Physico-chemical Properties of Solutions of Lithium Bis(fluorosulfonyl)imide (LiFSI) in Dimethyl Carbonate, Ethylene Carbonate, and Propylene Carbonate

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Abstract

Battery performance strongly depends on the choice of the electrolyte-solvent system. Lithium bis(fluorosulfonyl)imide (LiFSI) is a highly interesting novel electrolyte. Information on physico-chemical properties of solutions of LiFSI, however, is scarce. Therefore, the density, shear viscosity, and electrical conductivity of solutions of LiFSI in three pure solvents that are interesting for battery applications: dimethyl carbonate (DMC), ethylene carbonate (EC), and propylene carbonate (PC), were studied experimentally at temperatures between 273 K and 333 K at 1 bar and concentrations of LiFSI up to 0.45 mol mol⁻¹ in the present work. Empirical correlations of the experimental data are provided. The comparison of the data of this work with the corresponding LiPF₆ data underpins the attractiveness of LiFSI as an electrolyte in lithium ion batteries. *Keywords:* lithium bis(fluorosulfonyl)imide (LiFSI), electrical conductivity, density, shear viscosity, lithium ion battery, electrolyte solution

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1. Introduction

Lithium-ion batteries (LiB) are well established for the storage of electrical energy, and there is a continuously growing demand for both smaller and more powerful LiB [1–3]. The performance of the batteries depends on many factors,
5 among which the choice of the electrolyte-solvent system is one of the most important [4–10].

Since its introduction to market in the 1990’s, lithium hexafluorophosphate (LiPF₆) is the most common electrolyte in LiB. One of the strong points of
10 LiPF₆ is its high electrical conductivity in organic solvents. A promising new electrolyte for LiB is lithium bis(fluorosulfonyl)imide (LiFSI). It has an even higher electrical conductivity in organic solvents than LiPF₆, and has other advantages like a better stability regarding hydrolysis and lower aluminium corrosion [11–16].

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Despite the high interest in LiFSI, little is known up to now on the physico-chemical properties of its solutions in the commonly used solvents: dimethyl carbonate (DMC), ethylene carbonate (EC), and propylene carbonate (PC).
In practice, often solvent mixtures are used in LiB. The data on LiFSI in the
20 single solvents that are presented here is needed as a prerequisite for modeling solutions in solvent mixtures. Tab. 1 gives an overview of literature data on physico-chemical properties of solutions of LiFSI.

Tab. 1 shows that the data on physico-chemical properties of solutions of
 25 LiFSI in DMC, EC, and PC, are spotty. Therefore, a systematic experimental
 study on the density, shear viscosity, and electrical conductivity of solutions of
 LiFSI in these solvents was carried out in the present work. The three properties
 were determined for mole fractions of LiFSI up to 0.45 mol mol⁻¹, correspond-
 ing to a molarity of about 5.5 M, and temperatures between 273 K and 333 K.

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Empirical correlations of the new experimental data are provided that en-
 able a systematic comparison of the present data of LiFSI with data of LiPF₆
 available in the literature.

Table 1: Overview of literature data on physico-chemical properties of solutions
 of LiFSI in organic solvents.

Solvent (mixture)*	$c_{\text{LiFSI}} / \text{M}$	T / K	Properties	Reference
ACN	0.4 - 4.0	233 - 373	σ, η, ρ	Han et al. [12]
DMC	0.5 - 5.5	303	σ, η, ρ	Wang et al. [16]
DMC	0.1 - 5.0	223 - 323	σ	Li et al. [17]
DME	1.0 - 5.0	298	σ	Qian et al. [18]
EC	0.6 - 5.7	303	σ, η, ρ	Wang et al. [16]
DEC-EC (7:3)	1.0	253 - 293	σ, η	Takekawa et al. [19]
DMC-EC (1:1, 9:1)	1.0	298	σ, η	Uchida and Ishikawa [20]
DMC-EMC (3:7)	1.0	223 - 323	σ	Li et al. [17]
DMC-EC (1:1)	0.6 - 5.3	303	σ, η, ρ	Wang et al. [16]
EMC-EC (7:3)	1.0	253 - 333	σ, η	Han et al. [11]
DMC-EMC-EC (2:3:5)	1.0	253 - 323	σ	Li et al. [17]

σ electrical conductivity, ρ density, η shear viscosity; *: volume ratio.
 Abbr.: ACN: acetonitrile; DME: 1,2-dimethoxyethane; DEC: diethyl carbonate;
 DMC: dimethyl carbonate; EMC: ethyl-methyl carbonate; EC: ethylene carbonate.

2. Experimental Section

35 2.1. Chemicals

Lithium bis(fluorosulfonyl)imide (LiFSI, $\geq 0.999 \text{ g g}^{-1}$) was supplied by Budan Process UG. Dimethyl carbonate (anhydrous, $\geq 0.999 \text{ g g}^{-1}$), ethylene carbonate (anhydrous, 0.99 g g^{-1}), and propylene carbonate (anhydrous, 0.997 g g^{-1}) were purchased from Sigma Aldrich. All chemicals were used as
40 received. The water content of the pure components was determined by coulometric Karl-Fischer titration (Metrohm 831 KF coulometer) and were found to be below $50 \cdot 10^{-6} \text{ g g}^{-1}$ for all solvents, and below $30 \cdot 10^{-6} \text{ g g}^{-1}$ for LiFSI.

