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Electrical conductivity of random silver–potassium chloride composites

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The complex alternating current (a.c.) impedance of random silver–potassium chloride (Ag–KCl) composite specimens near the percolation threshold has been measured in the frequency range 5 Hz to 13 MHz. The impedance of these composites as a function of metal volume fraction and direct current (d.c.) potential field are presented. This a.c. response, which is correlated with structural and compositional characterization of these composites, is used to examine the applicability of several different theoretical models as well as to determine the important factors in the electrical conductivity of such materials.

1. Introduction

Composite materials generally have properties very different from those of their constituents. For example, it is well known that as the metal volume fraction in a metal–insulator composite increases the electrical conductivity increases. Near some critical metal volume fraction the conductivity of such a composite increases by several orders of magnitude [1, 2]. This critical point is known as the percolation threshold. In addition, these random small-particle metal–insulator (or normal–superconducting) composites are known to have anomalous far-infrared absorption [3, 4] and divergent dielectric constant near the percolation threshold [5]. However, alternating current response in the long radio wave frequency range of these composites has not been measured. The complex a.c. impedance between 5 Hz and 13 MHz, which covers the range well below that accessible to the infrared spectrometers, should provide a comprehensive picture of the electronic properties of the composites near percolation.

The phenomenon of conductivity in a mixture of metal particles in a non-conducting media was first observed by Branly in 1890 [6, 7]. More recently, the d.c. conductivity of silver–thermosetting polyester composites have been studied by Kwan *et al.* [8]. A switching effect, i.e. dramatic increase in conductivity when the applied voltage is beyond a certain value, in this silver–polyester composite was observed. It is also reported that the conductivity is highly unstable after the composite had switched-on. Furthermore, this composite exhibits more stable electrical conductivity if it had been "pre-conditioned" at high voltage for a long period of time.

In this study, the complex impedance or admittance of a series of Ag–KCl composites has been measured between 5 Hz and 13 MHz as a function of metal volume fraction, and external d.c. potential field. Particle distribution, cluster structure, and phase analysis of the constituents of the composite have been characterized by using electron microscopy and X-ray emission microanalysis. These results indicate the relative importance of the metal–insulator distribution and the interparticle spacing on the percolation threshold. The correlation between the peculiar structure of metal particle clusters that form near the percolation threshold as well as several physical models that describe these effects are also discussed.

2. Experimental procedure

All experiments discussed here were performed on random composite specimens of small silver particles (mean particle diameter 20 nm) randomly distributed in KCl matrix which were previously prepared by Garland and his colleagues in the Department of Physics of the Ohio State University [5]. The detailed procedure of small silver particle preparation has been previously described [5].

The a.c. impedance measurements were made using a two-terminal pair technique which minimized the effect of lead impedance. All the measurements were made using an HP 4192A LF Impedance Analyser in the frequency range from 5 Hz to 13 MHz with 20 points per decade (Fig. 1). The measured data were recorded using an IBM personal computer through an IEEE-488 interfacing system. Stray impedances due to the cell and leads were measured over the entire frequency range by measuring the impedance of the cell without a sample present. All data presented have been corrected for these stray impedances where significant.

A curve-fitting program written in BASICA was used for the curve fitting of the real and imaginary values in complex plane. This program is capable of fitting either a straight line and/or a semicircle to the data using least square criteria. Critical values such as intersection points, slopes, and radius of semicircle were then extracted to calculate the resistance and capacitance of an equivalent circuit.

