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The physicochemical properties of a [DEME][TFSI] ionic liquid-based electrolyte and its influence on the performance of lithium–sulfur batteries

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Graphical abstract

Abstract

Electrolyte choice is an important decision on the quest for higher-energy batteries. Besides general guidelines on the required properties of an electrolyte suitable for use in lithium–sulfur batteries, the influence of more specific physicochemical properties on its characteristics is not well understood. For this purpose, binary mixtures based on the [DEME][TFSI] and dioxolane electrolyte system for lithium–sulfur batteries was investigated in this work. Selected physicochemical properties were determined for different mixtures of solvents and lithium salt concentrations. All the electrolytes prepared were also tested in the lithium–sulfur battery system. The capacity, Coulombic efficiency, overpotentials and impedance spectra were analyzed and a connection between them and the determined electrolyte properties elucidated. We show that the electrolyte's conductivity does not have a direct connection to any of the battery system properties measured. The highest specific
capacities were obtained with batteries compromising 1.0 M LiTFSI and the highest ratio of dioxolane in the binary solvent mixture. On the other hand, the best Coulombic efficiencies were obtained with batteries having high ratios of ionic liquid. Resistance and overpotential are connected parameters and are a function of the ionic liquid content. None of the monitored parameters prevail, since the best electrochemical performance in terms of specific capacity and stability was obtained with the 1.0 M LiTFSI in X[DEME][TFSI] = 0.199 electrolyte.

**Keywords**

Lithium–sulfur batteries, ionic liquid electrolyte, physicochemical properties, conductivity, viscosity, density, impedance spectroscopy

**Introduction**

The world's increasing energy demand is, besides putting a burden on the environment, increasing the pressure on electrochemistry researchers to improve the available technologies and to develop new and reliable high-energy sources. One of the possible alternative systems in the energy storage field is the lithium–sulfur (Li–S) battery system\(^1\). Due to lighter materials and the two-electron charge transfer reaction of sulfur, this technology promises better theoretical capacities and energy densities\(^2\). However, the problems of short life cycle, poor cycling efficiency, component safety and high self–discharge rate still persist.

Li–S batteries function on the basis of a redox reaction between lithium and sulfur, where the latter gets reduced to Li\(_2\)S during discharge through intermediate lithium polysulfide species (Li\(_2\)S\(_x\), \(x = 2–8\)). A typical voltage profile exhibits two plateaus. The one in the range of 2.3–2.4 V belongs to the transformation of cyclic S\(_8\) molecules into long-chained polysulfide species, while the low voltage plateau at 2.0–2.1 V pertains to the reduction of these to shorter-chained polysulfides and Li\(_2\)S\(^3\). The first voltage plateau is controlled by the dissolution of solid sulfur into the electrolyte, while the lower one forms when the solubility product of Li\(_2\)S is exceeded and the precipitation starts. In the transition between them, it is believed that all the electroactive species are dissolved into the electrolyte\(^4\).

In general, electrolytes must have good ionic conductivity for facile ion transport and must be electronically insulating to minimize self-discharge. They should be thermally, mechanically and electrochemically stable in a wide potential window, non-toxic and environmentally friendly. Besides that, side reactions of electrolyte with the battery components (separator, electrodes and casing) should be avoided. The solvent should enable the sufficient dissolution
of the supporting salt (high dielectric constant) but also allow facile ionic transport (low viscosity). Due to these sometimes contradicting demands, binary mixtures of electrolytes and diverse solvents with different physical and chemical properties are most commonly used in practice.

As is evident from the discharge mechanism, the electrolyte in a Li–S battery acts in numerous roles in different processes of dissolution, redox reaction and crystallization. At the beginning of polysulfide electrochemistry, the research was mainly based on electrolytes in tetrahydrofuran (THF) solutions. Today a combination of solvents from linear (glymes) and cyclic ethers (dioxolane) employing lithium bis(trifluoromethanesulfonil)imide (LiTFSI) salt is commonly used. Besides these mixtures, ionic liquids are an interesting group of compounds for this application because they have low volatility, high conductivity and good thermal stability. Furthermore, since they supposedly exhibit lower polysulfide solubility than conventional electrolytes, their application would hinder and reduce the polysulfide redox shuttle, which is one of the most pressing problems in the Li-S battery system and causes a loss of active material, poor Coulombic efficiencies during cycling and a high self-discharge rate.

