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Solid electrolyte cells with a copper ion conductor $Rb_4Cu_{16}I_7Cl_{13}$. IV. Mixed-phase cathodes containing metal oxides

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Solid electrolyte cells Cu, X/X/(MO, C, X), have been investigated (X; $Rb_4Cu_{16}I_7Cl_{13}$, MO; metal oxide, and C; graphite). An electrolytic manganese dioxide was used as a model oxide for preparing three types of cathode: (1) only MO, (2) a mixture of MO and C, and (3) a mixture of MO, C and X. Cell performances depended not only on the composition of the mixed-phase cathode, but also on the uniformity of the mixture of the materials. Several cells with metal oxides such as MnO_2, V_2O_5, and WO_3, showed high and stable electromotive forces of 0.546–0.575 V and good discharge behaviour at room temperature.

1. Introduction

Solid electrolytes have attracted considerable interest recently because of the possibility of fabricating solid-state galvanic cells which offer solutions to several problems encountered with aqueous systems such as corrosion of materials, leakage of liquid and limited temperature range. Low-rate, small-size power sources have been developed using solid electrolytes for use in electronic watches, pocket calculators, heart pacemakers, memory back-up, etc. However, most of the cells are under trial production.

Recently, good copper ion conduction was found in the RbCl–CuI–CuCl system. The solid electrolytes, $RbCu_4Cl_3(I_{2-x}Cl_x)$ [1] and $Rb_4Cu_{16}I_{7-x}Cl_{13+x}$ [2], show very high ionic conductivity ($0.34\,S\,cm^{-1}$) at room temperature, which is the highest value in ambient-type solid ionic conductors.

The present authors have been fabricating galvanic cells using a copper ion conductor. Primarily, cells were fabricated with metallic copper as the anode active material and copper selenides as the cathode active materials [3, 4]. Electromotive forces (emfs) were very low, e.g. 0.268 and 0.385 V. In the second place, we looked for cells with high and stable emfs. Cells with Cu_xTiS_2 ($0.3 \leqslant x \leqslant 0.5$) for the cathodes were found to have emfs of 0.5–0.6 V and to show slight reduction of the emf values over 200 days, the cause of which seemed to be slow degradation of the cathode materials [5].

A series of studies on solid electrolyte cells has been projected for producing cells with high reliability over long periods [6]. In this study, metal oxides (especially electrolytic manganese dioxide) were chosen for the cathode active materials. To determine fundamental factors, mixed-phase cathodes, consisting of a metal oxide and other materials were examined in relation to the cell performance.

2. Experimental details

The solid electrolyte, $Rb_4Cu_{16}I_7Cl_{13}$, was prepared by the same procedure as reported in an earlier paper [2]. Chemicals, RbCl, CuI and CuCl, were purified and dried, and appropriate amounts of them were ground together. Tablets were formed by pressing the mixed powders at 300 MPa, heated at 200° C in an evacuated glass tube and annealed at 130° C. The electrolytic manganese dioxide (EMD), used as a representative metal oxide, was an international common sample, I.C. No. 3 EMD. Other metal oxides such as V_2O_5 and WO_3 were commercial grade powders and used without further purification. An international common sample of graphite powder, ICC, was used as an auxiliary conductive agent.

Galvanic cells Cu, X/X/(MO, C, X)(I) were made up where X is $Rb_4Cu_{16}I_7Cl_{13}$, MO is the metal oxide and C is ICC. The anode of the cell was a mixture of 0.1 g of copper powder and 0.1 g of the electrolyte. The anode and the electrolyte layers were pressed at 400 MPa to form a tablet 13 mm in diameter. The cathode of the cell was a mixture of MO, C, and X, the composition of which was varied. The electrolyte and the cathode layers were pressed in a similar manner as the anode. Two tablets thus obtained were combined, and leads were fitted on both electrodes. Finally, the cell was sealed with polyester resin.

Polarization was measured by passing certain discharge currents using a power supply. Cells were held at each current level for 30 s. To analyse the mixed-phase cathodes, distributions of grain sizes of both the EMD and the ICC were examined and profiles by

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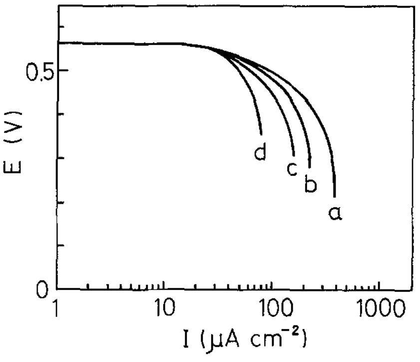

Fig. 1. Polarization curves of the cells Cu, X/X/EMD, C. Contents of C in the cathodes are (a) 22.5 wt %, (b) 20.0 wt %, (c) 25.1 wt % and (d) 9.9 wt %.

