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AC IMPEDANCE ANALYSIS OF CuS-C COMPOSITE SUPERIONIC CONDUCTOR

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ABSTRACT

AC IMPEDANCE ANALYSIS OF CuS-C COMPOSITE SUPERIONIC CONDUCTOR. CuS-C composite superionic conductor has been synthesized by powder metallurgy method. The frequency response of frequency dependent conductivity has been measured by AC complex impedance bridge methods at room temperature, 100 °C and 200 °C. The AC conductivity of superionic materials takes the form $\sigma=\sigma(0) + A\omega^n$. The carrier hopping rate ω_p is obtained from the new expression $\sigma(0)= A\omega_p^n$. The conductivity data is analyzed, to obtain the ionic conductivity parameters and hopping rates of CuS-C composite superionic conductor. *Arrhenius* plot of the conductivity shows a smooth slope change or transition at 323 K or 50 °C and the activation energy for conduction is found to be 0.154 eV. The experimental data for all temperatures shows a clear anomaly at frequencies of 9.0 kHz and higher. For frequencies from 0.1 Hz to up to 9.0 kHz the curve is mainly flat and practically no frequency dispersion at all temperatures is observed. The estimated DC conductivity is 0.5708 Scm^{-1}. The ionic parameters such as prefactor A, exponential power n and hopping frequency ω_p are in fact temperature dependent and this is a strong indication that hopping mechanism is the predominant mode of ionic conduction in CuS-C composite.

Key words : Composite superionic conductor, Impedance analysis, Hopping ionic conductivity, Hopping mechanism

ABSTRAK

ANALISIS IMPEDANSI AC KONDUKTOR SUPERIONIK KOMPOSIT CuS-C. Konduktor superionik komposit CuS-C telah berhasil dibuat melalui metode metalurgi serbuk. Respon frekuensi konduktivitas arus bolak-balik telah diukur menggunakan metode jembatan impedansi kompleks pada daerah suhu ruang, 100 °C dan 200 °C. Konduktivitas arus bolak-balik suatu konduktor superionik memiliki bentuk fungsional $\sigma = \sigma(0) + A\omega^n$. Frekuensi loncatan *hopping* ω_p diperoleh dari ekspresi baru $\sigma(0) = A\omega_p^n$. Data konduktivitas dianalisis untuk memperoleh parameter konduktivitas ionik dan laju *hopping* komposit konduktor superionik CuS-C. Plot *Arrhenius* konduktivitas menunjukkan perubahan *slope* mulus atau transisi pada 323 K atau 50 °C dan energi aktivasi konduksi ialah 0,154 eV. Data konduktivitas percobaan pada ketiga suhu pengukuran menunjukkan anomali pada frekuensi 9,0 kHz atau lebih tinggi. Pada rentang frekuensi mulai 0,1 Hz hingga 9,0 kHz kurva konduktivitas umumnya menunjukkan pola datar untuk semua suhu dan tidak diamati dispersi frekuensi. Harga konduktivitas DC diestimasi 0,5708 Scm^{-1}. Parameter konduksi ionik yaitu prafaktor A, pangkat eksponensial n dan frekuensi *hopping* ω_p menunjukkan ketergantungan pada suhu dan ini merupakan indikasi kuat bahwa mekanisme *hopping* merupakan modus dominan pada bahan komposit CuS-C.

Kata kunci : Konduktor superionik komposit, Analisis impendansi, Konduktivitas ionik loncatan, Mekanisme loncatan

INTRODUCTION

Copper based ionic solids, such as solid solutions, chemical compounds and composites have been a subject of study of physics for a long past [1-4]. The transport in such materials is partly or wholly governed by ions. Recently, one of the technologically very important electrolyte materials for all solid state batteries is the CuS compound. CuS compounds have been used in metallic nano-wires, either formed in break junctions or between a scanning tunnelling microscope tip and suitable substrates, and have been studied and used in molecular electronics and quantized conductance measurements [5]. Previous research on copper sulfides, resulted in the classification of copper-sulfides into three-groups, namely monosulfides, mixed monosulfide and disulfide (which is the subject of this research) and lastly copper disulfide [6]. Crystal structure and ionic

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conductivity of an Cu-S based compound have been studied [7]. Also it has been shown that silver nanowires can be reversibly grown between silver (or copper) and gold electrodes through a copper sulphide layer with wires exhibiting fractal geometry and spanning inter electrode distances of up to 1 cm through the solid electrolyte (copper sulphide) layer [8]. A thin film Li/copper sulphide on silicon battery has also been constructed. The application varies as miniaturized power source for applications including implantable medical devices, remote sensors, MEMS, smart cards and miniature transmitters [9]. Both CuS and AgS have been used as components in an electro-chemical cell as a volatile memory device [10].