All chemicals were handled in an inert gas glove box (GS Glovebox Tech-
45 nik) that maintained an nitrogen atmosphere with a water content of less than $2 \cdot 10^{-6} \text{ g g}^{-1}$. A laboratory balance (Mettler-Toledo AG204) with an accuracy of $\pm 0.0001 \text{ g}$ according to the calibration protocol was used for the gravimetric sample preparation. The total mass of each prepared sample was larger than 30 g . The samples were hermetically sealed in 40 ml glass vials. The uncertainty
50 of the mass fraction of LiFSI is estimated to be $\pm 0.00015 \text{ g g}^{-1}$.

Some relevant physico-chemical properties of the employed solvents and electrolytes are shown in Tab. 2, wherein M is the molar mass, T_{nmp} and T_{nbp} are the normal melting point and the normal boiling point, respectively, ρ is the
55 density, η is the shear viscosity, D is the self-diffusion coefficient and ϵ is the dielectric constant.

Table 2: Overview of some pure component physico-chemical properties. The numbers for ρ , η , and ϵ for DMC, EC, and PC refer to the liquid state at 313.15 K and ambient pressure.

Property	DMC	EC	PC	LiFSI	LiPF ₆

	C ₃ H ₆ O ₃	C ₃ H ₄ O ₃	C ₄ H ₆ O ₃	F ₂ LiNO ₄ S ₂	LiPF ₆
M / g mol ⁻¹	90.1	88.1	102.1	187.1	151.9
T_{nmp} / K	278.2 ^a	311.2 ^a	220.3 ^a	418.2 ^k	473.2 ^l
T_{nbp} / K	363.15 ^b	517.15 ^b	513.15 ^b		
ρ / g cm ⁻³	1.0434 ^c	1.3216 ^d	1.1893 ^e		
η / mPa s	0.4880 ^f	1.9000 ^g	1.9120 ^e		
D / 10 ⁻⁹ m s ⁻²	26.0 ^{h,*}	8.0 ^h	5.8 ^{h,*}		
ϵ	3.2 ⁱ	89.7 ^j	61.4 ^j		
References: ^a [21], ^b [22], ^c [23], ^d [24], ^e [25], ^f [26], ^g [27], ^h [28], ⁱ [29], ^j [30]. ^k [11], ^l [31]. * Measured at 303.15 K.					

2.2. Measurements

2.2.1. Density and Shear Viscosity

For the measurements of the density and the shear viscosity a combined in-
 strument of Anton Paar (SVM 3000) was used. In this instrument, the density is
 measured with the vibrating tube technique and the shear viscosity is measured
 by a Stabinger viscosimeter. The measurements of the density were conducted
 according to the ASTM method D4052 and the measurements of the dynamic
 viscosity according to the ASTM method D7042. Before and after each set of
 the measurements the apparatus was cleaned with toluene, water and ethanol
 and flushed with dry nitrogen. The measurements were carried out at ambient

pressure.

70 The apparatus was calibrated with a calibration standard provided by the manufacturer. Three other standards purchased from Paragon Scientific Ltd. (D5, N14, and N100) were used for testing. Deviations between the reported value and the own measurements were found to be below 0.05 % for the density and below 0.7 % for the viscosity in the studied temperature range which was
75 between 273 K and 333 K. All measurements of the present work were repeated three times for a given temperature and sample composition. Thus, the results listed in this work are the arithmetic mean of the three measurements. The relative standard deviation of the three measurements was ≤ 0.15 % for the density and the viscosity. Therefore, we conclude that the uncertainty of the
80 density data reported here is about ± 0.15 % and that of the viscosity is about ± 0.7 %. The temperature was measured with a built-in thermometer for which the manufacturer reports an uncertainty of ± 0.05 K. This may be to optimistic. Our estimate for the uncertainty is ± 0.1 K.

2.2.2. Electrical Conductivity

85 A conductivity meter was used (Mettler-Toledo Seven Multi equipped with an inLab 720 probe) for the measurements of the electrical conductivity. The measurements were carried out at ambient pressure. The conductivity meter was calibrated at 298.15 K using aqueous solutions of NaCl with a maximum concentration of NaCl of 0.3 mol l⁻¹. The reference data were taken from
90 Wadsworth [32]. The maximum relative deviation of an individual result from

the calibration curve was 0.8 %. That number is taken for the relative uncertainty of the measurement of the electrical conductivity. The temperature was controlled using a thermostat (Julabo F32 HE) and measured with the built-in thermometer provided by the instrument's supplier, which was calibrated in our
95 laboratory using a certified standard. The uncertainty of the temperature measurement was ± 0.1 K. Before and after each set of measurements the apparatus was cleaned with toluene, water and ethanol and flushed with dry nitrogen.