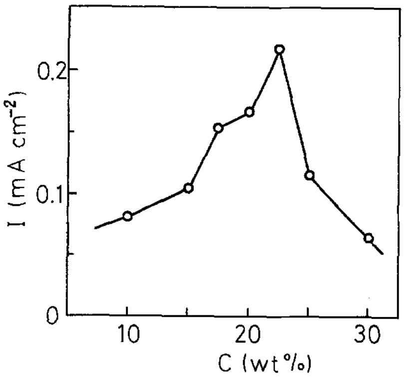

Fig. 3. The current densities read from Fig. 1 by the procedure shown in Fig. 2.

scanning electron microscope (SEM) and electron probe microanalyser (EPMA) were taken for a cross-section of the cathode.

3. Results and Discussion

3.1. *Three types of cathode*

The EMD as a model oxide was used for a cathode active material. The emf of the cell I was 0.575 V which could be observed even in cells without the graphite and/or the electrolyte. This fact suggested that the reaction between copper and manganese dioxide was as follows:

anode reaction

$$x\mathrm{Cu} \longrightarrow x\mathrm{Cu}^{+} + xe^{-}$$

cathode reaction

$$\mathrm{MnO_2} + x\mathrm{Cu}^{+} + xe^{-} \longrightarrow \mathrm{Cu}_x\mathrm{MnO_2}$$

total reaction

$$x\mathrm{Cu} + \mathrm{MnO_2} \longrightarrow \mathrm{Cu}_x\mathrm{MnO_2}.$$

Polarization behaviour of cell I was examined for three types of cathode: (1) only EMD; (2) a mixture of EMD and C, and (3) a mixture of EMD, C, and X.

In the first case, the polarization was marked. The discharge current was 0.04 mA cm^{-2} at a cell voltage of 0.4 V. This low performance resulted mainly from cathode polarization, since anode polarization was not significant, as shown in a previous paper [3]. The EMD seemed to have active sites for intercalation of copper ion. However, the resistance of the EMD to migration of both electron and copper ion is probably high. Therefore, the resistance- and diffusion-polarizations of the homogeneous cathode are dominant in the total polarization. In addition, concentration-polarization resulting from insufficient supply of copper ion to the bulk of the cathode would be considerable, since copper ion was supplied only at the electrolyte/EMD interface.

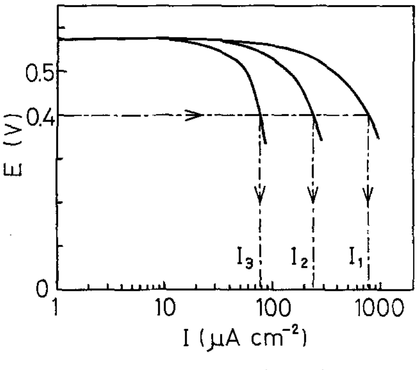

Fig. 2. A schematic diagram for estimating polarization curves. The current densities can be read at the cell voltage of 0.4 V.

In the second case, to decrease the electronic resistance mentioned above, some cathodes were composed of mixtures of the EMD and the graphite. Fig. 1 shows representative polarization curves of the cells. Polarization behaviour was found to depend on the graphite content. To evaluate the characteristics of the cells from the polarization curves, currents were read at a cell voltage of 0.4 V which corresponds to about 70% of the emf. A schematic diagram is shown in Fig. 2 where the order of the current, $I_1 > I_2 > I_3$, indicates the superior order of the polarization behaviour of the cells concerned.

Fig. 3 shows the currents thus obtained. The current gradually increased with increase of the graphite content up to 22.5 wt % and decreased with additional graphite. The maximum current is more than five times the current of the cathode with only EMD. This result confirms that the addition of graphite to the EMD is effective in decreasing the electronic resistance of the cathode.

Thirdly, various amounts of the solid electrolyte were added to the mixture of the EMD and the graphite mentioned above. In this procedure, both amounts of 0.2 g of the EMD and 0.058 g of the graphite were kept constant. Fig. 4 shows polarization curves of the cells. The polarization characteristics have been clearly improved by the addition of the electrolyte. The currents at 0.4 V were read in the same way as in the previous case and were plotted against the electrolyte content as shown in Fig. 5.

