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OPTIMIZING IONIC CONDUCTIVITY OF POLYMER ELECTROLYTES THROUGH SALT COMPOSITION AND THERMAL CONDITIONS

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ABSTRACT

For electrochemical application, polymer electrolytes need to be optimized in both composition and operating temperature, so as to obtain high ionic conductivity. The impact of lithium-salt chemistry, salt concentration, and thermal condition on the ionic conductivity of poly(ε-caprolactone)-based polymer electrolytes has been assessed based on 711 experimental observations, which correspond to 17 salt chemistries and 51 salt–molality formulations. Median conductivity was used to summarize replicate measurements and $\log_{10}$ conductivity was used for distributional comparisons at the four key thermal conditions (30, 50, 70 and 90 °C). The median conductivity increased from 3.03×10^{-7} S cm^{-1} at 30 °C to 4.39×10^{-5} S cm^{-1} at 90 °C, with a significant and highly consistent thermal effect across complete formulations. The conductivity and salt concentration had a non-linear relationship, with intermediate salt loadings often proving superior. LiFSI at 1.0 mol kg^{-1} showed the best overall performance throughout the entire thermal range, while LiBOB at 0.6 mol kg^{-1} and LiDFOB at 2.2 mol kg^{-1} showed the highest performance at about 70 and 90 °C, respectively. Arrhenius-type analysis further demonstrated formulation-specific temperature sensitivity. In general, optimization of ionic conductivity was best achieved by considering the salt, its concentration and thermal condition together. The results provide a set of optimum conductivities for the compositions and as a function of temperature, and they support the selection of polymer-electrolyte formulations for transport performance under multiple conditions.

1. Introduction:

Advanced electrochemical energy-storage systems are increasingly looking to polymer electrolytes as alternatives to traditional liquid electrolytes, given the desirable properties of safety, flexibility, and processability, and compatibility with high-energy-density battery designs. Solid and gel polymer electrolytes can reduce leakage and flammability risks while also providing mechanically flexible ion-conducting matrices. Nevertheless, insufficient ionic conductivity, particularly at moderate and ambient temperatures, remains a major limitation to their widespread application. The factors that affect the transport of ions in polymer electrolytes are closely correlated and involve polymer-chain mobility, ion dissociation, polymer–ion coordination, salt chemistry, salt concentration and operating temperature (Han et al., 2020).

The polymer matrix provides coordination sites through which dissolved ions can migrate, while the physicochemical properties of the incorporated salt govern the concentration and mobility of charge carriers. Thus, the polymer structure and the electrolyte chemistry need to be taken into account simultaneously for developing high conductivity systems. The degree of dissociation and mobility of ions in the polymer phase depends on the structural features of the polymer, including crystallinity, segmental flexibility, functional groups, and molecular architecture. Therefore, reviews of battery polymer electrolytes have focused on the balance between favorable ion–polymer interactions and segmental mobility to achieve high conductivity, instead of maximizing either of these properties on their own (Rollo-Walker et al., 2021). Furthermore, the choice of lithium salt and its compatibility with the host polymer affects the performance of solid polymer electrolytes, which affects their ion dissociation, segmental dynamics, and transport efficiency (Mauger & Julien, 2022).

Salt composition represents a particularly important design parameter. The addition of salt may at first increase the conductivity due to enhanced number of mobile charge carriers; however, further addition of salt may lead to ion aggregation, more coordination of the ions to the polymer, immobility of the polymer chains, and finally, a decrease in the transport efficiency. Experimental studies of hybrid polymer electrolytes (HPE) containing LiTFSI have shown that the conductivity can be enhanced up to a certain composition, after which the other properties of the material might be degraded (Mohanty et al., 2022). Based on these observations, salt concentration should be considered an optimization parameter rather than assuming a linear relationship between salt concentration and conductivity.

The type of salt is also significant, as the properties of the cations and anions affect the dissociation of the salt, its coordination strength, ion pairing, and transport processes. Recent investigations revealed that alterations in the cation chemistry can lead to significant changes in the conductivity, related to the interactions of the ions with the polymer coordination sites, and that the major transport mechanism also varies with polymer molecular characteristics (Papamichail et al., 2025). Polycaprolactone-based systems are particularly relevant in this context because their carbonyl-containing chains can support lithium-ion coordination and transport. Experimental solid polymer electrolytes based on PCL with LiTFSI have been reported to show that the electrolyte composition has a significant influence on the ionic conductivity and electrochemical performance (Bergfelt et al., 2018). The recent development of the gel polymer electrolytes based on PCL has similarly shown that excellent ionic conduction properties can be achieved by proper modification of the polymer architecture and electrolyte composition (Fan et al., 2023). Likewise, composite polymer electrolytes (CPEs) based on PCL were investigated with inorganic ion conducting additives, achieving compositional tuning to achieve stable operation of solid-state batteries at room temperature (Tang et al., 2024).

