



Zwitterionic imidazolium compounds with high cathodic stability as additives for lithium battery electrolytes

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ABSTRACT

A series of imidazolium-based zwitterionic compounds having both a propylsulfonate group at 3-position and an ester group at 1- or 2-position are synthesized and their interactions with LiPF_6 are investigated. FT-IR study and theoretical calculation using density functional theory show that the interactions of the zwitterionic compound with LiPF_6 varies significantly with the location of the ester group on the imidazolium ring. The electrochemical stability of the imidazolium-based zwitterionic compound is significantly improved by introducing an ester group at the C-2 position of the imidazolium ring. Cycle performance tests show that the initial cell capacity remains almost unchanged up to 100 cycles at 1/2 C when 2.5 wt.% of 2-(acetoxymethyl)-1-butylimidazolium-3-propylsulfonate is added to the model electrolyte consisting of ethylene carbonate (EC), dimethyl carbonate (DMC), and ethylmethyl carbonate (EMC) (EC/DMC/EMC = 1/1/1 v/v/v), whereas the capacity of the cell containing an unsubstituted or methyl-substituted imidazolium compound at the C-2 position, 1-(acetoxymethyl)imidazolium-3-propylsulfonate or 1-(acetoxymethyl)-2-methylimidazolium-3-propylsulfonate as an additive, starts to decrease rapidly just after a few cycles.

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1. Introduction

Current electrolyte systems used for lithium-ion batteries have inherent safety problems arising from the use of volatile and flammable organic carbonates, including ethylene carbonate (EC), dimethyl carbonate (DMC), and ethylmethyl carbonate (EMC) [1,2]. In addition to the safety concern, organic carbonate-based electrolytes possess many other drawbacks in terms of charge/discharge capacity, operating temperature limit, and ionic conductivity. In this regard, the development of safer electrolyte systems with higher performance is strongly desired [3,4].

Recently, room-temperature ionic liquids (RTILs) have received considerable interest as promising alternatives to replace completely or partly the traditional carbonate-based electrolytes because of their favourable properties such as a wide electrochemical window, high conductivity, non-flammability, and wide operating temperature range [5–7]. Among various types of ionic liquids (ILs), imidazolium-based ILs have been most extensively

studied due to their ease of preparation, high ionic conductivity and relatively low viscosity. Nevertheless, the electrochemical application of these ILs has been restricted due to the low cathodic stability caused by the C-2 hydrogen atom [8–11]. To improve the cathodic stability of imidazolium-based ILs, the alkyl-substituted ILs at the C-2 position have been proposed, but they still suffer from low ionic conductivity and poor cycle performance, possibly due to their relatively high viscosities and/or low electrochemical stability of the alkyl group at the C-2 position towards oxidation [12–15].

Since the discovery of zwitterionic-type ILs by Ohno and other workers [16–19], many attempts have been made to use these compounds as electrolytes for lithium batteries and fuel cells. It has been found [20–22] that the addition of pyrrolidinium-based zwitterionic ILs significantly enhance lithium ion diffusivity and conductivity in polyelectrolyte gels. We also have reported [23] that the cell performance of a pyrrolidinium-based zwitterionic compound can be greatly improved by the introduction of an ester group at the 1-position. Such a favourable effect of the ester group was also demonstrated in a previous paper [24] that showed an improvement in ionic conductivity of 1,2-dimethylimidazolium trifluoromethanesulfonimide by the substitution of a methyl group with an ester group at the 1-position. Unfortunately, however,

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attempts to use imidazolium-based zwitterionic compounds have not been very successful.

This study examines dual-functional imidazolium-based zwitterionic compounds with an ester at the C-2 position and a propylsulfonate group at the 3-position, which exhibit excellent electrochemical stability. Cell performances of electrolytes containing these compounds as additives are compared with those containing zwitterionic imidazolium compounds with an ester group at the 1-position. The interactions between imidazolium-based zwitterionic compounds and LiPF₆ are also investigated by means of FT-IR spectroscopy and a theoretical calculation using density functional theory.

