Rechargeable Solid Electrolyte Cells with Copper Ion Conductor and Vanadium-Tungsten Complex Oxide

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A rechargeable solid electrolyte cell has been developed using a high copper ion conductor, $\text{Rb}_4\text{Cu}_{16}\text{I}_7\text{Cl}_{13}$, a copper anode, and a vanadium-tungsten complex oxide cathode, $(\text{WV}_2)_2\text{O}_{15}$. The open circuit voltage was 0.57 V at 25°C. Ten microamperes were gained from the cell at ambient temperature without appreciable polarization. The charge-discharge performance was good, and the cell voltage was held at a level higher than 0.50 V during 500 or more cycles. The fine rechargeability of the cell was attributed to the use of the complex oxide with Wadsley-Roth type open structure.

1 INTRODUCTION

Considerable interest has been attracted in the field of rechargeable cells which are useful for driving electronic devices working at very low current density. Among them, solid electrolyte cell systems are promising for such devices because they have long shelf-life stability and have no problem of leakage after prolonged storage at ambient temperature. Studies of practical solid electrolyte cells were begun in 1950's. In the age, AgI was exclusively used for the solid electrolyte, and S and I_2 were employed as cathode materials so as to form a single shot battery or long life battery ^{1,2}). Afterward, the performance of cells with various silver ion conductors was examined using cathode materials such as I_2 and MeNI_5 ³⁻⁵).

Studies on solid electrolyte cells other than silver cells are also prosperous. Intense attention has been paid to solid state lithium batteries. A cell with LiI was practically developed for the power source of heart pace-maker, in which a charge transfer complex acted as the best

cathode⁶). A composite lithium ion conductor in the $\text{LiI-Al}_2\text{O}_3$ system was reported as the electrolyte of a lithium cell with mixture cathode of PbI_2 , PbS , and $\text{Pb}^{7)}$. MnO_2 and TiS_2 were shown to act as the excellent cathode materials of all solid state or solid thin film secondary lithium cell ^{8,9}). Recently, various secondary lithium cells with solid polymer electrolytes (SPE) have been reported extensively ¹⁰⁻¹⁵). However, the performance of the cells is not always so good at ambient temperature, since ionic conductivities of SPE are not yet so high as those of electrolyte solutions.

One excellent solid electrolyte of the highest ionic conductivity at room temperature was found in the RbCl-CuI-CuCl system ¹⁶⁻¹⁹). Several rechargeable cells with the copper ion conductor were developed by using cathode materials such as transition metal chalcogenides and copper Chevrel phase ²⁰⁻²²). Quite recently, ionic conductor sheets were made with the aid of organic binder and synthetic fiber to expand the application of the solid electrolyte ²³), and the rechargeable battery was reported using the paper form solid electrolyte and copper Chevrel electrodes ²⁴). We have been searching transition metal compounds for the cathode materials in order to develop all-solid-state cells and have found some good oxides MnO_2 , V_2O_5 , and

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WO₃^{25,26}). These compounds, however, did not show the characteristics suitable for secondary cells. In the recent paper ²⁷), we have developed a cell with V₆O₁₃ and have shown that the oxide containing crystallographic cavity is a possible cathode material for rechargeable copper cells.

We are able to expect that the cavity concentration in vanadium oxides may be changed by substituting elements with higher valency for vanadium. The class of compounds known as Wadsley-Roth phases affords many chemically similar compounds with different types and amounts of crystallographic shear ²⁸). We have examined complex oxides in the V-Cr-O, V-Mo-O, and V-W-O systems as cathode active materials. The complex oxide containing chromium is troublesome for preparation and poisonous, while the complex oxide with molybdenum showed the cathode behavior somewhat lower than that of the complex oxide with tungsten. This paper describes the possibility of the vanadium-tungsten complex oxide for the rechargeable copper cell.

2 EXPERIMENTAL

2.1 Preparation of solid electrolyte

The copper ion conductor, Rb₄Cu₁₆I₇Cl₁₃, was prepared by the method reported by Takahashi et al ¹⁷). The appropriate amounts of RbCl, CuI, and CuCl were ground and mixed by using a planet-type ball mill. After removing toluene used as dispersing reagent, the powder was pressed under a pressure of 300 MPa to form sample pellets which were heated at 200°C in an evacuated Pyrex tube and annealed at 130°C.

2.2 Anode and cathode materials

The anode active material was copper powder which was purified in flowing hydrogen gas at 150°C. The powder was mixed with the solid electrolyte (1:1 in weight) immediately before assembling cells.