Another important dimension to consider for maximizing conductivity is temperature. An increase in temperature will generally result in an increase in the polymer segmental motion and ease the migration of ions, although the extent of this effect will vary significantly with salt concentration and the type of electrolyte. Molecular studies of salt-doped polymers show that the combination of temperature and salt concentration on the polymer dynamics, ion diffusivity, and ion conductivity cannot be separated, and they should be studied together (Tsamopoulos & Wang, 2024). The study of polymer-electrolytes in experiments over a range of temperatures also shows that temperature and polymer-electrolyte formulation have a significant influence on the conductivity of the polymer-electrolytes (Czerwiński et al., 2024).

Therefore, a systematic study of the chemistry, concentration, and temperature of salts can create a more solid ground for finding polymer-electrolyte formulations having a high, steady ionic conductivity. The analysis of experimental conductivity measurements under various salts, salt concentrations, and thermal conditions allows for characterizing the transport properties depending on composition, determining the degree of thermal response and finding the conditions for maximum ionic conductivity.

Research Objectives

1. To evaluate the influence of salt type and salt concentration on the ionic conductivity of polymer electrolytes.
2. To assess the effect of thermal conditions on ionic conductivity and characterize temperature-dependent conductivity behavior across electrolyte formulations.
3. To identify the optimal salt–concentration combinations that maximize ionic conductivity under different thermal conditions.

2. Methodology

2.1 Research Design and Data Source

A quantitative secondary-data design was used to examine the effects of the polymer electrolyte chemistry (lithium salts), the salt concentration, and the thermal conditions on the polymer electrolyte ionic conductivity. The analysis was conducted based on the experimental data on ionic conductivity measurements of poly(ε-caprolactone) (PCL)-based polymer electrolytes formulated with various lithium salts and their concentrations, and tested across different temperatures (Ruza & Stolberg, 2025). The analytical data consisted of 711 experimental observations, corresponding to 17 lithium-salt chemistries and 51 different salt–molality formulations. The measurement temperatures were in the range of around 29-90 °C, with the temperature range around four main thermal conditions 30, 50, 70 and 90 °C.

2.2 Study Variables

The variable considered as the main dependent variable was ionic conductivity (S cm^{-1}). The three independent variables were the type of lithium salt, the concentration of the salts (molality, mol kg^{-1}) and the temperature of the measurement (°C). Where appropriate, salt identity was treated as a categorical variable while molality and temperature were treated as quantitative variables. The explanatory factors of polymer identity and molecular weight were not included because they did not vary between the observations. The experimental batch information was kept for data verification and sensitivity assessment and was not considered to be an independent physicochemical determinant of conductivity.

2.3 Data Preparation and Thermal Classification

The data was checked for missing data, duplicate data, non-positive conductivity data, incorrect identification of salt, and irregular temperature data. There were no missing values nor any exact duplicate observations found. Ionic conductivity covered a wide range of electrical conductivities, spanning over seven orders of magnitude, so conductivity was transformed as $\log_{10}(\sigma)$ for graphical comparison and assessment of conductivity distributions, while the original S cm^{-1} scale was retained for descriptive reporting.

Replicate observations were grouped according to lithium-salt identity, molality, and thermal condition. For grouped comparisons, individual recorded temperatures were assigned to the nearest nominal thermal condition of 30, 50, 70, or 90 °C. Continuous temperature dependent analyses preserved the original recorded temperature. Due to the variability in the number of replicates, and the high dispersion of some formulation–temperature combinations, the median conductivity was used as the main robust measure to compare formulation levels.

2.4 Analysis of Salt Composition and Thermal Effects

The distribution of ionic conductivity was summarized using descriptive statistics for the salt

chemistries, salt concentrations, and thermal conditions. Since the concentration range tested was different for various lithium salts, the effects of salt concentration were examined for each lithium chemistry. This avoided imposing a common linear concentration–conductivity relationship across chemically distinct electrolyte systems.

