

Ionic liquids for rechargeable lithium batteries

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Abstract

We have investigated possible anticipated advantages of ionic-liquid electrolytes for use in lithium-ion batteries. Thermal stabilities and phase behavior were studied by thermal gravimetric analysis and differential scanning calorimetry. The ionic liquids studied include various imidazoliumTFSI systems, pyrrolidiniumTFSI, BMIMPF₆, BMIMBF₄, and BMIMTf. Thermal stabilities were measured for neat ionic liquids and for BMIMBF₄-LiBF₄, BMIMTf-LiTf, BMIMTFSI-LiTFSI mixtures. Conductivities have been measured for various ionic-liquid lithium-salt systems. We show the development of interfacial impedance in a Li|BMIMBF₄ + LiBF₄|Li cell and we report results from cycling experiments for a Li|BMIMBF₄ + 1 mol/kg LiBF₄|C cell. The interfacial resistance increases with time and the ionic liquid reacts with the lithium electrode. As expected, imidazolium-based ionic liquids react with lithium electrodes. We seek new ionic liquids that have better chemical stabilities.

Introduction

A general trend in modern chemical engineering is to move to environmentally friendly processes. New chemical processes should be designed to reduce or eliminate generation of hazardous wastes. Ionic liquids are expected to provide alternatives for a variety of industrial-scale applications and for electrochemical devices. Numerous ionic liquids are known but only a small number has been investigated; for most of them, only a few properties have been studied. Because ionic liquids are nonvolatile at ordinary temperatures, and because they are non-flammable, they provide potential environmental advantages relative to conventional solvents. Properties and applicability of ionic liquids are not easily predicted. Solutes, impurities, undesired or desired reaction products alter the physical, chemical, and electrochemical behavior of a particular system. Interactions of ionic liquids with materials, or unwanted chemical reactions can eliminate the anticipated advantages in industrial applications. Knowledge of pure-component properties of ionic liquids is essential but not sufficient.

Recently, there has been increased interest in research toward using ionic liquids in chemical- process and electrochemical applications (e.g. Abraham 1993; Abraham et al. 2003; Anthony et al. 2002; Brenneke and Maginn 2001; Dupont 2002; Marsh 2004; Poole 2004; Rogers and Seddon 2002; Welton 1999, Abbot et al. 2005; Diez et al. 2005; Nakashima et al. 2005). These reviews tend to be concerned primarily with using ionic liquids for separation operations or as media for synthesis of organic and bio-organic products. However, other possible applications of ionic liquids include sensors, solar cells, light-emitting electrochemical cells and electrochromic devices, including displays (Lee and Chou 2004; Wang 2003; Lu 2002; Paulsen 2003; Yang 2003; Lu 2004). Ionic-liquid electrolytes are promising new electrolyte materials in power sources for electric vehicles, hybrid cars, electronic and power-storage devices, especially at extreme conditions. An advantage of ionic liquids is that they are not only conducting, but also nonvolatile at ordinary temperatures and, in most cases, thermally stable.

Ionic liquids show a large liquid range that allows a large temperature range for electrochemical devices. For rechargeable lithium-ion batteries, we require that any electrolyte, provide adequate durability, high conductivity, good transport properties and, very important, chemical and electrochemical stability with safety (Howlett 2004; Passerini 2003; Garcia 2004). We seek a salt/ionic-liquid system that provides chemical stability with electrode materials equal or better than that using a conventional salt-solvent system. We anticipate that a well-chosen salt/ionic-liquid system may be especially useful at low and elevated temperatures where conventional systems often give poor performance.

Ionic liquids studied and experimental methods

An ionic liquid typically contains a large organic cation and an inorganic anion. Figure 1 shows some pertinent cations and anions.

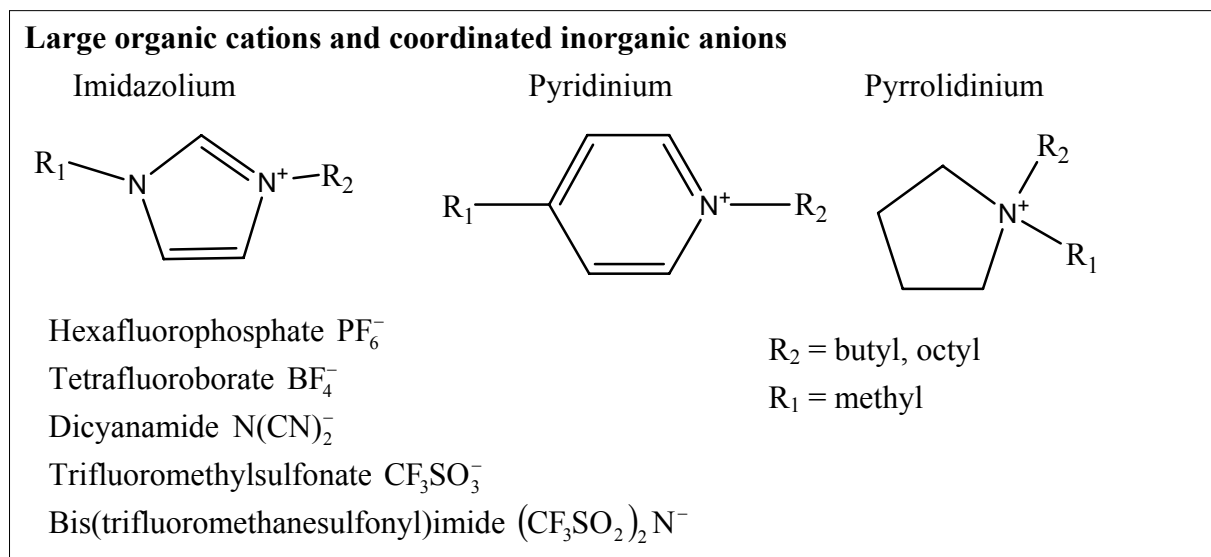


Figure 1. Ions for typical ionic liquids.

Table 1 lists ionic liquids used here and Table 2 lists our experimental equipment for measuring some battery-oriented physical properties of ionic liquids.