The first report on employing ionic liquid-based electrolytes in Li–S batteries was in 2006 with 1 M LiTFSI in [PP14][TFSI]. The properties of ionic liquids used as electrolytes in Li–S batteries are designed by changing the cation structure, while the anions are typically the same as in Li salts. The most common anion is [TFSI], which is supposed to enhance the formation of a stable and effective solid electrolyte interface (SEI) on the metallic lithium anode, although other compositions have also been tested. Ionic liquids in Li-S systems have been used on their own or in combination with various organic solvents, with the aim of adjusting the electrolyte properties (viscosity, wettability, conductivity). Special applications include polymeric ionic liquid electrolytes. The ionic liquid [DEME][TFSI] (N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulphonmethyl)imide) is one of the ones that have been successfully tested as an electrolyte in both Li-ion and Li–S batteries.

Besides the basic requirements explained in the preceding paragraphs, the role of the physicochemical properties of electrolytes in the complex working mechanism of Li–S batteries is not well understood, although this knowledge is essential for the targeted improvement of the system. For this reason, we first investigated the binary mixture of
[DEME][TFSI] ionic liquid and 1,3-dioxolane and then LiTFSI salt was added in the binary systems to check the influence of the presence of the lithium ion on the properties of the electrolyte solutions. The physicochemical properties (conductivity, viscosity and density) of different mixtures were determined and their influence on the specific capacities, cycling efficiencies and overpotentials of the batteries was studied. Finally, the extent of polysulfide dissolution into the electrolyte was evaluated with the help of impedance spectroscopy.

**Experimental part**

**Materials:**

Ionic liquid [DEME][TFSI] was obtained from Solvionic and was used without further purification. The LiTFSI (≥ 99 %, 19F-NMR) and 1,3-dioxolane (DOL, anhydrous) were both from Sigma-Aldrich. The LiTFSI was vacuum-dried at 140 °C, while dioxolane was dried in a multi-step process using molecular sieves, Al₂O₃ and distillation. Solutions were prepared by mass in a glove box (water and oxygen content below 1 ppm).

Unless stated otherwise, the term "electrolyte" is used for the mixture of ionic liquid, DOL solvent and Li⁺ salt in this publication.

**Physicochemical properties determination:**

The electrical conductivity of the electrolyte systems was measured using a set of capillary cells with different cell constants, \(B'\), as is usual for concentrated solutions of electrolytes\(^{23}\) (\(\sim 3 < B'/\text{cm}^{-1} < \sim 85\)). An assembly lid equipped with nine conductivity cells and switch equipment connecting them to the PC-interfaced LCR Meter Agilent 4284 A permits measuring the conductivity of nine different solutions at each temperature. The cells were calibrated with dilute potassium chloride solutions\(^{24}\) with the reproducibility of estimated cell constants better than 0.05 %. The lid with cells was immersed in the high-precision thermostat described previously.\(^{25}\) The oil bath was set to each temperature in the temperature program with a reproducibility within 0.005 K. The temperature was checked with a calibrated Pt100 resistance thermometer (MPMI 1004/300 Merz) connected to an HP 3458 A multimeter. Solutions of different concentrations were transferred under nitrogen into the capillary cells and measurements were carried out over a temperature cycle beginning and ending at 278.15 K. A home-developed software package was used for temperature control and the acquisition of conductance data. The equipment and measuring procedure are described in detail in the...
Taking into account the sources of error (calibration, measurements, impurities), the specific conductivities are certain within 0.5\%.

The density of the prepared electrolyte solutions was measured at atmospheric pressure with a vibration type density meter, the Anton Paar DMA 500 with a declared reproducibility of $1 \cdot 10^{-3}$ kg·m$^{-3}$. Calibration of densimeter was performed using the density data of milipore water. The measurements were carried out at the same temperatures as the conductivity and viscosity measurements and the instrument was thermostated within $\pm 0.001$ K. The relative standard uncertainty of determined density was estimated to be 0.4\%.