3. Correlations

3.1. Density

100 In previous works of our group [33, 34], it was found that the specific density of electrolyte solutions is a linear function of the mole fraction of cations if the concentration of cations in the solution is small ($x_{c^+} \leq 0.05 \text{ mol mol}^{-1}$). Thus, the density of the electrolyte solution is described in this work as a function of the mole fraction of Li^+ . However, as the maximum concentration of Li^+ in the
105 solution was much higher in this work ($x_{\text{Li}^+} \leq 0.45 \text{ mol mol}^{-1}$), a quadratic term was added resulting in the correlation given in Eq. (1).

$$\left(\frac{\rho}{\text{g cm}^{-3}} \right) = A_{0,k} + A_{1,k}x_{\text{Li}^+} + A_{2,k}x_{\text{Li}^+}^2 \quad (1)$$

x_{Li^+} is the true mole fraction of Li^+ -ions

$$x_{\text{Li}^+} = \frac{n_{\text{Li}^+}}{n_{\text{Li}^+} + n_{\text{FSI}^-} + n_k} \quad (2)$$

wherein n_i is the mole number of species i . The correlations of the present work are established assuming that LiFSI is always dissociated in the solutions. They remain applicable independent of the physical validity of that assumption. The $A_{0,k}$ is the density of the pure solvent k (with $k = \text{DMC, EC, PC}$). The temperature dependence of the parameters $A_{i,k}$ is described by:

$$A_{i,k} = a_{i,k} + b_{i,k} \left(\frac{T}{T_0} \right) \quad (3)$$

with $i = (0, 1, 2)$ and $T_0 = 273.15$ K. $a_{i,k}$ and $b_{i,k}$ are adjustable parameters.

The molar volume of the mixture v can be calculated from the specific density (cf. Eq. (1)) and the molar mass of the mixture M :

$$v = \frac{M}{\rho} \quad (4)$$

Further, the partial molar volume of LiFSI in solution can be calculated from Eq. (5)

$$v_{\text{LiFSI}} = \left(\frac{\partial V}{\partial n_{\text{LiFSI}}} \right)_{T,p,n_k} \quad (5)$$

where n_{LiFSI} is the apparent mole number of LiFSI and V is the volume of the solution and n_k refers to the solvent.

3.2. Shear viscosity

The dependence of the dynamic viscosity η of the studied electrolyte solutions on the composition of the solution and on the temperature is described by Eq. (6):

$$\ln \left(\frac{\eta}{\text{mPa s}} \right) = A_{0,k} + A_{1,k} x_{\text{LiFSI}} + A_{2,k} x_{\text{LiFSI}}^2 \quad (6)$$

where x_{LiFSI} is the apparent mole fraction of LiFSI in solution and the $A_{i,k}$ are empirical temperature dependent functions

$$A_{i,k} = a_{i,k} + \frac{b_{i,k}}{\left(\frac{T}{T_0} \right)} + \frac{c_{i,k}}{\left(\frac{T}{T_0} \right)^2} \quad (7)$$

with $i = (0, 1, 2)$, $k = \text{DMC, EC, PC}$ and $T_0 = 273.15 \text{ K}$. Due to the strong temperature dependence (see Section 4.2) a quadratic functions was used.

$a_{i,k}$, $b_{i,k}$ and $c_{i,k}$ are adjustable parameters.

3.3. Electrical conductivity

For correlating the electrical conductivity of the studied electrolyte solutions, we found Eq. (8) to be suitable.

$$\left(\frac{\sigma}{\text{mS cm}^{-1}} \right) = A_{0,k} + A_{1,k} X_{\text{LiFSI}} + A_{2,k} X_{\text{LiFSI}}^2 + A_{3,k} X_{\text{LiFSI}}^3 + A_{4,k} X_{\text{LiFSI}}^4 \quad (8)$$

where X_{LiFSI} is the apparent molar loading of the pure solvent k with LiFSI.

$$X_{\text{LiFSI}} = \frac{n_{\text{LiFSI}}}{n_k} \quad (9)$$

The $A_{i,k}$ are empirical temperature dependent functions

$$A_{i,k} = a_{i,k} + b_{i,k} \left(\frac{T}{T_0} \right) \quad (10)$$

135 with $i=(0,...,4)$ and $T_0 = 273.15$ K. $a_{i,k}$ and $b_{i,k}$ are adjustable parameters.

3.4. Parameter estimation

All adjustable parameters in the equations listed above were estimated by the method of least squares. The sum of the squared relative errors between the experimental data and the correlation $e_j = (z_j^{\text{corr}} - z_i^{\text{exp}})/z_i^{\text{exp}}$ was employed as
 140 objective functions for all properties z_i . The optimization procedure was carried out in Mathworks Matlab 2016b using the solver `lsqnonlin`.

4. Results and Discussion

4.1. Density

The experimental data obtained in the present work for the density of so-
 145 lutions of LiFSI in the pure solvents DMC, EC, and PC are reported in the Appendix in Tables A1, A2, and A3, respectively. The parameters of the correlation of that data (cf. Section 3.4) are reported in the Appendix in Tab. B1.