The conductivity of an ionic conductor is determined by the rate at which they are able to hop from site to site in the material. The a.c. conductivity $\sigma(\omega)$ is found to vary with angular frequency ω as

$$\sigma(\omega) = \sigma(0) + A\omega^{n} \quad \text{....................................} \quad (1)$$

where $\sigma(0)$ is the d.c. conductivity, A is a temperature dependent parameter and n is found to take values 0 and 1. Jonscher [11] has suggested that this power law is a 'universal' property of materials that is related to the dynamics of hopping conduction. Almond *et al* have shown [12], that there is a simple relationship between $\sigma(0)$ and A. From the theory of random walk, the DC conductivity $\sigma(0)$ is related to the hopping rate ω_p of ions as follows:

$$\omega_p = (\sigma(0)/A)^{1/n} \quad \text{.......................................} \quad (2)$$

Another morphology of the CuS based ionic conductors is in the form of a composite, in which each constituent is expected to retain its own physical (conductivity) property. It is expected that the composite sample would exhibit the high ionic conductivity of the CuS compound enhanced by the addition of C as a composite constituent. So far not many research works have focused on composites of CuS. Previously this group have studied copper based alumina composites. In 2004, Purwanto *et al.* reported that copper based composite of alumina $(CuI)_x(\beta\text{-}Al_2O_3)_{1-x}$ (x = 0.1, 0.2 and 0.3) has the highest d.c. conductivity in the range of (1.99 – 16.1) x 10^{-4} S/cm for x = 0, and decreases with increasing addition of CuI, and at x=0.3 the ionic conductivity is only 1.62 x 10^{-5} S/cm [13]. The values for the ionic conductivity σ_O are quite low. As a continuation of the previous works, and also to find alternative composites with possibly better conductivity, another copper-based composite CuS-C have been prepared and the conductivity data analyzed. The purpose of adding C to form the composite is in order to enhance the ionic conduction of the sample, since the presence of C may provide more pathways for the ionic conduction. The crystal structure is investigated using the X-ray diffractometer, and the frequency- and temperature dependent conductivity data are analyzed to obtain the conduction and ionic hopping parameters using equations (1) and (2).

EXPERIMENTAL METHOD

The samples of CuS-C composite superionic conductor were prepared by solid state reaction. The appropriate quantities of CuS and C were mixed together, ground and pressed into pellets, and heated for 2 hours at 200 °C in Pyrex tubes and then quenched. The X-ray diffraction intensity was collected using the Phillips X-Ray diffractometer. Conductive silver paint is painted on the surfaces of the pellet samples to make good Ohmic contacts. The powder samples for electrical conductivity were pressed at 700 kgcm^{-2} into cylindrical pellets; the geometrical data is as follow, length is equal to 1.70 mm and the diameter is around 13.0 mm.Conductivity data is measured using the computerized RLC spectrometer located at the BKAN-PTBIN laboratory in the frequency range of 0.1 Hz – 0.1 MHz, at room temperature 100 °C and 200 °C.

RESULTS AND DISCUSSIONS

X-ray Diffraction

Rietveld refinements of the x-ray diffraction intensities show the composition to be 79% CuS and 21 % C. The refinement results are shown in Table 1. The lattice parameters *a* and c are shown with the reliability indices (R factors). The crystal system of the CuS compound and carbon is preferably the hexagonal model, represented by the Space group: P 63/m m c (VOL. I, 194).

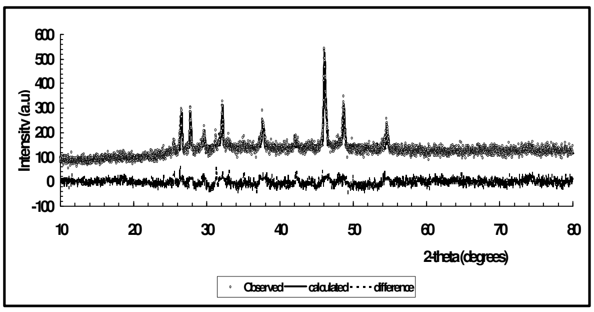

Figure 1. RIETAN results of the diffraction pattern of CuS-C composite sample.

