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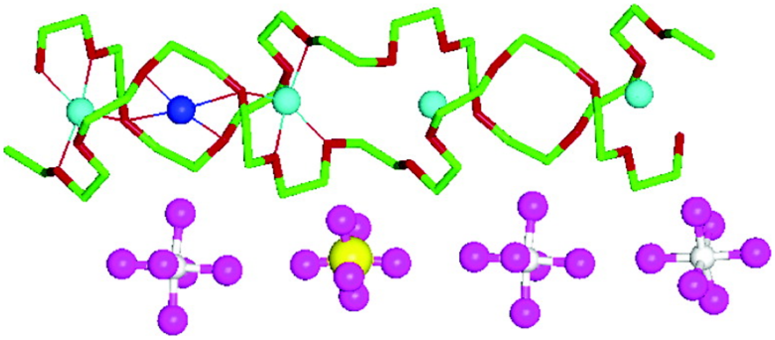

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Raising the Conductivity of Crystalline Polymer Electrolytes by Aliovalent Doping

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Abstract: Polymer electrolytes, salts dissolved in solid polymers, hold the key to realizing all solid-state devices such as rechargeable lithium batteries, electrochromic displays, or SMART windows. For 25 years conductivity was believed to be confined to amorphous polymer electrolytes, all crystalline polymer electrolytes were thought to be insulators. However, recent results have demonstrated conductivity in crystalline polymer electrolytes, although the levels at room temperature are too low for application. Here we show, for the first time, that it is possible to raise significantly the level of ionic conductivity by aliovalent doping. The conductivity may be raised by 1.5 orders of magnitude if the SbF_6^- ion in the crystalline conductor poly(ethylene oxide)$_6$:$LiSbF_6$ is replaced by less than 5 mol % SiF_6^{2-}, thus introducing additional, mobile, Li^+ ions into the structure to maintain electroneutrality.

Introduction

Polymer electrolytes are composed of salts dissolved in solid polymers, usually polyethers, in which the cations of the salt are coordinated by the ether oxygens, as in a crown ether complex.[1−3] These materials hold the key to developing important all solid-state devices such as electrochromic displays, SMART windows, and rechargeable lithium batteries. Polymer electrolytes may be prepared as amorphous or crystalline phases. For 25 years the belief had been that ion transport occurred only in amorphous phases above their glass transition temperature, in which state the segmental motion of the polymer chains plays a critical role in facilitating ion transport. As a result, all crystalline polymer electrolytes were believed to be insulators. Recently, this view has been overturned by demonstrating that the crystalline polymer−salt complexes poly(ethylene oxide)$_6$:$LiXF_6$, X = P, As, Sb can conduct, and by showing, more generally, that order, organization, and crystallinity in polymer electrolytes can lead to higher levels of conductivity.[4−7] Although the discovery of ionic conductivity in the crystalline 6:1 complexes represented an important breakthrough, their conductivities are not high (typically 10^{-7} S cm^{-1} at room temperature).[8] The major challenge, therefore, is how to raise significantly the conductivity of crystalline polymer electrolytes.

It has been shown that replacement of a small number (less than 5 mol %) of AsF_6^- ions in poly(ethylene oxide) (PEO_6):$LiAsF_6$ by the isovalent imide ion, $N(SO_2CF_3)_2^-$, results in an increase in the conductivity compared with the stoichiometric material, despite the fact that no extra Li^+ ions or vacancies are introduced.[9] Here we report, for the first time, a quite different doping mechanism for polymer electrolytes involving the introduction of additional Li^+ ions into the crystal structure. We show that it is possible to replace XF_6^-, specifically monovalent SbF_6^-, by an aliovalent ion, specifically divalent SiF_6^{2-}, resulting in the introduction of extra Li^+ ions, to maintain electroneutrality, into the 6:1 structure and leading to an increase in the conductivity compared with the undoped material of 1.5 orders of magnitude. These results demonstrate an important new route by which the conductivity of crystalline polymer-salt complexes may be raised. The crystal structures of the 6:1 complexes, PEO_6:$LiXF_6$, X = P, As, Sb, are broadly similar and are composed of pairs of PEO chains each of which folds to form a half cylinder with the cylinders interlocking to form tunnels, within which Li^+ ions reside in 5 coordinate sites (3 ether oxygens from one chain and 2 from the other).[4,10] The anions are located between the tunnels. The specific crystal structure for the PEO_6:$LiSbF_6$ is shown in Figure 1.

