. Although the cells are limited to low rates of use due to the low migration rate of the mobile ion in the electrolyte and/or due to the low rate of the charge transfer reaction at the boundary between the electrolyte and the electrode, they can drive electronic devices which work at very low current density owing to the remarkable progress in electronic techniques. Nevertheless, it is desirable for them to supply a voltage as high as possible.

The open circuit voltage (OCV) of a cell cannot exceed the decomposition voltage of the solid electrolyte used, even if the anode and the cathode materials are combined most successfully. This is the reason why high ionic conductors with high decomposition voltage must be developed. It is also necessary to obtain fundamental data on solid electrolyte cells with a view to obtaining higher voltages through an appropriate technique such as multi-layerbuilt cells.

In a previous paper [1], a solid electrolyte cell with copper selenide as a cathode material was studied using an excellent copper ion conductor $\text{Rb}_4\text{Cu}_{16}\text{I}_7\text{Cl}_{13}$ [2-4]. Copper selenide, $\text{Cu}_{2-\alpha}\text{Se}$, shows ionic and electronic mixed-conduction and its ionic conductivity has a maximum at $\alpha = 0.25$ [5]. The OCV of the cell $\text{Cu}_2\text{X}/\text{X}/\text{Cu}_{1.75}\text{Se}$ ($X = \text{Rb}_4\text{Cu}_{16}\text{I}_7\text{Cl}_{13}$) was not always high (268 mV at 25°C), although the discharge performance was very good [1]. This paper describes the essential characteristics of single cells using a mixture of selenium and cuprous selenide (Cu_2Se) powder as cathode material. In addition, multi-layerbuilt cells were prepared and their discharge behaviour was examined prior to subsequent work on multi-layerbuilt cells of solid thin films.

2. Experimental details

The solid electrolyte, $\text{Rb}_4\text{Cu}_{16}\text{I}_7\text{Cl}_{13}$, was prepared by the procedure reported previously [2, 3]. The anode was composed of a mixture of copper powder (0.1 g) and the electrolyte (0.05 g). The cathode material was a mixture of selenium and cuprous selenide powder. Cuprous selenide was prepared from powdered copper and selenium (99.999%) [5]. The powders were mixed in the atomic ratio of 2:1, packed into a Pyrex capsule, sealed under vacuum and heated at 200°C for

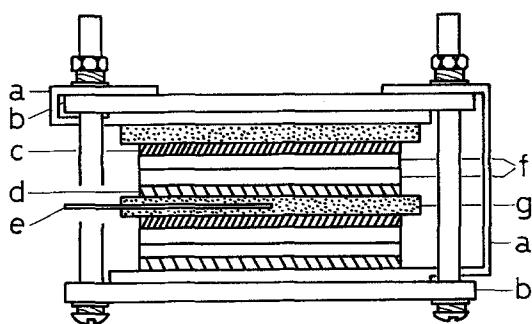


Fig. 1. Arrangement of two-layer built cell. a is copper plate, b is bakelite plate, c is cathode, d is anode, e is copper wire, f is solid electrolyte and g is a separator of graphite, copper plate or a pair of copper and graphite.

48 h. After pressing into a tablet, it was heated again under vacuum at 400°C for 48 h.

The single cell $\text{Cu}_x\text{X}/\text{X}/\text{Cu}_2\text{Se},\text{Se}$ was assembled as follows. The Cu_xX anode of the cell (0.15 g) and the electrolyte (0.7 g) were pressed simultaneously at 400 MPa into a tablet (13 mm dia.) to reduce contact resistance between the electrode and the electrolyte. The $\text{Cu}_2\text{Se},\text{Se}$ cathode (0.2 g) and the electrolyte (0.7 g) were pressed in a similar manner. These two tablets were combined so that the electrolyte surfaces were in contact. To measure the anodic and cathodic polarization, a copper wire (0.17 mm dia.) was inserted into the electrolyte and used as a reference electrode. A copper plate and a pair of graphite and copper plates were used as current collectors of the anode and cathode, respectively. The cell was sealed with polyester resin.

The multi-layer built cells were assembled from two, three and five unit cells. The arrangement of a two-layer built cell is shown as an example in Fig. 1. In this cell a copper wire was inserted into the graphite separator in order to examine the individual performance of each of the two unit cells. A copper plate and a pair of graphite and copper plates were also examined as separating materials in multi-layer built cells.