Table 1. Ionic liquids studied in this work.

n-Butylmethylimidazolium hexafluorophosphate	BMIMPF ₆
n-Butylmethylimidazolium tetrafluoroborate	BMIMBF ₄
n-Butylmethylimidazolium triflate	BMIMTf
n-Butylmethylimidazolium bis(trifluoromethanesulfonyl)imide	BMIMTFSI
n-Butylmethylpyrrolidinium bis(trifluoromethanesulfonyl)imide	P _{1,4} TFSI
Octylmethylimidazolium tetrafluoroborate	OMIMBF ₄
Octylmethylimidazolium bis(trifluoromethanesulfonyl)imide	OMIMTFSI
Octylmethylimidazolium triflate	OMIMTf
Butylmethylpyridinium bis(trifluoromethanesulfonyl)imide	BMPyrTFSI
Butylmethylpyridinium tetrafluoroborate	BMPyrBF ₄

Table 2. Experimental Equipment for Our Experimental Studies of Electrochemical Properties

Perkin-Elmer Differential Scanning Calorimeter, DSC 7
Perkin-Elmer Thermogravimetric Apparatus, TGA 7
Solartron, Schlumberger, 1254 four-channel frequency-response analyzer
Helium-Atmosphere Glove boxes

TGA measurements

Thermal stabilities of three ionic liquids have been studied using a Perkin-Elmer thermo-gravimetric analyzer, TGA 7. Thermal stabilities were measured for neat ionic liquids and for ionic-liquid / lithium-salt mixtures. All systems studied are thermally stable below 200°C. The thermal analysis was carried out in a platinum pan with similar sample size (23 mg) and with a 10°C / min scanning rate under dry-nitrogen flow. Prior to measurement, all ionic liquids were kept in a 1-mbar vacuum 24-48 h in the presence of P₂O₅. Figure 2 shows results for neat butylmethylimidazolium based ionic liquids.

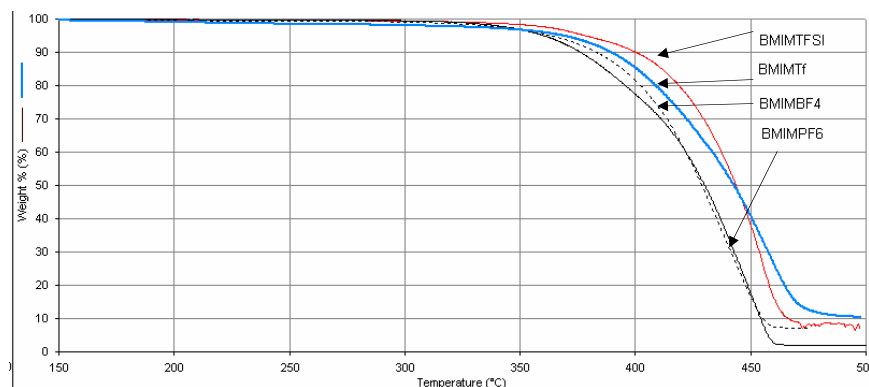


Figure 2. Thermal stabilities of several neat butylmethylimidazolium (BMIM) salts. All of these systems are thermally stable below 250°C.

Results for several octylmethylimidazolium- and pyridinium salts are shown in Figure 3.

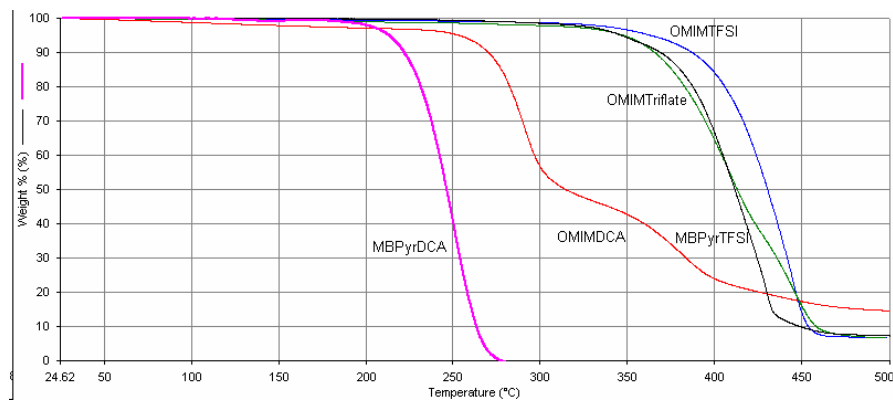


Figure 3. Thermal stabilities of various OMIM- and pyridinium-based ionic liquids.

Figures 4 and 5 show thermal stabilities for BMIMBF₄ + LiBF₄ and BMIMTf + LiTf salt mixtures.

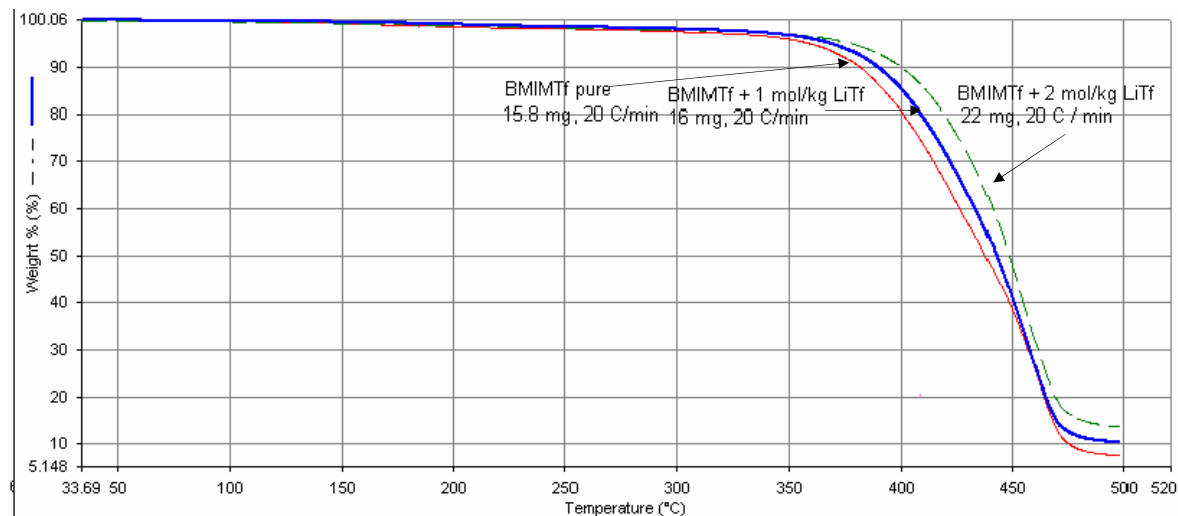


Figure 4. Thermal stabilities of pure BMIMTf and with added LiTf salt, 1 mol/kg and 2 mol/kg. Stability increases with added lithiumtriflate salt.

