



FREQUENCY DEPENDENT CONDUCTIVITY STUDIES ON FAST ION CONDUCTING COMPOSITE ELECTROLYTE SYSTEM

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Abstract: Frequency-dependent ionic conductivity studies on new silver ion conducting two-phase composite electrolyte system: $(1-x)$ $[0.75\text{AgI}:0.25\text{AgCl}] : x\text{CeO}_2$, where $0.1 \leq x \leq 0.5$ in mol. wt. (%), are reported here in this paper. CeO_2 has been dispersed in a “quenched/annealed $[0.75\text{AgI}:0.25\text{AgCl}]$ mixed system/solid solution” to obtain two phase composite electrolyte system. Here $[0.75\text{AgI}:0.25\text{AgCl}]$ has been established a better host salt which yields better silver ion electrolyte systems by Agrawal & Coworkers. The composition dependence of electrical conductivity was carried out on the system, to identify the optimum conducting composition (OCC). The present system exhibits highest conductivity at composition $x = 0.15$ (i.e., composite electrolyte system: $0.85 [0.75\text{AgI}:0.25\text{AgCl}]:0.15\text{CeO}_2$) prepared by melt quench method has already reported earlier. The conductivity data as a function of frequency was also studied and plotted at different temperatures for a two-phase composite electrolyte system prepared by two different routes. It has been observed from these investigations that the dispersion is attributed to low-frequency regions. ($f < 1\text{KHz}$) which is associated with electrode polarization effects.

Index Terms - Frequency, Conductivity, Ionic Conductivity, Polarization Effect, Composite Electrolyte System

I. INTRODUCTION

The study of ion transport behavior in solids electrolytes has been drawing considerable attention in the recent year due to their high ionic conduction at ambient temperature. These materials exhibit high ionic conductivity, and unique transport behavior and potential application towards solid state batteries, fuel cell, sensor and electrochromic display devices etc. [1-3]. Composite electrolyte systems are separate and special class of these solid electrolytes, which are also considered as two-phase electrolyte systems. A large number of investigations have already reported earlier [3-8]. A significant enhancement in ionic conductivity by the dispersion of second phase materials so these also referred as “dispersed solid electrolyte system” which have become important for scientists for their applications in power source devices [7-10]. A newly synthesized two-phase composite electrolyte system $(1-x) [0.75 \text{AgI} : 0.25\text{AgCl}] : x \text{CeO}_2$ has been synthesized by different routes of material preparations and then investigated & characterized by various techniques such as transport properties measurements were done by IS Technique. Also, it is characterized by XRD and MDSC (Thermal Characterization) these investigations have been carried out and reported [11-12]. In the present study the following investigations and studies are reported here in this paper are as:

1. Ionic conductivity as a function of frequency for composite electrolyte system: $(1-x) [0.75 \text{AgI} : 0.25\text{AgCl}] : x \text{CeO}_2$ at room temperature,
2. Ionic conductivity as a function of frequency for OCC: $0.85 [0.75\text{AgI} : 0.25\text{AgCl}] : 0.15\text{CeO}_2$ (quenched and annealed) at different temperature

II. EXPERIMENTAL DETAILS:

(a) Sample preparation: Commercially available extra pure chemicals AgI, AgCl [Purity >98% Reidel (India)] and CeO_2 [purity >99% Loba pvt. Ltd. (India)] were used for sample preparation. Homogeneous mixture of $(1-x)[0.75\text{AgI}:0.25\text{AgCl}] : x\text{CeO}_2$ in different mol. wt. % ($0.1 \leq x \leq 0.5$) were heated and then cooled rapidly to $\sim 10^\circ\text{C}$ with the quenching rate of $\sim 10^2 \text{K/sec}$. Optimum conducting composite electrolyte system: $0.85[0.75\text{AgI}:0.25\text{AgCl}]:0.15\text{CeO}_2$ was heated at $\sim 700^\circ\text{C}$ for different soaking time in electric furnace, than cooled rapidly. Highest conductivity was achieved at ~ 10 min soaking time, referred as Optimum conducting composition (OCC). Similar composition was also heated at $\sim 700^\circ\text{C}$ for 10 minutes soaking time and then left to cool in the electric furnace referred as “Annealed system”. The detail of sample preparation has already been reported [11-12].

(b) Ionic Conductivity as a function of temperature and frequency: In the present investigation, the true bulk resistances of the composite electrolyte systems were computed from the complex impedance plots with the help of LCR Bridge (HIOKI, model 3532-50, Japan) operating in the frequency range of 42 Hz to 5MHz. Colloidal silver paint was used as reversible (non-blocking) electrodes. Temperature and frequency dependence studies were carried out by placing the whole sample holder along with specimen in an insulated laboratory-built electric furnace. The dc conductivity has been obtained from $\log \sigma$ vs. $\log f$ plots, and was compared with ac conductivity. The detail of measurement of ionic conductivity as a function of composition and temperature were done and reported earlier [11-12].

