Preparation and electrical conductivity of thin films of $Rb_4Cu_{16}I_7Cl_{13}$

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A thin film of the copper ion conductor $Rb_4Cu_{16}I_7Cl_{13}$ was prepared on a glass plate by vacuum evaporation. An appropriate thin film was obtained by controlling the amount of the electrolyte mounted in a boat, the evaporation time etc. and by heating the deposited film at a temperature between 130 and $210°$ C. The electronic and ionic conductivities of the film measured by d.c. and a.c. techniques were nearly equal to those of a dense tablet of the solid electrolyte.

1. Introduction

Solid electrolytes with high ionic conductivity are interesting because of their application in power sources and other electrochemical devices. Since the devices are fabricated entirely from solid-state materials, they can be miniaturized with no anxiety about electrolyte leakage. Use of thin films of electrolyte are sufficient in many of the applications, such as as electrolyte for solid-state cells [1, 2] and as the source or sink of atoms for electrochromic devices [3–5]. These films have been prepared by chemical reactions [1, 2], vacuum evaporation [3, 4] or by slicing an ingot of solid electrolyte [5].

Recently, a new copper ion conductor has been found in the system CuCl–CuI–RbCl [6, 7], which is characterized by high conductivity and stability at room temperature; it also has the advantage of low cost compared with silver ion conductors. One of the authors has reported previously on a cell with a solid electrolyte tablet of copper ion conductor [8]. In the present paper, the conditions for the preparation of thin films of copper ion conductor and the conduction behaviour of the film will be described.

2. Experimental procedure

The evaporation source of copper ion conductor $Rb_4Cu_{16}I_7Cl_{13}$ was prepared by the method described in previous papers [6, 7], and was held in a boat made of copper plate, 0.1 mm thick. A glass plate ($18\,mm \times 18\,mm \times 0.14\,mm$) was cleaned chemically and used as a substrate. A conventional vacuum evaporator (Tokuda Seisakusho Co. Ltd, Model CU-4) was used to deposit the thin film of the conductor at 1×10^{-5} Torr. The thickness of the thin film was controlled by the evaporation conditions, such as the amount of electrolyte present (0.03–0.5 g), the evaporation time (10–60 s) and the temperature of the boat (500–$650°$ C). The evaporated film was annealed in a furnace at various temperatures *in vacuo* for 12 h to stabilize the structure of the electrolyte which had partially decomposed during evaporation. The film thus prepared was examined by X-ray diffraction and scanning electron microscopy (SEM).

The electronic and the ionic conductivity was measured parallel to the surface of the film from room temperature up to $160°$ C under a flow of nitrogen. The electronic conductivity was determined by Wagner's polarization method [9] using the arrangement of the sample and the electrodes shown in Fig. 1. The thin film was deposited onto a copper plate acting as a cathode using a direct current up to $100\,\mu A$. Fig. 2 shows two schematic arrangements for the measurement of ionic conductivity: one is for a d.c. four-probe technique in which a current of $1–60\,\mu A$ was passed from A to B with the voltage being detected between C and D; the other is for an a.c. complex impedance
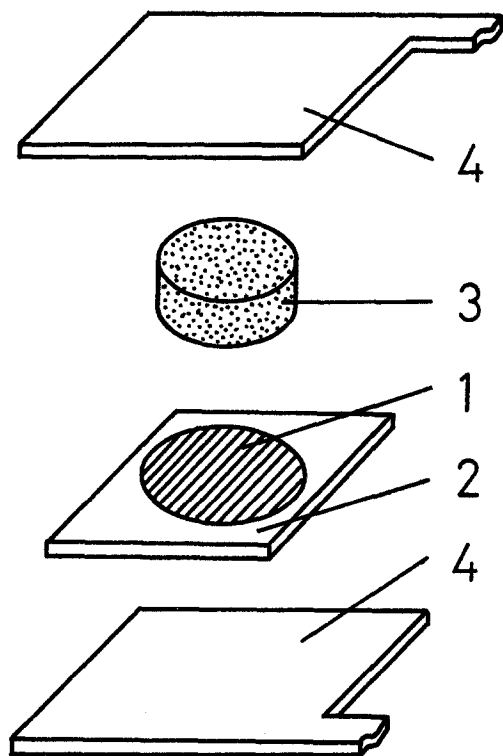
Fig. 1. Arrangement of the evaporated film and the electrode for measurement of electronic conductivity by the polarization method. 1. evaporated film, 2. copper plate, 3. graphite and 4. silver plate.
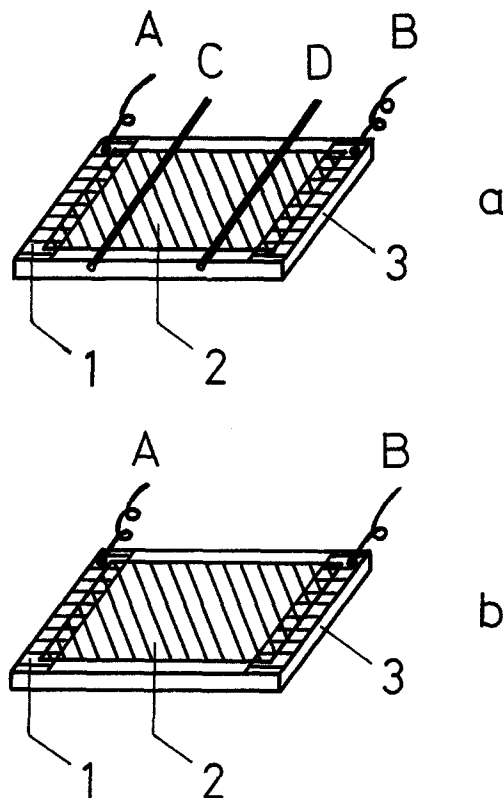

