Improved electrolytes for Li-ion batteries: Mixtures of ionic liquid and organic electrolyte with enhanced safety and electrochemical performance

A. Guerfi, M. Dontigny, P. Charest, M. Petitclerc, M. Lagacé, A. Vijh, K. Zaghib*

Institut de Recherche d'Hydro-Québec, 1800 Lionel Boulet, Varennes, QC J3X 1S1, Canada

A B S T R A C T

Physical and electrochemical characteristics of Li-ion battery systems based on LiFePO$_4$ cathodes and graphite anodes with mixture electrolytes were investigated. The mixed electrolytes are based on an ionic liquid (IL), and organic solvents used in commercial batteries. We investigated a range of compositions to determine an optimum conductivity and non-flammability of the mixed electrolyte. This led us to examine mixtures of ILs with the organic electrolyte usually employed in commercial Li-ion batteries, i.e., ethylene carbonate (EC) and diethylene carbonate (DEC). The IL electrolyte consisted of (trifluoromethyl sulfonylimide) (TFSI) as anion and 1-ethyl-3-methyleimidazolium (EMI) as the cation. The physical and electrochemical properties of some of these mixtures showed an improvement characteristics compared to the constituents alone. The safety was improved with electrolyte mixtures; when IL content in the mixture is ≥40%, no flammability is observed. A stable SEI layer was obtained on the MCMB graphite anode in these mixed electrolytes, which is not obtained with IL containing the TFSI-anion. The high-rate capability of LiFePO$_4$ is similar in the organic electrolyte and the mixture with a composition of 1:1. The interface resistance of the LiFePO$_4$ cathode is stabilized when the IL is added to the electrolyte. A reversible capacity of 155 mAh g^{-1} at C/12 is obtained with cells having at least some organic electrolyte compared to only 124 mAh g^{-1} with pure IL. With increasing discharge rate, the capacity is maintained close to that in the organic solvent up to 2 C rate. At higher rates, the results with mixture electrolytes start to deviate from the pure organic electrolyte cell. The evaluation of the Li-ion cells; LiFePO$_4$//Li$_4$Ti$_5$O$_{12}$ with organic and, 40% mixture electrolytes showed good 1st CE at 98.7 and 93.0%, respectively. The power performance of both cell configurations is comparable up to 2 C rate. This study indicates that safety and electrochemical performance of the Li-ion battery can be improved by using mixed IL and organic solvents.

1. Introduction

Lithium-ion batteries are at the heart of modern advances in portable electronic devices and are being improved and further developed for a myriad of other applications, especially in hybrid electric vehicles (HEVs) and plug-in HEV (PHEV) [1–4]. Notwithstanding a recent report of their use in a commercial PHEV [5], the general consensus is that further developments are needed before their widespread applications in HEs and PHEVs are realized. Much research is being conducted to achieve lower cost, higher calendar life, high-power capability, and above all, improved safety.

Our previous work [6,7] showed that one promising avenue for safer Li-ion batteries is the use of electrolytes based on room-temperature molten salts called ionic liquids (ILs). The most popular ILs consist of quaternary ammonium cations such as imidazolium, pyridinium, pyrrolidinium, sulfonium, ammonium and

phosphonium with anions having low Lewis basicities, such as BF$_4$, PF$_6$, CF$_3$SO$_3$ and (CF$_3$SO$_2$)$_2$N. The quaternary ammonium ions have low melting points, compared to the inorganic salts of the same anions, which approaches room temperature (RT). These RTILs are known as green solvents [8] due to their advantages of non-flammability, high electrochemical stability, low vapor pressure and high conductivity [9,10]. Many materials have been evaluated with IL, silicon anodes [11], and, SiOx:graphite mixtures [12,13] and LiFePO$_4$ [14,15].

Ionic liquids are the ultimate *non-volatile* solvents and show great thermal, chemical and electrochemical stability; they exhibit very low vapor pressure and high non-flammability – properties that are of central importance in their use as safe electrolytes in lithium-ion batteries [8,9,19]. The chemical structure of some ionic liquids of interest in Li-ion batteries is shown in Fig. 1. Both anion and cation in an IL are extremely large, with the result that charge to radius ratio of each ion is small; this leads to low lattice energies, weaker electrostatic bonding and lower melting points. The large ions cause high viscosity which leads, together with low charge to radius ratio, to low conductivity, which makes them less attractive

* Corresponding author. Tel.: +1 450 652 8019; fax: +1 450 652 8424.
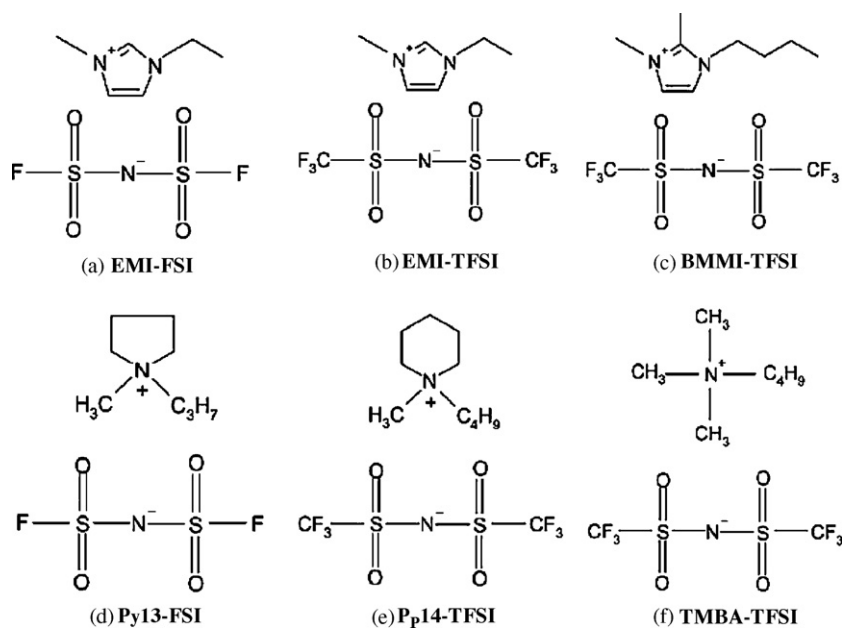E-mail address: zaghib.karim@ireq.ca (K. Zaghib).

