Ionic Transport in Nano-Heterogeneous Structured Materials[1]

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Summary

Although the concept of ”coupling-decoupling” by A.Angell is useful to characterize the ionic transport in supercooled liquid and glasses, another factor of ”percolation probability” is also of importance in complex materials. In case of organic-inorganic hybrid glasses, the ion conduction channel of AgI is interapted by organic ions to show a percolation transition from superionic to insulator at low AgI composition. Also in chalcogenide glasses, a transition from semicondctor to superionic conductor is seen at a silver concentration. This transition is accompanied by spinodal decomposition due to the large concentration fluctuation in the supercooled liquid state. Thirdly, a proton conducting polymer membrane of Nafion also exhibits a percolation transition at low water content region, which is due to a possible isolation of the inverse micels of the polymer and water.

1. Introduction

Ionic transport in supercooled liquid, glass and complex maters has been studied for more than three decades mainly from fundamental interests [1-3]. Recently it has been recognized also of great importance in engineering purpose especially for energy devices. For example, fast lithium ion motion in glass and polymer is now used for lithium ion batteries. Also, fast proton transport in polymer membrane is applied for fuel cells [4,5]. In these applications, the ionic conductivity of lithium or protons in electrolytes is a key factor of the performance, which should be as high as 10^{-1} to 10^{-3} S/cm in operating conditions. However, the ionic conductivity of these materials is strongly dependent on the environment conditions, especially on temperature and humidity, which is a serious restriction of the device performance.

In order to improve the device performance, it is necessary to know the ionic transport mechanism in not only simple liquids and crystals but also in so called complex matters such as complex liquids, glasses, polymers, and their composites. This is still remaining as a wide frontier field in science in comparison with the well sophisticated methodology for crystalline solids [6]. Thanks to the concept of “coupling and decoupling” by A. Angel [2], we have one guiding principle for searching high ionic conductivity in complex system; i.e. the mobile ion should be decoupled from the surrounding other ions and molecules by optimizing the chemical bond strength, coordination number, etc. Although this concept is of great importance in developing new ionic conductors for applications, there are some exceptions which can not be explained by simple coupling-decoupling concept.

One example is demonstrated in case of “organic-inorganic hybrid glasses”, which is composed of silver iodide (AgI) and some organic molecules, where the conductivity depends strongly on the amount of AgI to show a transition from superionic conductor to insulator [7]. Another is so called “mixed ion effect”, where ionic conductivity shows drastic decreasing when two mobile ions are mixed, ex. Na and Li in B_2O_3 glasses [8]. In both cases, the mobile ion is found to be decoupled from surrounding counter anions to allow the ion to move fast. However the observed conductivity

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shows very low, almost insulating, in some compositions. Now, these anomalous behavior of conductivity is believed to be relating to a "percolation transition", which is a special feature of the complex materials not observed in simple liquids or single crystals of homogeneous structure [9,10].

The authors have been investigated the composition dependence of ionic conductivity in some different systems; among them are found some interesting evidence of the percolation transitions in ionic conductivity all are relating to the heterogeneous structure in nano-meter scale. In this paper are shown some different examples of the importance of "percolation transition" for ionic transport in complex materials. One is organic-inorganic hybrid superionic glasses, 2nd is a silver chalcogenide glasses, and third is a proton exchange membrane of Nafion.

2. Organic-Inorganic Hybrid Glasses

First example is the organic-inorganic hybrid glasses composed of AgI and alkylammonium iodides [7,10,11]. The AgI is know to have high silver ion conductivity up to 1 S/cm above 150 °C, but is unstable at room temperature. However, if it is solved in organic substances, the silver ion conductivity still remains high up to 10^{-2} S/cm at room temperature. Thus, various organic materials have been hybridized so far with silver, copper and lithium ion conductors with organic molecules.

However, the ionic conductivity has been found strongly depend on the glass composition. An example is shown in figure 1, which is plotted as a function of the volume fraction of AgI. It is seen a clear transition from insulator to superionic state. The origin of this behavior is relating to the nano-scale heterogeneity observed by SAX experiments as shown in Figure 2, where clear intermediate range ordering is seen at 1Å^{-1}. Ionic conductivity shows large frequency dependence, which shows high conductivity in microwave (10 GHz) frequency even the insulator region of DC conductivity [7,10,11].

All these evidences strongly suggest that the silver ions are decoupled from surrounding iodine matrix and are moving fast in nano-scale domains, but are not diffuse to infinity due to the blocking of the percolation pass by the organic molecules. The conductivity is analyzed based on the percolation scaling formula [9,10] as,

$$\sigma[\phi]\approx(\phi-\phi_0)^{\mu} \tag{1}$$

which is in good agreement with the experiments.

