Graphical Abstract

Highlights:
• electrochemical measurement procedure with additional outcomes verification by a visual inspection of a symmetry
• comprehensive approach to a battery electrolyte characterization
• newly developed approach to the estimation of the salt diffusion coefficient and the diffusion domain
• subdiffusive motion of ions has been confirmed experimentally
The electrochemical measurement of salt diffusion coefficient, apparent cation transference number and ionic conductivity for a thin-film electrolyte.

Karol M. Pożyczka

To the memory of Professor Józef R. Dygas

Abstract—Further development of the electrochemical measurement procedure, namely the Symmetric Polarization Procedure (SPP), is described. The SPP allows for additional verification of measurement assumptions through a quick and simple inspection of a symmetry between the procedure outcomes. It also improves the precision of estimated transport properties. A considerable emphasis was also put on detailed outcomes analysis. In particular, a newly developed approach to the analysis of restricted diffusion data is proposed. This approach is based on the power law which is a common form for the rate equation, therefore it allows for a precise estimation of the salt diffusion coefficient and, innovatively, the diffusion domain. Importantly, as a result of this approach, the subdiffusive motion of species is recognized in every electrolyte examined herein. Additionally, four approaches that lead to a quantification of the apparent cation transference number are also extensively discussed. It has been demonstrated, how a knowledge about the salt diffusion coefficient, the apparent cation transference number and the ionic conductivity can be used to evaluate the electrochemical performance of an electrolyte. It is also shown, how these properties can be utilized to approximate the limiting-current density and the deviation from Nernst-Einstein equation.

Keywords:
Anomalous diffusion; Electrochemical equivalent circuit; LiTFSI; Lithium borate salts; Poly (ethylene oxide).

1. INTRODUCTION

Market demand for portable electronic devices, electric vehicles and energy storage facilities is higher than ever and everything indicates that it will grow even further. This demand prioritizes the research over batteries which would store more energy per volume, recharge faster, withstand more charging-discharging cycles, provide higher instantaneous power and above all be safe. To fulfill these expectations, new electrolytes must be engineered. The task is not trivial, considering almost an infinite number of substrate combinations. Therefore, in a search of the most optimal solution, the electrolytes should not be evaluated based on a single property (i.e. the ionic conductivity). In theory, as long as ion exchange and aggregation reactions are fast enough to be in equilibrium, three transport properties are necessary to properly describe a binary electrolyte. These properties are: the ionic conductivity, the salt diffusion coefficient and the cation transference number [1][2]. There are many techniques that are used to estimate these properties [3][4]. But, as it can be concluded based on examination of Fig. 1 and Fig. 2, the value of a transport property may differ substantially, even though it was estimated with similar or essentially the same technique.

![Fig. 1. Effective salt diffusion coefficients of the PEO+LiTFSI electrolytes measured by different research groups.](image-url)

Such discrepancies may be attributed to many technique-specific assumptions, which are not always fulfilled or to a research & development stage of the materials being examined.

This work has been supported by Polish National Science Centre NCN (grant 2014/15/N/ST5/03909).
K. M. Pożyczka (e-mail: kpozyczka@protonmail.com, orcid.org/0000-0002-7144-6611) made the measurements at the Warsaw University of Technology, Faculty of Physics, Koszykowa 75, 00-662 Warsaw, Poland.
© 2022. This manuscript version is made available under the CC-BY-NC-ND 4.0 license https://creativecommons.org/licenses/by-nc-nd/4.0/
Human made mistakes, which are sometimes very hard to spot, probably also contribute substantially. A proper design of the measuring routine together with a validation of outcomes should reduce or maybe even eradicate the burden of such mistakes. Accurate data about already-known-compounds is also of great importance to harvest the power of the Artificial Intelligence and Molecular Dynamics calculations. With help of AI and MD, subtle patterns could be spotted, which will presumably lead to many improvements or even to some spectacular breakthroughs.

In this work the electrochemical techniques are chosen to estimate the transport properties. These techniques should output the ensemble-averaged properties, which could differ from the temporal properties of relatively small number of markers, especially, in systems where the ergodicity is not fulfilled [14].

The remaining three lithium salt variants are a part of the Lithium AlkylTriAlkoxyBorates (LiATAB) (Fig. 3b) family. They were engineered at the Warsaw University of Technology by E. Zygadło-Monikowska et al. [21]. The main future of these salts is the ability to obtain a salt variant with the desired length of the oligomer arms (i.e. proportional to the number of ethylene oxide repeat units – n) by controlling the conditions of the synthesis process. The reader is kindly referred to the inventor’s publication [21] to see the details of synthesis process, as well as some properties obtained by means of the DSC, the NMR and the EIS measurements. In the [21], the three borate salt variants used herein are called: “salt 1”, “salt 3” and “salt 7”, respectively.

Lastly, the high molecular weight ($M_w \sim 5 \times 10^6$ g/mol) poly(ethylene oxide) was obtained from Sigma-Aldrich/Merck (abbreviated here as PEO).

Solid polymer electrolytes (SPE) studied here were prepared by a casting from solution technique. Weighted portions of the PEO and the anhydrous salt variant were dissolved in acetonitrile solvent. A magnetic stirrer was used to thoroughly mix the substrates. Then, the solution was poured onto flat PTFE dishes and subjected to a two-step drying process. The first step resulted in formation of a thin foil/film. It lasted up to a day and consisted of evaporating solvent under low vacuum. In the second step, which lasted at least one week, the remaining solvent was removed under a high vacuum. Prior to measurement, a dry polymer electrolyte foil (0.150 to 0.400 mm thick) was cut into discs, 16 mm in diameter. The thickness of every disc was estimated at a room temperature (RT, ca. 25 °C) with a micrometer. Prior to measurements, to minimize the influence of convection, the electrolytes that were liquid at RT, were soaked into the battery separator discs. The discs were cut out of the Celgard® 2500 battery separator sheet (type: monolayer PP, thickness: d=25 µm, porosity: ε=55%, PP pore size: 0.064 µm, tortuosity: δ=2.5, MacMullin number: Ns=4.5 [22]). In the measurements a single fully soaked disc was used. To provide a good surface contact, the lithium-
metal electrodes were gently pressing on the disc from both sides.

2.1.1. Electrolytes consisting of LiTFSI and PEO

Four SPE samples (see Tab. 1.) were studied. They were prepared by mixing the weighted amounts of the PEO and the LiTFSI. The weight of the compounds was calculated to obtain samples with a certain molar proportion of the ether oxygen (EO) atoms to the lithium (Li) atoms. The 16:1, 10:1, 5:1 and 3:1 EO:Li proportions were chosen. These proportions are equivalent to the salt mass fractions ($W_s$ [wt%]) 28.9%, 39.5%, 56.6% and 68.5%, respectively. Additionally, as a handy indicator of an electroactive specie content, the lithium mass permille ($W_{Li}$) is also shown in Tab. 1. It is a ratio of the lithium mass to the combined mass of all electrolyte constituents. To shorten the notation, it is expressed in permilles. At RT all samples had a form of semitransparent foil.

For convenience, the designation, composition and graph symbol of each measured electrolyte is summarized in Tab. 1.

Table 1. Designation and composition of the LiTFSI–PEO electrolytes.

| Electrolyte designation | Graph symbol | $W_s$ [wt%] | $X_s$ [mol%] | EO:Li | $W_{Li}$ [wt%] |
|-------------------------|-------------|-------------|--------------|-------|----------------|
| EO16TF                  |             | 28.9        | 5.9          | 16:1  | 7.0            |
| EO10TF                  |             | 39.5        | 9.1          | 10:1  | 9.5            |
| EO5TF                   |             | 56.6        | 16.7         | 5:1   | 13.7           |
| EO3TF                   |             | 68.5        | 25.0         | 3:1   | 16.6           |

2.1.2. Electrolytes containing a LiATAB salt variant

Six electrolytes (see Tab. 2.), each containing one of three LiATAB salt variants, were measured. At RT two samples were in a form of a viscous liquid (i.e. AB3 and AB7), thus they were soaked into the battery separator. Four remaining samples were made by mixing a chosen LiATAB salt variant with the PEO.

Table 2. Designation and composition of the LiATAB salt based electrolytes.

| Electrolyte designation | Graph symbol | $W_s$ [wt%] | $X_s$ [mol%] | EO:Li | $W_{Li}$ [wt%] |
|-------------------------|-------------|-------------|--------------|-------|----------------|
| LiATAB + PEO n=1        |             | 19.0        | 3.3          | 29:1  | 32:1 4.4       |
| LiATAB n=3              |             | 100         | 0:1          | 9:1   | 12.3           |
| LiATAB + PEO n=3        |             | 35.8        | 4.2          | 23:1  | 32:1 4.4       |
| LiATAB n=7              |             | 100         | 0:1          | 22.5:1| 6.0            |
| LiATAB + PEO n=7        |             | 73.5        | 9.5          | 9.5:1 | 32:1 4.4       |
| LiATAB + PEO n=7        |             | 48.9        | 3.5          | 27.5:1| 50:1 2.9       |

At a RT, the EO29AB1 polymer electrolyte (the LiATAB salt variant with three oligomer arms, each arm contains a single oxyethylene substituent, n=1) is in a form of a semitransparent, white foil. The AB3 electrolyte (neat LiATAB salt variant with three oxyethylene substituents, n=3) is in a form of a clear, viscous, yellow liquid. The EO23AB3 polymer electrolyte (n=3) has a form of a semitransparent, white foil. The AB7, a neat LiATAB salt electrolyte (seven oxyethylene substituents on average, n≈7), is in a form of transparent, brown and highly viscous liquid. The EO9AB7 polymer electrolyte (n≈7) has a form of semitransparent, light-brown wax. Lastly, the EO27AB7 polymer electrolyte (n≈7) has a form of semitransparent, white foil, with very good mechanical properties.

2.2. Apparatus

The main part of the experimental setup consisted of an examined electrolyte sandwiched between two, parallel, equal-area, mirror-symmetry, cation-reversible (e.g. lithium) electrodes. The electrolyte was in a form of a thin-film polymer electrolyte or a liquid electrolyte soaked into the battery separator. From an experimental-effort point of view, such setup is fairly easy to assemble. Also, from the application perspective, it mimic conditions that are likely to be encounter in batteries.

![Image of apparatus](image-url)
a thin (ca. 50 μm) PTFE tape was placed between the piston and the slice. Then, the force, acting on the piston, smeared the slice over the top surface of the mushroom-shaped SS. By this operation, the top of the SS was covered by a few hundred micrometers thick layer of lithium metal, creating a lithium electrode. After the compression, the PTFE tape was gently exfoliated from the lithium electrode surface. The exfoliation produced a clean, metallic surface. A lithium excess, extruded beyond the SS circumference, was gently cut-off. For each sample two such electrodes were prepared. Then a stack consisting of a sample sandwiched between the electrodes was mounted into a custom-made, gas-tight measuring cell (to see construction details reader is kindly referred to Fig. 2 in [19]). After being fully assembled, the cell was placed on a custom-build Peltier thermoelectric cooling and heating device, located outside of the glove-box and connected to the Potentiostat/Galvanostat Autolab PGSTAT 30 in a 2-electrode configuration (see Fig. 4). The sample temperature was controlled with ±0.1 °C precision by a thermocouple placed close to the sample. Every stage of the materials preparation and the cell assembly was performed in an argon-filled glove-box. Relatively large area of the electrodes assured a minimal distortion from any edge effects.

### 2.3. Measuring Procedure

The Symmetric Polarization Procedure (SPP) [19] is an ordered set of particular electrochemical measurements (measuring steps). A graphical representation of the SPP is shown in the upper part of Fig. 5 in a form of a flow diagram. The measuring steps that are essential for calculations are marked by a pair of curly brackets with single digit in between (e.g. \{1\}). Such nomenclature will be used consistently throughout this paper. The lower part of Fig. 5 contains graphs with an exemplary data, which was obtained by an exemplary data, which was obtained by an exemplary data, which was obtained by the essential measuring steps that are marked as colored rectangles. Below the diagram, the subsequent measuring steps, the \( V_{ZC} \) determined relative to the lithium anode. In

![Flow diagram representing the Symmetric Polarization Procedure (SPP)](image)

**Fig. 5.** Flow diagram representing the Symmetric Polarization Procedure (SPP). The measuring steps are marked as colored rectangles. Below the diagram, the plots of outcomes for deliberately chosen sample are shown. The outcomes were obtained for the LiTAB n=7 and PEO sample \( W_e=48.8\% \) EO:Li=50:1 (EO27AB7) measured at 80 °C.

- **Temperature Setting (TS).**
  Temperature of the measuring cell is controlled by a custom-made Peltier thermoelctric cooling and heating device. During this measuring step the rate of temperature change does not exceed 0.5 °C/min. Simultaneously to a temperature change, the measuring cell is externally short-circuited, allowing only very low electric current to flow (less than 10 nA/cm² of the electrode area). The external short-circuiting together with a slow pace of temperature change should prevent from the formation of any unintended salt concentration gradient in the sample. When the temperature of a sample converges to a desired value, it remains constant throughout all subsequent measuring steps. The precision of temperature setting is ±0.1 °C.