Fig. 1. Chemical formulas of ionic liquids and anions of interest in this study.

as electrolytes in batteries that need high conductivity for good performance [7,8].

On the anode side, ionic liquids are an attractive area of research due to the unstable formation of the SEI layer on graphite. Decomposition of ionic liquids on the graphite anode has restricted their application in Li-ion batteries. Considerable effort has been focused to improve the stability of the SEI layer. The addition of vinylene carbonate (VC) can suppress the reduction of this IL based on TFSI [16–19].

In this work we explored ways to increase the conductivity of battery electrolytes based on ILs but without compromising their stability, especially non-flammability. This led us to examine mixtures of ILs with organic electrolytes usually employed in commercial Li-ion batteries, i.e., ethylene carbonate (EC) and diethylene carbonate (DEC); the properties of these mixtures are described below.

2. Experimental

The ionic liquids selected in this study are based on the TFSI-anion; 1-ethyl-3-methylimidazolium-bis(fluorsulfonyl)imide (EMIm-TFSI), propyl-methyl-imidazolium-bis(fluorsulfonyl) imide (PMIm-TFSI) and hexyl-methyl-imidazolium-bis(fluorsulfonyl) imide (HMIm-TFSI) from Hydro-Québec (Fig. 1). These ionic liquids contain less than 10 ppm (w/w) of moisture and less than 2 ppm (w/w) of halide and alkali metal-ion impurities. Our interest in these ILs is with the TFSI-anion in combination with high conductivity and lower viscosity cations such as EMI. The organic electrolyte that is used is ethylene carbonate/diethylcarbonate carbonate with 2% vinylcarbonate; EC/DEC (2% VC) −1 M LiPF$_6$ (from UBE, Japan). The sources and procedures for these electrolytes have been described recently [19]. Although the price of these electrolytes is rather high today, it will come down through mass manufacture when and if they are extensively adopted by the battery industry.

The in situ Scanning Electron Microscope (SEM) was used to study the thermal behavior of the electrolyte using drops that were deposited on a flat surface. A Peltier devise was used to heat the sample, and the temperature range was precisely controlled from −20 to 180 °C.

To evaluate the electrochemical properties of LiFePO$_4$, natural graphite and Li$_4$Ti$_5$O$_{12}$ (Hydro-Québec), a stainless-steel coin type cell was used for this study. The anode was a composite electrode containing 5 wt.% PVDF (Kureha, Japan), 93 wt.% MCMB graphite (1028 from Osaka Gas, Japan) and 2 wt.% VGCF (vapor growth carbon fiber, Showa-Denko, Japan). The cathode contained 5 wt.% PVDF (Kureha, Japan), 89 wt.% carbon-coated LiFePO$_4$ (Hydro-Québec), 3 wt.% carbon black and 3 wt.% VGCF. The Li$_4$Ti$_5$O$_{12}$ was prepared in the same manner as the LiFePO$_4$ composite electrode. The slurries were cast on copper for the graphite and on aluminum for LiFePO$_4$ and Li$_4$Ti$_5$O$_{12}$ and then dried in an oven at 110 °C overnight. For the cell assembly, the Celgard (3501) separator was soaked in the electrolyte, organic solvent, ionic liquid or their mixture. The active surface area of the electrode is 2 cm^2. The cell was fabricated in the glove box with lithium metal as the counter electrode. The 18650-cell configuration was assembled by PHET (Pihsiang Energy Technology Co., Ltd., Taiwan). The electrochemical measurements were performed by using a VMP-cycler (Biologic, France). The first formation cycles were obtained at constant charge–discharge at C/24. The electrodes were evaluated for power performance with the C-rate test, by varying the discharge current from C/12 to 40 C. The d.c. conductivity was measured with a model CM-30R conductivity meter (DKK-TOA Corp., Japan). The viscosity was measured in a MCR-30 viscometer (Anton-Paar, USA).

The different compositions of mixed electrolytes were prepared by adding 0–100% of the ionic liquid to the quaternary organic solvent (see Table 1). The flammability of the electrolyte solutions was examined by directly observing the flame on the surface of the electrolytes for a couple of seconds, as shown in Photo 1 in Fig. 5. The thermogravimetric analysis (TGA) of mixed electrolyte solutions was carried out by using a Perkin Elmer Model TGA7 under argon atmosphere at the rate of 1 °C min^{-1}.

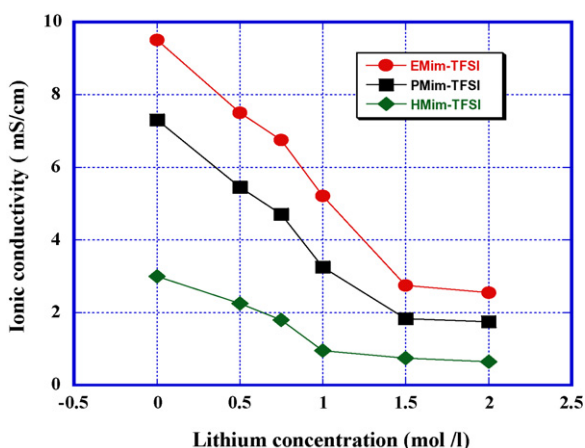## 3. Results and discussion

3.1. Mixed electrolytes

The effect of the salt concentration on the ionic conductivity in different ILs (EMIm-TFSI, PMIm-TFSI, HMIm-TFSI) was measured. The high viscosity and relative low conductivity of ILs is com-

