

Imidazolium-Based Protic Ionic Liquids as Electrolytes for Lithium-Ion Batteries

Timo Stettner,^[a] Florian C. Walter,^[a] and Andrea Balducci^{*[a]}

Protic ionic liquids (PILs) have been indicated as a promising class of ionic liquids (ILs) for the realization of high-performance lithium-ion batteries (LIBs). In this work we synthesize four different PILs containing the imidazolium-based cations 1,2-Dimethylimidazolium ($1,2\text{-DMim}^+$) and 1-Methylimidazolium (1-Mim^+), and the anions bis(trifluoromethanesulfonyl)imide (TFSI^-) and bis(fluorosulfonyl)imide (FSI^-). We show that these PILs display good conductivities and low viscosities and that they can be successfully used in combination with lithium iron phosphate (LFP) electrodes. Among the investigated electrolytes, 0.5 M LiTFSI in 1,2-DMIMTFSI appears as the most promising candidate for the realization of systems with high capacity retentions at high C-rates and high cycling stabilities.

In the last decade ionic liquids (ILs) have been extensively investigated as electrolytes for electrochemical energy storage devices due to the favorable combination of properties like low viscosity, high conductivity, low flammability and low vapor pressure that these molten salts might display.^[1] Several studies showed that ILs could positively contribute to the safety of batteries, e.g. lithium-ion batteries (LIBs).^[2–5] Until now, however, the performance of IL-based systems do not match that of conventional devices containing organic liquid electrolytes.^[6] Furthermore, the cost of ILs is typically higher than that of conventional electrolytes. For this reason, further efforts are required to realize IL-based LIBs with performance and costs comparable with those of the state-of-the art electrolytes. These efforts should be directed toward the realization of IL with designed properties for a specific device.

ILs can be divided in three subgroups: aprotic ionic liquids (AILs), protic ionic liquids (PILs) and zwitterionic ionic liquids. While the latter ones are often used in polymer gel electrolytes, in the field of batteries in general, AILs have been the most utilized subgroup.^[7–14] In the last years, however, the interest on the use of PILs as electrolytes for LIBs increased.^[6] It has been shown that PILs might display favorable transport and thermal properties, and that the presence of one or more proton(s) on the cation of these ILs, although limiting their cathodic stability, has a positive impact on the coordination of the lithium ions. This set of properties appears especially advantageous during tests at high current densities.^[15] PIL-based electrolytes have

been successfully used in combination with several cathodic materials, e.g. lithium iron phosphate (LFP), and anodic materials, e.g. graphite, used in LIBs.^[16–17] Nevertheless, many aspects related to the use of this subgroup of ILs in LIBs need to be further investigated.

So far, only a limited number of cations and anions have been utilized for the realization of PIL-based electrolytes.^[17–19] It is well known, however, that the chemical composition of the cation and the anion of ILs is dramatically affecting their properties.^[20] Therefore, investigations dedicated to the influence of the cation-anion combination on the properties of PIL-based electrolytes suitable for LIBs are of importance for the realization of devices containing these electrolytes.

Imidazolium based AILs have been intensively investigated as electrolytes for LIBs but, to the best of our knowledge, only a very limited number of studies reported the use of PIL based on this cation as electrolytes for LIBs. Nevertheless, taking into account the favorable properties of imidazolium-based ILs, their use could be of great interest for the realization of advanced LIBs. In this communication we report for the first time an investigation about a series of imidazolium-based PIL suitable for battery application containing the cations 1,2-Dimethylimidazolium ($1,2\text{-DMim}^+$) and 1-Methylimidazolium (1-Mim^+), and the anions bis(trifluoromethanesulfonyl)imide (TFSI^-) and bis(fluorosulfonyl)imide (FSI^-). In the first part of the manuscript, the chemical-physical properties of the electrolytes are investigated in detail. In the second part, the impact of these electrolytes on the chemical physical performance of LFP electrodes is reported.

