

Effect of concentration and grain size of alumina filler on the ionic conductivity enhancement of the $(\text{PEO})_9\text{LiCF}_3\text{SO}_3:\text{Al}_2\text{O}_3$ composite polymer electrolyte

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Abstract

Nano-composite polymer electrolytes are receiving attention as potential candidates to be used as electrolyte membranes in lithium polymer batteries and other devices. However, a survey of literature reveals that a systematic study of the effect of concentration and surface area of ceramic fillers on the conductivity enhancement of micro- and nano-composite polymer electrolytes is lacking. In this work, we have studied the thermal and electrical properties of the composite polymer electrolyte $(\text{PEO})_9\text{LiCF}_3\text{SO}_3 + \text{Al}_2\text{O}_3$ incorporating alumina filler grains of four different sizes with different specific surface areas. The results show that the PEO crystallite melting temperature decreased by a few degrees in samples with fillers exhibiting a minimum for samples with high conductivity. The presence of the filler enhanced the ionic conductivity substantially above as well as below 60 °C, and the nano-porous alumina grains with 5.8 nm pore size and 150 m²/g specific area and 15 wt.% filler concentration exhibited the maximum enhancement. The observed conductivity enhancement has been attributed to Lewis acid–base type surface interactions of ionic species with O/OH groups on the filler surface, with an additional contribution below 60 °C coming from the retention of an increased fraction of the amorphous phase due to the presence of the filler. The conductivity versus filler concentration curves exhibit two conductivity maxima which has been explained in terms of the surface interactions, blocking effect and grain consolidation. The conductivity enhancement appears to saturate beyond 100 m²/g grain surface area.

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Keywords: Alumina filler; Ionic conductivity; Composite polymer electrolyte; PEO

1. Introduction

Plasticizer free, ionically conducting polymer electrolyte membranes are emerging as potential candidates for replacing the liquid electrolytes currently used in lithium batteries. This would enable the fabrication of flexible, compact and lightweight batteries that can be laminated and produced in large scale. Polymer electrolytes presently being investigated in many laboratories for this purpose are complexes of a lithium salt (LiX) with a high molecular weight polymer such as polyethylene oxide (PEO). One of the major drawbacks of PEO-LiX electrolytes, however, is their low ionic conductivity at ambient temperatures. This is due to the presence of crystalline phases at temperatures below 60 °C which impedes lithium ion transport whereas the high ionic conductivity is generally associated with the high tempera-

ture amorphous phase. Much of the recent research efforts to improve the ambient temperature conductivity while retaining the mechanical properties and the stability towards metallic lithium anode have been directed towards the addition of ultra-fine particles of ceramic fillers such as Al_2O_3 , SiO_2 and TiO_2 into PEO based polymer electrolytes [1–5].

In most of the PEO based nano-composite and micro-composite polymer electrolytes reported so far, the filler concentration has been confined to 10 wt.% irrespective of the grain size and a conductivity enhancement of up to two orders of magnitude has been achieved depending on the grain/pore size and the type of the filler used. However, to our knowledge, a systematic study of the conductivity variation with the concentration as well as the grain size of the filler particles is lacking. Such a study is vital in order to optimise the electrolyte composition and to understand the role played by filler particles in enhancing the conductivity. In this work, we have studied the dependence of ionic

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conductivity of the composite polymer electrolyte (PEO)₉-LiCF₃SO₃:Al₂O₃ on the concentration of four different types of alumina grains. Three of these types have grain sizes <10 μm, 37 and 10–20 nm while the fourth type has 104 μm size grains with a pore size of 5.8 nm according to the manufacturers specifications. In a related work, we have studied in detail the effect of different surface groups (acidic, weakly acidic, neutral and basic) of alumina filler on the conductivity enhancement in the nano-composite polymer electrolyte (PEO)₉LiTFSI + 10 wt.% Al₂O₃ [6].