Vanadium-tungsten oxides were prepared in the following manner. Commercial grade V₂O₅ and WO₃ were weighed in mole ratios 1:2, 1:1, and 2:1. After mixing the powders in ball mill, pellets were formed under 200 MPa and heated at

650°C for 24 h. The products were identified by powder X-ray diffraction. The complex oxides were mixed with the solid electrolyte and graphite powder (IC sample) in the same procedure as in the previous paper ²⁵).

2.3 Galvanic cells

Solid state galvanic cells (13 mm diam and 3 mm thick) were formed by the same way as in the early study ²⁹). The electromotive force (e.m.f.) and the polarization were measured in a usual manner. The constant load and constant current discharge behavior was examined to evaluate the performance of the test cells at ambient temperature. The charge-discharge cycling tests were carried out at a current of 10 μ A.

3 RESULTS AND DISCUSSION

3.1 Apparent polarization behavior

The polarization behavior was obtained for cells with three complex oxides, (WV)₂O₁₀, (WV₂)₂O₁₅, and (WV₄)₂O₂₅. Figure 1, A shows the polarization curve of the cell with (WV₂)₂O₁₅. The curves of the cells with two other oxides were closely similar to the curve shown in Fig. 1, A and independent of the composition of the complex oxides. The cell voltages plotted in the figure were measured immediately after passing current which was held at each level for 30 s and was stepwise increased. Strictly speaking, observed cell voltages were not equilibrium values except for the value of e.m.f. 0.57 V at 25°C. Therefore, the polarization curve must be regarded as an apparent polarization curve of the cell. Such an experimental procedure is, however, quite convenient for instant evaluation of cathode materials and/or the composition of the cathode mixture ²⁵). The apparent polarization performance in this study was superior to that of the cells containing binary metal oxides such as MnO₂, V₂O₅, and V₆O₁₃ ^{25,27}). Thus, the complex oxide (WV₂)₂O₁₅ was exclusively used as the cathode active material in the following experiments.

Figure 1, B indicates the curve measured after 24 h of the first apparent polarization test (Fig. 1, A). It is clear that profiles of the two

curves are very similar with each other although the voltage at the second operation is fairly low. The fact that the starting voltage of the curve B was lower than that of the curve A suggests that copper ions migrated deeply into the cathode active material at the first operation could not always easily return from the cathode to the electrolyte if the inverse voltage was not applied. On the other hand, the similarity of the shape of both curves suggests that the complex oxide at the starting point of the second operation had the capacity to accommodate copper ions further.

Fig. 1 Apparent polarization behavior of the cell with complex oxide $(WV_2)_2O_{15}$ at ambient temperature.

- A: curve obtained at the first polarization test
B: curve obtained at the second test after 24 h of the first test

3.2 Constant load and constant current discharges

The constant load discharge test was performed by using four loads 1, 10, 20, and 50 k Ω . Table 1 shows several data which were obtained at the cut-off voltage 0.52 V. The average current was calculated from the midpoint value of both initial and cut-off voltages and the corresponding load, ignoring the cell own resistance. The discharge result at 50 k Ω suggested that the discharge capacity of about 2 mAh was possible at the current of about 10 μ A. The efficiencies of both electrodes were obtained on the basis of the capacities estimated from the active material weights and the following reaction

(84 mAh for anode and 6.6 mAh for cathode). The cathode efficiency of about 30% could be taken at 50 k Ω load.

Table 1 Constant load discharge performance of the cell with the complex oxide $(WV_2)_2O_{15}$ at ambient temperature.

Load /k Ω	Average current / μ A	Discharge capacity / μ Ah	Anode efficiency /%	Cathode efficiency /%
1	539	135	0.16	2.05
10	54.4	326	0.39	4.94
20	26.9	1740	2.07	26.4
50	10.9	1960	2.34	29.7

Table 2 Constant current discharge performance of the cell with the complex oxide $(WV_2)_2O_{15}$.

Current / μ A	Discharge capacity / μ Ah	Anode efficiency /%	Cathode efficiency /%
10	1000	1.2	15
50	100	0.12	1.5
100	47	0.056	0.71
300	43	0.051	0.65
500	30	0.036	0.45

Fig. 2 Constant current discharge performance of the cell with $(WV_2)_2O_{15}$.

