

Conductivity of a Confined Polymer Electrolyte: Lithium–Polypropylene Glycol Intercalated in Layered CdPS₃

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Lithium cations solvated by polypropylene glycol were confined, by intercalation, in the interlamellar space of an insulating layered solid, CdPS₃. The conductivity and the associated relaxation processes were investigated as a function of temperature and compared with corresponding bulk solid polymer electrolyte (SPE). The conductivity of the confined polymer electrolyte, which is comparable with that of bulk SPE, follows the Vogel–Tamman–Fulcher relation characteristic of ionic motion coupled to polymer relaxation modes and, surprisingly, these processes, although broadened, are faster than that in the corresponding bulk solid polymer electrolyte. The absence of ion-pair formation and anion transport makes Cd_{0.75}PS₃Li_{0.5}(PPG) an ideal system for investigating ionic motion in disordered polymer matrices.

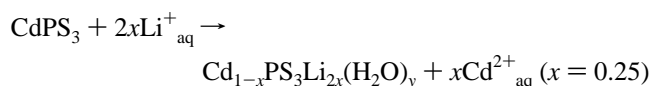
1. Introduction

The insertion, by intercalation, of polymers into the galleries of inorganic layered solids is a topic of current interest.^{1,2} It could, in principle, lead to new materials which combine the optical and electrical properties of the guest polymer with the mechanical strength and thermal stability of the inorganic host lattice and so possess properties which may not be achieved by either component separately. The intercalation of polyethers, e.g. polyethylene oxide (PEO) or polypropylene oxide (PPO), in Li/Na ion-exchanged layered solids is of particular significance since alkali metal salts dissolved in PEO/PPO–solid polymer electrolytes (SPEs)—are well-known ionic conductors.^{3,4}

SPEs have received considerable attention in the field of solid ionics, primarily in applications such as batteries and electrochromic devices, but they are also of fundamental interest for understanding ionic motion in disordered materials. It is now well established that significant ionic diffusion in these materials occurs only in the amorphous regions and that too in their elastomeric phase above the glass transition, T_g .⁵ Ionic motion is closely associated with local segmental motion of the polyether and shows two distinct dynamical regimes: a regime above T_g , where there is a strong coupling of ionic motion to polymer segmental motion and a regime below T_g where decoupling occurs.⁶ The experimental situation in the SPEs is, however, confused due to crystallization which leads to poor conductivities at ambient temperatures, anionic diffusion, and ion-pair formation. Intercalation of polymer electrolytes in layered solids, e.g. the mica-type silicates^{7,8} and metal thiophosphates,⁹ has been considered a promising approach to overcome some of these limitations since, in these systems, the anion is the host inorganic layer which is massive and immobile. It is, therefore, relevant to investigate and compare the dynamical process in the intercalated polymer electrolytes with those in the bulk SPEs. Because of the composite nature of the intercalated materials, many of the conventional techniques for investigating polymer motion—static and dynamic rheological

measurements, light scattering etc.—cannot be used. It is, however, possible, by choosing an inorganic host lattice which is electrically inert, to use ac electrical measurements to investigate dynamical processes in the confined polymer electrolyte. In this paper we report the temperature and frequency dependence of the conductivity of a polymer electrolyte, lithium cations solvated by polypropylene glycol (PPG) confined in the interlamellar space of an insulating layered solid, cadmium thiophosphate, CdPS₃. In particular, we are interested to know how the dc conductivity, its temperature variation, and the relaxation times associated with it compare with those of the analogous conventional solid polymer electrolytes (SPEs) formed by dissolving lithium salts, e.g. LiClO₄, in PPG of similar molecular weight.

CdPS₃ is a member of the layered transition metal chalcogenophosphate family of the general formula MPX₃, where M is a divalent metal and X = S or Se. CdPS₃ crystallizes in the C2/m space group with lattice parameters $a = 6.218$ Å, $b = 10.763$ Å, $c = 6.867$ Å, and $\beta = 107.58^\circ$.¹⁰ The structure consists of CdS₆ and P₂S₆ polyhedra which edge share to form CdPS₃ sheets which are separated by a van der Waals gap (Figure 1). The insertion of Li-PPG ($M_w = 4000$) into the van der Waals gap of cadmium thiophosphate was effected by a two-step ion-exchange–solvation shell exchange reaction to give Cd_{0.75}PS₃Li_{0.5}(PPG) in which lithium cations solvated by PPG are confined between negatively charged Cd_{0.75}PS₃ sheets.⁹ The first step is an ion-exchange intercalation reaction in which hydrated lithium ions from an aqueous solution are inserted in the interlamellar space of CdPS₃ with an equivalent loss of cadmium ions from the layer.