Fig. 2. Schematic diagrams for (a) the d.c. four-probe technique and (b) the a.c. complex impedance technique. 1. evaporated copper electrode, 2. electrolyte film and 3. glass slide.

plot technique in which the frequency was changed in the range 200 Hz to 100 kHz.

3. Results and discussion

3.1. Deposition of the thin film

Fig. 3 shows the X-ray diffraction patterns of typical deposits. As seen in this figure, the as-deposited film exhibits a different pattern from that of the source electrolyte (Fig. 3d). The diffraction peaks of the as-deposited film were ascribed mainly to $Rb_4Cu_{16}I_7Cl_{13}$, but a few peaks to CuI, CuCl or unknown compounds. This suggests that the electrolyte decomposed partially during vacuum evaporation. Therefore, the as-deposited film was heated at various temperatures in order to recover the original structure of the electrolyte. Recombination or recrystallization begins above $70°$ C and the heat treatment at $110°$ C is sufficient to obtain the film with the original structure (Fig. 3b and c).

Samples prepared at a low evaporation rate and with a short separation of the substrates from the boat were thermally treated at two temperatures (Fig. 4). The half-spheres may be formed by bumping of the electrolyte. They tend to be nearly fully spherical due to surface tension effects at high temperatures. Thus, the evaporation conditions were selected so that the partial decomposition and the bumping of the electrolyte were suppressed. The amount of electrolyte in the boat was 0.03–0.05 g, the evaporation time about 20 s, the temperature of the boat $650°$ C and the distance between the boat and the substrate 30 mm.

The typical appearance of the thin films after heat treatment is shown in Fig. 5; the surface is fairly fine, but several small grains can be observed. A large number of tiny domains other than the grains are seen on the surface of the film heated at $130°$ C, and these domains and grains grow uniformly over the whole surface of the thin film heated at $210°$ C. Fig. 6 shows the relationship
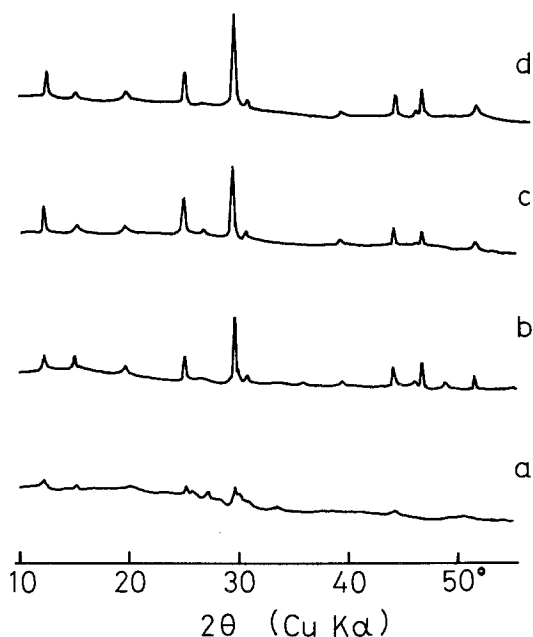
Fig. 3. X-ray diffraction patterns of (a) the as-deposited thin films, (b) heated at 130° C, (c) heated at 210° C and (d) of the dense tablet of the electrolyte.