- **Open-circuit Potential Determination (OCPD).**
  This measuring step is introduced to evaluate the open circuit potential \( (V_{ZC}) \) of the measuring cell. At first, the cell is conditioned by performing a medium to low frequencies open circuit EIS, with gradually decreasing amplitude (starting form 5mV), until the amplitude converges to zero. Then the \( V_{ZC} \) is determined relative to the lithium anode. In the subsequent measuring steps, the \( V_{ZC} \) is used as “a reference potential”, meaning that all the potential perturbation values are set relative to the \( V_{ZC} \) value.

- **Electrochemical Impedance Spectroscopy (EIS; \{1\}, \{4\}, \{7\}).**
  The amplitude of the sinusoidal potential perturbation is not greater than 10 mV root mean square (rms). For every sample, the value of that amplitude is tuned to be similar in magnitude to \( |ΔV| \) (see \{1\}). The \( V_{ZC} \) is set as the DC-potential-bias (the offset potential), thus the impedance measure-
ments are done close to open-circuit conditions. The Kramers-Kronig tests are performed to validate the outcomes.

- **Sample conditioning (cond)**
  This measuring step is intended to alleviate any charge or salt concentration gradient in the sample. Such gradient could have been introduced in the preceding measuring steps. Conditioning is also responsible for bringing the sample into similar state as it was just after the OCPD measuring step. It consists of medium to low frequencies EIS, with a decreasing amplitude (starting form 5 mV). The AC potential amplitude decreases until eventually converging to zero. The bias is equal to V_{ZC}.

- **ChronoAmperometry aka potentiostatic polarization (CA; \{2\}, \{5\})**
  During ChronoAmperometry (CA) measuring steps \{2\} and \{5\}, the current flowing through the measuring cell is registered. Its flow is induced by applying the perturbation between the electrodes (ΔV – electric potential difference) relative to the V_{ZC}. (Remark: The current should not flow if potential difference between electrodes is equal to the V_{ZC}). The perturbation is applied in a form of a single-step function. At selected moment (here at 20th second) the potential is changed from V_{ZC} to V_{ZC}+ΔV (during CA \{2\}) or to V_{ZC}−ΔV (during CA \{5\}). The ΔV should be small enough to cause a linear response of the cell, thus its value should fulfill the condition:

\[
|ΔV| ≤ \left| I_{db} \right| \cdot \left( R_e + R_{PEI} \right) \ll \frac{2 \cdot R \cdot T}{F}
\]

Where:
- \( I_{db} = I(t=1/f_{db}) \) – electric current flowing at the beginning of diffusion (A),
- \( R_e \) – electrolyte resistance (Ω),
- \( R_{PEI} \) – Polymer Electrolyte Interphase (PEI) layer resistance (Ω),
- \( R \) – gas constant (~8.31 J·K\(^{-1}\)·mol\(^{-1}\)),
- \( T \) – absolute temperature (K),
- \( F \) – Faraday constant (~96485 C·mol\(^{-1}\)).

It is assumed that for experimental conditions discussed here, a change of the perturbation value does not affect the salt concentration gradients that exist in the sample until the time \( t=1/f_{db} \). Thus, the mass transport is not affected until the inverse of this system characteristic frequency (\( f_{db} \)). The \( f_{db} \) can be estimated based on an EIS measurement (see Fig. 7b).

The “SPE overpotential” accounts for the Ohmic/IR loss component in the SPE. For samples presented here, the “SPE overpotential” did not exceed several dozens millivolts (mV). Also, the \( I_{db} \) should be small enough to observe a correspondingly low current density but high enough to minimize the noise to signal ratio. That is why, initially, the \( I_{db} \) corresponds to a current density, which does not exceed 0.1 mA/cm\(^2\). At a later stage of outcomes analysis, the \( I_{db} \) is additionally tested if it is lower than 5% of the limiting current (\( I_{lim} \), see (29)).

Additionally, the CA measuring steps are tweak to improve measurements and facilitate data analysis. Each CA measuring step consists of 2 parts, differing in the interval between sampling. The duration of parts and sampling rates given below are arbitrary. The first part has a fast sampling (1 reading per 10ms, \( f^{slow} \)) and it lasts 80 seconds. During first 20 seconds the perturbation is equal to the V_{ZC}. In this period none or negligibly small current should be measured. At the 20th second since beginning of the CA measuring step, an instantaneous change of the perturbation is imposed. The perturbation changes from V_{ZC} to V_{ZC}+ΔV during CA \{2\} and from V_{ZC} to V_{ZC}−ΔV during CA \{5\}. In response, the absolute magnitude of current raises to a maximum value and then starts to attenuate. This attenuation is registered for a remaining 60 seconds of the first part. Immediately after the first, the second part begins, where the sampling rate is lowered in order to save the disk space (1 reading per 1s, \( f^{slow} \)). The slow sampling rate persists until the system reaches a steady state. The steady state is inferred when the current does not change in time for at least 50% of the overall CA measuring step duration.

- **ElectroMotive Force (EMF; \{3\}, \{6\})**
  Immediately after each CA measuring step there is a potential relaxation measurement in open-circuit conditions (the current passing through the Potentiostat/Galvanostat is zero). During these measuring steps, the ElectroMotive Force (EMF) of the measuring cell is registered as a function of time. Here the sampling rate is deliberately set to 0.2 second. The duration of the EMF measuring steps is correlated with the duration of the preceding CA measuring steps.

- **High Frequency EIS with DC bias (HF EIS)**
  On the Fig. 5, the HF EIS measuring steps are marked by a dashed border, because they are treated as being optional. They are meant to be performed during the CA measuring steps when the system is in a steady state. The HF EIS have the DC potential bias set to V_{ZC}+ΔV during the CA \{2\} or to V_{ZC}−ΔV during the CA \{5\}. The amplitude of an AC signal is not greater than 10 mV rms. In those measurements the frequency range is deliberately set from 1kHz to 1MHz. After each HF EIS the respective CA measuring step is continued to assure that the sample is brought back to the steady state.
3. Calculations

During the work with the experimental setup, it was noticed that certain electrochemical states of the sample are more easily induced and more precisely measurable (i.e. a build up of a salt concentration gradient). In practice, it is very difficult to completely get rid of the concentration fluctuations in the sample. The probable causes are small deviations from the experimental setup symmetry, non-homogeneity, the existence of interfaces between the diffuse layer and the bulk or hysteresis effects. To mitigate the influence of departure from pristine state the idea of symmetric perturbation and the averaging was introduced. In case of the effective salt diffusion coefficient the averaging is expressed by formula:

$$D_s = \frac{D_s^3 + D_s^6}{2}$$  \hspace{1cm} (2)

And for the apparent cation transference number the suitable equation is:

$$T_+ = \frac{T_+^2 + T_+^6}{2}$$  \hspace{1cm} (3)

The results presented on figures in sections 4.1. and 4.2. are the outcome of such averaging.

3.1. Effective salt diffusion coefficient ($D_s$)

The effective salt diffusion coefficient ($D_s$) of an electrolyte consisting of a neutral solvent, a univalent cation and a univalent anion is given by the formula [23][24][25][26]:

$$D_s = \frac{2 \cdot D_{0+} \cdot D_{0-}}{D_{0+} + D_{0-}} \cdot \frac{c_T}{c_0} \cdot \left[1 + \frac{d \ln \left( \gamma_s \right)}{d \ln \left( m \right)} \right]$$  \hspace{1cm} (4)

Where:
• $D_{0+}$ – diffusion coefficient for interaction of solvent and cation (cm$^2$/s),
• $D_{0-}$ – diffusion coefficient for interaction of solvent and anion (cm$^2$/s),
• $c_T$ – total solution concentration, sum of ionic species and monomers in solvent (mol/cm$^3$),
• $c_0$ – monomers in solvent concentration (mol/cm$^3$),
• $\gamma_s$ – mean molal activity coefficient of the mobile species,
• $m$ – molality of electrolyte (mol/kg).

Experimentally, $D_s$ can be estimated by the method of restricted diffusion, developed by Harned and French [27]. This method was later refined by Newman and Chapman [28]. Additionally, Thomson and Newman [29] pointed out that the EMF induced at cation-reversible electrodes reflects the salt concentration gradient near electrodes.

In the sample, a monotonic, one-dimensional salt concentration gradient is introduced by a potentiostatic polarization imposed until at least the steady state is reached, that is by the CA measuring step. Each restricted diffusion measurement (aka EMF) begins immediately after the CA step (see Fig. 5). During the restricted diffusion measurement a flow of current is forbidden (the open-circuit condition is impose no the cell).

A decline of the EMF is registered as a function of time (as in EMF{3} and EMF{6} measuring step). The data from both EMF decays/relaxations is used to estimate the $D_s$. Prior to the proper outcome analysis, a validation of shape-symmetry between EMF{3} and EMF{6} decay is performed. Shapes of the EMF decays must be acceptably symmetrical to each other, with a line of symmetry lying in the vicinity of zero volts. In cases were the shapes show high degree of symmetry but the line of symmetry is slightly shifted from zero volts (less than 0.5 mV), the EMF decays data is altered by adding or subtracting the value of such shift, causing the line to move to zero volts. Additionally, prior to the calculation of the numerical derivatives, the long time part of the EMF decays was smoothed by averaging a number of EMF values. That number was proportional to time since beginning of the decay. Such treatment calmed noise and equipment-introduced analog-to-digital conversion artifacts.

Under the “ideal” conditions (a Fickian, one-dimensional diffusion, with the reflective boundaries, no diffuse layers) the EMF decays can be expressed by an infinite series [30][29][7][13]:

$$\hat{E} = \frac{E}{E_0} = \frac{8}{\pi^2} \sum_{k=0}^{\infty} \exp \left[ -\left(2k + 1\right)^2 \cdot \frac{\pi^2 \cdot D_s \cdot t}{L^2} \right] \left(2k + 1\right)^2$$  \hspace{1cm} (5)

$$E = E(t) \quad E_0 = E(t \to 0) \quad \hat{E} = \hat{E}(t)$$

Where:
• $t$ – time (s),
• $L$ – restricted diffusion length (cm),
• $E$ – electromotive force measured at any given time ($V$), a function,
• $E_0$ – electromotive force measured at the beginning of the EMF decay/relaxation ($V$), herein – the first value measured at the beginning of the EMF decay, a scalar,
• $\hat{E}$ – rescaled/normalized electromotive force, a function.

For a polymer electrolyte the restricted diffusion length is equal to the sample thickness, and for a liquid electrolyte soaked into a battery separator, the length is calculated according to the formula:

$$L = \sqrt{\frac{\delta}{\varepsilon}} \cdot d = \sqrt{N_M} \cdot d$$  \hspace{1cm} (6)

Where:
• $d$ – thickness of the battery separator (cm),
• $\delta$ – tortuosity of the battery separator,
• $\varepsilon$ – porosity of the battery separator,
• $N_M$ – the MacMullin number.

It is troublesome to fit (5) to measured EMF decay, therefore, in order to extract the $D_s$, the approximation at long time is commonly in use:

$$\hat{E} = \frac{E}{E_0} = \frac{8}{\pi^2} \exp \left[ -\frac{\pi^2 \cdot D_s \cdot t}{L^2} \right]$$  \hspace{1cm} (7)

$$\hat{E} = \hat{E}(t) \quad E = E(t) \quad E_0 = E(t \to 0)$$
But, to make a proper use of equation (7), the time at equivalence point ($\tau_{EP}$) needs to be known. Without this knowledge it is tricky to recognize which part of the relaxation data is the “long time” part. Under the “ideal” conditions, the $\tau_{EP}$ would be the time since beginning of the relaxation until which the salt concentration gradient in the middle cross section of the sample remains constant (how long it takes for the diffusion fronts to reach the half length). The value of $\tau_{EP}$ is proportional to the restricted-length squared divided by the $D_S$ (see (B.1)). Because the $D_S$ is about to be estimated, the $\tau_{EP}$ cannot be known a priori. But, it should be possible to approximate $\tau_{EP}$ based on the experiment data. Herein it was assumed that the $\tau_{EP}$ is equal to the time coordinate of the maximum of the plot shown on Fig. 6b. The ordinate of each point at this plot was

**Fig. 6.** Data representations suitable for the estimation of the effective salt diffusion coefficient ($D_S$), the time at equivalence point ($\tau_{EP}$) and the relaxation order ($n$). Data from EMF[3] and EMF[6] measured for the PEO+LiTFSI electrolyte, (EO16TF, $W_c$=28.9%, EO:Li=16:1) at 105 °C by means of the SPP.
equal to the $\hat{E}$ value multiplied by a square root of the $\hat{E}$-corresponding time. For an unbiased and diffusion-only data a single maximum is expected to appear on such plot. The time coordinate of this maximum is herein inferred to be the $\tau_{EP}$.

In the present paper, two approaches were deployed to obtain the $D_s$ from the analysis of EMF decays, namely:

- the “common” approach, which is very similar to one described in the literature [28][2][7][13],
- the “new” approach, first time proposed herein.