Figure 1 shows the chemical structures of the PILs investigated in this work. For each PIL the used acronym as well as the state of aggregation at room temperature (RT) are also reported. As shown in the figure, the nature of the anion has a

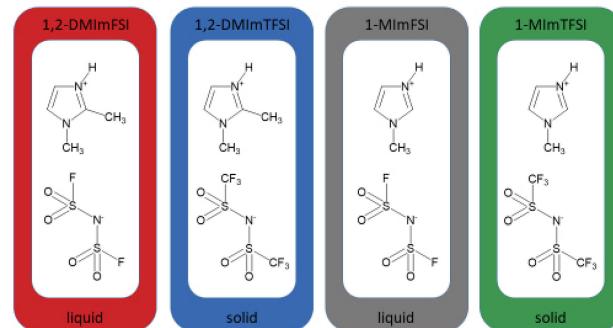


Figure 1. Overview of the synthesized and investigated PILs. The state of aggregation refers to RT.

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strong influence on the aggregation state at room temperature. At RT the PILs containing TFSI^- as anion are solids, while those containing the FSI^- anion are liquids. A similar behavior has been also reported for pyrrolidinium based ILs and, therefore, is not surprising.^[17] It is important to notice that the state of aggregation at RT is strongly depending on the water content of the PIL. When large amounts of water (1% or more) are present in the PIL, the large majority of these compounds are liquids.^[19,21] When the content is reduced to only a few ppm, as in the case of this work, the difference in terms of aggregation state becomes visible. Unfortunately, this aspect has not been always carefully considered in the past and several PILs have been indicated as room temperature ILs even if they are not.

Figure 2 compares the conductivity, viscosity and density of the PILs investigated in this work. As shown in the figure, the nature of the anion has a strong influence on the chemical-physical properties of these ILs. Figure 2a shows that among the investigated PILs, the 1,2-DMImTFSI displays the highest viscosity over the whole investigated range of temperature (27.2 mPa s at 60 °C). The replacement of the cation 1,2-DMIm $^+$ with the smaller cation 1-MIm $^+$ reduces the viscosity of the PIL, but not dramatically: 1-MImTFSI displays a viscosity of 22.3 mPa s at 60 °C. To the contrary, a significant change in viscosity is observed when the smaller FSI^- replaces the TFSI^- anion. As indicated in the figure, 1,2-DMImFSI and 1-MImFSI display viscosities of 16.0 mPa s and of 15.6 mPa s, respectively, at 60 °C. These values are approx. 30% lower than those observed for the TFSI-based PILs are. Considering these differences, it is reasonable to assume that the TFSI^- anion is responsible for higher ionic binding strengths, and thus higher viscosities, compared to the anion FSI^- . This effect is most likely related to the bigger size of the TFSI^- anion, which facilitates the sterical matching between anion and cation.^[22] Figure 2b shows a comparison of the conductivities of the investigated PILs. As shown, 1-MImFSI displays the highest conductivity over the whole temperature range. At 60 °C, it displays a conductivity of 20.8 mS/cm. At 30 °C this PIL displays a conductivity of 9.5 mS/cm.

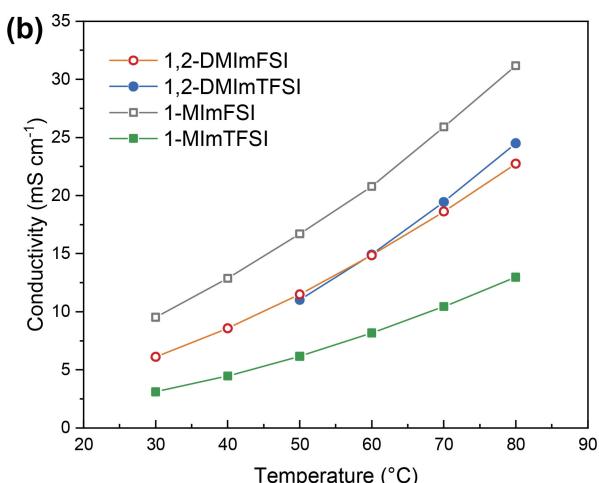


Figure 2. Influence of the temperature on the (a) viscosity, (b) conductivity, and (c) density of the PIL investigated in this work.

