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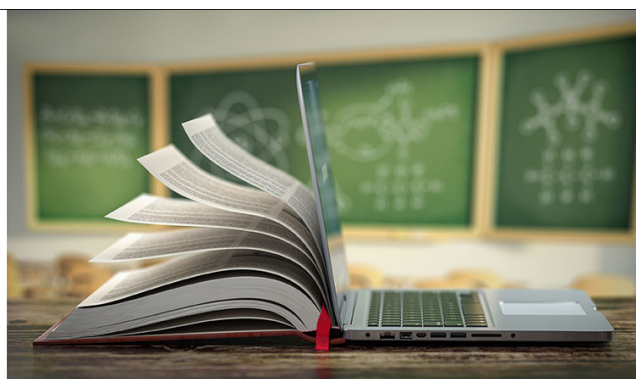
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RAPID COMMUNICATION

Role of the dielectric constant of ferroelectric ceramic in enhancing the ionic conductivity of a polymer electrolyte composite

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Online at stacks.iop.org/JPhysD/36/L93**Abstract**

The effect of dispersal of ferroelectric ceramic materials $\text{Ba}_{0.70}\text{Sr}_{0.30}\text{TiO}_3$ ($T_c \approx 30^\circ\text{C}$) and $\text{Ba}_{0.88}\text{Sr}_{0.12}\text{TiO}_3$ ($T_c \approx 90^\circ\text{C}$) on the ionic conductivity of an ion conducting polymer electrolyte (PEO : NH_4I) is reported. The addition of 3 wt% of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ($x = 0.30$ and 0.12) results in an increase in the conductivity by one to two orders of magnitude. Further, a study on the temperature dependence of conductivity of these composites shows that the conductivity enhancement ‘peaks’ as we approach the dielectric phase transition of the dispersed ferroelectric material where the ϵ changes rapidly from ~ 2400 to 7500 (for $x = 0.30$) and from 1100 to 5500 (for $x = 0.12$). This establishes the role of dielectric constant of the dispersoid in enhancing the ionic conductivity of the polymeric composites.

Ion conducting polymers are becoming increasingly important because of their application in solid state polymer batteries and fuel cells. The polymer films that can be used in electrochemical devices should be mechanically and chemically stable as well as highly ionically conducting. One class of polymer electrolytes that are widely studied is the ‘polymer–salt complex’ in which a dissociable salt is complexed with a polar polymer (polyethylene oxide (PEO); polypropylene oxide (PPO), etc.). Many good lithium ion conducting polymer electrolytes have been developed [1–4] by complexing polar polymers (e.g. PEO) with lithium salts like lithium perchlorate, lithium triflate, lithium tetrafluoroborate (LiBF_4), etc. Apart from Li^+ -ion conducting polymers, good proton (H^+) ion conducting polymer electrolytes have also been obtained by complexing ammonium salts [5–7] with polar polymers. To enhance the ionic conductivity, various approaches that have been pursued are to: (a) change the type of complexing polymer, (b) use polymers with

different chain lengths, (c) use different complexing salts, (d) modify the degree of crystallinity by using plasticizers and copolymerization, (e) form ‘composites’ by the dispersal of neutral/chemically inert fillers. Forming ‘composites’ by the dispersal of ceramic fillers is a very promising approach as it can enhance the conductivity as well as provide mechanical strength to the polymeric film. The mechanism of conductivity enhancement has been extensively studied [8–10] for crystalline–crystalline composites. The two important mechanisms suggested for the conductivity enhancement of these composites are:

- Adsorption–desorption model of Maier [8], who proposed that the ionic charge carrier concentration at the interface increases in the composites.
- Percolation model due to Bunde *et al* [10], who introduced the idea of the presence of a high conductivity path at the interface which develops connectivity or ‘percolation’ at a certain composition threshold of the dispersoid. The

situation in the case of the polymer composites is more complicated because the dispersal of a 'filler' changes the polymeric structure/morphology. Some of the important additional factors to be considered for the polymeric composites are:

- (i) change in glass transition temperature (T_g) and melting temperature of the polymer (T_m),
- (ii) change in the degree of crystallinity,
- (iii) size of the dispersoid particle because the interface contact area changes inversely as the radius of the particle ($1/r$), since the surface to volume ratio is approximately proportional to $(1/r)$,
- (iv) nature of the dispersoid, which may be acidic, alkaline or amphoteric.