A transmission electron microscope (TEM) was used for direct observation of the small silver particle distribution in the composite. TEM specimens were

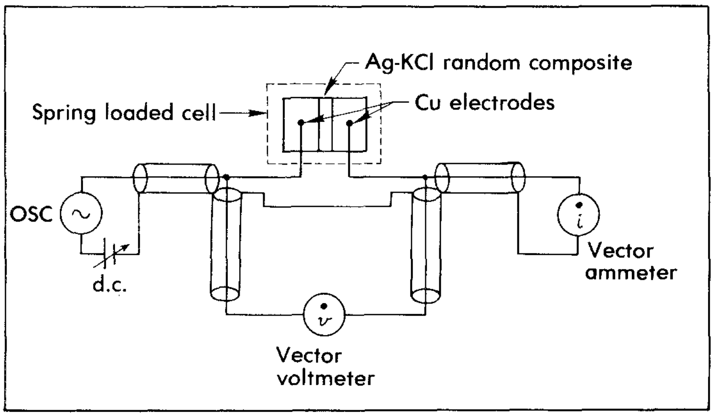

Figure 1 Schematic illustration of the a.c. impedance measurement apparatus.

prepared by scraping the composite powders off the random composite specimen, on to a thin carbon film supported by a copper grid. A cold stage specimen holder was used with operation temperature near − 180° C to prevent excess damage of the KCl matrix by the high-energy electrons. TEM observations were performed in a JEOL 200CX scanning transmission elecron microscope (STEM) with the acceleration voltage at 200 kV. Identification of the particle phases was obtained by X-ray energy dispersive spectrum (EDS) chemical analysis.

3. Results and discussion

3.1. Electrical properties of random composites in absence of external field

An electron micrograph (Fig. 2) of the composite shows silver particles in a KCl host distributed as single and agglomerated particles. EDS analysis in Fig. 2 shows that the dark spots are the silver phase while the white area is the KCl phase. A small silver peak is observed in the EDS of the white area although it is not clear whether the peak results from silver dissolution in the KCl matrix or from very small silver particles there. Complex a.c. response of a series of Ag–KCl specimens with silver volume fraction between 0.210 and 0.233, which surround the percolation fraction, P_c were measured at room temperature. Fig. 3 shows the a.c. response of these specimens in the complex admittance plane where G is the conductance and B the susceptance. Straight lines with a small angle inclined to the vertical are observed for the specimens with low silver volume fraction, i.e. 0.215 and below. The appropriate equivalent circuit, Fig. 4, is a parallel combination of an ideal resistor, R, and a non-ideal capacitor, $C(\omega)$, where ω is the angular frequency. The capacitor has a frequency independent loss term given by the dielectric loss tangent, tan α. At high metal volume fractions, e.g. 0.218 and above, the capacitance in Fig. 4 is small relative to the resistance, so that the impedance response shows a nearly ideal resistor.

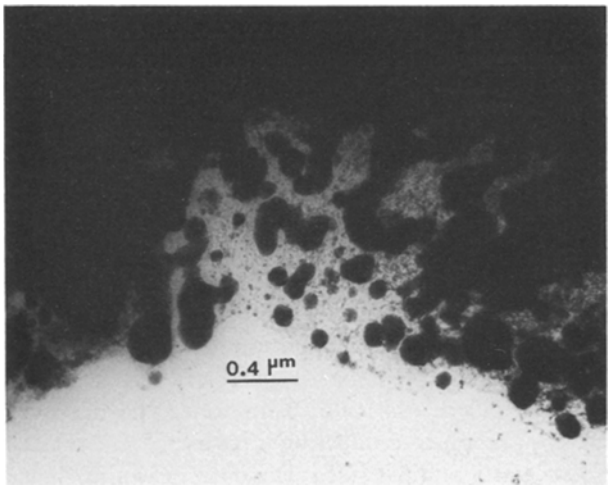

Figure 2 Electron micrograph of the edge of a debris from the Ag–KCl composite with silver volume fraction = 0.223. Dark area is silver and grey area is KCl matrix.

For the equivalent circuit shown in Fig. 4, the complex admittance Y can be expressed as

$$Y = G + iB = (1/R) - i\omega C(\omega) \qquad (1)$$

where $\omega = 2\pi \times$ frequency and i is $\sqrt{-1}$.