cm, a value comparable to that of conventional electrolytes for LIBs.^[23] On the other hand, 1-MImTFSI shows the lowest conductivity among all the PIL, with values of 3.1 mS/cm and 8.2 mS/cm at 30 °C and 60 °C, respectively. Taking these differences into account, the presence of the anion TFSI^- appears to have a rather strong (and negative) impact on the conductivity of PILs containing the cation 1-MIm $^+$. It is interesting to notice, however, that this impact appears much less significant when the cation 1,2-DMIm $^+$ is used. As shown in the figure, at 60 °C 1,2-DMImTFSI and 1,2-DMImFSI display conductivities of 14.9 mS/cm and 14.8 mS/cm, respectively. Taking these results into account it seems that the cation 1,2-DMIm $^+$ influences the conductivity much more than the cation 1-MIm $^+$. In order to confirm this assumption, however, a systematic investigation of the properties of PILs containing these cations and different anions would be necessary. This study, nevertheless, is out of the scope of the present work. Figure 2c compares the variation of the density over temperature of the investigated PILs. As shown, the 1-MIm $^+$ based PILs display a higher density than the corresponding 1,2-DMIm $^+$ PILs. Additionally, the PILs containing TFSI^- have a higher density compared to that containing the anion FSI^- . This latter finding could be related to the higher viscosity of the TFSI^- anion.

Figure 3 shows a comparison of the electrochemical stability window (ESW) of the investigated PILs. As shown, in all PILs the cathodic limit is located around -0.6 to -0.65 V vs. Ag. This limit is obviously defined by the reduction of the proton in the cation of the PIL. From the results reported in the figure, it is evident that the different number of methyl groups present on the imidazolium cations used in this work does not seem to have an impact on the stability of the "free" proton. The anodic limit of the PIL is related to the nature of the anion and, as shown, the TFSI-based are slightly more stable than the FSI-based PILs. This result is in line with the results available in literature.^[17] 1,2-DMImFSI decomposes around 1.9 V vs. Ag, while all other PILs appear to be stable up to 2.0 V vs. Ag. Consequently, the overall ESW of this latter PIL is of approx. 2.55 V, while those of all the others amounts to approx. 2.75 V.

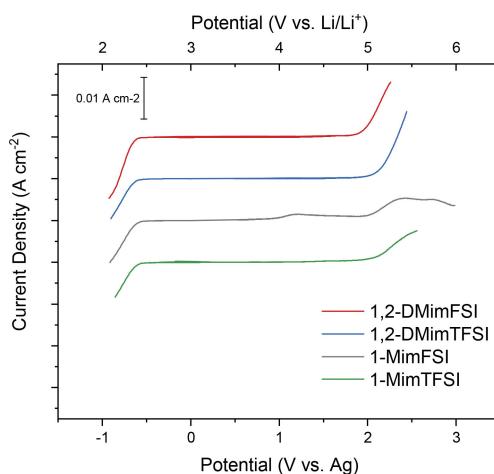


Figure 3. Electrochemical stability window of the pure synthesized PILs at 60 °C.

These values are slightly lower than those observed for pyrrolidinium based PIL.^[24] A similar trend has been also reported for AILs.^[25]

After the chemical-physical investigation described above, all the PIL have been mixed with 0.5 M LiTFSI to realize electrolytes suitable for a use in combination with LFP electrodes. After some initial test CVs which have been carried out to guarantee a good wetting of the LFP electrodes (results not shown), a C-rate test at 60 °C has been carried out. The results of these tests are reported in Figure 4. At 0.5 C the LFP