Fig. 1 depicts the density of the studied mixtures as a function of temperature and mole fraction of Li^+ -ions. The experimental data as well as the correlation are shown. The correlation describes the experimental data within the experimental uncertainty. The dependence of the density on the mole fraction of Li^+ -ions and the temperature is almost linear for all studied solvents. Still, for PC a slight deviation from linearity is visible. Fig. 1 also shows that the agreement between the correlation and the experimental results is excellent.

Fig. 2 depicts the molar volume of the studied mixtures as a function of temperature and mole fraction of LiFSI. The dependence of the molar volume on the temperature is linear in the studied range for all systems. The dependence of the molar volume on the mole fraction of LiFSI at constant temperature is found to be nearly linear for the solvent EC. In contrast, it is non-linear for the solvents PC and DMC. The non-linearity is strong for DMC for which a minimum of the molar volume is clearly observable in Fig. 2 for all studied temperatures, at a mole fraction of LiFSI of about 0.2 mol mol^{-1} .

Fig. 3 shows the partial molar volume of LiFSI which was calculated from the correlation of density (cf. Equations (1), (4), and (5)), as a function of the mole fraction of LiFSI at 333 K for all solvents. The trends shown in Fig. 3 are similar for other temperatures. Obviously, the partial molar volume of LiFSI is always positive for all studied systems. The partial molar volume at infinite dilution v_{LiFSI}^∞ in (DMC, EC, PC) is $(65.3, 85.1, 89.2) \text{ cm}^3 \text{ mol}^{-1}$. The mole

Figure 1: Specific density of solutions of LiFSI in a) DMC, b) EC, and c) PC as a function of the mole fraction of Li^+ -ions and temperature. Symbols: experimental data. Surface: correlation fitted to the experimental data, cf. Eq. (1).

Figure 2: Molar volume of solutions of LiFSI in a) DMC, b) EC, and c) PC as a function of the mole fraction of LiFSI and temperature. Symbols: experimental data. Surface: correlation fitted to the experimental data, cf. Eq (1) and (4).

Figure 3: Partial molar volume of LiFSI in solutions of LiFSI in DMC (blue), EC (red), and PC (grey) as a function of the mole fraction of LiFSI at 333 K.

fraction of LiFSI has a strong influence on the partial molar volume of LiFSI for DMC and PC, whereas it is less important for EC.

175 The addition of LiFSI has an influence on the structure of the fluid for all solvents. Quantum chemical calculations and molecular dynamics simulations indicate that the Li^+ -ion and carbonate molecules tend to form complexes with a maximal coordination number of 4. Complexes with higher coordination numbers may be possible geometrically but are reported to be unfavorable [22, 35–
180 39]. The size of the Li^+ -[DMC/EC/PC]₄ complexes is directly correlated with the size of the carbonate solvent molecules. Thus, the following relation holds:

$$\text{Li}^+[\text{PC}]_4 > \text{Li}^+[\text{EC}]_4 > \text{Li}^+[\text{DMC}]_4$$

This relation is confirmed by the numbers of the partial molar volume of LiFSI at infinite dilution reported above.

185 The results presented in Fig. 3 reveal important differences between the planar DMC and the cyclic EC and PC. The partial molar volume of LiFSI in DMC increases with increasing mole fraction of LiFSI, while it decreases for EC and PC. For all solvents the coordination number decreases with increasing mole fraction of LiFSI, starting from $n = 4$ at infinite dilution. However, the
190 volume of the complexes with $n < 4$ compared to that with $n = 4$ is different for the three solvents. It is smaller for the cyclic EC and PC, while it is larger for the planar DMC. This difference in the change in volume is a consequence of their geometric structure.

4.2. Shear viscosity

195 Fig. 4 depicts the viscosity of the studied mixtures as a function of the temperature and the mole fraction of LiFSI. The experimental data obtained in the present work for the viscosity of solutions of LiFSI in the solvents DMC, EC, and PC are reported in the Appendix in Tables A4, A5, and A6. The parameters of the correlation of that data (cf. Section 3.4) are reported in the Appendix in
200 Tab. B2. The parameter estimation procedure reveals that the parameter $c_{0,k}$ ($k = \text{DMC, EC, PC}$) and the parameter $c_{2,\text{EC}}$ (cf. Eq. 7) are not significant and thus they are set to zero. The correlation describes the experimental data for LiFSI in solutions of (DMC, EC, PC) within an maximal absolute deviation of (0.4, 3, 1.7) mPa s.

