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# NEW ANIONIC CONDUCTORS: CROWN ETHER COMPLEXES OF ALKALI-METAL IODIDES AND ALKALINE-EARTH METAL IODIDES

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Crown ether complexes of alkali-metal iodides or alkaline-earth metal iodides were found to be a new kind of iodide ion conductors. The more the kind of the component molecules in a complex was, the higher was the ionic conductivity. An iodine concentration cell was fabricated by using the complex as the electrolyte.

Crown ethers are known to accomodate metal cations in their cavities and form solid complexes with many inorganic and organic salts.[1] In such complexes, the Coulomb attraction force between metal cation and anion decreases considerably as compared with the original salts. This fact results in the so-called "naked anion", which is applied to the organic synthesis.[2] From the viewpoint of solid state chemistry, the anion of the crown ether complex may move under the electric field, since it is bound much less weakly to the metal cation than the original salt. Thus, the crown ether-metal halide complexes are expected to be a new kind of solid halide ion conductor. D. S. Newman et al. studied the halide ion conductivities of several crown ether-metal halide complexes.[3] However, detailed information is not available on this topic. Thus, we studied the iodide ion conductivities of crown ether complexes with alkali-metal iodides and/or alkaline-earth metal iodides.

The crown ether-metal iodide complexes were synthesized as follows. Crown ethers (18-crown-6 and/or "dicyclohexyl-18-crown-6")[4] and metal iodides (potassium iodide and/or barium iodide) were mixed in a glass tube. The glass tube was degassed, and then sealed. About 10 % excess molar amounts of crown ethers were used. When the sealed tube was heated, the crown ether melted at first at about 50°C, and the inorganic salt was found at the bottom of the tube. Sudden complex-formation was observed at about 160°C as evidenced by the solidification of the material in the tube. After cutting the tube, the unreacted crown ethers were washed out by diethyl ether. The white powder thus obtained was dried completely at about 100°C in vacuo.[5]

The ionic conductivity of the complex was measured as follows. The powder obtained by the above procedure was compressed to a pellet (13 mm diameter and about 1 mm thickness)[6], and it was sandwiched by electrodes. Two kinds of electrodes were used: one is a platinum plate, and the other is a pellet made of graphite powder. The sample sandwiched by two electrodes was mounted on a sample holder, and then inserted into a glass vessel as shown in Fig. 1. The

sample was dried by heating the vessel at 100°C in vacuo until the conductivity reaches a constant and a reproducible value. After that, nitrogen gas of about one atmosphere was introduced to the vessel. The conductivity was measured by a Vector Impedance Meter (Yokogawa Hewlett Packard 4800 A) in the frequency range of 5 Hz to 100 kHz at several temperatures. The vessel was heated by a heater, and the temperature of the sample was monitored by a chromel-alumel thermocouple.

In order to confirm the complexes synthesized here to be an ionic conductor, constant dc voltage (1 V) was applied to the complex at 110°C, using platinum plate electrodes; the complex was composed of equimolar amounts of 18-crown-6, "dicyclohexyl-18-crown-6", potassium iodide, and barium iodide. The most detailed studies were made on this sample, and hereafter "sample" denotes this complex unless specified. The resistance of the "sample" increased gradually from $5 \times 10^5$ to $1 \times 10^7 \Omega$ during 3 h; this is a characteristic phenomenon to the ionic conductor, and results from the formation of an ion depletion region in the "sample".

Next, the charge carrier was determined as follows. Figure 2 shows the experimental setup for this purpose.[7] A small gold electrode (2 mm x 1 mm) was made onto a "sample" pellet by evaporation, and another "sample" pellet was set on it. The two "sample"s were sandwiched between a graphite pellet and a graphite pellet containing iodine, and then compressed together by 2.2 t/cm$^2$. A copper wire had been attached to the above mentioned gold film. A constant dc current (1 μA) was applied for 1 h, and then the voltage difference ($\Delta V$) between the graphite-iodine electrode (B in Fig. 2), and electrode inside the sample (A in Fig. 2) was measured. The short circuit current between A and B ($I_s$) was also measured. No significant change of the value $\Delta V/I_s$ was observed after applying the constant current. Thus, the resistance between A and B was constant. On the other hand, a gradual increase of the value $\Delta V/I_s$ was found when the graphite electrodes without iodine was used. These results can be explained satisfactorily if the "sample" is an iodide ion conductor. In the former