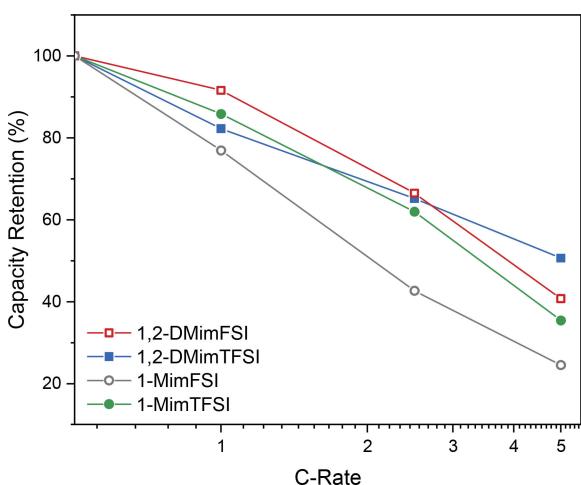


Figure 4. Capacity retention over increasing C-rate of LFP electrodes used in combination with electrolyte containing 0.5 M LiTFSI in PIL. The tests have been carried out at 60 °C.

electrodes display in 0.5 M LiTFSI in 1,2-DMImTFSI, 0.5 M LiTFSI in 1,2-DMImFSI, 0.5 M LiTFSI in 1-MimTFSI and 0.5 M LiTFSI in 1-MimFSI specific capacities of 158 mAh g⁻¹, 167 mAh g⁻¹, 113 mAh g⁻¹ and 143 mAh g⁻¹, respectively. These values indicate that in the investigated electrolytes the LFP electrodes can deliver good capacities, comparable or even higher of those observed in AILs or other PILs.^[17] When the C-rate is increased, the electrode capacity decreases, as expected. In spite of this, it is interesting to notice that overall the use of these PIL-based electrolytes allows a good retention capacity during tests carried out at high current densities. Among the investigated electrolytes, 0.5 M LiTFSI in 1,2-DMImTFSI appears as the most promising. The LFP electrode cycles in this electrolyte were able to retain more than 90% of their initial capacity at 1 C, and more than 50% at 5 C. For this reason, we decided to further investigate the behavior of the LFP electrodes in this electrolyte. In order to get information about the influence of the anion of the PIL on the electrochemical performance of LFP electrode, also the electrolyte 0.5 M LiTFSI in 1,2-DMImFSI has been considered.

Figure 5a shows a comparison of the capacity retention of LFP electrodes over 100 charge-discharge cycles carried out at 1 C and at 60 °C. As shown, the LFP electrode used in combination with 0.5 M LiTFSI in 1,2-DMImFSI was not displaying a good capacity retention, and after 25 cycles this electrode