This reaction, unique to the divalent metal thiophosphates, leaves immobile, randomly distributed, cationic vacancies in the layer^{11,12} and proceeds with a dilation of the lattice. In the

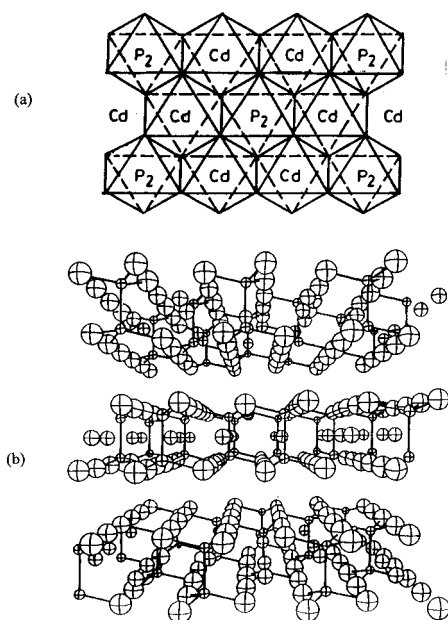
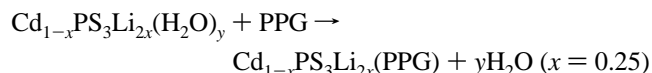


Figure 1. Structure of CdPS₃. (a) The in-plane structure in which CdS₆ and P₂S₆ polyhedra are linked to form CdPS₃ sheets. The P–P bond is collinear with the trigonal axis of the P₂S₆ polyhedra. (b) Perspective view of the structure viewed along the *b* axis showing the stacking of the CdPS₃ layers. The *a* axis is horizontal to the center of the figure. The circles represent P, Cd, and S with increasing size.

second step, the hydration shells of the intercalated lithium ions are replaced by the ether linkages of PPG with a further expansion of the lattice along the interlayer axis.



In these materials the negatively charged Cd_{0.75}PS₃ layers are electrically inert^{12,13} and consequently the electrical behavior of Cd_{1-x}PS₃Li_{2x}(PPG) would be entirely due to lithium ions solvated by PPG confined in the interlamellar space. The present study is restricted to an intercalated PPG of molecular weight 4000 since more detailed studies on the conductivity and associated relaxation times in the corresponding bulk Li–PPG SPEs have been reported for this molecular weight.^{14–17}

This restriction is not of much significance since the conductivities of the intercalated polymer electrolytes are independent of molecular weight (for MW > 700)¹⁸ just as in the corresponding SPEs.

2. Experimental Section

Cadmium thiophosphate was prepared from the elements following the procedure reported in ref 19. Cadmium metal powder, phosphorus, and sulfur in stoichiometric amounts were sealed in quartz ampules at 10^{−5} Torr and heated at 650 °C for a period of 2 weeks. The formation of CdPS₃ was confirmed by X-ray diffraction (XRD). Although Cd_{1-x}PS₃Li_{2x}(H₂O)_y can be prepared by the direct ion-exchange intercalation reaction, a more facile route is by exchanging the K ions in Cd_{1-x}PS₃K_{2x}(H₂O)_z with Li ions. The potassium ion exchanged intercalation compound was obtained by stirring CdPS₃ powder in an aqueous solution of KCl along with a complexing agent, EDTA. Complete ion-exchange intercalation was ascertained by the absence of 00*l* reflections of CdPS₃ and the appearance of new 00*l* reflections with lattice spacing (*d*) 9.3 Å.

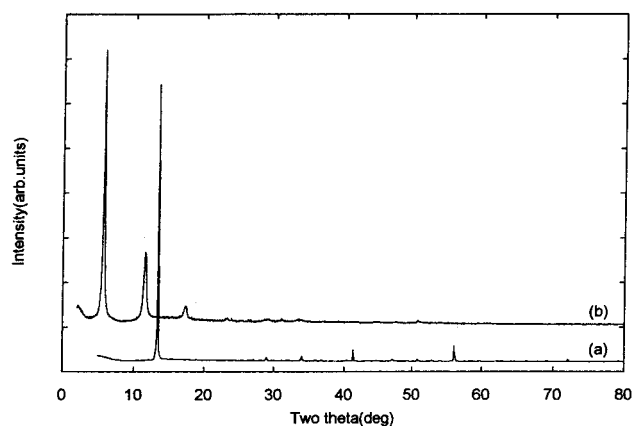
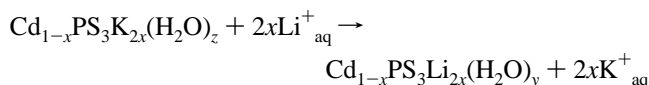


Figure 2. Powder X-ray (Cu Kα) diffraction pattern of (a) CdPS₃ and (b) Cd_{0.75}PS₃Li_{0.5}(PPG).

Cd_{1-x}PS₃Li_{2x}(H₂O)_y in turn was obtained by the following ion-exchange reaction.