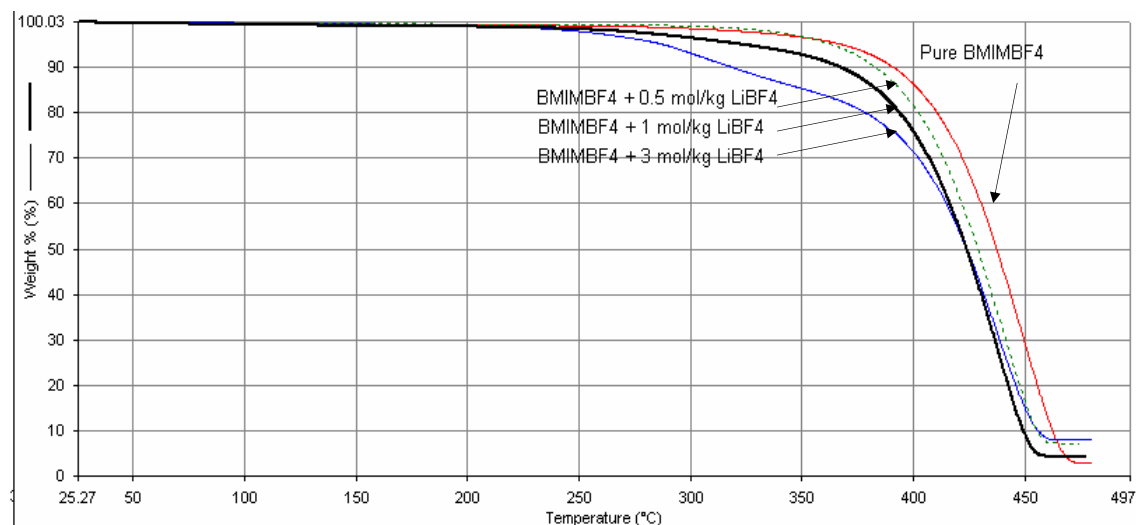


Figure 5. Thermal stabilities of pure BMIMBF₄ and with added LiBF₄ salt, 0.5, 1, and 3 mol/kg. Stability decreases slightly with added lithiumtetrafluoroborate salt.

Differential Scanning Calorimetry (DSC) measurements

DSC measurements provide data for the phase behavior of ionic liquids and their salt solutions. With DSC, we observe the glass-transition temperature T_g , melting point T_m , and crystallization temperature T_{cr} for different salt / ionic-liquid compositions. Table 3 presents DSC results. Ionic liquids form glasses at low temperatures. The glass-transition temperature T_g is the minimum temperature for the liquid. Some ionic liquids show only a glass-transition temperature while others can show multiple phase changes.

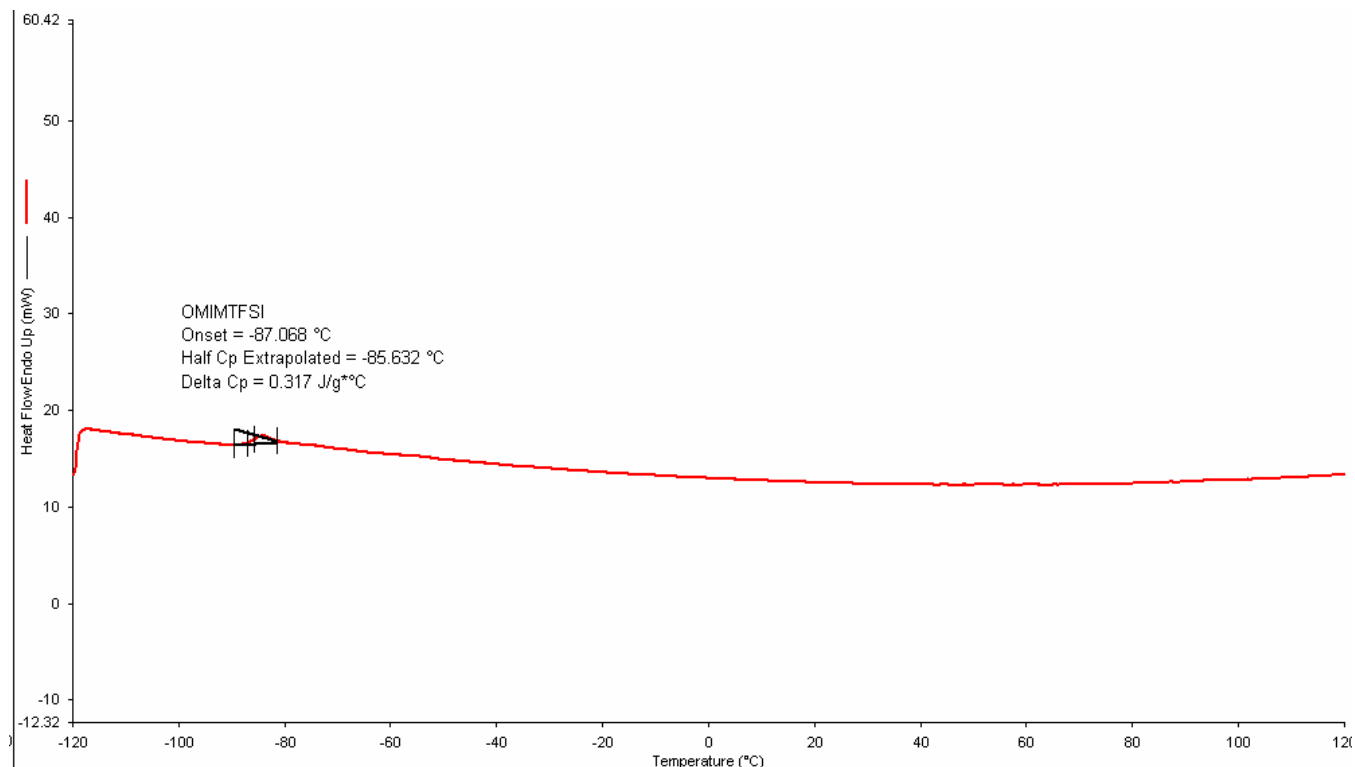


Figure 6. Octylmethylimidazolium TFSI shows only a glass-transition temperature. The absence of a melting point is observed for many ionic liquids with TFSI⁻ and BF₄⁻ anions.