Table 1. Refined structural parameters of CuS-C composite superionic conductor.

Phase[*)]	a (Å)[**)]	c(Å)	R_{wp} (%)	R_p (%)	R_F (%)	R_I (%)	"Goodness of Fit S"
CuS	3.754(7)	16.21(2)	17.25	11.83	17.98	17.51	1.20
C	2.428(2)	6.93(4)	17.25	11.83	18.80	17.83	
Composition	79%CuS and 21%C						

Frequency and Temperature Dependent Conductivity

The conductivity data pattern at several temperatures (room temperature, 100 °C and 200 °C) for CuS-C composite superionic conductor is shown in Figure 2. The data is clearly divided into two segments. For clarity, the two segments are reproduced in Figure 3 and Figure 4.

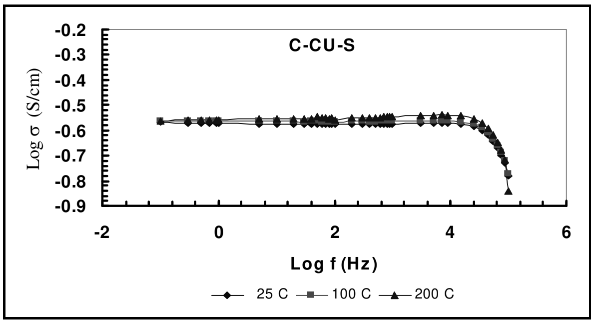

Figure 2. Frequency dependent conductivity data for CuS-C composite at various temperatures.

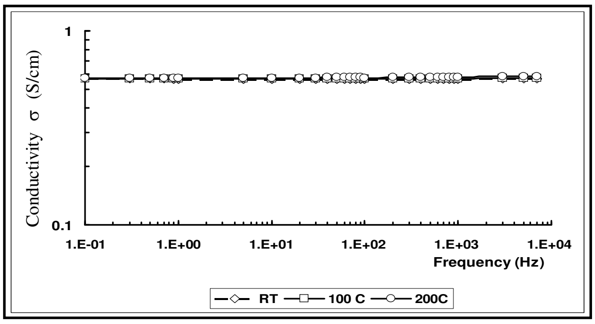

Figure 3. Frequency independent conductivity data for CuS-C composite at various temperatures.

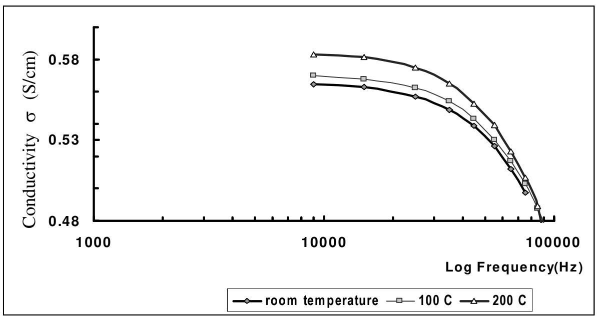

Figure 4. Anomalous frequency dependent conductivity data for CuS-C composite at various temperatures.

For frequencies from 0.1 Hz to up to 9.0 kHz the curve is mainly flat and practically no frequency dispersion is observed, this is shown in Figure 3 and the conductivity seems to converge to the steady-state value of 0.5708 Scm^{-1}. The experimental data for all temperatures shows a clear anomaly at frequencies of 9.0 kHz and higher, as shown in Figure 4. The frequency dependent part clearly indicates the predominance of ionic hopping conduction mechanism at these frequencies, and the ionic hopping rate ω_p could then be calculated by fitting the conductivity values to equation (1) and using equation (2).

Conductivity dispersion at the higher temperatures and higher frequencies is associated with electrode polarisation effects. The values of DC conductivity, $\sigma(0)$, as function of temperature are measured separately and plotted in conventional Arrhenius format as $\sigma(0)$ vs. $1000/T$ in Figure 5, where T is the absolute temperature.

