Ionic Liquid Hybrid Electrolytes for Lithium-Ion Batteries: A Key Role of the Separator–Electrolyte Interface in Battery Electrochemistry

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ⓢ *Supporting Information*

ABSTRACT: Batteries are multicomponent systems where the theoretical voltage and stoichiometric electron transfer are defined by the electrochemically active anode and cathode materials. While the electrolyte may not be considered in stoichiometric electron-transfer calculations, it can be a critical factor determining the deliverable energy content of a battery, depending also on the use conditions. The development of ionic liquid (IL)-based electrolytes has been a research area of recent reports by other researchers, due, in part, to opportunities for an expanded high-voltage operating window and improved safety through the reduction of flammable solvent content. The study reported here encompasses a systematic investigation of the physical properties of IL-based hybrid electrolytes including quantitative characterization of the electrolyte–separator interface via contact-angle measurements. An inverse trend in the conductivity and wetting properties was observed for a series of IL-based electrolyte candidates. Test-cell measurements were undertaken to evaluate the electrolyte performance in the presence of functioning anode and cathode materials, where several promising IL-based hybrid electrolytes with performance comparable to that of conventional carbonate electrolytes were identified. The study revealed that the contact angle influenced the performance more significantly than the conductivity because the cells containing IL–tetrafluoroborate-based electrolytes with higher conductivity but poorer wetting showed significantly decreased performance relative to the cells containing IL–bis(trifluoromethanesulfonyl)imide electrolytes with lower conductivity but improved wetting properties. This work contributes to the development of new IL battery-based electrolyte systems with the potential to improve the deliverable energy content as well as safety of lithium-ion battery systems.

KEYWORDS: ionic liquid, contact angle, electrolyte, lithium battery, separator
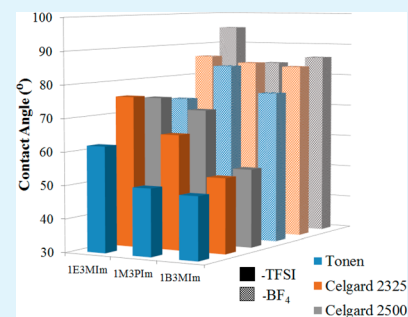
1. INTRODUCTION

The need for understanding the contributions to the deliverable energy content of batteries has taken on an increased significance because of an ever-expanding range of battery applications, including grid level systems and devices involving aerospace, transportation, portable electronics, and biomedical applications.[1] Along with energy content and power considerations, the safety of batteries under typical use and abuse conditions is a key consideration for practical implementation. Electrolytes and separators are often overlooked when it comes to battery performance because they do not affect the stoichiometric theoretical electron storage capacity of a battery. However, electrolytes and separators can affect charge transport within a battery, which ultimately affects the deliverable energy content under a specific application.

In addition, reducing the flammability of the battery electrolyte is a sound strategy toward increasing the safety of batteries especially under abuse conditions. Toward this end, ionic liquids (ILs) are being investigated as possible alternatives to conventional electrolytes.[2−4] While ILs have been known for

some time, the study of ILs in battery electrolytes is a more recent field of study.[5,6] For example, battery studies of neat ILs as well as for mixed solutions have been conducted to probe the effects of ILs on battery electrochemistry.[7−17]

Recent reports involving ILs in battery electrolytes include systematic investigations of IL–solvent mixtures, where the electrochemical stabilities and conductivities of the mixtures were assessed and correlated with the physical properties or structural characteristics of the ILs.[18,19] The physical and electrochemical properties of a series of ILs based on imidazolium and pyridinium cations with tetrafluoroborate (BF_4^-) and bis(trifluoromethanesulfonyl)imide ($TFSI^-$) anions neat and mixed with ethylene carbonate (EC) or propylene carbonate (PC) were reported. Higher conductivities were observed with imidazolium cations, BF_4^- anions, and shorter-chain-length substituents, while lower conductivities were

observed with pyridinium cations, TFSI⁻ anions, and longer-chain-length substituents. Investigation of ILs based on saturated ring cations, piperidinium and pyrrolidinium, were also conducted, showing further improvement of the electrochemical stability.

Investigating the physical and electrochemical properties of ILs and IL-based electrolytes in a systematic way provides the insight necessary to tune ILs for various battery applications. The conductivities of electrolytes are often a primary focus of electrolyte studies because the conductivity directly affects charge transport. However, another critical electrolyte property that is less studied is the ability of an electrolyte to wet the active and inactive surfaces in a battery. Electrolyte wetting properties, as determined by the contact angle, can be an illustrative measurement to assess electrolyte–electrode and electrolyte–separator compatibility and ultimately fundamental battery electrochemistry properties. Some previous studies of the ability of ILs to wet surfaces have been reported;[20−26] however, fewer reports address the contact angle of ILs on substrates relevant to lithium-ion batteries.[27]