The thermal effect was evaluated using formulations represented at all four principal temperature conditions. The Friedman test for repeated measurements was used to compare the conductivity between the four thermal conditions. The size and uniformity of the temperature effect was quantified using Kendall's coefficient of concordance (W). Two-sided $p < 0.05$ was considered statistically significant.

2.5 Optimization of Salt–Concentration Formulations

Electrolyte formulations were ranked separately at each thermal condition using replicate-level median ionic conductivity. This helped reduce the influence of extreme high or low values. For formulations with full thermal coverage, the geometric mean of the four median conductivities of 30, 50, 70 and 90 °C was estimated, to get an overall picture of performance over the entire temperature range. These rankings were used to select lithium-salt – concentration combinations that gave a relatively high conductivity over the temperature range, and to see if the best formulation varied with temperature.

2.6 Temperature-Dependent Transport Analysis

In addition, temperature-dependent ion transport was characterized using Arrhenius-type analysis for formulations with complete data at all four thermal conditions. For each formulation–thermal-condition combination, the median actual recorded temperature was converted from degrees Celsius to Kelvin and paired with the corresponding median ionic conductivity. The natural logarithm of median conductivity, $\ln(\sigma)$, was evaluated against reciprocal absolute temperature, $1/T$. Linear regression was used to estimate the apparent activation energy (Ea) and coefficient of determination (R^2) for each formulation. The apparent activation energies were interpreted as relative measures of temperature sensitivity and were not taken as evidence that all electrolytes followed exclusively Arrhenius ion-transport mechanisms.

3. Results

3.1 Characteristics of the Analytical Sample

A total of 51 distinct salt–molality formulations of poly(ε-caprolactone)-based polymer electrolytes containing different lithium salts were analyzed using 711 ionic-conductivity measurements. Replicate observations were grouped by salt identity, molality, and thermal condition, yielding 203 formulation–temperature conditions. Replication ranged from 1 to 6 measurements per condition, with a median of 3 replicates. A complete repeated-temperature structure for thermal comparisons as given in Table 1, was obtained with 50 of the 51 formulations represented at all four principal temperatures.

Table 1. Characteristics of the polymer-electrolyte conductivity observations

Characteristic	Value
Total ionic-conductivity measurements	711
Lithium-salt chemistries	17
Distinct salt–molality formulations	51
Formulation–temperature conditions	203
Complete four-temperature formulations	50
Salt molality range (mol kg^{-1})	0.2–7.0
Recorded temperature range (°C)	29.2–90.2
Principal thermal conditions (°C)	30, 50, 70, 90
Ionic-conductivity range (S cm^{-1})	5.06×10^{-11}–7.27×10^{-4}
Replicates per condition	1–6
Median replicates per condition	3

3.2 Effect of Thermal Conditions on Ionic Conductivity

Ionic conductivity increased markedly with increasing temperature across the polymer-electrolyte formulations. As given in Table 2, median condition-level conductivity increased from 3.03×10^{-7} S cm^{-1} at approximately 30 °C to 2.92×10^{-6} S cm^{-1} at 50 °C, 1.45×10^{-5} S cm^{-1} at 70 °C, and 4.39×10^{-5} S cm^{-1} at 90 °C. Relative to the 30 °C condition, median conductivity was approximately 9.65-fold higher at 50 °C, 47.92-fold higher at 70 °C, and 145.08-fold higher at 90 °C.

Table 2. Ionic conductivity across thermal conditions

Thermal condition (°C)	Conditions (n)	Median conductivity (S cm^{-1})	Interquartile range (S cm^{-1})	Fold relative to 30 °C
30	51	3.03×10^{-7}	2.26×10^{-8}–8.14×10^{-7}	1.00
50	51	2.92×10^{-6}	7.93×10^{-7}–1.24×10^{-5}	9.65
70	50	1.45×10^{-5}	4.51×10^{-6}–3.69×10^{-5}	47.92
90	51	4.39×10^{-5}	1.12×10^{-5}–9.74×10^{-5}	145.08

The progressive upward shift in log-transformed ionic conductivity across the four thermal conditions is shown in Figure 1. Among the 50 formulations represented at all four temperatures, 47 displayed a strictly increasing conductivity sequence from approximately 30 to 90 °C. The median within-formulation increase between these two conditions was approximately 133.7-fold. The Friedman test confirmed significant differences in conductivity across temperature conditions, $\chi^2(3) = 146.47$, $p < 0.001$. Kendall's coefficient of concordance was $W = 0.976$, indicating a very strong and consistent thermal effect across formulations.

