



Preliminary study of new electrolytes based on [MPPyr][TFSI] for lithium ion batteries

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ABSTRACT

The application of ionic liquids in lithium ion batteries has increased in recent years in order to find new electrolytes that improve both performance and safety. The gathering of experimental data in order to understand the behaviour of these systems will help us design electrolytes that can be optimized for a specific objective.

Data on electrolytes made up of a ternary mixture with an ionic liquid are missing in the literature. In this work, we provide new data on physical properties and refractive indexes for the ternary mixtures 1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([MPPyr][TFSI]) + acetonitrile (AN) or γ butyrolactone (GBL) or dimethyl sulfoxide (DMSO) + lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) with different concentrations of salt, specifically, 10%, 15%, 20%, 30%, 35%. The measured properties were density (ρ), viscosity (η) and ionic conductivity (κ) in the temperature range of 278.15 to 358.15 K except for the mixtures with acetonitrile whose temperature range was 278.15 K to 328.15 K and the refractive indexes (n_D) that were measured at a single temperature of 298.15 K.

In general, the addition of salt in the binary mixtures provokes an increase of density and viscosity and therefore a decrease of ionic conductivity. It is worth mentioning that some of the studied systems showed values of ionic conductivity even better than those obtained for electrolyte systems based on carbonate.

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1. Introduction

Nowadays, the increase of global demand of energy has led to the depletion of natural resources and the increase of emissions of greenhouse gases that have contributed significantly to global warming. This has caused research, in recent years, to be focused on solutions or alternatives that improve both the consumption natural resources and environmental conditions. Among these actions are the promotion of renewable energies (solar, wind...) as well as the development of energy-storage systems that improve energetic performance and reduce pollution. In this context, it is worth mentioning the importance of rechargeable batteries, particularly, the lithium-ion battery (LIB) whose role will be fundamental for the storage of non-programmable energy production, but is also significant in daily low power usage, where LIBs are present in devices such as mobile phones, laptops, pacemakers etc. However, although its success lies in its high energy density, low

cost, longevity, high cyclability... LIBs have a few limitations when we talk about using them on a large-scale in terms of energy, lifetime, safety and environmental sustainability.

The right design of Li-based batteries seeks to overcome the shortcomings mentioned above. For this reason, research has recently been focused on the study of the development of new or already known materials for anode, cathode and separators [1], the formulation of new electrolytes [2,3] as well as configuration and safety issues [4–7].

Ideally, electrolyte should be a good ionic conductor, non-flammable, nontoxic, environmentally friendly and it should have a long-term electrochemical stability over a wide temperature range. This latter implies that it has to be inert against both electrodes and the rest of the cell components (separators and current collectors) [8–10]. Unfortunately, these interactions exist and have a big impact on the properties of the cell such as efficiency, reliability and so on. With this in mind, it's obvious the difficulty for finding an electrolyte composed of one single component that meets all or nearly all these requirements. Consequently, the electrolytes are usually multi-component systems of (one or more

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lithium salts + one or more solvents) with the presence or not of additives [2,3,9,11–26].

In general, the commonly used electrolytes for LIBs are solutions of a lithium salt, lithium hexafluorophosphate (LiPF_6) in a mixture of organic carbonates: ethylene carbonate (EC) as solvent + linear carbonate mainly dimethyl and/or diethyl carbonate (DMC and DEC) as cosolvent [2]. The presence of EC in the mixture is essential due to its ability to form a protective film ionic conducting on the surface of carbonaceous anodes, SEI (solid electrolyte interface) which avoids the decomposition of the electrolyte on the anode. However, this cannot be used as a single solvent due to its high melting temperature; so it is necessary to mix it with a cosolvent to increase the fluidity of the electrolyte. Thus, although the composition of these electrolytes is well known, the complex handling of LiPF_6 because of its moisture sensitivity, along with safety problems at $T > 40^\circ\text{C}$, and the limits of voltage operation of carbonates mixtures, restrict its use in new applications. Therefore, its optimization requires the design of new formulations for these kind of compounds.

The attractive properties of ionic liquids (ILs) such as low flammability, high thermal stability, broad electrochemical window, high ionic conductivity and low vapour pressure, as well as their versatility because of their molecular structure make them promising candidates as electrolytes for LIBs. However, their properties vary enormously as a function of their molecular structure. Thus, the choice of the anion has a strong influence on the properties and the stability of the ionic liquids while the chemistry and functionality are, in general, controlled by the cation choice [27,28]. Because of this, the alternatives for an eligible ionic liquid for batteries are limited.

There are two main groups of ionic liquids, aprotic (A ILs) and protic ones (P ILs). The main difference between them is the absence or presence of an available proton on the cation. Ionic liquids are highly viscous liquids and the addition of a lithium salt, in order to realize electrolytes for LIBs, increase even more their viscosity, which means low conductivities, slow Li diffusion and weak wettability of electrode. All of this in addition to their lack of ability to form SEI on the surface both anode and cathode are critical issues in the design of ionic liquid based electrolytes. In order to overcome these difficulties, the addition of additives such as organic solvents is an usual practice in these systems.

Up to now, research has been focused on the search of A ILs based electrolytes, owing to their wide electrochemical window, although P ILs based electrolytes have also been proposed recently [29–31]. The most common A ILs are combinations of cations such as imidazolium, pyridinium, pyrrolidinium, and piperidinium and anions such (BF_4^-), (PF_6^-), (TFSI^-), (FSI^-) and (BCN_4^-). It has been shown that imidazolium cations have higher conductivities and a narrow electrochemical stability window (ESW) compared to those with pyrrolidinium and piperidinium cations. In addition, A ILs containing (TFSI^-) have higher thermal stability than those containing (PF_6^-), but higher viscosity respect to those with (FSI^-). This latter anion (FSI^-) has, moreover, the property of forming a protective film in carbonaceous electrodes without the presence of additives. At the same time, it has been reported that A ILs in mixtures with carbonates have improved electrochemical stability, cyclability, thermal stability, safety and sustainability of LIBs electrolytes. However, in spite of the large number of studies, an ILs based electrolyte whose performance is comparable with those obtained by conventional ones has not been achieved. [32–45].

With this in mind and on the basis of the existing literature, we have selected a pyrrolidinium-based ionic liquid 1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([MPPyr][TFSI]) due to their compatibility and versatility as electrolyte or additive in battery applications [46–49] a lithium salt of bis(trifluoromethylsulfonyl)imide (LiTFSI) with counter ion in common

with the IL, and a series of organic solvents, such as acetonitrile (AN), γ -butyrolactone (GBL) and dimethyl sulfoxide (DMSO) whose characteristics of solubility, dipolar moment, electrochemical window, dielectric constant and viscosity could make them suitable for use as electrolytes in batteries. The presence of these latter in electrolytes of Li-based batteries improves their electrochemical properties as well as their thermal and chemical stability [50–63].

In this work, we present the study of the physical properties and the refractive indexes of the ternary mixtures formed by mixtures (percent by weight (wt%)) 50 wt% [MPPyr][TFSI] + 50 wt% AN or GBL, or DMSO + LiTFSI , with five different concentrations of lithium salt. The measured properties were density (ρ), viscosity (η) and ionic conductivity (κ) in a broad temperature range, while the refractive index (n_D) was measured at a single temperature.

The chosen binary mixtures (IL + solvent) to be mixed with lithium salt were those that presented the highest ionic conductivity in the concentration range studied, according to the fit of a pseudolattice model recently developed by some of us [64]. In addition, the temperature behaviour of different magnitudes in the binary and ternary mixtures studied has been accurately fitted to the corresponding usual equations.

Literature reports data of pyrrolidinium-based ionic liquids mixtures in organic solvents, nitriles and the salt, LiFSI and LiTFSI [65–72]. Thus, combinations of pyrrolidinium-carbonate mixtures display good thermal stability, ionic conductivities similar to carbonate systems and electrochemical window wider than 5.5 V. However, not published data was found about the physical properties studied herein for any of the binary and ternary systems presented here.

The study of the physical properties of these mixtures hopes to be a small contribution to the understanding of IL-solvent interactions and in this way help with the selection and design of new electrolytes. Despite the refractive index has not impact in this study when assessing our mixtures as electrolytes for batteries, their knowledge can be useful in other fields. In general, these can provide us information about the purity and concentration of the substances as well as their volumetric and optical behaviour [73–81]. For this reason, we include it as part of the characterisation of our mixtures.

2. Experimental section

2.1. Chemicals

The studied compounds are included in Table 1, where we indicate the chemical name and the acronyms used here, as well as their provenance, mass fraction purity and CAS number. The compounds were used as they came from the dealer without any additional purification in our laboratory.

2.2. Experimental procedure

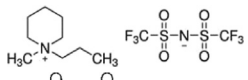
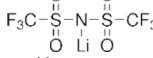
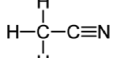
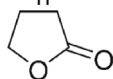
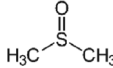
All chemicals used were taken from their original container, rebottled and sealed into a dry chamber with a relative humidity lower than 10% before taking them out.

As a first step, we measured the physical properties of density (ρ), viscosity (η), ionic conductivity (κ) and refractive index (n_D) of the ionic liquid [MPPyr][TFSI] and the solvents AN, GBL and DMSO, and their corresponding binary mixtures (IL + solvent) with different percent by weight of solvent 25, 50 and 75 wt%.

All measurements were carried out in the temperature range between 278.15 K and 358.15 K except for those containing AN, whose measured temperature range was between 278.15 K and 328.15 K, due to its low boiling point of 354.75 K. Also, the

Table 1

Chemical name, molar mass, provenance, mass fraction purity, CAS number and chemical structures of the compounds studied in this work.