III. RESULTS AND DISCUSSION:

To determination of dc conductivity as a function of composition and temperature, the conductivity has been studied as a function of frequency. Figure 1 represent the Log σ vs. log f plots for two-phase composite electrolyte at different composition of x (x = 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, 0.5) at room temperature. The conductivity data as a function of frequency was also plotted at different temperature for two-phase composite electrolyte system prepared by two different routes [11-12] as shown in Figure 2 & Figure 3.

depicted by region -I & region -II. The frequency dependence of conductivity is observed at higher frequency region and follows the Jonscher's power law [13 -17]. The temperature and composition dependence of dc conductivity $\sigma(0)$ is extracted from frequency independent plateau region of these plots. The behavior of conductivity with frequency is akin to those of two-phase composite electrolyte system: 0.9[0.75AgI: 0.25AgCl]: 0.1TiO2 as reported by us [18]. It is clearly seen in both the Figures that, at lower frequencies, the conductivity assumes a constant plateau value ' σ_{dc} ' which dispersion sets in at higher frequencies. As temperature increase the plateau value of dc conductivity (σ_{dc}) also increase. Finally, the high frequency dispersion region almost disappears at higher temperatures; since the jump frequency of the charge carriers increases with temperature.

The phenomenon of the conductivity dispersion in the high frequency region is analyzed using the power law exponent:

$$\sigma(\omega) = \sigma(0) + A \omega^n \tag{1}$$

where $\sigma(\omega)$ is conductivity at particular frequency, $\sigma(0)$ is dc conductivity of the sample at $\omega = 0$, A is a constant for a particular temperature and n is the power law exponent and varies from 0 to 1 ($0 < n < 1$). Composition & temperature dependence of dc conductivity (σ_{dc}) or (σ_0) is extracted from frequency independent plateau region. Furthermore, an abrupt jump in the conductivity value is observed at temperature around 135°C & at 145°C in Figure 2 & Figure 3 respectively, which corresponds to $\beta \rightarrow \alpha$ - like phase transition of the host salt in the region -I & -II.

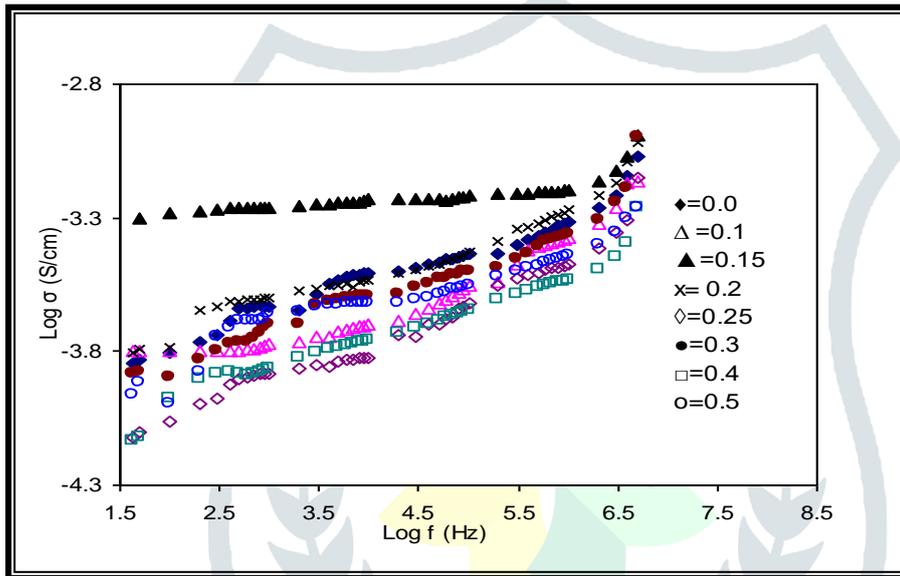


Figure 1. Log σ vs. log f plots for composite electrolyte system: (1-x) [0.75 AgI: 0.25AgCl]: x CeO2 at room temperature