Table 1
Viscosity, d.c. ionic conductivity and flammability as a function of % IL in EC–DEC–VC–1 M LiPF$_6$ electrolytes.
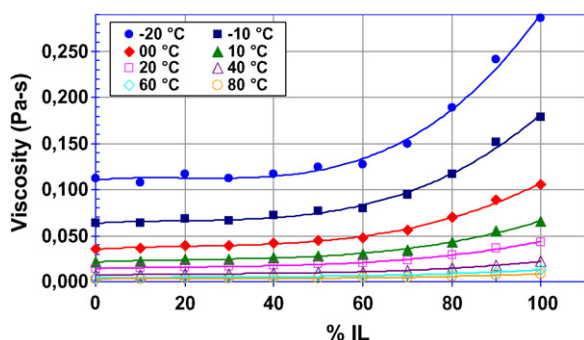
Ionic liquid (%)	At 25 °C		
	Viscosity (Pa S)	Conductivity (mS cm^{-1})	Flammability
0% EMI-TFSI	12.1	8.50	Yes
10% EMI-TFSI	12.7	9.45	Yes
20% EMI-TFSI	13.7	9.31	Yes
30% EMI-TFSI	14.1	9.41	Yes
40% EMI-TFSI	14.9	10.09	No
50% EMI-TFSI	16.3	10.11	No
60% EMI-TFSI	17	10.45	No
70% EMI-TFSI	19.9	10.26	No
80% EMI-TFSI	24.5	10.13	No
90% EMI-TFSI	30.5	9.78	No
100% EMI-TFSI	36.3	8.61	No

Fig. 4. Relative variation "Δ" of viscosity as a function of ionic liquid content in EC–DEC–VC–LiPF$_6$ electrolyte.
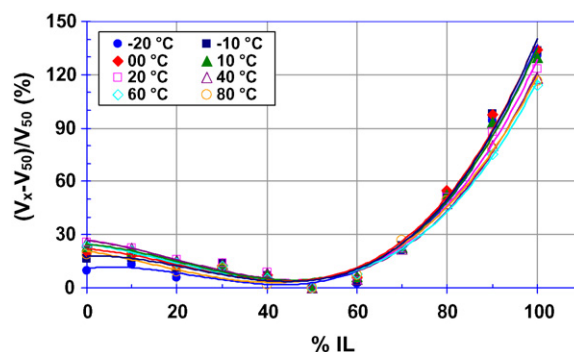

Fig. 2. D.c. conductivity of ionic liquid-TFSI based electrolytes as a function of LiTFSI salt concentration.

pounded by the fact that their conductivity *decreases* when a salt (e.g., LiTFSI) is added to make an electrolyte solution (Fig. 2); this behavior is contrary to that of conventional aqueous and non-aqueous solvents. One way to overcome this difficulty is to add some organic solvent such as EC and DEC. Some interesting properties were observed in our studies on these mixtures, as reported below.

The results obtained for the viscosity of the mixed and pure electrolytes at different temperatures from −20 to +80 °C is presented in Fig. 3. The viscosity varies inversely with the temperature; i.e., as the temperature increases, the viscosity decreases. The viscosity decreases 30–35 times when the temperature increases from −20 to +80 °C for mixed and pure electrolytes, respectively. The addition of IL in the electrolyte increases the viscosity of the mixture; before

Fig. 3. Viscosity at different temperatures as a function of ionic liquid content in EC–DEC–VC–LiPF$_6$ electrolytes.

reaching 1:1 ratio by volume, the variation is very slow which is probably due to the dominant properties of the organic electrolyte. Fig. 4 shows the relative variation of viscosity Δ ($\Delta = (V_x - V_{50})/V_{50}$) of the mixtures with IL percentage, where V_x is the viscosity at x% IL and V_{50} is viscosity when 50% IL is added. We can clearly observe the effect of the IL in the organic electrolyte on the viscosity of the mixture. A very small variation in the viscosity occurs when the amount of IL is less than 50%, but a rapid increase of Δ occurs when the IL ratio increases above 50% in the electrolyte mixture; the same correlation is observed at all of the temperatures that were investigated. This behavior indicates the possible unavailability of sufficient organic solvent for the solvation of ions, leading to some ion-pair formation as in a quasi lattice at IL concentration higher than 60%.

To clarify the effect of ionic liquids on battery safety, flammability tests of electrolytes with and without IL were carried out. Fig. 5 shows the photographs of a direct flame on the pure electrolytes and their mixtures, and Table 1 summarizes these results of these tests. The electrolyte flammability occurred with pure organic electrolyte in the first second of ignition; in contrast to this behavior, pure IL did not show any combustion even after more than 20 s of flame exposure. As soon as IL is added in the electrolyte, the flame exposure time increases before flammability occurs. After adding 40% IL in the electrolyte, no flammability is observed within the test periods, ca. 25 s. This result indicates that safety can be improved in Li-ion batteries when the % IL in the organic electrolyte is at least 40%.

The non-flammability characteristic of IL-based electrolytes, which is crucial for the safety of batteries, is maintained in these mixtures provided that at least 40% of the volume of the mixture is IL (see Fig. 5 and Table 1). When the conductivity and viscosity of the IL/EC–DEC mixtures are examined at different compositions, very interesting trends arise (see Fig. 6). When the IL in the mixtures increases from 0 to around 60%, the conductivity rises as one would expect if the "salt" (IL) concentration increases by adding it to the conventional solvent EC–EDC. On the other hand, additions of IL also increase the viscosity but not so steeply. Around 60% IL in the mixture, further increases of IL lead to decreases in conductivity because there is not sufficient organic solvent available to "solvate" all the IL present, and conductivity approaches that of pure IL. Correspondingly, and not unexpected, there is a steep rise in viscosity of the mixtures with increasing IL fraction (Fig. 6).