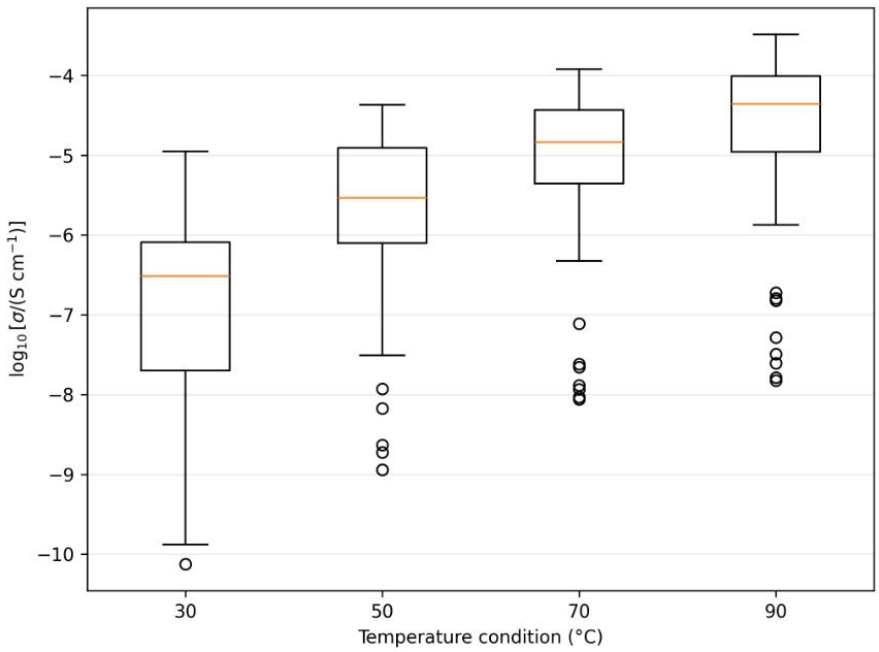

Figure 1. Distribution of log$_{10}$-transformed ionic conductivity [σ/(S cm^{-1})] across the four principal thermal conditions

3.3 Influence of Salt Chemistry and Concentration

Marked differences in ionic conductivity were observed across lithium-salt chemistries and concentration levels. The principal high-performing salts included lithium bis(fluorosulfonyl)imide (LiFSI), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), lithium bis(oxalato)borate (LiBOB),

lithium difluoro(oxalato)borate (LiDFOB), lithium bis(pentafluoroethanesulfonyl)imide (LiBETI), and lithium tetrafluoroborate ($LiBF_4$).

The relationship between salt concentration and conductivity was non-linear for several extensively sampled salts. For LiFSI-containing electrolytes, geometric-mean conductivity increased from 1.08×10^{-5} S cm^{-1} at 0.2 mol kg^{-1} to a maximum of 6.12×10^{-5} S cm^{-1} at 1.0 mol kg^{-1}, before decreasing to 1.37×10^{-5} and 2.11×10^{-5} S cm^{-1} at 3.0 and 3.7 mol kg^{-1}, respectively. LiTFSI displayed a similar intermediate-concentration optimum, increasing from 2.02×10^{-5} S cm^{-1} at 0.9 mol kg^{-1} to approximately 4.28–4.30 $\times 10^{-5}$ S cm^{-1} at 1.2–1.4 mol kg^{-1}, followed by a decline to approximately 3.25×10^{-6} S cm^{-1} at 4.4 mol kg^{-1}.

A comparable concentration-dependent pattern was observed for LiBETI, for which geometric-mean conductivity decreased from 3.10×10^{-5} S cm^{-1} at 1.2 mol kg^{-1} to 1.22×10^{-5} S cm^{-1} at 1.5 mol kg^{-1} and 1.34×10^{-6} S cm^{-1} at 5.5 mol kg^{-1}. For LiBOB, conductivity increased from 1.36×10^{-5} S cm^{-1} at 0.2 mol kg^{-1} to 2.16×10^{-5} S cm^{-1} at 0.6 mol kg^{-1}, whereas the 5.1 mol kg^{-1} formulation showed substantially lower performance. Thus, higher salt loading did not consistently correspond to higher ionic conductivity, and the concentration associated with favorable performance varied among salt chemistries.