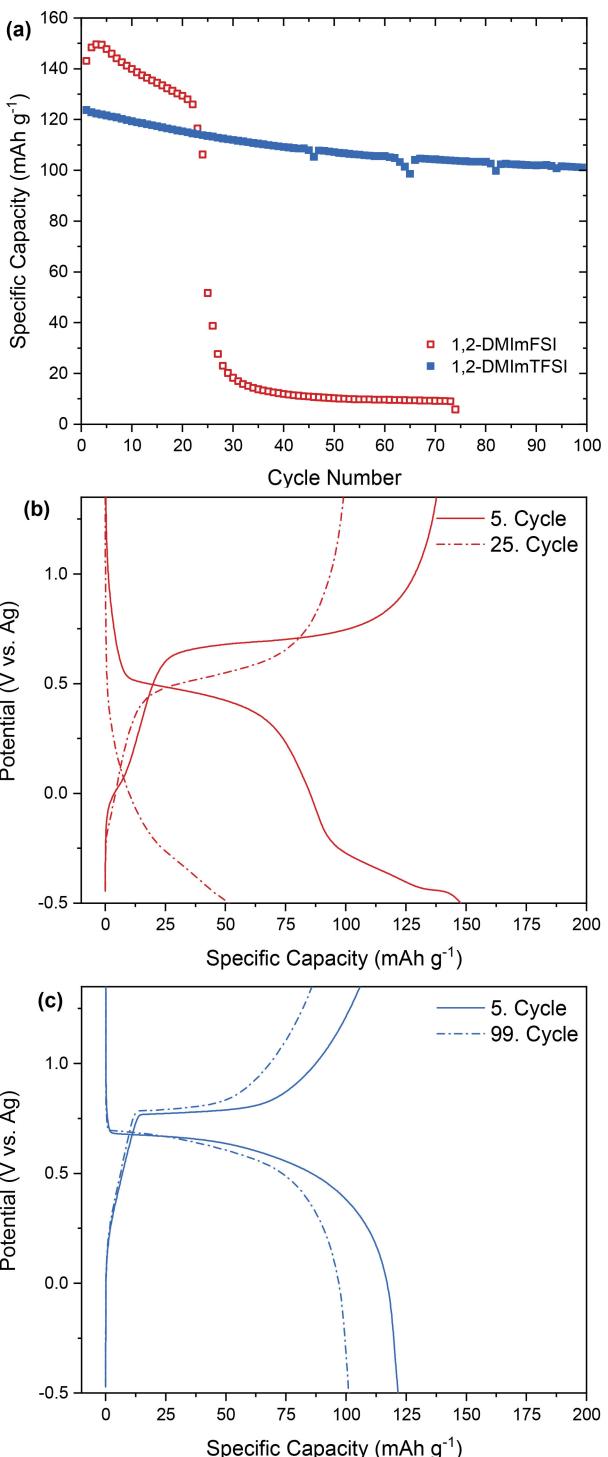


Figure 5. (a) Specific Capacity of LFP electrodes during test carried out at 60 °C and 1 C in combination with 0.5 M LiTFSI in 1,2-DMImFSI and 0.5 M LiTFSI in 1,2-DMImTFSI; (b) and (c) charge-discharge profiles of the LFP electrodes in the investigated electrolytes.

was not able to display a decent capacity. As shown in Figure 5b, this capacity fade was originated by the occurrence of (parasitic) reactions during the cycles, which were strongly reducing the efficiency of the charge-discharge process. To the contrary, the LFP electrode cycled in 0.5 M LiTFSI in 1,2-DMImTFSI was displaying a much more stable behavior, and it

was able to retain more than 80% of its initial capacity after 100 cycles. During the whole duration of the cycling process, no parasitic reactions were observed, and the efficiency of the charge-discharge was always close to 100% (Figure 5c). It has been shown that TFSI-based IL are typically displaying higher thermal stability compared to the FSI-based one^[6], and this difference could be one of the reasons of the better stability observed in 1,2-DMImTFSI. Study about this important point are currently in progress.

The realization of designed ILs is of crucial importance for the introduction of this class of electrolytes in electrochemical energy storage devices. In this manuscript we reported the chemical physical properties of four different imidazolium-based PILs, and we showed that these ILs display promising transport properties. Furthermore, we showed that despite their rather limited ESW, they can be successfully used as electrolytes for LIBs. Among the investigated PIL-based electrolytes 0.5 M LiTFSI in 1,2-DMImTFSI appears as the most promising. LFP electrodes utilized in combination with this electrolyte can deliver high capacity at low as well as at high C-rates and a good capacity retention during prolonged charge-discharge cycles carried out at 1 C and 60 °C. Further investigations are certainly needed to better understand the impact of imidazolium-based PILs on the electrochemical performance of other active cathodic and anodic active materials. Nevertheless, these results confirm that PILs can be seen as an interesting class of electrolyte for the realization of high-performance solvent-free LIBs.

Experimental

Synthesis of PILs

The PILs have been synthesized with a procedure similar to that reported in reference^[26]. The freshly distilled precursor, either 1,2-dimethylimidazole, or 1-methylimidazole (59.34 mmol, obtained by Aldrich) was put in a two-neck flask, topped by a reflux condenser and a dropping funnel. The latter one was filled with 5.35 ml HCl (35%, obtained by Merck). While dropping the HCl slowly to the precursor, the reaction mixture was stirred and cooled using an ice bath. After complete addition, the mixture was stirred at room temperature for 2 hours. Residual water was then evaporated using vacuum, to obtain a white salt, which was put into the two-necked flask for the next step. The flask was equipped with a reflux condenser and a dropping funnel. LiTFSI or LiFSI (59.34 mmol, obtained by Iolitec) was solved in 20 ml H₂O, filled into the dropping funnel and slowly dropped into the flask. Two phases were obtained during this metathesis, an aqueous on top and the PIL below. After complete addition and 2 h further stirring, the aqueous phase was removed using a separation funnel. To make sure no residual by-product LiCl was solved in the PIL, it was washed with water five times consecutively. The wash water was mixed with AgNO₃ to verify LiCl absence. As a last step, the PIL was dried under vacuum (10^{-3} mbar) and at 80 °C for three days. Following this procedure the PILs 1,2-dimethylimidazolium bis(trifluoromethanesulfonyl)imide (1,2-DMImTFSI), 1,2-dimethylimidazolium bis(fluorosulfonyl)imide (1,2-DMImFSI), 1-methylimidazolium bis(trifluoromethanesulfonyl)imide (1-MImTFSI) and 1-methylimidazolium bis(fluorosulfonyl)imide (1-MImFSI) were obtained. All PILs