Table 3. Melting (T_m) and glass-transition (T_g) temperatures for ionic liquids shown in Table 1. Reference literature data are shown for comparison.

	T_m / C	T_m / K	Ref. T_m / K	T_g / C	T_g / K	Ref. T_g / K
BMIMBF ₄	---	---	---	-86	187	188
BMIMPF ₆	7	280	281	-81	192	192
BMIMTf	15	288	289			191
BMIMTFSI	-5	268	NA	-91	182	NA
OMIMBF ₄	---	---	---			194, 192
OMIMTFSI	---	---	---	-87	186	189
OMIMTf	5	278	NA	-80	193	NA
MBPyrTFSI	10	283	---	-80	193	189
MBPyrBF ₄	---	---	---	-65	208	197
P ₁₄ TFSI			270			186

We measured the phase behavior of the BMIMTf–LiTf and BMIMBF₄–LiBF₄ systems. Addition of lithium triflate salt into BMIMTf decreases the melting point significantly. The glass-transition temperature for the 1 mol/kg LiTf system is slightly higher than that for the neat liquid (-80°C as opposed to -80°C).

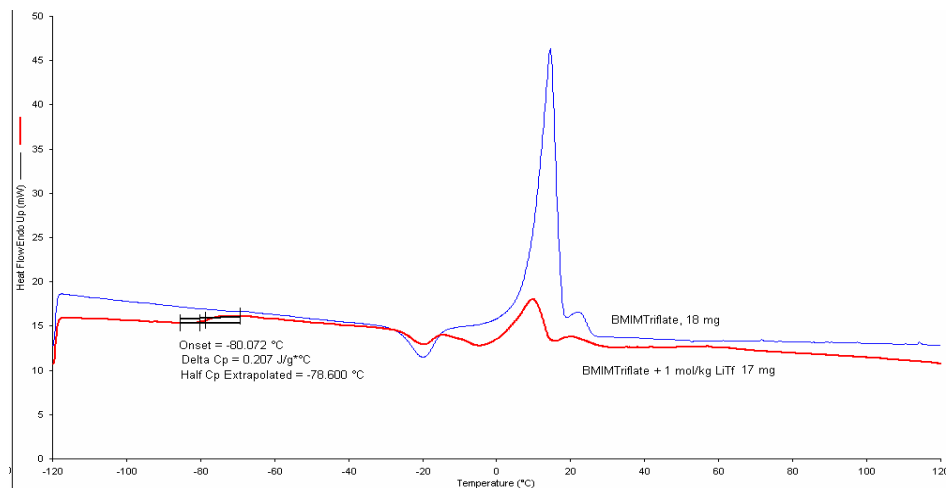


Figure 7. Addition of a lithium salt depresses the melting point. Result for neat BMIMTf and for BMIMTf + 1 mol/kg LiTf.

Neat BMIMBF₄ has no melting point nor does its solution with LiBF₄. Mixing BMIMBF₄ with LiBF₄ increases T_g .

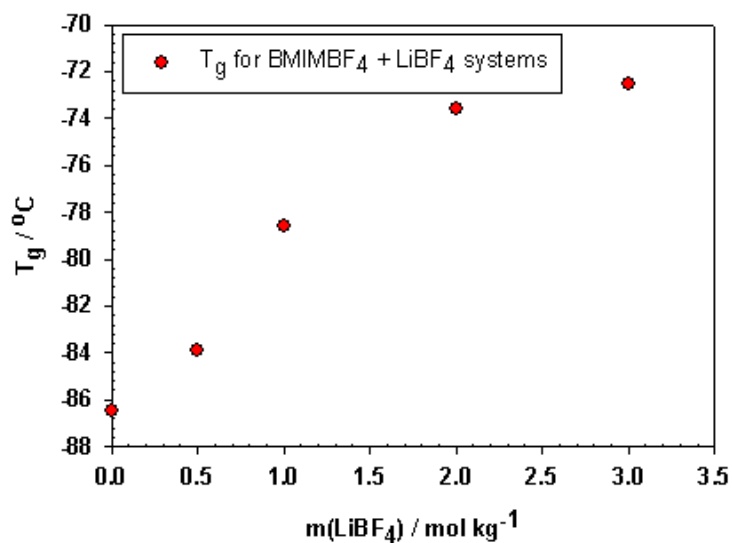


Figure 8. T_g increases as more LiBF₄ salt is added to BMIMBF₄.

Conductivity

We measured the electric conductivity of a lithium salt dissolved in an ionic liquid as a function of lithium-salt concentration over a wide range of temperature (about -20 to 100 °C). Conductivities were obtained by the AC impedance method. Conductivity measurements were carried out in a steel-(ionic liquid + lithium salt)-steel cell. Figure 9 shows the inner parts of the Swagelok-type cell. The frequency sweep was from 65535 Hz to 0.01 Hz at 5 mV AC amplitude.

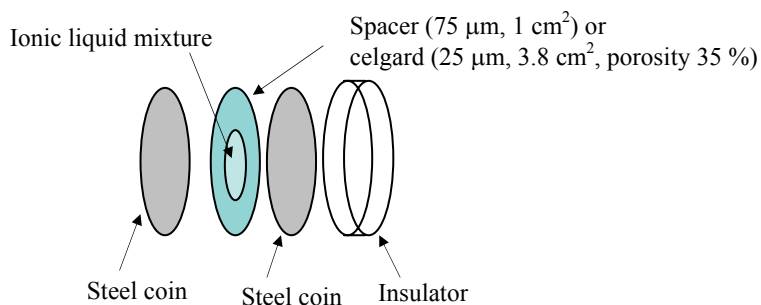


Figure 9. Swagelok-cell internal parts for conductivity measurements.