Ion exchange of the K ions by Li ions causes the lattice spacing to increase to 12.2 Å. The intercalation of PPG (Aldrich *M_w* = 4000) was carried out by refluxing the lithium ion exchanged intercalation compound, Cd_{1-x}PS₃Li_{2x}(H₂O)_y, with a methanolic solution of PPG. The progress of the reaction was monitored by the appearance of new 00*l* reflections with *d* = 15.3 Å in the powder XRD. Completion of the reaction was ascertained by the absence of the Cd_{0.75}PS₃Li_{0.5}(H₂O)_y reflections. Cadmium and lithium ion stoichiometries were established by atomic absorption spectroscopy after dissolving the compound in aqua regia. The value of *x* is 0.25. The amount of intercalated PPG was estimated by CHN elemental analysis. The Li to PPG ratio usually referred to as the ether–oxygen to lithium cation ratio (O:Li) is 3.6:1 in the intercalated compound. The material is stable in air.

The X-ray diffraction pattern of Cd_{0.75}PS₃Li_{0.5}(PPG) could be indexed in the same space group as CdPS₃, *C2/m*, with lattice parameters *a* = 6.37 Å, *b* = 10.58 Å, *c* = 16.04 Å, and β = 107.36°. A comparison of XRD's of CdPS₃ and the intercalated Cd_{0.75}PS₃Li_{0.5}(PPG) (Figure 2) showed that the only structural change on intercalation is a lattice expansion of 8.77 Å along the interlayer axis. Differential scanning calorimetry (rheometric scientific plus instrument) showed no evidence of a glass transition temperature in the temperature range 90–300 K. Electrical measurements were made on pelletized samples using platinum electrodes. Sample temperature could be varied from 10 to 330 K with ±0.5 K accuracy using a closed cycle cryostat (CTI Cryogenics). The complex admittance, *Y** = *Y*' + *iY*'', was measured in the frequency range 10–10⁵ Hz using a dual-phase lock-in analyzer (PAR 5208).²⁰ The physical quantities of interest, the real part of the frequency dependent conductivity, σ(*ω*), and the complex electrical modulus, *M** = 1/*Y**, which is the inverse of the complex dielectric permittivity, ε*, were derived from the complex admittance, *Y**. ε* = *Y**/*iωC*₀, where *C*₀ is the vacuum capacitance of the cell; *C*₀ = ε₀*A*/*d*. *A* is the area of the electrode, *d* is the thickness of the sample, and ε₀ is the permittivity of space (8.854 × 10^{−12} F/m). The values of *A* and *d* in the present measurements were 0.595 cm² and 0.125 cm, respectively. The real part of the conductivity, σ(*ω*), is related to the dielectric permittivity through the relation σ(*ω*) = ωε₀ε''. The dc conductivity, σ_{dc}, was obtained by fitting the

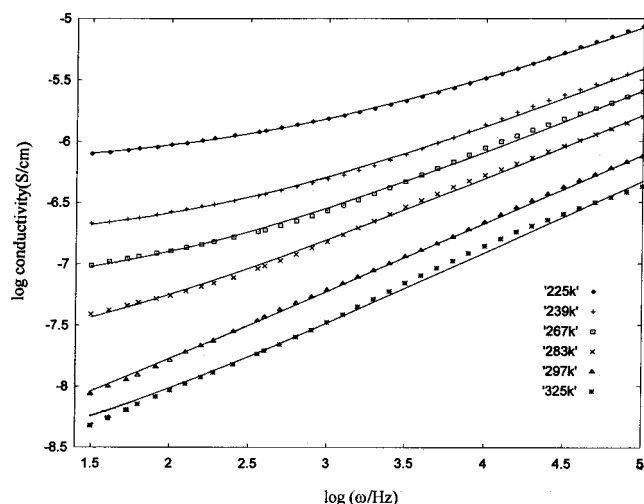


Figure 3. Conductivity vs frequency for $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PPG})$ presented in a double-logarithmic scale at different temperatures. Solid lines are fits to the expression $\sigma'(\omega) = \sigma_{\text{dc}} + a\omega^5$.

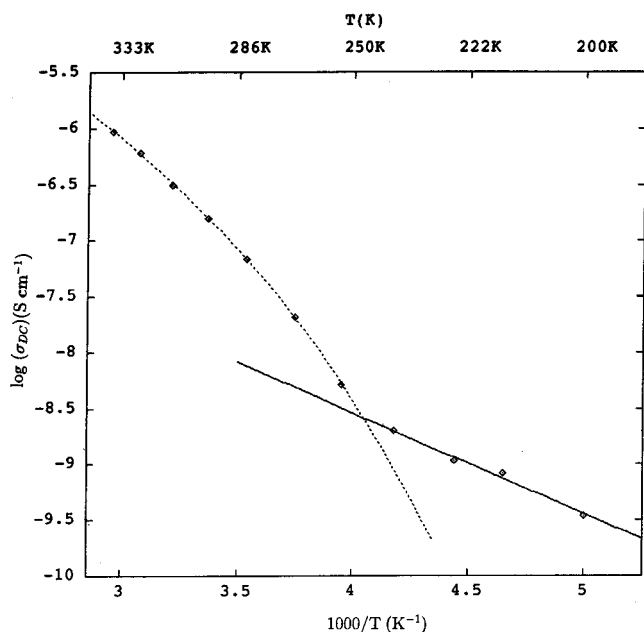


Figure 4. Temperature variation of the dc conductivity of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PPG})$. The solid line is the Arrhenius fit and the dashed line, the fit to the VTF equation (eq 1).