Chemical name	M/g·mol ⁻¹	Provenance	Purity	CAS number	Chemical structures
1-Methyl-1-propylpyrrolidinium bis(trifluoro methylsulfonyl)imide ([MPPyr][TFSI])	408.38	Io-li-tec	0.99	223437-05-6	
Lithium bis(trifluoro methylsulfonyl)imide (LiTFSI)	287.09	Acros organics	0.99	90076-65-6	
Acetonitrile (AN)	41.05	Panreac	0.997	75-05-8	
γ-Butyrolactone (GBL)	86.09	Merck	≥0.99	96-48-0	
Dimethyl sulfoxide (DMSO)	78.13	Panreac	0.999	67-68-5	

refractive indexes were measured at 298.15 K. All measurements have been performed at atmospheric pressure about 101 kPa.

Afterwards, a theoretical model was applied to the ionic conductivities data in function of composition for every temperature in all the binary mixtures, so as to select the proportion IL + solvent with higher ionic conductivity. These turned out to be those with a proportion around 50 wt%_{IL}-50 wt%_{solvent} for all studied systems. This model considers a pseudolattice nanostructure in the (IL + solvent) mixtures with an ion hopping mechanism of electrical conduction between adjacent cells instead the classical one, based on ion diffusion [64].

Once choice was made, we added to the binary mixtures different quantities of the LiTFSI salt, specifically 10, 15, 20, 30 and 35 wt %_{LiTFSI} and studied their physical properties of density, viscosity, ionic conductivity and refractive index at different temperatures (mentioned above). It should be noted that we stopped to add salt in at 35%, close to saturation.

In the Table S1, we show a summary of the measured magnitudes and temperatures with their corresponding concentrations of the different study systems.

Density and dynamic viscosity measurements were carried out in an Anton Paar SVM 3000 Stabinger viscodensimeter, which was thermostated with an internal Peltier cell with an uncertainty of 0.02 K. The procedure of measurement was detailed previously [82]. The combined expanded uncertainty in the measurement with a coverage factor, *k*, of 2 of density is about 0.5 kg·m⁻³ while for viscosity the relative combined expanded uncertainty is 0.01 of the measured value. This viscodensimeter automatically corrects the density value depending on the viscosity of the sample. Also, the viscosity value range goes from 0.2 up to 20,000 mPa·s, which is enough to measure these substances in a wide temperature range. This equipment is checked with reference chemicals recommended by the supplier M114 and C117 SH Calibration Service GmbH.

Ionic conductivities were measured using a Crison GLP31 conductivimeter which has a relative combined expanded uncertainty of 0.01. This conductivimeter uses a fixed 500 Hz ac current and 0.5 V rms. The samples were thermostated in an external bath with an uncertainty of 0.1 K. Details of the ionic conductivity measurement were published previously [83]. The reference fluids used to calibrate the measurement instrument were aqueous solutions of KCl 0.1 M and 0.01 M called P/N L7W9710.99 and P/N L7W9700.99.

Refractive index was measured in an Anton Paar Abbemat Automatic refractometer which was thermostated with an internal Peltier cell with an accuracy of ±0.03 K. Sample is measured in

direct contact with the measuring prism. The incident light of angles smaller than the critical angle of total reflection is partly refracted through the sample, while incident light of angles greater than the critical angle is totally reflected. A high-resolution sensor array measures the amount of this reflected light. The combined expanded uncertainty of the measurements of refractive indexes is 0.0005. The reference fluids used to calibrate were Milli-Q water and cyclohexane (Fluka > 0.995).

All measurements were carried out at atmospheric pressure of 101 kPa and standard uncertainty 1 kPa.

3. Results and discussion

3.1. Binary systems

As mentioned, we measured the physical properties of ρ , η and κ at atmospheric pressure of the binary systems [MPPyr][TFSI] + GBL, or DMSO, or AN at three concentrations and at different temperatures (Table S1).

The experimental data of densities and viscosities of our pure ionic liquid are in agreement with the only set of data given in the literature [84–86]. Regarding the binary mixtures studied, no published data were found. However, the literature reports some data of ρ , η and κ of binary mixtures of pyrrolidinium-based ionic liquids, specifically η and κ of 1-butyl-1-methylpyrrolidinium [TFSI] with GBL and ρ , η and κ of 1-methyl-1-pentylpyrrolidinium [TFSI] with AN and GBL [68,89] and ρ , η , κ and n_D of 1-methyl-1-butylpyrrolidinium [TFSI] with AN [87].

As can be seen in Fig. 1 (a), Figure S1 (a, b and c) and Table S2, density of binary mixtures presents a linear behavior with temperature and, as usual, its value decreases as temperature increases. If we pay attention how the addition of the solvent affects to the density Table S2, we observe as the density of the [MPPyr][TFSI] decreases with the addition of solvent. Particularly, the addition AN showed a significant drop of the density compared to the other two, whose values were similar in all the range of concentrations. This suggests that solvents molecules with little conformational flexibility, such as GBL and DMSO, have less interaction with molecules of ionic liquid than acyclic solvents molecules like AN. AN molecules are rigid molecules but shorter than GBL and DMSO molecules, that allow them to come into the gaps of the IL pseudolattice, breaking the interaction anion-cation, which would lead to a decrease of the density. This idea could be supported with the data of excess molar volume of mixtures of AN or GBL with other pyrrolidinium-based ILs reported in the literature [68,88].

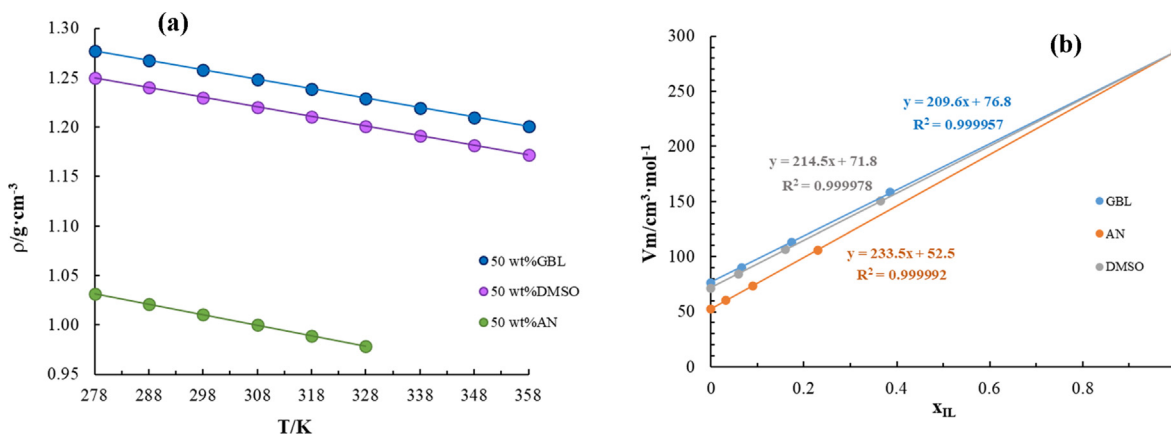


Fig. 1. (a) Densities versus T for the mixtures: [MPPyr][TFSI] + GBL; [MPPyr][TFSI] + DMSO and [MPPyr][TFSI] + AN at 50 wt%. Lines are the best fit of the data, (b) Molar volumes of binary mixtures (IL + solvent) in function of their molar fractions.

However, we should indicate that not always negative excess volumes imply stronger ion–solvent interactions as is the case of N-methyl-N-pentylpyrrolidinium TFSI with DMC [68,89]. In any case, we depict the molar volume of the mixtures, Fig. 1 (b), and we calculate their corresponding excess molar volumes. These latter were lower than 1% of the molar volume value for all binary mixtures, which indicates that they have a behaviour practically ideal.

In Fig. 2, Figure S2 (a, b and c) and Table S2, we present viscosity values, as expected, they decrease exponentially with temperature increases, following a Vogel-Fulcher-Tamman (VFT) trend [90–92]. VFT equation can be written as,

$$\eta = \eta_{\infty} \exp\left\{\frac{B_{\eta}}{T - T_{\eta}}\right\} \quad (1)$$

where η_{∞} , B_{η} and T_{η} are treated as fitting parameters, Table S3. The first one represents the limiting viscosity value at infinite temperature, the second one is related with a pseudo activation energy for ion hopping while T_{η} is usually near but above the glass transition temperature.

