



Gel electrolytes based on crosslinked tetraethylene glycol diacrylate/poly(ethylenimine) systems

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Abstract

Gel electrolytes were prepared by crosslinking low molecular weight poly(ethylenimine) (PEI) with tetraethylene glycol diacrylate (TEG) in the presence of 2-methoxyethyl ether (diglyme) and lithium triflate (LiTf). Impedance and infrared (IR) spectroscopies were used as complimentary tools for studying the mode of ion conduction in these gel electrolytes. Ionic conductivity measurements for all samples tested exhibited significant LiTf and diglyme composition dependency. The maximum ionic conductivity at 20 °C was 2×10^{-4} S/cm with moderate LiTf and high diglyme compositions. The calculated molal concentration of non-ionically bound 'free' triflate ion was found to vary directly with ionic conductivity with the highest molality 'free' triflate samples yielding the highest ionic conductivity. Lithium ion interactions with the triflate ion, diglyme and the crosslinked polymer matrix were observed with IR spectroscopy. A lower frequency shoulder on the $\nu_s(\text{C}=\text{O})$ vibrational mode increases in intensity as LiTf composition is increased. Curve fitting and molar calculations suggest that over 85% of the total lithium ions available are coordinated to the TEG carbonyl at dilute LiTf compositions.

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1. Introduction

The development and study of solid polymer electrolytes (SPE) has been extensive because of their potential application as ion transport membranes in batteries and other electrochemical devices. SPE are desirable because they offer form flexibility, decreased weight and improved safety as compared with other materials used as electrolytes in electrochemical devices [1]. Unfortunately, most SPE have lower than necessary ionic conductivity needed for high energy density electrochemical devices. Polymeric gel electrolytes have been developed and make certain improvements in the physical properties and conductivity of SPE. A polymeric gel electrolyte typically consists of a polymer matrix infused with a high boiling point organic solvent and a suitable electrolyte [2]. Ionic conductivity for these gel electrolytes can typically range from 10^{-3} to 10^{-4} S/cm and lower at room temperature [3–6]. For gel electrolytes to be a practical substitute for SPE, they also

must be dimensionally stable solids with suitable electrochemical stability. Further exploration of new and improved materials, along with further understanding of the link between molecular level interactions and ionic conductivity, is still necessary for the further development of polymeric ion transport membranes for electrochemical devices.

A Michael reaction [7] involving the nucleophilic amine functionality in PEI with the electrophilic acrylate functionality of TEG serves as the means of synthesis of the crosslinked material described herein (Fig. 1). To our knowledge, the use of TEG to produce gel electrolytes by condensation polymerization/crosslinking using the acrylate functionality as a Michael acceptor has not been reported. TEG has been described in the chemical literature for the preparation of crosslinked polymer gel electrolytes as a crosslinking agent [3,8–12]. However, in these examples, the alkene of the acrylate functionality has been used in addition polymerization reactions, typically radical, with other alkenes, and other TEG alkenes, in the presence of electrolyte and a solvent to yield gel electrolytes. These gel electrolytes also require initiation of polymerization by means of an initiator [3,8–11] or with a UV lamp [12]. With our system, only mixing is required for crosslinking.

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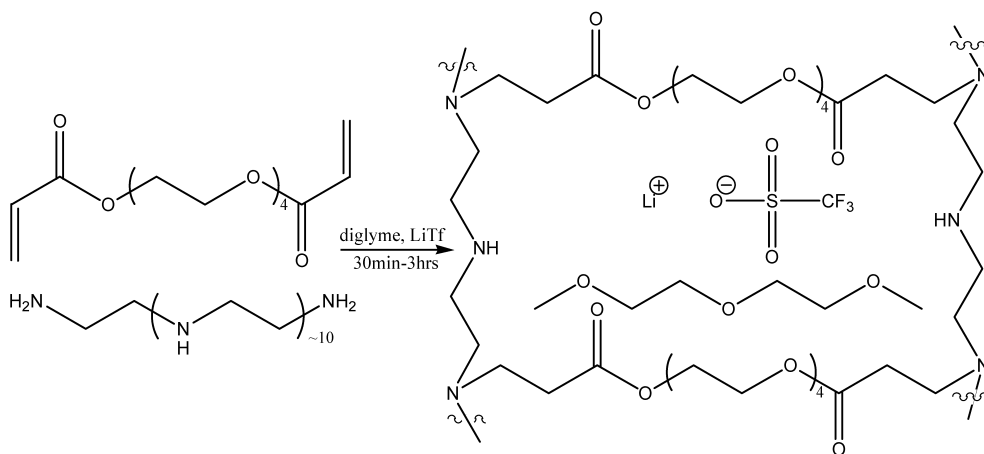


Fig. 1. Synthesis of TEG crosslinked PEI gel electrolytes.

Ionic conductivity measurements are presented for TEG crosslinked PEI gel electrolytes. Interactions of lithium ion with triflate, diglyme and the crosslinked polymer matrix have been examined with vibrational spectroscopy and have been used to help clarify certain aspects of ionic conduction occurring in these gel electrolytes.

2. Experimental

PEI (indicated by Aldrich to be a mixture of linear and branched chains, $M_w = 463$), diglyme (99.5% anhydrous), TEG (90%) and LiTf (96%) were obtained from Aldrich and stored in a dry air purge glove box. PEI, TEG and diglyme were used as received. LiTf was dried under reduced pressure at 110 °C for 32 h and stored in a dry air purge glove box. IR and NMR were used to verify the absence of spectroscopically meaningful amounts of water and other contaminants.