experimental $\sigma(\omega)$ to $\sigma(\omega) = \sigma_{\text{dc}} + a\omega^5$.²² The frequency dependence of $\sigma(\omega)$ is shown in Figure 3 for various temperatures. σ_{dc} was also obtained from the complex impedance plots; the values were identical to that obtained from the fits of Figure 3.

3. Results and Discussion

Figure 4 shows the temperature variation of the d.c conductivity, σ_{dc} , of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PPG})$. The conductivity shows two regions. Below 245 K, the conductivity values are small and the temperature dependence Arrhenius with an activation energy $E_a = 0.179$ eV (solid line in Figure 4). Above 245 K, σ_{dc} rises fairly rapidly, reaching a value of 1.58×10^{-7} S/cm at 300 K. It may be noted that this value is, in fact, higher than the conductivity values reported for the conventional Li-PPG-based SPEs which are typically 10^{-8} – 10^{-9} S/cm at 300 K.²³ Above 245 K, the temperature dependence of σ_{dc} of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PPG})$ is non-Arrhenius and is best described by the Vogel–

TABLE 1: Comparison of the VTF Parameters for the Dc Conductivity of the Intercalated Polymer Electrolyte $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PPG})$ with That of Bulk PPG Based Lithium SPEs

sample ^a	<i>B</i> (eV)	<i>T</i> ₀ (K)
Confined		
$\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}\text{PPG}$ (3.6:1)	0.117	142
Bulk (from ref 23)		
PPG–LiCF ₃ SO ₃ (6:1)	0.049	252
PPG–LiCF ₃ SO ₃ (8:1)	0.092	210
PPG–LiClO ₄ (8:1)	0.081	235
PPG–LiSCN (8:1)	0.126	203

^a The value in the parenthesis is the O:Li ratio.

Tamman–Fulcher (VTF) equation

$$\sigma = \sigma_0 T^{-0.5} \exp(-B/(T - T_0)) \quad (1)$$

with the pseudo activation energy $B = 0.117$ eV and $T_0 = 142.2$ K (dashed line in Figure 4).

In the SPEs, a VTF description for σ_{dc} is considered characteristic of ionic motion strongly coupled to polymer segmental motion, with T_0 in eq 1 identified as the temperature below which polymer segmental motion freezes.²⁴ Although in the intercalated polymer electrolyte, $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PPG})$, no DSC evidence for T_g is observed, it is still reasonable to identify the region above 245 K in Figure 4, where conductivity values are higher and show a VTF temperature dependence, as one where lithium ion motion is closely associated with segmental motion of the intercalated polymer. The lower values of σ_{dc} for $T < 245$ K would be due to a freezing of this motion so that conductivity now arises from an orthodox hopping of ions. It is known from cross-linking studies on PPO-based SPEs that changes in microviscosity are sufficient for enhanced conductivity; changes in the macroscopic viscosity on the length scale of the molecular weight are not a prerequisite.²⁵ A comparison of the VTF parameters of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PPG})$ with those of Li-PPG SPEs (Table 1) shows that while the value of the pseudo activation energies are comparable, the T_0 of the intercalated polymer electrolyte is lower. In fact, it is lower than that for bulk PPG ($T_0 \approx T_g - 50$ K = 150 K). The result is rather surprising since complexation with alkali salts is known to stiffen the PPG chains and hence shift T_g and T_0 to higher temperatures.²⁶

The dispersive behavior of the conductivity in the frequency domain (Figure 3) is more conveniently interpreted in terms of a conductivity relaxation time, τ_σ , using the electrical modulus, $M^* = 1/\epsilon^*$, representation.²¹ Although originally conceived as a formalism to separate space-charge effects from the bulk conductivity, the M^* representation is now widely used to analyze ionic conductivities by associating a conductivity relaxation time, τ_σ , with the ionic process.^{27,28}

$$M^* = M_\infty \left[1 - \int_0^\infty \exp(-i\omega t) \left(\frac{-d\phi(t)}{dt} \right) dt \right] \quad (2)$$

where $\phi(t)$ is a decay function of the electric field [$E(t) = E(0)\phi(t)$]. M_∞ is the high-frequency limit of the modulus. In the M^* representation, a relaxation peak is observed for the conductivity process in the frequency spectra of the imaginary component of M^* ; no peak occurs in the dielectric spectra. Comparison of the ϵ^* and M^* representations have been used to distinguish localized dielectric relaxation from long-range conductivity.²⁹