Electrolyte viscosity was determined using micro Ubbelohde viscometers (SI Analytics GmbH, 536 10 capillary I, 536 20 capillary II and 536 30 capillary III) and ViscoSystem_AVS 370. Each measurement was automatically repeated at least five times and yielded a reproducibility of the flow time of < 0.02\%. Kinematic viscosity was determined as a product of the average flow time and viscometer constant. By multiplying the kinematic viscosity with the determined density, the dynamic viscosity was obtained. The estimated errors from calibration and temperature control yield an uncertainty of about 1\% of absolute viscosity.

**Electrode preparation and electrochemistry:**

A carbon sulfur composite (1:2 ratio) was prepared by sulfur infiltration into carbon at 155°C (ENSACO 350G carbon obtained from Imerys). The composite material was mixed in a ratio of 80:10:10 wt.\% with a conductivity additive (Printex XE2 from Degussa) and PVdF (Sigma-Aldrich, average molar mass 543.000) in NMP (Sigma-Aldrich, chromasolv, >99 \%). The slurry was cast on carbon coated aluminum foil. The cathodes with loading close to 1 mgs/cm$^2$ were dried overnight at 50 °C. Li foil (FMC) was used as an anode and Celgard 2400 as separator. Pouch cells were prepared with 20 μL/mgs of the chosen electrolyte. The batteries for the performance studies were cycled at C/10 in the potential range 1.5–3.0 V at room temperature. Impedance spectroscopy measurements were performed on the freshly assembled cells and on charged cells after 10 cycles in the range of 1 MHz to 10 mHz with a potential amplitude of 10 mV (rms). Electrochemical measurements were done using a Biologic VMP3 or MPG2 galvanostat/potentiostat. The impedance spectra were fitted using ZView version 3.4f.
Results and discussion

Physicochemical properties of the electrolyte mixtures

To understand the basics behind the characteristics of the tested electrolytes, we first measured the physicochemical properties of the binary mixtures without added salt. For this, eight different mixtures of [DEME][TFSI] and DOL were prepared evenly on a molar scale. The conductivity of the binary mixtures without added salt first increases on increasing the ionic liquid content due to adding more charge carriers. This continues until a decline is caused due to high viscosity (Figure 1a). According to expectations, higher temperatures lead to higher conductivities, but peak conductivity remains at the same composition regardless of the temperature. A maximum conductivity is reached around the molar ratio \( X_{[\text{DEME}][\text{TFSI}]} = 0.2 \).

Viscosity is a function of temperature and ionic liquid content and increases from around 0.5 mPa·s to over 200 mPa·s for the higher ratios of ionic liquid measured at low temperatures. At high molar ratios of [DEME][TFSI], a temperature increase causes a greater increase of viscosity than at lower molar ratios (Figure 1b). The density has a steeper increment for low ionic liquid contents, which levels out with a low dioxolane content. Heating the mixtures decreases the density by approximately the same amount in all the different molar ratios tested (Figure 1c). Data for these measurements is included in the Supporting information file in Tables S1-S3.

For further tests, mixtures around the maximum conductivity were chosen (\( X = 0.101, 0.199, 0.401 \)) and three different concentrations of LiTFSI salt were prepared (0.1 M, 0.5 M, 1.0 M). The physicochemical properties of these nine electrolytes were tested in the same way as described above and the data can be found in Tables S4-S6, while for clarity only the values at room temperatures (298.15 K) are shown in Figure 2. For comparison, the values for electrolytes with the same molar ratios without LiTFSI addition are also depicted.