Differences between the crystal structures of the three 6:1 complexes are minor and confined to differences in the orientation of the anions and in the cross section of the tunnels, which can vary from circular, in the case of the PF_6 anion, to rectangular, in the case of SbF_6 anion. The location of the Li^+ ions within the polymer tunnels ensures that the Li^+ ions have pathways for facile transport through the polymer. In the ideal

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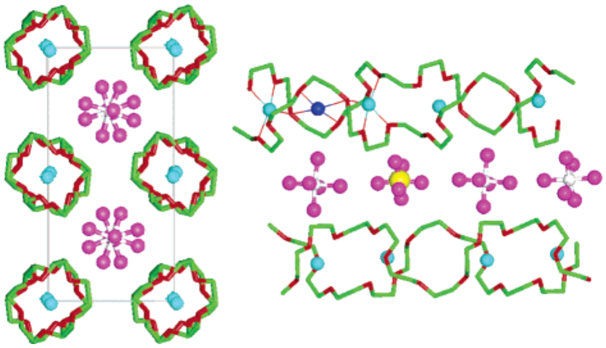

Figure 1. The structure of PEO_6:$LiSbF_6$. (Left) View of the structure along the polymer chain axis showing rows of Li^+ ions perpendicular to the page. (Right) View of the structure showing the positions and the conformation of the chains. Substitution of one of the SbF_6^- ions by SiF_6^{2-} and a possible position of an additional Li^+ ion (dark blue) in a 4-coordinate site are also shown. Light blue, lithium; green, carbon; red, oxygen; white, antimony; magenta, fluorine; yellow, silicon. Thin lines indicate coordination around Li^+ ions.

stoichiometric 6:1 compound all the Li^+ sites would be occupied, and ion transport could not occur. Of course the structure is not ideal, and the presence of a small number of defects is responsible for ion transport in the stoichiometric phase. In the case of isovalent doping, involving the replacement of XF_6^- by $N(SO_2CF_3)_2^-$, the different size and shape of the dopant anion is believed to disrupt the local structure sufficiently to modify the potential around the Li^+ ions, thus increasing the conductivity, by analogy with isovalent doping in ceramic materials.[9,11] However, in ceramic ionic solids the dominant method of increasing conductivity, compared with the stoichiometric solid, is to introduce either vacancies or interstitial ions. Indeed, it is generally the case that the latter doping mechanism leads to higher levels of conductivity than the former.[3,12,13] As a result, we have investigated doping PEO_6:$LiXF_6$ by replacement of the anion with a divalent anion, such that additional, interstitial, Li^+ ions may be introduced into the structure.

In an effort to maximize interstitial doping we selected an anion with a similar size and the same shape as the anion in the parent material, in this case SbF_6^-, but with a divalent charge, SiF_6^{2-}. This anion is octahedral, as is SbF_6^-, but smaller than the antimony-based anion and should therefore be suitable for substitution in the 6:1 structure.

Experimental Section

Poly(ethylene glycol) dimethyl ether of average molar mass 1000 Da (Fluka, ≥99.5%) was dried at 40 °C for 24 h and then dissolved in dry CH_3CN (Aldrich, 99.8%) along with appropriate mole ratios of $LiSbF_6$ (Fluorochem, 99%, used as received) and Li_2SiF_6 (Fluorochem, 98%, used as received). When the salts were fully dissolved, the solution was cast into vials and the solvent allowed to evaporate slowly. The resulting powders were dried at 30 °C under vacuum overnight.

Powder X-ray diffraction was carried out using a Stoe STADIP powder diffractometer with Cu Kα1 radiation operating in transmission mode and employing a small-angle position-sensitive detector (PSD). Data were collected with a step width of 0.02° in 2θ. To avoid contact with air, the polymer electrolyte samples were sealed in Lindemann (glass) capillaries or between Mylar films, depending on whether the samples were in the form of a powder or a film.

Differential scanning calorimetry (DSC) was carried out using a Netzch DSC 204 Phoenix with heating and cooling rates of 5°/min.