2. Experimental

Imidazole (99%), 2-methylimidazole (99%), 1-(2-hydroxyethyl)pyrrolidine (97%), pyridine (99%), chloromethyl acetate (98%), paraformaldehyde (95%), acetic anhydride (99%), 1-butylimidazole (99%), sodium hydride (dry, 99%), and 1,3-propanesultone (99%) were purchased from Aldrich Co. and used as-received. Solvents were obtained from J.T. Baker and distilled over appropriate drying agents prior to use. A LiPF₆ solution (1 M) of ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) (1/1/1 v/v/v) was donated from Cheil Industries, Inc. 1-(Methoxycarbonylmethyl)-2-methylimidazolium-3-propylsulfonate, **3d** and 1-(methoxycarbonylmethyl)imidazolium-3-propylsulfonate, **3e** were prepared according to procedures reported in the literature [23].

2.1. Synthesis of 1-methyl-2-(hydroxymethyl)imidazole (**1a**)

In a 100 mL high pressure reactor, 1-methylimidazole (8.2 g, 100 mmol) was reacted with paraformaldehyde (3.0 g, 100 mmol) in 40 mL of CH₃CN at 120 °C overnight. After the reaction was completed, CH₃CN was removed under a reduced pressure and the solid was collected, washed quickly with acetone (100 mL), then recrystallized from ethanol to give **1a** (yield: 71%). ¹H NMR (300 MHz, CD₃Cl, 25 °C): δ (ppm) = 6.81 (s, 1H, CH-Im), 6.78 (s, 1H, CH-Im), 6.74 (br, 1H, OH), 4.59 (s, 2H, CH₂O), 3.70 (s, 3H, NCH₃); calculated elemental analysis (%) for C₅H₈N₂O: C 53.6, H 7.2, N 25.0; found: C 53.2, H 7.4, N 7.0. 1-Butyl-2-(hydroxyethyl)imidazole, **1b** was prepared from 1-butylimidazole in a similar manner to that employed for the synthesis of **1a** (yield: 67%). ¹H NMR (300 MHz, CD₃Cl, 25 °C): δ (ppm) = 6.78 (d, 2H, CH-Im), 6.64 (br, 1H, OH), 4.57 (s, 2H, CH₂O), 3.95 (t, 2H, NCH₂), 1.71 (m, 2H, CH₂), 1.29 (m, 2H, CH₂), 0.89 (t, 3H, CH₃); calculated elemental analysis (%) for C₈H₁₄N₂O: C 62.3, H 9.2, N 18.2; found: C 61.9, H 9.3, N 18.0. 1-Methyl-2-(hydroxyethyl)imidazole, **1c** was prepared from 1,2-dimethylimidazole using a mixed solvent of dimethylformamide (DMF) and CH₃CN (v/v = 1/1) at 130 °C in an analogous manner to that used for the synthesis of **1a** (yield: 65%). ¹H NMR (300 MHz, CD₃Cl, 25 °C): δ (ppm) = 6.90 (s, 1H, CH-Im), 6.80 (s, 1H, CH-Im), 4.00 (t, 2H, CH₂O), 3.84 (br, 1H, OH), 3.56 (s, 3H, NCH₃), 2.84 (t, 2H, CH₂); calculated elemental analysis (%) for C₆H₁₀N₂O: C 57.1, H 8.0, N 22.2; found: C 56.8, H 8.4, N 21.9.

2.2. Synthesis of 1-methyl-2-(acetoxymethyl)imidazole (**2a**)

A mixture of **1a** (7.0 g, 62.4 mmol), acetic anhydride (30 mL, 31.7 mmol) and pyridine (30 mL, 37.0 mmol) in a 100 mL round-bottom flask was stirred for 6 h at room temperature. After the completion of the reaction, pyridine and acetic anhydride were removed by means of a rotary evaporator and the remaining solution was treated with Na₂CO₃ (7 g) in 50 mL of CH₂Cl₂ at room