3.4 Temperature-Specific Optimization of Salt–Concentration Formulations

Table 3 shows that the highest-performing salt–concentration combination varied according to thermal condition. At approximately 30 °C, LiFSI at 1.0 mol kg^{-1} produced the highest median conductivity of 1.12×10^{-5} S cm^{-1}, followed by $LiBF_4$ at 2.4 mol kg^{-1} and LiTFSI at 1.2 mol kg^{-1}. LiFSI at 1.0 mol kg^{-1} remained the leading formulation at 50 °C, with a median conductivity of 4.26×10^{-5} S cm^{-1}.

At approximately 70 °C, LiBOB at 0.6 mol kg^{-1} achieved the highest median conductivity of 1.20×10^{-4} S cm^{-1}, marginally exceeding LiFSI at 1.0 mol kg^{-1}. At approximately 90 °C, LiDFOB at 2.2 mol kg^{-1} became the highest-performing formulation, reaching 3.26×10^{-4} S cm^{-1}, followed by LiFSI at 1.0 mol kg^{-1} and LiBOB at 0.6 mol kg^{-1}. These results demonstrate that the optimal electrolyte formulation was dependent on temperature rather than being represented by a single universally dominant salt–concentration combination.

Table 3. Highest-performing salt–concentration formulations at each thermal condition

Thermal condition (°C)	Rank	Salt	Molality (mol kg^{-1})	Median conductivity (S cm^{-1})
30	1	LiFSI	1.0	1.12×10^{-5}
30	2	$LiBF_4$	2.4	9.33×10^{-6}
30	3	LiTFSI	1.2	7.30×10^{-6}
50	1	LiFSI	1.0	4.26×10^{-5}
50	2	LiTFSI	1.4	3.30×10^{-5}
50	3	LiTFSI	0.9	3.20×10^{-5}
70	1	LiBOB	0.6	1.20×10^{-4}
70	2	LiFSI	1.0	1.10×10^{-4}
70	3	LiTFSI	0.9	9.20×10^{-5}
90	1	LiDFOB	2.2	3.26×10^{-4}
90	2	LiFSI	1.0	2.68×10^{-4}
90	3	LiBOB	0.6	2.51×10^{-4}

The temperature-dependent profiles of the six strongest overall formulations are presented in Figure 2. Conductivity generally increased across successive thermal conditions, although the relative ranking of individual formulations changed. LiFSI at 1.0 mol kg^{-1} maintained comparatively high conductivity across the full temperature range, whereas LiBOB at 0.6 mol kg^{-1} showed a pronounced thermal response and LiDFOB at 2.2 mol kg^{-1} became the highest-performing formulation at approximately 90 °C.

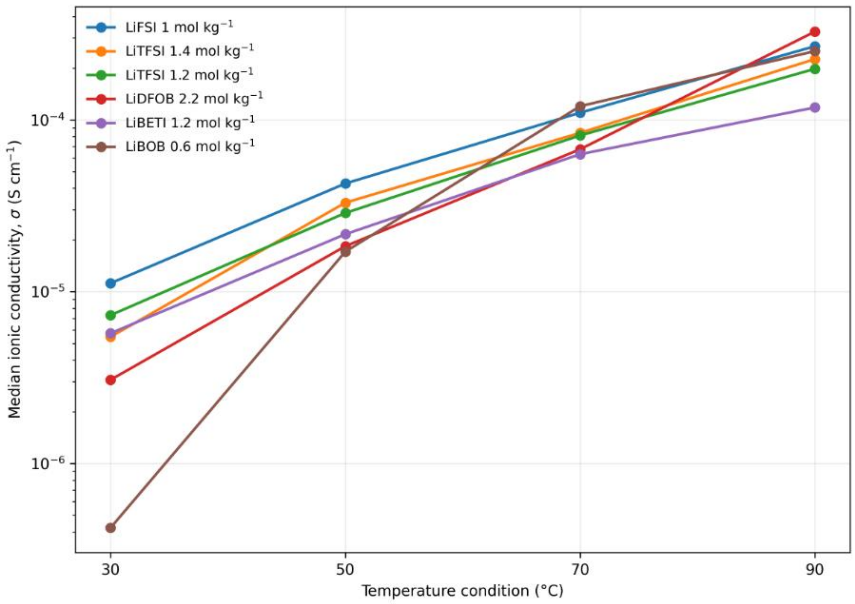

Figure 2. Temperature-dependent median ionic conductivity (S cm⁻¹) of the six highest-ranked salt–molality formulations