As expected, both the temperature and the concentration of LiFSI have a strong influence on the viscosity. Qualitatively, all studied systems show similar behavior, with a strong increase of the viscosity at low temperatures and high concentrations of LiFSI. The temperature dependence of the viscosity is more
 210 important in regions where the viscosity is high. For all temperatures and compositions of the electrolyte solutions $x_{\text{LiFSI}} > 0 \text{ mol mol}^{-1}$ reported here the following relation holds (cf. Supplementary Information Fig. S1):

$$\eta_{\text{DMC}} < \eta_{\text{PC}} < \eta_{\text{EC}}$$

The increase in viscosity with increasing concentration of LiFSI can be explained by the strong ion-dipole coordination of the Li^+ -ions and the carbonate
 215 molecules that leads to large, poorly mobile complexes. Additionally, FSI^- contributes to the increase of the viscosity. At high salt concentrations, also ion-pairing can play a role. Similar findings have been reported before for solutions of LiPF_6 [40, 41]. The size of the solvent molecules is important for the viscosity. Our findings show that the size effect dominates for the pure solvents
 220 ($\eta_{\text{DMC}} < \eta_{\text{EC}} < \eta_{\text{PC}}$). Interestingly, the viscosity of solutions of LiFSI in EC is higher than in PC (see Fig. S1 in the Supplementary Information), even though PC is slightly larger than EC. This observation may be attributable to the polarity of EC (cf. dielectric constants in Table 2), and the corresponding strong ion-dipole bond of the Li^+ -EC complexes. This is in line with the findings of
 225 Arai et al. [42] in solution of LiPF_6 in several carbonate solvents.

Figure 4: Shear viscosity of solutions of LiFSI in a) DMC, b) EC, and c) PC as a function of the mole fraction of LiFSI and temperature. Symbols: experimental data. Surface: correlation fitted to the experimental data, cf. Eq. (6).

4.3. Electrical conductivity

The experimental data obtained in the present work for the electrical conductivity of solutions of LiFSI in the pure solvents DMC, EC, and PC are reported in the Appendix in Tables A7, A8, and A9. The parameters of the correlation of that data (cf. Section 3.4) are reported in Tab. B3 in the Appendix. The correlation describes the experimental data within a maximal absolute deviation of (0.45, 0.17, 0.53) mS cm⁻¹ for solutions of LiFSI in (DMC, EC, PC), which is slightly higher than the experimental relative uncertainty of 0.8 %.

Fig. 5 depicts the electrical conductivity σ of the studied mixtures as a function of the temperature and the mole fraction of LiFSI. The electrical conductivity of the pure solvents is close to zero. With increasing mole fraction of LiFSI, the electrical conductivity increases first, goes through a maximum, and finally decreases for high mole fractions of LiFSI. That behavior is observed for all solvents and temperatures. Temperature and electrical conductivity are linearly related for all studied solutions. The maximal electrical conductivity of LiFSI solutions in (DMC, EC, PC) is (16.2, 15.5, 12.3) mS cm⁻¹ at 333 K and the corresponding mole fraction of LiFSI is (0.17, 0.10, 0.08) mol mol⁻¹. The electrical conductivity of the solutions of LiFSI in PC is always lower than that of solutions of LiFSI in EC at the same conditions. The comparison of the results for DMC with those for EC reveals that the increase in the electrical conductivity with increasing mole fraction of LiFSI is initially much stronger for the solvent EC. Furthermore, the maximum in the electrical conductivity is

reached at lower concentrations of LiFSI for that solvent than for DMC.

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Two counteracting effects influence the electrical conductivity in the studied solutions: with increasing mole fraction of LiFSI, more charge carriers are present in the solutions which leads to an increase in the electrical conductivity. However, with increasing mole fraction of LiFSI, the mobility of the charge carriers is hindered as a consequence of the increased viscosity (see previous section).

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4.4. Comparison of solutions of LiFSI and LiPF₆

The comparison of the electrical conductivity of solutions of LiFSI and LiPF₆ in the same solvent is presented here for all three solvents DMC, EC, and PC, as it is interesting both for practical and theoretical reasons. The data of LiPF₆ are taken from experimental studies found in the literature. Unfortunately, only spotty data for LiPF₆ is available in the literature, cf. Tab. 3 for a survey. As a direct comparison of the experimental data for LiPF₆ and LiFSI at the same conditions is not possible, the experimental data for LiPF₆ from the literature is compared to predictions of the correlation of the present work (cf. Section 3).

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Table 3: Overview on experimental data taken from literature.

System	$x_{\text{LiPF}_6} / \text{mol l}^{-1}$	T / K	Reference
LiPF ₆ -DMC	0.5-3.4, 0.3-2.0	298.15	[43, 44]
LiPF ₆ -EC	1.0	303.15-343.15	[45]
LiPF ₆ -PC	0.1-3.3, 0.1-1.0	298.15	[25, 46]

Fig. 6 depicts the electrical conductivity of solutions of LiFSI and LiPF₆ in DMC as a function of the molarity of the salt c_{salt} at a constant temperature of

Figure 5: Electrical conductivity of solutions of LiFSI in a) DMC, b) EC, and c) PC as a function of the mole fraction of LiFSI and temperature. Symbols: experimental data. Surface: correlation fitted to the experimental data, cf. Eq (8).

Figure 6: Electrical conductivity of solutions of LiFSI and LiPF₆ in DMC as a function of the molarity of salt for a temperature of 298.15 K. Red line: Regression for LiFSI-DMC (this work). Symbols: Experimental data for LiFSI-DMC taken from [17] (red square), and experimental data for LiPF₆-DMC taken from [43] (blue circle) and [44] (grey triangle) with lines as guide to the eye.