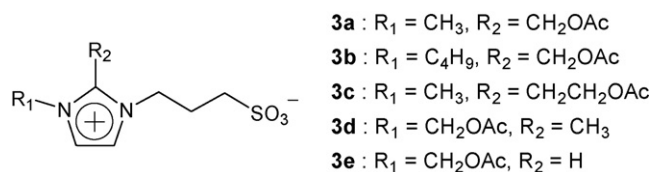
temperature to prevent the possible formation of protonated imidazole. The resulting mixture was filtered and washed with an aqueous solution of NaHCO₃ (30 mL). The organic layer was separated, washed twice with 5 mL portions of water, and dried over MgSO₄ (2 g). The filtrate was concentrated and the residue was purified on chromatography on silica gel with ethyl acetate to produce **2a** (yield: 73%). ¹H NMR (300 MHz, DMSO-*d*₆, 25 °C): δ (ppm) = 6.96 (s, 1H, CH-Im), 6.84 (s, 1H, CH-Im), 5.12 (s, 2H, CH₂O), 3.63 (s, 3H, NCH₃), 2.02 (s, 3H, COCH₃); calculated elemental analysis (%) for C₇H₁₀N₂O₂: C 54.5, H 6.5, N 18.2; found: C 54.2, H 6.8, N 17.9. 1-Butyl-2-(acetoxymethyl)imidazole, **2b** was prepared from **1b** similarly to that employed for the synthesis of **2a** (yield: 65%). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ (ppm) = 6.81 (d, 2H, CH-Im), 4.62 (s, 2H, CH₂O), 3.99 (t, 2H, CH₂), 2.11 (s, 3H, CH₃), 1.78 (m, 2H, CH₂), 1.36 (m, 2H, CH₂), 1.02 (t, 3H, CH₃); calculated elemental analysis (%) for C₁₀H₁₆N₂O₂: C 61.2, H 8.2, N 14.3; found: C 60.8, H 8.4, N 14.1. 1-Methyl-2-(acetoxymethyl)imidazole, **2c** was prepared from **1c** in an analogous manner to that used for **2a** (Yield: 69%). ¹H NMR (300 MHz, DMSO-*d*₆, 25 °C): δ (ppm) = 7.05 (s, 1H, CH-Im), 6.76 (s, 1H, CH-Im), 4.30 (t, 2H, CH₂O), 3.57 (s, 3H, NCH₃), 2.94 (t, 2H, CH₂), 1.99 (s, 3H, COCH₃); calculated elemental analysis (%) for C₈H₁₂N₂O₂: C 57.1, H 7.2, N 16.7; found: C 56.8, H 7.3, N 16.5.

2.3. Synthesis of 1-methyl-2-(acetoxymethyl)imidazolium-3-propylsulfonate (**3a**)

Compound **2a** (7.7 g, 0.05 mol) was reacted with 1,3-propanesultone (7.3 g, 0.06 mol) in 2-butanone overnight at 80 °C. After the completion of the reaction, the solid was collected by filtration, washed twice with 2-butanone (10 mL), and then recrystallized from MeOH (30 mL) to give **3a** (yield: 88%). ¹H NMR (300 MHz, DMSO-*d*₆, 25 °C): δ (ppm) = 7.87 (s, 1H, CH-Im), 7.79 (s, 1H, CH-Im), 5.42 (s, 2H, CH₂O), 4.39 (t, 2H, CH₂), 3.88 (s, 3H, NCH₃), 2.42 (t, 2H, CH₂), 2.10 (m, 3H, 2H, COCH₃, CH₂); calculated elemental analysis (%) for C₁₀H₁₆N₂O₅S: C 43.5, H 5.8, N 10.1; found: C 43.2, H 6.0, N 10.0. 1-Butyl-2-(acetoxymethyl)imidazolium-3-propylsulfonate, **3b** was prepared from **2b** in an analogous manner to that employed for the synthesis of **3a** (yield: 82%). ¹H NMR (300 MHz, D₂O, 25 °C): δ (ppm) = 7.65 (d, 2H, CH-Im), 5.49 (s, 2H, CH₂O), 4.48 (t, 2H, CH₂N), 4.29 (t, 2H, CH₂N), 2.97 (t, 2H, CH₂SO₃), 2.33 (m, 2H, CH₂), 2.17 (s, 3H, CH₃), 1.84 (m, 2H, CH₂), 1.36 (m, 2H, CH₂), 0.93 (t, 3H, CH₃); calculated elemental analysis (%) for C₁₃H₂₂N₂O₅S: C 49.0, H 7.0, N 8.8; found: C 48.8, H 7.2, N 8.9. 1-Methyl-2-(acetoxymethyl)imidazolium-3-propylsulfonate, **3c** was similarly prepared by reacting **2c** with 1,3-propanesultone (yield: 84%). ¹H NMR (300 MHz, DMSO-*d*₆, 25 °C): δ (ppm) = 7.83 (s, 1H, CHN), 7.75 (s, 1H, CHN), 4.36 (m, 2H, 2H, CH₂O, CH₂), 3.88 (s, 3H, NCH₃), 3.53 (t, 2H, CH₂), 2.50 (t, 2H, CH₂), 2.15 (q, 2H, CH₂), 2.07 (s, 3H, COCH₃); calculated elemental analysis (%) for C₁₁H₁₈N₂O₅S: C 45.5, H 6.3, N 9.7; found: C 45.4, H 6.5, N 9.6.