The maximum current, or the best polarization behaviour, was obtained at a composition of

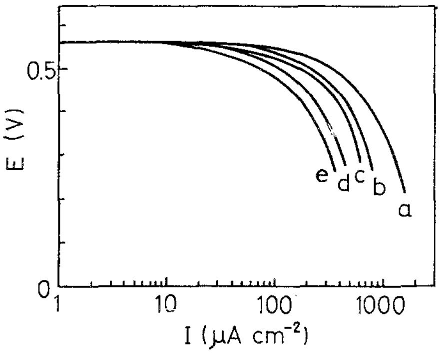

Fig. 4. Polarization curves of the cells Cu, X/X/EMD, C, X. Contents of X in the cathodes are (a) 43.7 wt %, (b) 53.8 wt %, (c) 60.8 wt %, (d) 66.0 wt % and (e) 27.9 wt %.

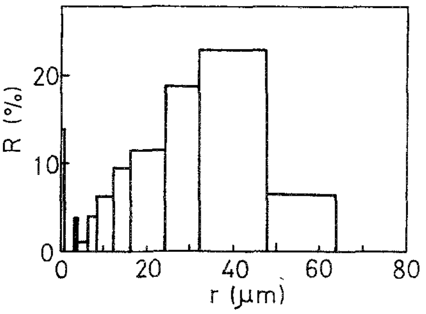

Fig. 6. Grain size distribution of the EMD after grinding.

43.7 wt % of electrolyte. The contents of the EMD and the graphite were 43.7 wt % and 12.6 wt % respectively. The existence of the electrolyte might contribute to lowering the concentration-polarization resulting from copper ion migration to the surface of the EMD and/or decrease the ionic resistance of the mixed-phase cathode. To evaluate polarization phenomena in more detail an appropriate reference electrode must be used, and iR-free data should be obtained. Further polarization studies will be reported later.

3.2. *Grain size and its distribution in the cathode mixture*

As shown above, the performance of the cell varied with the change in the composition of the cathode mixture. In addition to the composition, the grain size and the grain size distribution of the component materials were found to affect the cell performance.

The polarization curve shown in Fig. 4a represents that of the cathode with the best performance of all cathodes with the EMD, graphite, and the electrolyte. Before fabrication of the best cathode, both the as-received EMD and graphite were individually ground with the aid of an agate mortar and pestle. Figs 6 and 7 show grain size distributions of the pre-ground EMD and graphite powders respectively. The grain size of the EMD was distributed in a range smaller than 64 μm and the average grain size was 23.3 μm.

The grain size of the graphite was widely distributed and the average grain size was 18.8 μm, whereas, the solid electrolyte used here could be easily crushed into finer powder than the EMD and the graphite. These pre-ground materials were mixed to prepare the cathode powder using an agate mortar and pestle.

To obtain information about the mixed-phase powder, SEM photographs and EPMA images were taken. Fig. 8 shows an SEM image and EPMA profiles of the cathode mixture giving the data shown in Fig. 4a. The SEM image (Fig. 8a) indicates both isolated and aggregated grains. In the EPMA profiles (Figs. 8b, c and d), the mass of white dots indicates the existence of the element concerned. It can be seen from these profiles that carbon threw its shadow over the copper image, whereas manganese cast its shadow on the carbon image. The profiles show the following:

(i) Three materials, the EMD, graphite and the electrolyte were well mixed and distributed in good mutual contact.

(ii) The components were not homogeneously distributed over the cathode, but both graphite and the electrolyte individually had a continuous phase.

These facts suggest that the mixed-phase cathode mentioned above has a large contact area and a low charge-transfer impedance for the cathode reaction, since the performance of a cathode depends both on the magnitude of the operative contact area between the ionic and electronic conducting phases and on the charge-transfer impedance of the electrode reaction.

The cells composed of roughly ground powders of the EMD and graphite showed polarization behaviour

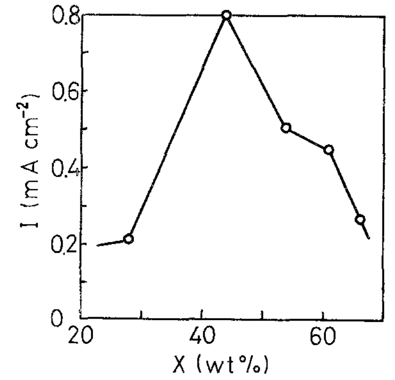

Fig. 5. Current densities read from Fig. 4.