We show in this paper that the dielectric constant of the dispersoid is also a controlling factor. To fulfil our motivation and to establish unambiguously the role of dielectric constant of the dispersoid in modifying the ionic conductivity of the polymer electrolyte, we have designed the composite used in our study in such a way that it avoids the confusion arising out of the factors listed above, as explained later in this paper.

The dielectric constant of the dispersoid is expected to change the ion transport in the polymer electrolyte since its presence modifies the local electric field distribution inside the polymeric composite ionic matrix. In the presence of dispersed 'ferroelectric' particles of dielectric constant higher than that of the basic polymer electrolyte ionic matrix, the electric field lines get modified such that the field would be higher 'near the interface' of the polymer and the high dielectric constant dispersoid (i.e. ferroelectric). This can have either of the following two effects:

- (a) the 'effective' conductivity due to the movement of the mobile ions near the interface may increase, as the effective local field for the same applied potential is higher; or
- (b) the dissociation of the complexed salt [11] in the polymer near the interface may increase resulting in an increase in the number of free mobile charge carriers ' n ' (and hence enhancement of the net conductivity) since $n = n_o \exp(-U/2\epsilon kT)$; where U is the dissociation energy.

In general, the high dielectric constant of the dispersoid may enhance n , the effective μ or both, resulting in an increase in the overall conductivity.

For experimentally verifying the above statements, a possible experiment could be to choose 'different dispersoid materials with widely different dielectric constants'. An argument against this is that the resulting effect in conductivity enhancement would not only be due to the dielectric constant but also will be the combined effect of factors (i)–(iv) discussed above. All the factors (including dielectric constant) are not mutually exclusive and hence it is experimentally difficult to 'unambiguously establish' the role of each separately. This constraint forces us not to change the type of dispersoid. Yet, our requirement is to create a condition of measurement such that the dielectric constant 'changes significantly'. To obtain these conditions, we chose a 'ferroelectric material' as dispersoid with 'dielectric phase transition' in a temperature range over which the changes

in the conductivity of the polymer electrolyte can be easily measured. The polymer electrolyte chosen by us is PEO : NH₄I (80 : 20 wt%) [7] in which a modified BaTiO₃ ferroelectric ceramic (Ba_{1-x}Sr_xTiO₃) is dispersed. It has been found earlier [12] that by changing x the dielectric phase transition temperature changes and can be so adjusted that it falls in the desired temperature range in which the conductivity can be easily measured. The choice of ' x ' (and corresponding transition temperature) of the dispersoid is 'crucial' to our experiment since PEO has $T_m \sim 60^\circ\text{C}$ above which the film becomes amorphous and the conductivity rises suddenly. We have chosen two values of ' x ', viz, $x = 0.30$ with $T_c \sim 30^\circ\text{C}$, which is lower than the T_m of PEO, and $x = 0.12$ with $T_c \sim 90^\circ\text{C}$, which is above the T_m of PEO.