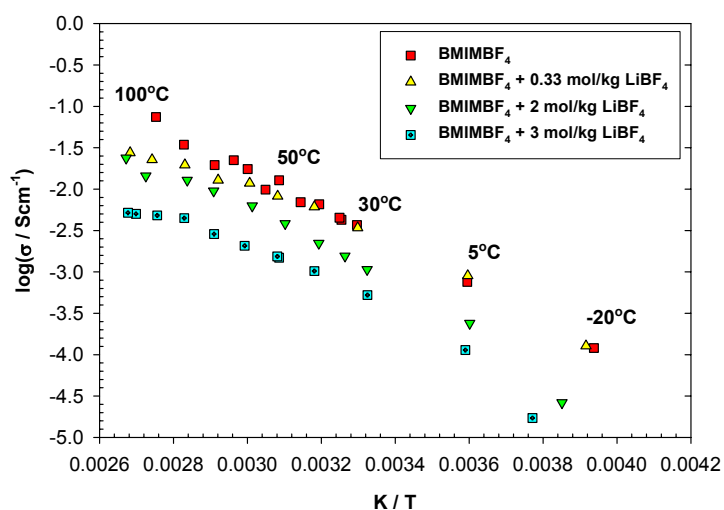


Figure 10. Conductivities of $\text{BMIMBF}_4 + \text{LiBF}_4$ systems as a function of temperature.

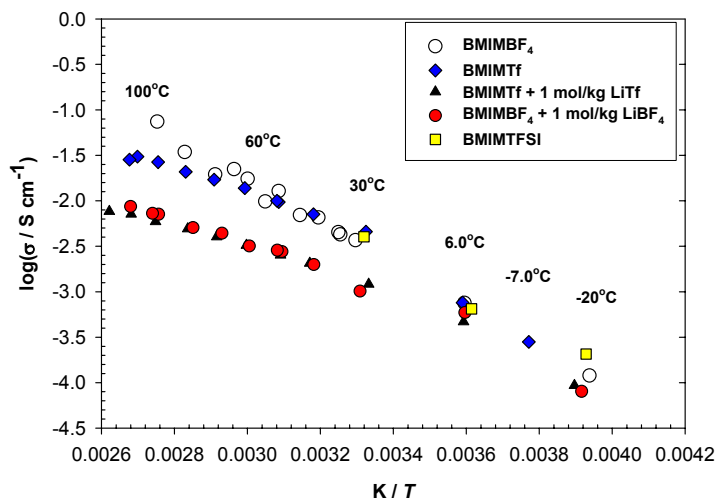


Figure 11. Conductivities of neat BMIMTf, BMIMBF₄ and BMIMTFSI. BMIMBF₄ + 1 mol/kg LiBF₄ and BMIMTf + 1 mol/kg LiTf mixtures.

Table 4. Summary of some thermal and transport properties of the ionic liquids studied. Those in italic have been measured in this work.

	M_w / g mol ⁻¹	T_m / °C	T_g / °C	Viscosity / cP	Density / g cm ⁻³	Conductivity / mS cm ⁻¹	Thermal Stability
BMIMBF₄	226.02	-	<i>-86.5</i> -85.3	120 (20°C) <i>219 (25°C)</i>	1.21 (20°C)	<i>3.8</i> <i>(30.2°C)</i>	<i><300°C</i>
BMIMPF₆	284.19	<i>10</i> 7.8	-81	281 (20°C) <i>450 (25°C)</i>	1.37 (20°C)		<i><300°C</i>
BMIMTf	288.29	16.4 17	-81.6	88.60 (20°C)	1.292 (20°C)	<i>4.6</i> <i>(27.6°C)</i>	<i><300°C</i>
BMIMTFSI	419.37	<i>-5</i>	<i>-91.2</i>	fluid		<i>4.0</i> <i>(28.0°C)</i>	<i><350°C</i>
OMIMBF₄	282.1	-	-79	439 (25°C)	1.12 (20°C)		<i><250°C</i>
OMIMTFSI	475.48	-	<i>-87.1</i>	fluid			<i><300°C</i>
BMPyTFSI	374.28	<i>10</i>	<i>-80.0</i>	fluid			<i><300°C</i>
P_{1,4}TFSI	422.41	-3 <i>(-50)</i>	-87	71.50 (20°C)	1.40 (20°C)	2.6 (25°C)	<360°C

Ref: Green Chem., 3 (2001) 156-164; J. Chromatograph A, 1037 (2004) 49-82; <http://www.ionicliquids-merck.de>; Electrochem. Solid State Lett., 7 No 5 (2004) A97-A101, J. Phys. Chem. B 107 (2003) 11749-11756

Interfacial resistance in a lithium-lithium cell

For electrochemical applications using lithium batteries, we must be sure that the ionic liquid is stable over a wide range of electric potential and, when lithium salt is added, that it be stable in a wide temperature range. For lithium batteries in hybrid vehicles, stability of the electrolyte with respect to the electrodes at high current densities is necessary to give sufficient energy for peak-power needs. In this case, the non-volatility and non-flammability of an ionic liquid provide an advantage. The electrochemical stability of a solution is provided by the experimentally-determined electrochemical window. In this window, we anticipate to see fewer undesired side reactions compared to those observed using conventional solvents. Electrochemical stability is obtained by measuring the interfacial impedance between electrode and electrolyte. Toward that end, we measure the temperature-dependent and time-dependent interfacial impedance using a frequency-response analyzer.

Our interfacial-resistance studies pertain to a symmetrical $\text{Li}|\text{BMIMBF}_4 + \text{LiBF}_4|\text{Li}$ cell. As shown in Figure 12, a Swagelok cell is used with a frequency sweep from 65535 Hz to 0.01 Hz at 5 mV AC amplitude.

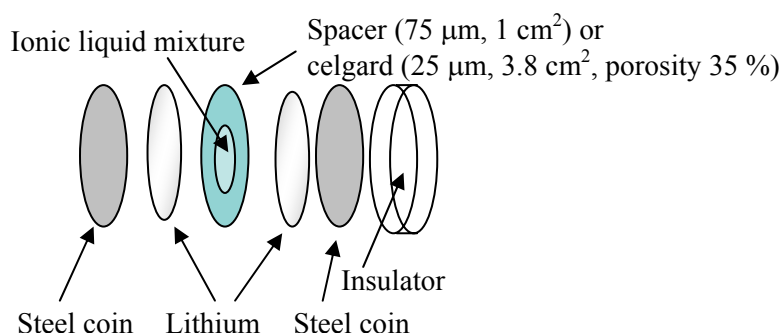


Figure 12. Swagelok-cell internal parts for interfacial-resistance measurements for cycling studies.

Reactivities of ionic liquid-lithium salt electrolytes were studied in Li-Li and Li-carbon cells. Figure 13 shows the increase of the interfacial impedance Z' in the presence of lithium metal in a $\text{Li}|\text{BMIMBF}_4 + 2 \text{ mol/kg LiBF}_4|\text{Li}$ cell at open circuit at 30°C. Z' is the real part of the interfacial impedance and Z'' is the imaginary part of the impedance. From Z' values one can observe the resistance of the system that, in this case, increases with time.

