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# The determination of the full set of characteristic values of percolation, percolation threshold and critical exponents for the artificial composite with ionic conduction $\text{Ag}_4\text{RbI}_5-(\beta\text{-AgI})$

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## Abstract

The dc electrical conductivity,  $\sigma_{\text{dc}}$ , of the composite system  $\text{Ag}_4\text{RbI}_5-(\beta\text{-AgI})$ , which is composed of a good ionic conductor and a bad one, was measured by the ac impedance method. The obtained  $\sigma_{\text{dc}}$  increases with the volume fraction,  $\phi$ , of the good conductor,  $\text{Ag}_4\text{RbI}_5$ . This  $\phi$  dependence of  $\sigma_{\text{dc}}$  was analysed based on the generalized effective medium (GEM) theory. The scaling law analysis was also applied. The obtained threshold value of the volume fraction,  $\phi_c$ , was  $0.162 \pm 0.005$ . The critical exponents,  $t$  and  $s$ , were determined to be  $2.0 \pm 0.05$  and  $0.88 \pm 0.005$  respectively. These values are in almost complete agreement with the universal values of  $\phi_c$ ,  $t$  and  $s$  predicted by the computer simulation for the electrical conduction. So far as the present authors know, this study is the first to provide the full set of universal characteristic values of percolation,  $\phi_c$ ,  $t$  and  $s$ , for the electrical conduction from a single experimental study for the artificial composite material.

## 1. Introduction

Materials containing heterogeneous phases have been very interesting from the practical and fundamental points of view [1, 2]. As such inhomogeneous materials, so-called composite materials have been developed for the important advanced uses [3]. In addition, even for the understanding of the homogeneous materials, it is very important to know the role of heterogeneous phase because of the inevitable existence of the grain boundary, which acts as something like a heterogeneous phase [4]. In addition, such heterogeneous or

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composite systems accompany the fascinating transition phenomena, such as metal–non-metal transitions [5, 6], sol–gel transitions etc [7].

In a composite system between an extremely high electrical conduction phase and an extremely low one, the electrical conductivity,  $\sigma$ , increases slowly with the increase of the volume fraction of highly conducting phase,  $\phi$ , in the small  $\phi$  range. Over some threshold value (critical value) of  $\phi$ ,  $\phi_c$ , it increases abruptly [8] and the transition of insulator to metal or to semiconductor occurs. These transition behaviours have been discussed by the power laws in the percolation theory [1, 2, 8, 9]. These phenomena are characterized by the  $\phi_c$  and the critical exponents,  $s$  and  $t$ . The critical exponent  $s$  relates to the tendency of the increase of  $\sigma$  from the electrical conductivity of low conduction phase,  $\sigma_L$ , in the  $\phi$  range,  $\phi < \phi_c$ . The critical exponent  $t$  relates to the approaching tendency of  $\sigma$  to the electrical conductivity of highly conducting phase,  $\sigma_H$ , in the  $\phi$  range  $\phi_c < \phi$ .

These characteristic values of percolation,  $\phi_c$ ,  $t$  and  $s$ , have been determined by the computer simulations [7, 8, 10, 11].  $\phi_c$  has been obtained by the Monte Carlo simulation of the site model, in which the site can be occupied by either a well conducting material or a poorly conducting (insulating) one. The group of neighbouring sites occupied by the well conducting material is called a ‘cluster’. The size of the ‘cluster’ increases with the increase of the probability of occupation of the site by the well conducting material,  $p$ . At the critical value of  $p$ ,  $p_c$ , the cluster starts to extend from one end of the sample to the other one and the sample becomes highly conducting. Scher and Zallen [10] inverted this  $p_c$  into the  $\phi_c$  by putting hard spheres of equal diameters on the site. In addition, they found that  $\phi_c$  is universal; that is, it is dependent only on the dimensionality and independent of the crystal structure considered. The obtained  $\phi_c$  in the three-dimensional case is  $0.16 \pm 0.02$ . Similar  $\phi_c$  has also been obtained by the resistance network model based on the bond model [12]. The critical exponents,  $s$  and  $t$ , have also been found to be universal. The universal value of  $t$  widely accepted is 2.0 [1] for the three-dimensional case. The widely accepted universal value of  $s$  is 0.88–0.89 [1, 13].