The Sr²⁺ modified BaTiO₃ ferroelectric ceramic, abbreviated as BST, was prepared using a novel semi-chemical route. First, we take stoichiometric amounts of BaCO₃ and SrCO₃ powders. The solutions of their nitrates, i.e. Ba(NO₃)₂ and Sr(NO₃)₂, were then obtained by dissolving these carbonates in minimum amount of dil. HNO₃. These nitrate solutions were then mixed together. Forced coprecipitation was carried out using saturated solution of ammonium carbonate so as to obtain Ba_{1-x}Sr_xCO₃ precipitate. The precipitate was thoroughly washed using distilled water so as to ensure that no ammonium ions remain stuck to the host matrix atoms. The filtrate is checked for the absence of Ba²⁺ and Sr²⁺ ions. After drying the precipitates at $\sim 100^\circ\text{C}$, x-ray diffractogram is collected to check the existence of only a single phase of Ba_{1-x}Sr_xCO₃ and to ensure the absence of undesirable phases. For the preparation of BST, TiO₂ powder and Ba_{1-x}Sr_xCO₃ were taken in the correct stoichiometric amounts and were hand mixed for 2 h followed by ball milling for 6 h in an agate jar having agate balls. Acetone was used as mixing media. This mixed powder was calcined at 1150°C for 6 h. Once again, the x-ray diffraction was recorded to check the single-phase formation of BST. To break the agglomerates, which get formed during the calcination stage, the calcined powder was once again ball milled for 2 h. For the purpose of sintering, disc shaped pellets (of diameter 12 mm and thickness 1 mm) were prepared at an optimum load of 80 kN using 2% polyvinyl alcohol (PVA) solution as binder. To remove PVA from the pellets, the pellets were heat treated at 500°C for 10 h. Sintering was carried out at 1300°C for 6 h and dense (99%) ceramic pellets were then obtained. Fine powders of BST was first obtained by crushing the sintered pellets in an agate pestle-mortar and then sieving it by using a 400 mesh sieve. Before dispersing this in the polymer, a highly viscous solution of the complexed polymer electrolyte is first obtained. PEO (mol. wt. 6×10^5) was dissolved in methanol to which 20 wt% of NH₄I was added and stirred at 40°C by a magnetic stirrer for 4–5 h. Then, the fine powder of BST (3 wt%) was added and again stirred thoroughly till the solution became highly viscous. This viscous solution was poured in a polypropylene petri dish and solution casted films were obtained after thoroughly drying in air followed by vacuum drying. Our earlier study on the composition dependence of this composite has shown [11] that the composite with 3 wt% of BST has highest conductivity and so this composite was chosen for this work. The bulk conductivity was evaluated by complex impedance spectroscopy [13, 14] technique using a Hioki Hi

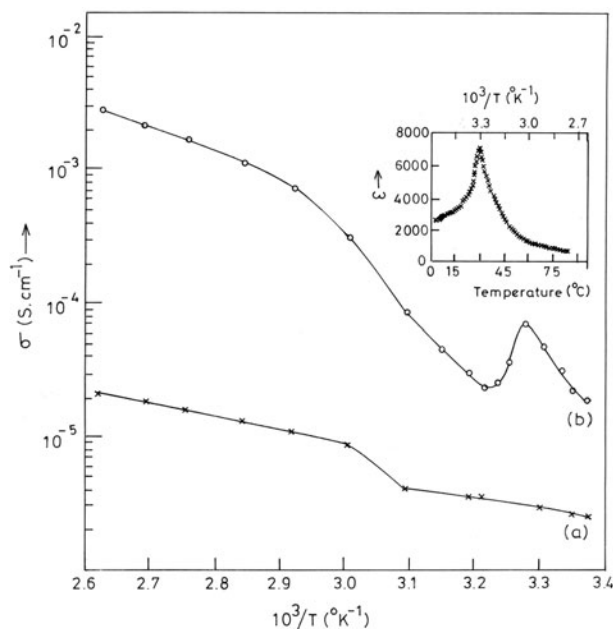


Figure 1. Temperature dependence of conductivity for (a) (PEO : NH₄I) electrolyte and (b) its composite with ferroelectric ceramic, viz (PEO : NH₄I) + 3 wt% Ba_{0.70}Sr_{0.30}TiO₃ at 70% relative humidity of the ambient. The inset shows the temperature dependence of the dielectric constant of BST at a frequency of 1 kHz.

