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Short communication

Electrical conductivity of KCu_4I_5

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Bradley and Greene [1] reported the formation, in the system KI–CuI, of the intermediate compound KCu_4I_5, stable between 257 and 332 °C. Because of the relationships between this compound and the corresponding silver compound, KAg_4I_5, which is characterized by an exceptionally high ionic conductivity, it appeared of interest to us to determine the electrical conductivity of the compound.

KI Merck Suprapur[R] and CuI reagent grade recrystallized from HI were used.

The existing data on the stability of the compound were tested by differential scanning calorimetry: a Perkin Elmer DSC Mod. 1–B was used. We observed that during the first heating cycle of the KI–4CuI mixture the temperature of formation of the compound was somewhat higher than 257 °C. During the subsequent heating cycles, the temperature of reaction was nearly coincident with that observed by Bradley and Greene. Therefore the conductivity measurements were performed on mixtures previously heated at 280 °C.

The mixtures were pressed in cylindrical pellets 12.0 mm in diameter and 2 - 3 mm thick, at a pressure of 2,500 kg/cm^2. For the total conductivity measurements, the pellets were assembled between copper electrodes in a Pyrex cell fluxed with pure argon. Electrical contact was maintained by means of steel springs. The ac bridge (Wayne & Kerr B 331 MK 11) operated at 1592 Hz. All the measurements were performed after having maintained the cell for 15 hours at 150 °C in a current of pure argon.

In Fig. 1 the total conductivity σ is reported as a function of temperature. The σ values at temperatures lower than that of formation of KCu_4I_5 are very close to those of pure CuI [2], while at 260 °C an increase in σ of more than three orders of magnitude is observed.

In Fig. 2, log σ values are reported as a function of temperature, for different samples in the temperature range 257 - 330 °C. A limited hysteresis between the heating cycle and the subsequent cooling or heating cycles was observed.

From the data of Fig. 2 an energy of activation of about 2 kcal/mol can be deduced.

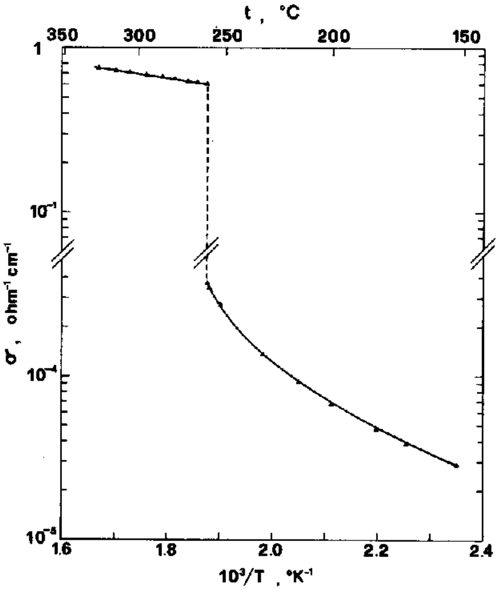

Fig. 1. Total electrical conductivity of the mixture KI–4CuI and of KCu_4I_5 between copper electrodes *vs.* reciprocal temperature.

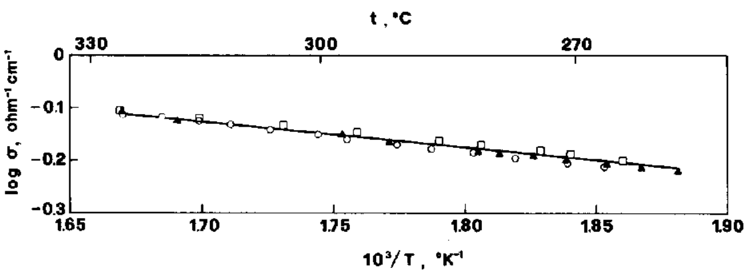

Fig. 2. Total electrical conductivity of KCu_4I_5 between copper electrodes *vs.* reciprocal temperature.

The conductivity of KCu_4I_5 is essentially ionic: this has been demonstrated by means of polarization measurements on $Cu/KCu_4I_5/Pt$ cells, according to Wagner's method and analysis [3]. The results obtained at 281.5 °C by forcing a current I through the cell (Pt being the positive) and measuring the steady state voltage E are reported in Fig. 3. The experimental points follow satifactorily (Fig. 4) the equation:

$$\log I = \log \sigma_{\oplus} (sRT/lF) + \log [\exp(EF/RT) - 1] \qquad (1)$$

where $\sigma_{\oplus}$ is the electronic conductivity due to electron holes, s and l are the cross-sectional area and thickness respectively of the sample, and the other symbols have their usual meaning. A value of $\sigma_{\oplus}$ of about 2×10^{-7} (ohm cm)$^{-1}$ is calculated at 281.5 °C.

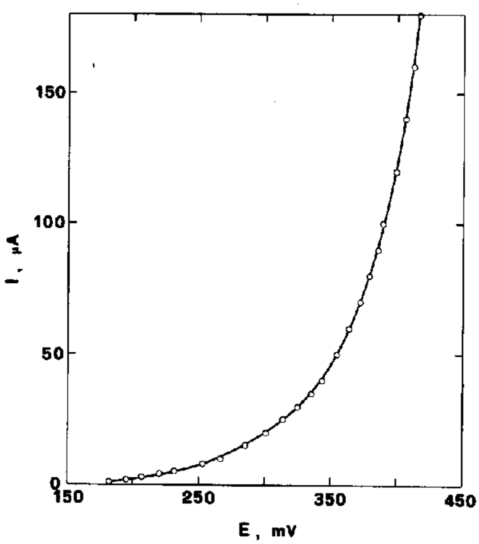

Fig. 3. *I vs. E* for a KCu_4I_5 pellet (l/s = 0.184 cm^{-1}) at 281.5 °C.

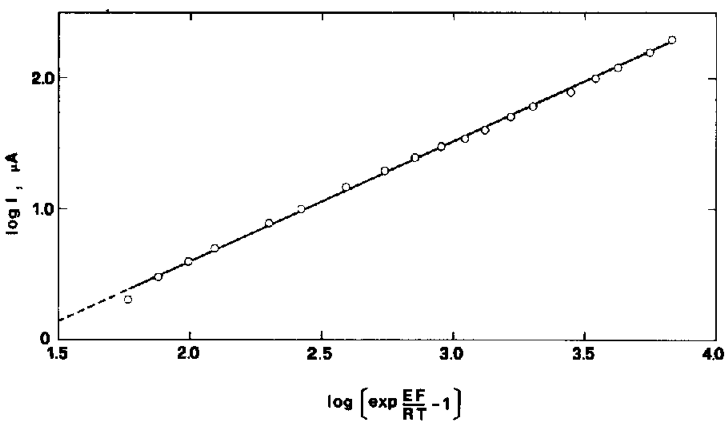

Fig. 4. Log *I vs.* log [exp (EF/RT) −1] for a KCu_4I_5 pellet (l/s = 0.184 cm^{-1}) at 281.5 °C.

The contribution of the electronic conductivity to the total conductivity of KCu_4I_5 equilibrated with copper is therefore negligible* and the compound can be considered a solid with high ionic conductivity, presumably due to Cu^+ ions. The compound cannot be quenched at room temperature, so its practical application as a solid electrolyte is limited to a narrow temperature range. Nevertheless the ascertained electrical properties of KCu_4I_5 could be very important in clarifying the role of the cation in stabilizing copper solid electrolytes [4 - 6].

*The ratio $\sigma_{\oplus}/\sigma$ at 281.5 °C is less than about 10^{-6}; the same ratio for pure CuI has the value of about 5×10^{-2} [2].

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