3.5 Overall Formulation Performance

When conductivity was integrated across all four thermal conditions using the geometric mean of condition-specific median values, LiFSI at 1.0 mol kg⁻¹ ranked first overall, with a geometric-mean conductivity of 6.12×10^{-5} S cm⁻¹, as shown in Table 4. LiTFSI at 1.4 and 1.2 mol kg⁻¹ ranked second and third, with closely comparable values of 4.30×10^{-5} and 4.28×10^{-5} S cm⁻¹, respectively. LiDFOB at 2.2 mol kg⁻¹ and LiBETI at 1.2 mol kg⁻¹ ranked fourth and fifth. LiBOB at 0.6 mol kg⁻¹ ranked sixth overall despite its particularly high conductivity at 70 and 90 °C.

Table 4. Overall performance and temperature-response characteristics of the ten highest-ranked formulations

Rank	Salt	Molality (mol kg⁻¹)	Geometric-mean conductivity (S cm⁻¹)	Apparent Ea (kJ mol⁻¹)	R^2
1	LiFSI	1.0	6.12×10^{-5}	47.99	0.997
2	LiTFSI	1.4	4.30×10^{-5}	55.80	0.986
3	LiTFSI	1.2	4.28×10^{-5}	50.28	0.998
4	LiDFOB	2.2	3.34×10^{-5}	69.80	0.997
5	LiBETI	1.2	3.10×10^{-5}	46.62	0.989
6	LiBOB	0.6	2.16×10^{-5}	97.43	0.940
7	LiFSI	3.7	2.11×10^{-5}	60.17	0.992
8	LiTFSI	2.0	2.04×10^{-5}	55.81	0.991
9	LiTFSI	0.9	2.02×10^{-5}	94.94	0.857
10	LiTFSI	2.2	1.98×10^{-5}	60.29	0.999

The top 10 formulations are ranked in the comparative ranking in Figure 3. The overall conductivity was the highest for LiFSI at 1.0 mol kg^{-1} over the entire temperature range. A few other LiTFSI formulations were also included in the top-ranked combinations, but the best performance of the LiTFSI was obtained at the intermediate concentrations used (around 1.2 to 1.4 mol kg⁻¹), not at the highest concentrations tested.

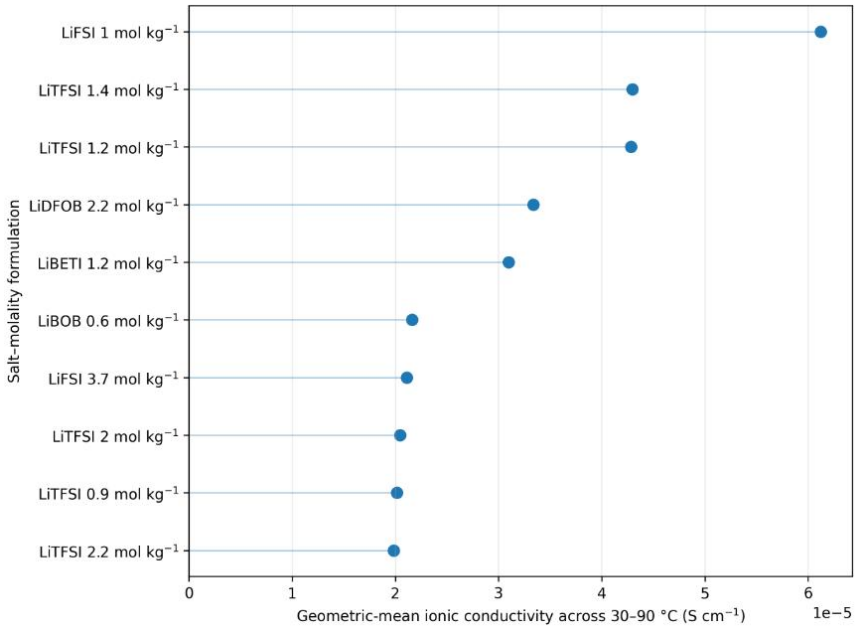

Figure 3. Overall ranking of the ten highest-performing salt–molality formulations based on geometric-mean ionic conductivity (S cm⁻¹) across approximately 30–90 °C

3.6 Temperature-Dependent Transport Characteristics

Arrhenius-type analysis was performed for the 50 formulations represented at all four principal thermal conditions. The median apparent activation energy (*E*a) was 73.23 kJ mol⁻¹, with an interquartile range of 61.76–85.91 kJ mol⁻¹. The median coefficient of determination was $R^2 = 0.990$, indicating that the relationship between ln(σ) and reciprocal absolute temperature was closely approximated by linear Arrhenius-type behavior for most formulations.