All gel electrolytes were prepared in a dry air purge glovebox. A typical sample was prepared by adding appropriate amounts of PEI, diglyme and LiTf to a vial and stirring until complete dissolution of each component occurred. The desired amount of TEG was added, and the mixture was stirred to ensure complete dissolution of TEG. A solid material resulted within 30 min to 3 h depending on the LiTf and diglyme concentrations. After initial dissolution of TEG, the pre-cured solution was partitioned out for IR, Raman and conductivity measurements.

IR samples were prepared by placing a very small drop of the pre-cured solution onto a NaCl plate, sandwiching the drop with another NaCl plate, applying a tape seal along the interface between the two NaCl plates and allowing an appropriate amount of time for curing. IR spectra were acquired for samples with a Bruker IFS66V FT-IR spectrometer over a range of 4000–600 cm^{-1} at a resolution of 1 cm^{-1} . Raman samples were prepared by dispensing the pre-cured

solution into a 5 cm long standard quartz NMR tube and allowing the solution to cure. Raman spectra were recorded using a Bruker Equinox 55 FT-IR spectrometer outfitted with an FRA 106 FT-Raman accessory and a Nd:YAG laser providing an excitation line at a power of 300 mW. Curve fitting analysis was performed using Galactic Grams software, version 7.0. Each spectral region was fit with a mixed gaussian–lorentzian function and a linear baseline. The frequency at which the calculated maximum band height occurred was set as the frequency for each band. A typical R^2 value, or coefficient of determination, between the curve produced by the sum of each deconvoluted peak and the actual spectrum was 0.99992. A typical fit is displayed in Fig. 2.

AC conductivity measurements were obtained for the cured material that remained in the original vial. The solid gels were easily removed and sandwiched between two 12.5 mm stainless steel electrodes in an airtight cell. Constant temperatures were maintained using a circulating water/ethylene glycol bath. Impedance measurements were made over the range of 5 Hz to 10 MHz using an HP 4192A LF impedance analyzer, and impedance plots were fitted using a commercial program (LEVM version 7.1).

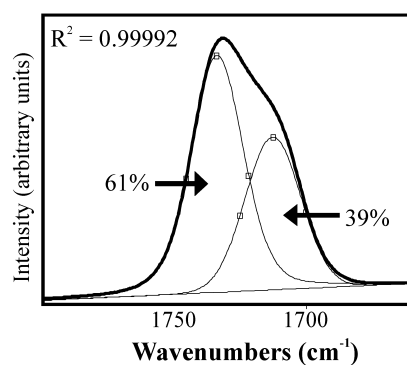


Fig. 2. A fit of the $\nu_s(\text{C}=\text{O})$ region with a typical R^2 value between actual and composite spectrum.

3. Results

3.1. General

IR and Raman spectroscopies were used to evaluate the degree of crosslinking of the cured gel electrolytes. A complete disappearance of the alkene stretching bands of TEG at 1637 and 1619 cm^{-1} , and the alkene CH_2 twist at 810 cm^{-1} was noted in the IR spectra for all samples discussed in this paper. An absence of the alkene stretching mode at 1636 cm^{-1} was also observed in Raman spectra. In both IR and Raman spectra, a higher frequency shift of the $\nu_s(\text{C}=\text{O})$ from 1724 cm^{-1} in pure TEG to 1734 cm^{-1} in the crosslinked samples was observed. Curve fitting of each carbonyl stretching mode indicated only one component contributes to the peak area in the samples prepared with diglyme but no LiTf. The combined evidence suggests essentially complete reaction of the acrylate groups of TEG with the amine groups of PEI. An infrared spectra stack plot of each of the gel components as well as two gels with different diglyme compositions is presented in Fig. 3 to show the spectral origins of the gel electrolytes and the disappearance of the alkene stretch.

All samples cited in this paper were prepared with a constant theoretical crosslinking ratio of five moles of PEI nitrogen to one mole of TEG (2.5N:1acrylate functionality), abbreviated 5N:1TEG (this composition was used because it produced samples that subjectively had good physical properties). The diglyme composition of each sample is listed as a ratio of the number of PEI nitrogens to diglyme oxygens (no TEG or Tf^- oxygens included). A sample with five nitrogens for every two diglyme molecules is abbreviated N:O = 5:6. When indicating the molar composition of a sample, the contribution of TEG is excluded

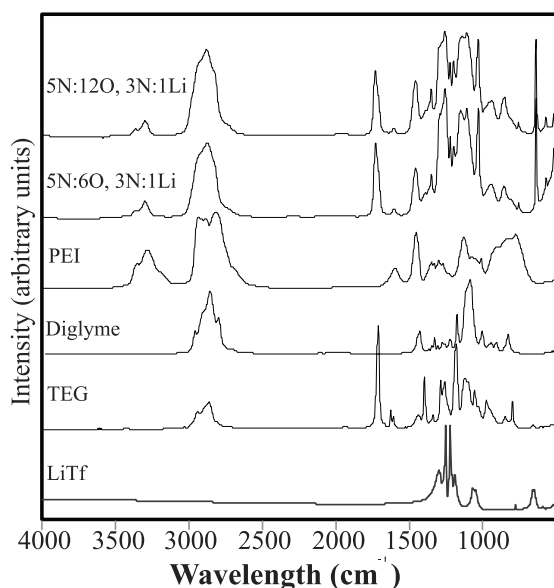


Fig. 3. Stack plot of each component in the gel electrolytes and a high and low diglyme composition gel.

because the molar ratio of PEI to TEG is held fixed in all samples.