As was the case with densities, Table S2, the addition of solvent to the [MPPyr][TFSI] lead to a decrease of the viscosity but in contrast to the density the values obtained decrease exponentially. Again, AN is the solvent that produces a higher decrease of viscosity of the IL while DMSO and GBL show similar values. According to the literature [93], the variations of the viscosity observed are correlated

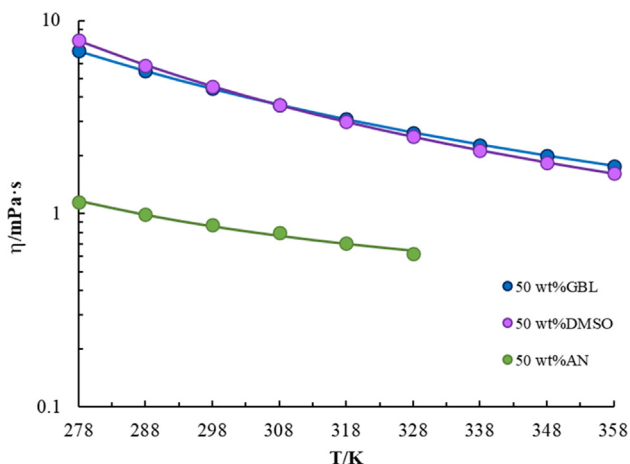


Fig. 2. Viscosities versus T for the mixtures: [MPPyr][TFSI] + GBL; [MPPyr][TFSI] + DMSO and [MPPyr][TFSI] + AN at 50 wt%. Lines are a VFT-type equation.

with the nature of the solvent (permittivity, the presence of electron lone pairs, size/shape. . .) and its concentration. So, as we add solvent to the ionic liquid, the strength of ion-ion interactions within the ionic liquid are weakened and the pseudolattice broken, as a consequence there is a significant decrease of the viscosity of the mixture up to 50 wt%_{solvent}, thereafter the values decrease slower. The similar viscosity values obtained for the mixtures of IL with DMSO and GBL could be explained because both are voluminous molecules with comparable permittivity and with more than one electron lone pair. This latter is relevant when we compare these data with those obtained for the mixtures of IL with AN, even though the AN is a small rigid molecule with a permittivity lower than DMSO and GBL, because the presence of a single lone pair in the AN may be an important factor that could explain the unexpected viscosity values obtained for these mixtures. In any case, the viscosity variations of the mixtures are influenced by multiple factors [68], including the fact that viscosity of pure AN is about four times lower than those of GBL or DMSO.

The ionic conductivity data measured for the binary mixtures studied are shown as a function of temperature and wt%_{solvent} in Fig. 3 (a), Figure S3 (a, b and c) and Table S2. As it was expected, the ionic conductivity increases with temperature following a Vogel-Fulcher-Tamman equation for the samples measured, as was expected [92,94]. VFT equation for electrical conductivities, is similar to that given in Equation (1),

$$\kappa = \kappa_{\infty} \exp\left\{\frac{-B_{\kappa}}{T - T_{\kappa}}\right\} \quad (2)$$

where again κ_{∞} , B_{κ} and T_{κ} are fitting parameters, Table S3. The first one, represents the limiting value of κ at infinite temperature and the second one is related with the activation energy for ion charge transport, while T_{κ} , called Vogel temperature is when ion hopping is suppressed, and so electrical conduction becomes negligible.

As happens for all IL mixtures with solvent [94,95], ionic conductivity increases with the addition of solvent to the IL up to a maximum value, and thereafter the ionic conductivity decreases. In our systems, that peak is around a solvent concentration of 50 wt% as observed in Fig. 3d. The mentioned pseudolattice model for electrical [64] conduction gives an equation which relates electrical conductivity with the partial molar volume occupied by each compound in the mixture, thus, it reads,

$$\kappa = \kappa_{IL}(\phi_{IL}\phi_S\nu_B + \phi_{IL}^2 + \phi_{IL}^2\phi_S\Delta\nu) \quad (3)$$

where κ_{IL} is the electrical conductivity of the pure IL, ϕ_{IL} and ϕ_S the molar partial volume of the IL and the solvent respectively (obviously $\phi_{IL} + \phi_S = 1$ in a binary mixture), Table 2.

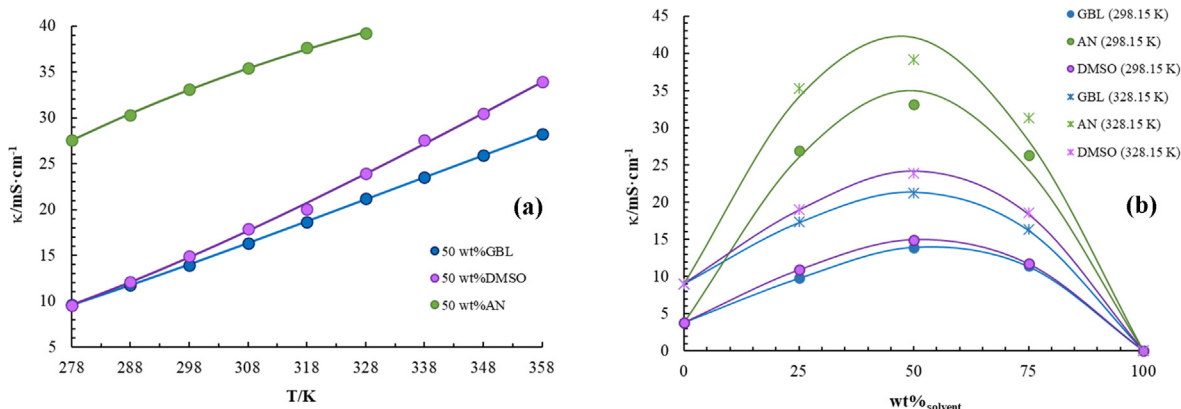


Fig. 3. (a) Ionic conductivities versus T for the mixtures: [MPPyr][TFSI] + GBL; [MPPyr][TFSI] + DMSO and [MPPyr][TFSI] + AN at 50 wt%, where lines are the best fit of VFT Eq. (2). (b) Ionic conductivities versus $\text{wt}\%_{\text{solvent}}$ composition for the binary systems [MPPyr][TFSI] + GBL; [MPPyr][TFSI] + DMSO; [MPPyr][TFSI] + AN at the temperatures 298.15 K and 328.15 K, where curves are the best fit of Eq. (3).

Table 2
Pseudolattice model parameters for binary mixtures.

Mixture	v_B	Δv
[MPPyr][TFSI] + GBL (298.15 K)	21.2	-16.2
[MPPyr][TFSI] + GBL (328.15 K)	12.3	-7.95
[MPPyr][TFSI] + DMSO (298.15 K)	21.9	-15.2
[MPPyr][TFSI] + DMSO (328.15 K)	14.3	-9.66
[MPPyr][TFSI] + AN (298.15 K)	56.3	-46.9
[MPPyr][TFSI] + AN (328.15 K)	27.6	-21.7

The term v_B represent the jumping frequency of ion hopping between adjacent cells, while Δv takes into account the different frequencies of jumping depending on the cell type, but both will be used as free parameters to fit the corresponding data. The resulting curves have been plotted in Fig. 3 (b), where we observe the high quality fit of Eq. (3) to the data except for the samples with AN.

The increase may be linked with the viscosity and solvents permittivity. Thus, the solvents used in the mixtures have comparable

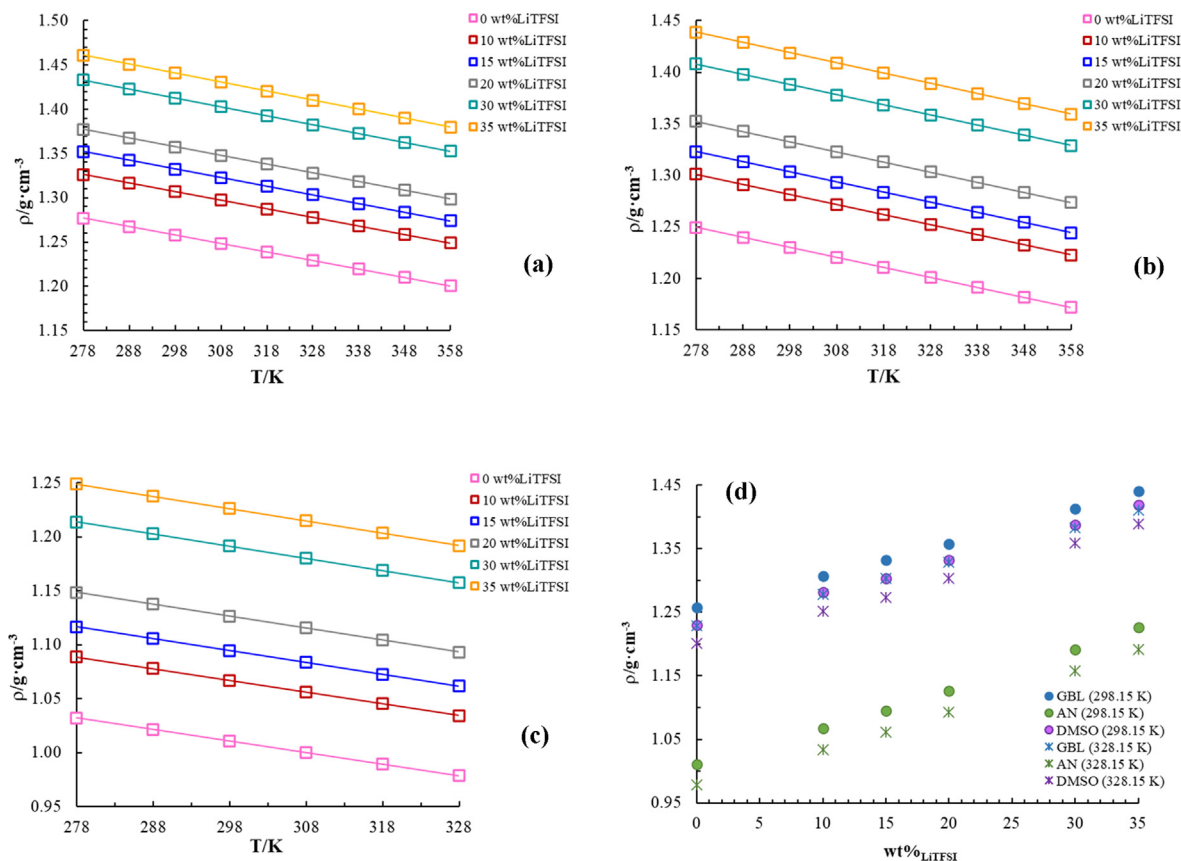


Fig. 4. Densities versus T for (a) ([MPPyr][TFSI] + GBL) + LiTFSI; (b) ([MPPyr][TFSI] + DMSO) + LiTFSI; (c) ([MPPyr][TFSI] + AN) + LiTFSI, (d) Densities versus $\text{wt}\%_{\text{LiTFSI}}$ for the ternary systems [MPPyr][TFSI] + GBL + LiTFSI; [MPPyr][TFSI] + DMSO + LiTFSI; [MPPyr][TFSI] + AN + LiTFSI at the temperatures 298.15 K and 328.15 K. Lines are the best fit of the data.

permittivities but the mixtures of IL + AN show a higher increase of the ionic conductivity due to their lower viscosity. Mixtures IL + GBL and IL + DMSO have similar ionic conductivities, being slightly higher the ionic conductivities of the IL + DMSO, this can be attributed to the permittivity of the DMSO that is somewhat higher than GBL.