2.4. Instruments

¹H NMR spectra were taken on a Varian UNITY plus-300. FT-IR spectra were recorded on a PerkinElmer Spectrum GX spectrophotometer using a specially designed gas cell to avoid contact with atmospheric water [25]. Thermogravimetric analysis was conducted with a Mettler TGA 50 system in a nitrogen atmosphere at a heating rate of 10 °C min⁻¹ in the temperature range 20–500 °C. The melting temperatures of the zwitterionic compounds were determined by means of a TA Instruments Q10 differential scanning calorimeter in the range from 10 to 300 °C at a scan rate of 10 °C min⁻¹ under a nitrogen atmosphere. The ionic conductivities were measured with a Solatron 1260A frequency response analyzer. The electrochemical stabilities of the electrolytes were analyzed



Scheme 1.

by means of cyclic voltammetry (CH Instruments Electrochemical Workstation) at an ambient temperature. A glassy-carbon working electrode of 3 mm diameter was used with a platinum wire as the counter electrode and a silver wire as a quasi reference electrode. Galvanostatic charge–discharge tests were performed in one-stack laminated cells that each consisted of a LiCoO_2 cathode, a graphite anode, LiPF_6 (1 M) in EC, DMC, EMC (1/1/1 v/v/v), and a zwitterionic compound. All the cells were assembled in a dry room and the charge–discharge tests were performed with a battery cycler (Won A Tech WBC 3000) at a constant rate of 1/20 C for the first cycle, 1/5 C for the next three cycles, and 1/2 C for the remainder of the cycles.

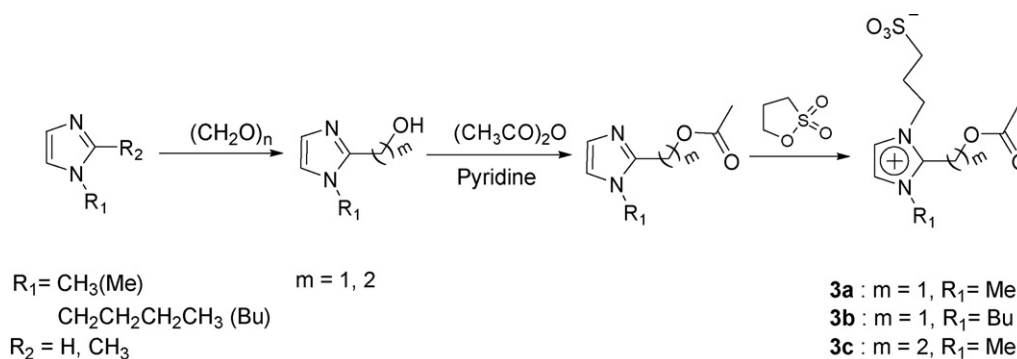
2.5. Computational details

The electronic energy and optimized structures of the stationary species of interest in the gas phase have been calculated using density functional theory method with the Amsterdam Density Functional (ADF) program, developed by Baerends et al. [26,27]. The electronic configurations of the molecular systems are described by double- ζ STO basis sets with polarization functions for the H, N, O, and C atoms, while triple- ζ Slater type basis sets are employed for the S and Ag atoms [28]. The 1s electrons of N, O, and C, the 1s–2p electrons of S are treated as frozen cores. Energy differences are calculated by augmenting the local exchange–correlation potential by Vosko et al. [29] with Becke's [30] non-local exchange corrections and Perdew's [31,32] non-local correlation corrections (BP86). ZORA scalar relativistic corrections [33,34] are added variationally to the total energy for all systems. In view of the fact that all systems investigated in this work show a large HOMO–LUMO gap, a spin-restricted formalism is used for all calculations.

