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Rechargeable solid electrolyte cells with a copper ion conductor, $Rb_4Cu_{16}I_{7-\delta}Cl_{13+\delta}$, and a titanium disulphide cathode

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A rechargeable solid electrolyte cell has been developed using a high copper-ion-conductivity solid electrolyte, $Rb_4Cu_{16}I_{7-\delta}Cl_{13+\delta}$, a copper anode, and an intercalation cathode, TiS_2. The open-circuit voltage was 0.59 V at 25° C. The cell yielded a current of several tens of microamperes at room temperature without appreciable polarization. The cell could be submitted to one hundred or more charge–discharge cycles without showing appreciable deterioration.

1. Introduction

Recently, considerable interest has been shown in the area of microwatt rechargeable batteries coupled with solar cells. These batteries could be used for electronic wrist watches and electronic calculators. The most important characteristic for these applications is reliability over long periods. Button-type rechargeable silver oxide batteries have been developed for use in electronic watches. There are, however, some unresolved problems in practical application, for example, poor leahaye resistance and rapid self-discharge. Solid electrolyte battery systems are promising for these applications, because of their long shelf-life stability and because there is no leakage after prolonged storage at room temperature or elevated temperatures. The most serious problem of the solid electrolyte cell is the low rate capability. However, remarkable progress in the field of electronic devices has reduced the current necessary to drive them to levels at least partially compatible with solid electrolyte battery systems.

Many types of solid electrolyte cells have been reported [1]. Except for a few cases, most of them were primary cells. Lazzari *et al.* [2] and Scrosati *et al.* [3] reported rechargeable copper solid electrolyte cells. The cells consisted of a high copper ion conductivity solid, *N. N′*-dimethyltriethylenediamine dibromide–copper(I) bromide double salt or *N*-methylhexamethylenetetramine bromide–copper(I) bromide double salt, and an intercalation cathode, TiS_2. TiS_2 was considered a very promising cathode for rechargeable copper solid electrolyte cells. The copper anode–electrolyte interface showed serious kinetic limitations, however, and the rechargeability of the cell was poor. More recently, Takahashi *et al.* [4, 5] found an extremely high copper ion conductivity solid, $Rb_4Cu_{16}I_{7-\delta}Cl_{13+\delta}$ ($-0.2 \leqslant \delta \leqslant 0.5$). This compound has a conductivity as high as 0.37–0.28 S cm^{-1} at room temperature, a value which is comparable to that of an aqueous electrolyte solution. In this study, the performance of the cell with the solid electrolyte, $Rb_4Cu_{16}I_{7-\delta}Cl_{13+\delta}$, a copper anode, and the intercalation cathode, TiS_2, was examined.

2. Experimental procedure

The solid electrolyte, $Rb_4Cu_{16}I_{7-\delta}Cl_{13+\delta}$, was prepared by the method described in a previous paper [5]. The appropriate quantities of CuCl, CuI, and RbCl were ground together; to remove water the mixture was heated in a vacuum, utilizing a liquid-N_2 trap, for 12 h at 130–140° C. Pellets of the sample were pressed under 300 MPa, heated at 200° C in an evacuated Pyrex tube, and then annealed at 130° C. Commercial grade titanium disulphide was used without further purification.

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The chemical composition of the titanium disulphide determined by thermogravimetric analysis was $TiS_{2.00}$.

The anodic polarization was measured by the cell

$$\begin{array}{c} \text{Cu}, Rb_4Cu_{16}I_{7-\delta}Cl_{13+\delta}|Rb_4\underset{\substack{\uparrow \\ \text{Cu}}}{Cu_{16}}I_{7-\delta}Cl_{13+\delta}| \\ \text{Cu}, Rb_4Cu_{16}I_{7-\delta}Cl_{13+\delta} \end{array} \qquad (1)$$

with the help of the copper wire reference electrode inserted into the electrolyte. A mixture of powdered copper (325 mesh) and the electrolyte (2 : 1 weight ratio) served as the electrodes. About 1.0 g of the electrolyte was placed between two electrodes and pressed at 300 MPa to form a pellet of 13 mm diameter.