Conductivity data were obtained from alternating current (ac) impedance measurements carried out on a Solatron 1255 frequency response analyzer and 1286 electrochemical interface, both under the control of a PC. A polarizing potential of 15 mV (rms) was employed and data was collected over the frequency range 10^{-1} to 10^5 Hz. The polymer electrolyte disks, formed by pressing the powdered material, were sandwiched between 2 stainless steel plates in a 2-electrode cell which was itself located within an argon filled stainless steel chamber. The chamber was placed in a thermostatic bath in order to control the temperature of the cells. Analysis of the ac impedance plots obtained from the variable frequency measurements (supplementary data) revealed that there is only one semicircle and that the capacitance values are ~1 pF cm^{-1}. These results indicate that the electrical response of the electrolyte and, in particular, the extracted conductivities correspond to that of the bulk material, i.e., no grain-boundary resistances were observed.

Results and Discussion

Conductivity isotherms demonstrating the variation of conductivity on replacing SbF_6^- by SiF_6^{2-} are shown in Figure 2a. The conductivity rises very rapidly with small amounts of doping, increasing at room temperature by 1 order of magnitude with only 1 mol % of the dopant and then increasing more slowly to reach a plateau with an overall increase in conductivity compared with the stoichiometric material of 1.5 orders of magnitude. The rapid rise in conductivity on introducing small amounts of dopant is reminiscent of the results obtained on doping PEO_6:$LiAsF_6$ by $N(SO_2CF_3)_2^-$, where the TFSI anion has been incorporated into the crystal structure.

The variation of the conductivity with temperature for different dopant levels is shown in Figure 2b. For all levels of doping the temperature dependent conductivity is well described by an Arrhenius expression $A = \exp(-E_a/RT)$. Linearity of the log σ vs $1/T$ plots is indicative of ion hopping in a crystalline lattice rather than the curved plots more typical of ion transport in an amorphous polymer above T_g.[1-3] The variation of activation energy with doping level is shown in Figure 2c. There is a drop in the activation energy on moving from the undoped (77 kJ mol^{-1}) to the doped materials. Thereafter, it is difficult to discern any clear trend in the variation of activation energy with the level of doping; however, the range of activation energies for the doped materials is, in any case, small, 63−68 kJ mol^{-1}.

To understand the origin of the conductivity and its increase on doping, it is necessary to consider the phases present in the doped complexes as a function of Li_2SiF_6 content. Powder X-ray diffraction patterns collected for various doping levels up to $x = 0.1$ in PEO_6:$(LiSbF_6)_{1-x}(Li_2SiF_6)_x$ are shown in Figure 3 along with the most prominent peak from the powder X-ray diffraction pattern of Li_2SiF_6 at 43° in 2θ.

The powder diffraction patterns are dominated by the peaks of the 6:1 complex, with peaks from Li_2SiF_6 appearing for $x \geq 0.05$ in PEO_6:$Li(SbF_6)_{1-x}(SiF_6)_x$, indicating that the Li_2SiF_6 salt is present at these compositions. This is consistent with the incorporation of SiF_6^{2-} in the 6:1 crystal structure at lower doping levels. There is no significant shift in the lattice parameters; however the difference in the size of the anions (X−F bond lengths of the XF_6^- anions: SiF_6^{2-}, 1.68 Å; SbF_6^-, 1.81 Å) is small, and since the solubility limit for incorporation of Li_2SiF_6 is <0.05, the absence of a shift is not unexpected.