2. Experimental

PEO (molecular weight, 5×10^6) and LiCF₃SO₃ (lithium triflate, LiTf) were purchased from Aldrich. The nanoporous Al₂O₃ powder (Aldrich) had a pore size 5.8 nm, particle size 104 μm, surface area 155 m²/g and acidic surface groups. The Al₂O₃ powder with <10 μm, 37 and 10–20 nm grain size were purchased from Alfa Aesar. All four types of alumina powder had a purity of 99.5% or better. Prior to use, PEO and LiTf were vacuum dried for 24 h at 50 and 120 °C, respectively. Appropriately weighed quantities of PEO and LiTf required for an ether oxygen to Li⁺ ratio of 9:1 were dissolved in anhydrous acetonitrile. Al₂O₃ powders were vacuum dried at 200 °C for 24 h and added to the above solution which was magnetically stirred at room temperature for at least 24 h, until a homogenous solution was obtained. For each Al₂O₃ type, the amount of filler added was varied from 5 to 25 wt.% of the total PEO + LiTf weight. The resulting slurry after stirring was cast on to a Teflon plate and then left in order to let the solvent slowly evaporate. After subsequent vacuum drying for 24 h, this procedure yielded visually homogenous composite polymer electrolyte films of average thickness 100–200 μm which were stored in the vacuum oven.

The PEO crystallite melting temperatures of different samples were determined using a Mettler Toledo DSC 30 differential scanning calorimeter. The measurements were carried out at a heating rate of 10 °C min⁻¹ from -140 to 140 °C in the heating cycle. A flow of nitrogen gas was maintained over the perforated pan to avoid any contact with atmospheric moisture. Complex impedance measurements were made on disc shaped samples sandwiched between two stainless steel electrodes of 13 mm diameter, using a computer controlled Schlumberger SI 1260 impedance analyser in the 1 Hz to 10 MHz frequency range. The temperature of the sample was varied from 25 to 110 °C and the measurements were taken at approximately 10 °C intervals on heating. The ionic conductivity was derived from the complex impedance data.

3. Results and discussion

Table 1 shows the DSC results of the (PEO)₉LiCF₃SO₃:Al₂O₃ composite polymer electrolyte samples incor-

Table 1

Crystallite melting temperatures T_m (in °C) of the (PEO)₉LiCF₃SO₃:Al₂O₃ composite polymer electrolyte incorporating the four different types of alumina grains mentioned in the text

Al ₂ O ₃ (wt.%)	<10 μm	37 nm	10–20 nm	5.8 nm (pore)
0	58.2	58.2	58.2	58.2
5	58.1	59.9	59.4	58.1
10	54.7	57.1	56.7	57.2 (12 wt.%)
15	56.1	56.1	43.9	54.2
20	57.3	59.7	59.1	56.6
25	58.9	59.8	59.8	56.7

For pure PEO, $T_m = 60.4$ °C.

porating alumina filler of four different grain types all taken during the heating cycle. The crystallite melting temperatures are obtained from the onset temperature in the DSC traces. The crystallite melting temperature of 58.2 °C for the (PEO)₉LiCF₃SO₃ electrolyte agrees well with the value reported in literature for this material [7,8]. From the table it can generally be seen that the crystallite melting temperature of the composite polymer electrolyte goes through a minimum.

Fig. 1a–d show the variation of conductivity with inverse temperature for the composite polymer electrolytes (PEO)₉LiCF₃SO₃ + Al₂O₃ incorporating up to 25 wt.% of Al₂O₃ filler of four different grain types. A closer inspection of these figures reveal the following features: (i) the conductivities of both the amorphous phase above 60 °C and the partly crystalline phase below 60 °C have increased substantially due to the presence of the ceramic filler, (ii) the conductivity enhancement is much greater in the crystalline phase compared to that in the amorphous phase, (iii) the discontinuity in the log σ versus $1/T$ plots around 60 °C becomes less visible for the filler concentrations that correspond to higher conductivities, (iv) for electrolytes with large surface area per gram, i.e. for 10–20 nm (grain size) and 5.8 nm (pore size) grains, the VTF behaviour extends down to ambient temperatures for filler concentrations that correspond to high conductivities, (v) the highest room temperature conductivity enhancement of more than two orders of magnitude is obtained for electrolytes with 10–20 nm (grain size) and 5.8 nm (pore size) filler.