The galvanic cells,

$$\begin{array}{c} \text{Cu}, Rb_4Cu_{16}I_{7-\delta}Cl_{13+\delta}|Rb_4Cu_{16}I_{7-\delta}Cl_{13+\delta}|TiS_2, \\ \text{graphite}, Rb_4Cu_{16}I_{7-\delta}Cl_{13+\delta} \end{array} \qquad (2)$$

were examined. The anode of the cell was a mixture of 0.2 g of the electrolyte and 0.4 g of copper powder. The electrolyte (0.8 g) and anode layers were pressed at 300 MPa to form a pellet 13 mm in diameter. The cathode of the cell was a mixture of 0.3 g of the electrolyte, 0.2 g of TiS_2, and 0.07 g of graphite: The electrode material was pressed at 300 MPa to form a pellet 13 mm in diameter in a nitrogen filled glove box. In order to measure the anodic and cathodic polarizations, a copper wire was inserted into the electrolyte and used as a reference electrode. The cells were placed in a glass vessel with silica gel.

3. Results and discussion

The previously reported solid electrolyte cells with copper ion conductors exhibited a predominant anodic polarization [2, 6]. In order to obtain a high performance cell, an electrolyte having a small polarization at the boundary between the electrolyte and the copper electrode must be found, in addition it must also have a high ionic and low electronic conductivity. $Rb_4Cu_{16}I_{7-\delta}Cl_{13+\delta}$ has an extremely high copper ion conductivity of 0.37–0.28 S cm^{-1} at room temperature and low electronic conductivity of about 10^{-12} S cm^{-1} at 60° C [5]. However, no anodic polarization data for cell 1 have been reported. In this study, $Rb_4Cu_{16}I_{7-\delta}Cl_{13+\delta}$ with various values of δ were prepared. The anodic polarization of these compounds was examined at room temperature as a function of δ and is shown in Fig. 1. In these measurements, all the potentials were recorded within one minute. At higher current densities, as the anode potentials became rapidly more positive with time they are indicated by the dotted lines in Fig. 1.

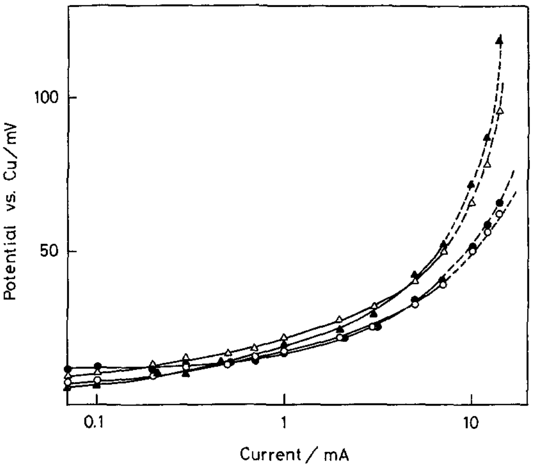

Fig. 1. Anodic polarization curves of cell 1 at room temperature: (○) $Rb_4Cu_{16}I_7Cl_{13}$, (●) $Rb_4Cu_{16}I_{6.8}Cl_{13.2}$, (△) $Rb_4Cu_{16}I_{7.4}Cl_{12.6}$ and (▲) $Rb_4Cu_{16}I_{7.6}Cl_{12.4}$.