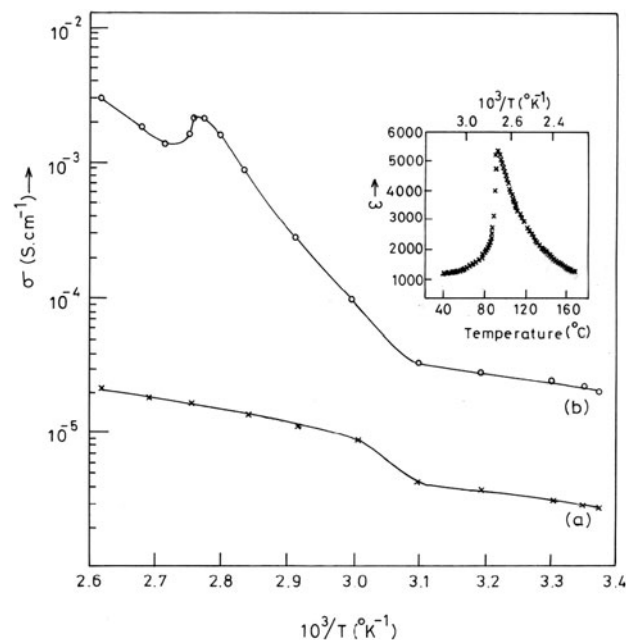


Figure 2. Temperature dependence of conductivity for (a) (PEO : NH₄I) electrolyte and (b) its composite with ferroelectric ceramic, viz (PEO : NH₄I) + 3 wt% Ba_{0.88}Sr_{0.12}TiO₃ at 70% relative humidity of the ambient. The inset shows the temperature dependence of the dielectric constant of BST at a frequency of 1 kHz.

Tester model 3520 in the frequency range of 40–100 kHz. The dielectric constant was measured using a Hioki Hi Tester 3532.

The values of the dielectric constant of BST at different temperatures for $x = 0.30$ and 0.12 are shown as ‘insets’ in figures 1 and 2. The dielectric constant for the $x = 0.30$

sample at the low temperature end, i.e. at $T \sim 20^\circ\text{C}$, is 2400. It suddenly peaks to a value of 7500 at $\sim 30^\circ\text{C}$ and then decreases again to 700 or lower. For the case of BST with $x = 0.12$, we observe a similar change in the dielectric constant at its transition temperature $T_c \sim 90^\circ\text{C}$ (ϵ at 20°C is 1100 and ϵ at 90°C is 5500).

The σ vs $1/T$ plot for polymer electrolyte composite (PEO : NH₄I) + 3 wt% Ba_{1-x}Sr_xTiO₃ ($x = 0.30$) is shown in figure 1 along with that for the PEO : NH₄I polymer electrolyte without the dispersoid. It is to be noted that the values of σ for the polymeric samples with and without the dispersoid were measured at the same relative humidity of $\sim 70\%$ for a meaningful inter-comparison of the two values (since PEO : NH₄I, being a proton conductor, shows strong humidity dependence). It is obvious from figure 1 that the dispersal of BST has resulted in an overall increase in the conductivity of the polymer electrolyte. Further, we see that the conductivity increases rapidly and peaks (at 34°C) as we pass through the dielectric phase transition temperature ($T_c \approx 30^\circ\text{C}$), establishing the role of dielectric constant in conductivity enhancement. The conductivity peaking temperature ($T \approx 34^\circ\text{C}$) is slightly higher than the actual T_c of 30°C . Without effecting the general conclusion about the role of dielectric constant in the conductivity enhancement, this small difference in the peaking and dielectric phase transition temperature could be due to one or more of the following reasons: (a) the σ vs $1/T$ measurement was a dynamic measurement and hence effective T may be different; (b) in a composite, being a heterogeneous dielectric system, the dielectric phase transition temperature may slightly differ; or (c) the presence of the dispersoid may change the T_g or amorphosity and hence its temperature dependence overlapping the effect of the dielectric constant of the dispersoid may ‘apparently’ shift the peaking temperature. Apart from the peaking of σ at $T \sim 34^\circ\text{C}$, the data in figure 1 also show that there is another sharp increase in σ at $50\text{--}55^\circ\text{C}$ as we approach the T_m value of the polymer PEO. This increase in the conductivity at T_m is a general observation and has been assigned to the high amorphosity beyond T_m .

For the polymer samples containing a BST ferroelectric dispersoid with $x = 0.12$, $T_c \sim 90^\circ\text{C}$, the change in conductivity in the $30\text{--}40^\circ\text{C}$ range is not observed as is expected (see figure 2), since in this temperature range the values of the dielectric constant do not change much. However, we do see a small hump in the values of σ near the dielectric phase transition temperature of this BST ceramic ($T_c \sim 90^\circ\text{C}$). This change in conductivity is not as clearly observed as that in figure 1 because beyond T_m the conductivity of the base polymer electrolyte itself is large and the changes in σ , introduced by the dispersoid BST, are masked.

In brief, we have conclusively shown that in polymer electrolyte–ceramic composites the high dielectric constant of the dispersed ferroelectric ceramics has a definite role in the enhancement of the conductivity of the composite, possibly as a result of the high effective electric field at the dispersoid polymer interfaces.

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