From the experimental side, many studies have been performed for the percolation behaviour of insulator–metal composites, insulator–semiconductor composites, etc. It is a fact that an extremely small value of  $\phi_c$  (smaller than 0.01) has been reported for rather complicated systems, such as carbon fibres with layer structures in plastic material [14–16]. However, except for such a special case with complicated structures, many studies have reported values around the universal value, 0.16, as the  $\phi_c$  though considerably larger values can be found in table 1 in [6]. Reported values of the critical exponent,  $t$ , scatter between 0.38 and 2.0. McLachlan [17] also presented many examples of non-universal values for the critical exponent,  $t$ , of composite materials between graphite and boron nitride.

Compared with  $\phi_c$  and  $t$ , the determination of the critical exponent,  $s$ , has so far been insufficient because of the lack of experimental studies of  $s$ . The value 0.85 was obtained by Granman *et al* [18], though the value of  $\phi_c$  determined at the same time was 0.20–0.22, which is larger than the universal value, 0.16. It should be noted that the value of the critical exponent, 0.73, reported in the original manuscript, was derived from the form of scaling law  $((\phi_c - \phi)/\phi_c)^{-s'}$ , and can be changed into 0.85 as the critical exponent  $s$  in the form of scaling law  $(\phi_c - \phi)^{-s}$ . McLachlan [17] also presented many examples of non-universal values for the critical exponent,  $s$ . Thus, to date, there have been no experimental studies which report universal values of  $\phi_c$ ,  $t$  and  $s$  at the same time for a single composite system. As a result, it is still now open to question whether or not universal values of  $\phi_c$ ,  $t$  and  $s$  are established in real composite materials.

Unfortunately, most of these studies described above have been performed only for electron conducting systems. The percolation behaviour of ionic conduction systems has not been studied so much. In addition, most of the studies for such ionic conducting systems have

been performed for the homogeneous glass systems. Mangion and Johari [19] determined that the critical composition of AgI in the homogeneous glass of  $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$  ( $0 < x < 0.6$ ) is 0.30. As the  $\phi_c$  of organic–inorganic glasses, Kawamura *et al* [20] reported 0.35, which is far larger than the universal value. A composite system of ionic conduction,  $(\text{ZrO}_2:8 \text{ mol\% Y}_2\text{O}_3) + m \text{ mol\% Y}_2\text{O}_3$ , was studied by Fonseca and Muccillo [21]. A larger  $\phi_c$ ,  $\sim 28 \text{ vol\%}$ , was reported by the simplified GEM analysis ( $t = s$  in equation (3)). This large value of  $\phi_c$  was speculated to be derived from the grain size and the porosity.

Quite recently the present authors [22] studied the percolation behaviour of a composite system of the  $\text{Ag}^+$  ion conductor, AgI–BN, by which two kinds of percolation behaviour were able to be studied, that is the  $\alpha$ -AgI–BN composite system at 453 K and the  $\beta$ -AgI–BN composite at room temperature. The determined  $\phi_c$  and  $t$  for both systems were in good agreement with universal values. In principle the ionic system has advantages for the study of the percolation phenomena because of the freedom from the scattering or tunnelling phenomena in the boundary region, which may occur in the case of electron conduction systems. Unfortunately, the determination of  $s$  was not performed in that previous study [22] because of the too small electrical conductivity of the lower conductivity phase, BN.