Among the leading formulations, LiFSI at 1.0 mol kg⁻¹ exhibited an apparent activation energy of 47.99 kJ mol⁻¹ with $R^2 = 0.997$. LiTFSI at 1.2 and 1.4 mol kg⁻¹ showed apparent activation energies of 50.28 and 55.80 kJ mol⁻¹, respectively. LiDFOB at 2.2 mol kg⁻¹ had a higher apparent activation energy of 69.80 kJ mol⁻¹ but achieved the greatest median conductivity at approximately 90 °C. LiBOB at 0.6 mol kg⁻¹ showed a comparatively high apparent activation energy of 97.43 kJ mol⁻¹, corresponding to its pronounced increase in conductivity toward the higher thermal conditions.

In general, the ionic conductivity was found to be a combined effect of the lithium-salt chemistry, salt concentration and thermal condition. Intermediate concentration levels often yielded higher conductivity than the high-concentration formulations, and higher temperatures resulted in significant, and consistent improvement in ionic transport. Overall, LiFSI at 1.0 mol kg⁻¹ showed the best performance over the range of temperatures investigated, while LiBOB at 0.6 mol kg⁻¹ and LiDFOB at 2.2 mol kg⁻¹ showed the highest performance at around 70 and 90 °C, respectively.

4. Discussion

The results show that the lithium-salt chemistry, salt concentration and thermal condition all play a role in the ionic conductivity of PCL-based polymer electrolytes, but no single factor alone is the sole determinant of conductivity. There were three patterns which were especially prominent. For all but a few formulations, conductivity rose sharply with temperature. Second, the relationship between the salt concentration and the conductivity was found to be non-linear with intermediate salt concentrations often yielding better results than high salt concentrations. Thirdly, the best salt–concentration combination was found to shift with temperature but LiFSI at 1.0 mol kg⁻¹ showed the best overall performance over the entire thermal range. The results directly support a multi-variable approach to the optimization of polymer electrolytes.

The effect of temperature was the most uniform on the ionic conductivity. The median conductivity increased from 3.03×10^{-7} S cm⁻¹ at approximately 30 °C to 4.39×10^{-5} S cm⁻¹ at 90 °C, representing an increase of more than two orders of magnitude. Furthermore, 47 out of 50 formulations tested followed a strictly increasing conductivity profile ranging from about 30 to 90 °C for all the thermal

conditions. This behavior is typical of ionic transport in polymer matrices which are temperature dependent. The higher temperatures accelerate the rate of segmental motion of the polymer chains and the free volume, which allows for ion migration and decreases the polymer domain constraints of order. In lithium-salt containing polymer system, the ionic conductivity has been found to get enhanced with the increase of temperature, which affects the crystallinity, molecular mobility, and efficiency of ion transport (Olmedo-Martínez et al., 2021).

The effect of salt concentration was also an important but composition-specific one. The conductivities of LiFSI were better overall at 1.0 mol kg^{-1}, while LiTFSI exhibited a particularly good conductivity range between 1.2–1.4 mol kg^{-1}. However, at higher concentrations, conductivity decreased for both systems and similar behavior was seen for LiBETI and LiBOB. The trends show that the conductivity does not increase proportionately with the salt loading. Beyond a relatively low concentration, further salt can increase the number of available charge carriers, but too much salt can lead to increased ion pairing, larger aggregates of ions, more effective polymer–ion coordination, and reduced segmental mobility. Competing effects may decrease the fraction or mobility of ions that are conducting. Maximum ionic transport was often observed within an intermediate concentration range rather than at the highest salt concentration (Olmedo-Martínez et al., 2019).

The observed differences between salts also indicate that the effects of concentration should not be understood without the consideration of salt chemistry. The conductivity profiles and optimal concentration ranges of LiFSI, LiTFSI, LiBOB, LiDFOB, LiBETI and $LiBF_4$ differed substantially. The variable size, charge delocalisation, coordination strength, dissociation tendency and interaction with PCL functional groups can affect both the concentration and mobility of the carriers. Thus, the same molality cannot be assumed to produce similar transport properties across chemically different salts. The current interpretation is in line with the studies of polymer gel electrolytes, which indicated that the increase in salt concentration has an impact on the association of salts and polymer interactions, leading to a conductivity maximum at an intermediate salt concentration followed by a decrease at higher concentrations (Rizzuto et al., 2022).