The whole process of EMF data analysis by both approaches is illustrated on Fig. 6 and described in details below.

### 3.1.1. The “common” approach ( \[\text{(1)}\] )

The data representation showed on the Fig. 6c is a consequence of a rearrangement of the equation (7) to a time-linearized form:

$$\ln(\hat{E}) = \ln \left( \frac{E}{E_0} \right) = \left( -\frac{\pi^2 D_S}{L^2} \right) \cdot t + \ln \left( \frac{8}{\pi^2} \right)$$

$$E = E^{|k|}(t) \quad E_0 = E^{|k|}(t=0) \quad D_S = D^{|k|}_S \quad \alpha = \alpha^{|k|} \quad k = 3, 6;$$

This representation is only useful for the long time part of the EMF decay, thus for the part measured some time after the $\tau_{EP}$. Such representation facilitates the estimation of the “slope($\alpha$)”, thus of the bracket underscored in the equation (8). This slope is obtained by fitting a linear function to a subrange of transformed EMF decay. Herein, the subrange was deliberately chosen to span from $1.5 \cdot \tau_{EP}$ to $2.0 \cdot \tau_{EP}$ due to of the data within a wide temperature range. Additionally, under the “ideal” conditions, the $D_s$ estimated using the equation (7) based on that subrange, differs by less than 0.2% from the $D_s$ derived by fitting the infinite series (5) to the “ideal” condition data. Knowing “slope($\alpha$)”, two values of $D_s$ by the “common” approach were calculated according to below formula:

$$D^{|k|}_S = -\frac{\alpha^{|k|}}{\pi^2} L^2 \quad \land \quad k = 3, 6;$$

and then those values were averaged, as in (2), to give the final result.

### 3.1.2. The “new” approach ( \[\text{(2)}\] )

Similarly to the “common” approach, the “new” approach is only suitable for the EMF data registered after the $\tau_{EP}$. The “new” approach is based on the assumption, that after a sufficiently long time the EMF decay has the form of a power law (10) which is a common form for the rate equation. According to this law the relaxation rate of the $\hat{E}$ is proportional to the $\hat{E}$ raised to a system-specific power:

$$- \frac{d \hat{E}}{dt} = \left( \frac{\pi^2 D_S}{L^2} \right) \cdot \hat{E}^n$$

In present paper that system-specific exponent will be called the “relaxation order (n)”. It is worth noticing that the “common” approach is a special case of the “new” approach, in which the exponent is equal to one ($n=1$).

A plot used to evaluate the relaxation order is presented on Fig. 6d and described below. It is a “log-log” plot with the same logarithm base on both axes (here the natural logarithm “ln” was chosen). The values of rescaled/normalized EMF are marked by a hat/circumflex above a capital E letter ($\hat{E}$) and are obtained by dividing the EMF value by the first value of the EMF decay ($E_0$). To obtain Fig. 6d each $\hat{E}$ value is transformed into two coordinates. The first coordinate, the ordinate, is a logarithm of the $\hat{E}$ value. The second coordinate, the ordinate, is a logarithm of the relaxation rate of the $\hat{E}$, calculated at the same point in time as the value chosen for abscissa. The relaxation rate of the $\hat{E}$ is mathematically expressed as a derivative with respect to time of the $\hat{E}$. Herein, the derivatives were calculated numerically. Finally, the relaxation order is the “slope(n)” of a straight line fitted to the long time part (the part at times greater than $1.5 \cdot \tau_{EP}$) of this “log-log” plot. Since in every case measured herein the relaxation order was greater than one, the equation (8) is replaced by:

$$\left( \frac{E}{E_0} \right)^{(1-n)} = \left( \frac{(n-1) \cdot \pi^2 D_S}{L^2} \right) \cdot t + \left( \frac{8}{\pi^2} \right)^{(1-n)}$$

$$E = E^{|k|}(t) \quad E_0 = E^{|k|}(t=0) \quad n = n^{|k|} \quad D_S = D^{|k|}_S \quad \beta = \beta^{|k|} \quad k = 3, 6;$$

The relaxation order estimated with help of Fig. 6d enables a transformation of the EMF decay to the representation presented on Fig. 6e. Such time-linearized representation facilitates the determination of the “slope($\beta$)”, underscored in the equation (11). To allow a comparison with the “common” approach, the same subrange (from $1.5 \cdot \tau_{EP}$ to $2.0 \cdot \tau_{EP}$) was used to fit a straight line by means of least squares method, and thus to obtain the $D_s$.

Two values of $D_s$ by the “new” approach were calculated according to the formula:

$$D^{|k|}_S = \left( \frac{\beta^{|k|}}{(n^{|k|}-1) \cdot \pi^2} \right) \cdot L^2 \quad \land \quad k = 3, 6;$$

and then those values were averaged, as in (2), to give the final result.

### 3.2. Model of the electrolyte-electrode interface

In this section an attempt will be made to translate known micro- and macroscopic phenomena happening on the polymer electrolyte-lithium metal electrode interface into an electrochemical model. Later, this model will be frequently used in the analysis of the outcomes. Additionally, other concepts that will be used in the subsequent sections are also introduced and justified herein.

A schematic representation of the electrolyte-electrode interface together with the electrochemical equivalent circuit is showed on Fig. 7a. The representation renders a LiTFSI+PEO polymer electrolyte, being in contact with a lithium metal
electrode. The schema depicts a cross-section, which is perpendicular to electrode surface. The interface structure is approximated by four layers, differing in electrochemical properties. This Gedanken cross-section consists of (right to left):

- solid, lithium-metal electrode,
- compact layer,
- diffuse or Polymer Electrolyte Interphase (PEI) layer,
- bulk electrolyte.

The solid, lithium-metal electrode is the source/sink of the lithium.

The compact layer, according to studies of Zaban et al. [31] and Eshetu et al. [32], contains Li$_2$O, Li$_2$CO$_3$, LiOH together with other products of LiTFSI salt decomposition. Presumably, this layer is very thin, dense and ionically conductive. It forms almost immediately, due to very high reactivity of the lithium.

Moreover, such shorter chains may accumulate in excess at the surface of polymer electrolyte sample due to excluded-volume/entropic-segregation effects [35][36][37]. Also, the end-groups of the PEO chains (those present at the surface of a polymer electrolyte sample) may react with lithium and anchor-in/adhere-to the compact layer (see pink dots on Fig. 7a). In consequence, the conformation freedom of a part of the chain that is directly connected to such end group may be reduced, what should affect the migration and diffusion of ions in the PEI layer. Such effect presumably intensifies with decreasing length of polymer chains (due to higher concentration of the end groups). Such effect could explain vary interface properties of samples with different PEO chain lengths as observed by Pesko et al. [6].

The bulk electrolyte is listed as last, but the estimation of its electrochemical properties is the main goal of this work.

In general, it is worth mentioning that the thickness and active contact area of the compact and PEI layers may evolve with time, temperature and the magnitude of an external perturbation. Also, throughout this work, the assumption is made that the thickness of the compact layer and the PEI layer is much smaller (much less than 5%) than the thickness of the bulk electrolyte, thus the sample thickness is approximately equal to the bulk thickness.

The lower part of Fig. 7a contains the electrochemical equivalent circuit, which is intended to mimic an electric response of the upper schematic representation. The circuit consists of two Randles circuits [38], which are connected in series. The resistances are denoted by capital “R”. The Constant Phase Elements (denoted as “CPE”), are used to model a space-separated charge at non-ideal interfaces. The non-idealities in the system most likely arise from a distribution of resistances [39]. The Generalized Finite Warburg elements (denoted as “$W^\gamma$”) served as an electric analogue of the anomalous diffusion (the Warburg-type mass transport impedance, bounded/finite-length anomalous diffusion with an absorbing/transmissive boundary condition). The diffusive part of the impedance spectra is well modeled by equation (35) presented in the work of Bisquert and Compte [40]:

\[
Z(\omega) = R_w \cdot \tanh \left( i \cdot \frac{\omega}{\omega_d} \right)^{\gamma/2} \quad \land \\
\omega_d = \frac{2 \cdot \pi \cdot D_S}{(L/2)^2} \quad \land \quad 0 < \gamma \leq 1
\]  

The anomalous resistance parameter of $W^\gamma$ is denoted as $R_w$ or $R(W^\gamma)$. For $\gamma=1$ the bounded diffusion impedance is obtained. The equation (13) is probably more suitable for well dissociated electrolytes. In case of systems with poorly dissociated salt, thus an extensive ion aggregation, the modified Gerischer impedance [41][42][43] seems a better choice:

\[
Z(\omega) = Z_0 \cdot \frac{1}{\sqrt{1 + \left( i \cdot \frac{\omega}{\omega_d} \right)^\alpha}} \quad \land \quad 0 < \alpha < 1
\]  

Next, there is the Polymer Electrolyte Interphase (PEI) layer. This layer is electronically insulating, but it allows for diffusion of ionic species. High viscosity of polymer electrolytes contributes to poor electrode wettability, thus many empty voids are expected to exist in this layer [33]. These voids are the major factor affecting the character of ion transport in this layer. Additionally to the voids, other factors may also affect the electrochemical properties of this layer. According to Thiam et al. [34], during a sample preparation process (i.e. during stirring in the casting from solution) some of monodisperse, long PEO chains may break into much shorter pieces. Depending on the degree of such breaking the polymer chains in the sample may become polydisperse.
The subscripts next to the letters denoting an electric analogue on the circuit have the meaning:

- \( dl \) – double layer,
- \( ct \) – faradaic charge transfer,
- \( PEI \) – Polymer Electrolyte Interphase,
- \( b \) – bulk/solution,
- \( mt \) – mass transport,

Theoretically, an EIS measurement in a wide range of frequencies (usually from MHz to \( \mu \)Hz) should allow to distinguish the transport processes occurring in a sample. But, in case of polymer electrolytes, such measurement would usually last for a very long time. Moreover, the impedance measured at very low frequencies could be tampered by an external noise or by a time evolution of the system. Such tampered impedance spectrum could be very hard to recognize and to analyze. Therefore in this work, the chronoamperometric (CA) measurements are utilized to obtain a very low frequency part of the impedance spectrum. The CA outcome, after being checked for any artifacts, is Numerically Laplace Transformed (NLT) from a time-domain to the frequency-domain, using an algorithm similar to that proposed by Takano et al. [44]. The EIS technique is used to measure and deconvolute fast electrochemical processes occurring at high to medium frequencies. Ultimately, the CA NLT outcomes are merged with the EIS outcomes to give impedance spectrum from very wide frequency range. Exemplary spectrum together with data transformation process is shown on Fig. 7b.

Another concept, namely the “optimal time” (\( \tau_{\text{opt}} \)), is introduced here. In essence, this concept is similar to the concept proposed by Wohde et al. [45]. The \( \tau_{\text{opt}} \) is utilized to estimate the value of \( I_0 \) (as in (16) and (18)). Herein, the \( \tau_{\text{opt}} \) is the time that it takes to affect the salt concentration gradient in the bulk electrolyte by applying the potential perturbation. The \( \tau_{\text{opt}} \) is estimated based on the optimal frequency (\( f_{\text{opt}} \)). The relation between the two is:

\[
\tau_{\text{opt}} \frac{f_{\text{opt}}}{k} = 1
\]

The \( f_{\text{opt}} \) (see Fig. 7b) is the frequency at which the real part of impedance (\( Z' \), resistance) is equal to the sum of electrolyte bulk resistance (\( R_b \)) and interface resistance (\( R_x \)). Whereas, the \( R_i \) is a sum of the PEI layer resistance (\( R_{\text{PEI}} \)), the charge transfer resistance (\( R_{\text{ct}} \)) and the PEI layer anomalous diffusion resistance (\( R(W_{\text{PEI}}) \)) (see Fig. 7b).

The content of the subsequent sections should be more clear knowing all the concepts mentioned in this section.

### 3.3. Apparent cation transference number (\( T_+ \))

The apparent cation transference number (\( T_+ \)) is the fraction of the overall current that flows through an electrolyte when only one electroactive constituent of the salt, e.g. lithium is allowed to be reduced or oxidized at the electrodes. In practice, the overall current should be small enough not to cause large salt concentration gradients, thus the system should obey the Ohm’s law. The \( T_+ \) is also called the limiting current fraction [4]. For an ideal electrolyte with fully dissociated salt, the \( T_+ \) is equal to the cation transference number [46]. But, if mobile associated species (like ion pairs, triplets etc.) exist in an appreciable amount than those two quantities may differ substantially. Nevertheless, a high value (ideally equal to one) of \( T_+ \) is desired for an effective battery operation.

In the upcoming subsections four approaches to an estimation of \( T_+ \) are presented. The outcomes of the chronoamperometric and the EIS measurements (from measuring steps marked by \{1\}, \{2\}, \{4\}, \{5\} and \{7\} on Fig. 5) serve as the input to these approaches.