The constant current discharges were carried out at 10, 50, 100, 300, and 500 μ A/cell. The performance of the cell is shown in Fig. 2. It can be seen from the figure that the cell is available for low current discharge. The discharge capacity and the electrode utilization efficiencies are listed in Table 2. The discharge capacity at 10 μ A was 1 mAh which was nearly half of the value obtained at the constant load of 50 k Ω (Table 1). This discrepancy seems to be due to the fact that the cell own resistance was ignored at the average current estimation in the constant load experiment. The internal resistance of the cell will be investigated in the near future. As the current or discharge reaction rate increased, the

electrode efficiencies decreased. It appears from the fact that in the case of high current discharge the reaction predominantly proceeded at the surface of the electrode active materials. Considering that in this work thick tablets for both electrodes were evaluated in order to handle them with ease, the electrode utilization efficiencies will be considerably raised if thin electrode tablets are used.

3.3 Charge-discharge behavior

As mentioned above, the apparent polarization performance of the cell with $(WV_2)_2O_{15}$ was better than that of the cells reported in the previous papers ^{25,27}. Because the oxide, V_6O_{13} , is a promising cathode material for rechargeable cell, the complex oxide $(WV_2)_2O_{15}$ will also have the possibility for the candidate of the cyclable cathode material. Thus, the charge-discharge cycling test was done concerning the cell used for the first apparent polarization experiment. The current passed to the cell was 10 μA /cell and the duration of each charge and discharge was 30 min. The cycling was simply carried out without rest. The cell voltage gradually increased from 0.30 V and reached the initial e.m.f. value of the cell after the cycle number of 50. Then, the discharge end voltage decreased very slowly as the cycling was continued. This result suggested the availability of the complex oxide.

Another cycling test was performed using a virgin cell under the same conditions as in the case mentioned above. Figure 3 shows the representative charge-discharge cycling curves. The form of the curve changed little by little with increase of cycling number. Although the result

Fig. 3 Representative charge-discharge curves in the course of cycling at 10 μA /cell.

Fig. 4 Discharge end voltage curve illustrating the charge-discharge cycling performance of the cell.

suggested gradual deterioration of the cell, the cell voltage decreased very slowly. The profile of the cell voltage change is shown in Fig. 4. The discharge end voltage was higher than 0.50 V even after 500 cycles. Such a cycling performance was the best of all the performance of the cells prepared using oxides.

Since both the anode and the solid electrolyte were the same as those used for the previous cells ^{26,27}, the improvement of the cell performance seems to be owing to the use of the complex oxide, $(WV_2)_2O_{15}$, as the cathode active material. The vanadium-tungsten complex oxide takes the Wadsley-Roth phase ²⁸. Figure 5 displays idealized structure of the complex oxide. The basic structural units of the phase are blocks consisted of distorted MO_6 octahedra sharing corners, which are joined to adjacent blocks either through edge sharing or a combination of edge sharing and

Fig. 5 Idealized crystal structure of the vanadium-tungsten complex oxide $(WV_2)_2O_{15}$ ²⁸.

tetrahedrally coordinated metal atoms at the block corners. Such structures generally show open tunnel like regions bound by regions of extensive edge sharing³⁰. In this study, copper ions may be able to easily enter from the electrolyte to the complex oxide through the open tunnel, and on the contrary, copper ions at the charging operation may return with ease from the oxide to the electrolyte by way of the tunnel. The decay curves shown in Fig. 3 include IR drop and other overvoltages. Detailed analyses of the curves were not carried out in this study.

4 CONCLUSION

Vanadium-tungsten complex oxides, $(WV)_2O_{10}$, $(WV)_2O_{15}$, and $(WV)_4O_{25}$, were prepared and were used as the cathode active materials in the cells $Cu, X/X/V-W-O, X, C$, where X was copper ion conductor $Rb_4Cu_{16}I_7Cl_{13}$ and C was graphite. The three oxides showed almost the same cathode behavior in apparent polarization curves.

Both constant load and constant current discharges using the complex oxide $(WV)_2O_{15}$ indicated the cell capacity of about 1 mAh at a current of 10 μA /cell without significant drop of the working voltage. Although the cathode utilization efficiency calculated from the amount of the complex oxide was low, i.e. about 15% at 10 μA discharge, this value will be raised by making thinner cathode layer. The cycling performance was the best of all the cells with oxide cathodes so far examined, and the cell voltage was kept higher than 0.50 V even after 500 cycles. Such high performance seems to originate in the cathode improvement by using the complex oxide with open tunnel structure.

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