In order to explain the above observations, we shall make use of the ideas proposed by Wieczorek et al. and further developed by Croce et al. and Mellander et al. regarding the role played by the alumina fillers in nano- and micro-composite polymer electrolytes [6,9–17]. According to these ideas, Lewis acid–base type oxygen and OH surface groups on alumina grains interact with cations and anions and provide additional sites creating favourable high conducting pathways in the vicinity of grains for the migration of ions. According to recent dielectric relaxation studies on the PEO:LiTFSI + Al₂O₃ nano-composite electrolyte, this is reflected as an increased mobility for the migrating ions

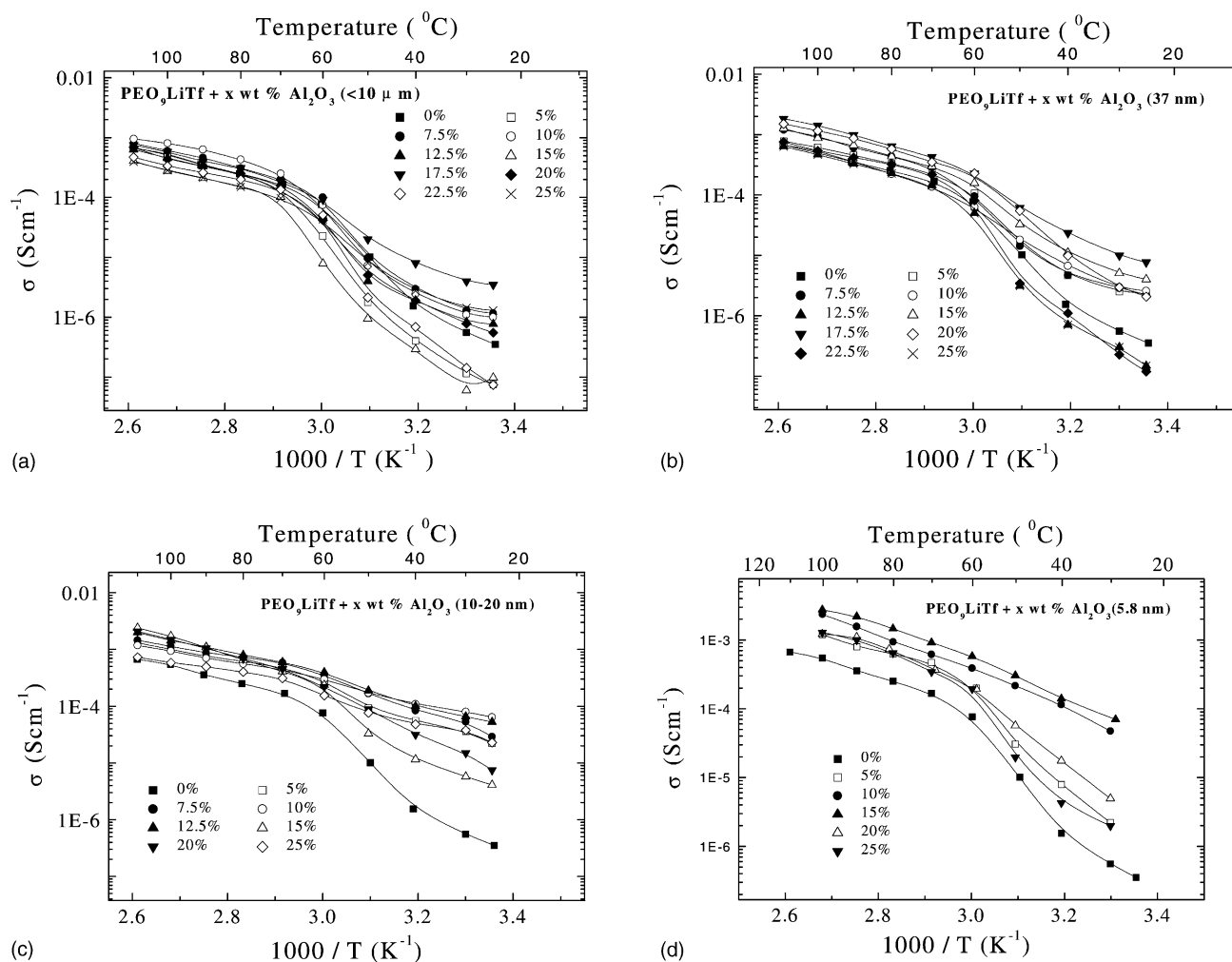


Fig. 1. Variation of ionic conductivity with inverse temperature for the composite polymer electrolyte system, $(\text{PEO})_9\text{LiTf} + \text{R}_2\text{O}_3$ incorporating up to 25 wt.% of Al_2O_3 fillers taken on the heating run: (a) grain size $<10 \mu\text{m}$, (b) grain size 37 nm, (c) grain size 10–20 nm and (d) pore size 5.8 nm.

[6]. This mechanism is quite likely to be the dominant conductivity enhancement mechanism operating in the composite polymer electrolytes $(\text{PEO})_9\text{LiCF}_3\text{SO}_3 + \text{Al}_2\text{O}_3$ at temperatures above and below 60°C . However, an additional substantial contribution to the conductivity enhancement below 60°C appears to come from the increased fraction of the amorphous phase retained due to the presence of the filler at these temperatures. This is evidenced from the lower PEO crystalline melting temperatures seen in the DSC traces and the VTF type behaviour seen for the high con-

