JOURNAL OF APPLIED ELECTROCHEMISTRY **16** (1986) 23–27

An investigation of the solid-state cell $Cu/Rb_4Cu_{16}I_7Cl_{13}/Cu_xTiS_2$

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Received 8 November 1984; revised 18 December 1984

The solid electrolyte cell Cu,Z/Z/Cu_xTiS_2,Z,graphite (Z = $Rb_4Cu_{16}I_7Cl_{13}$) was investigated in a search for a cell with high and stable open circuit voltage (OCV). The cells Cu/Cu_xTis_2 (x = 0 and 0.3–0.5) showed only a small reduction in OCV values over 200 days. The cause of the slight decrease of OCV was discussed from the viewpoint of degradation of the cell-component materials. Polarization curves and constant load discharge curves were obtained to indicate that the cathode polarization was predominant and that Cu_xTiS_2 of $0.3 \leqq x \leqq 0.5$ performed well, as did TiS_2.

1. Introduction

Recently, promising copper ion conductors were found in the system CuCl–CuI–RbCl. The solid electrolytes $RbCu_4Cl_3(I_{2-x}Cl_x)$ [1, 2] and $Rb_4Cu_{16}I_{7-x}Cl_{13+x}$ [3, 4] have wide ranges of solid solution, $0.00 \leqq x \leqq 0.40$ and $-0.5 \leqq x \leqq 0.2$, respectively. At ambient temperature, the materials show a high ionic conductivity of $0.33 \pm 0.05\,S\,cm^{-1}$ which is comparable to that of an aqueous electrolyte solution.

Cells with such a solid electrolyte may be applied in the field of electronics. At room temperature, the cells are limited to low rates of use due to the low migration velocity of the mobile ion in the electrolyte and also due to the low rate of the charge transfer reaction at the electrolyte/electrode boundary. However, they are useful for driving electronic devices which work at very low current density.

When metallic copper is used as anode, the open circuit voltage (OCV) of a cell is still low for applications in electronics, e.g. 0.268 V for the cell Cu,Z/Z/$Cu_{1.75}Se$ (Z = $Rb_4Cu_{16}I_7Cl_{13}$) [5] and 0.385 V for the cell Cu,Z/Z/Cu_2Se, Se (Se/Cu_2Se = 3 in weight) [6], although the stability of the OCV and the discharge performance are satisfactory. It is desirable for the cell to supply a voltage as high as possible, though multilayer cells can supply a required voltage as described in a previous paper [6].

As part of a study relating to the application of the electrolyte $Rb_4Cu_{16}I_7Cl_{13}$, the present authors have searched for cells with high and stable OCV. Recently, a solid galvanic cell

$$Cu,Z/Z/Cu_xTiS_2,Z,graphite$$

was reported to show a comparatively high OCV of about 0.6 V and to display fairly good rechargeability [7]. In this paper, the OCV stability, polarization and constant load discharge were investigated using a cell with the ionic conductor $Rb_4Cu_{16}I_7Cl_{13}$ as the electrolyte and Cu_xTiS_2 as the cathode active material.

2. Experimental procedure

The solid electrolyte, $Rb_4Cu_{16}I_7Cl_{13}$, was prepared from cuprous chloride, cuprous iodide and rubidium chloride by the same procedure as reported in an earlier paper [3]. The starting material, TiS_2, was prepared by heating a mixture with an appropriate weight ratio of spongy titanium (> 98%) and sulphur powder (99.99%) in a sealed silica tube at 600° C for 145 h. Cu_xTiS_2 ($0 < x \leqq 0.6$) were prepared by heating the mixtures of copper powder and pulverized titanium sulphide in sealed silica tubes at 800° C for 72 h.

The galvanic cell

$$\mathrm{Cu,Z/Z/Cu_{\mathit{x}}TiS_2,Z,graphite}$$

was examined, where Z was $Rb_4Cu_{16}I_7Cl_{13}$. For simplicity, the cell is abbreviated hereafter as Cu/Cu_xTiS_2. 0.1 g of the electrolyte and 0.1 g of copper powder were mixed for use as the anode material. The anode material and the electrolyte (0.2 g) were pressed simultaneously at 400 MPa into a tablet (13 mm diameter). The cathode of the cell was prepared from a mixture of 0.2 g of Cu_xTiS_2, 0.2 g of the electrolyte and 0.1 g of graphite by pressing together with the electrolyte (0.2 g) into a tablet (13 mm diameter) at 400 MPa. In order to measure the anode and cathode polarizations, the anode was divided into two parts (3 : 10 in area) and the smaller one was used as a temporary reference electrode.