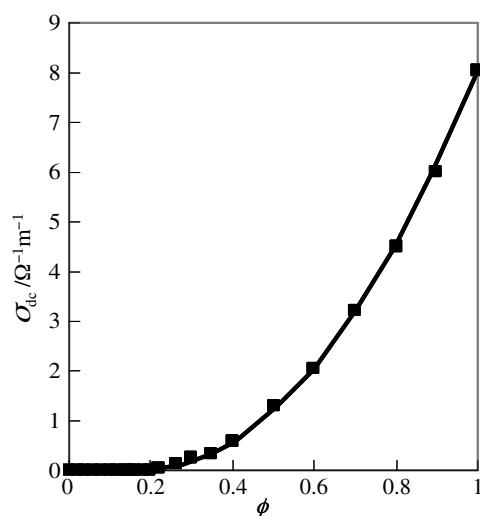
The purpose of this paper is to determine all characteristic values of percolation,  $\phi_c$ ,  $t$  and  $s$ , for a single composite system, in which both component phases have a finite ionic conductivity. The composite system  $(\text{Ag}_4\text{RbI}_5)_x$ –( $\beta$ -AgI) $_{1-x}$  was adopted in the present study. The high ionic conductivity phase,  $\text{Ag}_4\text{RbI}_5$ , has the highest electrical conductivity at room temperature [23] among superionic conductors. The low conductivity phase,  $\beta$ -AgI, has a low but a measurable ionic conductivity.

## 2. Experimental details

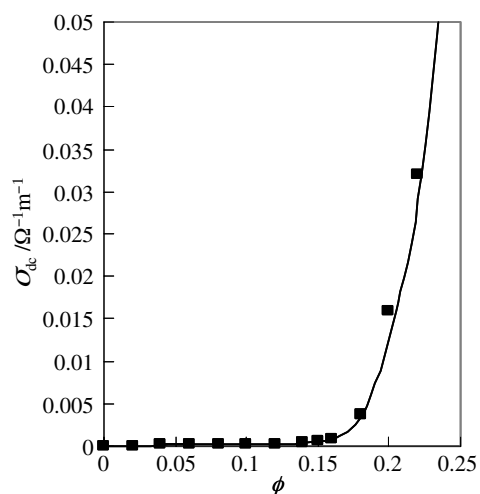
The reagents,  $\text{Ag}_4\text{RbI}_5$  and AgI, were ground together into fine powders of a few micrometres in a mortar with the use of a pestle. The  $\text{Ag}_4\text{RbI}_5$  used was a special grade (99%) from Soekawa Chemical Co. Ltd. The AgI used was also a special grade (over 99%) from Kojima Chemical Co Ltd. The obtained fine powders were pressed into a cylindrical pellet with 3 mm depth and 13 mm diameter together with thin Ag powder layers (as electrodes) on both sides. The composition range studied was  $x = 0$ –1 for  $(\text{Ag}_4\text{RbI}_5)_x$ –( $\beta$ -AgI) $_{1-x}$ . The impedance measurements were made for this pellet at room temperature by using a HIOKI 3532-20 high tester in the frequency range from 47 Hz to 5 MHz. The dc part of the electrical conductivity,  $\sigma_{\text{dc}}$ , was extracted from the measured impedance by the conventional method.

The reproducibility of the present measurements for the electrical conductivity was very good, judging from the comparison of  $\sigma_{\text{dc}}$  for  $\beta$ -AgI at 298 K between independent measurements (first run,  $1.66 \times 10^{-4} \Omega^{-1} \text{ m}^{-1}$ ; second run,  $1.65 \times 10^{-4} \Omega^{-1} \text{ m}^{-1}$ ), for which the preparation of samples was also performed independently. In addition, the present data of  $\sigma_{\text{dc}}$  for  $\beta$ -AgI at 298 K ( $1.6$ – $1.66 \times 10^{-4} \Omega^{-1} \text{ m}^{-1}$ ) were compared with the literature value ( $1.75 \times 10^{-4} \Omega^{-1} \text{ m}^{-1}$ ) [24]. A slight difference, 6%, is present between them. However, as is well known, the AgI reagent decomposes easily into metallic Ag and molecular iodine. The value of  $\sigma_{\text{dc}}$  of  $\beta$ -AgI is sensitive to the quality of the sample, particularly such decomposition and the purity. Taking into account these conditions, the accuracy of the present measurements for  $\sigma_{\text{dc}}$  was very high.

The density was calculated from values of the mass, the surface area, and the thickness of the pellet. A value of over 99.9% was obtained for the ratio of this estimated density to the density obtained by assuming the additive law of volume between two component phases.