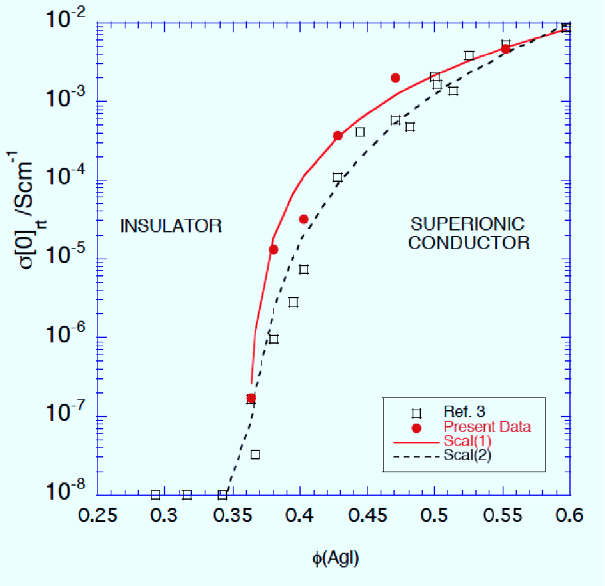

Fig.1 Ionic conductivity of AgI-alkylammoniumiodide glasses compared with scaling formula of eq. (1) [from Ref. 11].

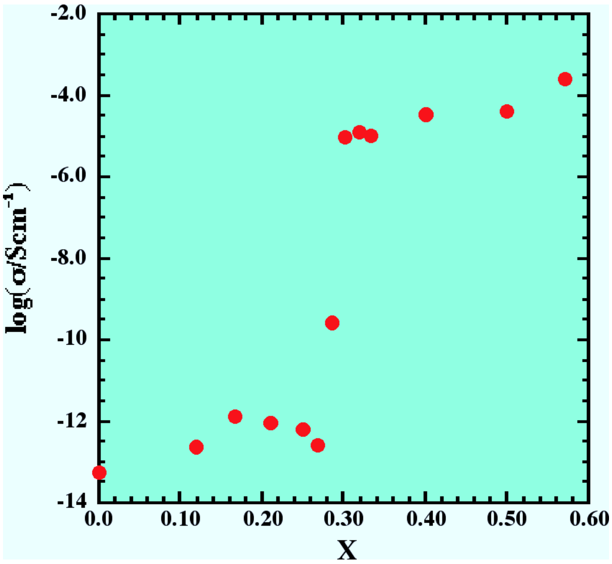

Fig.2 Ionic conductivity of Ag_x-$(GeSe3)_{1-x}$ glasses at room temperature

3. Silver Chalcogenide Glasses

Since the discovery of chalcogenide semiconductor glasses in 1950 th., there have been reported a large number of studies on the electrical properties

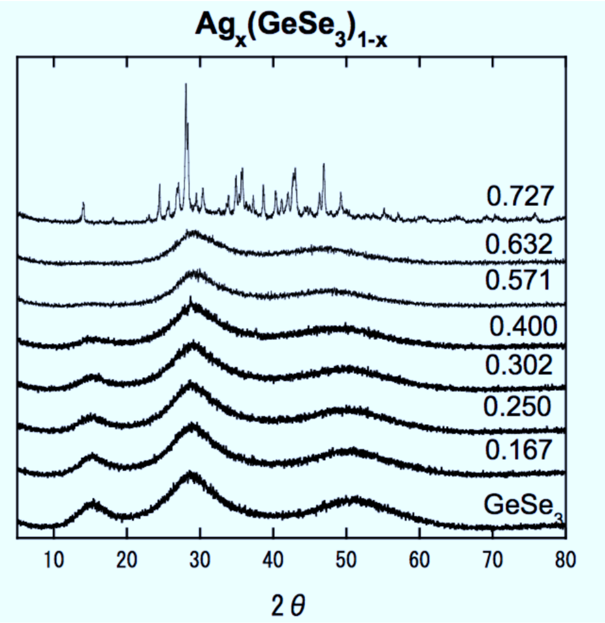

Fig.3 X-ray diffraction of Ag$_x$(GeSe$_3$)$_{1-x}$ glasses: ⟶ shows the FSDP.

of similar glasses [12,13]. In particular, the chalcogenide glasses containing silver have some interesting photo-electrical properties such as photo-doping, photo-deposition, photo-voltage, photo-chemical modification etc. These unique phenomena are probably related to both electronic (or hole) and silver ionic transport triggered by photo-excitations, however the detailed mechanism of which is still unsolved.

Among them, Ag-Ge-Se(S) system is known to show strange photoelectrical behavior such as photo doping, semiconductor-superionic conductor transition etc [13]. In figure 2 is shown a composition dependence of the conductivity of Ag-Ge-Se glasses, which depends strongly on the concentration of the amount of silver. The sudden increase in conductivity is observed at silver composition $x = 0.3$, below which the glass is hole conducting semiconductor and jumps to fast silver ionic conduction above $x = 0.3$ [14].