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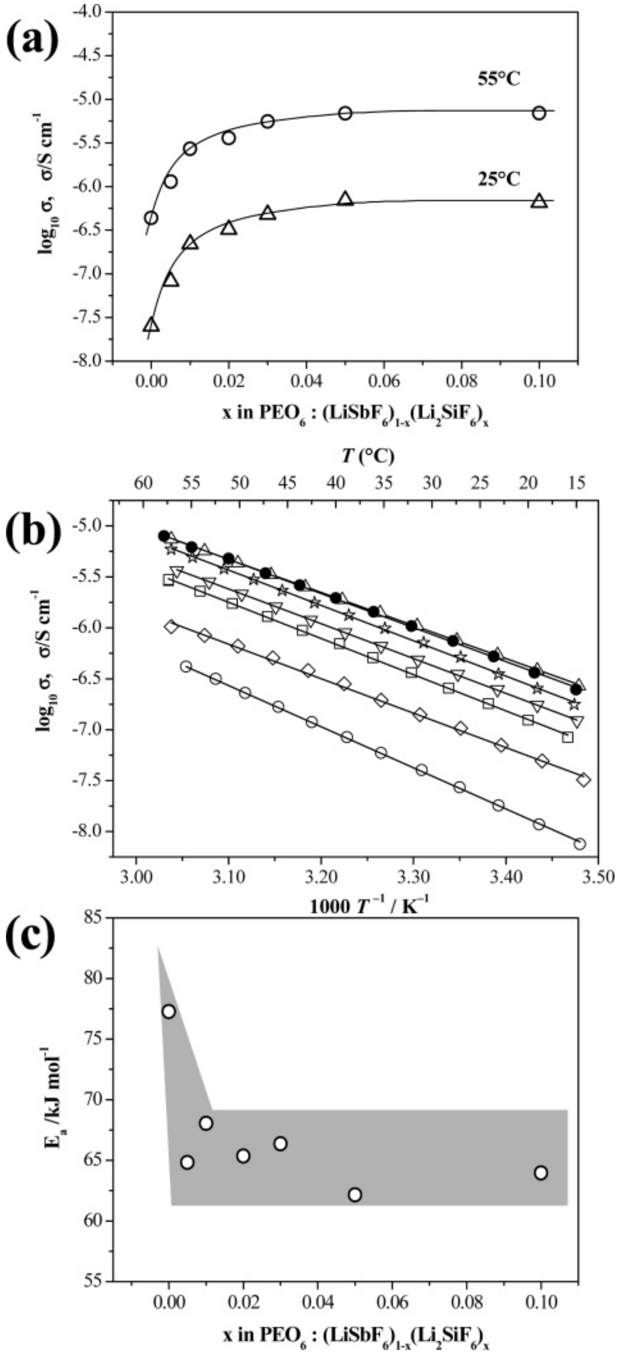

Figure 2. Conductivity of PEO_6:$(LiSbF_6)_{1-x}(Li_2SiF_6)_x$. (a) Conductivity isotherms as a function of x. (b) Ionic conductivity as a function of temperature. Open circles, $x = 0$; diamonds, $x = 0.005$; squares, $x = 0.01$; down triangles, $x = 0.02$; stars, $x = 0.03$; up triangles, $x = 0.05$; filled circles, $x = 0.1$. Solid lines represent best least-squares fits to the Arrhenius equation. (c) Activation energies as a function of x.

Despite the lack of a shift in lattice parameters, the significant rise in conductivity at low doping levels is consistent with incorporation of Li_2SiF_6 in the 6:1 crystal structure. It is not possible to detect directly the presence of such low dopant contents in the crystal structure. In fact, changes in conductivity have classically been used as probes of doping in ceramic ionic conductors because of the sensitivity of conductivity to small quantities of dopants. Unfortunately, it proved impossible to dissolve significantly larger amounts of Li_2SiF_6 in any reasonable quantity of acetonitrile or other suitable solvents, to explore compositions with $x > 0.1$. It is anticipated that for $x \gg 0.1$ the increasing presence of insulating Li_2SiF_6 (the conductivity of which at room temperature is below the detection limit of our equipment, $<10^{-10}$ S cm^{-1}) would lead to an overall reduction in the conductivity.