298 K. The data set for LiFSI from the Li et al. [17] is in good agreement with our regression for LiFSI-DMC. The two data sets for LiPF₆ from the literature [43, 44], are found to be contradictory. Compared to the LiPF₆ data from [43], LiFSI leads to a slightly higher electrical conductivity at constant molarity of salt, whereas the increase is important if the LiPF₆ data of [44] is used as reference. The maximal value of the electrical conductivity is obtained at molarity of salt about 1.7 mol l⁻¹ for both salts. It is 10.7 mS cm⁻¹ for LiFSI. For LiPF₆, it is 10.2 mS cm⁻¹ according to [43] whereas [44] reports only 8.2 mS cm⁻¹.

Results for the electrical conductivity of solutions of LiFSI and LiPF₆ in EC are compared in Fig. 7 for a molarity of the salt of 1.0 mol l⁻¹ and temperatures between 313 and 333 K. Using LiFSI instead of LiPF₆ leads to a higher

Figure 7: Electrical conductivity of solutions of LiFSI and LiPF₆ in EC with a molarity of $c_{salt} = 1.0 \text{ mol l}^{-1}$ as a function of temperature. Red line: Regression for LiFSI-EC (this work). Symbols: Experimental data for LiPF₆-EC taken from [45] (blue) with line as guide to the eye.

280 electrical conductivity in the entire range depicted in Fig. 7. The relative differences are about 10 % for the lowest and 3 % for the highest studied temperature.

Fig. 8 depicts the electrical conductivity of solutions of LiFSI and LiPF₆ in PC as a function of the molarity of salt at a constant temperature of 298 K. Also for that solvent, the two data sets from literature for solutions of LiPF₆ [25, 46] are found to be contradictory. No matter which of the data sets for LiPF₆ is used, the solutions of LiFSI feature a higher electrical conductivity in the entire studied range.

290 At a first glance, the results presented here are astonishing. The PF₆⁻-ion has a molar mass of only 145 g mol⁻¹ whereas that of the FSI⁻-ion is 180 g mol⁻¹. Also in terms of mobility, the bulky shape of the FSI⁻-ion with a volume of 95 Å³

Figure 8: Electrical conductivity of solutions of LiFSI and LiPF₆ in PC as a function of the molarity of salt for a temperature of 298.15 K. Red line: Regression for LiFSI-PC (this work). Symbols: Experimental data for LiPF₆-PC taken from [46] (blue circle) and [25] (grey triangle) with lines as guide to the eye.

is disadvantageous compared to PF₆⁻ (69 Å³) [11]. Hence, the higher electrical conductivity of LiFSI compared to LiPF₆ must stem from different interactions of the anion (PF₆⁻, FSI⁻) with the solvents and the counter-ion (Li⁺). The negative charge of the FSI⁻-ion is delocated over the large volume, explainable by the multiple possible resonance structures. This delocation weakens the attractive interactions with the solvent as well as with the counter-ion Li⁺ [47].

The delocation of the negative charge is much smaller for PF₆⁻ than it is for FSI⁻, which leads to a strong binding of the solvent shell and counter-ion cloud. This effect increases the viscosity (reduced mobility of the anion), decreases the degree of dissociation and thus results in a lower electrical conductivity for solutions of LiPF₆. This conclusion is also in line with a result of a comparison of the shear viscosity of solutions of LiFSI and LiPF₆ in PC which is presented

305 in Fig. S2 in the Supplementary Information. Solutions of LiFSI in PC have a lower viscosity than solutions of LiPF₆ in PC at the same molarity of salt and temperature. Also this finding supports that the interactions of the FSI⁻-ion in solution are weaker compared to those of the PF₆⁻-ion.

4.5. Conclusions

310 In the present work, a systematic investigation of the density, shear viscosity and electrical conductivity of solutions of LiFSI in dimethyl carbonate (DMC), ethylene carbonate (EC), and propylene carbonate (PC) was carried out at ambient pressure, temperatures between 273 and 333 K, and mole fractions of LiFSI up to 0.45 mol mol⁻¹. Empirical correlations are provided, which are faithful
315 representations of the experimental data. Our findings show that solutions of LiFSI have superior properties, with regard to the electrical conductivity and shear viscosity, as compared to solutions of LiPF₆. The higher electrical conductivity and lower shear viscosity must stem from weaker attractive interactions of the FSI⁻-ion with the solvents and the counter-ion Li⁺ compared to PF₆⁻.
320 The findings underpin that LiFSI is a promising candidate to replace LiPF₆. The data and correlations presented here provide a sound basis for the design and optimization of LiFSI-based electrolyte systems for LiB.

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Appendix A. Experimental data

Tables A1, A2, and A3 list the experimental data of the density of solutions
of LiFSI in DMC, EC, and PC. The experimental data of the shear viscosity
of solutions of LiFSI in DMC, EC, and PC are given in Tables A4, A5, and
510 A6. Tables A7, A8, and A9 present the experimental data of the electrical
conductivity of solutions of LiFSI in DMC, EC, and PC. All experiments were
carried out at ambient pressure. Uncertainties are discussed in the text.