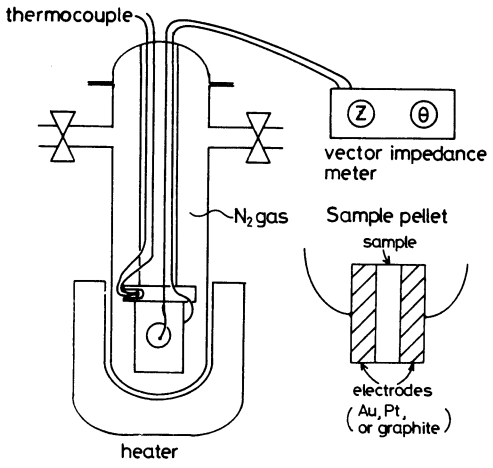


Fig. 1 The apparatus for the ionic conductivity measurements.

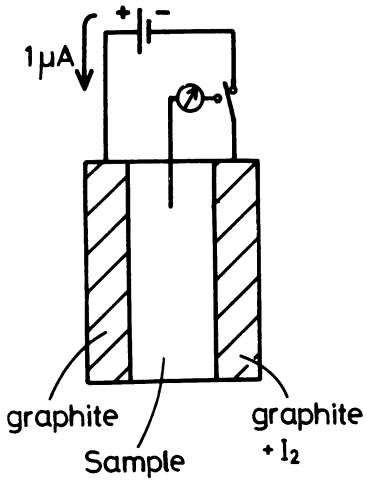


Fig. 2 The experimental setup for the determination of the charge carrier.

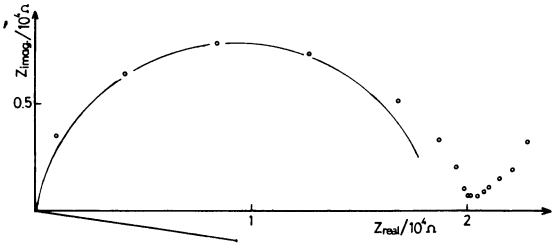


Fig. 3 The plots of the real and imaginary parts of the impedance of the "sample" measured at 111 °C.

experiment, the resistance between A and B does not change, since iodide ions are supplied from the graphite-iodine electrode. On the other hand, the resistance in question in the latter experiment increases because of the lack of iodide ion supply. Thus, the complexes of alkali-metal iodides and alkaline-earth metal iodides with crown ethers have been found to be a new type of iodide ion conductor.

Figure 3 shows the plot of the real and imaginary parts of the impedance of the "sample" measured at 111°C, using platinum plate electrodes. The curve deviated from the arc in the low frequency range. This experimental observation shows that the equivalent circuit can be expressed as the polarization processes in the complex and at the interface of the electrodes as shown in Fig. 4.[9,10] The resistances of the complexes were obtained from the intercept of the left arc to the abscissa.

Figure 5 shows temperature dependences of the iodide ion conductivities of several complexes.[11] The order of the anionic conductivity is as follows; the complex composed of two kinds of crown ethers and two kinds of inorganic salts > the complex composed of two kinds of crown ethers and one kind of inorganic salt or the complex composed of one kind of crown ether and two kinds of inorganic salts > the complex composed of one kind of crown ether and one kind of inorganic salt. These experimental observations may be explained as follows; the more the kind of the component molecules in a complex is, the poorer is the molecular packing in the solid; this fact results in the more channels of the iodide ion conduction.