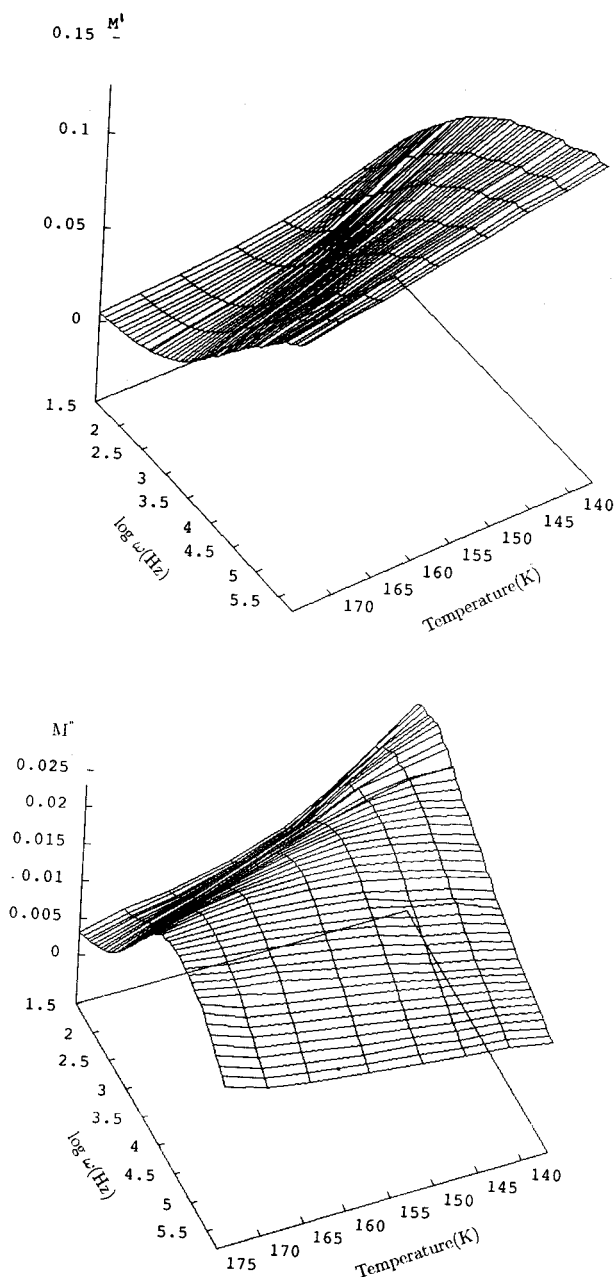


Figure 5. Real (M') and imaginary (M'') component of the electrical modulus of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}$ (PPG) as a function of frequency and temperature.

The real and imaginary components of the modulus spectra of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}$ (PPG) are shown in Figure 5. The M'' spectra shows a single well-defined relaxation peak. The corresponding dielectric spectra, $\epsilon''(\omega)$ (Figure 6), on the other hand shows a simple dispersion; no maximum characteristic of a dielectric relaxation is seen in the spectra of the imaginary component $\epsilon''(\omega)$ in Figure 6b. This may be interpreted, as in the case of SPEs,¹⁴ as indicating that in $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}$ (PPG), the segmental relaxation modes of the PPG and the lithium ion motion are coupled.

It may be seen from Figure 7, where the imaginary component of the modulus as function of frequency has been plotted for various temperatures, that it has a strong non-Debye-like character. The modulus spectra at all temperatures could be

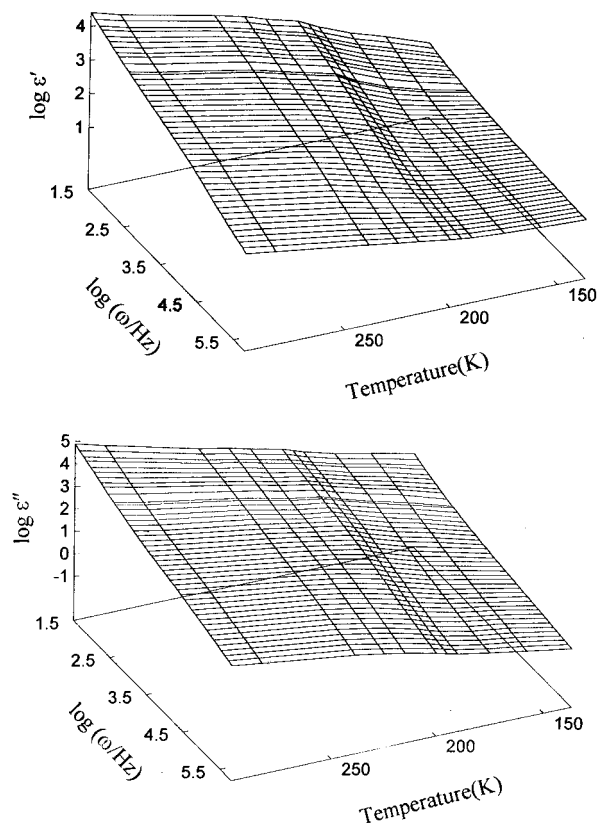


Figure 6. Real and imaginary components of the complex dielectric permittivity as a function of temperature for $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}$ (PPG).