between the surface appearance and the film thickness. The tiny semi-spherical domains combine with each other to make the planar, larger domains as the thickness of the film increases. Since the thin film has a high surface energy per unit volume, the film tends to decrease its surface area to stabilize itself. Figs. 5 and 6 seem to illustrate this tendency. The evaporated film begins to melt at as low a temperature as 210° C which is much lower than the melting temperature of the dense tablet of $Rb_4Cu_{16}I_7Cl_{13}$ (234° C) [7].
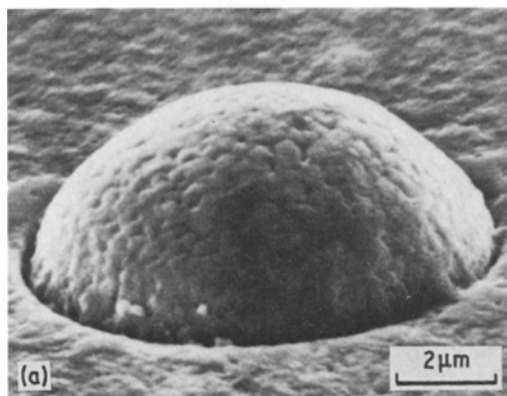
Fig. 7 shows the cross-section of the films after heat treatment. Although the sample heated at 130° C shows a similar structure to that of as-deposited film, the cross-section of the film treated at 210° C is composed of large grains, which are supposed to have melted and/or sintered. The grains are larger nearer the surface than near the interface between the film and substrate glass. This difference in the grain size would arise from a difference in the grain size distribution or in the temperature change with depth.

3.2. Conductivity of the thin film

The electronic and ionic conductivities of the dense tablet of the electrolyte $Rb_4Cu_{16}I_7Cl_{13}$ are of the order of 10^{-12} Scm^{-1} at 60° C and 10^{-1} Scm^{-1} at 25° C, respectively [6, 7]. In order to apply these thin films to any devices, it is important to know whether the thin films deposited onto a glass plate have a similar order of conductivity as those of tablets or not. Fig. 8 shows typical plots of the logarithm of the direct current (I) versus applied cell voltage (E), from which a linear relationship is clearly seen. According to Wagner's theory, the linear relationship between $\log I$ and E means that electronic conduction is not due to excess electrons but to electronic holes [9]. The gradient of the linear lines are less than those calculated by Wagner's theory. When contact between the thin film and the graphite anode is poor, a voltage higher than the theoretical one may be necessary for a certain current to flow. With increasing temperature, such a contact resistance
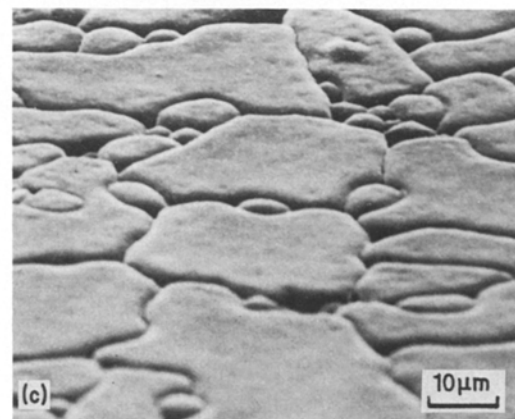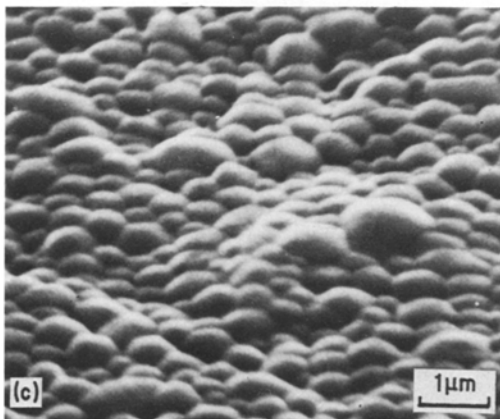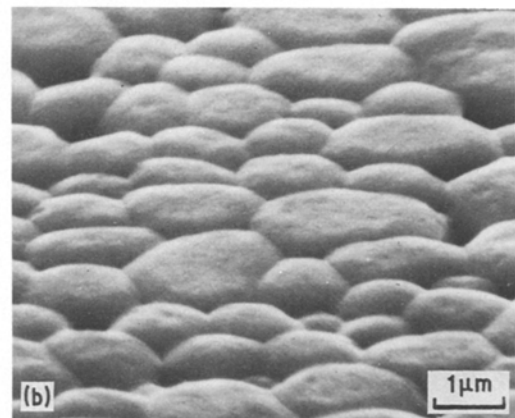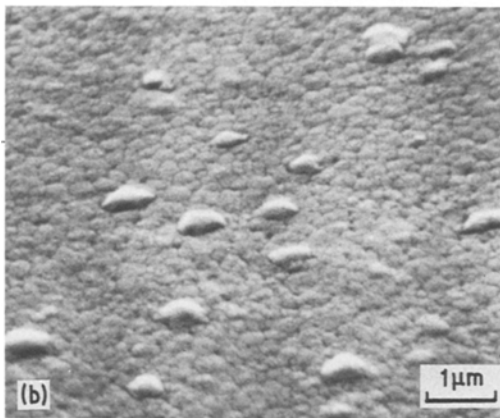