### 3.3.1. Steady-state to initial current ratio (ISS)

In this approach the \( T_+ \) of the bulk is calculated as a ratio of the steady-state to the initial current [47]. It is the most primitive approach. Mathematically, it is expressed by the formula:

\[
T_+^k = \frac{I_0^k}{I_0^l} \quad k=2,5; \quad l=1,4;
\]

Where:

- \( I_0 \) – “steady-state” or “stationary” electric current. It is a steady in time electric current measured after applying a small potential difference (\( \Delta V \) in (1)) to the system. For a typical polymer electrolyte, it takes quite some time for transient effects to die out, and thus to converge to the steady state (see current vs time plot on Fig. 7b). To esti-
mate the value a statistically significant number of the steady-state readings was averaged to obtained more precise value of \( I_s \).

- \( I_0 \) — “initial” electric current. It is an electric current measured at the beginning of the salt concentration gradient build up in the bulk of the electrolyte. To assess this moment, the analysis of the EIS data was carried out (see Fig.7b and description of the \( \tau_{opt} \) at the end of the preceding section).

Remark: Typically, by this approach, the analysis of EIS spectra was not carried out and thus, the \( I_0 \) was equal to the first/maximal output of an ammeter (or an oscilloscope or a potentiostat/galvanostat), that is, the current value measured immediately after the application of the perturbation. Clearly, this methodology introduces additional errors resulting from maximal sampling rate of the equipment, thus it leads to the indeterminacy of such calculated \( T_\ast \).

The ISS approach neglects/disregards the influence of the electrode-electrolyte interface on the value of \( T_\ast \). It also assumes that the electrochemical characteristic of that interface is unaffected by a change in the external conditions i.e. by the perturbation or the temperature.

3.3.2. By Sorensen-Jacobsen & NLT (SJ NLT [1])

Equation (17) is the SPP adjusted version of the formula used by Sorensen and Jacobsen [48] in 1982:

\[
T_{\ast}^{[k]} = \frac{R_b^{[m]}}{R_b^{[m]} + R_d^{[k]}} \quad k=2, 5; \quad m=4, 7; \tag{17}
\]

Where:
- \( R_b \) — bulk electrolyte resistance,
- \( R_d \) — diffusional resistance of the bulk electrolyte.

The \( R_d \) is an additional resistance of the bulk electrolyte due to the steady-state salt concentration gradient induced by the potentiostatic polarization. It is represented by an anomalous resistance parameter of the \( W_b \) denoted as a \( R(W_b) \) (see Fig. 7b and description in the previous section). In practice, the \( R(W_b) \) should be approximately equal to \( (\Delta V/I_s - R_b - R_s) \). The \( R_b \) value is evaluated based on the data from the CA & the EIS measuring steps and the \( R_s \) is estimated based on EIS data only. The superscripts in formula (17) point to a source of input data (the measuring steps). As indicated, the CA measuring step always precedes the EIS measuring step. Such order is intended to minimize the influence of possible changes in the system properties (i.e. due to very long CA measuring step).

In the author’s opinion, the SJ NLT approach is the most appropriate way to calculate the \( T_\ast \). It verifies the agreement between the EIS and the CA data, and is based on a thorough analysis of the impedance spectrum covering a broad frequency range.

3.3.3. By Bruce-Vincent (BV [2])

In 1989 the \( T_\ast \) measurement approach, combining EIS and chronoamperometry, was described [49]. The EIS was used to deconvolute the contributions of high rate processes, like those occurring at the electrolyte-electrode interface. The chronoamperometry was applied to characterize more sluggish processes, namely the diffusion. The formula for \( T_\ast \) calculation was also presented:

\[
T_{\ast}^{[k]} = \frac{S_k^{[m]} \left( \Delta V^{[k]} - I_0^{[k]} R_{S_1}^{[m]} \right)}{I_0^{[k]} \left( \Delta V^{[k]} - I_S^{[k]} R_{IS}^{[m]} \right)} \quad k=2, 5; \quad l=1, 4; \quad m=4, 7; \tag{18}
\]

Where:
- \( \Delta V \) — potential perturbation imposed upon the measuring cell during a chronoamperometric measurement (same as in (1)),
- \( I_0 \) and \( I_s \) are described in the ISS section (3.3.1.).
- \( R_{S_1} \) and \( R_{IS} \) are the interface resistances (similarly to subscripts in \( I_0 \) and \( I_s \), characters “0” and “S” mean “initial” and “steady state” respectively).

Formula (17) accounts for the influence of the electrolyte-electrode interface, thus is a much more advanced approach than the equation (16). The major difficulty of this approach lies in proper estimation of the \( R_s \). The EIS measurements in conditions other than open circuit potential (i.e. with a bias/offset potential as in the HF EIS) are much more difficult to interpret. Moreover, such biased EIS distorts the steady state, especially when it is performed to low frequencies. This in turn may affect the validity of \( I_s \) estimation or considerably elongate the duration of the measurement routine.

Remark: For systems and experimental conditions discussed herein (i.e. a small perturbation and salt concentration gradient, no convection, a linear, stable and causal system response) the relations based on the Ohm’s law should be valid:

\[
\Delta V = [R_b + R_{S_1}] I_0 \tag{19}
\]

\[
\Delta V = [R_b + R_{S_1} + R_s] I_s \tag{20}
\]

The (19) and (20) relations make the equations (17) and (18) equivalent to each other.

3.3.4. By Watanabe (W [3])

One can omit an estimation of the \( I_0 \) and \( R_{S_1} \) by merging (17) together with (20), to obtain the formula similar to one presented by Watanabe et al. [50]:

\[
T_{\ast}^{[k]} = \frac{R_{S_1}^{[m]}}{\Delta V^{[k]} - R_{IS}^{[m]}} \quad k=2, 5; \quad m=4, 7; \tag{21}
\]

In general, for systems in which properties may evolve/flucluate with time the interface resistance should be inferred based on EIS measured at an open-circuit potential and after the potentiostatic polarization from which the \( I_0 \) was obtained. It is also of great importance to precondition the measuring cell with fresh sample to accelerate convergence to a relatively stable thermodynamic state.
3.4. Conductivity

3.4.1. Ionic conductivity ($\sigma^+$)

The ionic conductivity of electrolyte is estimated based on data obtained by EIS (from measuring steps \{4\} and \{7\}, see Fig. 5) and the geometrical dimensions of the sample. In case of polymer electrolyte the bulk solution resistance ($R_b$) is obtained by fitting an electrochemical equivalent circuit showed on Fig. 7a and Fig. 7b. Then the average of two resistances is calculated, as it is expressed by the formula:

$$R_b = \frac{\sum R_b^k}{2} \quad k = 4, 7; \quad (22)$$

Finally, the ionic conductivity is calculated according to the formula:

$$\sigma = \frac{L}{A \cdot R_b} \quad (23)$$

Where:
- $L$ – thickness of the sample (cm),
- $A$ – contact area (apparent) between a single electrode and the sample (cm$^2$).

For a liquid electrolyte soaked into the battery separator, the ionic conductivity is calculated according to the formula:

$$\sigma = \frac{\delta}{\epsilon} \frac{d}{A \cdot R_b} = \frac{\delta}{\epsilon} \frac{d}{(A \cdot R_b)} \quad (24)$$

Remark: In previous work [19], it was shown that the bulk conductivities measured with use of cation (i.e. lithium) reversible/transmissive electrodes were similar to those estimated with blocking/reflective (i.e. stainless steel) electrodes.

3.4.2. Apparent diffusional conductivity ($\sigma_d$)

The apparent diffusional conductivity (conductivity based on the $D_s$) is calculated via:

$$\sigma_d = \frac{2 \cdot F^2}{R \cdot T} c_s \cdot D_s \quad (25)$$

Where:
- $F$ – Faraday constant (96485.33212 C mol$^{-1}$),
- $R$ – gas constant (8.31446261815324 J K$^{-1}$ mol$^{-1}$),
- $\epsilon$ – elementary charge (1.602176634×10$^{-19}$ C),
- $k_B$ – Boltzmann constant (1.380649×10$^{-23}$ J K$^{-1}$),
- $N_A$ – Avogadro constant (6.02214076×10$^{23}$ mol$^{-1}$),
- $T$ – absolute temperature (K),
- $c_s$ – molar concentration of salt (mol cm$^{-3}$),
- $D_s$ – effective salt diffusion coefficient calculated by the “new” approach via (12) and then averaged as in (2) (cm$^2$/s).

Additionally, the apparent diffusional conductivity amendment ($\chi_d$) is defined as:

$$\chi_d = \frac{c_0}{4 \cdot c_T \cdot T^* \cdot (1 - T^*)} \left[1 + \frac{d \ln \gamma_s}{d \ln (m)}\right]^{-1} \quad (26)$$

Where:
- $T^*$ – apparent cation transference number calculated by (17) and then averaged as in (3),
- $c_T$ – total solution concentration, sum of ionic species and monomers in solvent (mol/cm$^3$),
- $c_0$ – monomers in solvent concentration (mol/cm$^3$),
- $\gamma_s$ – mean molal activity coefficient of the mobile species,
- $m$ – molarity of electrolyte (mol/kg).

The derivation of the equation (26) and the underlying assumptions are presented in Appendix C.

3.4.3. Effective conductivity ($\sigma^+$)

The effective (cationic) conductivity is calculated according to the formula:

$$\sigma^+ = \sigma \cdot T^+ \quad (27)$$

Where:
- $T^+$ – apparent cation transference number calculated by (17) and then averaged as in (3).

3.5. Limiting-current density ($I_{lim}$)

Formula (28) was used to calculate the limiting-current density:

$$J_{lim} = \frac{2 \cdot F \cdot c_s \cdot D_s}{(1 - T^+) \cdot L^*} \quad (28)$$

Where:
- $L^*$ = 100 µm – reference thickness of an electrolyte sample. The value was deliberately chosen to facilitate possible conversions.

Originally, this formula was derived to be used with the lithium transference number rather than $T^+$ and for a Fickian-type diffusion [51]. Based on below presented results and considerations, this is apparently not the case, but the $I_{lim}$ should still be a good and useful estimator.

The limiting current ($I_{lim}$) could be calculated based on $J_{lim}$:

$$I_{lim} = \frac{J_{lim} \cdot L^* \cdot A}{L} \quad (29)$$

The $I_{lim}$ calculated via (29) is used to check whether acceptably small current (less than 5% of the $I_{lim}$) flowed through each sample during the potentiostatic polarization measuring steps. Fulfillment of this condition allows to neglect salt concentration variations near the electrodes. In such cases only the ohmic potential drop and the interface overpotentials determine the distribution of currents [25].
4. RESULTS AND DISCUSSION

In the present work the measurements were performed at temperatures between 60 °C and 110 °C. This temperature range was deliberately chosen to minimize the influence of heterogeneity (i.e. crystal grains) or phase transitions in the electrolyte structure. For some samples, temperature range was narrower because of materials used or experimental errors.

To facilitate comparisons between examined electrolytes, ten unique symbols are used to present the results on the following figures. Each symbol shape is associated with one composition, as summarized in Tab. 1. and Tab. 2. Dotted or dashed lines linking data points are guides for the eye only. For every data point, the experimental uncertainty has been calculated and expressed by the error bars (sometimes barely visible due to small error).

4.1. Effective salt diffusion coefficient (Dₜₚ) 

Based on the EMF decays, the “common” and the “new” approaches (see section 3.1.) were used to estimate the effective salt diffusion coefficients (Dₜₚ). The difference between outcomes of these approaches can be compared by studying pairs of figures. Figures 8a and 9a depict results by the “common” approach, while figures 8b and 9b are showing results by the “new” approach. Each Dₜₚ on the “a” figure has its equivalent on the “b” figure.

Recalling: the equivalents resulted from the same input data i.e. the same subrange of each EMF decay. The difference in value between the equivalents is solely caused by the approach used to process the data.

It is also worth noticing, that the Dₜₚ obtained by the “new” approach are independent of a deliberately chosen subrange, in contrary to the Dₜₚ evaluated by the “common” approach. Such independence is due to the linearity of the long-time-part of the plot shown on Fig. 6e. Therefore, only the Dₜₚ by the “new” approach were used to calculate τₚₑ, Jₘₑ and Iₘₑ.

The secondary ordinate axis on the “a” figures is related to the time at equivalence point (τₚₑ, light-gray points) determined in a way described in the section 3.1. Whereas, the secondary ordinate axis on the “b” figures refers to the relaxation order values (n, gray points).

4.1.1. Electrolytes consisting of LiTFSI and PEO

The Dₜₚ, τₚₑ and n of four polymer electrolytes consisting of the LiTFSI salt and the PEO polymer (see Tab. 1.) are presented in this part. The results are grouped by the two approaches.

- The “common” approach

The results of the “common” approach are depicted on Fig. 8a and listed below.

At 70 °C on Fig. 8a, the Dₜₚ values, ordered from highest to lowest, are:

- EO16TF  =  30.97 ± 1.02 × 10⁻⁹ cm²s⁻¹
- EO10TF  =  25.63 ± 5.28 × 10⁻⁹ cm²s⁻¹
- EO5TF   =  17.25 ± 2.73 × 10⁻⁹ cm²s⁻¹
- EO3TF   =  6.72 ± 0.80 × 10⁻⁹ cm²s⁻¹

The Dₜₚ of the EO16TF sample are changing the least with temperature and they have the highest values at low temperatures. Apparently a trend can be recognized, the more LiTFSI salt in polymer electrolyte contains, the greater the variation of Dₜₚ with temperature is.