Finally, as part of the characterization of our binary mixtures, we include Figure S4 and Table S2 with the values of their refractive indexes at 298.15 K.

3.2. Ternary mixtures

As mentioned before, we prepared ternary mixtures of the (IL + solvent) + lithium salt, in which there are two salts and one of the molecular solvents. Specifically, in the literature, no published data was found about the physical properties of our mixtures, we could only find some data of ionic conductivities for a single ternary mixture 1-butyl-3-methylimidazolium [TFSI] + Li-TFSI + AN [96].

From the binary mixture with higher ionic conductivity (50 wt%_{IL} and 50 wt%_{solvent}) we prepared five ternary mixtures adding Li-TFSI in five compositions given in Table S4, and we measured their physical properties in a broad range of temperatures and atmospheric pressure.

Density data measured for the three studied systems are plotted in Fig. 4, while viscosity is presented in Fig. 5 and ionic conductivity in Fig. 6 and their corresponding values are in Table S5. In these figures, a) is for the system IL + GBL, b) for IL + DMSO and c) for IL + AN. Respecting temperature behavior, density and viscosity decrease while the ionic conductivity increases with temperature as usual. As it happened for the binary systems, the experimental

data of viscosity and ionic conductivity for all mixtures in the temperature range studied are very well fitted by the VFT equation given in Eq. (1) and Eq. (2) respectively (Table S3)

Concerning the values obtained at a given temperature according to the salt concentration, Figs. 4, 5 and 6(d), Table S5, we observed that the higher the salt concentration the higher the density and the viscosity, but the lower the ionic conductivity.

As was the case with the binary mixtures, the ternary mixtures with AN are those with lower viscosities and higher ionic conductivities. At the same time, the ternary mixtures with GBL and DMSO show similar values of both viscosities and ionic conductivities but we observe a peculiar behavior in the data. Thus, the ternary mixtures of GBL and DMSO in low concentrations (10 wt%_{LiTFSI}) have similar values of viscosity, but subsequent additions (15 and 20 wt%_{LiTFSI}) show values of the viscosity for mixtures with GBL higher than those with DMSO up to 30 wt%_{LiTFSI} at which point both viscosities rejoin. However, at 35 wt%_{LiTFSI}, the viscosities of the mixture with GBL and DMSO again have different values; but now viscosity of mixtures with DMSO are higher than those with GBL contrary to what happened with the samples at 10 wt%_{LiTFSI}.

In the literature we found different works about the study of binary mixtures (solvent + lithium salt) [93,97,98]. They describe that when a lithium salt is dissolved in an aprotic solvent, it produces a competition between the anions and the solvent for coordinating the Li⁺, giving rise to different solvent complexes (solvent separated ion pairs (SSIPs), contact ion pairs (CIPs) and aggregates (AGGs)) which determines the structure of the mixture and therefore their physical properties. In these kind of mixtures, factors such as salt concentration, anion and cation nature, temperature... are relevant in the final behavior of the mixture. Thus,

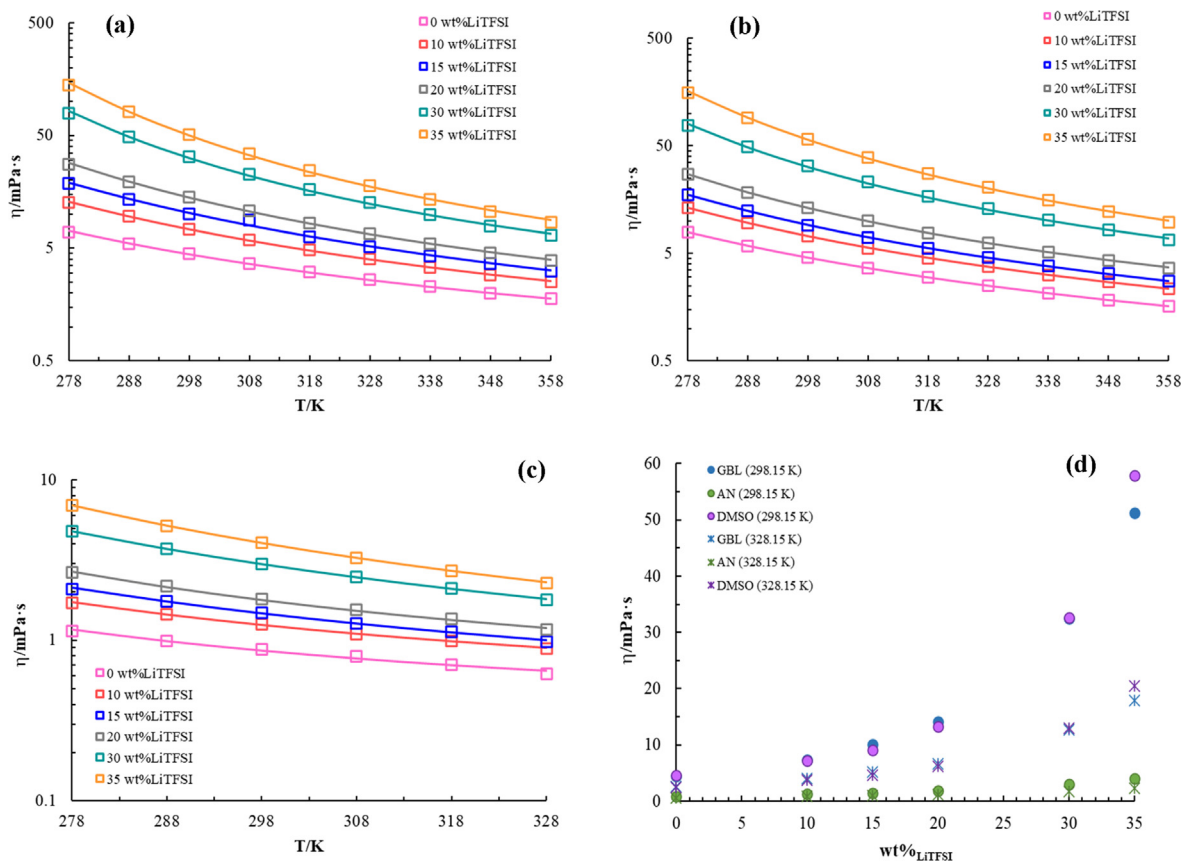


Fig. 5. Viscosities versus T for (a) ([MPPyr][TFSI] + GBL) + LiTFSI; (b) ([MPPyr][TFSI] + DMSO) + LiTFSI; (c) ([MPPyr][TFSI] + AN) + LiTFSI, (d) Viscosities versus wt%_{LiTFSI} for the ternary systems [MPPyr][TFSI] + GBL + LiTFSI; [MPPyr][TFSI] + DMSO + LiTFSI; [MPPyr][TFSI] + AN + LiTFSI at the temperatures 298.15 K and 328.15 K. Lines are a VFT-type equation.