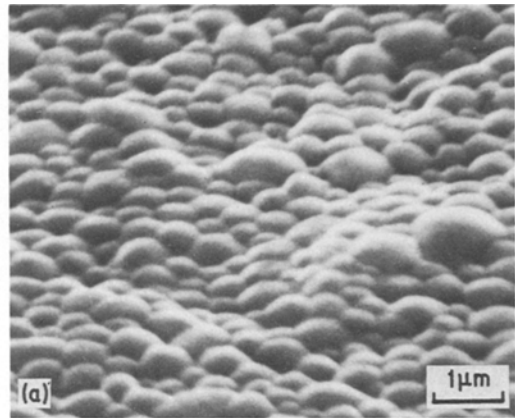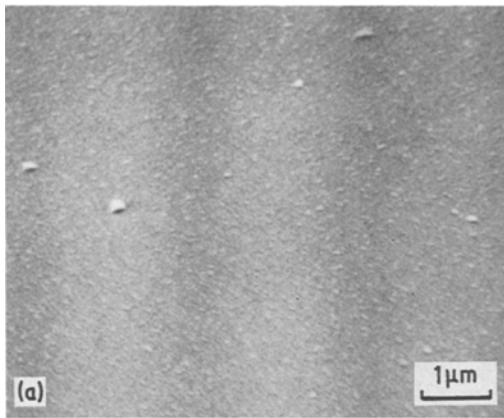Fig. 4. SEM photographs of the evaporated thin films heated at (a) 130° C and (b) 210° C.

Fig. 5. Surface features of the thin films (0.6 μm thick) (a) as-deposited, (b) heated at 130° C and (c) at 210° C.

Fig. 6. Surface features of the thin films heated at 210° C with a thickness of (a) 0.6 μm, (b) 1.3 μm and (c) 4.9 μm.

tends to decrease, and the discrepancy between the experimental and the calculated gradients may increase, in accordance with the above result.