A remarkable *optimum* composition range has been discovered for a promising battery application when the proportion of IL in the mixture is 40–60%, which provides the key desirable properties of a battery electrolyte – high conductivity, low viscosity and non-flammability (Figs. 5 and 6 and Table 1). These findings are the main new observations of the present work.
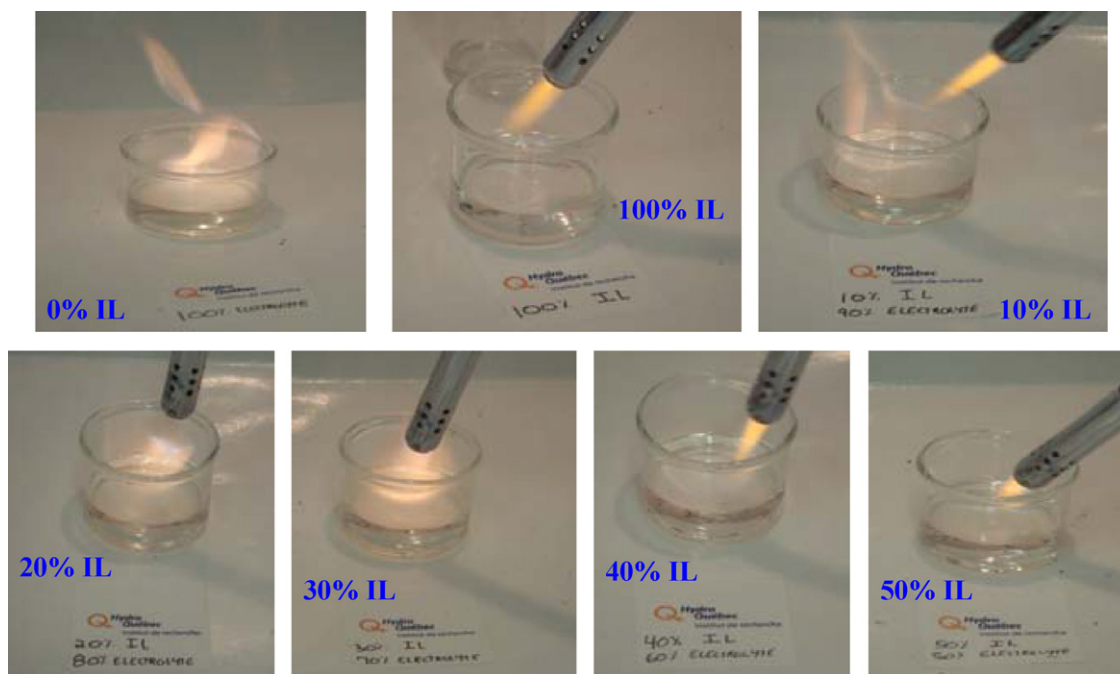
Fig. 5. Flammability test on different EC–DEC–VC mixtures with EMI-TFSI electrolyte.

The expected inverse correlation between conductivity and viscosity (Table 1) of the electrolytes is not followed by the mixtures trend because the organic solvent has covalent bonding and few ions (by auto-ionization) and hence low conductivity, whereas, the ionic liquids are by definition full of ions, and therefore have higher conductivity than the organic solvents. Although the viscosity increases when IL is added in the mixture, the conductivity shows a maximum at 60% IL and then decreases with increasing IL (see Fig. 6 and related comments in the text above).

We also conducted in situ measurements of the evaporation temperatures and the vapor pressure of some electrolyte mixtures in the SEM by using a Peltier device to scan the temperature range from −20 to 180 °C. Fig. 7 shows the SEM picture of drops of IL, organic electrolyte and their mixture (30, 50% IL). For the pure IL drop, no decrease in the drop size was observed up to the highest temperature limit of the device, 182 °C. On the other hand, the organic electrolyte starts evaporating at around 50 °C. When IL is added, the mixture drops show a strong direct relationship between IL content in the electrolyte and evaporation temperature. Hence adding IL to the organic electrolyte increases the evaporation temperature, which is related to flammability. When 30% IL is added, the evaporation temperature increases to ~125 °C, and it reaches 176 °C when the IL concentration is 1:1 with organic solvent. Therefore, the evaporation temperature of the mixture is increased by
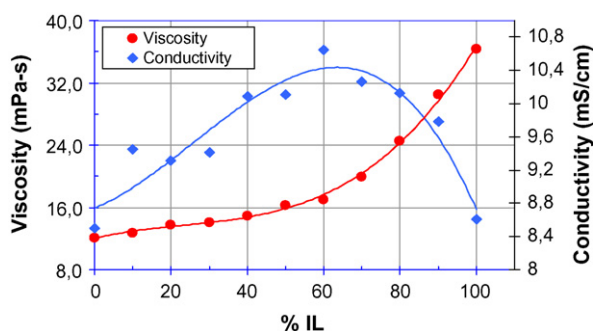
252% with 50% IL in the organic solvent. The rise of temperature rate in these experiments was 2 °C per minute.

The thermal properties of the electrolyte are the key to battery safety. Thermal gravimetric analysis (TGA) of the electrolytes with IL concentrations – 0, 30, 50, 70 and 100% – is shown in Fig. 8. There is essentially no weigh loss for the pure IL up to 350 °C, and less than 3% loss was measured at 350 °C. These results explain the thermal stability of IL and confirm that little volatile species are released. In contrast, the weight loss is 30% when the organic electrolyte is heated from 25 to 100 °C, and 80% loss at 160 °C. By adding IL to the organic electrolyte, the thermal stability of the mixed electrolyte does not show a big improvement up to 100 °C. The electrolytes with 30, 50 and 70% IL show losses of 23, 15 and 10% at 100 °C, respectively. This result confirms the in situ SEM analysis where the electrolyte drops evaporated at different stages depending on the proportion of IL in the mixtures. Although IL improves the thermal stability of the organic electrolyte, the mixed electrolyte does not form a new phase. However, the initial weight loss from 25 to 100 °C is attributed to the decomposition of salt and organic solvent in the mixtures.

3.2. Anode, cathode and cell behavior

The electrochemical behavior of the Li-ion battery electrode materials, i.e., graphite and LiFePO$_4$, as well as Li-ion cell behavior is described in this section.