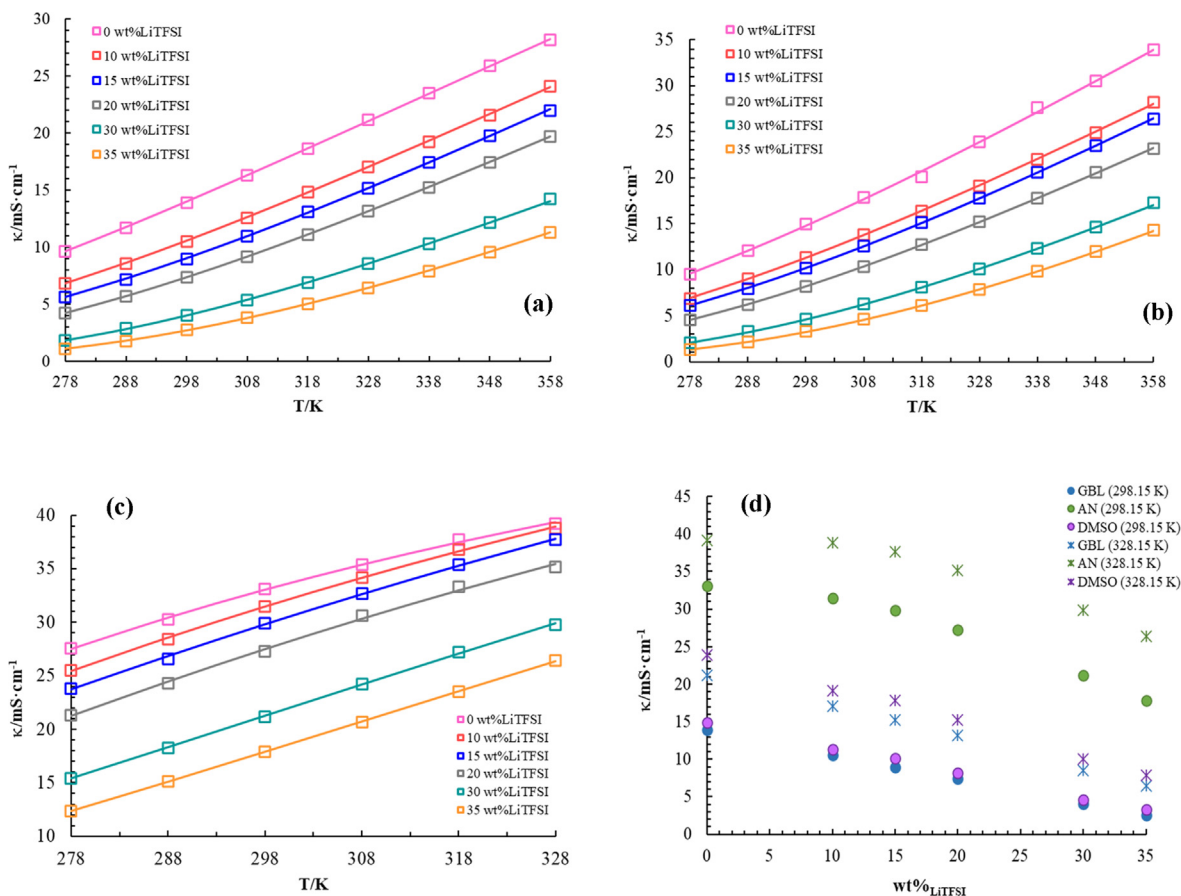


Fig. 6. Ionic conductivities versus T for (a) ([MPPyr][TFSI] + GBL) + LiTFSI; (b) ([MPPyr][TFSI] + DMSO) + LiTFSI; (c) ([MPPyr][TFSI] + AN) + LiTFSI. (d) Ionic conductivities versus $\text{wt}\%_{\text{LiTFSI}}$ for the ternary systems [MPPyr][TFSI] + GBL + LiTFSI; [MPPyr][TFSI] + DMSO + LiTFSI; [MPPyr][TFSI] + AN + LiTFSI at the temperatures 298.15 K and 328.15 K. Lines are a VFT-type equation.

the increase of the salt concentration favors the ionic association, which leads to changes in the viscosity of the mixture that affect ionic conductivity. Generally, the ionic conductivity shows an increase at lower salt concentrations up to a maximum value, thereafter this decreases as a consequence of the increase of the viscosity that reduces the ion mobility.

Our systems have two salts, an IL and Lithium salt (with the anion in common) and one solvent and their behaviour is different to the mixtures (solvent + lithium salt). Thus, the ionic conductivity of our mixtures (IL + solvent + lithium salt) decreases, for all cases, with the addition of the lithium salt as usual, in part because of the increase of the viscosity because of the solvation of the Li cations. We think that this is due to the addition of lithium salt increases the anions content and therefore favors the interaction of the Li^+ with more than an anion giving rise to formation of contact ion pairs and ionic aggregates. For this reason, the higher the addition of lithium salt, the lower the ionic conductivity.

In any case, the values obtained for the ionic conductivity are for some of our systems even better than those obtained for electrolyte systems based on carbonate solvents with IL and lithium salt [45,95]. These systems are the ternary mixture with GBL or DMSO up to 20 $\text{wt}\%_{\text{LiTFSI}}$, and those with AN for all salt concentrations.

As we did with the binary mixtures, we include the measurements of their refractive indexes at different proportions of lithium salt at the temperature of 298.15 K (Figure S5 and Table S5). In spite of this property not affecting the behaviour of our mixtures as electrolytes, we think that this is an interesting find for other applications of these mixtures.

4. Conclusions

The aim of this work was to try to design an electrolyte for lithium ion batteries with an ionic liquid as a component, in order to find one combination to improve conventional electrolyte characteristics. The study of the physical properties of this kind of mixtures (IL + solvent + Lithium salt) as well as their functionalities from the point of view of their structure and behavior is a preliminary contribution to the study of battery technologies.

The ternary mixtures studied were prepared from a selected 50 wt% binary mixtures, [MPPyr][TFSI], + GBL; DMSO, or AN; to which was added five different percentages by weight of LiTFSI salt up to near saturation (35 $\text{wt}\%_{\text{LiTFSI}}$).

The addition of salt in the binary mixtures provokes, as in other mixtures with ILs, an increase of density and viscosity and therefore a decrease of ionic conductivity. In spite of that, the values obtained for this latter property are for some of our systems even higher than those obtained for electrolyte systems based on carbonate. Among these systems are: [MPPyr][TFSI] + GBL or DMSO + LiTFSI at 0–20 $\text{wt}\%_{\text{LiTFSI}}$ and [MPPyr][TFSI] + AN + LiTFSI at 0–35 $\text{wt}\%_{\text{LiTFSI}}$.

These results should be analysed with caution, and it must be seen whether the loss of ionic conductivity after the addition of lithium salt is compensated by other factors in the battery. It is well known that the use of highly concentrated electrolytes in salt improves aspects such as the reductive and oxidative stability, thermal stability, enlargement of useful life etc. Taking this into account, we plan to test these electrolytes in a real battery using commercial and the new generation electrodes in order to carry out an overall study of the applicability of these mixtures as real electrolytes.

CRediT authorship contribution statement

S. García-Garabal: Conceptualization, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Data curation. **M. Domínguez-Pérez:** Conceptualization, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Data curation. **D. Portela:** Investigation, Data curation. **L.M. Varela:** Conceptualization, Writing – original draft, Data curation. **O. Cabeza:** Conceptualization, Methodology.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2022.119758>.