From the complex admittance diagram, R can be calculated as the reciprocal of the intercept of the G axis; the dielectric loss tangent tan α can be deduced from the slope of B against G; and the capacitance C is the slope of B against ω. Fig. 5 shows the resistivity measurement based on the calculation described above. The resistivity drops 7 orders of magnitude with a 1% Ag volume fraction increment. Such behaviour is similar to that observed by Kwan *et al.* [8] in the silver–thermosetting plastic composites which had been conditioned at 150 V for several hours.

Fig. 6 shows the dielectric constant, K, and dielectric loss tangent, tan α, as a function of silver volume fraction. Both the dielectric constant and dielectric loss tangent diverge as the silver volume fraction approaches the percolation threshold. The divergent behaviour of the dielectric constant at percolation threshold can be explained by the percolation model [5, 9]. The divergent behaviour of the dielectric loss tangent, which is the ratio of the real to imaginary part of the dielectric constant, indicates that the dramatic increase in dielectric constant as the metal volume fraction approaches the percolation threshold is primarily due to the increase of real part rather than the imaginary part of the dielectric constant. The dielectric constant has not been measured above the percolation threshold.

Based upon the percolation model [10–12] the electrical properties such as resistivity and dielectric constant should diverge as the metal volume fraction approaches the percolation threshold with a scaling

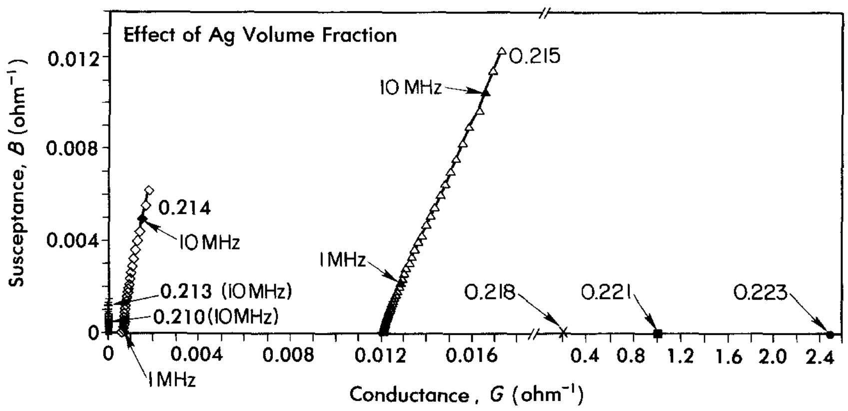

Figure 3 The a.c. response in the complex admittance plane of a series of Ag–KCl composite samples with different silver volume fractions in the frequency range 5 Hz to 13 MHz. The abscissa is linear but changes by a factor of 200 at 0.019 ohm^{-1}. Ag volume fraction: □, 210; +, 0.214; ◇, 0.213; △, 0.215; x, 0.218; ■, 0.221; ●, 0.223.

equation as:

$$E = K' g^s \qquad (2)$$

where E is the electrical property of interest, K' is the proportional constant, g is the geometric parameter which is correlated to the metal volume fraction, and s is the critical exponent [12]. The values of g and s depend upon the exact nature of the composite. Resistor network models show that the resistivity for a three-dimension random composite should have a critical exponent about 2 [2, 12] and the geometric parameter g equal to $(P - P_c)$, where P is the metal volume fraction and P_c is the percolation fraction. The dielectric constant for a three-dimensional random composite should have a critical exponent about 0.7 and the geometric parameter equal to $(P - P_c)/P_c$ [5].

Least-square fitting of the measured resistivity and dielectric constant data show that the critical exponents for the resitivity and for the dielectric constant are higher than those predicted in resistor–insulator network simulations, though the trend of the electrical properties does follow the prediction of the percolation model. Previous measurements of the dielectric constant on a wider volume fraction range of Ag–KCl composites prepared in the same laboratory gave a critical exponent very close to that predicted theoretically [5]. Thus, the high values of the critical exponent found here are probably due to the limited number of specimens and narrow compositional region that have been investigated.