ductivity filler compositions (Fig. 1). Similar observations have been reported for the PEO-LiClO_4 and $\text{PEO-LiCF}_3\text{SO}_3$ composite polymer electrolytes incorporating nano-sized Al_2O_3 , TiO_2 and $\gamma\text{-LiAlO}_2$ [11–14].

Plots of the variation of $\log \sigma$ versus wt.% Al_2O_3 for the $(\text{PEO})_9\text{LiCF}_3\text{SO}_3:\text{Al}_2\text{O}_3$ composite electrolyte incorporating the four types of filler grains are shown in Fig. 2a–d. For filler particles of grain size $<10 \mu\text{m}$, 37 and 10–20 nm, the figures a–c clearly show the existence of two conductivity maxima within the concentration range studied. However,

Table 2

Values of conductivity maxima at 30°C for different filler concentrations for the $(\text{PEO})_9\text{LiCF}_3\text{SO}_3:\text{Al}_2\text{O}_3$ composite polymer electrolyte

Filler type (surface area/g)	σ of the filler free electrolyte (S cm^{-1})	σ_{max}^1 at peak 1 in S cm^{-1} (filler concentration in wt.%)	σ_{max}^2 at peak 2 in S cm^{-1} (filler concentration in wt.%)
$<10 \mu\text{m}$ grain size ($0.17 \text{ m}^2/\text{g}$)	5.55×10^{-7}	1.29×10^{-6} (10%)	3.96×10^{-6} (17.5%)
37 nm grain size ($45 \text{ m}^2/\text{g}$)	5.55×10^{-7}	2.96×10^{-6} (7.5%)	9.91×10^{-6} (17.5%)
10–20 nm grain size ($100 \text{ m}^2/\text{g}$)	5.55×10^{-7}	5.31×10^{-5} (7.5%)	6.58×10^{-5} (12.5%)
5.8 nm (pore size) ($150 \text{ m}^2/\text{g}$)	5.55×10^{-7}	7.00×10^{-5} (15%)	7.00×10^{-5} (15%)