References

- [1] X. Yuan, H. Liu, J. Zhang, *Lithium-Ion Batteries: Advanced Materials and Technologies*, CRC Press, 2011.
- [2] K. Xu, Nonaqueous liquid electrolytes for lithium-based rechargeable batteries, *Chem. Rev.* 104 (2004) 4303–4418, <https://doi.org/10.1021/cr030203g>.
- [3] K. Xu, Electrolytes and interphases in Li-Ion batteries and beyond, *Chem. Rev.* 114 (23) (2014) 11503–11618, <https://doi.org/10.1021/cr500003w>.
- [4] M.J. Lain, J. Brandon, E. Kendrick, Design strategies for high power vs. high energy lithium ion cells, *Batteries* 5 (4) (2019) 64, <https://doi.org/10.3390/batteries5040064>.
- [5] X. Wu, K. Song, X. Zhang, N. Hu, L. Li, W. Li, L. Zhang, H. Zhang, Safety issues in lithium ion batteries: materials and cell design, *Front. Energy Res.* 7 (2019) 65, <https://doi.org/10.3389/fenrg.2019.00065>.
- [6] T.O. Ely, D. Kamzabek, D. Chakraborty, Batteries safety: recent progress and current challenges, *Front. Energy Res.* 7 (2019) 71, <https://doi.org/10.3389/fenrg.2019.00071>.
- [7] B. Liu, Y. Jia, C. Yuan, L. Wang, X. Gao, S. Yin, J. Xu, Safety issues and mechanisms of lithium-ion battery cell upon mechanical abusive loading: A review, *Energy Storage Mater.* 24 (2020) 85–112, <https://doi.org/10.1016/j.ensm.2019.06.036>.
- [8] D. Aurbach, B. Markovsky, G. Salitra, E. Markevich, Y. Talyossef, M. Koltypin, L. Nazar, B. Ellis, D. Kovachev, Review on electrode–electrolyte solution interactions, related to cathode materials for Li-ion batteries, *J. Power Sources* 165 (2007) 491–499, <https://doi.org/10.1016/j.jpowsour.2006.10.025>.
- [9] J. Wang, Y. Yamada, K. Sodeyama, C.H. Chiang, Y. Tateyama, A. Yamada, Superconcentrated electrolytes for a high-voltage lithium-ion battery, *Nat. Commun.* 7 (2016), <https://doi.org/10.1038/ncomms12032>.
- [10] A. Jana, D.R. Ely, E. García, Dendrite-separator interactions in lithium-based batteries, *J. Power Sources* 275 (2015) 912–921, <https://doi.org/10.1016/j.jpowsour.2014.11.056>.
- [11] S. Tobishima, K. Hayashi, Y. Nemoto, J. Yamaki, Multi-component nonaqueous electrolytes for rechargeable lithium cells, *Electrochimica Acta*, 43, 8 (1998) 925–933. DOI: [https://doi.org/10.1016/S0013-4686\(97\)00264-8](https://doi.org/10.1016/S0013-4686(97)00264-8)
- [12] I. Cekić-Lasković, N. von Aspern, L. Imholt, S. Kaymaksiz, K. Oldiges, B.R. Rad, M. Winter, Synergistic effect of blended components in nonaqueous electrolytes for lithium ion batteries, *Top. Curr. Chem.* 375 (2017) 37, <https://doi.org/10.1007/s41061-017-0125-8>.
- [13] K. Xu, M. Ding, S. Zhang, J. Allen, R. Jow, An attempt to formulate nonflammable lithium ion electrolytes with alkyl phosphates and phosphazenes, *J. Electrochem. Soc.* 149 (5) (2002) 622–626, <https://doi.org/10.1149/1.1467946>.
- [14] E.-G. Shim, T.-H. Nam, J.-G. Kim, H.-S. Kim, S.-I. Moon, Effects of functional electrolyte additives for Li-ion batteries, *J. Power Sources* 172 (2007) 901–907, <https://doi.org/10.1016/j.jpowsour.2007.04.089>.
- [15] L. Xiao, X. Ai, Y. Cao, H. Yang, Electrochemical behavior of biphenyl as polymerizable additive for overcharge protection of lithium ion batteries, *Electrochim. Acta* 49 (2004) 4189–4196, <https://doi.org/10.1016/j.electacta.2004.04.013>.
- [16] Y. Watanabe, H. Morimoto, S. Tobishima, Electrochemical properties of aryladamantanes as new overcharge protection compounds for lithium cells, *J. Power Sources* 154 (2006) 246–254, <https://doi.org/10.1016/j.jpowsour.2005.03.221>.
- [17] C. Dippel, R. Schmitz, R. Müller, T. Böttcher, M. Kunze, A. Lex-Balducci, G.-V. Röschenhaler, S. Passerini, M. Winter, Carbene adduct as overcharge protecting agent in lithium ion batteries, *J. Electrochem. Soc.* 159 (2012) 1587–1590, <https://doi.org/10.1149/2.006210jes>.
- [18] C. Korepp, H.J. Santner, T. Fujii, M. Ue, J.O. Besenhard, K.C. Möller, M. Winter, 2-Cyanofuran—A novel vinylene electrolyte additive for PC-based electrolytes in lithium-ion batteries, *J. Power Sources* 158 (2006) 578–582, <https://doi.org/10.1016/j.jpowsour.2005.09.021>.
- [19] H.J. Santner, C. Korepp, M. Winter, J.O. Besenhard, K.C. Möller, In-situ FTIR investigations on the reduction of vinylene electrolyte additives suitable for use in lithium-ion batteries, *Anal. Bioanal. Chem.* 379 (2004) 266–271, <https://doi.org/10.1007/s00216-004-2522-4>.
- [20] K.C. Möller, H.J. Santner, W. Kern, S. Yamaguchi, J.O. Besenhard, M. Winter, In situ characterization of the SEI formation on graphite in the presence of a vinylene group containing film-forming electrolyte additives, *J. Power Sources* 119–121 (2003) 561–566, [https://doi.org/10.1016/S0378-7753\(03\)00289-1](https://doi.org/10.1016/S0378-7753(03)00289-1).
- [21] G.H. Wrodnigg, J.O. Besenhard, M. Winter, Ethylene Sulfite as Electrolyte Additive for Lithium-Ion Cells with Graphitic Anodes, *J. Electrochem. Soc.* 146 (1999) 470–472, <https://doi.org/10.1149/1.1391630>.
- [22] C. Korepp, W. Kern, E.A. Lanzer, P.R. Raimann, J.O. Besenhard, M. Yang, K.C. Möller, D.T. Shieh, M. Winter, Ethyl isocyanate—An electrolyte additive from the large family of isocyanates for PC-based electrolytes in lithium-ion batteries, *J. Power Sources* 174 (2007) 628–631, <https://doi.org/10.1016/j.jpowsour.2007.06.140>.
- [23] J. Xia, N.N. Sinha, L.P. Chen, J.R. Dahn, A comparative study of a family of sulfate electrolyte additives, *J. Electrochem. Soc.* 161 (2014) 264–274, <https://doi.org/10.1149/2.015403jes>.
- [24] E. Krämer, R. Schmitz, S. Passerini, M. Winter, C. Schreiner, 1-Fluoropropane-2-one as SEI-forming additive for lithium-ion batteries, *Electrochem. Commun.* 16 (2012) 41–43, <https://doi.org/10.1016/j.elecom.2011.12.021>.
- [25] E. Krämer, R. Schmitz, P. Niehoff, S. Passerini, M. Winter, SEI-forming mechanism of 1-Fluoropropane-2-one in lithium-ion batteries, *Electrochim. Acta* 81 (2012) 161–165, <https://doi.org/10.1016/j.electacta.2012.07.091>.
- [26] L. Hu, A. Tornheim, S.S. Zhang, Z. Zhang, Additives for Functional Electrolytes of Li-Ion Batteries, in: Z. Zhang, S. Zhang (Eds.), *Rechargeable Batteries*, Springer, Green Energy and Technology, 2015, pp. 263–290.
- [27] J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation, *Green Chem.* 3 (2001) 156–164, <https://doi.org/10.1039/b103275p>.
- [28] E. Rilo, J. Vila, M. García, L.M. Varela, O. Cabeza, Viscosity and Electrical Conductivity of Binary Mixtures of CnMIM-BF4 with Ethanol at 288 K, *J. Chem. Eng. Data* 55 (2010) 5156–5163, <https://doi.org/10.1021/j100687x>.
- [29] A. Lewandowski, A. Świdarska-Moczek, Ionic liquids as electrolytes for Li-ion batteries—An overview of electrochemical studies, *J. Power Sources* 194 (2009) 601–609, <https://doi.org/10.1016/j.jpowsour.2009.06.089>.
- [30] S. Menne, J. Pires, M. Anouti, A. Balducci, Protic ionic liquids as electrolytes for lithium-ion batteries, *Electrochem. Commun.* 31 (2013) 39–41, <https://doi.org/10.1016/j.elecom.2013.02.026>.
- [31] T. Stettner, P. Huang, M. Goktas, P. Adelhelm, A. Balducci, Mixtures of glyme and aprotic-protic ionic liquids as electrolytes for energy storage devices, *J. Chem. Phys.* 148 (2018), <https://doi.org/10.1063/1.5013117> 193825.
- [32] H. Sakaebe, H. Matsumoto, N-Methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide (PP13-TFSI) – novel electrolyte base for Li battery, *Electrochem. Commun.* 5 (2003) 594–598, [https://doi.org/10.1016/S1388-2481\(03\)00137-1](https://doi.org/10.1016/S1388-2481(03)00137-1).
- [33] H. Matsumoto, H. Sakaebe, K. Tatsumi, M. Mikuta, E. Ishiko, M. Kono, Fast cycling of Li/LiCoO₂ cell with low-viscosity ionic liquids based on bis (fluorosulfonyl)imide [FSI], *J. Power Sources* 160 (2006) 1308–1313, <https://doi.org/10.1016/j.jpowsour.2006.02.018>.
- [34] J. Jin, H.H. Li, J.P. Wei, X.K. Bian, Z. Zhou, J. Yan, Li/LiFePO₄ batteries with room temperature ionic liquid as electrolyte, *Electrochem. Commun.* 11 (2009) 1500–1503, <https://doi.org/10.1016/j.elecom.2009.05.040>.
- [35] H. Sakaebe, H. Matsumoto, K. Tatsumi, Discharge-charge properties of Li/LiCoO₂ cell using room temperature ionic liquids (RTILs) based on quaternary ammonium cation – Effect of the structure, *J. Power Sources* 146 (2005) 693–697, <https://doi.org/10.1016/j.jpowsour.2005.03.071>.
- [36] V. Borgel, E. Markevich, D. Aurbach, G. Semrau, M. Schmidt, On the application of ionic liquids for rechargeable Li batteries: High voltage systems, *J. Power Sources* 189 (2009) 331–336, <https://doi.org/10.1016/j.jpowsour.2008.08.099>.
- [37] M. Armand, P. Axmann, D. Bresser, M. Copley, K. Edström, C. Ekberg, D. Guyomard, B. Lestriez, P. Novák, M. Petranikova, W. Porcher, S. Trabesinger, M. Wohlfahrt-Mehrens, H. Zhang, Lithium-ion batteries – Current state of the art and anticipated developments, *J. Power Sources* 479 (2020), <https://doi.org/10.1016/j.jpowsour.2020.228708> 228708.