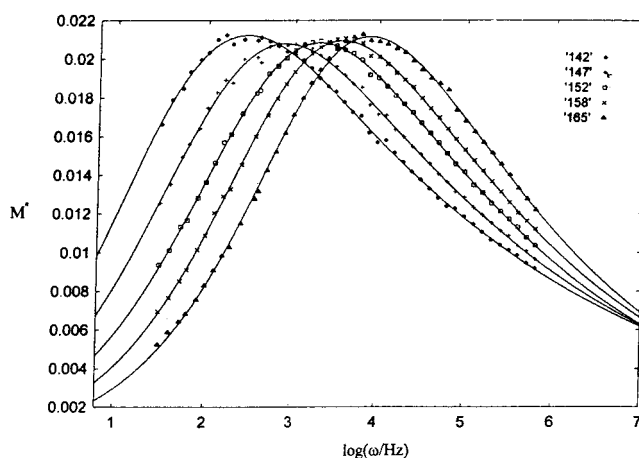


Figure 7. Imaginary part of the electric modulus vs frequency for $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}$ (PPG) at various temperatures. Solid lines are fits of $M''(\omega)$ to HN equation (eq 4).

fitted to the empirical Havriliak–Negami (HN) equation³⁰

$$M^*(\omega) = M_{\infty} \left[1 - \frac{1}{(1 + (i\omega\tau)^{1-\alpha})^{\beta}} \right] \quad (3)$$

where $0 \leq \alpha, \beta \leq 1$ are the shape parameters. The imaginary part of the HN equation is given by

$$M''(\omega) = M_{\infty} \frac{\sin \beta \varphi}{[1 + 2(\omega\tau_0)^{1-\alpha} \sin^{1/2} \pi \alpha + (\omega\tau_0)^{2(1-\alpha)}]^{\beta/2}} \quad (4)$$

where $\varphi = \arctg[(\omega\tau_0)^{1-\alpha} \cos^{1/2} \pi \alpha / (1 + (\omega\tau_0)^{1-\alpha} \sin^{1/2} \pi \alpha)]$. The experimental $M''(\omega)$ was fitted to eq 4 by floating the HN parameters α , β , and τ . The HN fits are shown as the solid lines in Figure 7 and the best-fit parameters in Table 2.

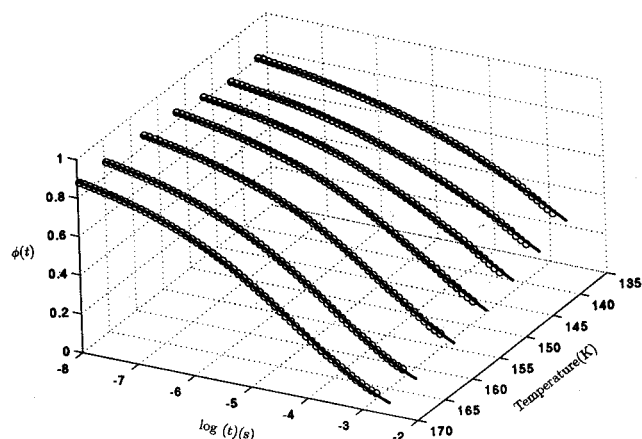


Figure 8. Decay function, $\phi(t)$, for the conductivity relaxation of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PPG})$ at various temperatures. The solid line is the fit to the stretched exponential function (eq 6).

TABLE 2: HN Best-Fit Parameters for $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PPG})$

temp (K)	τ (s)	α	β
142	3.50×10^{-2}	0.41	0.24
147	1.12×10^{-2}	0.45	0.29
152	3.41×10^{-3}	0.47	0.35
158	1.64×10^{-3}	0.47	0.37
165	6.19×10^{-4}	0.48	0.43

TABLE 3: Temperature Dependence of the Stretched Exponential Fit Parameters Which Describe the Decay Function (Figure 8) Calculated from the Modulus Spectra (Figure 7) of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PPG})$

temp (K)	τ_{SE} (s)	β_{SE}	$\langle\tau_a\rangle$ (s)
142	9.50×10^{-4}	0.22	4.88×10^{-2}
147	5.41×10^{-4}	0.24	1.73×10^{-2}
152	3.05×10^{-4}	0.25	6.55×10^{-3}
158	1.85×10^{-4}	0.26	3.42×10^{-3}
165	1.06×10^{-4}	0.27	1.73×10^{-3}