The study reported here is an investigation of the wetting properties of ILs and IL–carbonate solvent blends, with and without salt on battery-relevant substrates, on composite electrode surfaces and separators by contact-angle measurements. The impact of the substituent chain length, the cation type, and the anion type of the ILs was determined. Further, the influence of adding either PC or EC to the IL was studied. Finally, the wetting properties of the electrolytes including lithium-based salts were measured. An inverse trend in the conductivity and wetting properties was observed for a series of IL-based electrolyte candidates. Both the electrolyte and electrolyte–separator interface contribute to the cell conductivity; thus, although the ionic conductivity plays an important role in the cell conductivity, without appropriate wetting of the battery components, the cell conductivity will be low. Electrochemical test cells containing lithium-metal anodes, IL-based hybrid electrolytes, separators, and lithium–iron phosphate (LiFePO₄) cathodes were used to evaluate the electrochemical performance, where the influence of the IL anion, carbonate cosolvent, and separator type was probed during the study. This work provides the fundamental insight necessary for the development of new IL battery-based electrolyte systems designed to improve the deliverable energy content and safety of lithium-ion batteries.

2. EXPERIMENTAL SECTION

ILs used for these experiments were purchased from Iolitec Inc. and dried under vacuum prior to use. The water content after drying was measured to be below 50 ppm for all ILs. After drying, the IL solutions and electrolytes were prepared in an inert-atmosphere glovebox. Contact-angle measurements were carried out using a Kyowa DropMaster DM-501 series instrument, using the sessile-drop method. Values were averaged over six measurements for a given solution on a substrate. Commercially obtained samples of separator [Tonen E25 (Toray Battery Separator Co., Ltd.), polyethylene; Celgard 2325 (Celgard, LLC.), trilayer polypropylene/polyethylene/polypropylene; Celgard 2500 (Celgard, LLC.), polypropylene] were evaluated as substrates.

Composite electrodes were prepared in-house by coating mixtures onto aluminum foil. The mixtures consisted of active material (LiFePO₄ (MTI Corp.) or Li₄Ti₅O₁₂ (MTI Corp.), carbon, and poly(vinylidene difluoride) (PVDF). Viscosity measurements were taken at 23 °C with a Brookfield LVT viscometer with a cone/plate attachment. Contact-angle and viscosity measurements were com-

pleted in a dry room at −45 °C dew point to minimize water uptake during measurement.

Electrochemical test cells were constructed with LiFePO₄ electrodes opposite lithium-metal anodes, using IL hybrid electrolytes as described in the Results and Discussion section. Control cells utilized EC and dimethyl carbonate (DMC) based solvents with lithium tetrafluoroborate (LiBF₄), lithium hexafluorophosphate, or lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salts. Cells were cycled between 4.2 and 2.0 V versus lithium at ∼10 mA/g.

3. RESULTS AND DISCUSSION

ILs continue to hold interest as possible electrolytes for lithium-based batteries. Therefore, characterization of ILs with regard to their conductivity, electrochemical stability, and thermal safety has been pursued.[18,19] Prior reports indicate that saturated cation-based ILs, in particular pyrrolidinium, exhibit high upper voltage limits of stability as well as wide windows of voltage stability.[18,19,28−30] The imidazolium-based ILs demonstrate high conductivities compared to ILs based on other cations. Therefore, ILs based on pyrrolidinium and imidazolium cations were selected for the bulk of this study. Piperidinium- and pyridinium-based ILs were also investigated to enable a broader comparison of the compositional features important to ILs.

The specific objective of this study was to assess the wetting properties of material surfaces contained in batteries by IL-based hybrid electrolytes. As noted above, the conductivity, electrochemical stability, and lithium-ion transference numbers are important for an effective electrolyte. However, the wetting properties of electrolytes should also be considered because the electrochemistry takes place at a solid surface and batteries contain membranes (separators) that must provide facile ion transport. For these studies, the wetting properties of four classes of solutions were investigated utilizing contact-angle measurements on a variety of battery-relevant substrates. The first group of solutions used neat ILs comprised of a series of cations (piperidinium, pyrrolidinium, imidazolium, and pyridinium) with variation of the organic substituents and two anions, either BF₄⁻ or TFSI⁻. The abbreviations and general structures for each of the ILs are provided for clarity (Table 1). The second group of solutions incorporated blends of ILs with carbonate solvents, specifically EC or PC. The third group of solutions included ILs and dissolved electrolyte salts, either LiBF₄ or LiTFSI. The fourth and final group contained ILs, carbonate solvents, and dissolved electrolyte salts.