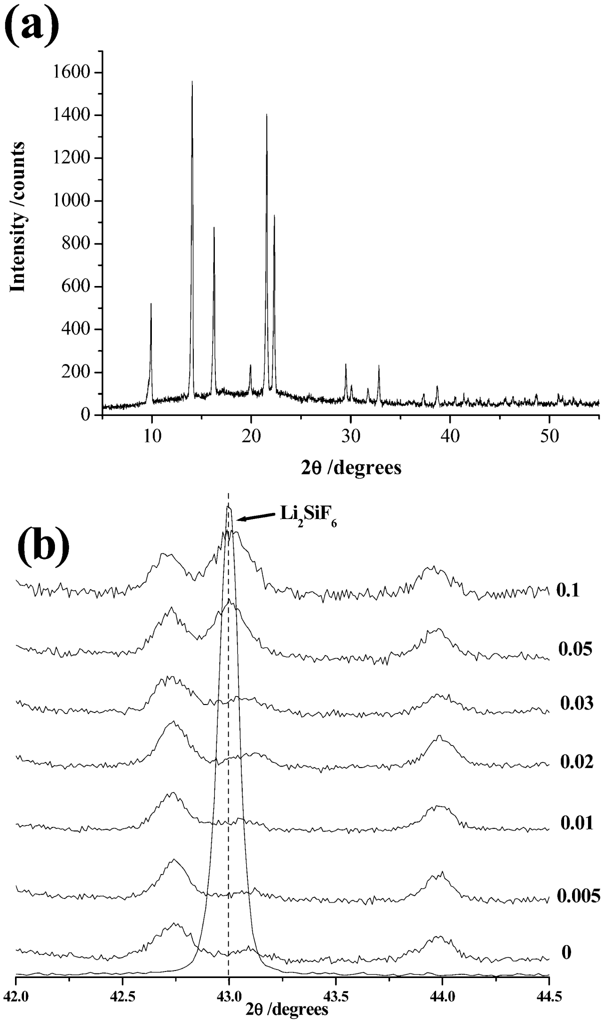

Figure 3. X-ray powder diffraction patterns of (a) PEO_6:$(LiSbF_6)_{0.95}(Li_2SiF_6)_{0.05}$; (b) PEO_6:$(LiSbF_6)_{1-x}(Li_2SiF_6)_x$ and Li_2SiF_6. Numbers indicate the values of x.

The presence of Li_2SiF_6 as a second phase implies the coexistence of PEO as well as the 6:1 structure. There is however no evidence for crystalline PEO in the powder diffraction patterns, therefore we investigated whether an amorphous phase was present. DSC measurements were carried out on the pure 6:1 complex and the materials with different levels of doping, Figure 4.

In all cases two endotherms were evident on heating. The first is associated with transformation from the α to the β polymorph, and the second corresponds to melting of the β phase.[14,15] Of more relevance here is the presence of a T_g in the region of −53 to −42 °C, Figure 4b, for all compositions except $x = 0$. The value of T_g varies little with dopant content (and shows no systematic trend) indicative of an amorphous phase with an invariant composition, i.e., Li_2SiF_6 does not appear to dissolve in the amorphous phase. Efforts to dissolve

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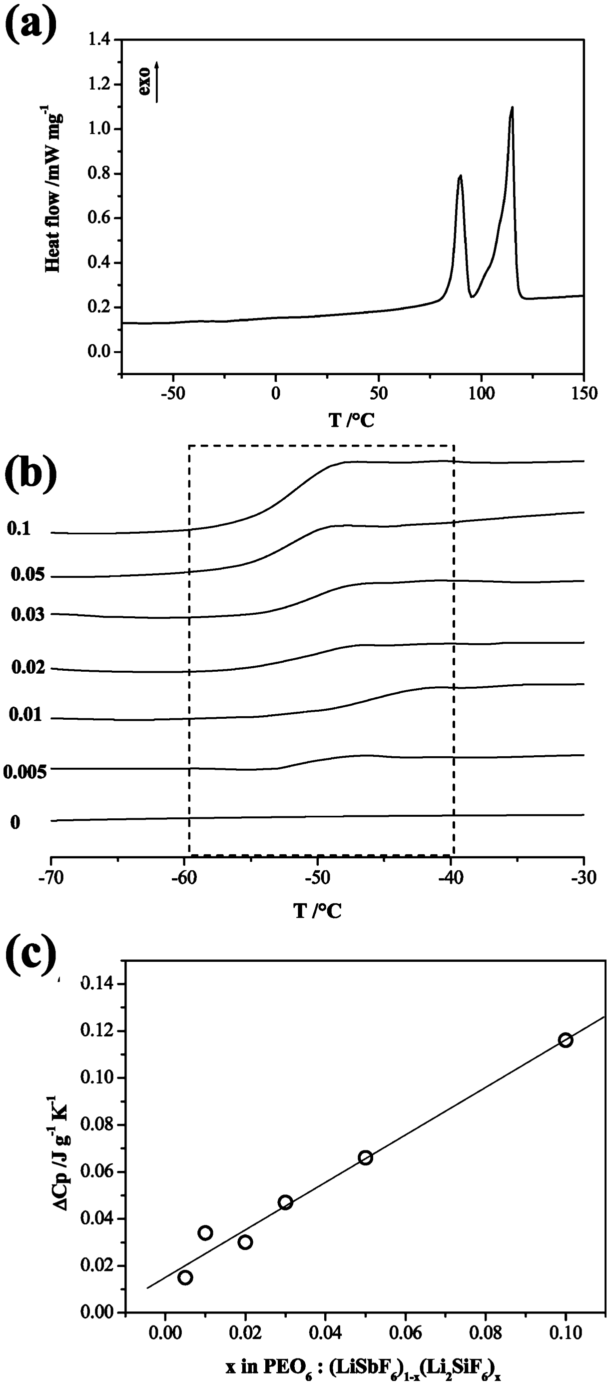