Table A1: Experimental data of the density of solutions of LiFSI in DMC.

$x_{\text{LiFSI}} / \text{mol mol}^{-1}$	$\rho / \text{g cm}^{-3}$			
	283.15 K	293.15 K	313.15 K	333.15 K
0.0000	1.0827	1.0697	1.0432	1.0162
0.1027	1.2105	1.1981	1.1735	1.1480
0.2001	1.3250	1.3132	1.2898	1.2663
0.2502	1.3759	1.3644	1.3415	1.3185
0.3001	1.4239	1.4128	1.3907	1.3687
0.3500	1.4700	1.4592	1.4375	1.4159
0.3999	1.5165	1.5069	1.4850	1.4632
0.4493	1.5634	1.5527	1.5313	1.5103

Table A2: Experimental data of the density of solutions of LiFSI in EC.

$x_{\text{LiFSI}} / \text{mol mol}^{-1}$	$\rho / \text{g cm}^{-3}$			
	T / K			
	303.15	313.15	323.15	333.15
0.0000	-	1.3200	1.3052	1.2938
0.0501	1.3837	1.3734	1.3621	1.3510
0.1004	1.4382	1.4237	1.4126	1.4048
0.2000	1.5253	1.5144	1.5034	1.4921
0.2500	1.5656	1.5543	1.5446	1.5340
0.3000	1.6040	1.5934	1.5828	1.5723
0.3500	1.6415	1.6308	1.6202	1.6098
0.4001	1.6799	1.6689	1.6580	1.6551
0.4500	1.7165	1.7048	1.6938	1.6832

Table A3: Experimental data of the density of solutions of LiFSI in PC.

$x_{\text{LiFSI}} / \text{mol mol}^{-1}$	$\rho / \text{g cm}^{-3}$			
	T / K			
	273.15	293.15	313.15	333.15
0.0000	1.2262	1.2048	1.1835	1.1623
0.1000	1.3229	1.3017	1.2808	1.2601
0.2000	1.4135	1.3927	1.3719	1.3516
0.2500	1.4559	1.4359	1.4153	1.3934
0.2996	1.4983	1.4770	1.4567	1.4367
0.3501	1.5418	1.5198	1.4991	1.4791
0.4000	1.5851	1.5629	1.5414	1.5211
0.4488	1.6279	1.6040	1.5830	1.5623

Table A4: Experimental data of the shear viscosity of solutions of LiFSI in DMC.

$x_{\text{LiFSI}} / \text{mol mol}^{-1}$	$\eta / \text{mPa s}$			
	T / K			
	283.15	293.15	313.15	333.15
0.0000	0.828	0.730	0.581	0.455
0.1027	2.567	2.099	1.483	1.112
0.2001	10.571	7.769	4.664	3.163
0.2502	22.539	15.408	8.444	5.344
0.3001	47.954	27.250	15.285	9.027
0.3500	101.830	60.679	27.250	14.951
0.3999	228.600	129.170	50.214	25.119
0.4493	560.810	279.240	95.880	43.863

Table A5: Experimental data of the shear viscosity of solutions of LiFSI in EC.

$x_{\text{LiFSI}} / \text{mol mol}^{-1}$	$\eta / \text{mPa s}$			
	T / K			
	303.15	313.15	323.15	333.15
0.0000	-	1.900	1.595	1.387
0.0501	4.428	3.659	2.996	2.537
0.1004	9.715	7.086	5.610	4.740
0.2000	47.269	30.605	21.148	15.290
0.2500	94.365	56.674	37.692	26.166
0.3000	162.470	93.946	59.116	39.634
0.3500	261.850	145.370	88.380	57.895
0.4001	431.460	229.940	133.770	92.133
0.4500	742.160	370.310	206.980	126.280

Table A6: Experimental data of the shear viscosity of solutions of LiFSI in PC.

$x_{\text{LiFSI}} / \text{mol mol}^{-1}$	$\eta / \text{mPa s}$			
	T / K			
	273.15	293.15	313.15	333.15
0.0000	4.635	2.841	1.950	1.467
0.1000	23.269	10.999	6.336	4.120
0.2000	187.280	57.095	24.616	13.090
0.2500	467.030	120.600	45.689	21.766
0.2996	948.193	217.080	75.211	34.387
0.3501	1875.100	370.580	118.260	50.891
0.4000	3770.700	639.650	185.770	74.466
0.4488	8162.500	1129.000	296.470	110.460

Table A7: Experimental data of the electrical conductivity of solutions of LiFSI in DMC.