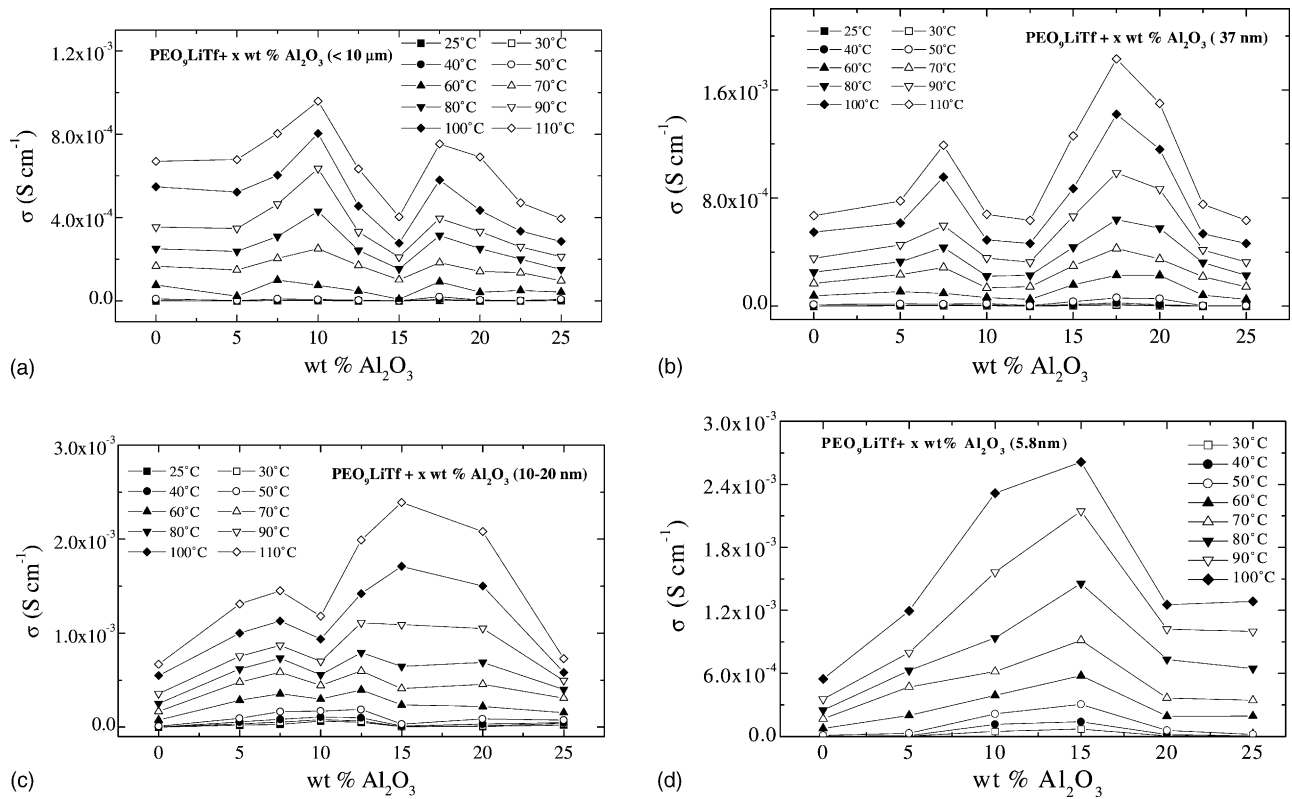


Fig. 2. Variation of $\log \sigma$ vs. wt.% Al_2O_3 for the four types of filler grains incorporated in the composite polymer electrolyte $(\text{PEO})_9\text{LiTf} + \text{Al}_2\text{O}_3$: (a) grain size $<10 \mu\text{m}$, (b) grain size 37 nm, (c) grain size 10–20 nm and (d) pore size 5.8 nm.

for filler grains of pore size 5.8 nm, (Fig. 2d), this double peak appears to merge to a single broad peak. In each case, these observations have been confirmed by two independent measurement runs. Values of the conductivity maxima at 30°C for different filler concentrations are given in Table 2. The variation of $\log \sigma$ at 30°C versus surface area of the grains is shown in Fig. 3. The observed trend clearly suggests that the conductivity enhancement increases with increasing specific surface area of filler grains. Accordingly,