Neat ILs. The impact of the substituent chain length, cation type, and anion type of the neat ILs was of interest for this study. Prior to undertaking the broader study of the influences of the factors noted, a series of substrates were tested with neat ILs. Three separator types (Tonen, Celgard 2325, and Celgard 2500) and composite electrodes with either LiFePO₄ or Li₄Ti₅O₁₂ were tested. In all cases, the contact angles for the aluminum foil, PVDF-coated copper foil, and Li₄Ti₅O₁₂ or LiFePO₄ composite electrodes (Figure 1a) were notably lower than the values measured for the separator materials (Figure 1b). For example, the contact angles for wetting by 1M1PPyrr-TFSI determined for the LiFePO₄ and Li₄Ti₅O₁₂ electrodes were 17.7° and 17.2°, while the separator contact-angle values ranged from 46.4° to 53.0°. Similar results were obtained using 1B3MIm-TFSI (or 1B3MIm-BF₄), where the contact angles for the LiFePO₄ and Li₄Ti₅O₁₂ electrodes were 11.9° and 14.8° (22.9° and 29.2°), while the separator contact-angle values ranged from 48.9° to 53.7° (from 75.9° to 85.9°). Thus, for the bulk of the studies, contact-angle measurements focused on the

Table 1. IL Names, Abbreviations, and Structures

Full Name	Abbreviation
1-methyl-1-propylpiperidinium-bis(trifluoromethylsulfonyl)imide	1M1PPi-TFSI
1-butyl-1-methylpiperidinium-bis(trifluoromethylsulfonyl)imide	1B1MPi-TFSI
1-ethyl-1-methylpyrrolidinium-tetrafluoroborate	1E1MPyrr-BF4
1-methyl-1-propylpyrrolidinium-tetrafluoroborate	1M1PPyrr-BF4
1-butyl-1-methylpyrrolidinium-tetrafluoroborate	1B1MPyrr-BF4
1-ethyl-1-methylpyrrolidinium-bis(trifluoromethylsulfonyl)imide	1E1MPyrr-TFSI
1-methyl-1-propylpyrrolidinium-bis(trifluoromethylsulfonyl)imide	1M1PPyrr-TFSI
1-butyl-1-methylpyrrolidinium-bis(trifluoromethylsulfonyl)imide	1B1MPyrr-TFSI
1-ethyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)imide	1E3MIm-TFSI
1-methyl-3-propylimidazolium-bis(trifluoromethylsulfonyl)imide	1M3PIm-TFSI
1-butyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)imide	1B3MIm-TFSI
1-ethyl-3-methylimidazolium-tetrafluoroborate	1E3MIm-BF4
1-methyl-3-propylimidazolium-tetrafluoroborate	1M3PIm-BF4
1-butyl-3-methylimidazolium-tetrafluoroborate	1B3MIm-BF4
1-propyl-3-methylpyridinium-bis(trifluoromethylsulfonyl)imide	1P3MPy-TFSI
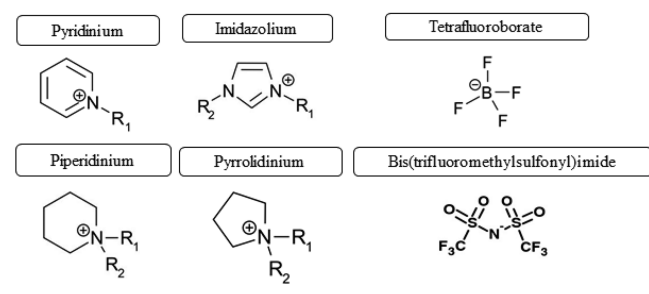
use of separators as substrates because they showed the largest values and most significant variation in the contact angle.

The effect of the cation in ILs on the conductivity has been studied;[19] therefore, it was also investigated by contact-angle measurements in this work. The contact-angle values comparing the pyrrolidinium, piperidinium, imidazolium, and pyridinium cations with the TFSI⁻ anion across three different separator materials were determined (Figure 1b). Specifically, commercially obtained samples of Tonen E25 polyethylene, Celgard 2325 trilayer polypropylene/polyethylene/polypropylene, and Celgard 2500 polypropylene were used for the studies. Some trends in the separator material are apparent from the data; all of the ILs have the smallest contact angle with Tonen (polyethylene), followed by Celgard 2325 (polyethylene/polypropylene layered material), with Celgard 2500 (polypropylene) showing the highest contact-angle values. The effect of the cation can be categorized by size and by a saturated versus unsaturated ring. For the unsaturated cations (pyridinium and imidazolium), the larger, six-membered-ring

pyridinium-based IL showed smaller contact angles than its five-membered-ring counterpart, imidazolium, across all three separator types. However, for the saturated ring ILs (pyrrolidinium and piperidinium), the smaller five-membered-ring pyrrolidinium-based IL has smaller contact angles across the three separator types compared to its piperidinium (six-membered ring) counterpart. This suggests that there are competing factors of size and saturation level affecting the wettability of the separators by ILs.