- [38] J. Kalhoff, G.G. Eshetu, D. Bresser, S. Passerini, Safer Electrolytes for Lithium-Ion Batteries: State of the Art and Perspectives, *ChemSusChem* 8 (2015) 2154–2175, <https://doi.org/10.1002/cssc.201500284>.
- [39] M. Li, J. Lu, Z. Chen, K. Amine, 30 Years of Lithium-Ion Batteries, *Adv. Mater.* 30 (2018) 1800561, <https://doi.org/10.1002/adma.201800561>.
- [40] T. Stettner, F.C. Walter, A. Balducci, Imidazolium-Based Protic Ionic Liquids as Electrolytes for Lithium ion batteries, *Batteries & Supercaps* 2 (2019) 55–59, <https://doi.org/10.1002/batt.201800096>.
- [41] H. Niu, L. Wang, P. Guan, N. Zhang, C. Yan, M. Ding, X. Guo, T. Huang, X. Hu, Recent advances in application of ionic liquids in electrolyte of lithium ion batteries, *J. Storage Mater.* 40 (2021), <https://doi.org/10.1016/j.est.2021.102659> 102659.
- [42] K. Liu, Z. Wang, L. Shi, S. Jungsuttiwong, S. Yuan, Ionic liquids for high performance lithium metal batteries, *J. Energy Chem.* 59 (2021) 320–333, <https://doi.org/10.1016/j.jechem.2020.11.017>.
- [43] L.T.M. Le, T.D. Vo, K.H.P. Ngo, S. Okada, F. Alloin, A. Garg, P.M.L. Le, Mixing ionic liquids and ethylene carbonate as safe electrolytes for lithium-ion batteries, *J. Mol. Liq.* 271 (2018) 769–777, <https://doi.org/10.1016/j.molliq.2018.09.068>.
- [44] S. Lee, K. Park, B. Koo, C. Park, M. Jang, H. Lee, H. Lee, Ionic liquid electrolytes: safe, stable cycling of lithium metal batteries with low-viscosity, fire retardant locally concentrated ionic liquid electrolytes, *Adv. Funct. Mater.* 30 (2020) 2070234, <https://doi.org/10.1002/adfm.202070234>.
- [45] F. Wu, A.R. Schür, G.-T. Kim, X. Dong, M. Kuenzel, T. Diemant, G. D'Orsi, E. Simonetti, M. Francesco, M. Bellucci, G.B. Appetecchi, S. Passerini, A novel phosphonium ionic liquid electrolyte enabling high-voltage and high-energy positive electrode materials in lithium-metal batteries, *Energy Storage Mater.* 42 (2021) 826–835, <https://doi.org/10.1016/j.ensm.2021.08.030>.
- [46] L.M. McGrath, J.F. Rohan, Pyrrolidinium containing ionic liquid electrolytes for Li-based batteries, *Molecules* 25 (2020) 6002, <https://doi.org/10.3390/molecules25246002>.
- [47] M. Ravia, S. Kim, F. Ranc, D.S. Kim, Y.M. Lee, M.-H. Ryou, Hybrid gel polymer electrolyte based on 1-methyl-1-propylpyrrolidinium Bis (Trifluoromethanesulfonyl) imide for flexible and shape-variant lithium secondary batteries, *J. Membr. Sci.* 621 (2021), <https://doi.org/10.1016/j.memsci.2020.119018> 119018.
- [48] R. Löwe, T. Hanemann, T. Zinkevich, A. Hofmann, Poly(ionic liquid) based composite electrolytes for lithium ion batteries, *Polymers* 13 (2021) 4469, <https://doi.org/10.3390/polym13244469>.
- [49] H. Qi, Y. Ren, S. Guo, Y. Wang, S. Li, Y. Hu, F. Yan, High-voltage resistant ionic liquids for lithium-ion batteries, *ACS Appl. Mater. Interfaces* 12 (2020) 591–600, <https://doi.org/10.1021/acsami.9b16786>.
- [50] L. Dagoussset, G.T.M. Nguyen, F. Vidal, C. Galindo, P.-H. Aubert, Ionic liquids and γ -butyrolactone mixtures as electrolytes for supercapacitors operating over extended temperature ranges, *RSC Adv.* 5 (2015) 13095–13101, <https://doi.org/10.1039/C4RA13933J>.
- [51] A. Lahiri, G. Li, M. Olschewski, F. Endres, Influence of Polar Organic Solvents in an Ionic Liquid Containing Lithium Bis(fluorosulfonyl)amide: Effect on the Cation-Anion Interaction, Lithium Ion Battery Performance, and Solid Electrolyte Interphase, *ACS Appl. Mater. Interfaces* 8 (2016) 34143–34150, <https://doi.org/10.1021/acsami.6b12751>.
- [52] J. Huang, Z. Jin, Z.-L. Xu, L. Qin, H. Huang, Z. Sadighi, S. Yao, J. Cui, B. Huang, J.-K. Kim, Porous RuO₂ nanosheet/CNT electrodes for DMSO-based Li-O₂ and Li ion O₂ batteries, *Energy Storage Mater.* 8 (2017) 110–118, <https://doi.org/10.1016/j.ensm.2017.05.004>.
- [53] M.L. Martins, R.L. Sacci, X. Lin, R. Matsumoto, I. Popov, J. Cui, T. Kobayashi, M. Tyagi, W. Guo, S. Dai, M. Pruski, P.T. Cummings, A.P. Sokolov, E. Mamontov, Beyond Simple Dilution: Superior Conductivities from Cosolvation of Acetonitrile/LiTFSI Concentrated Solution with Acetone, *J. Phys. Chem. C* 126 (5) (2022) 2788–2796, <https://doi.org/10.1021/acs.jpcc.1c09352>.
- [54] W. Zhang, H. Sun, P. Hu, W. Huang, Q. Zhang, Double-effect of highly concentrated acetonitrile-based electrolyte in organic lithium-ion battery, *EcoMat.* 3 (2021), <https://doi.org/10.1002/eom2.12128> e12128.
- [55] P. Hilbig, L. Ibing, B. Streipert, R. Wagner, M. Winter, I. Cekic-Laskovic, Acetonitrile-based electrolytes for lithium-ion battery application, *Curr. Top. Electrochem.* 20 (2018), <https://doi.org/10.31300/CTEC.20.2018.1-13>.
- [56] A. Lahiri, G. Pulletikurthi, M.S. Ghazvini, O. Höft, G. Li, F. Endres, Ionic liquid–organic solvent mixture-based polymer gel electrolyte with high lithium concentration for li-ion batteries, *J. Phys. Chem. C* 122 (2018) 24788–24800, <https://doi.org/10.1021/acs.jpcc.8b07745>.
- [57] X. Lu, J.M. Vicent-Luna, S. Calero, R.M. Madero-Castro, M.C. Gutiérrez, M.L. Ferrer, F. del Monte, EMIMBF₄ in ternary liquid mixtures of water, dimethyl sulfoxide and acetonitrile as “tri-solvent-in-salt” electrolytes for high-performance supercapacitors operating at -70 °C, *Energy Storage Mater.* 40 (2021) 368–385, <https://doi.org/10.1016/j.ensm.2021.05.026>.
- [58] P. Martínez-Crespo, M. Otero-Lema, O. Cabeza, H. Montes-Campos, L.M. Varela, Structure, dynamics and ionic conductivities of ternary ionic liquid/lithium salt/DMSO mixtures, *J. Mol. Liq.* 359 (2022), <https://doi.org/10.1016/j.molliq.2022.119188> 119188.
- [59] T.C. Lourenço, L.M.S. Barros, C.G. Anchieta, T.C.M. Nepel, J.P.O. Júlio, L.G. Dias, R. M. Filho, G. Doubek, J.L.F. Da Silva, Tuning Aprotic Solvent Properties with Long Alkyl Chain Ionic Liquid for Lithium-based Electrolytes, *J. Mater. Chem. A*, 2022, Advance Article. <https://doi.org/10.1039/D1TA10592B>
- [60] S. Wang, Y. Shi, X. Luo, M. Song, B. Ling, X. Zhu, Electrical Conductivities of DBU-Based Ionic Liquid in Its Binary Solutions with Nonaqueous Molecular Solvents, *J. Solution Chem.* 50 (2021) 558–575, <https://doi.org/10.1007/s10953-021-01070-x>.
- [61] Y. Gu, S. Fang, L. Yang, S.-I. Hirano, A safe electrolyte for high-performance lithium-ion batteries containing lithium difluoro(oxalato)borate, gamma-butyrolactone and non-flammable hydrofluoroether, *Electrochim. Acta* 394 (2021), <https://doi.org/10.1016/j.electacta.2021.139120> 139120.
- [62] S. Papović, S. Gadžurić, M. Bešter-Rogač, B. Jović, M. Vraneš, A systematic study on physicochemical and physical properties of imidazolium-based ionic liquids with γ -butyrolactone, *J. Chem. Thermodyn.* 116 (2018) 330–340, <https://doi.org/10.1016/j.jct.2017.10.004>.
- [63] L. Yu, G.Z. Chen, High energy supercapattery with an ionic liquid solution of LiClO₄, *Faraday Discuss.* 190 (2016) 231–240, <https://doi.org/10.1039/C5FD00232J>.
- [64] H. Montes-Campos, S. Kondrat, E. Rilo, L.M. Varela, O. Cabeza, Random-alloy model for the conductivity of ionic liquid–solvent mixtures, *J. Phys. Chem. C* 124 (2020) 11754–11759, <https://doi.org/10.1021/acs.jpcc.0c00531>.
- [65] C. Arbizzani, G. Gabrielli, M. Mastragostino, Thermal stability and flammability of electrolytes for lithium-ion batteries, *J. Power Sources* 196 (2011) 4801–4805, <https://doi.org/10.1016/j.jpowsour.2011.01.068>.
- [66] T. Vogl, S. Menne, A. Balducci, Mixtures of protic ionic liquids and propylene carbonate as advanced electrolytes for lithium-ion batteries, *PCCP* 16 (2014) 25014–25023, <https://doi.org/10.1039/C4CP03830D>.
- [67] R.S. Kühnel, N. Böckenfeld, S. Passerini, M. Winter, A. Balducci, Mixtures of ionic liquid and organic carbonate as electrolyte with improved safety and performance for rechargeable lithium batteries, *Electrochim. Acta* 56 (2011) 4092–4099, <https://doi.org/10.1016/j.electacta.2011.01.116>.
- [68] E.T. Fox, E. Paillard, O. Borodin, W.A. Henderson, Physicochemical properties of binary ionic liquid–aprotic solvent electrolyte mixtures, *J. Phys. Chem. C* 117 (2013) 78–84, <https://doi.org/10.1021/jp3089403>.
- [69] L. Lombardo, S. Brutti, M.A. Navarra, S. Panero, P. Reale, Mixtures of ionic liquid – alkylcarbonates as electrolytes for safe lithium-ion batteries, *J. Power Sources* 227 (2013) 8–14, <https://doi.org/10.1016/j.jpowsour.2012.11.017>.
- [70] I. Quinzeni, S. Ferrari, E. Quartarone, C. Tomasi, M. Fagnoni, P. Mustarelli, Li-doped mixtures of alkoxy-N-methylpyrrolidiniumbis (trifluoromethanesulfonyl)-imide and organic carbonates as safe liquid electrolytes for lithium batteries, *J. Power Sources* 237 (2013) 204–209, <https://doi.org/10.1016/j.jpowsour.2013.03.036>.
- [71] S.F. Lux, M. Schmuck, G.B. Appetecchi, S. Passerini, M. Winter, A. Balducci, Lithium insertion in graphite from ternary ionic liquid–lithium salt electrolytes: II. Evaluation of specific capacity and cycling efficiency and stability at room temperature, *J. Power Sources* 192 (2009) 606–611, <https://doi.org/10.1016/j.jpowsour.2009.02.066>.
- [72] Y. Wang, K. Zaghbi, A. Guerfi, F.F.C. Bazito, R.M. Torresi, J.R. Dahn, Accelerating rate calorimetry studies of the reactions between ionic liquids and charged lithium ion battery electrode materials, *Electrochim. Acta* 52 (2007) 6346–6352, <https://doi.org/10.1016/j.electacta.2007.04.067>.
- [73] S. Seki, N. Serizawa, S. Ono, K. Takei, K. Hayamizu, S. Tsuzuki, Y. Umabayashi, Densities, viscosities, and refractive indices of binary room-temperature ionic liquids with common cations/anions, *J. Chem. Eng. Data* 64 (2) (2019) 433–441, <https://doi.org/10.1021/acs.jced.8b00334>.
- [74] Q. Zhang, S. Cai, W. Zhang, Y. Lan, X. Zhang, Density, viscosity, conductivity, refractive index and interaction study of binary mixtures of the ionic liquid 1-ethyl-3-methylimidazolium acetate with methyldiethanolamine, *J. Mol. Liq.* 233 (2017) 471–478, <https://doi.org/10.1016/j.molliq.2017.03.036>.
- [75] X. Hu, S. Zhang, C. Qu, Q. Zhang, L. Lu, X. Ma, X. Zhang, Y. Deng, Ionic liquid based variable focus lenses, *Soft Matter* 7 (2011) 5941–5943, <https://doi.org/10.1039/C1SM05585B>.
- [76] X. He, Q. Shao, W. Kong, L. Yu, X. Zhang, Y. Deng, A simple method for estimating mutual diffusion coefficients of ionic liquids–water based on an optofluidic chip, *Fluid Phase Equilib.* 366 (2014) 9–15, <https://doi.org/10.1016/j.fluid.2014.01.003>.
- [77] S. Calixto, M. Rosete Aguilar, O.L. Torres Rocha, F.J. Sanchez Marin, M. Calixto Solano, E.M. Martínez Prado, Compound optofluidic small lenses with varifocal possibility, *Proceedings Volume 8287, Eighth Symposium Optics in Industry*; 828706, 2011. <https://doi.org/10.1117/12.910196>
- [78] G.G. Meena, J.G. Wright, A.R. Hawkins, H. Schmidt, Greatly Enhanced Single Particle Fluorescence Detection Using High Refractive Index Liquid-Core Waveguides, *IEEE J. Sel. Top. Quantum Electron.* 27 (2021) 1–7, <https://doi.org/10.1109/JSTQE.2021.3055078>.
- [79] S. Calixto, M. Rosete-Aguilar, F.J. Sanchez-Marín, O.L. Torres-Rocha, E.M. Martínez Prado, M. Calixto-Solano, Applications of ionic liquids in Science and Technology, S. Handy, Ed. InTech, 2011. <https://doi.org/10.5772/1769>
- [80] S. Seki, S. Tsuzuki, K. Hayamizu, Y. Umabayashi, N. Serizawa, K. Takei, H. Miyashiro, Comprehensive Refractive Index Property for Room-Temperature Ionic Liquids, *J. Chem. Eng. Data* 57 (8) (2012) 2211–2216, <https://doi.org/10.1021/je201289w>.
- [81] C.D. Rodríguez-Fernández, E. López Lago, C. Schröder, L.M. Varela, Non-additive electronic polarizabilities of ionic liquids: Charge delocalization effects, *J. Mol. Liq.* 346 (2022), <https://doi.org/10.1016/j.molliq.2021.117099> 117099.
- [82] O. Cabeza, J. Vila, E. Rilo, M. Domínguez-Pérez, L. Otero-Cernadas, E. López-Lago, T. Méndez-Morales, L.M. Varela, Physical properties of aqueous mixtures of the ionic 1-ethyl-3-methyl imidazolium octyl sulfate: A new ionic rigid gel, *J. Chem. Thermodyn.* 75 (2014) 52–57, <https://doi.org/10.1016/j.jct.2014.04.016>.