The τₚₑ plots have a linear character, similar to the Dₜₚ, but the dependence on temperature is reversed. The overlapping of the τₚₑ plots is smaller compared to the Dₜₚ, because the τₚₑ additionally account the diffusion length of the sample.

- The “new” approach

Next, on Fig. 8b and below, the results due to the “new” approach are presented. At 70 °C the Dₜₚ values, ordered from highest to lowest, are:

- EO16TF  =  71.13 ± 1.26 × 10⁻⁹ cm²s⁻¹
- EO10TF  =  39.62 ± 2.13 × 10⁻⁹ cm²s⁻¹
- EO5TF   =  26.43 ± 3.04 × 10⁻⁹ cm²s⁻¹
- EO3TF   =  8.69 ± 0.89 × 10⁻⁹ cm²s⁻¹

In general, the order and the temperature dependencies of Dₜₚ between the samples and the approaches are quite similar, but the values calculated by the “new” approach are larger.
The relaxation orders of the EO16TF sample are the highest among the LiTFSI containing electrolytes. Apparently, the temperature variation of the relaxation orders increases with the salt content. This probably indicates a gradual change in the ion transport mechanism. The relaxation orders of all measured samples are greater than one, what appears to be an indicator of the anomalous diffusion i.e. the subdiffusion.

The subdiffusion of polymer segments in polymer melts has been recognized and measured long time ago [52][53][54][55]. The physics behind those observations was also figured out and described mathematically. At short times (between the shortest and the longest relaxation time of a Rouse chain, the latter often called the Rouse time) the subdiffusive motion of the segment results from a Rouse-like [56] relaxation process of a linear polymer chain. At longer times (between the Rouse time and the disentanglement time) and for long, entangled chains the exponent of subdiffusion is better quantified by the Tube Model [57][58].

However, according to the author’s knowledge, the subdiffusive motion of ions in polymer electrolytes was not recognized experimentally. However, the Molecular Dynamics simulations (MD) [59][60][61] showed that the subdiffusion of ions should exist in short-chain-PEO and LiTFSI system. By these simulations, it was discovered that the motion of the lithium cation (Li+) should be in part subdiffusive. It was postulated that Li+ subdiffusion is due to a Rouse-like relaxations of a polymer segment with which the cation is coordinated. Two mechanisms of Li+ motion have been identified. The first one was due to breaking of “most outer” coordination bond, one out of five, and then formation a new bond on the “other side”. The breaking and formation is probably triggered by the longitudinal Rouse-like modes. By this mechanism Li+ subdiffused along the polymer chain. The second one was an effect of Li+ being transported by the coordinated segment. During such transport the coordination bonds between Li+ and the segment did not change. This motion is likely caused by the transverse Rouse-like modes. These two subdiffusion mechanisms are intertwined by diffusive-in-character hops of Li+ to other segments or to low energy sites present in the cations surrounding. For electrolytes with high salt concentration those hops were predominantly assisted by anions. It was also pointed out that the motion of anions is strongly coupled with PEO ether oxygen atoms (EO) displacements.

Herein, for samples with high salt concentration, the relaxation order rapidly decreases with temperature towards value equal to one, thus towards the diffusive behavior. Such trend presumably indicates that when sample crystallizes the Rouse-like conformations are frozen and the motion of ions becomes purely diffusive.

Clearly, there are additional factors that are not accounted in the MD simulations, but may contribute to the subdiffusive behavior. Herein, the polymer matrix consists of much longer (than in the MD) polymer chains, which are entangled. The center of mass of these chains is practically immobile. The system is not as homogeneous and “pure” as the one modeled in the MD, thus it is possible that some of the ionic species get immobilized (trapped) in local electrochemical potential minima (i.e. percolation network cul-de-sacs/pockets etc.) for waiting-times that constitute the probability density function with long tail. Such shape of this function is characteristic for a subdiffusion [62][63]. For polymer electrolytes the longest waiting time should be limited by a time evolution of the polymer matrix (i.e. by the “renewal time”) as predicted by the Dynamic Bond Percolation [64][65] theory or, indirectly, by the Reptation Theory [57]. It is also possible that the aforementioned interfaces (i.e. the layered structures or the PEO matrix polydispersity described in section 3.2.) may mimic the subdiffusive response. Nonetheless, it is assumed that the contributions by these additional factors are of little account.

To the author’s knowledge, this is the first communication that presents a measure of diffusion domain in the restricted diffusion experiment, thus the results could not be compared. Also a more detailed studies are needed to discover causes of described behavior.

4.1.2. Electrolytes containing a LiATAB salt variant

Similarly, the Ds, τη, and n of six electrolytes based on three borate salt variants are shown. The electrolytes consist of the LiATAB salts with or without the PEO polymer (see Tab. 2.).

- The “common” approach ( kep)

The results obtained by the “common” approach are summarized on Fig. 9a.

At 70 °C the EO27AB7 sample has the highest value of Ds which is equal to $13.78 \pm 0.51 \times 10^{-9}$ cm².s⁻¹. At this temperature the Ds of remaining samples are aligned in descending order:

- EO29AB1 = $12.03 \pm 1.41 \times 10^{-9}$ cm².s⁻¹,
- EO23AB3 = $9.33 \pm 1.02 \times 10^{-9}$ cm².s⁻¹ at 73 °C,
• AB3 = $2.50 \pm 0.21 \times 10^{-9}$ cm$^2$s$^{-1}$,
• AB7 = $1.89 \pm 0.10 \times 10^{-9}$ cm$^2$s$^{-1}$,
• EO9AB7 = $3.31 \times 10^{-9}$ cm$^2$s$^{-1}$ (This $D_s$ value was obtained by a linear extrapolation based on two data points plotted in the Arrhenius representation).

Remark: Postmortem inspections of the cells with EO9AB7 sample (LiATAB+PEO n=7 EO:Li=9:1) exposed a greatly deteriorated surface of the electrodes. Probably, not-fully evaporated acetonitrile in the sample was the culprit. The acetonitrile leftovers continued to evaporate from the sample inside the assembled measuring cell and they reacted with the lithium electrodes. Additionally, at higher temperatures and during the electric perturbations the evaporation and the unwanted reactions proceeded at a faster pace. The persistently increasing resistivity of the system and the vast corrosion of the electrodes seem to confirm the above scenario. Even during extremely long potentiostatic polarizations, this system did not reach the steady state. Only the outcomes measured at the highest temperatures showed an acceptable level of uncertainty.

The correlation between the $\tau_{sp}$ and the $D_s$ has similar character to the one described in the subsection 4.1.1.

• The “new” approach

The results due to the “new” approach are depicted on Fig. 9b.

At 70 °C EO27AB7 sample has the highest value of $D_s$ which is equal to 85.94 ± 0.54 × 10$^{-9}$ cm$^2$s$^{-1}$. At this temperature the $D_s$ of remaining samples are aligned in descending order:
• EO29AB1 = $28.41 \pm 3.26 \times 10^{-9}$ cm$^2$s$^{-1}$,
• EO23AB3 = $23.63 \pm 0.66 \times 10^{-9}$ cm$^2$s$^{-1}$ at 73 °C,
• AB3 = $4.41 \pm 0.21 \times 10^{-9}$ cm$^2$s$^{-1}$,
• AB7 = $3.99 \pm 0.47 \times 10^{-9}$ cm$^2$s$^{-1}$,
• EO9AB7 = $2.95 \times 10^{-9}$ cm$^2$s$^{-1}$ (obtained by linear extrapolation in Arrhenius representation to 2.91 × 10$^3$ K$^{-1}$).

Before discussing the results showed on Fig. 9b in general, let us focus our attention on two data points of the EO29AB1 sample which are indicated by arrows. These points were obtained from two successive SPPs both performed at 80 °C. During the first SPP the absolute value of perturbations ($|\Delta V|$) was set to 30 mV and the absolute value of the first EMF values ($|E_0|$) was approximately equal to 26 mV. During the second SPP the $|\Delta V|$ was equal to 10 mV and $|E_0|$ = 9 mV respectively. When we compare the $|E_0|$ in case of those two SPPs, we notice that the ratio $|E_0|$ in case of those two SPPs, we notice that the ratio $|E_0| / |E_0|$ = 289%, but the ratio $D_s^{1st} / D_s^{2nd}$ ≈ 108%. Based on this observation a conclusion can be made: The $D_s$ by the “new” approach is a property which is independent of potential-perturbation magnitude (for perturbations fulfilling condition (1)). For comparison, the ratio $D_s^{1st} / D_s^{2nd}$ by the “common” approach (Fig. 9a) is on the order of 110%. It is also worth mentioning that the first SPP was preceded by the SPP during which the temperature of the sample was set to 90 °C. In contrast, in case of the second SPP, the preconditions were different. There, the Temperature Setting measuring step could be omitted because the sample was already well equilibrated at 80 °C. This difference in preconditions should explain why the ratio $D_s^{1st} / D_s^{2nd}$ is not equal to 100%. Additionally, the relaxation orders of these successive SPPs are very similar, what may be viewed as an another argument in favor of the “new” approach. Same as in the case of the $D_s$, the relaxation order is a property which is independent of a magnitude of $|\Delta V|$. In general it could be concluded that dissolving the Li-
ATAB salt in the PEO increases the $D_n$. This effect is clearly visible by comparing electrolytes containing the same salt variant, i.e. AB3 vs. EO23AB3 or AB7 vs. EO27AB7. Presumably, the PEO chains compete with the anions in the Li+ coordination. If the concentration of the chains is sufficiently high, the electrostatic interactions between ions are efficiently shielded. Also, long chains constitute an immobile 3D mesh which hampers the motion of big ionic species.

The relaxation orders of the EO27AB7 sample are considerably greater than those of the remaining LiATAB samples. It is reasonable to assume that for this sample a 3D mesh made of PEO is dense enough to successfully block the motion of fairly large and bulky ionic species. High concentration of PEO provides an environment for Li+ to percolate and effectively shields the cations from interactions with other ionic species. The relaxation order can also be used to explain the influence of the anion size on the diffusion. The EO27AB7 sample has a $n$ approximately equal to 2.2 and for the EO29AB1 sample $n=1.6$. These samples have similar molar content of PEO (EO:Li values are 27.5:1 and 29:1 respectively) but they differ in the borate salt variant. Recalling, in EO27AB7 the anion has long oligomer arms that comprise approximately $n=7$ oxyethylene substituents and in EO29AB1 the anion has the arms that are much shorter ($n=1$, see Fig. 3, and Tab. 2.). Two phenomena may be responsible for the difference in the subdiffusion extent. First, at a given PEO concentration, the longer the oligomer arms of the anion are, the more prone the anion is to be slowed down or even trapped by a dense PEO mesh. Second, such trapped anion or an ion cluster may additionally confine Li+ in pocket/cul-de-sac in between the oligomer arms. The probability of such confinement should increase with the length of the arms. The confinement of Li+ may be particularly effective in the vicinity of the boron atom.

The relaxation orders of the neat salts (AB3 $n=3$ and AB7 $n=7$) look particularly puzzling. Surprisingly, they are considerably greater than one ($n=1.5$ and $n=1.6$ respectively). Similarly as mentioned above, the Li+ in these neat salts may be confined/"slowed-down" by the oligomer arms. Also, in addition to the translational motion, the anions may have to rotate to move, what may contribute to the subdiffusion. The structure of the battery separator may also be the culprit. In particular, its greater than one tortuosity or the Knudsen friction which differs between ions may have an impact on the motion. The trapping caused by an aggregation and clustering seems also a plausible cause.

Broader and more advanced measurements, reaching beyond the scope of the present work, are needed to clarify the microscopic causes of such behavior.

### 4.2. Apparent cation transference number ($T_+$)

The $T_+$ presented in this section were calculated according to the four approaches described in section 3.3. On the plots below, a color of the symbol corresponds to the approach, namely:

- yellow (ISS) as in (16),
- orange (SJ NLT) as in (17),
- purple (BV) as in (18),
- green (W) as in (21).

Figures have a form of the apparent cation transference number plotted against the reciprocal of the absolute temperature.

#### 4.2.1. Electrolytes consisting of LiTFSI and PEO

The $T_+$ of four polymer electrolytes consisting of the LiTFSI salt and the PEO polymer (see Tab. 1.) are presented on Fig. 10 and discussed bellow.

![Fig. 10](image)

**Fig. 10.** Temperature dependence of the apparent cation transference numbers ($T_+$) calculated by four approaches (color coded as on inset). Results obtained for the PEO+LiTFSI electrolytes. Each symbol is related to an electrolyte composition (see Tab. 1.).