The effect of the substituent chain length on the conductivity and other properties of ILs has been previously assessed.[31−33] In line with investigation of this effect, Figure 2 shows the contact angle on the three separator types for a series of imidazolium-based ILs with substituent chain lengths ethyl, propyl, and butyl, having both BF₄⁻ and TFSI⁻ anions. For the Im-TFSI series on the Tonen separator, the ethyl substituent shows a contact angle of approximately 63°, with the propyl and butyl substituents showing lower values near 50.5° and 49°, respectively. Representative optical micrographs are shown in Figure 2a. For the Tonen substrate, the contact angle trends to lower values with longer chain length. This trend is consistent with other work in which different ILs were studied.[21,26,27] In this series, the property of longer length of the substituent aids in wetting the separator by adding to the hydrophobic nature of the IL,[34] thus making it more compatible with the hydrophobic separator membranes used as substrates for these studies. The role of the anion of the IL can be seen in Figure 2 as well. On Tonen, the BF₄⁻ anion-based ILs with ethyl, propyl, and butyl chain lengths have contact angles of 73°, 84°, and 76°, respectively, all higher than their TFSI⁻ counterparts (Figure 2b). The contact angles for the two anions for three different-chain-length ILs all show the trend that, for the imidazolium cation, ILs with the TFSI⁻ anions have lower contact angles than those with the BF₄⁻ anions, suggesting that they are better able to wet separators compared to BF₄⁻. The anion size does significantly influence the hydrophobic nature of the IL, with larger ions showing increased hydrophobic properties, which in this case leads to improved separator wetting.[34] The Celgard substrates show generally higher contact angles across the series, with similar values between the Celgard 2325 and 2500 separator in each case.

In order to probe further the behavior of the ILs, viscosity measurements of the ILs were also determined. The influence of both the anion type and substituent chain length on the
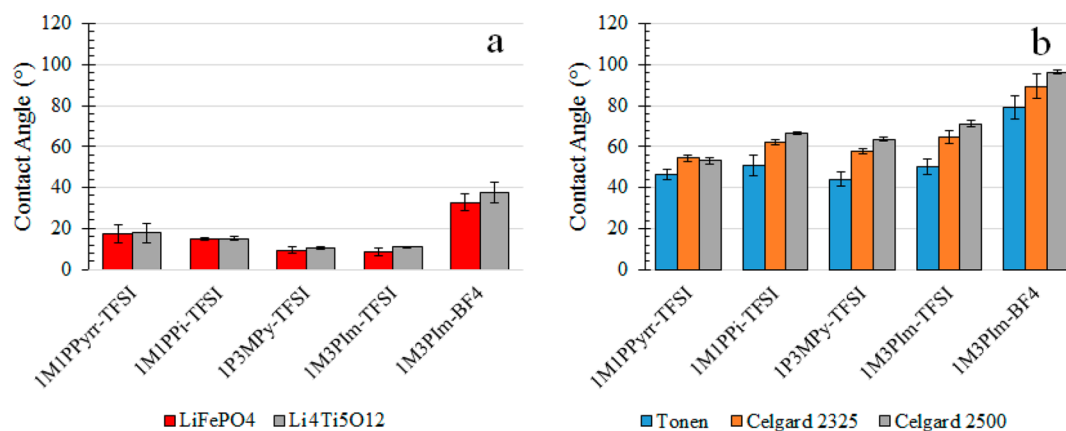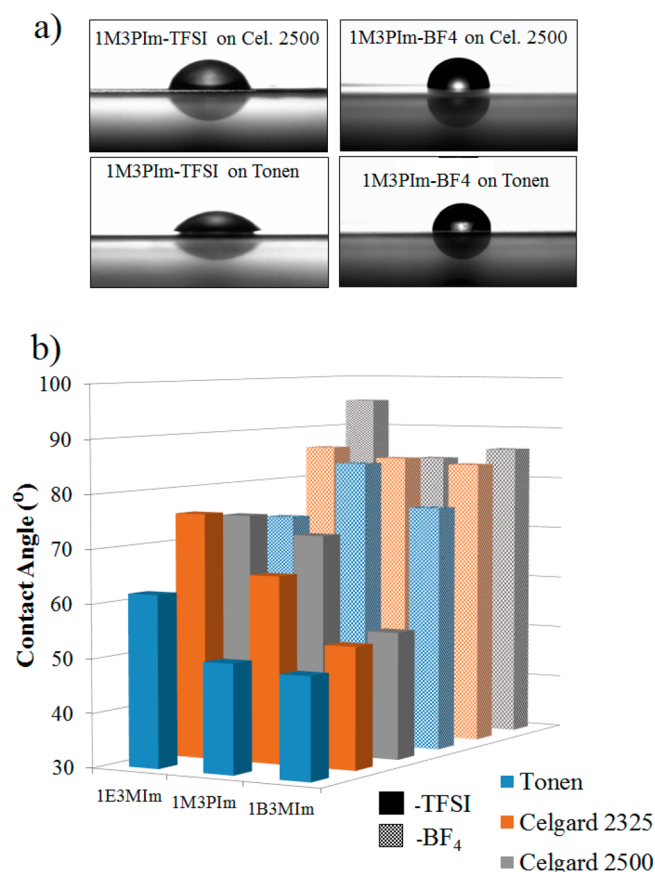

Figure 1. IL contact angles measured on various (a) electrode and (b) separator substrates. Error bars represent 1 standard deviation of six measurements for each IL and surface combination.

Figure 2. Contact angle as a function of the IL and separator type: (a) optical images; (b) quantitative data. Solid bars represent the TFSI⁻ anion, and hatched bars represent the BF₄⁻ anion.