$x_{\text{LiFSI}} / \text{mol mol}^{-1}$	$\sigma / \text{mS cm}^{-1}$					
	T / K					
	283.15	293.15	303.15	313.15	323.15	333.15
0.0000	0.00	0.00	0.00	0.00	0.00	0.00
0.0100	0.01	0.07	0.08	0.09	0.10	0.10
0.0340	1.89	2.11	2.32	2.53	2.71	2.89
0.0499	3.58	4.03	4.46	4.88	5.22	5.58
0.0749	6.05	6.87	7.66	8.41	9.09	9.86
0.0999	7.70	8.90	10.00	11.11	12.17	13.19
0.1249	8.40	9.83	11.24	12.61	13.98	15.27
0.1500	8.25	9.89	11.50	13.12	14.64	16.19
0.1706	7.71	9.39	11.10	12.84	14.58	16.20
0.2000	6.69	8.38	10.02	11.69	13.47	15.33

Table A8: Experimental data of the electrical conductivity of solutions of LiFSI in EC.

$x_{\text{LiFSI}} / \text{mol mol}^{-1}$	$\sigma / \text{mS cm}^{-1}$		
	T / K		
	313.15	323.15	333.15
0.0000	0.01	0.02	0.02
0.0114	2.98	3.43	3.89
0.0248	5.52	6.38	7.58
0.0503	8.75	10.22	11.73
0.0745	10.52	12.32	14.21
0.0994	11.15	13.27	15.45
0.1259	10.84	13.13	15.52
0.1493	9.70	12.01	14.60
0.1753	6.34	8.32	10.54

Table A9: Experimental data of the electrical conductivity of solutions of LiFSI in PC.

$x_{\text{LiFSI}} / \text{mol mol}^{-1}$	$\sigma / \text{mS cm}^{-1}$						
	T / K						
	273.15	283.15	293.15	303.15	313.15	323.15	333.15
0.0000	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.0100	1.27	1.63	2.01	2.42	2.86	3.31	3.76
0.0251	2.41	3.13	3.85	4.68	5.53	6.44	7.37
0.0499	3.16	4.26	5.44	6.71	8.05	9.42	10.82
0.0750	3.28	4.52	5.81	7.27	8.84	10.54	12.28
0.1000	2.80	4.00	5.39	6.91	8.59	10.30	12.21
0.1249	1.92	3.25	4.52	6.04	7.77	9.56	11.49
0.1499	1.54	2.54	3.71	5.04	6.60	8.29	10.18
0.1746	1.26	2.07	3.13	4.21	5.47	7.32	9.04

Table B2: Parameters of the correlation function (Eq. (6)) for the shear viscosity in the systems LiFSI-DMC, LiFSI-EC, and LiFSI-PC.

	LiFSI-DMC	LiFSI-EC	LiFSI-PC
$a_{0,k}$	-4.09	-4.65	-5.13
$b_{0,k}$	4.05	6.06	6.66
$a_{1,k}$	-2.08	132.24	25.95
$b_{1,k}$	15.85	-306.97	-59.09
$c_{1,k}$	-2.61	197.74	51.71
$a_{2,k}$	88.00	-9.88	69.96
$b_{2,k}$	-229.49	2.95	-173.59
$c_{2,k}$	152.22	-	99.36

Appendix B. Correlation parameters

Tables B1, B2, and B3 list the parameters of the empirical correlations for
515 the density, shear viscosity and electrical conductivity, developed in the present
work.

Table B1: Parameters of the correlation function (Eq. (1)) for the density in the systems LiFSI-DMC, LiFSI-EC, and LiFSI-PC.

	LiFSI-DMC	LiFSI-EC	LiFSI-PC
$a_{0,k}$	1.4596	1.7297	1.5170
$b_{0,k}$	-0.3634	-0.3578	-0.2909
$a_{1,k}$	1.0216	0.3424	0.7815
$b_{1,k}$	0.2792	0.6464	0.1374
$a_{2,k}$	0.8595	1.9822	1.6611
$b_{2,k}$	-0.1111	-1.3014	-0.4822

Table B3: Parameters of the correlation function (Eq. (8)) for the electrical conductivity in the systems LiFSI-DMC, LiFSI-EC, and LiFSI-PC.

	LiFSI-DMC	LiFSI-EC	LiFSI-PC
$a_{0,k}$	-0.000039	-0.045766	-0.013769
$b_{0,k}$	0.000036	0.051352	0.014345
$a_{1,k}$	39696.70	-277502.46	-119644.03
$b_{1,k}$	-66030.37	274159.77	139370.77
$a_{2,k}$	-97397.55	720691.16	297508.37
$b_{2,k}$	165890.90	-709875.76	-346118.91
$a_{3,k}$	78778.42	-626223.45	-248376.20
$b_{3,k}$	-137737.09	615333.70	288357.34
$a_{4,k}$	-21099.24	181778.11	69510.32
$b_{4,k}$	37923.42	-178283.82	-80484.08

Supplementary Information

Figure S1: Shear viscosity of solutions of LiFSI in a) DMC (blue), b) EC (red), and c) PC (grey) as a function of the mole fraction of LiFSI at 333 K. Symbols: experimental data. Lines: correlations fitted to the experimental data, cf. Eq. (6).

Figure S2: Shear viscosity of solutions of LiFSI and LiPF₆ in PC as a function of the molarity of salt for a temperature of 298.15 K. Red line: Regression for LiFSI-PC (this work). Symbols: Experimental data for LiPF₆-PC taken from [46] (blue) with line as guide to the eye.