3.2.1. Anode

For the graphite anode, we previously reported [6] that graphite is not intercalated when pure IL based on TFSI-anion is used. Fig. 9 shows the initial charge–discharge cycles at C/24 rate of a graphite electrode with pure and mixture electrolytes. As well-known, intercalation in the graphite usually occurs below 250 mV. However for pure IL, no intercalation occurs and a low coulombic efficiency is obtained. Also, some ex-foliation of the graphite is observed, which may or may not be related to the reduction of IL. This contrasts with the results we found with pure IL based on FSI anion, where the FSI anion plays a key role to stabilize the SEI layer and a Li-ion impermeable film [7]. When the organic solvent is added to
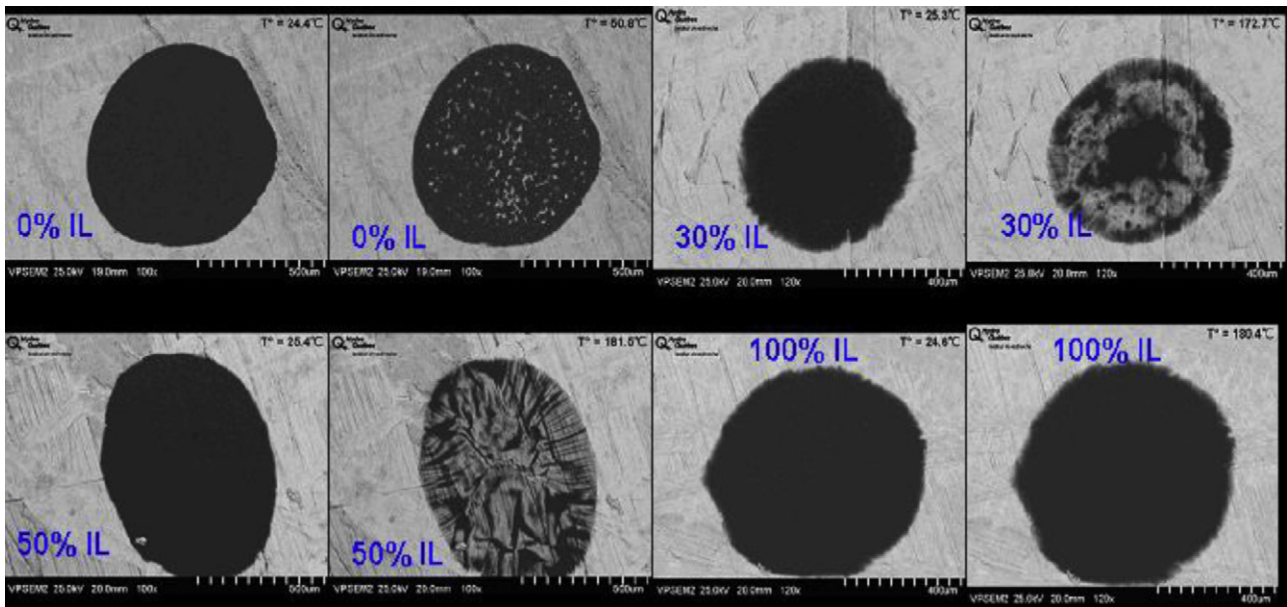

Fig. 6. Conductivity and viscosity of EC–DEC–VC–1 MLiPF$_6$ with EMI-TFSI.

Fig. 7. SEM photographs from in situ SEM analysis of evaporation temperature of electrolytes with different IL content.

the IL electrolyte in a ratio (1:1), a passivation SEI layer is obtained at 800 mV, followed by intercalation compound formation. This is due to the decomposition of the EC solvent during reduction in the range 800–250 mV. Hence, a more stable passivation layer is formed on the graphite particles. The coulombic efficiencies and reversible capacities were found to be sensitive to the % IL that is present. The effect of IL content in the electrolyte on the coulombic efficiencies (Ah. Eff.) of the graphite anode is shown in Fig. 10. The lowest 1st (Ah. Eff.) was obtained with pure IL electrolyte and the highest one is obtained with the pure organic electrolyte. Clearly, the presence of IL in the organic electrolyte reduces the coulombic efficiency. When the electrolyte is consists of a 1:1 ratio, the 1st coulombic efficiency is 80%, the same value we obtained with pure IL based on FSI anion [8]. Thus, we conclude that the mixture of IL-FSI with organic electrolyte should show an improvement in
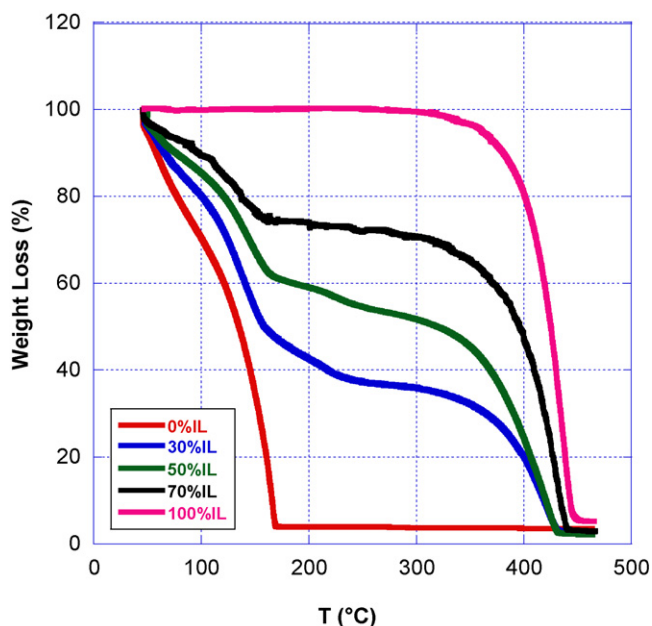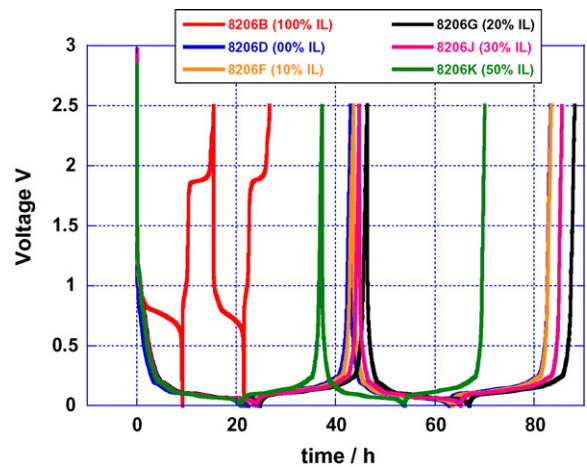

Fig. 9. First cycle behavior of Li/EC–DEC–VC–1 MLiPF$_6$/graphite cells with and without EMI-TFSI added.