All gel electrolytes described herein were free-standing and flexible materials. When blotted by tissue paper, diglyme bleeding out of the polymer matrix was not observed. Decreasing the diglyme composition yielded a tougher material, while increasing the LiTf composition had little effect except at the very high concentrations (N:Li = 1.5 and 2) where the material softened at $60\text{ }^\circ\text{C}$.

3.2. Ionic conductivity

3.2.1. General

Ionic conductivity measurements were taken for a variety of sample compositions at different temperatures. Each sample tested had a composition of 5N:1TEG, while the compositions of diglyme and LiTf were varied. Conductivity measurements were taken for all samples at $20\text{ }^\circ\text{C}$ and, for select samples, over a temperature range of $0\text{--}60\text{ }^\circ\text{C}$.

3.2.2. Ionic conductivity at $20\text{ }^\circ\text{C}$

The ionic conductivity of samples with a diglyme composition of N:O = 5:6 increased with increasing amounts of LiTf present at $20\text{ }^\circ\text{C}$ as shown in Table 1. Additional increases in LiTf composition were not possible due to limited LiTf solubility. Increasing the diglyme composition from N:O = 5:6 to 5:12 increased the conductivity about an order of magnitude for comparable LiTf compositions, (Table 1). The trend in conductivity values at $20\text{ }^\circ\text{C}$ for the N:O = 5:12 samples was different than that of the trend observed in the N:O = 5:6 samples. Ionic conductivity increased as the LiTf composition increased to a maximum value of $2 \times 10^{-4}\text{ S/cm}$ at a composition of N:Li:O = 3:1:7.2 and decreased in value for samples with increased amounts of LiTf. Increases in conductivity with increasing amounts of diglyme are considerable, as samples with constant N:Li = 30:1 and N:O ratios of 5:0, 5:6 and 5:12 had conductivities of 1×10^{-7} , 2×10^{-6} and $1 \times 10^{-5}\text{ S/cm}$, respectively.

3.2.3. Conductivity from 0 to $60\text{ }^\circ\text{C}$

Plots of ionic conductivity versus temperature over a temperature range of 0 to $60\text{ }^\circ\text{C}$ are presented in Figs. 4 and 5 for samples with N:O = 5:6 and 5:12 and LiTf compositions of N:Li = 3:1 to 40:1 for the N:O = 5:6 samples and N:Li = 3:1 to 30:1 for the N:O = 5:12 samples. All plots appear to display Arrhenius behavior in this temperature region although the temperature range is too narrow to distinguish between Arrhenius behavior and WLF or VTF behavior. The highest conductivity observed is $7 \times 10^{-4}\text{ S/cm}$ at $60\text{ }^\circ\text{C}$ for the N:O:Li = 3:7.2:1 sample. Apparent activation energies for ionic conduction were calculated for each 0 to $60\text{ }^\circ\text{C}$ data set and are presented in Table 2. Higher energies are noted for the samples with the N:O = 5:6 composition relative to the samples with

Table 1

Weight percent of each component, relative peak areas of the triflate anion species and the 20 °C ionic conductivity for each gel electrolyte

xN:1Li	PEI (wt%)	TEG (wt%)	Diglyme (wt%)	LiTf (wt%)	'Free' ion (%)	Ion pair (%)	Aggregate (%)	σ (S/cm)
5N:12O 30N:1Li:72O	19.9	27.9	49.8	2.4	100			1×10^{-5}
20N:1Li:48O	19.7	27.6	49.2	3.5				2×10^{-5}
10N:1Li:24O	19.0	26.6	47.5	6.8	93	7		6×10^{-5}
5N:1Li:12O	17.8	24.9	44.4	12.9	78	22		1×10^{-4}
3N:1Li:7.2O	16.4	22.9	41.0	19.7	51	48	1	2×10^{-4}
2N:1Li:5O	15.1	21.1	37.7	26.2	31	65	4	2×10^{-4}
1.5N:1Li:3.6O	13.7	19.1	34.2	33.0	28	64	8	5×10^{-5}
5N:6O								
30N:1Li:36O	26.5	37.1	33.2	3.2	100			2×10^{-6}
20N:1Li:24O	26.1	36.6	32.6	4.7				4×10^{-6}
10N:1Li:12O	24.9	34.9	31.2	9.0	67	33		8×10^{-6}
5N:1Li:6O	22.9	32.0	28.6	16.6	61	39		1×10^{-5}
3N:1Li:3.6O	20.6	28.8	25.7	24.9	44	51	5	2×10^{-5}

Table 2

Activation energies for ionic conduction for N:O = 5:6 and 5:12 samples over a range of LiTf compositions

N:O = 5:12	E_a (kJ/mol)	N:O = 5:6	E_a (kJ/mol)
1.5N:1Li:3.6	40	3N:1Li:3.6O	42
2N:1Li:5O	30	5N:1Li:6O	40
3N:1Li:7.2O	24	10N:1Li:12O	37
5N:1Li:12O	26	30N:1Li:36O	37
10N:1Li:24O	26	40N:1Li:48O	31
20N:1Li:48O	26		
30N:1Li:72O	25		