These results suggest that the anodic polarization increases with increasing δ in $Rb_4Cu_{16}I_{7-\delta}Cl_{13+\delta}$. Kleitz *et al.* [7] measured the complex impedance of $Rb_4Cu_{16}I_8Cl_{12}$ and $Rb_4Cu_{16}I_7Cl_{13}$ using copper electrodes, and indicated that $Rb_4Cu_{16}I_8Cl_{12}$ was unstable in contact with copper metal and a sort of passivation blocked the interface. The high anodic polarization at the interface $Cu/Rb_4Cu_{16}I_{7.6}Cl_{12.4}$ may be due to the formation of a nonconductive phase such as copper(I) iodide. The time dependences of the anodic polarization at a constant current of 100 μA for the cells $Cu|Rb_4Cu_{16}I_{7.6}Cl_{12.4}|Cu$ and $Cu|Rb_4Cu_{16}I_{6.8}Cl_{13.2}|Cu$ are shown in Fig. 2. A remarkable difference between the anodic behaviour of the two cells is found: the overvoltages increase rapidly with time after 70 h for $Rb_4Cu_{16}I_{6.8}Cl_{13.2}$ and 25 h for $Rb_4Cu_{16}I_{7.2}Cl_{12.8}$. Further, Takashi *et al.* [5] found that $Rb_4Cu_{16}I_{6.8}Cl_{13.2}$ has the highest conductivity, 0.37 S cm^{-1} at 25° C in the $Rb_4Cu_{16}I_{7-\delta}Cl_{13+\delta}$

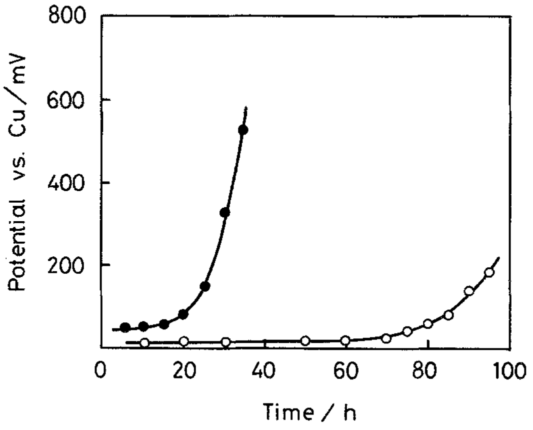

Fig. 2. Time dependence of the anode potentials at a constant current of 100 μA: (○) $Rb_4Cu_{16}I_{6.8}Cl_{13.2}$ and (●) $Rb_4Cu_{16}I_{7.2}Cl_{12.8}$.

system. These results indicate that in the $Rb_4Cu_{16}I_{7-\delta}Cl_{13+\delta}$ system, the sample with the highest content of chlorine, i.e., $Rb_4Cu_{16}I_{6.8}Cl_{13.2}$, is the best electrolyte for a cell with a copper anode. In the following experiments, $Rb_4Cu_{16}I_{6.8}Cl_{13.2}$ was used as the electrolyte in the cell.

The decomposition potential of $Rb_4Cu_{16}I_7Cl_{13}$ was measured (using the cell $Au|Rb_4Cu_{16}I_7Cl_{13}|Au$) as 0.69 ± 0.01 V at 22° C [4]. Therefore, the cathode material will be limited by the decomposition potential. Recently, the transition metal dichalcogenides and related materials have been used as the cathode in rechargeable batteries. The rechargeability is due to the formation of intercalation compounds with the layered dichalcogenides as hosts. The possibility of intercalating copper in TiS_2 has already been indicated by Whittingham [8] with liquid electrolyte cells and by Bottini *et al.* [9] with solid electrolyte cells.

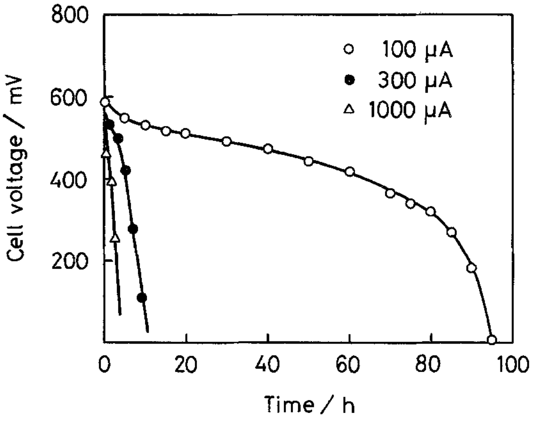

Fig. 3. Constant current discharge curves of cell 2 at room temperature.