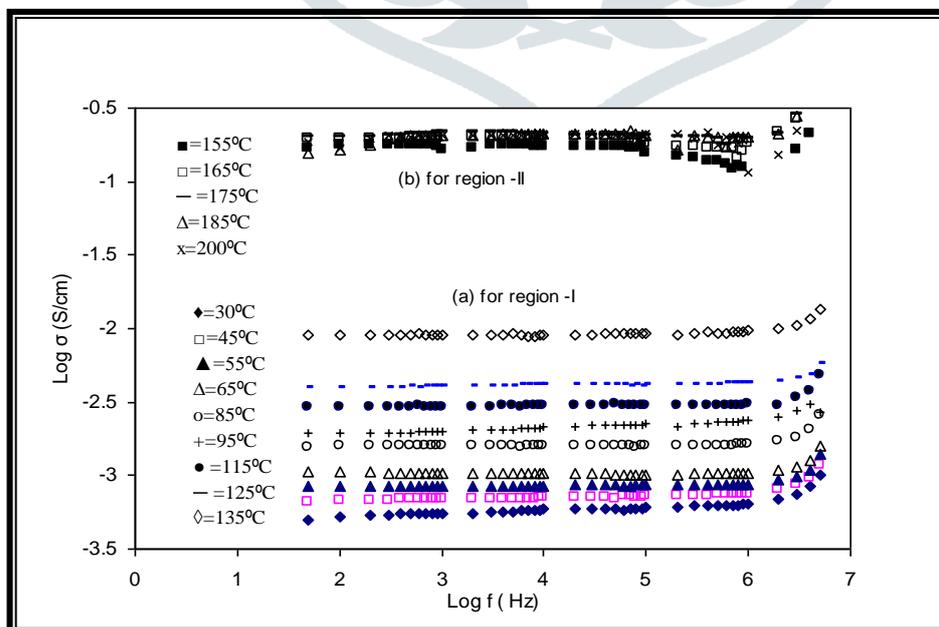


Figure 2. Log σ vs. log f plots for OCC: 0.85 [0.75 AgI: 0.25AgCl]: 0.15CeO2 (quenched) at different temperature

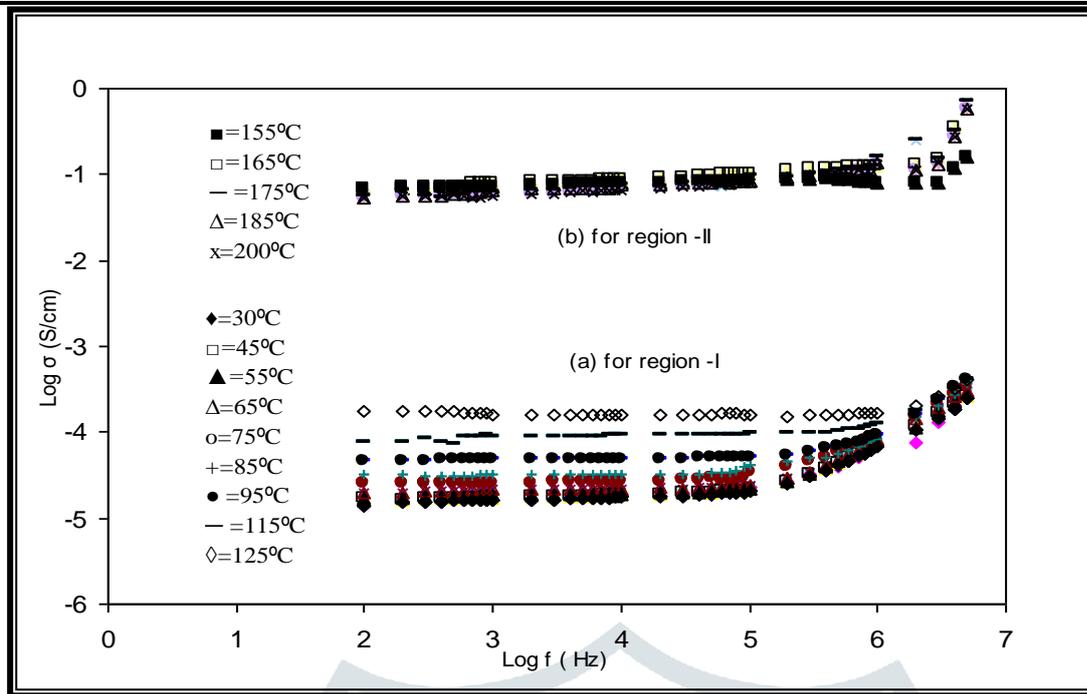


Figure 3 Log σ vs. log f plots for OCC: 0.85 [0.75 AgI: 0.25AgCl]: 0.15CeO₂ (annealed) at different temperature

IV. CONCLUSIONS:

A fast Ag⁺ ion conducting two-phase composite electrolyte system: (1-x) [0.75AgI:0. 25AgCl]: xCeO₂ and optimum conducting composition 0.85[0.75AgI:0. 25AgCl]:0. 15CeO₂ has been investigated and studied, the frequency dependence of ionic conductivity of this composite system has been analyzed. It is concluded from figure 1 the dispersion is attributed at low frequency region ($f < 1\text{KHz}$) which is associated with electrode polarization effects. The conductivity data as a function of frequency was also plotted at different temperature for OCC of this two-phase composite electrolyte system It is found in all three Figures (1, 2 & 3) that conductivity is almost independent at lower frequency region (plateau region) which corresponds to dc conductivity value and the high frequency ($f > 1\text{MHz}$) dispersion is predominant in the plots.

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