For a quantitative analysis of the modulus data, the decay function, $\phi(t)$, was calculated using the inverse transform of eq 2. Since the real and imaginary components of M^* are connected by the Kramers–Krönig transform, it is sufficient to use only M'' to calculate $\phi(t)$.

$$\phi(\tau) = \frac{2}{\pi} \int_0^\infty \frac{M''}{M_\infty} \frac{d\omega}{\omega} \cos \omega \tau \quad (5)$$

The transform was carried out for various temperatures using the analytical form of the HN equation eq 4 with the parameters α , β , and τ as obtained from the fitting of the experimental M'' spectra (Table 2).^{13,31,32} The resulting decay functions were found to be asymmetric with respect to time (Figure 8) and could be well described by the Kohlrausch–Williams–Watts or stretched exponential decay function

$$\phi(t) = \exp(-t/\tau_{\text{SE}})^{\beta_{\text{SE}}} \quad (6)$$

with the value of β_{SE} increasing with temperature (Table 3). The departure of β_{SE} from unity characterizes the departure from an ideal Debye relaxation. The average relaxation time associated with the stretched exponential decay function is²⁷

$$\langle\tau_a\rangle = \frac{\tau_{\text{SE}}}{\beta_{\text{SE}}} \Gamma\left(\frac{1}{\beta_{\text{SE}}}\right) \quad (7)$$

where Γ is the gamma function. These values for $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PPG})$ are tabulated in Table 3.

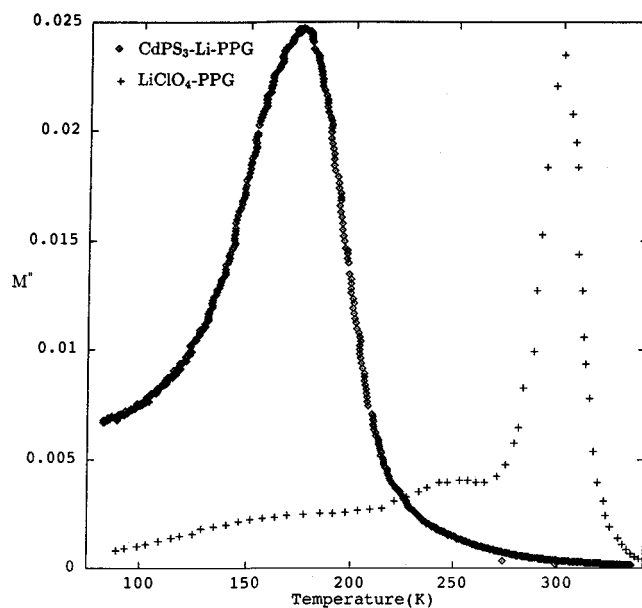


Figure 9. Comparison of the temperature variation of the imaginary component of the electrical modulus (M'') at 1 kHz of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PPG})$ with that of LiClO_4 PPG (O:Li = 4:1) from ref 16.

TABLE 4: Comparison of the Dc Conductivity Values Calculated from the M'' Spectra with that Obtained from the Complex Admittance

temp (K)	$\sigma_{\text{DC}} = \epsilon_0 \epsilon_\infty / \langle\tau_a\rangle$ S/cm	σ_{DC} S/cm (from $\sigma(\omega) = \sigma_{\text{DC}} + a\omega^S$)
142	1.07×10^{-9}	3.31×10^{-9}
147	3.18×10^{-9}	4.29×10^{-9}
152	8.91×10^{-9}	6.25×10^{-9}
158	1.77×10^{-8}	1.93×10^{-8}

Further confirmation that the peak observed in the M'' spectra is due to a conductivity relaxation was obtained by comparing the dc conductivity values as obtained from the modulus spectra, $\sigma_{\text{dc}}^{\text{mod}}$ with, the σ_{dc} obtained from the fits to the $\sigma(\omega)$ data (Figure 3) or the complex admittance. $\sigma_{\text{dc}}^{\text{mod}}$ may be calculated from the average relaxation time $\langle\tau_a\rangle$ of Table 3 using the relation $\sigma_{\text{dc}}^{\text{mod}} = \epsilon_0 \epsilon_\infty / \langle\tau_a\rangle$. The comparison is shown in Table 4. This confirmation implies that the observed dispersion in the dielectric spectra (Figure 6) is a manifestation of what is expected from a distribution of conductivity relaxation times.²¹