3. Results and discussion

3.1. Cathode materials

Fig. 2 shows the OCV values of several cells with various ratios of Se to Cu_2Se . The OCV increases slightly with increasing weight per cent (wt %) of Se. The OCV values in the range 25–75 wt %

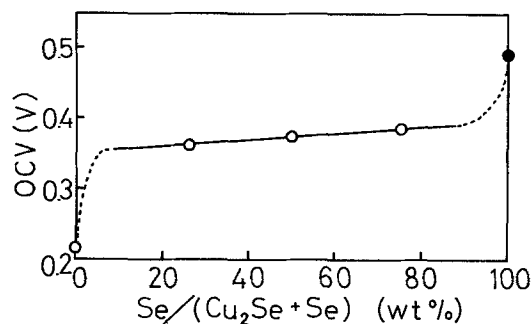


Fig. 2. Dependence of OCV of single cell $\text{Cu}_x\text{X}/\text{X}/\text{Cu}_2\text{Se},\text{Se}$ (X is $\text{Rb}_4\text{Cu}_{16}\text{I}_7\text{Cl}_{13}$) on the cathode composition.

of Se were stable over 250 days, as shown in Fig. 6a. The OCV value of a cell with a cathode consisting of only Se fluctuated vigorously. In contrast, the OCV of a cell containing only Cu_2Se as the cathode material was about 215 mV at the most. The standard free enthalpy changes of formation of cuprous selenide, Cu_2Se , and cupric selenide, CuSe , from copper and selenium are -71.8 and -45.2 kJ mol^{-1} , respectively [6], and the e.m.f.s calculated from these thermodynamic values are 372 and 468 mV, respectively. The fluctuation of the OCV suggested that the cell $\text{Cu}_x\text{X}/\text{X}/\text{Se}$ did not attain chemical equilibrium in a short time owing to low electrical conduction in selenium. On the other hand, Cu_2Se in the cell $\text{Cu}_x\text{X}/\text{X}/\text{Cu}_2\text{Se}$ cannot accommodate any further Cu^+ ions, although it has high electrical conductivity. The OCV value obtained implied that the standard free enthalpy change of formation of nonstoichiometric copper selenide ($\text{Cu}_{2+\beta}\text{Se}$) was less than that of Cu_2Se . From these facts the composition of 75 wt % of Se was regarded as most appropriate for the cathode in providing a stable and comparatively high OCV.

3.2. Polarization behaviour

Fig. 3 shows polarization curves in both electrodes with the best compositions. The iR drops included in the curves were negligibly small, i.e. only 10 mV even when the current passed was 1.0 mA cm^{-2} . The anodic and the cathodic overpotentials were 50 and 25 mV at 1.0 mA cm^{-2} , respectively. These low overpotentials were comparable to those obtained in the cell $\text{Cu}_x\text{X}/\text{X}/\text{Cu}_{1.75}\text{Se}$ [1]. When discharge was repeated daily up to about 75–50% of the OCV value for 50 days without charge,

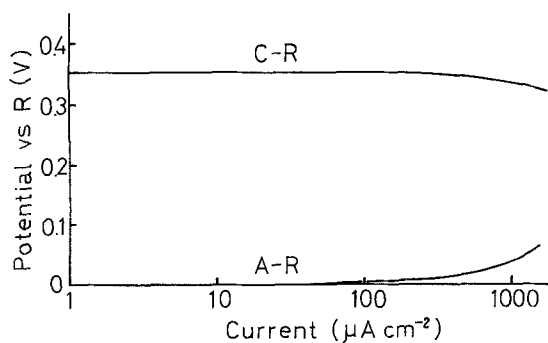


Fig. 3. Anode and cathode polarization in a single cell at room temperature.

typical polarization curves were obtained as shown in Fig. 4. The increase of the polarization of the discharge may be attributed to the increase of the concentration and the resistance overpotentials. The Cu^+ ion in the anode would be supplied slowly or the charge transfer reaction $\text{Cu} \rightleftharpoons \text{Cu}^+ + e^-$ would be slow as mentioned by Armstrong *et al.* [7]. The selenium powder in the cathode reacted with copper to produce a cuprous selenide layer which might hinder the successive electrochemical reaction between the unreacted selenium and the Cu^+ ion or which could act as resistance wall against the Cu^+ ion migration into the bulk of the cathode. In other words, the solid state electrochemical reactions seemed to proceed for the most part at the thin boundary layer between the electrolyte and the cathode. The overpotential mentioned above could be reduced notably if the current density was held low enough for Cu^+ ions to migrate through the cuprous selenide layer into the bulk of the cathode.