N:O = 5:12 composition, and an increase in energy was also noted as the LiTf composition was increased in the N:O = 5:6 samples. This trend was not observed in the N:O = 5:12 samples until the LiTf composition was greater

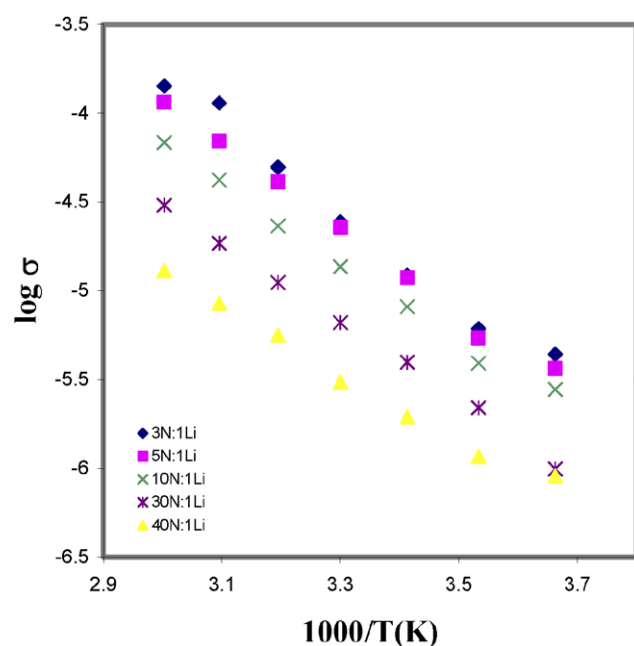


Fig. 4. Ionic conductivity from 0 to 60 °C for N:O = 5:6 samples with LiTf compositions of N:Li = 3:1 to 40:1.

than N:Li = 3:1 where the energy of activation increased with additional LiTf for both the N:Li = 2:1 and 1.5:1 samples.

3.3. Infrared spectroscopy

3.3.1. Li^+ interactions

Lithium ion coordinative interactions in the gel electrolytes were probed using IR spectroscopy. The lithium ion can potentially interact with the triflate as a triflate ion pair or an aggregate structure, the ether oxygens in diglyme and TEG, the ester functionality in TEG and the amine nitrogens of PEI.

3.3.2. Li^+ and Tf^- ionic association

The frequency of the triflate ion $\nu_s(\text{SO}_3)$ vibrational

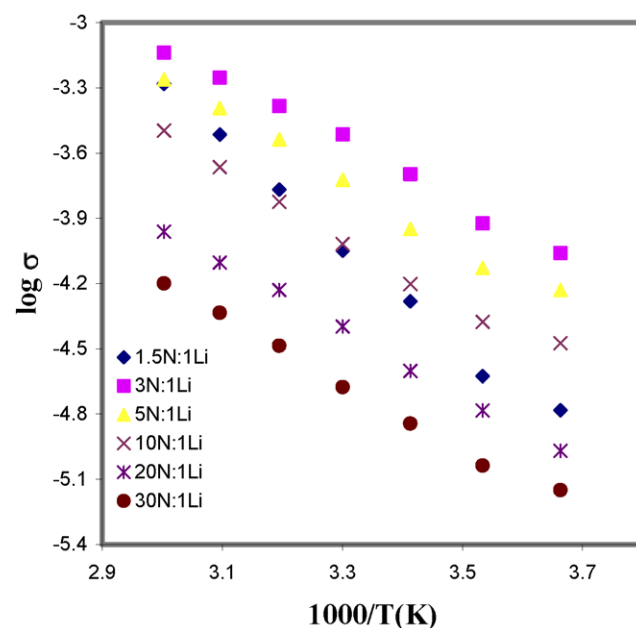


Fig. 5. Ionic conductivity from 0 to 60 °C for N:O = 5:12 samples with LiTf compositions of N:Li = 1.5:1 to 30:1.

mode has been shown to be sensitive to interactions with lithium ions and is indicative of its ionic coordination (Tf^- ('free'), LiTf (contact ion pair), $[\text{Li}_2\text{Tf}]^+$ (triple cation), etc.) [13,14]. 'Free' triflate in this paper is defined as triflate ion not coordinated to lithium ion and was determined, as with the other triflate species, through analysis of the infrared spectral region associated with the $\nu_s(\text{SO}_3)$. Fig. 6 shows IR spectra in the $\nu_s(\text{SO}_3)$ region for samples with compositions N:O = 5:12 and N:Li = 1.5:1 to 30:1 at room temperature. Semi-quantitative determination of the relative amounts of triflate species present was calculated by curve-fitting the $\nu_s(\text{SO}_3)$ region. Mixed gaussian-lorentzian bands were observed at 1031, 1039 and 1053 cm^{-1} and assigned to the spectroscopically 'free' Tf^- , the LiTf ion pair and the $[\text{Li}_2\text{Tf}]^+$ triple ion, respectively. These values are consistent with those in chemical literature [14,15]. Comparison of the $\nu_s(\text{SO}_3)$ region of spectra in samples with and without LiTf (5N:1TEG:4dig) indicate that the triflate bands are present in a significantly greater relative intensity to weak underlying bands even at the 30N:1LiTf composition and that these weak bands only impart a very small amount of error into the curve fitting analysis. Table 1 summarizes the curve-fitting results for both the N:O = 5:6 and 5:12 samples. At low compositions of LiTf , the only form of triflate observed was the spectroscopically 'free' form in all compositions of diglyme tested. At moderate LiTf composition (N:Li = 5:1 and 10:1 for both N:O = 5:6 and 5:12 compositions), an increase in ionic association is noted with an increase in the relative population of the LiTf ion pair without exceeding the amount of 'free' triflate present. Formation of the $[\text{Li}_2\text{Tf}]^+$ triple ion species is apparent at high LiTf compositions. Contact ion pairs predominate and increasingly become more dominant with increasing LiTf for both diglyme compositions. 'Free' triflate is notably still present in a significant percentage at the highest compositions of LiTf for both the N:O = 5:6 and 5:12 samples.