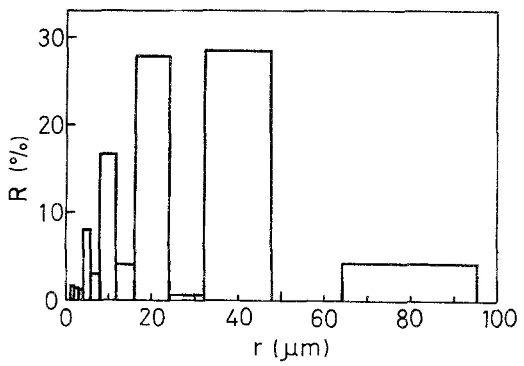

Fig. 7. Grain size distribution of C after grinding.

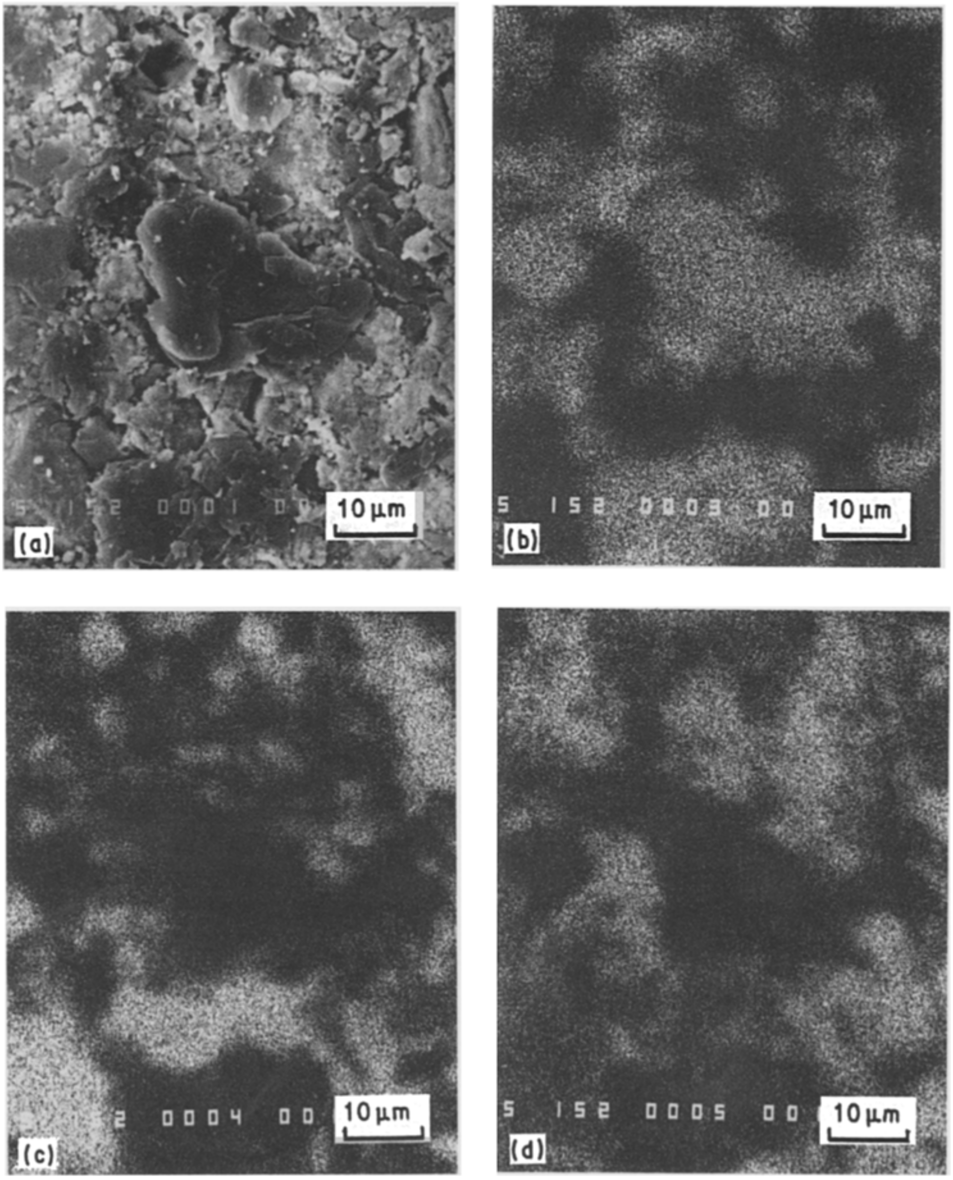

Fig. 8. Profiles of a cross-section of the mixed-phase cathode. (a) SEM picture taken at magnification of 1500. EPMA area profiles of (b) carbon, (c) manganese and (d) copper.

inferior to the polarization shown in Fig. 4. Namely, the discharge current at the cell voltage 0.4 V was lower than 0.1 mA cm^{-2}. The roughly ground EMD has plate-like shape resulting from the preparation method and the graphite has a flaky form originating from the crystal structure. The average grain size of the EMD was 35.7 μm and that of the graphite was 19.6 μm. The worst polarization behaviour seemed to be caused by the incomplete mixing of the materials due to their shapes and sizes.