Iodine concentration cell was fabricated by using the complex of crown ethers with inorganic salts. For example, a cell such as graphite+ "sample"|"sample"| graphite+"sample" +iodine was made.[12] Three pellets were made initially: one is used as the electrolyte, and the other two were used as the electrodes. They are compressed altogether at 2.2 t/cm$^2$. A pellet of 13 mm diameter and about 3 mm thickness was obtained. Voltage was found to be generated between the electrodes. The open circuit

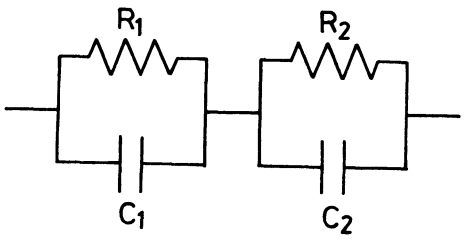


Fig. 4 Equivalent circuit for the specimen.
$R_1C_1$: Resistance and capacitance corresponding to electrode polarization process.
$R_2C_2$: Resistance and capacitance representing polarization process in electrolyte.

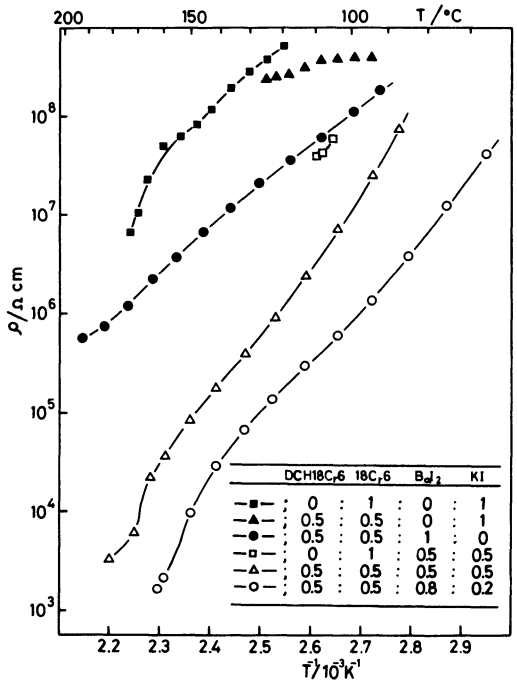


Fig. 5 Temperature dependences of the iodide ion resistivities. The values in the table denote the molar fractions of crown ethers and metal iodides in the complexes.

voltage ($V_{oc}$) and short circuit current ($I_{sc}$) in the typical examples are as follows; $V_{oc}$ = 0.23 V, $I_{sc}$ = 1 nA at 25°C, and $V_{oc}$ = 0.33 V, $I_{sc}$ = 1 μA at 100° C. By using the graphite electrodes containing "sample", very stable battery operation was observed; only a slight decrease of $I_{sc}$ was observed after connecting the two electrodes without load resistance for 12 h. On the other hand, $I_{sc}$ decreased gradually when the graphite electrodes without the "sample" was used. This fact results from the formation of insulating iodine layer at the surface of the anode in the latter case. The concentration cell may be used as an iodine sensor or an imaging device in principle.

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2) C. L. Liotta and H. P. Harris, J. Am. Chem. Soc., 96, 2250 (1974).

3) D. S. Newman, D. Hazlett, and K. F. Mucker, Solid State Ionics, 3-4, 389 (1981).

4) Formal name: perhydrobenzo[b,k][1,4,7,10,13,16]hexaoxacyclooctadecane.

5) The powder x-ray diffraction study of the complexes showed only broad diffraction characteristic of the amorphous state.

6) About 0.3 g of the complex was used.

7) The Tubandt method (see ref. 8) could not be used, because of the difficulty in the separation of the sample pellets after applying the current.

8) C. Tubandt, "Handbuch der Experimentallen Physik Bad XII", Berlin (1932).

9) "Solid Electrolytes and Their Applications", ed. by E. C. Subbaro, Plenum Press, New York, p 24 (1980).

10) The equivalent circuit in Fig. 4 was also confirmed by using graphite electrodes. In this case, almost the same arc with different deviation at the low frequency range was observed.

11) The plots of the resistivities against 1/T did not give straight lines. This may result from the softening of the sample as the elevation of the temperature.

12) The mixtures of graphite (0.15 g), iodine (0.05 g), and sample (0.15 g) were ground in an agate bowl, and then compressed to a pellet under a pressure of 2.2 $t/cm^2$.

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