Figure 3. Contact angle and viscosity as a function of the IL cation substituent and anion type. Contact-angle error bars represent 1 standard deviation for six measurements of each IL on Celgard 2325 separators. Viscosity error bars represent 1 standard deviation for six measurements of each IL.

contact angle is considered in relation to the viscosity of the IL (Figure 3). These data suggest some interesting trends in the behavior of the ILs. First, viscosity values increase with an increase of the substituent chain length across both anion types. Previous studies observed the same trend that longer alkyl chain lengths on the cation increase the viscosity of the IL.[34−36] The viscosities of BF₄⁻-based ILs scale from 52.8 to 93.6 to 166.1 cP from ethyl to propyl to butyl chain length, while those for TFSI⁻-based ILs increase from 43.5 to 62.1 to 69.4 cP (Figure 3). Thus, these data affirm higher viscosity values for the BF₄⁻-based ILs. The data imply that, for the smaller anion, more ordering of the IL contributes to higher viscosity. In addition to the viscosity trends, there is also a trend in contact-angle values with the chain length, where longer chain lengths have lower contact angles. This is very clear in the TFSI⁻ series, where the ILs have contact angles of 75.6°, 64.7°, and 52.6° for the ethyl, propyl, and butyl substituents, respectively. There may also be a trend in the contact angle for the BF₄⁻-based ILs, but the changes with the substituent chain length are much less apparent. Notably, the contact angles for the BF₄⁻-based ILs are also significantly larger than those for the TFSI⁻-based ILs, ranging from 83.5° to 86.2°. For the measurements shown on the substrates involved in this study, these observed trends suggest that while longer chain lengths give rise to higher and, thus, less desirable viscosity values, they show the opposite behavior in wettability as determined by contact-angle measurements, where longer substituents lead to improved wetting of the hydrophobic surfaces such as separator membranes.
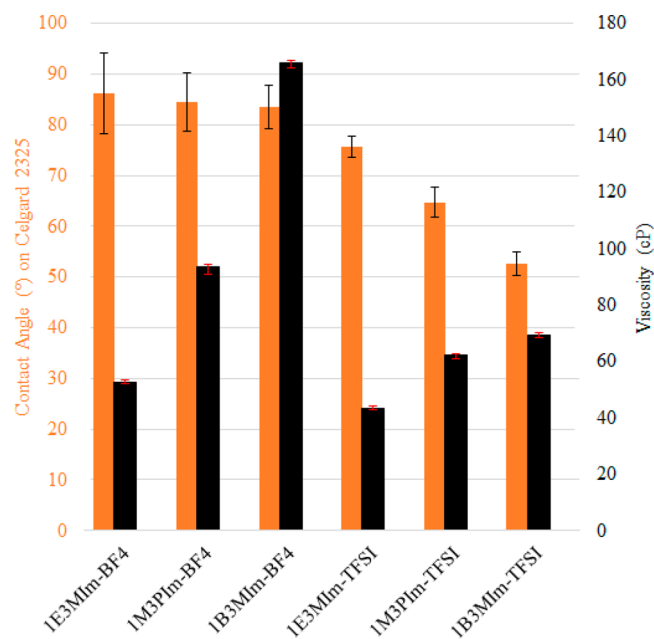
ILs and Carbonate Solvents. Previous studies have reported a reduction of the high-viscosity values and an accompanying increase in the conductivity of neat ILs by mixing with other solvents, in many cases carbonates.[8,19,37] In this work and in previous work by this group, the effect of mixing ILs with carbonate solvents was studied.[18,19] The effect of EC or PC in 1:1 (v/v) mixtures with ILs on the contact angle was studied. The contact angles of the IL/solvent mixtures were taken on Tonen and Celgard 2500 separator materials as substrates. Specifically, the contact angles of neat 1M3PIm-BF₄, 1M3PIm-TFSI, and 1M1PPyrr-TFSI and mixed with EC or PC were determined. When measured on Tonen, the IL 1M3PIm-BF₄ (an unsaturated cation and BF₄⁻ anion) has a rather high contact angle of 84°, while the addition of PC or EC lowers it to 73°. When measured on Celgard 2500, the pure IL 1M3PIm-BF₄ had the same high contact angle of 84°, while PC lowered the contact angle relative to the pure IL (75°), but the addition of EC did not (96°). For 1M3PIm-TFSI on Celgard 2500, contact-angle measurements were lower (71°) than those for 1M3PIm-BF₄ (84°). However, for 1M3PIm-TFSI, the addition of PC lowered the contact angle on Celgard 2500 (58°), while EC did not (78°). In comparison, the neat IL 1M1PPyrr-TFSI (a saturated cation and TFSI⁻ anion) has a low contact angle of 46° on Tonen. The addition of PC results in no change in the contact angle with a value of 47°, while the addition of EC slightly increases the value to 54° on a Tonen separator. On Celgard 2500, the neat IL 1M1PPyrr-TFSI has a low contact angle of 53°, while the addition of PC and EC results in an increase in the contact angle (70° and 73°, respectively). These results indicate that the addition of EC or PC to an imidazolium BF₄⁻-based IL may slightly improve the wettability of a hydrophobic separator membrane. This is consistent with the higher ordering of the BF₄⁻-based ILs, as reflected by the higher viscosity values of BF₄⁻-based ILs compared to their TFSI⁻-based counterpart

ILs.[19] In the case of TFSI-based ILs, there is no significant improvement in the contact angle resulting from addition of EC or PC.