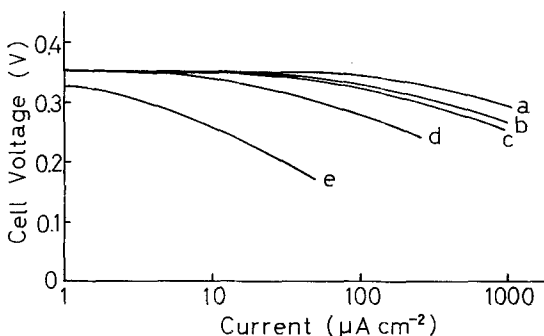


Fig. 4. Polarization curves of single cell for which the discharge was repeated daily up to about 75% of the OCV without charge. The curves were obtained at (a) first, (b) second, (c) third, (d) thirtieth and (e) fortieth discharge.

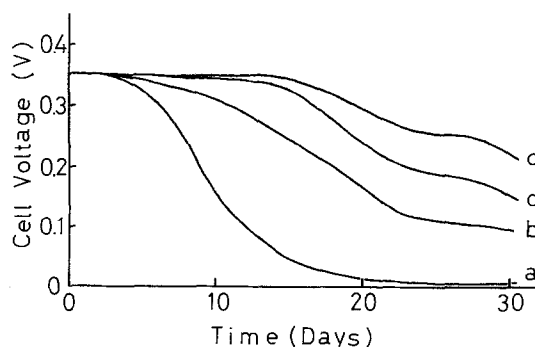


Fig. 5. Discharge curves of single cell with constant loads, (a) 20 k Ω , (b) 30 k Ω , (c) 50 k Ω and (d) 100 k Ω .

3.3. Cell capacity and efficiency

Fig. 5 shows the constant load discharge curves at ambient temperature. The anode capacity of the cells was 42.2 mA h, and the cathode capacity was 101.8 mA h. The average currents were 3.1 (2.3), 6.1 (4.6), 10.1 (7.6) and 15.3 μA (11.5 $\mu\text{A cm}^{-2}$), and the accumulated capacities to the cut-off voltage at 260 mV were 1.75, 2.78, 3.40 and 2.72 mA h corresponding to loads of 100, 50, 30 and 20 k Ω , respectively. The anode efficiencies calculated from the anode capacity and the accumulated capacity were 4.15, 6.59, 8.06 and 6.45% whilst the cathode efficiencies were 1.72, 2.73, 3.34 and 2.67% in the same order of the load. These low efficiencies suggest that the active materials in both electrodes were used only partially, presumably at the boundary layers adjacent to the electrolyte. Therefore, the solid electrolyte cell can be expected to work well even if both the anode and the cathode could be made to a thickness of only several tens of micrometres. This idea leads to the thin solid film batteries which are now under investigation [8].

3.4. Multi-layerbuilt cells

Single cells with the best compositions of both electrodes were stacked to compose multi-layerbuilt cells. The OCV of the two-layerbuilt cell is shown together with those of other multi-layerbuilt cells in Fig. 6. It can be seen from the figure that the OCV of a cell was approximately proportional to the number of the stacked single cells. The value of the OCV of any multi-layerbuilt cell was a little higher in the case of the graphite separator

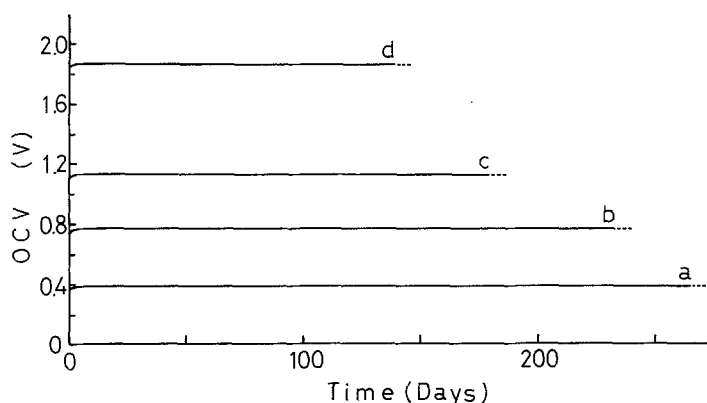


Fig. 6. OCVs of (a) single cell, (b) two-, (c) three- and (d) five-layer built cell.

than in the case of the copper separator. The surface of the copper plate, used as the inner separator and faced to the cathode, seemed to react slightly with selenium in the cathode material to form a rather resistive thin layer on the surface. Another feature in the figure is the slight increase of the OCV values in the initial stages.

A two-layer built cell using a couple of copper-graphite as inner separator was discharged up to about 75% of the OCV value repeatedly at intervals without charge. Fig. 7 shows the polarization curves which resemble those for the single cell. As expected, the overpotentials in these discharges were almost equal to twice the overpotentials obtained in the discharges for the single cell or to the sum of the overpotential of each single cell constituting the layer built cell. When the layer built cell was assembled by using only copper or graphite as the separator, the cell gave overpotentials a little higher than those shown in Fig. 7.