**Figure 1.** The dependence of the dc electrical conductivity,  $\sigma_{dc}$ , on the volume fraction of highly conducting  $\text{Ag}_4\text{RbI}_5$  phase,  $\phi$ , for the  $\text{Ag}_4\text{RbI}_5-(\beta\text{-AgI})$  composite system in the range from  $\phi = 0$  to 1.0; solid squares, experimental data; line, fitted curve to the GEM formula (equation (3) in the text).



**Figure 2.** The dependence of the dc electrical conductivity,  $\sigma_{dc}$ , on the volume fraction of highly conducting  $\text{Ag}_4\text{RbI}_5$  phase,  $\phi$ , for the  $\text{Ag}_4\text{RbI}_5-(\beta\text{-AgI})$  composite system in the range from  $\phi = 0$  to 0.25; solid squares, experimental data; line, fitted curve to the GEM formula (equation (3) in the text).

### 3. Results

In figure 1 the dc ionic conductivity,  $\sigma_{dc}$ , of  $(\text{Ag}_4\text{RbI}_5)_x-(\text{AgI})_{1-x}$  system is shown as a function of the volume fraction of  $\text{Ag}_4\text{RbI}_5$  phase,  $\phi$ , in the  $\phi$  range between zero and unity. Figure 2 corresponds to a magnified view of figure 1 in the  $\phi$  range below  $\phi = 0.25$ . As can be seen in figure 2,  $\sigma_{dc}$  increases abruptly with the increase of  $\phi$  around  $\phi = 0.16$ .

#### 4. Discussion and conclusions

Figures 1 and 2 indicate that the behaviour of  $\sigma_{dc}$  may be governed by the percolation process because of the abrupt increase with the increase of the volume fraction of well conducting phase,  $\text{Ag}_4\text{RbI}_5$ . The  $\phi$  dependence of  $\sigma_{dc}$  may be analysed by percolation theory.

To date, much analysis of percolation theory [1, 2, 7, 8, 11] has been performed by the scaling laws, which is described as follows:

$$\sigma \sim \sigma_L(\phi_c - \phi)^{-s} \quad \text{for } \phi < \phi_c. \quad (1)$$

$$\sigma \sim \sigma_H(\phi - \phi_c)^t \quad \text{for } \phi > \phi_c. \quad (2)$$

In these equations, the symbol  $\phi$  indicates the volume fraction of the electrically high conduction phase and  $\sigma_L$  and  $\sigma_H$  represent respectively the  $\sigma$  of low conduction phase and that of high conduction phase. Equation (1) represents the increasing tendency of  $\sigma$  with approach to the threshold value of  $\phi$ ,  $\phi_c$  on increasing  $\phi$ .  $\phi_c$  corresponds to the  $\phi$  at which  $\sigma$  increases abruptly due to the connection of the high conduction domains all over the sample. The critical exponent  $s$  relates to the tendency of the evolution of  $\sigma$  below  $\phi_c$ , as already mentioned. Equation (2) represents the saturation tendency to  $\sigma_H$  with the increase of  $\phi$ . The critical exponent  $t$  relates to the approaching tendency of  $\sigma$  to  $\sigma_H$ , as already explained. On the analysis based on the percolation theory, it is very important to determine the threshold value of the volume fraction,  $\phi_c$ , and the critical exponents,  $t$  and  $s$ .

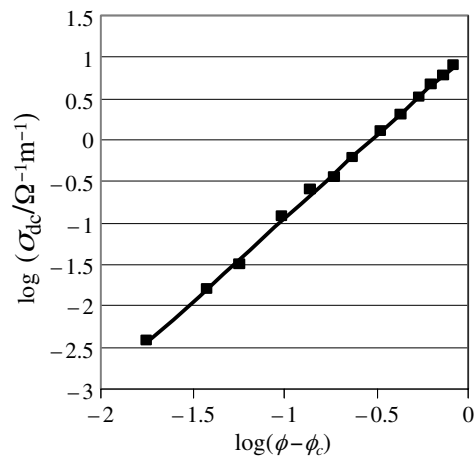
McLachlan [13, 17] presented the generalized effective medium (GEM) theory, whose form is similar to the effective medium theory and includes above two power laws as the limiting form around  $\sigma \sim \sigma_L$  and  $\sigma \sim \sigma_H$  respectively. Therefore, the GEM formula can represent the behaviour of  $\sigma$  in the whole range of  $\phi$  by a single formula. The explicit form is as follows:

$$\phi \left( \frac{\sigma_H^{1/t} - \sigma_m^{1/t}}{\sigma_H^{1/t} + A\sigma_m^{1/t}} \right) + (1 - \phi) \left( \frac{\sigma_L^{1/s} - \sigma_m^{1/s}}{\sigma_L^{1/s} + A\sigma_m^{1/s}} \right) = 0. \quad (3)$$

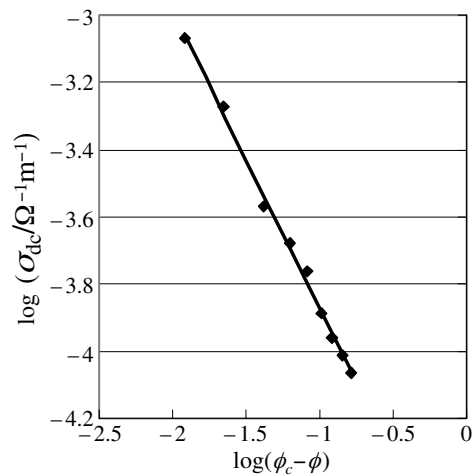
The critical exponents,  $s$  and  $t$ , in equation (3) have respectively the same meaning as those in equations (1) and (2). The percolation threshold,  $\phi_c$ , relates to the symbol  $A$  by the relation  $A = (1 - \phi_c)/\phi_c$ . As already described, the universal value of  $t$  widely accepted is 2.0 for the three-dimensional case [1, 7, 10]. The universal value of  $s$  is 0.88–0.89 [1, 13].

The characteristic values of percolation,  $\phi_c$ ,  $t$  and  $s$ , were determined by fitting the experimental  $\sigma$ – $\phi$  relation to equation (3) by the least square method. Obtained values are  $\phi_c = 0.162 \pm 0.005$ ,  $t = 2.0 \pm 0.05$  and  $s = 0.88 \pm 0.005$ . These characteristic values determined were in quite good agreement with universal values. To make doubly sure, the characteristic values of percolation were also determined by fitting the experimental  $\sigma$ – $\phi$  relation to equation (2) by the least square method. The  $\sigma$ – $\phi$  relation in the range  $\phi > \phi_c$  is drawn in the log–log form in figure 3. The determined characteristic values were  $\phi_c = 0.162 \pm 0.001$ ,  $t = 2.0 \pm 0.03$ . Similarly, the fitting of the experimental  $\sigma$ – $\phi$  relation to equation (1) was also performed in the range  $\phi < \phi_c$ , as shown in figure 4. The obtained characteristic values were  $\phi_c = 0.162 \pm 0.001$  and  $s = 0.89 \pm 0.005$ . The good agreement was obtained among these three sets of characteristic values of percolation. Therefore, the values of  $\phi_c$ ,  $t$  and  $s$  determined in the present study seem to be quite reliable.

Here it must be stressed that, up to now, characteristic values of percolation, particularly the critical exponent  $s$ , have not been well established from real conductivity measurements. In addition, there have been no real materials for which the universal values of  $\phi_c$ ,  $t$  and  $s$  have been given from a single conductivity measurement. Therefore, the present study is the first to provide the full set of universal values of  $\phi_c$ ,  $t$  and  $s$  for a real composite



**Figure 3.** The relation between  $\log \sigma_{dc}$  and  $\log(\phi - \phi_c)$  for  $\phi > \phi_c$ ;  $\sigma_{dc}$ , dc electrical conductivity;  $\phi$ , volume fraction of high conductivity  $\text{Ag}_4\text{RbI}_5$  phase;  $\phi_c$ , threshold value of  $\phi$ . The solid square indicates experimental data and the line the fitted curve to the power law (equation (2) in the text).