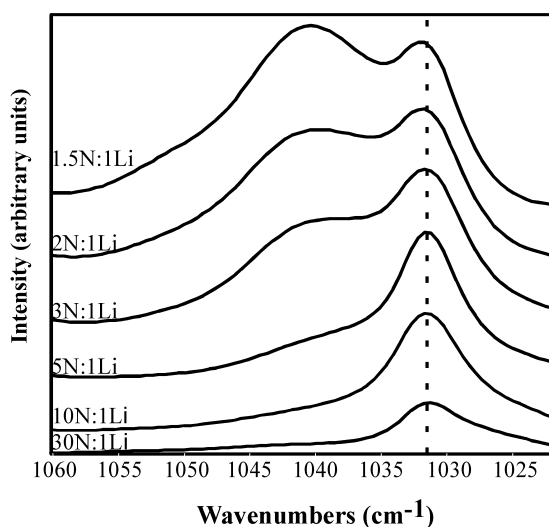


Fig. 6. Comparison of the infrared spectra from N:O = 5:12 samples at the indicated LiTf compositions in the $\nu_s(\text{SO}_3)$ spectral region.

Frequency shifts and band development are also noted in other lithium sensitive triflate bands, such as the $\nu_s(\text{CF}_3)$ and the $\delta_s(\text{CF}_3)$, when varying LiTf composition.

3.3.3. Li^+ interactions with diglyme

Studies of the interactions of Li^+ with the ether oxygens in ethylene oxide based compounds such as PEO, tetraglyme and diglyme indicate that the frequencies and intensities of bands attributed to a mixture of CH_2 rocking and C–O stretching motions reflect local conformations of the ethylene oxide unit through the correlation of these frequencies with the O–C–C–O dihedral angle [16,17]. Lithium ion interactions with the ether oxygens have been shown to affect this angle [18–20]. Fig. 7 shows the CH_2 rocking and C–O stretching region for samples with a constant diglyme composition of N:O = 5:12 and an increasing LiTf composition. A band, centered at 854 cm^{-1} , dominates at low LiTf composition with a weak band present at higher frequency. This band has been assigned in the literature in the case of diglyme– LiTf to be the result of a mixture of CH_2 rocking and C–O stretching motions related to the TGT and TGG conformer of diglyme [16]. As the LiTf composition is increased, the higher frequency band at 872 cm^{-1} increases significantly in intensity until it becomes the dominant feature at N:Li = 1.5:1. This band has been assigned in the literature in the case of diglyme: LiTf to a CH_2 rocking vibration of a conformation which is not observed in pure diglyme but is adopted by diglyme in order to coordinate the lithium ion as the LiTf composition is increased [16]. An increase in distinct band structure is also observed as two lower frequency bands relative to the original dominant band at 854 cm^{-1} increase in intensity at approximately 846 and 836 cm^{-1} . These bands may be the result of conformers

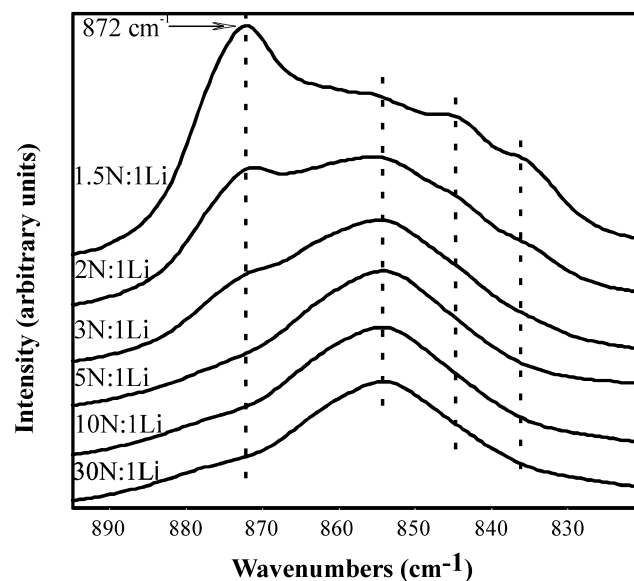


Fig. 7. Comparison of the infrared spectra from N:O = 5:12 samples at the indicated LiTf compositions in the CH_2 rocking spectral region.

with CH₂ rocking and C–O stretching motions related to diglyme conformations related to the TTG and TTT conformations [16]. Only a small development in band intensity of the 872 cm⁻¹ band at a N:Li = 3:1 composition is noticed relative to the dominant 854 cm⁻¹ band in the N:O = 5:6 samples from N:Li = 30:1 to 3:1. An additional band develops in the region between 900 and 1000 cm⁻¹ at 949 cm⁻¹ for both the N:O = 5:6 and 5:12 samples as LiTf composition is increased. Bands in this region also reflect local ethylene oxide conformations, which change as the lithium ion interacts with ether oxygens.