ILs and Lithium Salts. It is of interest to consider the impact of added salt because a lithium-based salt would be used for the formulation of a battery electrolyte. Lithium salt where the anion matched the anion of the IL, either LiTFSI or LiBF$_4$, was added. The contact angle and conductivity were determined for neat IL and 0.5 and 1.0 M concentrations of lithium salt in IL. Figure 4 shows the contact angles for these
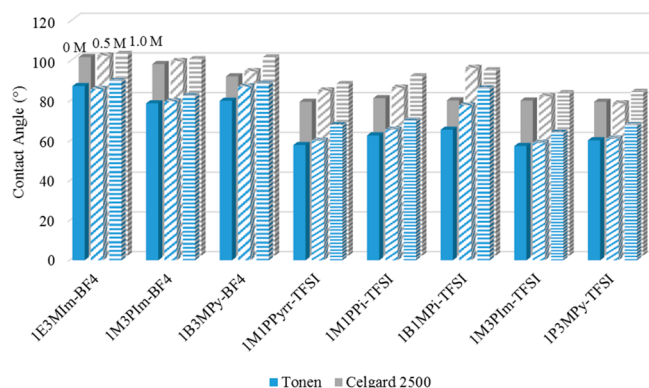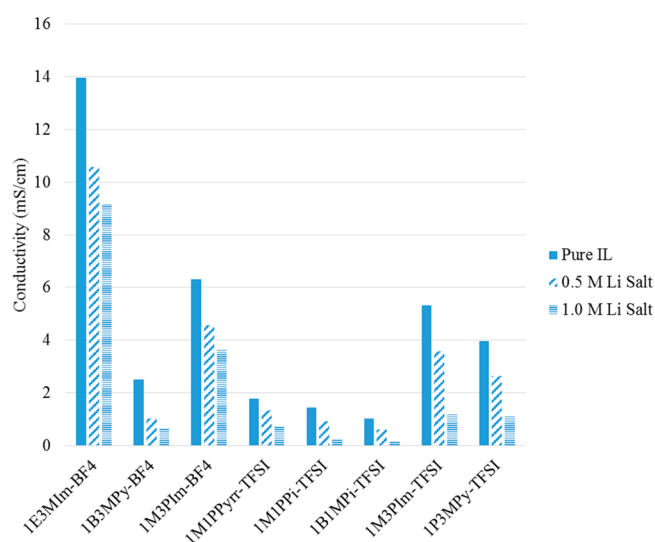

Figure 4. Contact angle on the Tonen and Celgard 2500 separator for (a) pure ILs and ILs with (b) 0.5 M and (c) 1.0 M added lithium salt. For each IL, the left column indicates pure IL, the middle column represents 0.5 M lithium salt, and the right column shows 1.0 M lithium salt.

lithium salt−IL solutions with 0 M, 0.5 M, and 1 M salt in various ILs. For each IL, there is a general trend of increasing contact angle with increasing lithium salt concentration. Also, contact angles measured on Celgard 2500 separators are consistently larger than the measurements on the Tonen separators. Most notable is the separation of the data based on the anion type. Samples with BF$_4^-$ anions consistently have higher contact angle than samples with TFSI$^-$ anions. This relationship is illustrated by fixing the cation and comparing 1M3PIm-BF$_4$ to 1M3PIm-TFSI. 1M3PIm-TFSI displayed much smaller contact angles than its BF$_4^-$ counterpart. This trend was observed over all measured cation types. Also worth noting is that the addition of salt has a much smaller impact on the contact angle of BF$_4^-$-based mixtures than that of TFSI$^-$ mixtures.

As lithium salt is added to the neat ILs, the conductivity is reduced with the 1.0 M salt, showing a further decrease in the conductivity than the 0.5 M salt concentration (Figure 5). Notably, the samples with BF$_4^-$ anions generally showed higher conductivity than the samples with TFSI$^-$ anions. With the addition of lithium salt, the conductivity is more significantly reduced for the TFSI$^-$ ILs than the BF$_4^-$-based samples. For example, the conductivity of 1E3MIm-BF$_4$ decreases from 14 to 9 mS/cm (about 36% loss in conductivity), while the conductivity of 1B1MPi-TFSI decreases from 0.95 to 0.125 mS/cm (about 87% loss in conductivity) compared to the salt concentrations of 0 and 1 M.