The $T_+$ values obtained by the ISS approach are significantly greater than those obtained by the three remaining approaches. Moreover, in case of the EO16TF and the EO10TF samples the $T_+$ by the ISS approach show a reverse temperature dependence. The dissimilarity of the $T_+$ by the ISS approach occurs, even though the influence of the interface is partially taken into account (see (15) and (16)).

At 70 °C the EO3TF sample gives the highest values of $T_+$:

- SJ NLT – 0.278 ± 0.023,
- W – 0.282 ± 0.021,
- BV – 0.289 ± 0.015.

At the same temperature the $T_+$ values of the remaining samples are more similar in value:

- EO16TF:
  - SJ NLT – 0.112 ± 0.004,
  - W – 0.100 ± 0.005,
  - BV – 0.166 ± 0.080,
- EO5TF:
  - SJ NLT – 0.072 ± 0.006,
  - W – 0.072 ± 0.009,
  - BV – 0.104 ± 0.001,
- EO10TF:
  - SJ NLT – 0.076 ± 0.003,
The $T_\varepsilon$ values obtained by the SJ NLT approach are quite similar to those derived by the W approach. The BV approach outputs somewhat greater $T_\varepsilon$ values, and the discrepancy in EO16TF case is quite significant. This particularly big discrepancy is prescribed to human errors in the chronoamperometric measurement settings, which lead to an inaccurate “initial” current values. The errors were discovered in the course of much later analysis of the measurement outcomes, when there was no possibility to repeat the measurements.

In general, $T_\varepsilon$ obtained herein (by further modified approaches) are somewhat lower than those from the previous work [19] but the trend in concentration dependence is similar. At first, with increasing salt concentration, the $T_\varepsilon$ gradually decreases until it reaches a minimum at around EO:Li=6:1. From there, the values of $T_\varepsilon$ start to grow rapidly with rising salt content.

Based on above results and a scientific literature study, it can be concluded what follows. At low salt concentrations, each Li$^+$ is solely coordinated by five ether oxygen (EO) atoms (on average) of the PEO chains [66]. The Li$^+$ and TFSI$^-$ are the dominant ionic species. High flexibility of the chains is maintained because of relatively small number of Li$^+$ coordination bonds. Interactions between ions are greatly diminished owing to a substantial spatial separation and the screening effect provided by EO [67]. Ions migrate almost independently from each other. The motion of cations is mainly induced by the PEO conformations. Although, at low salt concentration regime, the transport of cations is relatively very effective due to high elasticity of the chains, a low $T_\varepsilon$ is observed. The reasoning behind such observation is that the interactions of PEO with TFSI$^-$ are much weaker than with those with Li$^+$. Also, the anion has more than six times greater molecular mass than the PEO monomer, thus it has much greater inertia (oddly enough, the molecular mass of 6 PEO monomers and Li$^+$ is almost equal to one of TFSI$^-$). The direction of Li$^+$ motion is to a great extent determined by the arrangement of PEO segments surrounding the cation. Therefore, the migration path of the cations is much more tortuous than the one of the anions, what likely translates to a considerably higher mobility of the latter.

With increasing salt concentration, a PEO chain capability of Li$^+$ coordination gets progressively depleted. At around EO:Li=6:1 the chains are saturated, thus cannot solely complex more lithium. At this concentration the motion of Li$^+$ along the chains is almost brought to a halt. The coordination bonds affect the effective segment length and decrease chain conformational freedom [68], thus the characteristics of Rouse-like relaxations are changed. Further concentration rise perpetuates ion clusters emergence and their gradually growth in size. Also, at higher salt concentrations, the clusters have overall negative charge [61]. The structure becomes more compact and rigid, what in turn affects at most the motion of species with large size. Presumably at very high salt concentrations due to crystallization the hopping of cations becomes the dominating mechanism of charge transport.

### 4.2.2. Electrolytes containing a LiATAB salt variant

Similarly, the $T_\varepsilon$ of six electrolytes based on three borate salt variants are shown. The electrolytes consist of the LiATAB salts with or without the PEO polymer (see Tab. 2.). The results by four approaches are shown on Fig. 11 and discussed bellow.

![Fig. 11. Temperature dependence of the apparent cation transference numbers ($T_\varepsilon$) calculated by four approaches (color coded as on inset). Results obtained for the electrolytes containing LiATAB salt. Each symbol is related to an electrolyte composition (see Tab. 2.).](image)

For the LiATAB electrolytes, the $T_\varepsilon$ calculated by the BV, W and SJ NLT approach are quite similar to each other. Also, the influence of the interface on $T_\varepsilon$ value is not as severe as it is in the case of LiTFSI+PEO systems.

To facilitate the recognition of samples, the $T_\varepsilon$ values obtained by SJ NLT approach at 70 °C are listed (aligned in a descending order):

- EO27AB7 $= 0.331 \pm 0.014$,
- EO23AB3 $= 0.149 \pm 0.011$ at 73 °C,
- EO29AB1 $= 0.066 \pm 0.002$,
- AB7 $= 0.048 \pm 0.010$,
- AB3 $= 0.035 \pm 0.002$.

Additionally, based on the linear extrapolation, the $T_\varepsilon$ of the EO9AB7 sample has been evaluated to be equal to ca. 0.303.

The order in which the $T_\varepsilon$ values are aligned supports the following hypothesis: The greater the size of the anion and the denser the network of an entangled, thus immobile, PEO chains, the higher the $T_\varepsilon$. Anions with long oligomer arms seem to have a great difficulty in switching between positions due to necessity of squeezing through holes in polymer mesh. In case of the “big” anions (see Fig. 3) in a dense PEO matrix, the rise in temperature causes substantial increase in the $T_\varepsilon$. Such effect is probably caused by a decrease in enthalpy of mixing between anion and cation. Also, the pace of conformation change, especially of PEO chains, but also of the...
oligomer arms is more rapid. Presumably, polymer electrolytes with short-oligomer-arms anions show low $T_{\text{c}}$ values caused by a high mobility of anionic species.

### 4.3. Ionic conductivity ($\sigma$)

**Apparent diffusional conductivity ($\sigma_d$)**

The ionic conductivities ($\sigma$) were calculated according to equations (23) and (24). The apparent diffusional conductivities ($\sigma_d$), thus the conductivities based on the $D_2$ by the “new” approach, were evaluated by using (25). The effective (cionic) conductivities ($\sigma_i$) were obtained using the SJ NLT approach $T_{\text{c}}$, thus by (27).

#### 4.3.1. Electrolytes consisting of LiTFSI and PEO

The $\sigma$, $\sigma_d$, $\sigma_i$ of four polymer electrolytes consisting of the LiTFSI salt and the PEO polymer (see Tab. 1.) are presented on Fig. 12 and discussed bellow.

![Fig. 12. Arrhenius-type plot of the ionic conductivity (blue, $\sigma$), the cationic/effective conductivity by SJ NLT (orange, $\sigma_i$) and the conductivity based on the salt diffusion coefficient (magenta, $\sigma_d$) for the PEO+LiTFSI electrolytes. Each symbol is related to an electrolyte composition (see Tab. 1.).](image)

To facilitate the recognition of the results on Fig.12, the values obtained at 70 °C are listed (aligned in descending order):

- $\sigma$:
  - EO16TF: $4.94 \pm 0.06 \times 10^{-4}$ $\Omega^{-1}\text{cm}^{-1}$
  - EO10TF: $4.61 \pm 0.05 \times 10^{-4}$ $\Omega^{-1}\text{cm}^{-1}$
  - EO5TF: $1.90 \pm 0.02 \times 10^{-4}$ $\Omega^{-1}\text{cm}^{-1}$
  - EO3TF: $0.45 \pm 0.01 \times 10^{-4}$ $\Omega^{-1}\text{cm}^{-1}$

- $\sigma_d$:
  - EO16TF: $5.85 \pm 0.10 \times 10^{-4}$ $\Omega^{-1}\text{cm}^{-1}$
  - EO5TF: $5.02 \pm 0.58 \times 10^{-4}$ $\Omega^{-1}\text{cm}^{-1}$
  - EO10TF: $4.62 \pm 0.25 \times 10^{-4}$ $\Omega^{-1}\text{cm}^{-1}$
  - EO3TF: $2.16 \pm 0.22 \times 10^{-4}$ $\Omega^{-1}\text{cm}^{-1}$

- $\sigma_i$:
  - EO16TF: $0.55 \pm 0.04 \times 10^{-4}$ $\Omega^{-1}\text{cm}^{-1}$
  - EO10TF: $0.35 \pm 0.04 \times 10^{-4}$ $\Omega^{-1}\text{cm}^{-1}$
  - EO5TF: $0.14 \pm 0.03 \times 10^{-4}$ $\Omega^{-1}\text{cm}^{-1}$
  - EO3TF: $0.13 \pm 0.01 \times 10^{-4}$ $\Omega^{-1}\text{cm}^{-1}$

The $\sigma$ on Fig. 12 and those from the previous work [19] show that a maximal value of the ionic conductivity is presumably located somewhere between EO:Li=16:1 and 10:1. The location of this maximum is supported by the Flory–Huggins mean-field theory [69]. According to this theory, the change in the entropy of mixing (per lattice site and for flexible, monodisperse, linear polymer chains mixed with solvent molecules of a monomer size) is proportional to:

$$\Delta S_{\text{mix}} \propto \frac{\Phi}{N} \ln(\Phi) + (1-\Phi) \ln(1-\Phi)$$

(30)

Where:
- $\Phi$ – volume fraction of the polymer,
- $N$ – number of lattice sites taken by the polymer.

Let us assume (very roughly) that:
- $\Phi$ is related to the salt mass fraction as $\Phi \approx 1 - W_s$,
- $N$ is proportional to the number of monomers in the chain, and that:
- the chain has the entanglement molecular weight ($M_e$). For the PEO, the $M_e=2000\text{g/mol}$ [70]. Thus, the $N$ is approximately equal to 45. By performing mathematical operations on the (30), we obtain that the maximum of the entropy is located at $\Phi=0.636$, thus $W_s=0.364$ or EO:Li=11:1. Clearly, this value is a very rough estimate, because of the approximations, and because the influence of the enthalpy of mixing was not comprised here. In polymer electrolytes, in addition to the theory, the enthalpy should also account for the electrostatic ion-ion interactions.

For the EO16TF sample the $\sigma$ are quite similar to the $\sigma_d$. Such similarity is apparently an indicator of a well dissociated salt. Additionally, the molar conductivities of this sample are the highest among the samples. The motion of ions in this sample appears to be uncorrelated. Also, in case of the EO10TF sample the $\sigma$ and $\sigma_d$ are alike, but the molar conductivities for this sample are somewhat lower. For the EO5TF sample the differences are much bigger (the $\sigma_d$ to $\sigma$ ratio is equal to ca. 3). Presumably, ion aggregates are additionally present in this sample. For the EO3TF sample the ratio is equal to about 7. This suggests that the level of ion association is high, thus to the correlation between the motion of ions is strong.

Additionally, the $\chi_e$ was calculated (according to (26)) in an attempt to have a better sense of the deviation from the Nernst-Einstein relation. The estimation was made only for PEO+LiTFSI system and only at one temperature equal to 90 °C. Because the evaluation of the thermodynamic factor is not incorporated in the present work, the values (these in the square brackets below) were extracted from Fig. 3b of Pesko et al. [6] communication:

- EO16TF: $2.12 \cdot [3.0]^{-1} = 0.71$
- EO5TF: $2.86 \cdot [4.5]^{-1} = 0.63$
- EO10TF: $2.68 \cdot [2.7]^{-1} = 0.99$
Noticeably, all $\chi_a$ values are less than one. This apparently means that the motion of ions is less correlated than concluded based on the $\sigma_a$ to $\sigma$ ratio. But, because of many simplifying assumptions (see Appendix C) and the thermodynamic factor measured elsewhere, high uncertainties of these $\chi_a$ are expected.

As stated above, significant differences between $\sigma$ and $\sigma_d$ presumably indicate a high concentration of ion pairs or other ion aggregates. In such cases additional measurements can be made at varied perturbation values ($|\Delta V|$). The results of such measurements should provide better insight into the type of the dominating species [4].

The plots on Fig. 12 look linear, thus a thermally activated charge transport can be recognized (i.e. Arrhenius-type transport). To facilitate the comparison of an energy landscape, the apparent activation energies ($E_a$) were extracted from Fig. 12 into Tab. 3. Each $E_a$ listed in that table is proportional to the slope of a linear function fitted to the data points. Clearly, the $E_a$ values shown in Tab. 3 are only a rough estimate of an actual energy landscape. The Vogel–Fulcher–Tamman fittings should give a more accurate view. Nevertheless, due to a relatively small number of data points such analysis was omitted. To further clarify, for every type of conductivity presented on Fig. 12, a type of $E_a$ was extracted. The ionic $E_a$ values stem from the fittings to the $\sigma$ data points, the diffusional $E_a$ are based on the $\sigma_d$ data and the cationic $E_a$ is related to the $\sigma_c$.