3. Results and discussion

3.1. *Open circuit voltage (OCV)*

A typical OCV-composition curve of the galvanic cell is shown in Fig. 1 together with the data reported by Bottini *et al.* [8]. The two curves behave in a similar manner in the range $0.3 \leqq x \leqq 0.5$. The samples, Cu_xTiS_2, in the x region of 0.3 to 0.5 were confirmed to have a single phase by X-ray diffraction. Le Nagard *et al.* [9] described $Cu_{1-y}Ti_2S_4$ as having a normal spinel structure and a single phase over a wide range, $0 \leqq y \leqq 0.44$. This range is equivalent to $0.28 \leqq x \leqq 0.50$ in the formula Cu_xTiS_2. Therefore, the range $0.3 \leqq x \leqq 0.5$ in Fig. 1 corresponds to the spinel phase of the cathode material Cu_xTiS_2.

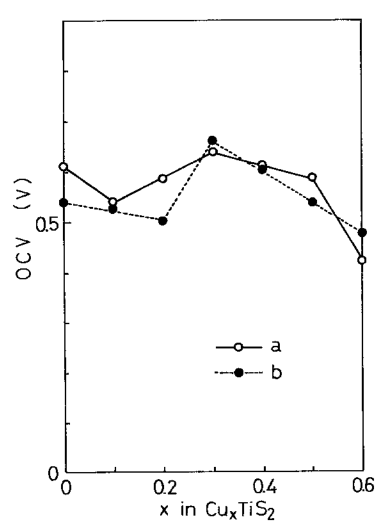

Fig. 1. OCVs of the cells, (a) Cu/Cu_xTiS_2 and (b) from reference [8].

On the other hand, in the range $0 \leqq x < 0.3$ the OCV values of the cells Cu/Cu_xTiS_2 showed poor reproducibility except for the cell Cu/TiS_2 ($x = 0$ in Cu_xTiS_2). X-ray diffraction profiles of Cu_xTiS_2 with $x = 0.1$ and 0.2 showed mixed phases of TiS_2 and $Cu_{0.3}TiS_2$.

3.2. *OCV changes of the cells Cu/Cu_xTiS_2 with time*

The changes in OCV values of the cells with Cu_xTiS_2 ($x = 0$, 0.3 and 0.5) are shown in Fig. 2 together with those reported by Lazzari *et al.* [10, 11]. OCV values of the cells Cu/Cu_xTiS_2 are very stable, although very slow and slight changes are observed. The cell with TiS_2 described by Lazzari *et al.* [10] is essentially the same typical copper galvanic cell as the present cell except for the electrolyte of N-N′-dimethyltriethylenediamine dibromide ($DTDBr_2$)–cuprous bromide. Nevertheless, the OCV value of the cell is relatively low. The other copper solid electrolyte cell, $Cu/DTDBr_2\text{–}CuBr/Br_2$, showed rapid lowering of the OCV value [11], and such a behaviour was explained by oxidation of CuBr and the increase in the electronic conduction of the electrolyte. As can be seen from Fig. 2, the cells with Cu_xTiS_2 in this study show the highest and the most stable OCV values among the various types of copper cell. The very slow and small changes in OCV values of the cells Cu/Cu_xTiS_2 are suggested to be caused by the deterioration of the solid electrolyte and/or the degradation of the electrode active material.