IL, Carbonate Solvents, and Lithium Salts. To complete the full analysis of the effects of adding carbonate solvents and lithium salts, electrolytes with ILs, carbonates, and lithium salts were also investigated. Figure 6 shows the contact-angle measurements for 50% by volume of ILs (1M3PIm-BF$_4$,

Figure 5. Conductivity of (a) pure ILs and ILs with (b) 0.5 M and (c) 1.0 M added lithium salt. For each IL, the left column indicates pure IL, the middle column represents 0.5 M lithium salt, and the right column shows 1.0 M lithium salt.
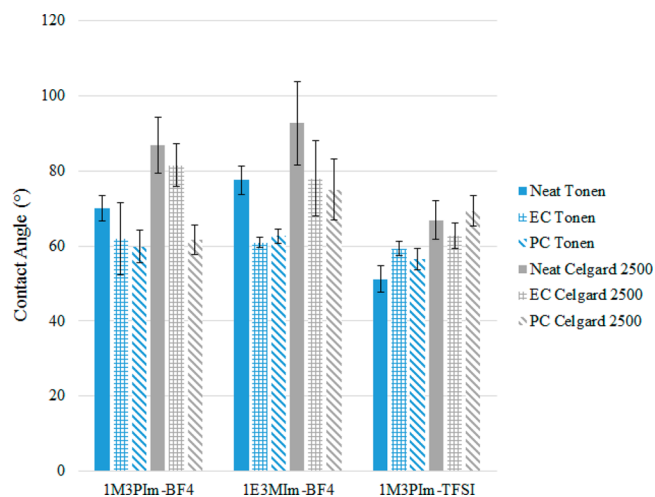

Figure 6. Contact angles for electrolytes consisting of 50% by volume IL (1M3PIm-BF$_4$, 1E3MIm-BF$_4$, or 1M3PIm-TFSI), 50% by volume carbonate (EC or PC), and 0.5 M lithium salt (LiBF$_4$ or LiTFSI). Neat IL with no carbonate and no lithium salt is also plotted for reference. Error bars represent 1 standard deviation of 10 measurements for each IL and separator combination.

1E3MIm-BF$_4$, and 1M3PIm-TFSI) blended with 50% by volume of either EC or PC and 0.5 M lithium salt with the corresponding anion BF$_4^-$ or TFSI$^-$. The contact angles were significantly smaller for Tonen compared to Celgard 2500, which agrees with the results in Figure 2. This suggests that Tonen has a better wettability with these types of electrolytes as well. In general, electrolytes with PC solvent produced contact angles smaller or similar to those mixed with EC. For all combinations except 0.5 M LiTFSI in 1M3PIm-TFSI with PC, the mixtures of IL, carbonate, and salt produced smaller contact angles and showed better wettability than the neat ILs. These 6 combinations of IL, carbonate, lithium salt, and separator were chosen for electrochemical testing in coin cells with the Tonen E25 and Celgard 2500 separators.

Electrochemical Performance. Electrochemical performance assessment of the IL hybrid electrolytes was conducted using LiFePO$_4$ cathodes versus lithium-metal anodes. In order to probe the behavior of the lithium salt anion, a control group of cells containing lithium salts based on TFSI$^-$, BF$_4^-$, or PF$_6^-$ anions dissolved in carbonate solvents (EC/DMC) with a Celgard 2500 separator were prepared and tested. All of the cells from this control group delivered ~140 mAh/g of active cathode material. Cells using the hybrid electrolytes were assembled to explore the variables of the separator (Tonen E25 vs Celgard 2500), anion (BF$_4^-$ vs TFSI$^-$), organic solvent additive (EC vs PC), and substituent length (ethyl vs propyl) using imidazolium-based ILs. These variables cover a range of conductivities and contact angles for the separators and electrolyte combinations.

The performance of the cells under cycle testing was observed to cluster into two groups: (1) cells that showed good performance delivering ~140 mAh/g of active cathode material and (2) those that functioned very poorly, typically delivering <10 mAh/g of active cathode material (Figure 7). The anion
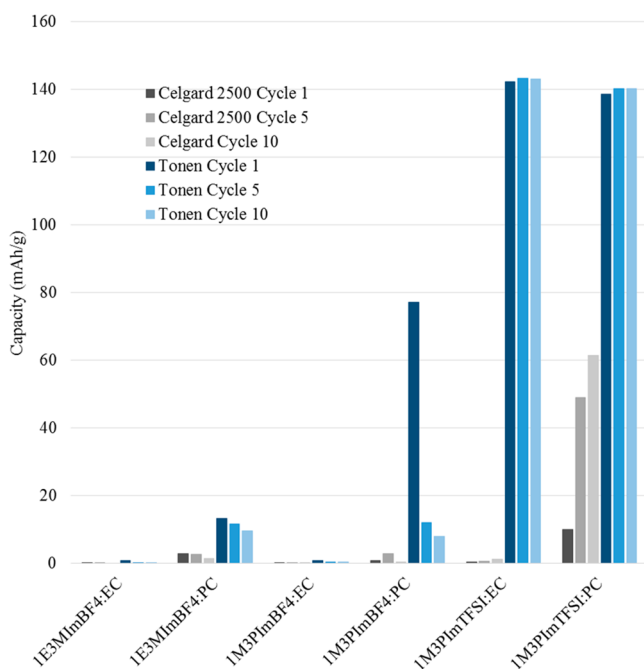
Figure 7. Discharge capacities of the 1st, 5th, and 10th cycles for cells with LiFePO$_4$ cathodes, lithium-metal anodes, and IL hybrid electrolytes with 0.5 M lithium salt.