![Table 3](image)

| EO:Li | ionic | diffusional | cationic |
|-------|-------|-------------|----------|
| LiTFSI+PEO 16:1 | 32 / 0.33 | 32 / 0.33 | 35 / 0.36 |
| LiTFSI+PEO 10:1 | 40 / 0.42 | 46 / 0.47 | 48 / 0.50 |
| LiTFSI+PEO 5:1 | 70 / 0.72 | 68 / 0.70 | 64 / 0.67 |
| LiTFSI+PEO 3:1 | 83 / 0.86 | 98 / 1.02 | 79 / 0.82 |

The EO16TF sample has the lowest $E_a$ values and the values between the types are also very similar. Such observations additionally confirm the superiority of this electrolyte. A gradual increase of each type of $E_a$ with increasing salt concentration is also noticeable.

Based on possessed knowledge, the influence of salt content in LiTFSI+PEO polymer electrolytes can be summarized as follows. Long and entangled polymer chains constitute a relatively immobile matrix. At low salt concentrations, the LiTFSI salt is well dissociated by the PEO. Each of the $\text{Li}^+$ is preferably coordinated to 5 ether oxygen atoms (EO) [66], therefore there are plenty of “free” EO available for $\text{Li}^+$ coordination at low salt concentrations. Above the melting temperature the PEO, the chains are very flexible, but the $\text{Li}^+$ coordination bonds make the section of the chain more rigid [68]. Such section has presumably the length of 6 consecutive EO for a coordination by a single chain. The $\text{Li}^+$ shifts position mostly with assist of the chains via the subdiffusion. The direction of $\text{Li}^+$ motion is highly influenced by the alignment of a chain segment to which the $\text{Li}^+$ is currently bonded to. A large spatial separation and the screening effect of the EO's diminish the ion-ion electrostatic interactions [67]. A relatively small positive charge of PEO hydrogen atoms and a considerable charge delocalization on TFSI contribute to a more fluid and less tortuous motion of the TFSI. Additionally, there is a substantial difference in the inertia because of more than six times higher molecular mass of a TFSI compared to a PEO monomer. Therefore, the majority of TFSI move swiftly in the direction of the electric field. Nevertheless, some of the TFSI may be trapped by the polymer matrix (i.e. especially in the cross-linking points) for long waiting times. The trapping could be caused by a large size and bulkiness of the TFSI, and thus may contribute to the subdiffusion.

With increasing salt concentration the influence of Rouse-type conformations on the $\text{Li}^+$ motion is fading, but the volumetric number of ions rises. A high number of ions is a prerequisite of a high ionic conductivity. At EO:Li=6:1 ratio, energetically favorable structures consisting of pairs of PEO coils which interlock to form cylinders with inner cation channels are believed to be predominant [68]. Such chains arrangement apparently hampers an efficient $\text{Li}^+$ motion by impairing the effect of Rouse-type chain conformations. A constructive synchronization of chain conformations in both coils seems possible but unlikely, also the orientation and “clogging” of the channels may be an issue. Above the salt concentrations of EO:Li=6:1, additionally to $\text{Li}^+$ and TFSI, other ionic species (i.e. ion pairs, triplets etc.) begin to emerge and play an important role in charge transfer between electrodes. In this concentration regime an addition of salt not necessarily translates to an increase of number of charge carries. A sole $\text{Li}^+$ transport via a percolating network of the chains becomes rare. The $\text{Li}^+$ are forced to frequently modify their coordination environment between the EO atoms and the oxygen atoms belonging to the TFSI. Frequent changes of the coordination character further impedes a motion of the $\text{Li}^+$ [71], thus most of the charge is transported with assist of anionic species.

### 4.3.2. Electrolytes containing a LiATAB salt variant

At 70 °C the AB3 sample has the highest ionic conductivity ($\sigma$), equal to 4.84 ± 0.29 × 10⁻² Ω⁻¹cm². At this temperature $\sigma$ of the remaining samples are aligned accordingly:

- AB7 = 1.25 ± 0.16 × 10⁻² Ω⁻¹cm²
- EO29AB1 = 9.02 ± 1.10 × 10⁻² Ω⁻¹cm²
- EO27AB7 = 5.90 ± 0.29 × 10⁻² Ω⁻¹cm²
- EO23AB3 = 1.29 ± 0.10 × 10⁻² Ω⁻¹cm² at 73 °C
- EO9AB7 = 2.81 ± 0.72 × 10⁻² Ω⁻¹cm²

Substantial differences between $\sigma$ and $\sigma_a$ of the polymer electrolytes (EO29AB1, EO27AB7, EO23AB3, EO9AB7) can be noticed on Fig. 13. As already mentioned above, such differences likely indicate a poorly dissolved salt. In contrast, $\sigma$ and $\sigma_a$ of the neat borate salts (AB3, AB7) are relatively similar to each other. Probably, the PEO chains disturb a spatially symmetric disposition of identical interactions acting upon each ion in the neat salts. Thus, the chains facilitate an emer-
gence of ion pairs or even larger aggregates [46]. In particular, species that have no net charge (like ion pairs, etc.), don’t contribute to the ionic conductivity, but they should participate in the diffusional conductivity ($\sigma_d$). For the case of the borate salts, and especially for variants with long oligomer arms, ion pairs should have similar size as ATAB$^-$ anions.

Furthermore, the denser the PEO matrix is, the better it is in restraining the motion of species based on their size. Probably, for LiATAB polymer electrolytes, the electrode reactions are the main source of relatively small ionic species i.e. Li$^+$ and ATAB$^-$. Also, the battery separator, used in case of AB3 and AB7, should be quite effective in diminishing convection but it may not inhibit the motion of large size ionic species.

### 4.4. Limiting-current density

The limiting-current densities ($J_{\text{lim}}$) are presented on Fig. 14. They were calculated using (28). To facilitate possible conversions, in those calculations the reference electrolyte thickness was deliberately chosen to have 100 $\mu$m.

To assist a recognition of the samples on Fig. 14, the $J_{\text{lim}}$ obtained at 70 °C, are listed below. The values are aligned in descending order:

- EO16TF $- 1.947 \pm 0.040$ mA·cm$^{-2}$
- EO5TF $- 1.600 \pm 0.186$ mA·cm$^{-2}$
- EO10TF $- 1.477 \pm 0.080$ mA·cm$^{-2}$
- EO27AB7 $- 1.357 \pm 0.023$ mA·cm$^{-2}$
- EO3TF $- 0.887 \pm 0.095$ mA·cm$^{-2}$
- EO29AB1 $- 0.480 \pm 0.055$ mA·cm$^{-2}$
- EO23AB3 $- 0.444 \pm 0.014$ mA·cm$^{-2}$ at 73 °C,
- AB3 $- 0.203 \pm 0.010$ mA·cm$^{-2}$
- AB7 $- 0.091 \pm 0.011$ mA·cm$^{-2}$
- EO9AB7 $- 0.072$ mA·cm$^{-2}$ when extrapolated to 70 °C.

At relatively low temperatures (from 60 to 70 °C) the EO16TF sample has the highest limiting-current density accompanied by the highest ionic conductivity. Interestingly, at higher temperatures, the LiTFSI-rich polymer electrolytes should have the ability to sustain higher charging-discharging current.

Overall, as a result of better salt dissociation, the LiTFSI based polymer electrolytes have higher limiting-current densities than electrolytes based on the LiATAB salts. Apparently, the high amount of large ionic aggregates significantly reduces the number of charge carriers in the latter electrolytes.
5. CONCLUSIONS

In the beginning of the present work, the details of Symmetric Polarization Procedure were described. The SPP is an ordered set of measurements, which in addition to a precise estimation of the properties, facilitates a simple and fast detection of experimental mistakes. These mistakes are discovered by a visual examination of a symmetry in the SPP outcomes. Thus, an information about any inconsistency is available instantaneously and the SPP can be repeated or the additional measurements can be performed to explain the source of confusion. Thanks to this simple preliminary validation task an ad hoc advanced data analysis can be avoided and the outcomes inspection can be made by less qualified staff.

Also, a new approach to the analysis of restricted diffusion measurement was proposed, together with a quantitative measure of the diffusion domain, namely the relaxation order. This approach not only improves the precision of evaluated salt diffusion coefficient, but also it provides an important information on the character of the salt gradient relaxation. Such accurate and complete information should lead to the design of more optimal battery charging/discharging protocols as well as more precise electrochemical sensors. Herein, in case of all examined electrolytes, the subdiffusive ion motion was observed. Two presumable reasons were given as the sources of such motion: the motion of lithium cations coordinated by wriggling polymer chains and the trapping events of ions.

Finally, it has been shown how the combination of the apparent cation transference number, the salt diffusion coefficient and the ionic conductivity, can be used as a proper indicator of an electrochemical fitness of an electrolyte.

ACKNOWLEDGMENTS

I am grateful to Prof. Andrzej Lasia (Université de Sherbrooke) for kindly sharing his vast knowledge about the EIS technique. I would also like to express my gratitude to Asst. Prof. Ewa Zygałko-Monikowska and coworkers (Warsaw University of Technology) for supplying the lithium borate salts. Help by Asst. Prof. Michał Marzantowicz (Warsaw University of Technology) with the synthesis of the polymer electrolytes and a configuration the measuring equipment is also greatly appreciated.

Funding Sources: This work has been supported by Polish National Science Centre NCN (grant 2014/15/N/ST5/03909).

Declaration of Competing Interest: The author declares no competing financial interest.

APPENDICES

A. Abbreviations of the measuring methods from Fig. 1 and Fig. 2.

Letters in front of temperatures in Fig. 1 legends have the meaning:
- GP – the salt gradient relaxation is introduced by the Galvanostatic Polarization of a sample, analysis based on the long time part of the relaxation curve, as in [2],
- PP – the salt gradient relaxation is introduced by the Potentiostatic Polarization to a steady state, as in [9],
- LT – analysis based on data from long time part of relaxation, similar to the “common” approach, see 3.1.1.,
- ST – as LT but on data from short time, see (B.2),
- SPP – Symmetric Polarization Procedure, the result is an average of two relaxations introduced by two opposite sign PP,
- EIS – analysis based on the Electrochemical Impedance Spectroscopy data,
- EP – Equivalence Point or the “new” approach, see section 3.1.2.

Letters in front of temperatures in Fig. 2 legends have the meaning:
- M – measurements and result analysis proposed by Ma et al. [2],
- BV – measurements and result analysis proposed by Evans et al. [49],
- SJ – measurements and result analysis proposed by Sørensen and Jacobsen [48],
- A – measurements similar to BV and result analysis proposed by Abraham et al. [72],
- SPP W – measurements similar to BV with two potentiostatic polarizations with equal-magnitude but opposite sign of potential perturbation and result analysis proposed by Watanbe et al. [50],
- SPP SJ NLT – measurements similar to SPP W and result analysis proposed by Sørensen and Jacobsen et al. see section 3.3.2.

B. Time at equivalence point

The equation (4) being an infinite sum can be approximated in two time regions, namely at the short time (st) (B.2) and at the long time (7) or (B.6). Each approximation if multiplied by the square root of time gives a function that has a single maximum which is localized in the vicinity of $\tau_{pp}$. Here mathematical formula for $\tau_{pp}$ is obtained by equating a time derivative of mentioned single maximum functions to zero as in (B.3) or (B.7).
Another characteristic time is correlated with a salt diffusion at the restricted length ($\tau_d$) given by formula below:

$$\tau_d = \frac{L^2}{D_S}$$  \hfill (B.1)

The $\tau_{EP}$ derived from the short-time approximation:

$$\frac{E(t)}{E_0} = 1 - 4 \sqrt{\frac{t}{\pi \tau_d}}$$  \hfill (B.2)

$$\frac{d}{dt} \left( 1 - 4 \sqrt{\frac{t}{\pi \tau_d}} \right) = 0$$  \hfill (B.3)

$$\tau_{EP}^\text{st} = \frac{\pi}{64} \tau_d \approx 0.049087 \tau_d$$

$$E_{EP} = E(t = \tau_{EP}^\text{st}) \quad E_0 = \frac{E_{EP}}{2}$$  \hfill (B.4)

$$E(t)^\text{st} = \left( 1 - 4 \sqrt{\frac{t}{2 \pi^3 \tau_{EP}^\text{st}}} \right) \left( \frac{E_{EP}}{1 - \frac{4}{\sqrt{2 \pi^3}}} \right)$$  \hfill (B.5)

The $\tau_{EP}$ derived from the long-time approximation:

$$\frac{E(t)}{E_0} = \frac{8}{\pi^2} \exp \left( -\pi^2 \frac{t}{\tau_d} \right)$$  \hfill (B.6)

$$\frac{d}{dt} \left( \frac{8}{\pi^2} \exp \left( -\pi^2 \frac{t}{\tau_d} \right) \right) = 0$$  \hfill (B.7)

$$\tau_{EP}^\text{lt} = \frac{1}{2 \pi^2} \tau_d \approx 0.050661 \tau_d$$

$$E_{EP} = E(t = \tau_{EP}^\text{lt}) \quad E_0 = \frac{E_{EP}}{\left( 1 - \frac{4}{\sqrt{2 \pi^3}} \right)^{0.5}}$$  \hfill (B.8)