3. Results and discussion

3.1. Thermal properties

The structures of the various zwitterionic imidazolium compounds and the synthesis of zwitterionic imidazolium compounds bearing a propylsulfonate group at the 3-position and an ester group at the 2-position are depicted in Schemes 1 and 2, respectively.



Scheme 2.

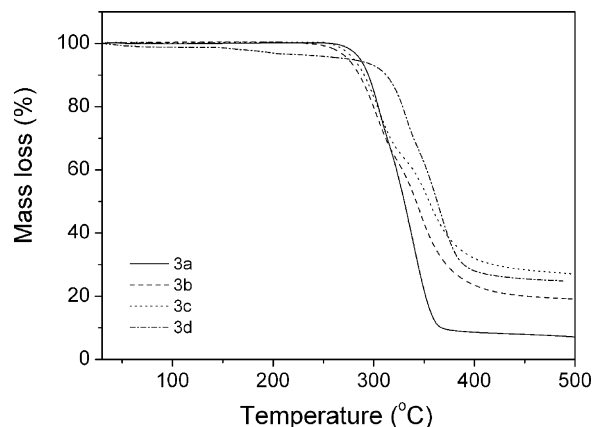


Fig. 1. Thermogravimetric analysis of zwitterionic imidazolium compounds with an ester group.

As demonstrated in Fig. 1, thermogravimetric analysis shows that all the zwitterionic compounds exhibit similar thermal behaviour. Two distinct decomposition temperatures are observed between 270 and 350 °C, except for **3a**. The decompositions at lower temperatures are probably due to decomposition of the ester group. The zwitterionic compounds bearing an ester group at the C-2 position decompose at a lower temperature than those with an ester group at the 1-position, possibly on account of the relatively low thermal stability of the ester group at the C-2 position of the imidazolium ring. The melting points of the zwitterionic compounds with an ester group at the C-2 position are higher than those with the ester group at the 1-position, as determined by differential scanning calorimetry (see Table 1).

3.2. Electrochemical properties

The effect of added zwitterionic compound on the electrochemical properties of a model electrolyte consisting of 1 M LiPF_6 in a mixture of EMC, DMC, and EMC (EC/DMC/EMC = 1/1/1 v/v/v) was

Table 1
Thermal properties of zwitterionic imidazolium compounds with an ester group

| | T_m (°C) ^a | T_{Decomp1} (°C) ^b | T_{Decomp2} (°C) ^b |
|-----------|-------------------------|--|--|
| 3a | 256.4 | 283.9 | – |
| 3b | 217.7 | 273.8 | 330.7 |
| 3c | 203.7 | 277.9 | 341.3 |
| 3d | 215.2 | 311.6 | 347.2 |
| 3e | 192.2 | 304.3 | 346.1 |

^a Melting temperature.

^b Decomposition temperatures.

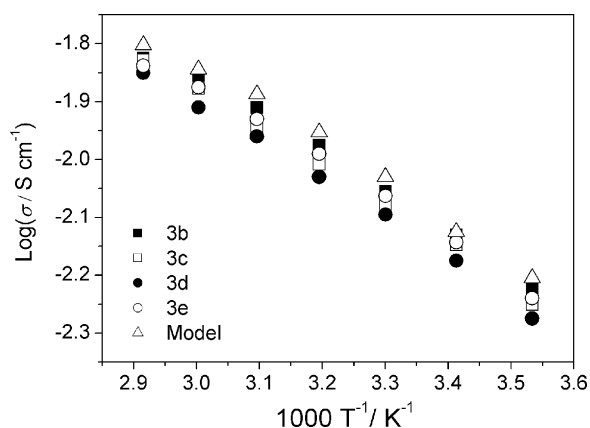


Fig. 2. Conductivities of electrolytes containing an zwitterionic imidazolium compound (2.5 wt.%).