Another interesting character of the chalcogenide glass is an appearance of so called first sharp diffraction peak (FSDP) at about $q = \text{Å}^{-1}$, which corresponds to a intermediate range order between layer-like region of Ge-Se networks. X-ray or neutron diffraction of a Ag-Ge-Se glass shows a pronounced FSDP at $q = 1.0\text{Å}^{-1}$, however, when the amount of silver or the temperature is increased the intensity of the FSDP decreases as shown in figure 3; the disappearance of the FSDP is at the same composition of the conductivity transition in case of Ag-Ge-Se glasses.

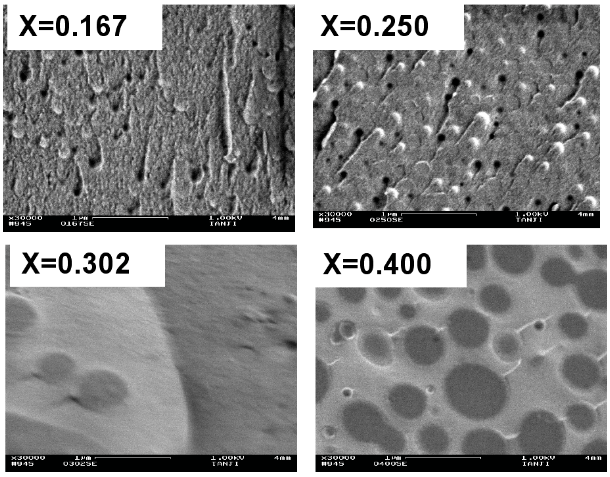

Fig.4 FE-SEM pictures of Ag$_x$(GeSe$_3$)$_{1-x}$ glasses at different compositions x.

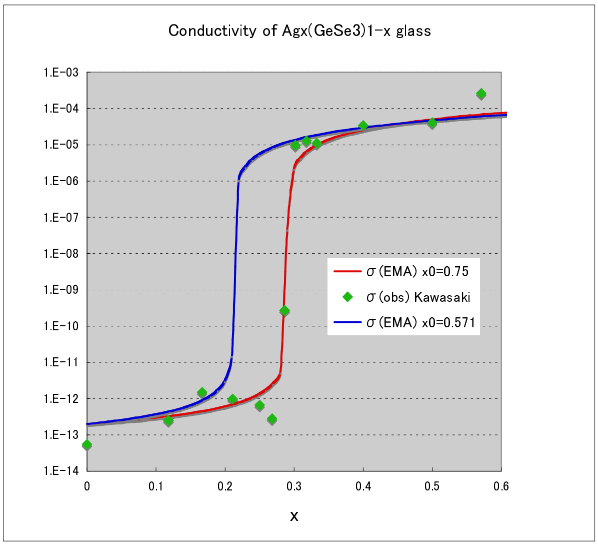

Fig.5 Comparison of the conductivity values calculated from Effective Medium Approximation (EMA) and experiment on Ag$_x$(GeSe$_3$)$_{1-x}$ glasses:

The origin of this jump is now attributed to a nano-scale phase separation due to the immiscibility, which is evidenced by recent FE-SEM measurements shown in figure 4, where clear phase separation in nano to micro meter scale is observed [15,16].

The macroscopic conductivity observed in figure 3 is now considered as a result of the heterogeneous structure of the glass. then we can employ theoretical formula to calculate the conductivity of the heterogeneous medium. One simplest way is effective medium approximation (EMA) [9], in which the each constituent domain with conductivity σ_i is considered to be embedded in the effective medium with conductivity of σ_m, the polarization of the domain should be consistent to the surrounding to give rise to the following condition for the effective medium conductivity σ_m.

$$\left\langle \frac{\sigma_i - \sigma_m}{\sigma_i + 2\sigma_m} \right\rangle = \sum_i \eta_i \frac{\sigma_i - \sigma_m}{\sigma_i + 2\sigma_m} = 0 \tag{2}$$

where, η_i is the volume fraction of the component i.

A tentative result of the calculation using eq. 2 is shown in figure 5, where the two different compositions x0 are assumed for the second phase. The result is fairly in good agreement with the experimental results although the estimated composition (x0=0.75) is larger than that of determined EPMA analysis (x0=0.571).

The existence of heterogeneous structure of chalcogenide glass is relating to the dynamical concentration fluctuation in supercooled liquid state of this material, where the two locally stable structures are competing with each other to show two minima in free energy diagram to result in spinodal or binodal decomposition tendency. In this case, some NMR and Raman scattering data suggest that the stability of edge and corner sharing of $GeSe_4$ units are probably relating to this fluctuation.