3.2. Effect of superimposed d.c. field on the conductivity

The effect of an external electric field on the electronic properties of the random composite specimen can be measured by applying a d.c. field in addition to the small a.c. signal. Fig. 7 shows the a.c. response of a specimen (volume fraction = 0.213) under different external d.c. potentials. For low external d.c. potentials (0 to 1 V), the admittance of the specimen is relatively independent of the external d.c. potentials. At about 1 V d.c., a dramatic increase in conductivity is observed. One possible explanation of this effect is that the KCl matrix undergoes dielectric breakdown [13]. Direct measurement of the silver-particle agglomerates in TEM (Fig. 2) shows the spacing in the range of tens of nanometres between agglomerates. Thus, local electric field intensity is of the order of $10^8\,\text{V m}^{-1}$ which could very well cause local dielectric breakdown in such regions.

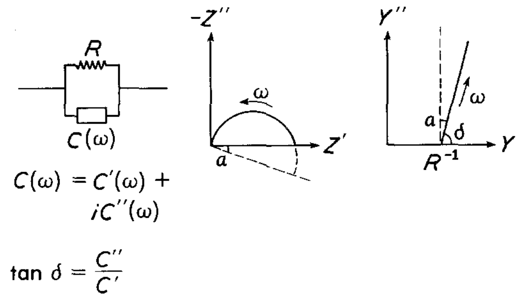

Figure 4 Schematic illustration of a circuit combination of an ideal resistor R, and non-ideal frequency-dependent capacitor $C(\omega)$. The complex impedance plot, Z, and complex admittance plot, Y, of its corresponding circuit are shown in the second and third columns, respectively.

Another possible explanation is electrical conductivity caused by electron migration [14] between two narrowly separated silver clusters. Owing to the high current density in the limited number of newly created conducting paths, mass flow caused by the momentum exchange between conducting electrons and metal ions in the crystal lattice may become important. This metal mass flow in the narrowly separated metal clusters could create excess or wider conducting paths which allow a dramatic increase in the electrical current in the bulk. Since electron migration phenomenon is strongly temperature dependent [15] and the dielectric breakdown [16] is a less temperature-dependent phenomenon, a study of the effect of temperature on the conductivity should elucidate the real electron transport mechanism. However, the effect of different thermal expansion coefficients between the metal and the insulating phases may tend to mask the desired response.

The admittance increase observed along the horizontal axis in the conductance plane at high d.c. external potentials as frequency is increased is believed to be due to a time-dependent dielectric breakdown and/or electron migration process [14]. When the a.c. measurements were made in the reverse direction (from high frequency to low) immediately after the forward scan at the same d.c. potential, the horizontal region was not observed. Thus, once the dielectric material becomes conducting it requires some time to return to its original state. The data shown in Figs 7 and 8 are reproducible to within 5% as long as the material is given sufficient time to relax back to its initial state. The exact time constant for this "healing"

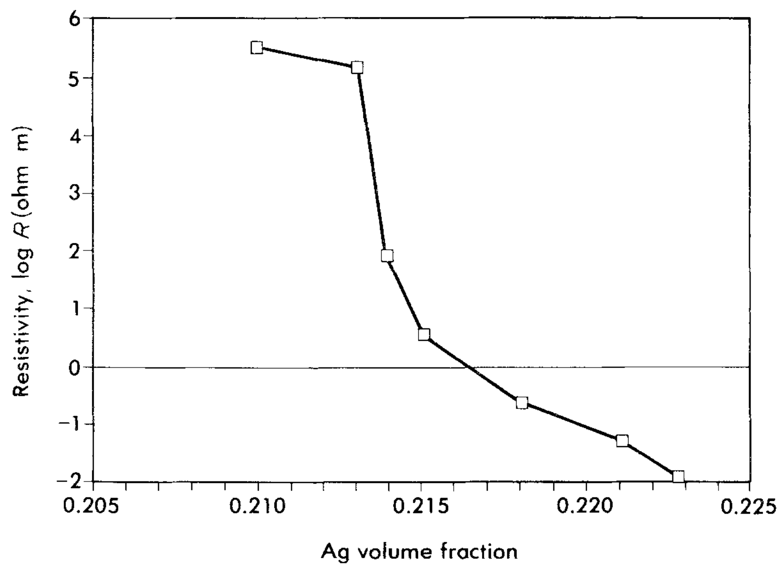

Figure 5 The resistivity, R, of Ag–KCl specimens with different metal volume fractions based on the equivalent circuit shown in Fig. 4.

process has not been measured, but appears to be of the order of minutes at room temperature.