\section*{C. Diffusional conductivity}

Based on the Nernst-Einstein relation we can write the diffusional conductivity expression:

$$\sigma_d^* = \frac{F^2 \cdot D_S \cdot c_s \cdot c_0}{2 \cdot R \cdot T \cdot c_T \cdot t_s \cdot (1-t_s)} \cdot \left[ 1 + \frac{d \ln (y_\pm)}{d \ln (m)} \right]^{-1}$$  \hfill (C.1)

Combining (4) with (C.1) and (C.2) gives:

$$\sigma_d^* = \frac{F^2 \cdot D_S \cdot c_s \cdot c_0}{2 \cdot R \cdot T \cdot c_T \cdot t_s \cdot (1-t_s)} \cdot \left[ 1 + \frac{d \ln (y_\pm)}{d \ln (m)} \right]^{-1}$$  \hfill (C.2)

Assuming that $t_s$ can be approximated by $T_+\text{ in (C.3)}$ and utilizing (25) we get:

$$\sigma_d^* = \frac{c_0}{2 \cdot R \cdot T_+ \cdot (1-T_+)} \cdot \left[ 1 + \frac{d \ln (y_\pm)}{d \ln (m)} \right]^{-1}$$  \hfill (C.3)

Finally, combining (26) and (C.4) we get an expression for Nernst-Einstein relation based on the apparent diffusional conductivity:

$$\sigma_d^* = \sigma_d \cdot \chi_d$$  \hfill (C.5)

Assuming that $t_s$ can be approximated by $T_+$ in (C.3) and utilizing (25) we get:

$$\sigma_d^* = \sigma_d \cdot \chi_d$$  \hfill (C.5)

Additionally, the transference numbers (with respect to solvent) in concentrated solution theory are defined as:

$$t_+ = \frac{D_0^+}{D_0^+ + D_0^-} \quad \land \quad t_- = 1 - t_+$$  \hfill (C.2)
REFERENCES

[1] L. Onsager, Ann. N.Y. Acad. Sci. 46 (1945) 241.
[2] Y. Ma, M. Doyle, T.F. Fuller, M.M. Doeff, L.C. De Jonghe, J. Newman, The measurement of a complete set of transport properties for a concentrated solid polymer electrolyte solution, J. Electrochem. Soc. 142 (1995) 1859.
[3] P. G. Bruce, Polymer Electrolytes and Interconnection Electrodes: Fundamentals and Applications, In Fast Ion Transport in Solids Springer, Dordrecht (1993) 87.
[4] P. G. Bruce, C. A. Vincent, Effect of ion association on transport in polymer electrolytes. Faraday discussions of the Chemical Society 88 (1994) 43.
[5] L. Edman, A. Ferry, G. Orriëld, Analysis of diffusion in a solid polymer electrolyte in the context of a phase-separated system, Physical Review E 65 (2002) 042803.
[6] D. M. Pesko, Z. Feng, S. Sawhney, J. Newman, V. Srinivasan, N. P. Balsara, Comparing Cycling Characteristics of Symmetric Lithium-Polymer-Lithium Cells with Theoretical Predictions, Journal of The Electrochemical Society 165 (2018) A3186.
[7] I. Rey, J.-L. Brunee, J. Grondln, L. Servant, J.-C. Lassègues, Raman spectroelectrochemistry of a lithium/polymer electrolyte symmetric cell, J. Phys. Chem. Soc. 145 (1998) 3034.
[8] L. Edman, M.M. Doeff, A. Ferry, J.B. Kerr, L.C. De Jonghe, Transport properties of the solid polymer electrolytes system P(EO)₅LiTFSI, J. Phys Chem B 104 (2000) 3476.
[9] Y.-T. Kim, E. S. Smotkin, The effect of plasticizers on transport and electrochemical properties of PEO-based electrolytes for lithium rechargeable batteries, Solid State Ionics 149 (2002) 29.
[10] R. Bouchez, S. Lascaud, M. Rosso, An EIS study of the anode Li/PEO-LiTFSI of a Li polymer battery, Journal of the Electrochemical Society 150 (2003) A1385.
[11] O. E. Geiculescu, R. Rajagopal, S. E. Creager, D. D. DesMarteau, X. Zhang, P. Fedkii, Transport properties of solid polymer electrolytes prepared from oligomeric fluorosulfonimide lithium salts dissolved in high molecular weight poly (ethylene oxide), The Journal of Physical Chemistry B 110 (2006) 23130-23135.
[12] S. A. Mullin, G. M. Stone, A. Panday, N. P. Balsara, Salt diffusion coefficients in block copolymer electrolytes, Journal of the Electrochemical Society 158 (2011) A619.
[13] M.M. Hiller, M. Joost, H.J. Gores, S. Passerini, H.-D. Wiemhofer, The influence of interface polarization on the determination of lithium transference numbers of salt in polyethylene oxide electrolytes, Electrochim. Acta 114 (2013) 21.
[14] A. Lubelski, I. M. Sokolov, J. Klafer, Nonergodicity mimics inhomogeneity in single particle tracking. Physical review letters, 100/25 (2008) 250602.
[15] F. Lemaitre-Augier, J. Prüihomme, Ion–ion, short-range interactions in PEO-LiX rubbery electrolytes containing LiSCN, LiIn(CF₃SO₃)₂ or Li[CF₃SO₃(N(CH₃)₃)OCH₃] as deduced from studies performed on PEO-LiX-KX ternary systems, Electrochim. Acta 46 (2001) 1359.
[16] Z. Zhao, R. Tao, T. Fujinami, Enhancement of ionic conductivity of LiX-KX ternary systems, Electrochim. Acta 133 (2014) 529.
[17] J. Mindemark, B. Sun, E. Törmä, D. Brandell, High-performance solid oxide (SOX) polymer electrolyte, Electrochimica Acta 133 (2014) 529.
[18] A. Thiam, C. Martinez-Cisneros, Y. Molmèret, C. Joioju, J. Y. Sanchez, PEO: An immobile solvent?. Electrochimica Acta 302 (2019) 338.
[19] P. J. Flory, Thermodynamics of high polymer solutions. The Journal of Chemical Physics 100/1 (1942) 51.
[20] P. J. Flory, The configuration of real polymer chains. The Journal of Chemical Physics 17/3 (1949) 303-310.
[21] P. Mahnoudi, W. S. R. Forrest, T. M. Beardsley, M. W. Matsen, Testing the universality of entropic segregation at polymer surfaces. Macromolecules 51/3 (2018) 1242.
[22] J. E. B. Randles, Kinetics of rapid electrode reactions. Discussions of the faraday society 1 (1947) 117.
[23] A. Lasia, Electrochemical Impedance Spectroscopy and its Applications, Springer, New York, NY, (2014).
[24] J. Bisquert, A.Compte, Theory of the electrochemical impedance of anomalous diffusion. Journal of Electroanalytical Chemistry 499/1 (2001) 112.
[25] H. Gerischer, Alternating-current polarization of electrodes with a potential determining step for equilibrium potential. Z. Physik. Chem. 198 (1951) 268.
[26] S. Havrilak, S. Negami, A complex plane representation of dielectric and mechanical relaxation processes in some polymers. Polymer 8 (1967) 161.
[27] B.A. Boukamp, H.J.M. Bouwmeester, Interpretation of the Gerischer impedance in solid state ionics. Solid State Ionics 157 (2003) 29.
[28] K. Takano, K. Nozaki, Y. Saito, K. Kato, A. Negishi, Impedance Spectroscopy by Voltage-Step Chronoamperometry Using the Laplace Transform Method in a Lithium-Ion Battery. Journal of the Electrochemical Society 147/3 (2000) 922.
[29] F. Woehde, M. Babajews, B. Roling, Li⁺ transference numbers in liquid electrolytes obtained by very-low-frequency impedance spectroscopy at variable electrode distances, Journal of The Electrochemical Society 163 (2016) A1714.
[30] P. G. Bruce, C. A. Vincent, Polymer electrolytes. Journal of the Chemical Society, Faraday Transactions 89/17 (1993) 3187.
[31] P. M. Blonsky, D. F. Shriver, P. Austin, H. R. Alcock, Complex formation and ionic conductivity of polyphosphazene solid electrolytes. Solid State Ionics 18 (1986) 258.
[48] P.R. Sørensen, T. Jacobsen, Conductivity, charge transfer and transport number an ac-investigation of the polymer electrolyte LiSCN-poly(ethylene oxide), Electrochim. Acta 27 (1982) 1671.
[49] J. Evans, C.A. Vincent, P.G. Bruce, Electrochemical measurement of transference numbers in polymer electrolytes, Polymer 28 (1987) 2324.
[50] M. Watanabe, S. Nagano, K. Sanui, N. Ogata, Estimation of Li+ transport number in polymer electrolytes by the combination of complex impedance and potentiostatic polarization measurements, Solid State Ionics 28–30 (1988) 911.
[51] J. O. M. Bockris, A. K. N. Reddy, M. Gamboa-Aldeco, Modern Electrochemistry 2A. Fundamentals of Electroics. (2000). DOI:10.1007/b113922
[52] D. Richter, B. Ewen, B. Farago, T. Wagner, Microscopic dynamics and topological constraints in polymer melts: A neutron-spin-echo study. Physical review letters 62/18 (1989) 2140.
[53] H. W. Weber, R. Kimmich, Anomalous segment diffusion in polymers and NMR relaxation spectroscopy. Macromolecules 26/10 (1993) 2597.
[54] E. Fischer, R. Kimmich, N. Fatkullin, NMR field gradient diffusometry of segment displacements in melts of entangled polymers. The Journal of chemical physics 104/2 (1996) 9174.
[55] A. Wischnewski, M. Monkenbusch, L. Willner, D. Richter, G. Kali, Direct observation of the transition from free to constrained single-segment motion in entangled polymer melts. Physical review letters 90/5 (2003) 058302.
[56] P. E. Rouse Jr, A theory of the linear viscoelastic properties of dilute solutions of coiling polymers. The Journal of Chemical Physics 21/7 (1953) 1272.
[57] P. G. de Gennes, Reptation of a polymer chain in the presence of fixed obstacles. The journal of chemical physics 55/2 (1971) 572.
[58] M. Doi, S. F. Edwards, S. F. Edwards, The theory of polymer dynamics, Oxford University Press. Vol. 73 (1988)
[59] O. Borodin, G. D. Smith, Mechanism of ion transport in amorphous poly(ethylene oxide)/LiTFSI from molecular dynamics simulations. Macromolecules 39/4 (2006) 1620.
[60] D. Diddens, A. Heuer, O. Borodin, Understanding the lithium transport within a rouse-based model for a PEO/LiTFSI polymer electrolyte. Macromolecules 43/4 (2010) 2028.
[61] D. J. Brooks, B. V. Merinov, W. A. Goddard III, B. Kozinsky, J. Mailoa, Atomistic description of ionic diffusion in PEO-LiTFSI. Effect of temperature, molecular weight, and ionic concentration. Macromolecules 51/21 (2018) 8987.
[62] R. Metzler, J. Klafter, Boundary value problems for fractional diffusion equations. Physica A: Statistical Mechanics and its Applications 278 (2000) 107.
[63] R. Metzler, J. Klafter, The restaurant at the end of the random walk: recent developments in the description of anomalous transport by fractional dynamics. Journal of Physics A: Mathematical and General 37/31 (2004) R161.
[64] S. D. Drager, A. Nitzan, M. A. Ratner, Dynamic bond percolation theory: A microscopic model for diffusion in dynamically disordered systems. I. Definition and one-dimensional case. The Journal of chemical physics 79/6 (1983) 3133.
[65] A. Nitzan, M. A. Ratner, Conduction in polymers: dynamic disorder transport. The Journal of Physical Chemistry 98/7 (1994) 1765.
[66] G. Mao, M. L. Saboungi, D. L.Price, M. B. Armand, W. S. Howells, Structure of liquid PEO-LiTFSI electrolyte. Physical review letters 84/24 (2000) 5536.
[67] K. Kang, G. Ceder, Factors that affect Li mobility in layered lithium transition metal oxides. Physical Review B 74/9 (2006) 094105.
[68] B. K. Annis, M. H. Kim, G. D. Wignall, O. Borodin, G. D. Smith, A study of the influence of LiI on the chain conformations of poly(ethylene oxide) in the melt by small-angle neutron scattering and molecular dynamics simulations. Macromolecules 33/20 (2000) 7544.
[69] P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca (1953).
[70] L. J. Fetters, D. J. Lohse, S. T. Milner, W. W. Graessley, Packing length influence in linear polymer melts on the entanglement, critical, and reptation molecular weights. Macromolecules, 32/20 (1999) 6847.
[71] Y. Wang, W. D. Richards, S. P. Ong, L. J. Miara, J. C. Kim, Y. Mo, G. Ceder, Design principles for solid-state lithium superionic conductors. Nature materials 14/10 (2015) 1026.
[72] K. M. Abraham, Z. Jiang, B. Carroll, Highly conductive PEO-like polymer electrolytes. Chemistry of materials 9/9 (1997) 1978.