4. Proton Exchange Membrane & Water

In case of a proton exchange polymer membrane as Nafion 117, which is used for fuel cells, the ionic conductivity strongly depends on the humidity of the environment. The main reason is the water content in the membrane depends on the humidity and the proton conductivity strongly depends on the water contents [17].

We have recently investigated the relation between the water content of the membrane and the mobility of protons in the membrane by using pulsed field gradient NMR (pfg-NMR) [18]. The amount of the water molecules in the membrane is evaluated by NMR and is plotted as a function of relative humidity RH shown in figure 6. In combining the DSC measurements, we can evaluate the freezing and non freezing water in the membrane.

The diffusion coefficient of proton is plotted in figure7 scaled by pure water value as a function of

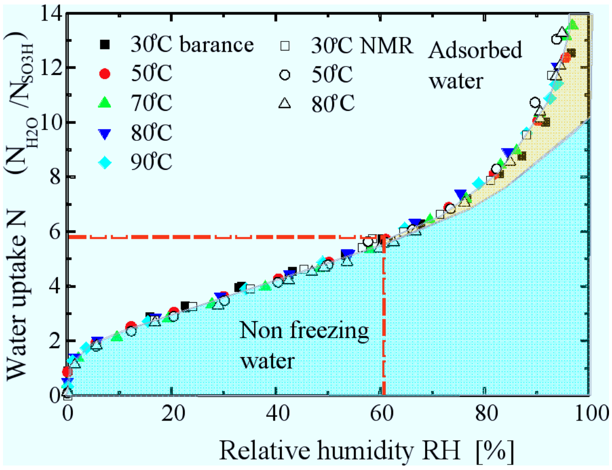

Fig.6 Water uptake ratio of Nafion 117 membrane as a function of relative humidity RH.

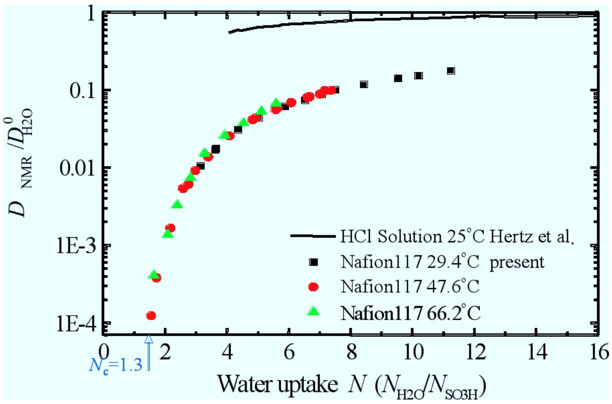

Fig.7 Diffusion coefficient of protons in Nafion 117 membrane as a fucntion of water uptake ratio N.

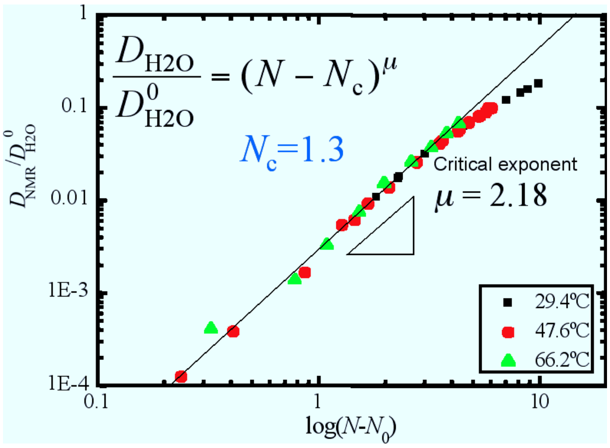

Fig.8 Scaling plot of diffusion coefficient of Nafion 117, where the peroration threshold $N_c = 1.3$ is used.

water uptake ratio N.

Here is also seen a clear transition from high proton diffusing region to insulator at $N\sim1.3$. Here, the origin of this transition is due to the nano-micelle structure of the Nafion and water system. At high water content region the inverse micelles containing acid water inside are connecting with each other, however they are separated into the isolated micelles below N_c.

5. Summary

As the summary of these observations in various materials, it can be concluded that the percolation problem is often effective to the ionic transport in complex matter as ion conducting glass, polymers and composite materials. The origin of this phenomenon is the concentration or compositional fluctuation in complex liquids, which tends to create various kinds of heterogeneous structure in nano to submicron scales. Although it is time fluctuating in liquid state (dynamical fluctuation), it is frozen into static inhomogeneity in glassy state. Ionic conduction in these inhomogeneous structure is dominated by the migration through conduction channels. The transport in the random conduction channel is well characterized by percolation theories.

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