the graphite anode performance. In the second cycle, the coulombic efficiency reaches 97% with the mixture (1:1). The other parameter of interest here is the reversible capacity; a low reversible capacity of 94 mAh g^{-1} was obtained with pure IL. This reversible capacity increases with the amount of organic solvent in the electrolyte.
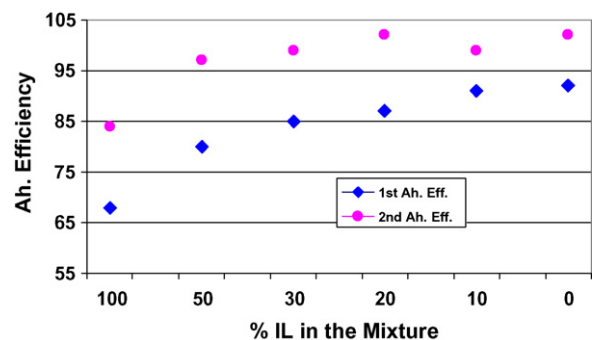

Fig. 8. Thermogravimetric analysis of EC–DEC–VC–1 MLiPF$_6$ s with different EMI-TFSI ratios.

Fig. 10. First and second coulombic efficiencies of Li/EC–DEC–VC–1 MLiPF$_6$/graphite cells with electrolyte containing different EMI-TFSI ratios.

Table 2

The first cycle electrochemical characteristics of MCMB graphite anode in EC–DEC–VC–LiPF$_6$/EMI-TFSI mixed electrolyte.

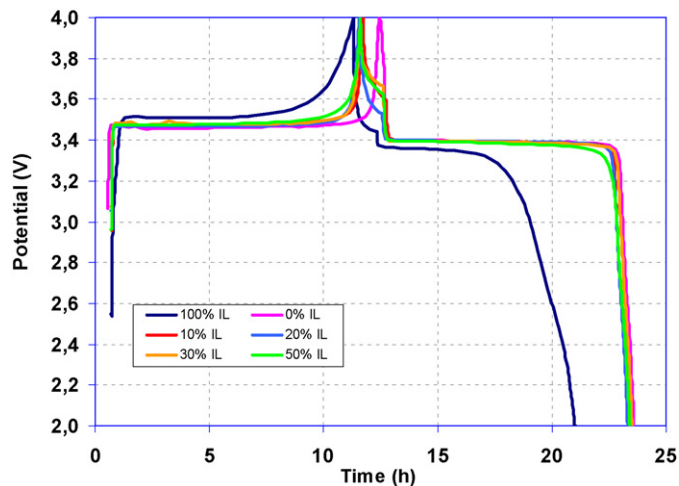| % IL	Dis. Cap. 1st/2nd	Cha. Cap. 1st/2nd	Ah. Eff. 1st/2nd
100	141/94	96/79	68/84
50	311/255	250/248	80/97
30	372/314	315/312	85/99
20	388/324	337/331	87/102
10	362/306	329/302	91/99
0	362/306	316/312	92/102

Fig. 11. First cycle behavior of Li/EC–DEC–VC–1 MLiPF$_6$/LiFePO$_4$ cells with electrolyte containing different EMI-TFSI ratios.

Passivation layer formation improved with increasing amounts of organic electrolyte in the mixture, allowing the subsequent formation of intercalation compounds and a higher reversible capacity. The results for efficiencies and capacities are summarized in Table 2. The highest reversible capacity is obtained with the pure organic solvent, followed by the mixture containing 10% IL, and decreasing proportionally as the % IL in the electrolyte increases.

3.2.2. Cathode

The salient features of the LiFePO$_4$ cathode in these mixed electrolytes are described. The first and the second cycles of LiFePO$_4$ at C/12 rate are shown in Fig. 11. The coulombic efficiencies and reversible capacities are given in Table 3. The 1st Ah. Eff. for pure IL is low, 82%, which is probably related to high viscosity of the IL. The low wettability of the carbon coating layer affects the reversible capacity, which is only 123 mAh g^{-1}. Nevertheless, the performance is reasonably good, independent of the IL content in the electrolyte mixture. The cells containing the mixed electrolyte perform well, comparable to that for the pure organic electrolyte. Thus, the IL-based electrolytes exhibit excellent behavior for cathode but less so for anodes.

Table 3

The first cycle electrochemical characteristics of LiFePO$_4$ cathode in organic/IL mixed electrolyte.

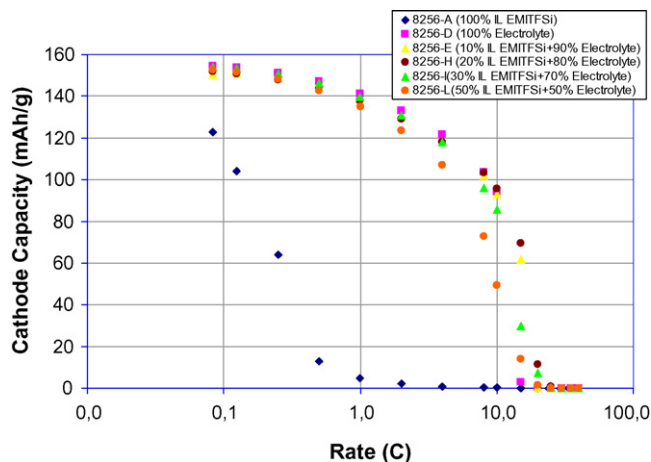| % IL	Capacity (mAh g^{-1})		Ah. Eff. (%)
	Charge	Disch.	
100	150	123	82
50	154	153	99
30	154	154	100
20	154	152	99
10	154	154	100
0	155	156	100

Fig. 12. Rate capability of Li/EC–DEC–VC–1 MLiPF$_6$/LiFePO$_4$ with electrolyte containing different EMI-TFSI ratios.