The temperature dependence of the electronic conductivity can be obtained from log I versus E curves as shown in Fig. 9, in which the average thickness over the thin film was used to calculate the conductivity. Deviation from the straight line in the low temperature region may be attributed to the low gradients of the log I versus E curves
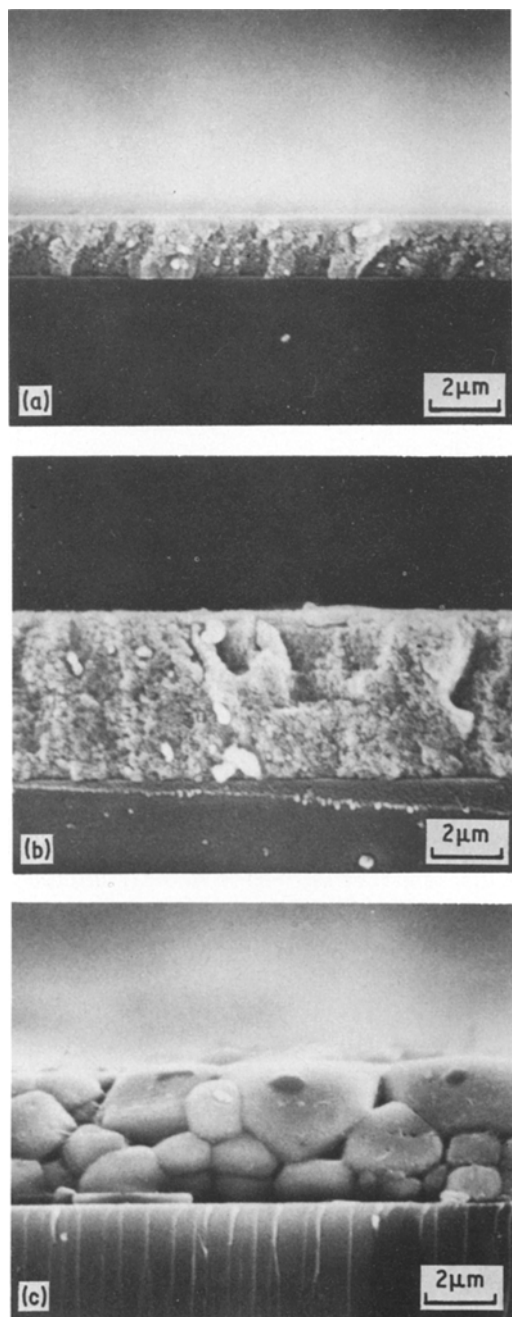
Fig. 7. Cross-sections of the films (a) as-deposited, (b) heated at 130° C and (c) heated at 210° C.

Fig. 8. Logarithm of the d.c. current versus cell voltage curves obtained at (a) 51° C, (b) 69° C, (c) 90° C and (d) 109° C.

at such temperatures. The electronic conductivity of the thin film is of the order of 10^{-13} Scm^{-1} at 60° C, lower than that of the tablet (10^{-12} Scm^{-1}), but these values agree within experimental error considering the microscopic roughness of the surface of the thin film.
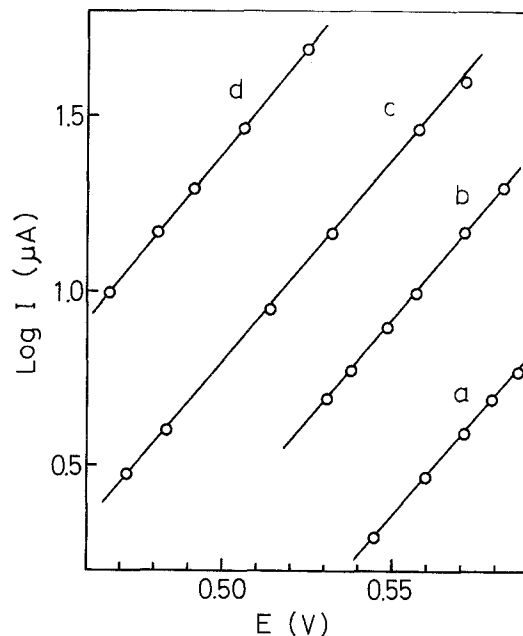
The ionic conductivity obtained by the d.c. four-probe method is shown in Fig. 10 and is 2.9×10^{-1} Scm^{-1} at 25° C, which is comparable with the ionic conductivity of the dense tablet of 3.1×10^{-1} Scm^{-1}. The apparent activation energy for copper ion conduction was estimated from the gradient of the conductivity curve to be 9.2 kJ mol^{-1} compared with 7.0 kJ mol^{-1} for the dense tablet [7]. The discrepancy between these two values for activation energy cannot be explained although it is only small if one considers the great difference of the forms. The resistance of the grain boundary may play a role in the total conductivity of the thin film. The a.c. conductivities of the thin films with different thickness were obtained from the complex impedance plots (Fig. 11). The conductivity curve of the thin film consists of two parts; one is the higher temperature part which has the smaller slope, and the other is the low temperature part which has the larger slope. On the other hand, a thicker film showed an almost linear response over the whole temperature range. The results from a.c. measurements are slightly larger than the ionic conductivity obtained by the d.c. technique, and the averaged activation energy for conduction is calculated to be 8.6 kJ mol^{-1}.
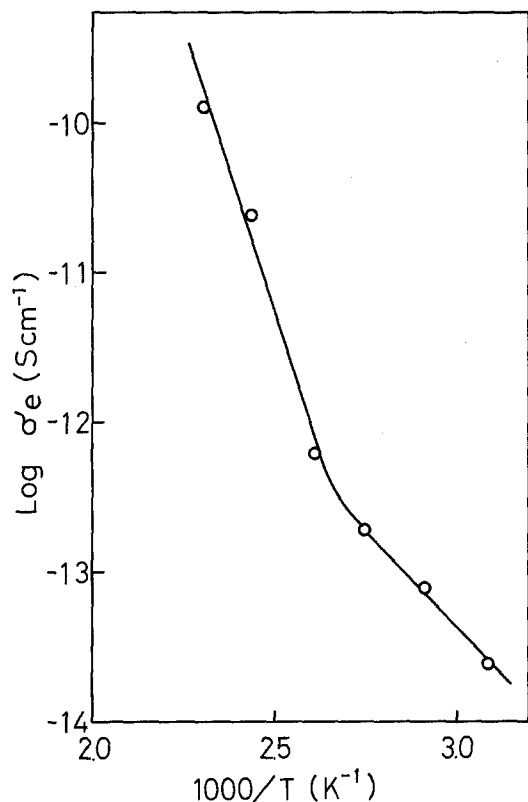
Fig. 9. Electronic conductivity of an evaporated thin film of $Rb_4Cu_{16}I_7Cl_{13}$.