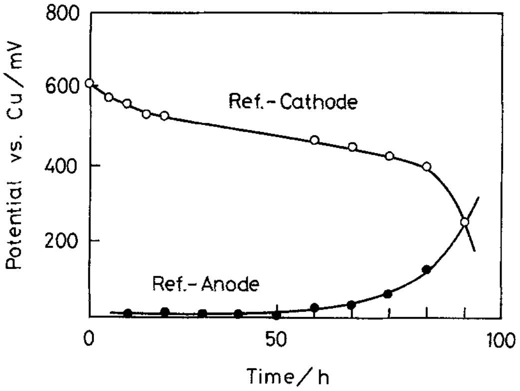

Fig. 4. Polarization curves of cell 2 at room temperature.

The open-circuit voltage (OCV) of cell 2 was 0.59 ± 0.01 V at room temperature, a value which is lower than the decomposition potential of $Rb_4Cu_{16}I_7Cl_{13}$, 0.69 ± 0.01 V. No appreciable change of the OCV with time has been observed at room temperature. In Fig. 3, the constant current discharge curves of cell 2 at room temperature are shown. At a higher current density, 300 μA (225 μA cm^{-2}), the cell voltages rapidly decrease with time and the capacity was 1.5 mAh to the cut-off voltage of 0.4 V. On the other hand, the capacity increased to 6.3 mAh at a lower current intensity of 100 μA (75 μA cm^{-2}).

The cathode and anode potentials at a constant current discharge (100 μA) with respect to the copper reference electrode for cell 2 are shown in Fig. 4. The cathode potentials decrease gradually with time, and then rapidly after discharging for the period of about 100 h. Le Nagard *et al.* [10, 11] have reported that the Cu–TiS_2 system has two intermediate phases, namely, $Cu_{1-y}Ti_2S_4$ spinel ($0 < y < 0.44$), and Cu_xTiS_2 intercalated ($0.7 < x < 1$). The OCV–composition curve at 80° C was determined electrochemically by passing a constant current of 20 μA through cell 2 where the cathode was a mixture of 0.3 g of the electrolyte, 0.01 g of TiS_2, and 0.07 g of graphite. The curves showed that the OCV decreased gradually to 0.25 V at $\delta \simeq 0.63$ and then rapidly to 0.1 V at $\delta \simeq 0.73$. The results of Bottini *et al.* [9] were confirmed in this work. The lower cathode potentials after discharging for 100 h in Fig. 4 may be due to the formation of the phase

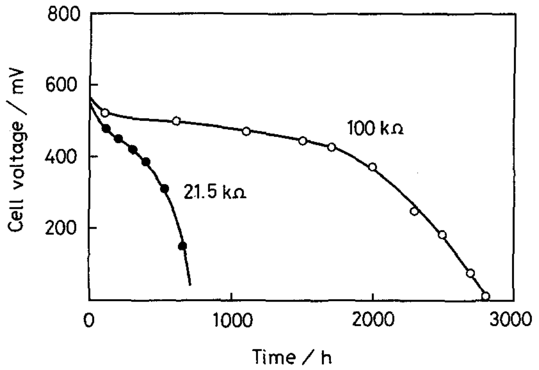

Fig. 5. Constant load discharge curves of cell 2 at room temperature.

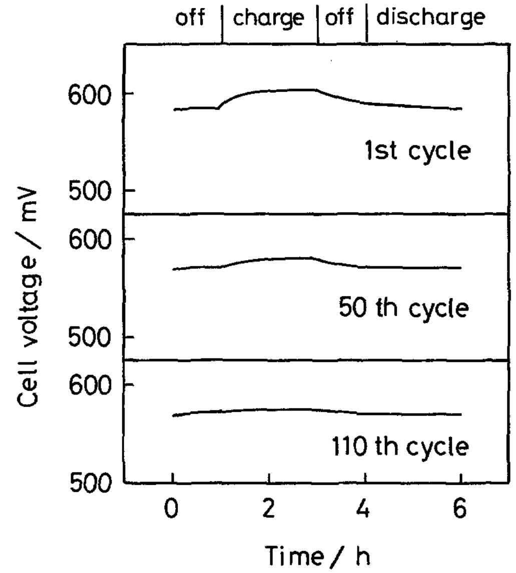

Fig. 6. Charge–discharge cycles at 10 μA and at room temperature of cell 2.