One of the most significant findings was that the formulation that was most effective varied with temperature. LiFSI at 1.0 mol kg^{-1} showed the highest median conductivity at approximately 30 and 50 °C and also ranked first when performance was evaluated across the complete temperature range using the geometric mean. However, at the temperature of about 70 °C, LiBOB at 0.6 mol kg^{-1} was the highest conductor with a median conductivity of 1.20×10^{-4} S cm^{-1}, while LiDFOB at 2.2 mol kg^{-1} was the highest at about 90 °C with a median conductivity of 3.26×10^{-4} S cm^{-1}. The change shows that an electrolyte which is optimized at medium temperature may not be optimal at higher temperatures. Selection of the formulation should therefore be based on the operating temperature, and not upon conductivity data obtained at one thermal condition.

The overall good performance of LiFSI at 1.0 mol kg^{-1} is particularly interesting, as it had relatively high conductivity at low temperatures, and improved with increasing temperature. This led to the maximum geometric-mean conductivity over the range examined. The positive results of systems containing LiFSI are in line with the findings that a lithium-salt concentration optimization can enhance conductivity and minimize energetic barriers for ion transport in polymer electrolytes (Zhang et al., 2022). However, the results also indicate that LiFSI is not necessarily better than LiBOB or LiDFOB because the conductivity of these latter materials was higher at some higher temperature conditions.

Arrhenius-type analysis also showed that there was formulation-dependent thermal sensitivity. The median apparent activation energy of the 50 complete formulations was 73.23 kJ mol^{-1} and the median R^2 was 0.990. LiFSI at 1.0 mol kg^{-1} exhibited an apparent activation energy of 47.99 kJ mol^{-1} with R^2 = 0.997, whereas LiBOB at 0.6 mol kg^{-1} showed a substantially higher apparent activation energy of 97.43 kJ mol^{-1} with R^2 = 0.940. The latter one is consistent with the sharp rise in the conductivity of LiBOB at high temperatures. These differences validate the idea that the polymer-electrolyte conduction is not based on a universal mechanism for ion transport, but on the coupling of four processes: salt dissociation, segmental polymer dynamics, ion–polymer coordination, and the temperature-dependent ion mobility (Li et al., 2023).

Findings must be understood within the range of the experiment investigated. Only one polymer

matrix was studied and the concentrations tested were not the same for all 17 salts. Therefore, it is important to note that the identified optima should not be taken as generally applicable for all polymer-electrolyte systems, but instead as formulation-specific. Despite these constraints, the analysis shows the need to consider lithium-salt identity, concentration and temperature together for effective conductivity optimization. The intermediate concentrations and the temperature-dependency of the formulation selection then become key variables to consistently high ionic conductivities.

5. Conclusion

The analysis shows that the ionic conductivity in PCL-based polymer electrolytes is strongly influenced by the combined effects of lithium-salt chemistry, salt concentration, and thermal conditions. Conductivity increased with rising temperature, and the median conductivity increased from 3.03×10^{-7} S cm^{-1} at about 30 °C to 4.39×10^{-5} S cm^{-1} at 90 °C. This significant and very uniform thermal response is representative of the importance of temperature as a parameter of ionic transport in the formulations investigated.

Salt concentration also exerted a substantial but non-linear influence. The conductivity of the corresponding high concentrations was not always superior to that of the intermediate concentrations, suggesting that the transport performance of high concentrations is not necessarily better than that of medium concentrations. LiFSI at 1.0 mol kg^{-1} showed the best overall results for the entire thermal range while LiTFSI formulations in the range 1.2–1.4 mol kg^{-1} exhibited good conductivities. The best formulation was however dependent on temperature: LiBOB (0.6 mol kg^{-1}) gave the best median conductivity at around 70 °C, while LiDFOB (2.2 mol kg^{-1}) was best at around 90 °C.

The Arrhenius-type analysis also revealed formulation dependent thermal sensitivity, highlighting the need to take thermal sensitivity into account in addition to the conductivity magnitude. In summary, it has been concluded that the optimization of polymer electrolytes should consider lithium-salt identity, salt concentration, and operating temperature together. The findings provide a basis for identifying composition-specific and temperature-dependent conductivity optima and support further validation across different polymer matrices and operating conditions.

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