Figure 4. DSC of PEO$_6$:(LiSbF$_6$)$_{1-x}$(Li$_2$SiF$_6$)$_x$. (a) Trace of PEO$_6$:(LiSbF$_6$)$_{0.99}$(Li$_2$SiF$_6$)$_{0.01}$; (b) sections of the traces showing T_g, numbers indicate the values of x; (c) heat capacity difference associated with T_g as a function of x.

Li$_2$SiF$_6$ in PEO to form either an amorphous phase or a crystalline complex proved fruitless, resulting only in a mixture of crystalline PEO and Li$_2$SiF$_6$. Although the T_g is invariant, indicating a constant composition, the proportion of the amorphous phase does increase with increasing x, Figure 4c. The proportion of amorphous phase continues to grow throughout the composition range over which the conductivity does not change $0.05 < x < 0.1$. This is inconsistent with conductivity arising from the amorphous phase, since, under such circumstances, we anticipate that the conductivity would continue to rise, as was observed in the case of the N(SO$_2$CF$_3$)$_2^-$ doping where, at levels of imide content above the solubility limit in the 6:1 structure, conducting amorphous phase appeared which led to a slow increase in the conductivity at higher doping levels.

We may conclude therefore that the dramatic rise in conductivity on replacement of a small amount of SbF$_6^-$ with SiF$_6^{2-}$ is not due to an increase in the amount of an amorphous phase or an increase in the amount of free Li$_2$SiF$_6$ (a poor conductor). Instead, the X-ray, DSC, and conductivity data all point to incorporation of Li$_2$SiF$_6$ within the crystal structure of PEO$_6$:LiSbF$_6$ compound, which results in incorporation of additional Li ions into the structure leading to the substantial rise in conductivity.

Since the solubility limit for Li$_2$SiF$_6$ in the 6:1 phase is low, it is not possible to locate the exact position of the additional Li$^+$ ions by powder diffraction methods. Visual examination of the crystal structure for the 6:1 complexes does reveal the presence of an intermediate 4-coordinate site for Li$^+$ ions lying between the normal 5-coordinate sites in the crystal structure, Figure 1. A Li$^+$ ion located in this site would be coordinated by four equidistant ether oxygens with a very reasonable coordination distance of approximately 2 Å, thus making the site a possible candidate for the incorporation of extra Li$^+$, although this is of course speculative. Such a Li$^+$ ion would imply an interstitial mechanism of Li$^+$ ion migration in which the extra 4-coordinate Li$^+$ ions displace neighboring 5-coordinate ions into the next empty 4-coordinate sites. This mechanism is reminiscent of Ag$^+$ migration in AgCl where tetrahedrally coordinated interstitial Ag$^+$ ions migrate by displacement of Ag$^+$ ions from the normal 6-coordinate sites by an interstitialcy mechanism. Recently molecular dynamics simulations have been performed on the doped complex PEO$_6$:Li(PF$_6$)$_{0.99}$(SiF$_6$)$_{0.01}$. They revealed several possible Li$^+$ sites, explored possible conduction mechanisms and emphasized that ionic conduction is influenced by limited local motion of the polymer chains within these soft crystalline solids.[16]

In conclusion, a rise of 1.5 orders of magnitude in the conductivity has been demonstrated by replacement of less than 5 mol % SbF$_6^-$ with SiF$_6^{2-}$ and incorporation of an equivalent amount of additional Li$^+$ ions within the structure of the 6:1 polymer−salt complex PEO$_6$:LiSbF$_6$. This demonstrates that a substantial increase in conductivity by addition of a small number of divalent anions can take place in such materials, thus establishing a new route for enhancing the conductivity of crystalline polymer electrolytes.

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Supporting Information Available: ac impedance plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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