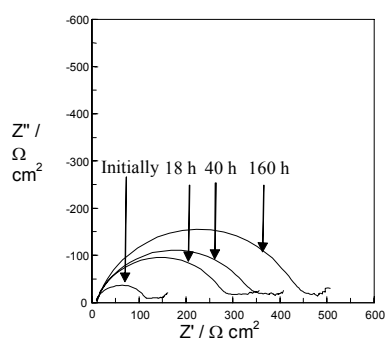


Figure 13. Increase of interfacial impedance as a function of time in $\text{Li}|\text{BMIMBF}_4 + 2 \text{ mol/kg LiBF}_4|\text{Li}$ cell at open circuit at 30°C.

As shown in Figure 14, initial interfacial resistance for a 2-mol / kg solution is smaller than that for a 1-mol / kg LiBF₄ solution.

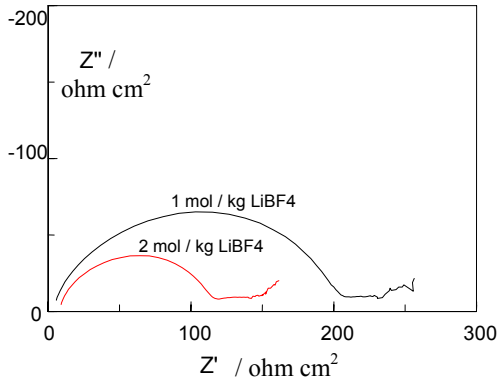


Figure 14. Initial interfacial impedance in Li | BMIMBF₄ + 1 or 2 mol/kg LiBF₄ | Li cells at open circuit at 30°C.

Cycling tests

Cell cycling has been carried out in Li-Li cells and in Li-carbon anode cells shown schematically in Figure 15.

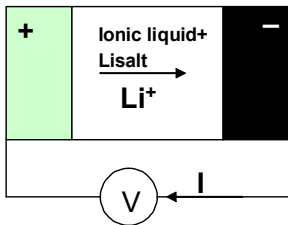


Figure 15. Rechargeable lithium-ion battery.

Figure 16 shows cycling results for the Li | BMIMBF₄ + 1 mol/kg LiBF₄ | Li cell. After five cycles passing ±0.1 mA/cm² current and 15 min open circuit potential, the growth of dendrites is evident. Also, the interfacial impedance rises to a few thousand Ω cm².

Figure 17 shows the effect of cycling in a Li-Li cell.

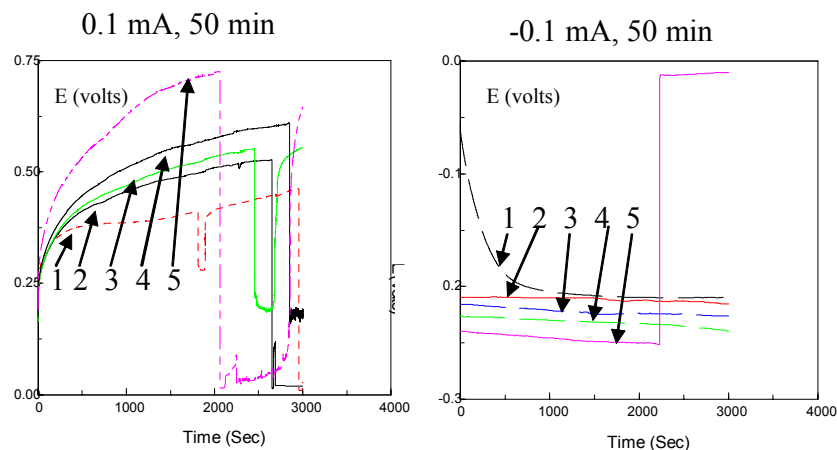


Figure 16. First five charging curves for the Li | BMIMBF₄ + 1 mol/kg LiBF₄ | Li cell. The curves indicate surface roughening and the formation of dendrites, a common feature with all currently used electrolytes (Newman and Monroe 2004).



Figure 17. The presence of lithium coins after 10 cycles passing $\pm 0.1 \text{ mA/cm}^2$ current in a Li | BMIMBF₄ + 1 mol/kg LiBF₄ | Li cell.

Figure 18 shows evidence for surface roughening and dendrite formation in a Li-Li cell.