The conductivity change due to an increase in ionic liquid content at different salt concentrations exhibits a different trend (Figure 2a). This result is coherent with the conductivity dependence on ionic liquid content (Figure 1a). At low LiTFSI salt concentrations, the conductivity maximum is still \( X = 0.199 \). A further increase in LiTFSI molarity exhibits the same change as increasing the molar ratio of the ionic liquid – a decrease in the conductivity of the electrolyte. Consequently, the electrolyte with high LiTFSI
concentrations has the highest conductivity at the lowest ratio of ionic liquid. Here we should emphasize that the conductivity values represent both anion and cation migration.

The viscosity (Figure 2b) and density (Figure 2c) of all the electrolyte solutions increase with high ionic liquid ratios and high LiTFSI salt concentrations. If we compare the change influenced by increasing the lithium salt concentration while maintaining the same molar content of the ionic liquid, we see that with density, the absolute increase is approximately the same with all the different ionic liquid contents tested (Figure 3c). On the contrary, with viscosity, the absolute difference in the same scenario increases on increasing the ionic liquid content.

**Polysulfide solubility determination with impedance spectroscopy:**

Polysulfides dissolved during battery operation change the physicochemical properties of the electrolyte. To test how the difference in polysulfide solubility influences the electrochemical behavior, we performed electrochemical impedance spectroscopy measurements on freshly assembled cells and on charged cells after 10 cycles. The resistive intercept values were obtained and their inverse values (conductance) are plotted in Figure 3.

The resistive intercepts of fresh batteries were compared to the conductivity measurements of the electrolytes (Figure 2a). The conductance trends are in good agreement with the obtained conductivities, although the values cannot be directly compared since the "cell constant" was not determined and the pouch cell setup is not sufficiently advanced to eliminate the measurement disturbance effects. No attempt was made to differentiate between the resistance of the electrolyte in the cathode and separator pores. We attribute the small discrepancies with the data from electrolytes with $X_{[\text{DEME}]\text{TFSI}} = 0.2$ to not regulating the temperature conditions for battery cell measurement.

After 10 cycles of discharge and charge accompanied by polysulfides dissolution and diffusion, the resistive intercept was measured again. Large change can be observed in the resistance of the electrolytes with low LiTFSI salt concentration and for electrolytes with high dioxolane content (Figure 3b). For these electrolyte compositions, higher polysulfide solubility is proposed. Comparison of the conductivity values obtained from the resistive intercept between fresh and cycled cells show the least difference when 1.0 M electrolyte was used. This is in agreement with papers showing that highly concentrated electrolytes can effectively prevent polysulfides dissolution. The least change is observed with high
The connection between the physicochemical properties and electrochemical performance:

The comparison of the electrochemical performance of the nine different mixtures of electrolytes was done on two different bases. We compared the change due to the difference in ionic liquid content at the same concentration of LiTFSI salt and the opposite, the influence of changing the concentration of the lithium salt in the same [DEME][TFSI]:DOL mixture. The Coulombic efficiencies, specific capacities and overpotentials are compared.

Coulombic efficiencies range from close to 90% for electrolytes with low LiTFSI salt concentrations to almost 100% for 1.0 M LiTFSI as evident from Figure 4a-4c. A uniform trend is also visible in Figures 4d-4f, from which it can be concluded that a higher dioxolane content also equals a lower Coulombic efficiency. These results can be linked to the polysulfide solubility (Figure 3b). The electrolytes, which poorly solvate polysulfides, exhibit a smaller extent of the polysulfide shuttle, which in turn results in better charging efficiencies. In this study, the difference in the passivation nature of lithium by using two different solvents has a minor impact as can be deduced from the observed results.

The overpotential contains the contributions of the ohmic, activation and concentration polarization. The values were calculated as half the difference of the potentials difference between the charge and discharge curves at approximately 50 % DOD for a given battery cell experiment. They range from 50 mV to 170 mV. The trend is different to the one for cycling efficiencies. The largest overpotentials are exhibited for electrolytes with low lithium salt concentrations (Figure 5a-5c) and with high ionic liquid content (Figure 5d-5f). For the latter, we attribute this difference to the difference in viscosity.