The high-rate performance of LiFePO$_4$ was investigated as function of IL content (see Fig. 12). The reversible capacity at high rates decreases with increasing IL content, more precipitously with pure IL, perhaps due to its high viscosity and poor electrode wettability. With highly viscous electrolytes such as pure ionic liquids, the wettability of the carbon layer is more difficult due to its large inaccessible (to electrolyte) surface area arising from micro-roughness. Moreover, the high viscosity inhibits wettability of the electrode interior of both anodes and cathodes. This is likely to be the case because of the quasi three-dimensional fractal nature of the electrodes, which contains not only meso-pores (easily accessible by the electrolyte) but also micro-pores that limit electrolyte accessibility. With the electrolyte mixture (1:1), the high-rate performance is sharply improved and resembles the pure organic electrolyte up to the 2 C rate, above which it starts decreasing slightly, although it continues this trend to the 10 C rate. At rates higher than 10 C, some departures are noticeable; the cells containing the electrolyte mixtures with 10% IL and 20% IL showed a slightly higher capacity than the pure organic electrolyte. This result may be attributed to their higher conductivity, but still responding like the pure organic electrolyte. In other words, the higher quantity of salt in the mixture electrolyte during the peak power, arising
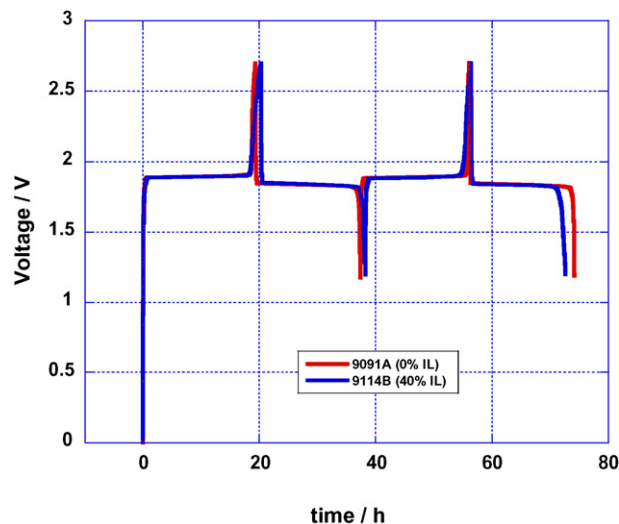

Fig. 13. First cycle behavior of Li$_4$Ti$_5$O$_{12}$/LiFePO$_4$ at C/24 in electrolyte with 40 and 0% ionic liquid.

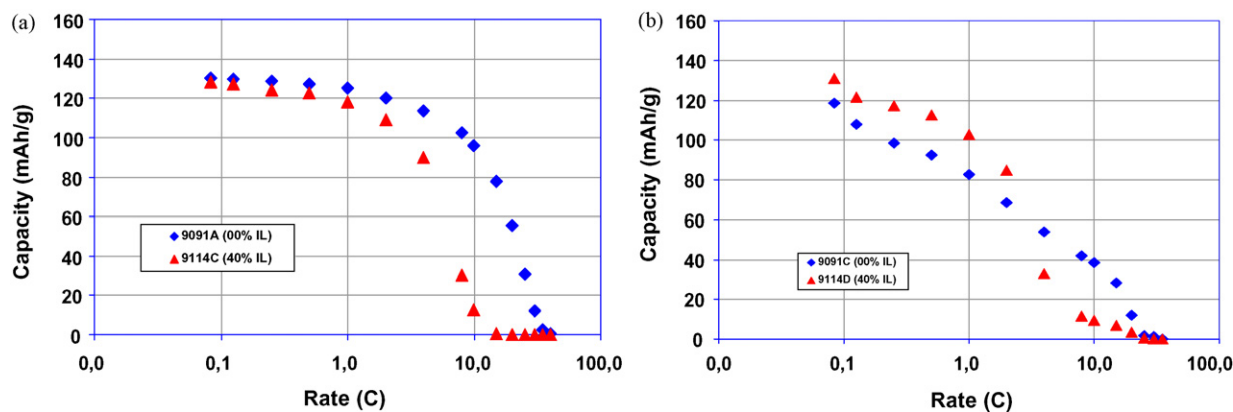**Fig. 14.** Rate capability of $Li_4Ti_5O_{12}/LiFePO_4$ with electrolyte containing 40% IL.

from some IL in the electrolyte by increasing the salt concentration without yet creating high ion-pair-interaction.

3.2.3. Li-ion cell

Unfortunately, these electrolyte compositions containing 10–30% IL exhibited flammability during the flame test (Fig. 5), even though they are attractive because of their conductivity and electrochemical properties. In order to improve the battery performance without compromising safety, other mixed electrolyte compositions were evaluated. Thus, Li-ion cells were assembled with electrolyte mixture containing 40% IL with $LiFePO_4$ and $Li_4Ti_5O_{12}$ as the cathode and anode, respectively. Fig. 13 shows the first cycles at C/24 of Li-ion cells with this electrolyte (40% IL) and an electrolyte with no IL. At C/24 rate, the cells yielded 89 and 94% coulombic efficiency in the first cycle and reversible capacity of 115 and 128 mAh g^{-1}, respectively. The discharge and charge voltage plateaus are located at 1.84 V and at 1.88 V, respectively, for the two cells. The low polarization of around 40 mV between the charge and discharge curves reflects the high-rate performance of these Li-ion cells. To investigate the rate capability, we evaluated the high-rate charge and discharge of Li-ion cells. The charge and discharge performance of a Li-ion cell containing electrolyte with 40% IL was compared to a cell with pure organic electrolyte (0% IL). The high-rate discharge of the Li-ion cells is shown in Fig. 14a. The two cells have comparable capacity up to the 2 C rate – 119 and 109 mAh g^{-1}, respectively, for electrolytes with 0% IL and 40% IL. At rates higher than 2 C, the discharge capacity of the cell with mixed electrolyte decreases faster than the cell without IL, and the difference between capacities increases with the rate. In contrast, the high-rate charge capability of the cell with the electrolyte containing 40% IL shows better performance up to 2 C rate, and then at higher discharge rates the cell with

Fig. 15. Cycle life of $Li_4Ti_5O_{12}/LiFePO_4$ 18650-cell at discharge: 10 C, charge: 5 C with organic electrolyte.

pure organic electrolyte has higher capacity (see Fig. 14b). In both high-rate charge and discharge at greater than the 2 C rate, the cell containing 40% IL shows lower performance than the cell with pure organic electrolyte. This pattern is attributed to the lower concentration of organic solvent molecules that are available for ion solvation needed for high-rate charge and discharge when IL is present in the electrolyte. However, the rates are still attractive, and the safety is acceptable for many battery applications.