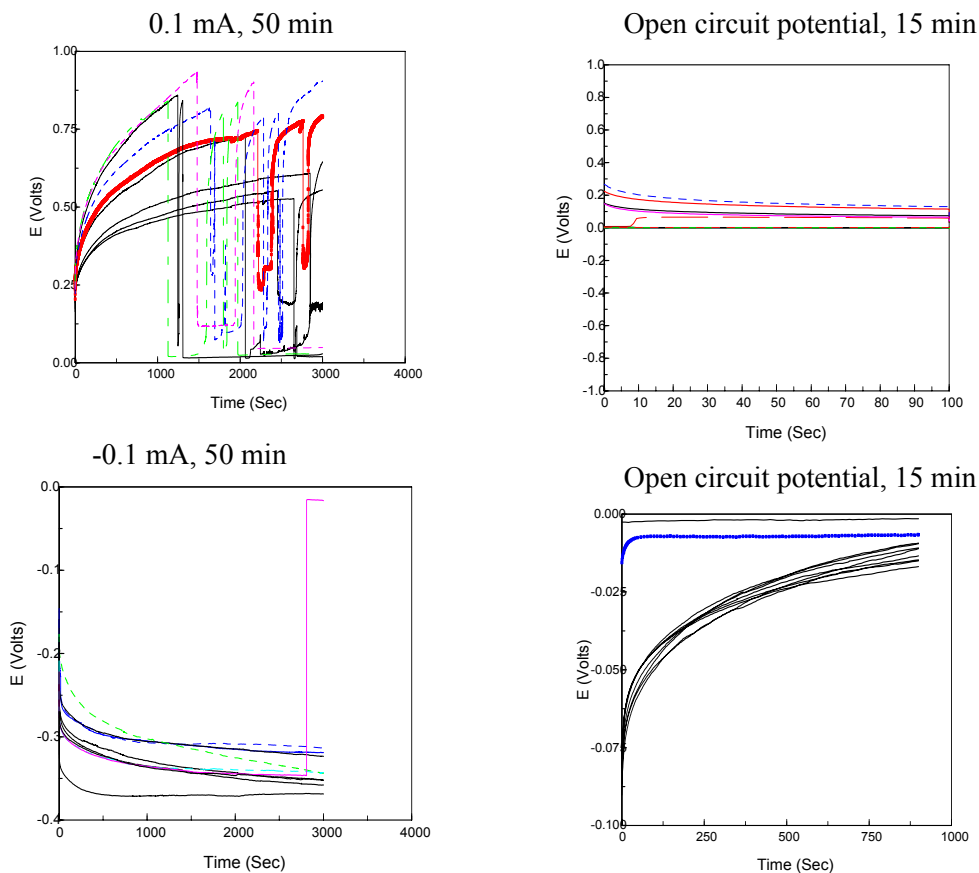


Figure 18. Ten charging curves for the Li | BMIMBF₄ + 1 mol/kg LiBF₄ | Li cell. The curves indicate surface roughening and the formation of dendrites, a common feature with all currently used electrolytes (Newman and Monroe 2004).

A stable ionic liquid decreases the (undesirable) tendency to form side reactions that contribute to power- and capacity-fade of a battery. We have studied chemical and structural changes in the electrodes including possible (undesirable) formation of dendrites that lead to battery short-out. A few cycling tests were made with Lithium | BMIMBF₄ + 1 mol/kg LiBF₄ | Gen2-Carbon cell. The cell components are shown in Figure 19.

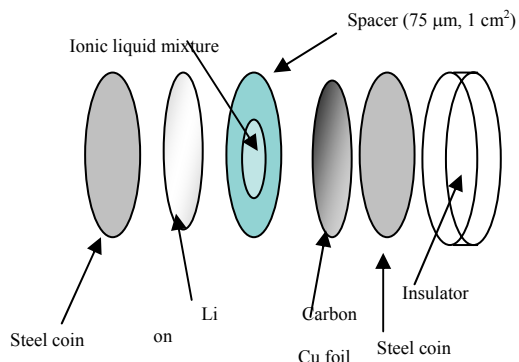


Figure 19. Li-(BMIMBF₄ + LiBF₄)-Carbon cell cycling tests.

Cycling experiments were made for a Lithium | BMIMBF₄ + 1 mol/kg LiBF₄ | Gen2-Carbon cell. (Li C4 cell). On the first day of testing, starting impedance was 65 Ω cm² and the open-circuit potential was 3.1 V. The programme set-up was: Loop repeat 10 times, Charging 500 s, 50 μA, Rest 1.5 min, Discharging 500 s, -50 μA, Rest 1.5 min, Loop end. The cell voltage changed between 3.5 V to 1.8 V as shown in Figure 20. Figures 21, 22, and 23 show the development of interfacial impedance during cycling.

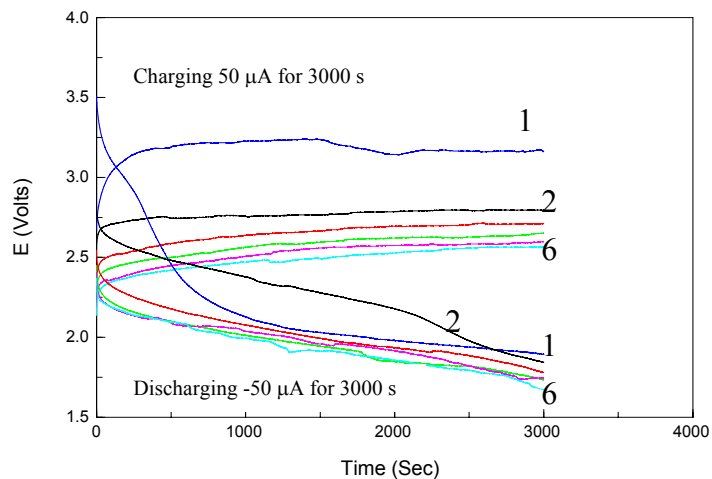


Figure 20. The cell voltage changed between 3.5 V to 1.8 V in Lithium| BMIMBF₄ + 1 mol/kg LiBF₄ |Gen2-Carbon cell. Cycling tests were made passing a current of ± 50 μA/cm². After charging and discharging, the system was at open-circuit potential for 1.5 minutes.

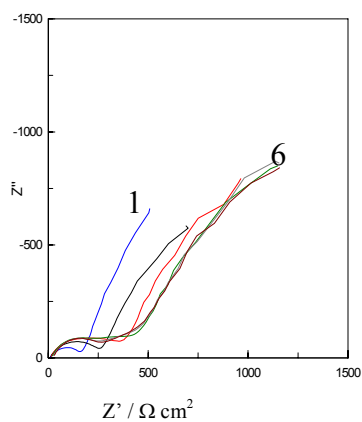


Figure 21. Impedance after charging

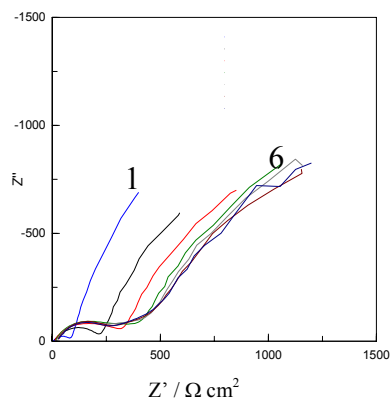


Figure 22. Impedance after discharging

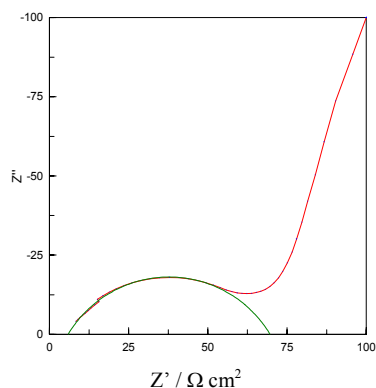


Figure 23. Initial interfacial impedance. Impedance at the beginning, near $65 \Omega \text{ cm}^2$, increases to $400 \Omega \text{ cm}^2$ after 6 cycles.

Second-day testing was carried out with the same Lithium|BMIMBF₄ + 1 mol/kg LiBF₄|Gen 2 Carbon cell. The starting impedance was $500 \Omega \text{ cm}^2$ and at the end it was $4000 \Omega \text{ cm}^2$. The cycling routine was: Loop repeat 10 times, Charging 500 s, $100 \mu\text{A}$, Rest 1.5 min, Discharging 500 s, $-100 \mu\text{A}$, Rest 1.5 min, Loop end. Results are shown in Figures 24, 25 and 26.