Cu_xTiS_2 $(0.7 < x < 1)$ at the electrolyte–electrode interface. The cathode utilization was 18% with a discharge period of 90 h. Therefore, the formation of Cu_xTiS_2 $(0.7 < x < 1)$ may be due to low diffusivity of copper in the reaction product. The cathode and anode polarization curves at higher current intensity such as 1 mA showed a predominant anode polarization. The anode potentials increased rapidly after discharging for a period of two hours. On the other hand, the cathode potentials gradually decreased from 0.58 to 0.44 V during that period.

The constant load discharge curves at room temperature for cell 2 are shown in Fig. 5. The anode capacity of these cells was 168 mAh, and the cathode capacity was 48 mAh. In the case of the 21.5 KΩ load the average current was 23 μA (18 μA cm^{-2}) and the capacity was 8.3 mAh to the cut-off voltage of 0.4 V. The cathode efficiency was 17%. In the case of the 100 kΩ load, the average current was 5 μA (3.8 μA cm^{-2}), the capacity was 9.5 mAh to the cut-off voltage of 0.4 V, and the cathode efficiency was 20%. The energy density of the cell calculated from the total weight (2 g) of the anode, cathode, and electrolyte was about 2.5 Whkg^{-1}, the value of which is comparable to the solid silver compound electrolyte cells reported previously [1].

The rechargeability of cell 2 has been examined. Typical charge–discharge curves of cell 2 are shown in Fig. 6, where charge and discharge currents are 10 μA (7.7 μA cm^{-2}). The depth of discharge (the ratio of coulombs of discharge to the cathode capacity) was 0.04%. Since the current consumption of a typical modern watch is 2–3 μA, the depth of discharge (20 μAh) will be equivalent to a half-day discharge. As shown in Fig. 6, the cell may be submitted to more than one hundred charge–discharge cycles without showing appreciable deterioration. The charge–discharge curves of the 1st cycle and 50th cycle show a slightly different performance, but those of the 50th cycle and the 110th cycle are exactly the same. At higher current density such as 100 μA cm^{-2}, the cell 2 had a poor cycling capability; the cell sustained only 100 cycles at 200 μAh before showing detectable breakdown. The solid state rechargeable cells with the copper ion conductor, Cu anode, and TiS_2 cathode reported by Lazzari *et al.* [2] sustained 25 cycles before showing detectable breakdown at the current density of 160 μA cm^{-2} for a period of 2 h. More recently, Takahashi *et al.* [12] reported the charge–discharge performance of the cell $Cu|Rb_4Cu_{16}I_7Cl_{13}|Cu_{1.75}Se$, the open-circuit voltage of which was 0.26 V at 25° C. The cell showed that the potential decreased gradually with repeating cycles at 100 μA cm^{-2}. The poor rechargeability of the solid electrolyte cells with the copper ion conductors, especially at a high current drain, may be due to a poor reversibility of the copper electrode, which was pointed out by Armstrong *et al.* [13]. To obtain a rechargeable cell at a higher current density, the anode must be improved and it is in progress in our laboratory.

4. Conclusion

The solid electrolyte cell with a titanium disulphide cathode and a copper ion conductor, $Rb_4Cu_{16}I_7Cl_{13}$, was capable of achieving a current density in the range of several tens of microamperes at room temperature and has the significant advantage of good rechargeability. This type of cell may have an application as a practical recyclable power source, because solid state cells have the advantage of a long shelf-life and no leakage.

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