The cells with finely ground cathode materials also gave lower performance than that shown in Fig. 4. The current, at a cell voltage 0.4 V, was smaller than 0.1 mA cm^{-2}. In the mixing of the cathode materials, a ball-mill was used, together with toluene or acetone, as the dispersion reagent. Although the average grain sizes of the three components were smaller than 10 μm and the mixing appeared to be satisfactory, the performance was lower than that of the best cell shown in Fig. 4a. The reason why the polarization of the cell with the well-mixed cathode was high could not be analysed in this work.

Nairn *et al.* reported on the mixed-phase electrodes of solid state cells [7]. They used solid solution materials such as transition metal dichalcogenides and mixed the solid solution material with a solid electrolyte. According to their chronopotentiometric analysis for the mixed-phase region under the influence of a short galvanostatic pulse, for designing the best mixed-phase electrode it is necessary to balance the attainment of a large contact area among the component particles (to reduce the reaction impedance) with that for a minimum thickness and tortuosity of conducting pathways (to reduce the electrolyte resistance).

In the present study, the mixed-phase cathode with the roughly ground materials consisted of unsatisfactorily mixed grains, whereas the mixed-phase cathode with the finely ground grains may have a large contact area. In any case, it is clear from our experimental results that the control of both the size and its distri-

*Table 1. Electromotive forces of cells Cu, X/X/MO, C, X**

MO	*emf (V)*	*MO*	*emf (V)*
MnO_2	0.575	Ta_2O_5	0.520
V_2O_5	0.560	NiO	0.518
In_2O_3	0.558	Co_2O_3	0.516
Fe_2O_3	0.549	Cr_2O_3	0.505
MoO_3	0.547	Sb_2O_3	0.494
WO_3	0.546	SnO_2	0.459
TiO_2	0.535	Bi_2O_3	0.415
Nb_2O_5	0.529	SnO	0.300
Fe_3O_4	0.523	ZnO	0.284

* X: $Rb_4Cu_{16}I_7Cl_{13}$, MO: metal oxide

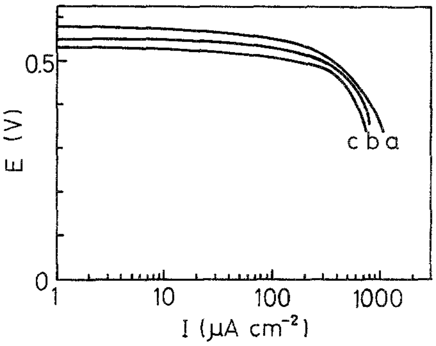

Fig. 9. Polarization curves of the cells Cu, X/X/MO, C, X. MO is (a) MnO_2, (b) V_2O_5 and (c) WO_3.

bution of the powders used for the cathode materials is very important in improving the performance of the mixed-phase cathode.

3.3. *Cells with metal oxides other than EMD*

On the basis of the information obtained from cells containing the EMD, various solid electrolyte cells were fabricated with mixed-phase cathodes using metal oxides other than the EMD. Table 1 summarizes the emfs of the cells at room temperature. Several cells containing transition metal oxides show emfs higher than 0.5 V. The emfs obtained in this study are seen to be higher than values obtained in cells with metal chalcogenides [3, 4].

Cells with high emfs do not always give good performance. Most of the cells gave considerable polarization even at low current densities. Fig. 9 shows representative polarization curves. The high emf values and low polarizations suggest the possibility of developing practical cells with high performance. Constant current and constant load discharges, stability of the emf and charge–discharge cycles should be examined for such solid electrolyte cells. This study on improved cells is in progress.

4. Summary

Solid electrolyte cells were investigated using a good copper ion conductor $Rb_4Cu_{16}I_7Cl_{13}$, a mixed-phase anode and mixed-phase cathodes. Three kinds of typical cathodes were prepared by the use of EMD as a model oxide, and the compositions and the uniformity of the mixed-phase cathode were examined. Several cells with metal oxides, such as manganese dioxide, were found to show comparatively high emfs of 0.546–0.575 V and good performance at room temperature.

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