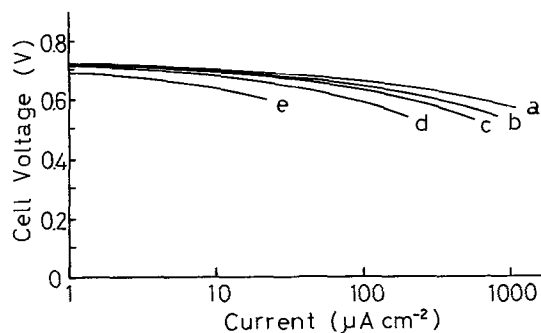


Fig. 7. Polarization curves of two-layer built cell examined in a similar manner to Fig. 4. (a) first, (b) second, (c) third, (d) thirtieth and (e) fortieth discharge.

The constant load ($100\text{ k}\Omega$) discharge curve at room temperature is shown in Fig. 8. Comparing this with Curve d shown in Fig. 5, the stability of the cell voltage is considerably better in the two-layer built cell than in the single cell. The average current was $6.8\text{ }\mu\text{A}$ and the cell capacity was 4.9 mA h to the cut-off voltage of 650 mV . The energy density of the cell was estimated from the total weight of the electrodes and the electrolyte to result in a value of 1.5 Wh kg^{-1} , which is comparable to the value of the single cells with the solid silver compound electrolyte reported previously [9].

Fig. 9 shows the discharge curves of the multi-layer built cells with graphite separator. The polarization of the two-layer built cell at 1.0 mA cm^{-2} was about 250 mV which was larger than the sum of the overpotential of each single cell. As mentioned above, polarization in the single cell was about 80 mV at 1.0 mA cm^{-2} . The apparent extra overpotential ($250 - 2 \times 80 = 90\text{ mV}$) appears to be due to contact resistance in the mechanical stacking of the unit cell. Similarly,

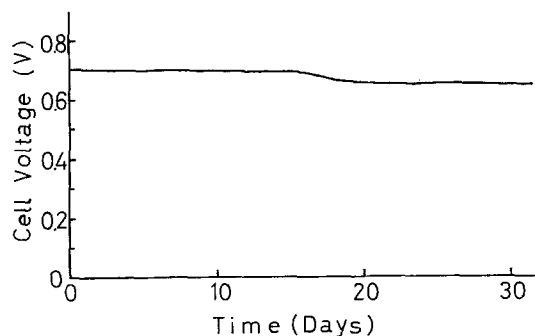


Fig. 8. Constant load ($100\text{ k}\Omega$) discharge curve of two-layer built cell at room temperature.

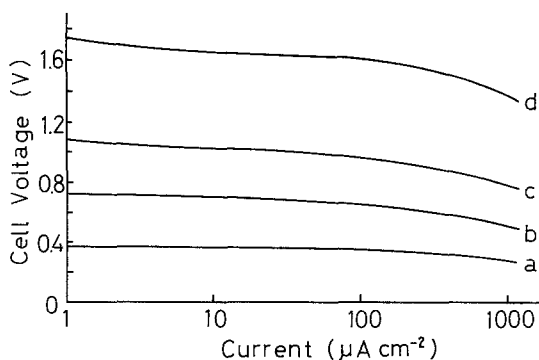


Fig. 9. Discharge curves of (a) single cell, (b) two- (c) three- and (d) five-layerbuilt cell.

the overpotentials of three- and five-layerbuilt cells at the current density of 1.0 mA cm^{-2} were about 350 and 525 mV, respectively. The differences between these values and 80 mV multiplied by three and five were 110 and 125 mV, respectively. That is to say, the extra overpotential increased gradually with the number of the cells stacked. These facts suggest that the contact resistance would increase with increasing number of layers in a tablet-stacking type cell. The overpotential based on the iR component may be reduced sharply if the multi-layerbuilt cell is prepared from thin films by a technique such as vacuum evaporation.

4. Summary

A solid electrolyte cell was prepared using the high copper ion conductor $\text{Rb}_4\text{Cu}_{16}\text{I}_7\text{Cl}_{13}$ as an

electrolyte, a mixture of copper and the electrolyte (2:1 in weight) as anode material, and a mixture of selenium and cuprous selenide as cathode material. The highest and most stable open circuit voltage was 385 mV at a ratio $\text{Se}/\text{Cu}_2\text{Se}$ of 3 in the cathode material. At a discharge rate of 1.0 mA cm^{-2} , the overpotential was about 80 mV. The multi-layerbuilt cells were assembled by stacking two, three and five single cells. The OCVs and the polarization of these cells were approximately proportional to the number of the single cells stacked up.

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