3.3.4. Li⁺ interactions with crosslinked polymer

Lithium ion interactions with the polymer matrix can be examined with IR spectroscopy. A lower frequency shoulder develops on the $\nu_s(\text{C}=\text{O})$ mode with increasing LiTf composition for both the N:O = 5:6 and 5:12 samples (Fig. 8). The C=O stretching mode commonly develops this spectral signature in the presence of Lewis acids as a result of coordination between the Lewis acid and the more electronegative oxygen in the carbonyl [21,22]. At sufficient LiTf compositions, curve fitting the $\nu_s(\text{C}=\text{O})$ mode in the gel electrolytes reveals the presence of two bands, one at 1733 cm⁻¹ (indicated by a dashed line in Fig. 8) and the other, typically, between 1714 and 1711 cm⁻¹. In the absence of LiTf, only one band is observed at 1733 cm⁻¹. This band is assumed to be the result of non-lithium ion coordinated ester carbonyl and will be called ‘free’ carbonyl in this paper. The other band will be described as the lithium ion coordinated band. Curve fitting of the $\nu_s(\text{C}=\text{O})$ region for the N:O = 5:12 samples shows a distinct increase in the peak area of the coordinated band with increasing LiTf composition. As seen in Table 3, essentially all of the carbonyl groups are present in the free form at dilute LiTf compositions in the N:O = 5:12 samples. Sharp increases in the percent area of the coordinated carbonyl are noted going from the N:Li = 30:1 to the 10:1 samples. At the highest

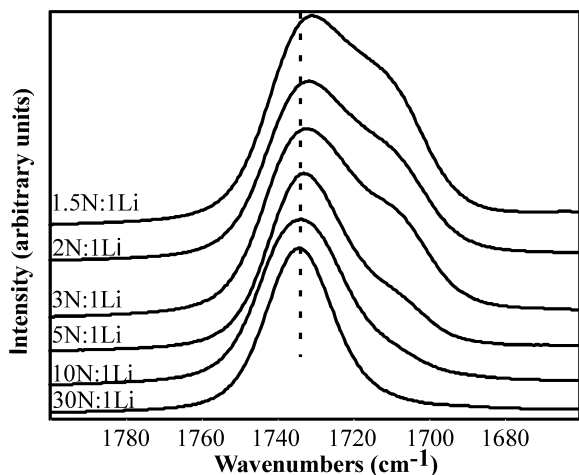


Fig. 8. Infrared spectra from the $\nu_s(\text{C}=\text{O})$ spectral region for N:O = 5:12 samples at the indicated LiTf compositions.

Table 3

Curve fitting results from N:O = 5:12 samples indicating the percentage area of the $\nu_s(\text{C}=\text{O})$ represented by ‘free’ carbonyl and lithium ion coordinated carbonyl

N:O = 5:12 composition (N:Li)	‘free’ C=O (%)	Li ⁺ coordinated C=O (%)
1.5	61	39
2	62	38
3	65	35
5	75	25
10	79	21
30	100 ^a	0 ^a

^a At dilute LiTf composition, curve fitting software could not detect a second band.

composition of LiTf, the ‘free’ carbonyl represents only 60% of the total peak area.

N:Li = 10:1 and 30:1 samples were prepared without addition of diglyme, and the 800–1000 cm⁻¹ TEG O–C–C–O conformation region was examined for evidence of increased band structure as a result of the interaction of the lithium ion with the TEG ether oxygens. One dominant band centered at 859 cm⁻¹ is present with bands of weak intensity on each side in both spectra and does not change appreciably as LiTf composition is increased from N:Li = 30:1 to 10:1. The spectral region between 4000 and 2000 cm⁻¹ remains largely unchanged for the sample compositions cited in this paper. The N–H stretching bands broaden slightly at lower LiTf compositions, while the C–H stretching region is largely unaffected by changes in LiTf composition.

4. Discussion

Examination of the various lithium ion interactions and ionic conductivity in these gel electrolytes provides insight into the relative concentration of charged species and qualitatively how ionic coordination trends correlate with ionic conductivity trends. Extensive coordination of the ionic species present can either, depending on the strength of coordination, hinder ionic mobility and decrease ionic conductivity or facilitate ion mobility and increase ionic conductivity.

In the binary system of diglyme–LiTf, the lithium ion has been suggested to prefer four fold coordination in solution and five fold coordination in the crystalline phase [20]. The solution phase structure of lithium ion (present as LiTf) in pure diglyme was found to preferentially coordinate three oxygens from diglyme and one oxygen from triflate as a contact ion pair [20]. A relatively rigid three-dimensional network of crosslinked polymer, i.e. TEG crosslinked PEI, infused with diglyme and LiTf, increases the number of coordinative sites possible for the lithium ion. Instead of the lithium ion being limited to diglyme oxygens and triflate ionic species, amine nitrogens, ester oxygens and TEG ether

oxygens are available for potential coordination thus not allowing treatment of the polymer matrix as an inert framework for the diglyme and LiTf.