The modulus spectra of the intercalated polymer electrolytes (Figures 5b and 7) clearly shows that only a single relaxation is present. The modulus spectra of the conventional bulk $\text{LiClO}_4\text{-PPG}(4000)$, on the other hand, is more complicated.^{14–17} At low O:Li ratio, the conductivity relaxation and segmental dielectric relaxation are decoupled with the latter appearing at higher frequencies. At higher O:Li ratio, the two features merge to give a coupled conductivity–dielectric relaxation.^{14,15} This relaxation, however, appears at a higher temperature for the same frequency window as in Figures 5b and 7. Even in such situations, the interpretation of M'' spectra of the SPEs is rarely as straightforward as that of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PPG})$. This is because at higher O:Li concentration cation–anion pair formation gives rise to a distinct dielectric feature.¹⁶ In the case of intercalated polymer electrolytes, since the anion is the massive, immobile negatively charged $\text{Cd}_{0.75}\text{PS}_3$ layer, ion-pair formation is absent even for the high O:Li ratio in $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PPG})$. This may be clearly seen in the plots of M'' at 1 kHz versus temperature of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PPG})$ compared with data for $\text{LiClO}_4\text{-PPG}$ (O:Li = 4:1) from ref 16 (Figure 9). The data for $\text{LiClO}_4\text{-PPG}$ shows a conductivity relaxation peak at 295 K;

the shoulder at 250 K has been assigned to a relaxation due to ion-pair formation.¹⁶ Such a feature is absent for the intercalated polymer electrolytes, although the O:Li ratio is higher. Second, the conductivity relaxation in the intercalated polymer electrolyte appears at a much lower temperature (175 K) and is considerably broader. The broadening of the conductivity relaxation may also be inferred from the β_{SE} values (Table 3) which are smaller than those observed in the bulk polymer electrolyte. Although there is an element of ambiguity in the β_{SE} value for the Li-PPG-based SPEs—it depends on the frequency range analyzed—they are typically ≈ 0.5 and are claimed to be temperature independent.¹⁷

The lower value of the VTF T_0 , for the temperature dependence of σ_{dc} of the intercalated polymer electrolyte (Table 1), and the faster conductivity relaxation times (Table 3) may be understood by considering the density of the intercalated PPG. The density of the intercalated PPG may be calculated from the observed X-ray diffraction lattice parameters for $Cd_{0.75}PS_3Li_{0.5}(PPG)$ and the stoichiometry as determined from elemental analysis. The unit cell volume of the host, $CdPS_3$, is 438.1 \AA^3 . The formation of $Cd_{0.75}PS_3Li_{0.5}(PPG)$ occurs with a dilation of the lattice along the interlayer axis (*c*-axis). The increase in volume, ΔV , of the unit cell due to intercalation is 593.6 \AA^3 . The volume available for the PPG in the unit cell may be obtained by subtracting the ionic volume of Li^+ ion (1.7 \AA^3) from ΔV . Assuming that the entire volume is available for the PPG, the density of the intercalated PPG is calculated to be 0.65 g/cm^3 . This is considerably lower than that of bulk PPG (1.004 g/cm^3). Thus, the free volume, defined as the difference in the volume available to a molecule and its van der Waals volume, is larger for PPG confined in $Cd_{0.75}PS_3Li_{0.5}(PPG)$ than in the bulk. A consequence of the increased free volume is that polymer segmental relaxation modes are faster and since lithium ion motion coupled with these, the conductivity relaxation appears at a lower temperature (higher frequency) as compared to the bulk Li-PPG-based SPEs. Since ion-pair formation is absent in $Cd_{0.75}PS_3Li_{0.5}(PPG)$, the increase in the width of the conductivity relaxation is an intrinsic feature of the intercalated polymer electrolyte. The broadening probably arises due to a slowing down of the polymer segmental motion near the $CdPS_3$ layer interface. It is well-known that nonmetallic interfaces can slow rotational dynamics of a polar liquid due to dipolar interaction.³³ It is interesting to compare these results with that of a recent report³⁴ on the dielectric relaxation of PPG confined in a porous glass. There, too, a broadening of the relaxation due to the presence of the interface is observed. However, unlike the present system, there is a decrease in free volume on confinement and consequently a retardation of relaxation times.

4. Conclusions

In summary, we have presented results on the conductivity and associated relaxation, of a polymer electrolyte confined, by intercalation, in a layered solid; $Cd_{0.75}PS_3Li_{0.5}(PPG)$. The dc conductivity of this material follows the VTF behavior with T_0 lower than that in the bulk PPG based lithium SPEs. Ionic motion in the intercalated polymer electrolyte is coupled with

the PPG relaxation modes so that the modulus representation of the ac electrical response shows a single relaxation. A comparison shows that the conductivity relaxation, although broadened, is faster than that in the corresponding bulk SPEs. The absence of ion-pair formation and anion transport makes $Cd_{0.75}PS_3Li_{0.5}(PPG)$ an ideal system for investigating ionic motion in disordered polymer matrixes.

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