investigated. The electrochemical properties of compound **3a** were not tested due to the formation of an insoluble complex when added to the model electrolyte. Elemental analysis and ^1H NMR spectroscopic results indicate that the complex is a 1:1 adduct of **3a** and LiPF_6 [35]. As shown in Fig. 2, the ionic conductivities of the electrolytes consisting of the model electrolyte and a zwitterionic compound (2.5 wt.%) increase with increasing temperature, possibly due to the decrease in viscosity at high temperature. As a whole, the conductivities of the electrolytes containing a zwitterionic compound are lower than that of the model electrolyte. This can be ascribed to the increase in viscosity by the addition of a zwitterionic compound. It is worth noting, however, that the electrolytes containing a zwitterionic compound with the ester group at the C-2 position exhibit higher conductivities than those with the ester group at the 1-position, which implies that the 2-ester group is more effective for the dissociation of LiPF_6 . In a previous paper [23], we have demonstrated that the presence of a zwitterionic compound bearing an ester group at the 1-position can enhance the dissociation of LiPF_6 through a multi-interaction of Li^+ with sulfonate and ester groups. Similarly, such a multi-interaction can be conceivable with the zwitterionic compound bearing the ester group at the C-2 position.

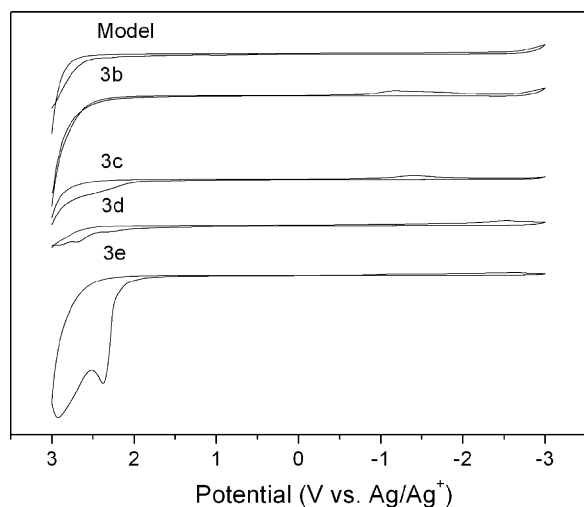


Fig. 3. Cyclic voltammograms of electrolytes containing an zwitterionic imidazolium compound (2.5 wt.%).

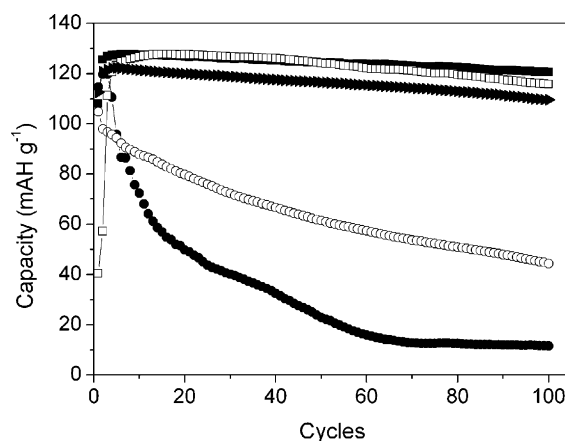


Fig. 4. Cycling performances for LiCoO_2 cathode and graphite anode using an electrolyte consisting of 1 M LiPF_6 in EC, DMC, EMC (1/1/1 v/v/v), and 2.5 wt.% zwitterionic compound (1/2 C rate, 3.0–4.2 V): (■) model, (□) **3b**, (▴) **3c**, (○) **3d**, and (●) **3e**.

The electrochemical stabilities of the electrolytes containing a zwitterionic compound at a concentration of 2.5 wt.% were analyzed by means of cyclic voltammetry at ambient temperature. As shown in Fig. 3, the electrolyte containing a zwitterionic compound with the ester group at the C-2 position has a slightly wider electrochemical window than those the ester group at the 1-position. This demonstrates a favourable effect of the ester group C-2 position.