Comparison of the spectral data from N:O = 5:12 samples of the diglyme–LiTf–TEG–PEI gels and only diglyme–LiTf samples reveals markedly different diglyme conformational behavior and triflate speciation at comparable diglyme oxygen to lithium ratios. As seen in Fig. 9, diglyme–LiTf at a composition of O:Li = 5:1 exhibits a strong band at 874 cm^{-1} with two smaller bands at 835 and 844 cm^{-1} . This is in contrast to the gel O:Li = 5:1 spectrum in which a slightly weaker higher frequency band at around 872 cm^{-1} appears superimposed on the broad 854 cm^{-1} band. Bands at 835 and 844 cm^{-1} appear as only weak features on the low frequency side of the 854 cm^{-1} band. The increase in band structure as LiTf composition is increased suggests an increase in the amounts of lithium ion/ether coordinative interactions.

In diglyme–LiTf, contact ion pairs are the dominant triflate species from O:Li = 80:1 to 10:1, while, at the O:Li = 5:1 composition, the triple cation $[\text{Li}_2\text{Tf}]^+$ form dominates [23]. This is significantly different from both the N:O = 5:6 and 5:12 gel samples where ‘free’ triflate is the only component at dilute LiTf compositions, and ion pair develops at moderate LiTf compositions but does not dominate until high LiTf composition. The formation of higher order ionic species appears to be significantly impeded in the gel electrolyte samples when compared to the diglyme–LiTf samples.

The polymer matrix must play a key role in coordinating the lithium ion so as to produce the marked spectral differences between the diglyme–LiTf and diglyme–LiTf–TEG–PEI samples. As mentioned earlier, the polymer matrix provides several different coordinative heteroatoms as part of ester, ether and amine functionalities. Slight changes are seen in the C–N stretching region over the LiTf concentration ranges examined, but meaningful

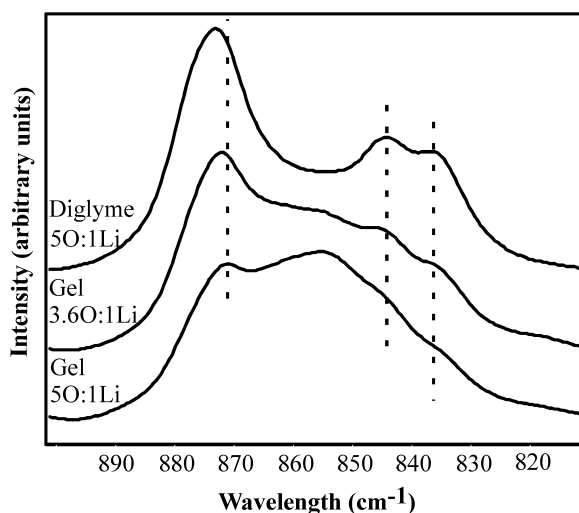


Fig. 9. Comparison of CH₂ rocking region of N:O = 5:12 samples and diglyme–LiTf at the indicated LiTf compositions.

interpretation is not possible due to a medley of other bands that appear in this region. Interaction of the lithium with the TEG ether oxygens in the O–C–O conformation regions could not be observed because of the dominance of diglyme bands in these regions. IR spectra were taken of only TEG–LiTf at a low LiTf concentration and the maximum allowable LiTf concentration (O:Li = 10:1), and virtually no changes in band structure in the O–C–O conformation regions were observed when compared to pure TEG. This suggests that there are only a few conformation-restricting lithium ion interactions with the TEG ether oxygens. A slight carbonyl–lithium ion interaction did appear at the higher LiTf concentration.

The only direct evidence of lithium interaction with the polymer matrix is through observation of the shoulder that develops on the carbonyl symmetric stretch. As seen from the curve fitting results in Table 3, the peak area of the low frequency shoulder on the carbonyl increases significantly from essentially 0 to 39% of the total peak area over the complete LiTf composition range in the N:O = 5:12 samples. Assuming the absorptivity of the shifted carbonyl vibrational mode is approximately the same as the stationary carbonyl vibrational mode and that the lithium ion coordinates to only one carbonyl, the percentages of total lithium coordinated to carbonyls were calculated. This calculation is possible because the compositions of TEG and LiTf and the relative compositions of ‘free’ and coordinated carbonyl are known. Table 4 lists the percentages of lithium ion coordinated to carbonyls over all the LiTf concentrations for the 5N:12O samples. At the N:Li = 1.5:1 composition, the ratio of lithium ion to carbonyl is 1.7:1, the shoulder comprises 39% of the total carbonyl peak area and 23% of the total lithium ions are coordinated to a carbonyl. At the 10N:1Li concentration, the ratio of lithium ion to carbonyl is 0.25:1, the shoulder comprises 21% of the total carbonyl peak area and 85% of the total lithium ions are coordinated to a carbonyl. This information coupled with the curve fitting data indicating the triflate speciation to be 28 and 93% ‘free’ triflate for the N:Li = 1.5:1 and 10:1 samples, respectively, strongly suggests that the carbonyl dominates the competition for lithium ion at moderate compositions. It also suggests that the carbonyl significantly coordinates the lithium ion not forced into coordination with

Table 4

Data indicating the results of the calculation of the percentage of total lithium ion coordinated to a carbonyl with a comparison to the amount of ‘free’ triflate present for N:O = 5:12 samples

N:Li	Moles of CO–Li	Li ⁺ coordinated (%)	‘Free’ triflate (%)
1.5	3.6×10^{-4}	24	28
2	3.4×10^{-4}	31	31
3	3.2×10^{-4}	42	51
5	2.2×10^{-4}	49	78
10	1.9×10^{-4}	85	93
30	~0	0.0	100

triflate at high LiTf composition. Although two peaks were not observed when curve fitting the N:Li = 30:1 sample, presumably due to the very small amount of LiTf, the trend suggests that at dilute LiTf composition greater than 85% of the total lithium is coordinated to the carbonyl. The overall coordinative influence of the carbonyl likely provides the basis for the prevalence of the lower order triflate species (free Tf^- and LiTf contact ion pairs) in the gel samples as compared with the diglyme–LiTf samples.