The d.c. conductivity, G_0, can be estimated from the impedance data by determining the real part of the admittance as the frequency approaches zero. This d.c. conductivity, G_0, is plotted as a function of d.c. field potential, $V_{\mathrm{d.c.}}$, in Fig. 8. If the conductivity increase results from high local electric fields described above, the shape in Fig. 8 can be understood physically as follows: the local electric field intensity is inversely proportion to the spacing of the particles. At low d.c. fields, there are no local regions with high enough fields to cause conduction. Thus the conductivity does not change significantly. As the bias is increased, regions with the smallest interparticle spacing would conduct first, then more and more regions would become conducting with increasing bias. If the interparticle spacing follows a normal distribution, the rise in conductivity would be given by the cumulative distribution function for the normal probability density function. Also the shape of the conductivity against d.c. field curve would be close to that of Gaussian (normal) cumulative distribution function [17]. Finally, nearly all of the interparticle regions would be conducting so that a linear relationship between conductance and d.c. bias would arise from simple ohmic behaviour.

Recent work [18] shows that the interparticle spacing does not actually follow a normal distribution, but rather has a distribution which depends on the fractal dimension, d_f, of the silver particles. Functionally, this leads to conductivity given by

$$G_0 = K[1 - \exp - (V_{\mathrm{d.c.}}/V_{\mathrm{d}0})^{d_f}] \qquad (3)$$

where K is a constant, $V_{\mathrm{d.c.}}$ is the d.c. field applied to the composite, $V_{\mathrm{d}0}$ is the voltage required to cause the metal clusters with the most probable separation distance to conduct, and d_f is the fractal dimension. The fractal dimension would have a value of 3 if the silver particles were randomly distributed and a value of 2 if the particles were ideal percolating clusters. Practically, particles are distributed somewhat differently from these two extreme cases and should have a value between 2 and 3. By fitting the experimental results to theory a value of 2.23 has been determined [18]. Thus, the silver particle distribution in the composite is closer to the percolating clusters than to a random distribution. Electron micrographs (Fig. 2) of the silver particle distribution in the composite, while showing some individual particles and some agglomeration of the particles, are consistent with this predicted value of d_f.

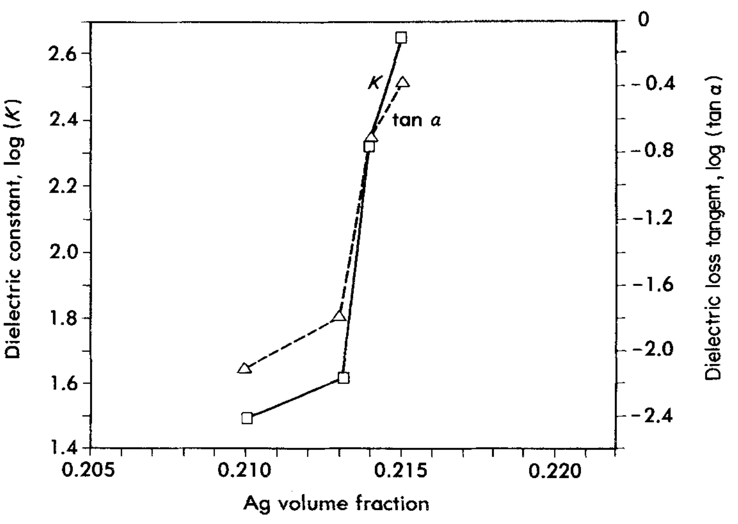

Figure 6 The dielectric constant (□), K, and dielectric loss tangent (△), tan α, of Ag–KCl random composite below the percolation threshold.