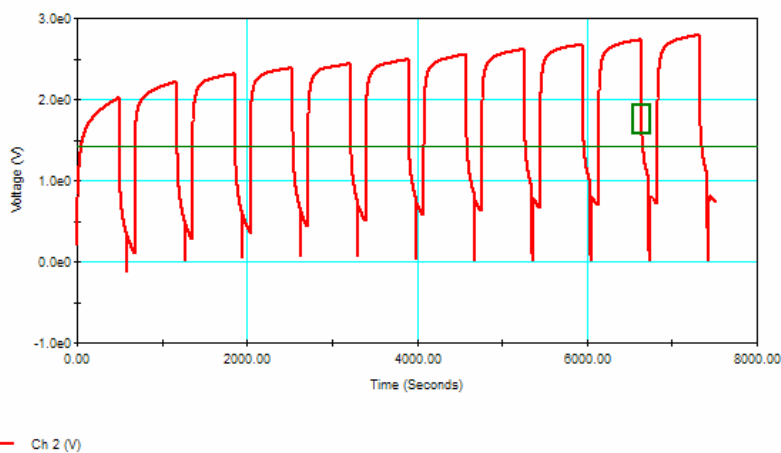


Figure 24. Second-day cycling with Lithium|BMIMBF₄ + 1 mol/kg LiBF₄|Gen 2 Carbon cell. Voltage-time curve is shown when charging 500 s at $\pm 100 \mu\text{A}$. After charging and discharging, the cell was at open-circuit potential for 1.5 min. Discharge is shown as the peak downwards after large potential drop. This indicates zero discharge capacity.

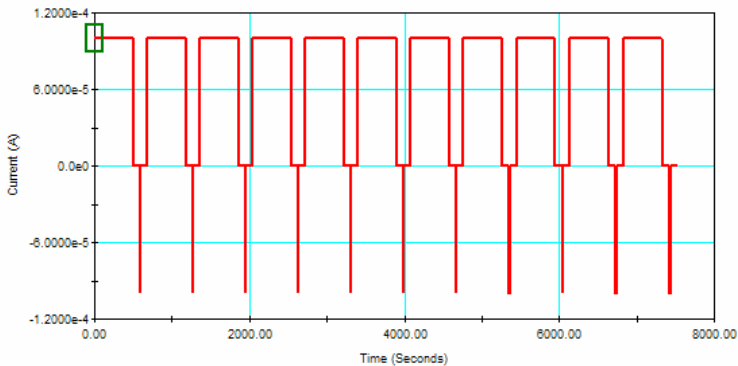


Figure 25. Second-day cycling with Lithium | BMIMBF₄ + 1 mol/kg LiBF₄ | Gen 2 Carbon cell. Current-time curve is shown when charging 500 s at $\pm 100 \mu\text{A}$. After charging and discharging, the cell was at open-circuit potential for 1.5 min.

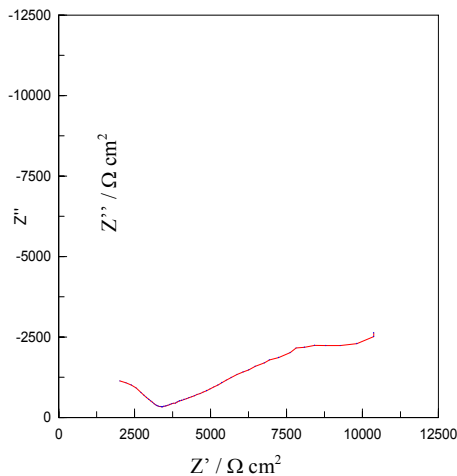


Figure 26. Impedance after second-day cycling with Lithium | BMIMBF₄ + 1 mol/kg LiBF₄ | Gen 2 Carbon cell. The interfacial impedance has increased to $4000 \Omega \text{ cm}^2$.

Conclusions

Thermal analysis shows that ionic liquids are stable up to around 250°C . Large liquid ranges were observed for the ionic liquids studied in this work. The addition of lithium salts alters the thermal stabilities but not much.

Absorbed water changes TGA results. Because ionic liquids take moisture from air, it is necessary to dry them and to store them in a glove box. Drying the samples in a drying pistol at 60°C in the presence of P_2O_5 was found to be adequate. Also, the lithium salt that is dissolved into the ionic liquid must be dry.

From DSC data, the melting-point endothermic peak declines or disappears completely when lithium salt is dissolved into an ionic liquid. Ionic liquids form glasses at low temperatures. For example, BMIMBF₄ does not show a melting point but a glass-transition temperature circa -85°C .

Measured conductivities were within 3-5 mS/cm at 25°C. That is a necessary but not sufficient condition for a working battery. It is essential that an ionic liquid – lithium salt system is chemically and electrochemically stable in the presence of lithium metal, lithium ions, and other electrode materials. This has to be valid both at open-circuit potential as well as at charging and discharging processes.

The ionic-liquid / lithium-salt system (BMIMBF₄ + LiBF₄) showed large interfacial impedance at open-circuit potential. The formation of dendrites was shown in both Li-Li cells as well as in Li-Carbon cells. The increase of interfacial impedance shows reactivity of the electrolyte with the electrode. In addition, cycling tests showed non-existing discharge capacity in Lithium | BMIMBF₄ + 1 mol/kg LiBF₄ | Gen2-Carbon and in LiFePO₄ | BMIMBF₄ + 1 mol/kg LiBF₄ | Carbon cells. The reason for the poor performance of the BMIMBF₄ is likely to be the reactivity of the BF₄⁻ ion. We expect PyrrolidiniumTFSI and other imidazoliumTFSI ionic liquids to show better electrochemical stability in a battery system.

Future work

It is necessary to analyze the reaction products from the electrode using gas chromatography and mass spectrometry. Experiments with different electrodes and TFSI ionic liquids will be carried out. We will use electrodes like LiFePO₄-carbon, LiMn₂O₄-carbon, LiFePO₄-LiTi₅O₁₂.

The observed reactivity of ionic liquids with the electrodes brings additional obstacles for their use in lithium-ion batteries. However, applications at elevated temperatures may be attractive due to increased safety. More research on side reactions with different electrodes will be carried out.

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