LiTf composition affects the ionic conductivity significantly as seen in Fig. 10 where molality (moles of LiTf/mass of PEI + TEG + diglyme) was used as an estimation of the LiTf concentration. In the N:O = 5:12 samples, conductivity increased to a maximum and then decreased with additional LiTf. This is in contrast to the N:O = 5:6 samples where conductivity increased as the LiTf molality increased for all LiTf compositions. At higher LiTf molality, the conductivity for N:O = 5:6 samples may also decrease as similar behavior has been noted in other gel electrolyte systems [3]. The largest ‘free’ triflate molality (moles ‘free’ triflate estimated from curve fitting data/mass of PEI + TEG + diglyme + other triflate species) observed was for the N:Li = 3:1 sample, and this was also where the highest conductivity was observed. The sample with the highest molality of ‘free’ triflate also yielded the highest conductivity in the highest composition LiTf, 5N:6O sample.

The ionic conductivity at 20 °C increased about an order of magnitude as the composition of diglyme was roughly doubled from the N:O = 5:6 to the 5:12 sample. This increase is presumably related to an increase in the mobility of the lithium and triflate ions as a result of increased amount of diglyme supported in the semi-rigid polymer matrix. The presence of more diglyme may also decrease some of the lithium ion coordination to the relatively stationary carbonyl in the polymer matrix as seen by the

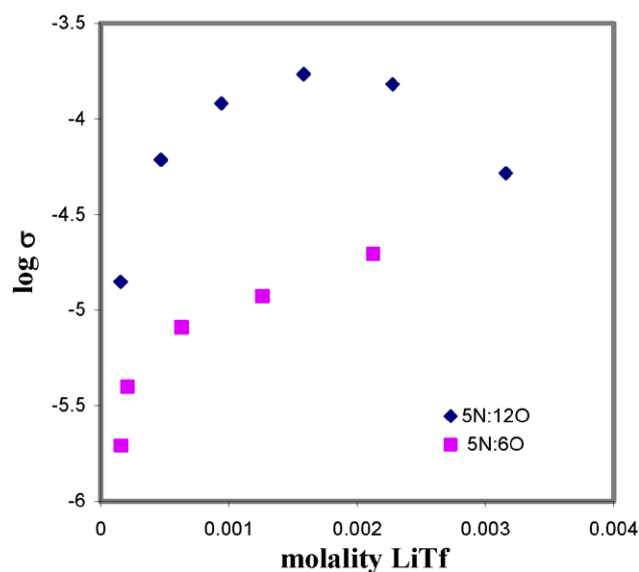


Fig. 10. Natural log of the conductivity versus LiTf molality for N:O = 5:6 and 5:12 samples over a range of LiTf compositions.

increase in the amount of coordinated carbonyl in the N:O = 5:6 samples at comparable LiTf compositions. Apparent activation energies for ionic conduction calculated from the variable temperature data for both the N:O = 5:6 and 5:12 samples indicate that higher activation energies are, not surprisingly, required in the N:O = 5:6 samples. This is in agreement with the lower conductivity values measured for these samples. In the N:O = 5:6 samples, the apparent activation energy actually increased with increasing LiTf concentration, which is not understood because the highest conductivity is observed with the highest molality of ‘free’ triflate, and composition of LiTf. The activation energies in this gel electrolyte are on average slightly higher than those in other gel systems. For example in a glyme plasticized polymerized diacrylate system with LiTf, a typical activation energy was 28 kJ/mol [24], while in a plasticized PAN gel electrolyte activation energies were between 10 and 15 kJ/mol [25].

5. Conclusions

New gel electrolytes composed of a TEG crosslinked low molecular weight PEI matrix infused with varying concentrations of diglyme and LiTf have been characterized by means of vibrational and impedance spectroscopies. The ionic conductivity was found to vary with LiTf composition with the N:O = 5:6 samples showing a continual, steady increase in conductivity and the N:O = 5:12 samples exhibiting a maximum conductivity at a N:Li = 3:1 composition. The ionic conductivity was the greatest in both the N:O = 5:6 and 5:12 samples when the ‘free’ triflate molality was at a maximum. Increases in diglyme concentration yielded increases in conductivity. Over a temperature range of 0–60 °C, activation energies for ionic conduction indicated more energy was required for conduction in the lower diglyme composition samples. In the N:O = 5:12 samples, the percentage of lithium ions coordinated to carbonyl groups was found to increase as the total amount of LiTf decreased and was observed to be the greatest at the N:Li = 10:1 composition where 85% of the lithium ion available was coordinated to a carbonyl group. This, along with the triflate speciation data, indicates that the lithium ion preferentially interacts with the carbonyl group relative to the triflate anion at dilute LiTf compositions. At higher LiTf compositions, a greater relative percentage of lithium ions interacting with the triflate ions rather than the additional ‘free’ carbonyl groups and increasing diglyme band structure indicates a complex coordinative environment that results in material with relatively high ionic conductivity. A closer examination of the effect of the interaction of the polymer matrix with lithium salts on ionic conductivity and evaluation of the electrochemical stability of this material are both part of future work planned.

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