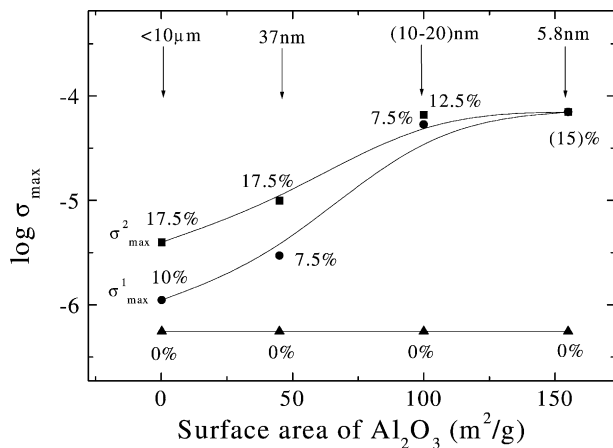


Fig. 3. Variation of ionic conductivity at 30°C with specific surface area of alumina grains for the composite polymer electrolyte $(\text{PEO})_9\text{LiTf} + \text{Al}_2\text{O}_3$.

the highest conductivity enhancement is obtained for the filler particles having the largest surface area per gram, i.e. for 10–20 nm (grain size) and 5.8 nm (pore size) grains. This trend is therefore consistent with the interpretation that the surface interactions, most likely of Lewis acid–base type, are largely responsible for the observed conductivity enhancement in these nano- and micro-composite polymer electrolytes both above and below 60°C . However, as stated earlier, an additional contribution appears to come from the increased fraction of the amorphous phase at temperatures below 60°C .

Our current viewpoint for describing these phenomena includes the following aspects. The composite polymer electrolyte system at low filler concentrations may be imagined as a conducting medium where filler grains are randomly and uniformly distributed throughout the volume. The presence of the filler grains could give rise to additional favourable conducting pathways in the vicinity of the surface of the grains as described earlier. The number of such additional high conductivity pathways is expected to increase with increasing filler surface area. At low enough filler concentrations, where the grains are still well separated these surface interactions can therefore account for the observed conductivity increase with increasing filler concentration.

At somewhat higher filler concentrations, however, the blocking effect or the geometrical constrictions imposed by

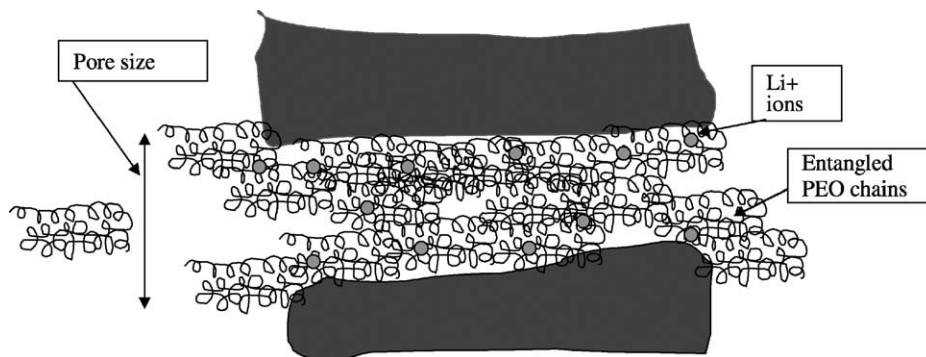


Fig. 4. Sketch depicting how PEO chains enter the nanoporous tunnels of alumina grains in a PEO based nano-composite electrolyte.

the more abundant alumina grains could make the long polymer chains more “immobilized” leading to a lower conductivity. This would lead to the appearance of the first conductivity maximum and the subsequent drop in conductivity. As the filler concentration is further increased, the filler grains get close enough to each other so that the high conducting regions in the vicinity of the grain surfaces start to get interconnected. The migrating ionic species can now travel along and between these interconnected high conducting pathways giving rise to the second increase in the conductivity. Finally, at still higher filler concentrations, the grains get so close to each other that the blocking effect due to the neutral filler becomes large and the conductivity starts to drop. This can explain the existence of the second maximum in the variation of the conductivity versus composition plots.