One of the safest combinations for electrode materials for Li-ion cell is $LiFePO_4/Li_4Ti_5O_{12}$. This cathode/anode configuration in the 18650-cell using the standard organic electrolyte demonstrated a remarkable cycling life (Fig. 15). A very stable discharge capacity for discharge at 10 C and charge at 5 C was obtained for cells with conventional electrolyte. The capacity is maintained constant at 800 mAh for more than 20,000 cycles. This type of accelerated aging is equivalent to 50 years of the real life of the battery. For safe EV and HEV applications, however, this technology based on $LiFePO_4$ cathode and $Li_4Ti_5O_{12}$ anode with a mixed electrolyte having around 40% IL is an interesting subject for further development and optimization. Although the energy density of LTO/$LiFePO_4$ is low (67.5 Wh kg^{-1} with Al anode and cathode) for vehicle applications, it is of great interest for stationary or storage applications because of its long cycle life.

4. Conclusions

We reported in previous work that IL is a good candidate for safer batteries, however, the performance need to be improved. In this work, we show that mixed organic EC–DEC–1 M LiPF$_6$ and EMI-TFSI (IL) electrolyte can improve the performance without compromising safety. An optimum range for the viscosity and ionic conductivity is between 30 and 40% IL in the organic electrolyte. By adding IL, the performance of the graphite anode was also improved and lithium intercalation occurred successfully, despite the utilization of IL based on TFSI-anion. This mixed electrolyte gave results comparable to the organic electrolyte for both graphite anode and $LiFePO_4$ cathode. From the point of view of a safer Li-ion battery, we evaluated a $LiFePO_4/Li_4Ti_5O_{12}$ cell with an electrolyte mixture (40% IL) and compared it to the results in the standard organic electrolyte. The results were comparable up to a 2 C rate for discharge, and then the capacity starts to decrease slightly with the cell containing IL. When the cells are evaluated at high charge rate, the cell with the electrolyte mixture electrolyte was better below 2 C, and then the cells exhibited the same behavior as in the previous test. In order to make the best choice of the electrolyte composition for use in a practical Li-ion battery, we should take into account the flammability, conductivity and viscosity of the electrolyte. The elec-
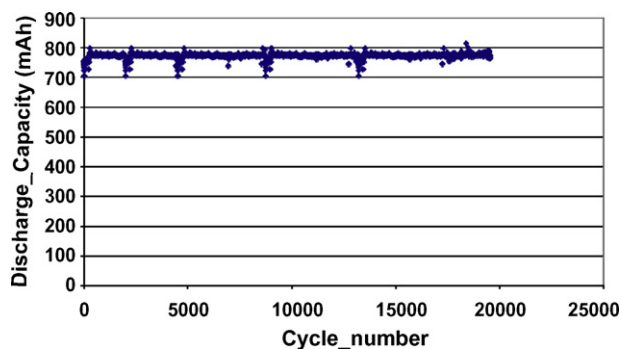
trolyte having the ionic liquid content between 30 and 70% should approach these requirements.

Acknowledgements

References

[1] T. Tanaka, K. Ohta, N. Arai, J. Power Sources 97–98 (2001) 2.
[2] R.A. March, S. Vukson, S. Sarampudi, B.V. Ratnakumar, M.C. Smart, M. Manzo, P.J. Dalton, J. Power Sources 97–98 (2001) 236.
[3] T. Takamura, Solid State Ionics 152–153 (2002) 19.
[4] K. Zaghib, P. Charest, A. Guerfi, J. Shim, M. Perrier, K. Striebel, J. Power Sources 134 (2004) 124.
[5] Anon., The Economist 390 (8622) (2009) 81.
[6] A. Guerfi, S. Duchesne, Y. Kobayashi, A. Vijh, K. Zaghib, J. Power Sources 175 (2008) 866.
[7] A. Guerfi, M. Dontigny, Y. Kobayashi, A. Vijh, K. Zaghib, J. Solid State Electrochem. 13 (2009) 1003 (Prof. J.O'M. Bockris, issue).
[8] J.S. Wilkes, Green Chem. 4 (2002) 73.
[9] K. Zaghib, P. Charest, A. Guerfi, M. Dontigny, M. Petitclerc, Canadian Patent, CA 2,482,003 (2004).
[10] J.G. Huddleston, H.D. Willaur, R.P. Swatloski, A.E. Visser, R.D. Rogers, Chem. Commun. (1998) 1765;
T. Emi, J.O'M. Bockris, J. Phys. Chem. 74 (1970) 159.
[11] L.A. Blanchard, D. Hancu, E.J. Beckman, J.F. Brennecke, Nature 399 (1999) 289.
[12] V. Baranchugov, E. Markevich, E. Pollak, G. Salitra, D. Aurbach, Electrochem. Commun. 9 (2007) 796.
[13] Y. Kobayashi, S. Duchesne, M. Dontigny, S. Seki, Y. Mita, H. Miyashiro, P. Charest, A. Guerfi, K. Zaghib, 211th ECS Meeting, 2007, Abst # 287.
[14] Y. Kobayashi, S. Seki, Y. Mita, Y. Ohno, H. Miyashiro, P. Charest, A. Guerfi, K. Zaghib, J. Power Sources 185 (2008) 542.
[15] L. Wu, Z. Song, L. Liu, X. Guo, L. Kong, H. Zhan, Y. Zhou, Z. Li, J. Power Sources 188 (2009) 570.
[16] M. Holzpfel, C. Jost, P. Novak, Chem. Commun. 4 (2004) 2098.
[17] M. Holzpfel, C. Jost, A. Prodi-Schaw, F. Krumeich, A. Wursig, H. Buqa, P. Novak, Carbon 43 (2005) 1488.
[18] T. Sato, T. Maruo, S. Marukane, K. Takagi, J. Power Sources 138 (2004) 253.
[19] Y. Wang, K. Zaghib, A. Guerfi, F.F.C. Bazito, R.M. Torresi, J.R. Dahn, Electrochim. Acta 52 (2007) 6346.