For a better understanding of the reasons behind the overpotential value trends for electrolytes with the same ionic liquid content and different Li⁺ salt concentrations, we also compared the impedance spectra of charged cells after 10 cycles (Figure 6a-6c) measured at OCV. Although the measured values cannot be directly compared, the impedance contributions still serve as a good indicator of the contributions. Here, smaller ohmic resistances are seen for lower salt concentrations (Figure 6 - insets). This elucidated that the concentration polarization
contribution should be taken into account when assessing the overpotentials for electrolytes with lower lithium salt concentrations.

**The specific capacities** fading trend during 100 cycles (Figure S1) follows a reverse trend of overpotentials (Figure 5).

The highest capacities reached were for the 1.0 M LiTFSI in X_{[DME][TFSI]} = 0.101. One would expect an additional capacity fade for electrolytes with higher dioxolane contents, which is somewhat visible in the data comparison for electrolytes with the same LiTFSI salt concentration (Table 1, Figure S1d-S1f). Higher dioxolane content equals larger capacity fades, which would likely result in lower capacities of the currently best performing electrolyte if the cells are cycled further.

**Discussion:**

From the gathered data, we can draw various conclusions about the influence of the measured electrolyte's physicochemical parameters on the Li–S battery performance.

The electrolyte's conductivity determined in our case does not have a direct connection to any of the battery system properties measured. It is worth noting that since an ionic liquid electrolyte was used, an array of charged species can migrate and contribute to the overall determined conductivity, while only the charge transferred by the Li$^+$ ion is important for battery cell function. This is further complicated by the fact that polysulphides are dissolved in the electrolyte during battery operation. Similarly, no influence of the density of the electrolytes was observed.

When comparing electrolytes with the same lithium salt concentration, a parallel can be drawn between the viscosity trend (Figures 2b) and the overpotential, ohmic resistance values (Figure 6) and specific discharge capacities achieved (Figure 5d-f, S1d-f). This can be explained by the hindered diffusion of electroactive species towards the electrode surface, which increases the low-frequency contributions in the EIS spectra (Figure 6). For electrolytes with different lithium salt concentrations, the connection is more complicated, since the overpotential in an electrochemical system is influenced by both the ohmic resistance and the concentration polarization. When using low concentrations of the dissolved Li$^+$ salt, the
concentration polarization becomes an important contribution to the overpotential, which consequently reduces the specific capacity (Figure 5a-c, S1a-c).

The polysulfide solubility is in our case a function of the amount of ionic species dissolved in the electrolyte (Figure 3). Higher lithium salt concentrations and higher molar ratios of the ionic liquid impede the dissolution of polysulfide species. In a binary electrolyte system, with two solvents in different ratios, this correlation would of course depend upon the solubility of polysulfides in the chosen components. The solubility of polysulfides has an influence on the Coulombic efficiencies (Figure 4) and can to some extent be linked to the increased capacity fade (Table 1, Figure S1).

The best electrochemical performance in terms of specific capacity retention and stability is obtained in the 1.0 M LiTFSI in X_{[DEME][TFSI]} = 0.199. The slightly lower capacity compared to the 1.0 M LiTFSI in X_{[DEME][TFSI]} = 0.101 in the formation cycles could be ascribed to the higher viscosity of the electrolyte with a higher ionic liquid content. The average Coulombic efficiency during 100 cycles is 97.0 %. Higher Coulombic efficiencies can be obtained with increased ionic liquid content but, due to increased viscosity and polarization, the obtained specific capacities are lower and not favorable for practical application. Further improvements with the introduction of a third co-solvent are probably possible and will be explored by our group in the future.

**Conclusions**

An electrolyte system consisting of [DEME][TFSI] ionic liquid, 1,3-dioxolane and LiTFSI salt was tested in a Li–S battery system. Nine different mixtures were prepared with three different molar ratios of ionic liquid and dioxolane solvent and three different concentrations of the LiTFSI salt. The viscosity, density and specific conductivity of the different electrolyte mixtures were determined. The difference in solubility of polysulfides was also approximated using the resistive intercept in the impedance spectra determined before and after the cycling of the Li-S batteries.