The electrolyte, $Rb_4Cu_{16}I_7Cl_{13}$, had been used for the solid copper cells $Cu,Z/Z/Cu_{1.75}Se$ and $Cu,Z/Z/Cu_2Se,Se$, and the experimental fact that OCV values of the cells were almost constant over 200 days verified the excellent stability and reproducibility of the electrolyte [5, 6]. But, if the electromotive force of a cell exceeds or is close to the decomposition potential of the electrolyte, the electrolyte in the cell will be

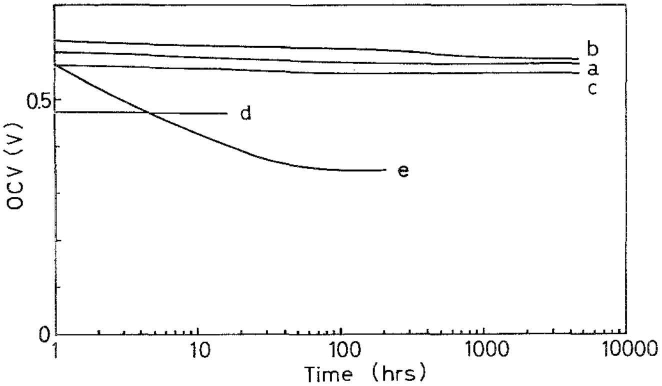

Fig. 2. OCV changes of cells with Cu_xTiS_2. x; (a) 0, (b) 0.3 and (c) 0.5. (d) and (e) are the data from references [10] and [11], respectively.

decomposed. Bottini *et al.* attributed the poor reproducibility of the cell Cu/Cu_xTiS_2 ($x \leqq 0.3$) to electrolyte decomposition [8]. The decomposition potential of the electrolyte $Rb_4Cu_{16}I_7Cl_{13}$ is reported to be 0.69 V [3] which was re-examined and confirmed by the present authors. In Fig. 1, rough extrapolation of the curve in the range of $0.3 \leqq x \leqq 0.5$ to the low x range of composition reveals voltages higher than 0.65 V which is close to the decomposition potential of the solid electrolyte.

To examine the possibility of deterioration of the electrolyte, a voltage of 0.70 V was applied for 5 min to the configuration,

graphite/electrolyte/graphite

Fig. 3 shows the X-ray diffraction patterns of the various states of the electrolyte. The sample without the voltage supply indicates the original diffraction pattern, while unidentified weak peaks at about 20.8° and 25.7° are found for the sample immediately after voltage supply. Further, after 400 days, more unidentified peaks are found over the whole range. These patterns suggest that the sample once decomposed continues to deteriorate until new stable phases are formed.

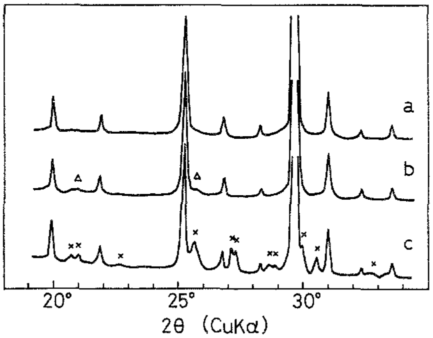

Fig. 3. X-ray diffraction patterns of the electrolytes. (a) before voltage supply, (b) immediately after voltage supply of 0.70 V for 5 min and (c) after 400 days from the state of (b).

The change in the electrical resistivity of the electrolyte is an important factor in the present problem. The specific resistivity change of the sample is shown in Fig. 4. The resistivity, 12.64 Ω cm, of the sample without voltage supply (0.70 V for 5 min) decreased to 12.06 Ω cm immediately after the voltage supply, and further to 10.63 Ω cm after 400 days. The decrease seems to be due not to the increase of copper ion conductivity but to the increase of the electronic conductivity arising from increase in the concentration of the cupric ion, since a cell with partially decomposed electrolyte showed an OCV value lower than 0.5 V and the value decreased rather quickly.

Even if the decreases in OCV values of the cells with x lower than 0.3 could be explained by the decomposition of the electrolyte, the OCV

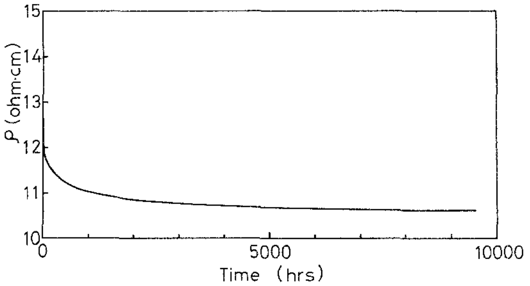

Fig. 4. Resistivity change of the electrolyte with time after supply of 0.70 V for 5 min.

changes in cells with x equal to or higher than 0.3 can not be interpreted in the same way since OCV values of cells with cathodes ($x \geqq 0.3$) were lower than the decomposition potential of the electrolyte as seen in Fig. 1. Therefore, the degradation of the electrode active materials was examined.