**Figure 4.** The relation between  $\log \sigma_{dc}$  and  $\log(\phi_c - \phi)$  for  $\phi < \phi_c$ ;  $\sigma_{dc}$ , dc electrical conductivity;  $\phi$ , volume fraction of high conductivity  $\text{Ag}_4\text{RbI}_5$  phase;  $\phi_c$ , threshold value of  $\phi$ . The solid square indicates experimental data and the line the fitted curve to the power law (equation (1) in the text).

material. The reason for this success may be derived from the selection of low conduction material with measurable  $\sigma$  and no chemical reaction between the two adopted materials. The latter may be partially derived from the low measurement temperature, namely room temperature. In addition, the present ion conducting composite system has the advantage of the absence of scattering phenomena or tunnelling phenomena, which occurs in the case of electron conducting composite systems. In fact, if the reaction occurs around the boundary, the characteristic values of percolation determined are not always in good agreement with the universal values, as was observed by Uvanov *et al* [25].

The high electrical conductivity of  $\alpha$ -AgI, with the highest electrical conductivity among superionic conductors, is considered to be derived from the average structure, in which many

site positions prepared among the large anions ( $\text{I}^-$ ) on the bcc sublattice are available for the migration of cationic  $\text{Ag}^+$  ions with shallow energy barriers [26–28]. The high electrical conductivity of solid  $\text{Ag}_4\text{RbI}_5$  itself is also derived from a similar mechanism though the structure of the anion sublattice is complicated [29]. In the unit cell, the arrangement of  $\text{I}^-$  ions provides 56 iodide tetrahedra, which share faces in such a manner as to provide the diffusion path for 16  $\text{Ag}^+$  ions [27]. The percolation mechanism does not bring into existence any higher conductivities of the mixed state than its constituent one. In this respect, the modification of the boundary layer may be important to obtain this higher conductivity.

As already described, there seems to be only a very small possibility of the quantum effect in the ion conducting systems. Here we discuss in more detail the possibility of the tunnelling phenomena in the superionic conductors, which may be a wave behaviour of  $\text{Ag}^+$  ions in the present case. In the extreme approximation, the  $\text{Ag}^+$  ions in superionic conductors migrate freely like molecules in gas. The de Broglie thermal wavelength  $\Lambda$  is 0.01 nm for  $\text{Ag}^+$  ions at 298 K.  $\Lambda$  was calculated by  $\Lambda = (2\pi\hbar^2/(mk_{\text{B}}T))^{1/2}$ , in which  $m$ ,  $\hbar$  and  $k_{\text{B}}$  are respectively the mass per ion, Planck's constant divided by  $2\pi$  and Boltzmann's constant. On the other hand, the average nearest neighbour distance,  $d$ , among  $\text{Ag}^+$  ions is 0.17 nm, which is estimated from the density data [30] of  $\text{AgI}$  at 298 K by assuming that  $d$  is equal to the cubic root of volume per  $\text{Ag}^+$  ion. Therefore, the quantum effect seems to be negligible for the superionic conductor at 298 K, judging from the fact that the ratio  $d/\Lambda$  is larger than unity. However, the present estimation is rather the zeroth approximation. There is a possibility that the velocity of  $\text{Ag}^+$  ions in superionic conductors is slower than the thermal velocity for free particles. Then, as is the case of electron conducting systems [31, 32], still now there is a possibility of the existence of the quantum tunnelling effect in the ion conducting systems particularly at low temperatures. The problem of the tunnelling effect in the ion conducting systems may be a future important field.

In this study, the determined characteristic values of percolation were  $0.162 \pm 0.005$  for the threshold value,  $\phi_c$ , and  $2.0 \pm 0.05$  and  $0.88 \pm 0.005$  respectively for critical exponents,  $t$  and  $s$ . The similar characteristic values of percolation were also obtained from the analysis based on the power law in the percolation theory. These values are in almost complete agreement with the universal values of  $\phi_c$ ,  $t$  and  $s$ . So far as the authors know, the present study is the first to provide the full set of universal characteristic values of percolation for electrical conduction from a single experimental study.

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