type influenced the cell performance significantly, where the cells based in the BF$_4^-$ electrolyte consistently delivered low capacities. Independent of the solvent, separator, or substituent types, the cells with the BF$_4^-$ anion delivered <10 mAh/g of the cathode material by cycle 10. However, in the TFSI$^-$-based cell group, the cells assembled using the Tonen E25 separator performed well, while the cells assembled using the Celgard 2500 separator showed first cycle capacities of ≤10 mAh/g. One cell with 0.5 M LiTFSI in the 1M3PImTFSI:PC electrolyte delivered 10 mAh/g on cycle 1 and 61 mAh/g on cycle 10, consistent with the gradual wetting of the separator during use of the cell. Notably, there was no strong correlation with the solvent type, PC or EC, or the imidazolium cation substituent. The results demonstrate a strong interaction

between the separator and anion types, where cells with a combination of the Tonen E25 separator and TFSI$^-$-based electrolyte performed well while the cells utilizing BF$_4^-$ salt or the Celgard 2500 separator overall performed poorly.

The observed cell performance is consistent with the contact-angle results obtained for the IL-based solutions where the Tonen E25 separator showed lower contact angles than the Celgard separators 2325 and 2500 (Figures 2, 4, and 6). Further, TFSI$^-$-based ILs showed lower contact angles and improved wetting compared to BF$_4^-$-based ILs, also consistent with the performance characteristics of the cells. Notably, the BF$_4^-$-based ILs with and without added lithium salt often show higher conductivity than the TFSI$^-$ analogues (Figure 5). However, they also consistently show higher contact angle with separator materials (Figures 2, 4, and 6). The cell testing results highlight that the influence of the contact angle and separator wetting may be a critical determining factor in the cell performance. In the data from this study, the electrochemical cell performance correlates more strongly with the contact angle than the conductivity.

4. SUMMARY

The contact angles for neat ILs, ILs blended with carbonate solvents, EC or PC, ILs with lithium salt, and IL−carbonate solvent blends with added lithium salt were determined on battery-relevant surfaces. The contact angles of the solutions on composite electrodes were generally low. However, significant differences in the contact angles could be seen among solutions studied when measured on the separator surfaces. Generally, the contact angles observed on Tonen E25 (polyethylene) separators were lower than those observed on Celgard 2325 (polyethylene/polypropylene layered material) and Celgard 2500 (polypropylene). The role of the substituent on the organic cation was explored. In this series, the property of the longer length of the substituent (ethyl, propyl, and butyl) aids in the wetting of the separator by adding to the hydrophobic nature of the IL, thus making it more compatible with the hydrophobic separator membrane.

The role of the anion of the IL was investigated, where imidazolium-based ILs with BF$_4^-$ or TFSI$^-$ anions were studied. The contact angles for the two anions for three different-chain-length ILs all show the trend for the imidazolium cation, that the ILs with the TFSI$^-$ anions have lower contact angles than those with the BF$_4^-$ anions, suggesting that they are better able to wet separators compared to BF$_4^-$. The anion size significantly influences the hydrophobic nature of the IL, with larger ions showing increased hydrophobic properties, which in this case lead to improved separator wetting.

The role of added carbonate-based solvents EC or PC was explored. The addition of EC or PC to a BF$_4^-$-based IL may improve the wettability of a hydrophobic separator membrane, but the addition of PC- or EC-based solvents to a TFSI$^-$-based IL did not provide any further enhancement of the wetting properties. This is consistent with the higher ordering of the BF$_4^-$-based ILs, as reflected by the viscosity values, where the viscosity of BF$_4^-$-based imidazolium ILs is higher than that of TFSI$^-$-based imidazolium ILs. The contact angles of the IL blends with the carbonate solvents typically either did not change or increased on the order of 5° with the addition of 0.5 or 1 M salt.

The full combination of IL, solvents EC or PC, and lithium salts of BF$_4^-$ or TFSI$^-$ was explored on the surfaces of Tonen

E25 and Celgard 2500. The Tonen separator showed significantly smaller contact angles and better wettability than Celgard 2500. Hybrid IL-based electrolytes prepared by the addition of carbonate solvent and lithium salt generally showed lower contact angles than the corresponding neat ILs.

The material compatibility and cell electrochemistry involving the hybrid IL electrolytes were tested in lithium-based coin cells utilizing LiFePO$_4$ cathodes. The anion type influenced the cell performance significantly, where none of the cells based in the BF$_4^-$ hybrid electrolyte performed well, uniformly delivering low capacities. However, some of the cells containing electrolytes based on TFSI$^-$-type ILs delivered capacities of ~140 mAh/g consistent with the lower contact angles and improved wetting compared to BF$_4^-$-based electrolytes. The results demonstrate a strong interaction between the separator type and IL anion type, where a combination of the Tonen E25 separator and TFSI$^-$-based hybrid IL electrolyte provided the best performance of the groups tested.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Contact-angle measurements as a function of time and a Walden plot. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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