The cathode material Cu_xTiS_2 is partially degraded by ambient moisture to form H_2S gas,

$$Cu_xTiS_2 + H_2O \longrightarrow Cu_xTiO_2 + H_2S \quad (1)$$

The compound, Cu_xTiO_2, could not be identified by X-ray diffraction analyses, whereas the presence of H_2S gas was confirmed by its characteristic smell. The formation of H_2S gas in the cathode may lead to the lowering of the OCV value by suppressing the electrochemical reaction between Cu^+ ion and Cu_xTiS_2.

H_2S gas produced by partial degradation of the cathode material may possibly cause damage to the anode material. The gas seems to pass through pin holes or to diffuse along the grain boundaries of the solid electrolyte and to react with metallic copper in the anode to produce a thin layer of copper sulphide. The fact that the anode polarization of the cell with Cu_xTiS_2 containing ambient moisture was higher than the polarizations shown in Fig. 6 suggested slight damage of the anode due to the formation of the hydrogen sulphide. These data suggest that the degradation of the cathode material is the most predominant cause of the behaviour observed.

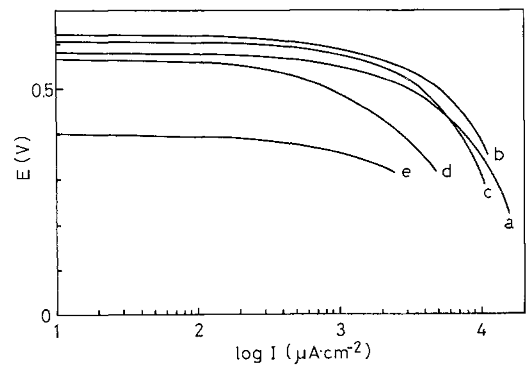

Fig. 5. Polarization curves of cells with Cu_xTiS_2. x; (a) 0, (b) 0.3, (c) 0.4, (d) 0.5 and (e) 0.6.

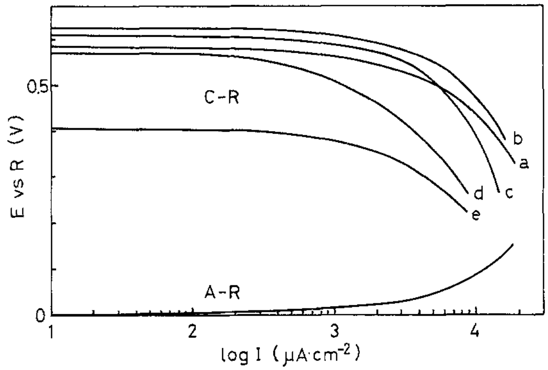

Fig. 6. Polarization curves of the anode (A–R) and the cathode (C–R) of the cells with Cu_xTiS_2. x; (a) 0, (b) 0.3, (c) 0.4, (d) 0.5 and (e) 0.6.

3.3. *Polarization curves*

Polarization behaviour was examined in the same manner as described in previous papers [5, 6] and Fig. 5 shows *E–I* curves of the cells with various cathodes. The curves include the *iR* drops which are negligibly small for low current densities but result in values higher than 10 mV in the region of high current densities ($> 1.0\,mA\,cm^{-2}$). In order to evaluate the performances of each cell, current densities corresponding to cell voltages of 70% of the OCV are selected as a measure of the usable limit. Current densities are 6.3, 7.6, 5.9, 2.4 and $3.2\,mA\,cm^{-2}$ for cathodes with $x = 0$, 0.3, 0.4, 0.5 and 0.6 respectively. As can be seen, the cells with the cathodes of $x = 0$, 0.3 and 0.4 can supply relatively high currents.