The electrolyte's performance was evaluated using three different parameters – Coulombic efficiency, overpotential and specific discharge capacity. The trends were explained by connecting the performance of the batteries with the determined physicochemical properties of the electrolytes.
Although only one electrolyte system was investigated, certain general directions describing the required physicochemical properties of a Li–S battery electrolyte can be concluded, which can serve as a basis for further improvements of Li-S battery performance. We found the following properties of high importance. Enough lithium salt should be dissolved so that there is no concentration polarization problem. The polysulfide solubility needs to be low enough for good efficiencies and minimum capacity fade, while the electrolyte should still maintain a low viscosity to enable low internal resistances and good capacities. Li stability and capacity fade due to loss of contact in the cathode pores was not evaluated, although we speculate that it could still play a role in electrolyte performance.

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Figures and tables:

**Figure 1:** The physicochemical properties of [DEME][TFSI]:DOL mixtures without LiTFSI salt at various molar ratios and temperatures between 278.15 K and 313.15 K: a) conductivity, b) dynamic viscosity, c) density.

**Figure 2:** The physicochemical properties of [DEME][TFSI]:DOL:LiTFSI mixtures at 298.15 K: a) conductivity, b) dynamic viscosity, c) density.

**Figure 3:** The conductance of different electrolyte mixtures determined from resistive intercept measurements with EIS: a) freshly assembled battery cells with no polysulfides dissolved, b) after 10\textsuperscript{th} charge.

**Figure 4:** Coulombic efficiencies during 100 cycles at C/10 current rate: a-c show a comparison of electrolytes with the same ionic liquid molar content and different concentrations of LiTFSI salt with a) X=0.101, b) X=0.199, c) X=0.401. d-f show a comparison of the performance of electrolytes with the same LiTFSI concentration with d) 0.1 M LiTFSI, e) 0.5 M LiTFSI, f) 1.0 M LiTFSI.

**Figure 5:** Overpotentials over 100 cycles at C/10 current rate: a-c show a comparison of electrolytes with the same ionic liquid molar content and different concentrations of LiTFSI salt with a) X=0.101, b) X=0.199, c) X=0.401; d-f show a comparison of the performance of electrolytes with the same LiTFSI concentration with d) 0.1 M LiTFSI, e) 0.5 M LiTFSI, f) 1.0 M LiTFSI.

**Figure 6:** Impedance spectra for charged battery cells after 10 cycles of discharge/charge, comparison of different lithium salt concentrations in the same compositions of dioxolane and [DEME][TFSI]: a) X=0.101, b) X=0.199, c) X=0.401 (Insets show the high-frequency regions of the spectra).
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**Figure 6:** Impedance spectra for charged batteries after 10 cycles of discharge/charge, comparison of different lithium salt concentrations in the same compositions of dioxolane and [DEM][TFSI]: a) X=0.101, b) X=0.199, c) X=0.401 (Insets show the high-frequency regions of the spectra).
Table 1: Initial specific discharge capacity, average capacity and the capacity fade over 100 cycles at C/10 for the different electrolyte mixtures.

| c(LiTFSI) | X([DEME][TFSI]) | 0.101 | 0.199 | 0.599 |
|-----------|------------------|-------|-------|-------|
| 0.1 M     | initial capacity [mAh/g₆] | 710.0 | 590.5 | 321.1 |
|           | average capacity [mAh/g₆] | 615.0 | 404.0 | 296.3 |
|           | capacity fade over 100 cycles [mAh/g₆] | 135.9 | 186.5 | 49.6 |
| 0.5 M     | initial capacity [mAh/g₆] | 925.3 | 513.2 | 344.7 |
|           | average capacity [mAh/g₆] | 667.4 | 490.0 | 353.7 |
|           | capacity fade over 100 cycles [mAh/g₆] | 392.1 | 23.2 | 11.3 |
| 1.0 M     | initial capacity [mAh/g₆] | 1007.1 | 826.0 | 527.8 |
|           | average capacity [mAh/g₆] | 668.1 | 634.0 | 487.2 |
|           | capacity fade over 100 cycles [mAh/g₆] | 339.0 | 192.0 | 52.3 |