- [83] M. Prego, E. Rilo, E. Carballo, C. Franjo, E. Jiménez, O. Cabeza, Electrical conductivity data of alkanols from 273 to 333 K, *J. Mol. Liq.* 102 (2003) 83–91, [https://doi.org/10.1016/S0167-7322\(02\)00049-1](https://doi.org/10.1016/S0167-7322(02)00049-1).
- [84] M. Geppert-Rybczynska, J.K. Lehman, A. Heintz, Physicochemical properties of two 1-alkyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl)imide ionic liquids and of binary mixtures of 1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl)imide with methanol and acetonitrile, *J. Chem. Thermodyn.* 71 (2014) 171–181, <https://doi.org/10.1016/j.jct.2013.12.009>.
- [85] Q. Liu, L. Zhao, L. Ma, J. Chu, J. Wang, Y. Zang, Hydroxyethyl Group Effect on Properties of Bis((trifluoromethyl)sulfonyl)imide-Type Ionic Liquids, *J. Chem. Eng. Data* 65 (2020) 4780–4789, <https://doi.org/10.1021/acs.jced.0c00187>.
- [86] B. González, E.J. González, Physical properties of the pure 1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquid and its binary mixtures with alcohols, *J. Chem. Thermodyn.* 68 (2014) 109–116, <https://doi.org/10.1016/j.jct.2013.08.021>.
- [87] R. Majdan-Cegincara, M.T. Zafarani-Moattar, H. Shekaari, The study of solute–solvent interactions in 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate + acetonitrile from solvent activity, density, speed of sound, viscosity, electrical conductivity and refractive index measurements, *J. Mol. Liq.* 203 (2015) 198–203, <https://doi.org/10.1016/j.molliq.2014.12.048>.
- [88] M. Vranes, A. Tot, S. Papovic, N. Zec, S. Dozic, S. Gadzuric, Ideal and non-ideal behavior of 1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl)imide + γ butyrolactone binary mixtures, *J. Chem. Thermodyn.* 81 (2015) 66–76, <https://doi.org/10.1016/j.jct.2014.10.002>.
- [89] O. Borodin, W.A. Henderson, E.T. Fox, M. Berman, M. Gobet, S. Greenbaum, Influence of solvent on ion aggregation and transport in PY₁₅TFSl ionic liquid aprotic solvent mixtures, *J. Phys. Chem. B* 117 (2013) 10581–10588, <https://doi.org/10.1021/jp406541e>.
- [90] H. Vogel, The law of the relationship between viscosity of liquids and the temperature, *Phys. Z.* 22 (1921) 645–646.
- [91] G.S. Fulcher, Analysis of recent measurements of the viscosity of glasses, *J. Am. Ceram. Soc.* 8 (1925) 339–355, <https://doi.org/10.1111/j.1151-2916.1925.tb16731.x>.
- [92] G. Tammam, W. Hesse, Die Abhängigkeit der Viskosität von der Temperatur bei unterkühlten Flüssigkeiten, *Z. Anorg. Allg. Chem.* 156 (1926) 245–257, <https://doi.org/10.1002/zaac.19261560121>.
- [93] Y. Yamada, A. Yamada, Review-Superconcentrated Electrolytes for Lithium Batteries, *J. Electrochem. Soc.* 162 (2015) A2406–A2423, <https://doi.org/10.1149/2.0041514jes>.
- [94] J. Vila, P. Ginés, E. Rilo, O. Cabeza, L.M. Varela, Great increase of the electrical conductivity of ionic liquids in aqueous solutions, *Fluid Phase Equilib.* 247 (2006) 32–39, <https://doi.org/10.1016/j.fluid.2006.05.028>.
- [95] R.A. Di Leo, A.C. Marschilok, K.J. Takeuchi, E.S. Takeuchi, Battery electrolytes based on saturated ring ionic liquids: Physical and electrochemical properties, *Electrochim. Acta* 109 (2013) 27–32, <https://doi.org/10.1016/j.electacta.2013.07.041>.
- [96] R.N.S. Rofika, W. Hongowiranto, H. Jodi, S.u. Sudaryanto, E. Kartini, R. Hidayat, The effect of acetonitrile as an additive on the ionic conductivity of imidazolium –based ionic liquid electrolyte and charge-discharge capacity of its Li-ion battery, *Ionics* 25 (2019) 3661–3671, <https://doi.org/10.1007/s11581-019-02919-4>.
- [97] D.M. Seo, O. Borodin, S.-D. Han, Q. Ly, P.D. Boyle, W.A. Henderson, Electrolyte solvation and ionic association I. Acetonitrile-lithium salt mixtures: intermediate and highly associated salts, *J. Electrochem. Soc.* 159 (2012) A553–A565, <https://doi.org/10.1149/2.jes112264>.
- [98] D.M. Seo, O. Borodin, D. Balogh, M. O'Connell, Q. Ly, S.-D. Han, S. Passerini, W.A. Henderson, Electrolyte solvation and ionic association III. Acetonitrile-lithium salt mixtures—physical properties, *J. Electrochem. Soc.* 160 (2013) A1061–A1070, <https://doi.org/10.1149/2.018308jes>.