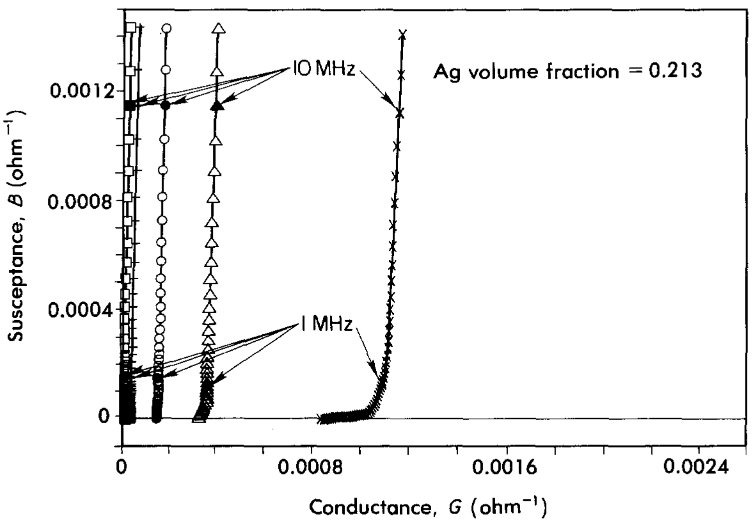

Figure 7 The a.c. response from 5 Hz to 13 MHz in the complex admittance plane of one specimen (volume fraction of silver = 0.213) under different external d.c. potential. □, 0 to 0.8 V; +, 0.9 V; ○, 1.3 V; △, 2.0 V; x, 3.0 V.

4. Conclusion

A simple combination of parallel $R-C$ circuit can be used to represent Ag–KCl random composite materials with metal volume below the percolation fraction. These composites with metal volume fractions above P_c behave as a pure resistor. Both dielectric constant and dielectric loss tangent show a singularity at percolation threshold. The resistivity, dielectric constant, and dielectric loss tangent generally follow the prediction given by the percolation theory when the metal volume fraction approaches the percolation threshold. TEM direct observation of the composite shows that silver particles are distributed as the prediction of percolation model that both clusters and isolated particles are presented. The observed dramatic increase in conductivity with increasing external d.c. potential is believed to arise from a distribution of inter-cluster spacing which follow a fractal dimension of distribution between ideal random and ideal percolating clusters. Further study of the effect of temperature on conductivity under external d.c. potential field should elucidate the conducting mechanism of the switching phenomenon. The variation of the fractal dimension as a function of metal volume fraction, particle size distribution, and different metal–insulator system will give a comprehensive understanding of the electric properties of this random composite system.

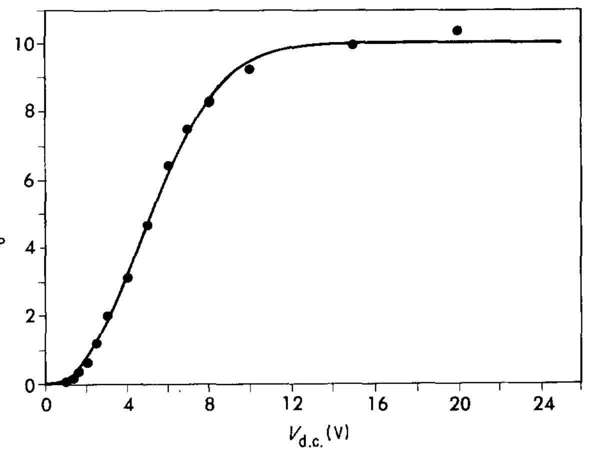

Figure 8 The effect of an external d.c. potential field, $V_{d.c.}$, on the estimated d.c. conductance, G_0. Points correspond to the experimental data and the solid line corresponds to the best fit of Equation 3 with $d_f = 2.23$, $V_{d_0} = 6.15$ V, and $K = 0.0100$.

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