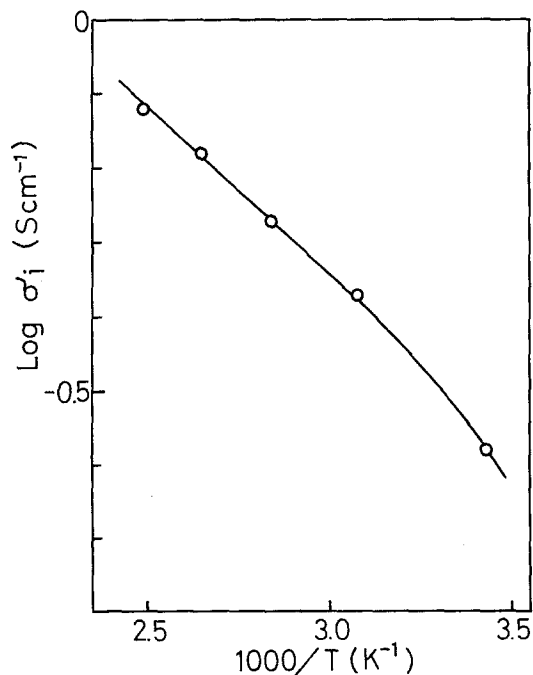Fig. 11. Total conductivities of the thin films with a thickness of 1.3 μm ($\square$), 2.4 μm ($\triangle$) and 5.9 μm ($\circ$) obtained from a.c. complex impedance plots.

Fig. 10. Ionic conductivity of a thin film measured by the d.c. four-probe method.

The inflection in the conductivity curve of the thin film cannot be ascribed to an order–disorder transition or another transition behaviour since the transition temperatures were reported to be -52 and $-103°$ C [6] or $-25°$ C [7]. The thin film consists of tiny semi-spherical domains as seen in Fig. 6a. Therefore, the resistance of the grain boundary may be significant, particularly in the low temperature region, and the activation energy for conduction in the grain boundary would become larger than that of the bulk of the electrolyte. The influence by the grain boundary would decrease with increasing temperature.

The contact between the electrolyte and the electrode must be good since both the electrolyte and the electrode were prepared by evaporation onto a glass substrate. In addition, the rather thick film has the large flat domains as seen in Fig. 6c. These facts support the assumption that the influence of the grain boundary in the thick film will be less than that in the thin film. The linear curve for the conductivity of the thick film can be considered to support this presumption.

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