These data, as well as OCV values, suggest that cells with $Cu_{0.3}TiS_2$ and $Cu_{0.4}TiS_2$ can achieve a performance comparable to the cell with TiS_2. The compound TiS_2 with a hexagonal layer structure is known to be a typical intercalation compound and is a promising cathode material for a rechargeable cell. Selected cations can migrate through the layers, but the ion cannot move in a direction perpendicular to the (0 0 1) plane. Control of the crystallographic orientation of the conductive plane is important in TiS_2. Kanehori *et al.* [12] developed an all solid-state lithium cell, $Li/Li_{3.6}Si_{0.6}P_{0.4}O_4/TiS_2$. TiS_2 in the form of thin films was prepared by LPCVD (low pressure chemical vapour deposition) so as to orientate its c-axis parallel to the substrate plane, and then the solid electrolyte was formed on the TiS_2 film by a radio frequency sputtering method and finally a lithium thin film was prepared on the electrolyte by vacuum evaporation. Excellent performance of the cell could be obtained by successful preparation of the oriented film of TiS_2. In contrast, the compound Cu_xTiS_2 of $0.3 \leqq x \leqq 0.5$ has the spinel structure indicating little anisotropy. Therefore, Cu_xTiS_2 has an advantage of the preparation of the thin film as cathode material without particularly orientating a crystallographic plane.

Polarization curves in both electrodes are shown in Fig. 6. Anode overpotentials are 15 and 85 mV at 1.0 and 10 mA cm^{-2}, respectively. Kanno *et al.* [13] examined the anodic polarization using copper ion conductors with various compositions of $Rb_4Cu_{16}I_{7-x}Cl_{13+x}$ and found $Rb_4Cu_{16}I_{6.8}Cl_{13.2}$ the best electrolyte for a cell with a copper anode. The anode polarization obtained in this study is as low as the data reported in the literature [13]. On the other hand, the cathode polarizations are comparatively high. Cells with cathodes of $x = 0$ and 0.3 give cathode overpotentials of 25 to 45 mV at 1.0 mA cm^{-2} which are comparable to the overpotentials in the cells $Cu,Z/Z/Cu_{1.75}Se$ and $Cu,Z/Z/Cu_2Se,Se$ described in previous papers [5, 6]. In spite of assembling sufficient cathode active material to promote the cell reaction, the concentration and the resistance overpotentials increase as the discharge progresses.

3.4. *Constant load discharge*

Fig. 7 shows constant load (1 MΩ) discharge curves at room temperature. The anode capacity of the cells used in this work was 42.2 mA h, and the cathode capacities were 47.9 and 40.9 mA h at cathodes of TiS_2 and $Cu_{0.3}TiS_2$, respectively. In the case of the cell Cu/TiS_2, the average current was 0.54 μA and the capacity was 1.08 mA h for a 2000 h discharge. The anode and the cathode efficiencies were estimated to be 2.6 and 2.3%, respectively. The amount of copper reacted with one mole of TiS_2 was calculated using the anode efficiency to be 0.023 gram atom. In the cell $Cu/Cu_{0.3}TiS_2$, the average current was 0.57 μA and the capacity was 1.14 mA h. The anode and the cathode efficiencies were 2.7 and 2.8%, respectively. The amount of copper reacted with one mole of $Cu_{0.3}TiS_2$ was 0.028 gram atom. From the facts that both the anode and the cathode efficiencies were very low, the solid-state electrochemical reaction is considered to proceed mainly at the thin electrode surface layer as expected. These results suggest that if a thin-film type solid galvanic cell is prepared, the efficiency of electrode materials will increase considerably.

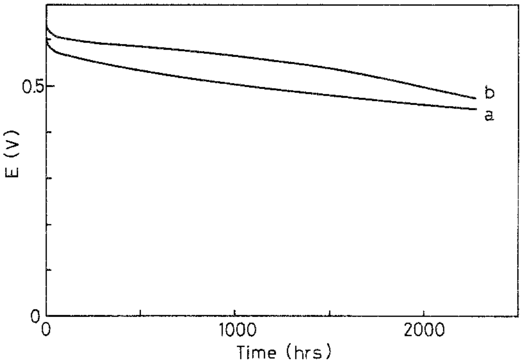

Fig. 7. Constant load (1 MΩ) discharge curves of the cells Cu/Cu_xTiS_2. x; (a) 0 and (b) 0.3.

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