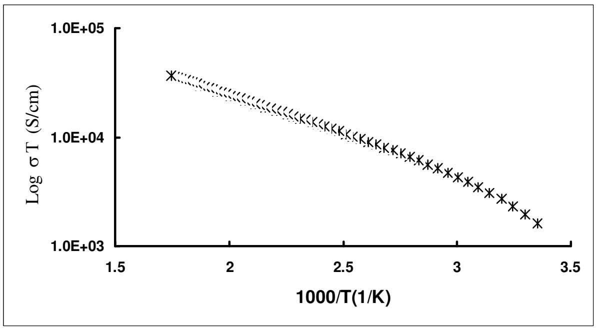

Figure 5. Arrhenius plot of σ vs. 1000/T

From the Arrhenius plot of the conductivity in Figure 5, there is a smooth slope change or transition at 323 K or 50 °C and the activation energy for conduction is found to be 0.154 eV. AC conductivity data at three temperatures were found to fit equations (1) and (2), providing the values of $\sigma(0)$, A, n and ω_p shown in Table 2.

Table 2. Parameters obtained in fitting a.c. conductivity measurements of CuS-C composite to $\sigma(\omega) = \sigma(0) + A\omega^n$

Temperature (K)	σ_O (Scm^{-1})	A ($Scm^{-1}rad^{-1/n}$)	n	ω_p (Hz)
Room temperature	0.5708	0.8474	0.0297	3,31 x 10^7
100	0.5708	0.969	0.0414	7,22 x 10^4
200	0.5708	1.0839	0.0518	3.52 x 10^3

It was observed from Table 2, that the values of A and n are strongly dependent upon temperature, indicating a hopping mechanism for ionic conductors [10]. The values of the parameter n and ion hopping frequency ω_p are also shown plotted as function of temperature T in Figure 6.

Kanno *et al* [2] reported smooth slope changes in the conductivity curves of $Rb_4Cu_{16}I_{7+x}Cl_{13-x}$ over a wide range of temperatures (110K-300K), due to dynamical ion correlation in the sample. Detailed structural study using neutron diffraction techniques by the same author showed that the movement of a copper ion from a Cu(1) site through faces shared by tetrahedra to four neighbouring sites namely, the Cu(3) site, another Cu(1) site or one of two Cu(2) site constitutes the most likely ion conduction mechanism in the samples.

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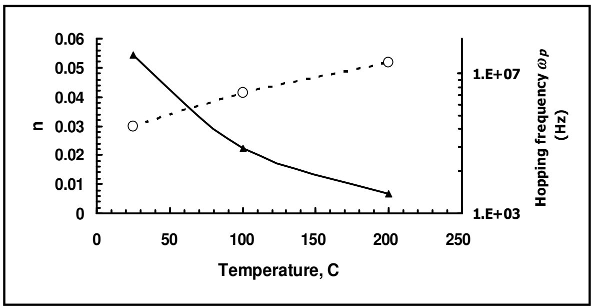

Figure 6. Plot of n (o) and ion hopping rates ωp (▲) versus temperature. The solid line is a guide to the eyes.

In an earlier work, Almond *et al* [10] contended that dynamical properties of ionic materials like β-alumina may be unified by the use of the "universal" dielectric response theory. In each case the response observed is attributed to the effects that many-body interaction amongst the ions have on relaxation processes. Dissado and Hill [11] have developed a microscopic theory which shows that in interactive many-body systems, dielectric perturbations decay after a short time as t^{-n}, rather than exponentially with time t. This in the frequency domain explains the ω^{n} dispersion in the conductivity, which has been suggested as a "universal" law by Jonscher. In this work it was shown that CuS-C compound appears to be an example which response is in support of this theory.

CONCLUSION

Using the analysis methods outlined above, the dynamical characteristics of AC conductivity, such as activation energies and ion hopping frequencies have been successfully utilized. The temperature activated properties confirmed. DC contributions to the overall conductivity have been estimated, and power law relationships between conductivity and frequency have been established for CuS-C compound. Smooth slope changes have been observed in the Arrhenius plot of the conductivity curves. The physical origin of this behaviour may be attributed to copper ion redistribution mechanism in the crystal lattice, as well as to conduction ions interaction in the samples. The results presented in this work seem to support the universal law of dielectric response in superionic conductors.

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