The observed trend in conductivity enhancement in samples with solid alumina grains of size $<10\ \mu\text{m}$, 37 and 10–20 nm clearly shows that the enhancement increases with the specific surface area of the grains. Although this trend has continued even up to the samples with nano-porous grains of pore size 5.8 nm, this case may need further clarification because of the very small pore size. From structural studies, it has been established that a PEO:LiX polymer electrolyte has a multiphase character consisting of crystalline and amorphous phases and the fraction of each phase present depends on several factors such as the temperature, thermal history, salt content, etc. The crystalline phase consists of long helical PEO chains with the diameter of the helix about 5 Å. The amorphous phase consists of stretched, flexible PEO chains. Spectroscopic studies have shown that, in the helical structure, polar oxygen atoms are directed inward, lining the tunnel cavity while the CH_2 groups all face outward [18]. This preferential orientation gives rise to tunnels of radius 1.3–1.5 Å, large enough to readily accommodate Li^+ cations of ionic radius 0.58 Å. The polyether helix may wrap somewhat more tightly to coordinate the small cations more effectively. It is however generally believed that the ion transport mainly takes place by intrachain hopping and interchain hopping of ionic species in the amorphous regions.

If one assumes that nano-porous alumina grains to consist of “tunnels” and “craters” of average diameter 5.8 nm or 58 Å, with the above structural information, it is reasonable to expect that not only linear PEO chains of diameter 5 Å but also entangled and folded PEO chains could enter these pores without much difficulty, especially when the fraction of the amorphous phase is high. Surface interactions due to O and OH groups of the filler surface can thus enhance the conductivity as described earlier (Fig. 4).

The possibility of Li^+ ion trapping inside these pores are also quite unlikely as the cations are surrounded and coordinated by ether oxygens or filler surface groups. Moreover, as the pore dimensions (58 Å) are much larger compared to the cationic radius of Li^+ (0.58 Å), ion trapping may be ruled out.

From the DSC results, see Table 1, it was observed that the melting temperature goes through a minimum near the composition that corresponds to the observed second conductivity maximum. This observation may suggest that the melting point in the phase corresponding to the high conducting pathways is lower than that of the bulk.

4. Conclusion

The results of electrical conductivity and thermal measurements on the $(\text{PEO})_9\text{LiTf} + \text{Al}_2\text{O}_3$ composite polymer electrolyte system reported in this paper demonstrate the following. The presence of filler particles enhances the ionic conductivity substantially, and the degree of enhancement depends on the surface area of the filler. Nanoporous alumina particles with 5.8 nm size pores have shown the highest conductivity increase. It is suggested that the conductivity enhancement at temperatures above as well as below 60 °C results from Lewis acid-base type surface interactions of ionic species with O/OH groups in the filler surface. These surface interactions are expected to create additional high conducting pathways for migrating ions. An additional contribution below 60 °C appears to come from the retention of an increased fraction of the amorphous phase due to the presence of the filler. The conductivity

versus filler concentration curves exhibit two conductivity maxima for fillers with $<10\ \mu\text{m}$, 37 and 10–20 nm grain size. The geometrical restrictions on the long polymer chains of the bulk polymer at moderately higher filler concentrations would give rise to the first conductivity drop. The subsequent conductivity increase is quite likely to come from the interconnected high conducting pathways due to the close proximity of the filler grains. At still higher filler concentrations, high volume fraction of inert fillers reduces the conductivity giving rise to the observed second conductivity maximum. Below $60\ ^\circ\text{C}$, and for certain filler concentrations, an additional contribution to reduce the conductivity may come from the formation of crystallites. The melting temperature of the $(\text{PEO})_9\text{LiTf}$ system changed appreciably due to the addition of the filler and passed through a minimum with increasing filler concentration with the exception for the porous grains. This minimum generally corresponds to the filler concentration range of the second conductivity maximum.

Acknowledgements

Authors wish to thank the International Programmes in the Physical Sciences (IPPS), Uppsala University, Sweden and the National Science Foundation (Grant: RG/2001/P/01) for research support.

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