display water contents lower than 30 ppm, as determined using Karl Fischer titration.

Electrolyte Preparation

Electrolytes containing the synthesized PILs and 0.5 M LiTFSI (Iolitec) have been prepared in an MBraun LABmaster[®] ECO glove box with <1 ppm H₂O and <1 ppm O₂. The water content of all electrolytes was lower than 30 ppm.

Chemical-Physical-Characterisation

The conductivities of the electrolytes were measured using a potentiostat ModuLabXM (Solartron analytical) in the temperature range comprised between -30 and 80 °C.^[27] The viscosity of the electrolytes was determined using a rheometer MCR 102 (Anton Paar) in the temperature range comprised between -30 and 80 °C.^[27] The density of the electrolytes was determined in the temperature range comprised between 10 and 80 °C, using a density meter DMA 4100 M (Anton Paar).

Electrode Preparation

LFP composite electrodes were prepared following a procedure identical to that used by Menne et al.^[28] The dry composition of the electrodes is 85 wt% of active material (LFP, Südchemie) 10 wt% of conducting agent (Super C65, Imerys) and 5 wt% of binder (carboxymethyl cellulose, Dow). The mass loading of the electrodes is comprised between 2.5 mg/cm² and 3.2 mg/cm²; the electrode area was equal to 1.13 cm².

As (oversized) counter electrodes, activated carbon-based electrodes were used. The electrodes were prepared following the procedure indicated in reference^[29]. The electrodes composition is 90 wt% of activated carbon (DLC Super, Norit), 5 wt% of carbon Black (Super C65, Imerys) and 5 wt% of binder (polytetrafluoroethylene, Aldrich). The mass loading of these electrodes is about 40 mg/cm², and their area 1.33 cm².

Electrochemical Measurements

The ESWs of the electrolytes were measured in a Swagelok cell using a platinum electrode as working electrode, an oversized carbon electrode as counter electrode, and a silver electrode as pseudo reference electrode. 150 µl of the pure synthesized PILs have been utilized. After a 1.5-hour open circuit voltage (OCV) measurement (needed to reach an equilibrium), the cells were swept from OCV towards either positive or negative direction using a scan rate of 1 mV/s. Since one of the investigated electrolytes (1-MimTFSI) was liquid only above 60 °C, all the ESW measurements have been carried out in an oven at 60 °C, to make a fair comparison between the PILs possible.

The electrochemical behavior of the LFP electrodes in the PIL-based electrolytes has been investigated in a Swagelok cell. In the case of these measurements, the LFP working electrode was coupled with an oversized carbon counter electrode. As reference, a silver electrode was used. 150 µl of the prepared 0.5 M LiTFSI in PIL has been used as electrolyte. The first step of the measurements has been an OPV measurement for 8 hours. Afterwards, 10 cycles of cyclic voltammetry (CV) were carried out using a scan rate of 5 mV/s. Subsequently, the LFP electrodes were charged-discharged using C-rates ranging from 0.5 C to 5 C. For this test, the theoretical capacity of LFP (170 mAh g⁻¹) was used to define 1 C. Finally, tests at 1 C were carried out to investigate the electrode stability over

cycling. All the electrochemical tests have been carried out in an oven at 60 °C.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: electrolytes • imidazolium • lithium-ion batteries • lithium iron phosphate • protic ionic liquids

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