3.3. Cell performance

Cell performance was also evaluated with electrolytes consisting of the model electrolyte and a zwitterionic compound. The data given in Fig. 4 show that the discharge capacities of the batteries are fairly stable up to 100 cycles at 1/2C when **3b** or **3c** is used as an additive. By contrast, the capacity of the cell containing **3d** or **3e** as an additive decreases drastically. These results strongly imply that substitution at the C-2 position by an ester group plays an important role in improving the electrochemical stability of the imidazolium compounds. The low electrochemical stabilities of **3d** and **3e** can be attributed largely to the acidic character of methyl hydrogen and C-2 hydrogen,

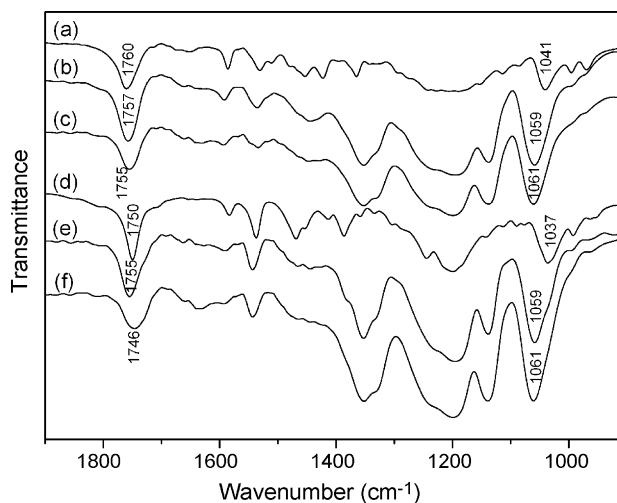


Fig. 5. FT-IR spectra showing: interaction of **3d** with LiPF_6 ; molar ratio of LiPF_6 /**3d** is (a) 0, (b) 1, (c) 2; and interaction of **3a** with LiPF_6 ; the molar ratio of LiPF_6 /**3a** is (d) 0, (e) 1, (f) 2.

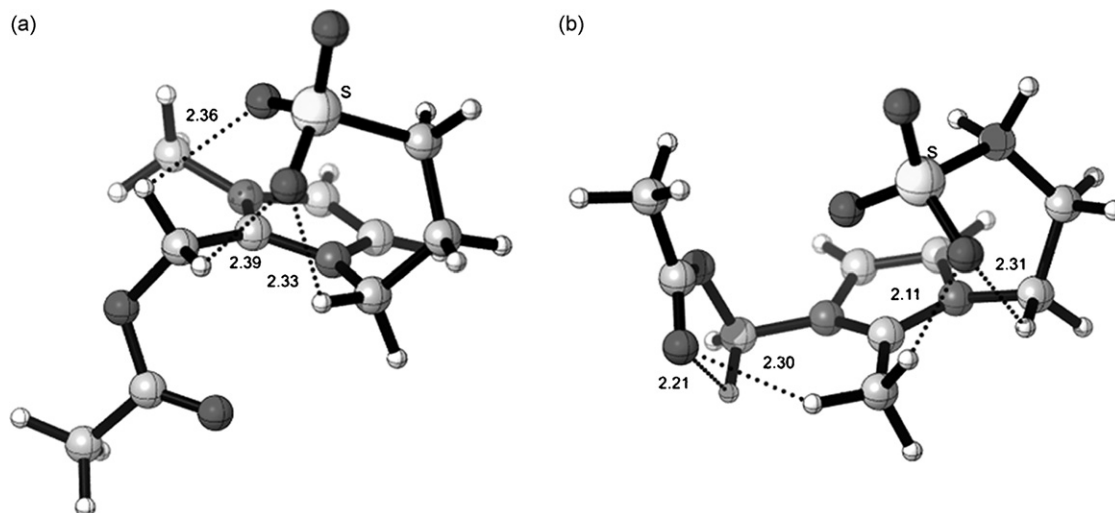


Fig. 6. Optimized structures of (a) **3a** and (b) **3d**.

respectively. It is well known that 2-H-imidazolium compounds are electrochemically unstable due to the acidic character of the C-2 hydrogen atom [8–11]. Like the C-2 hydrogen atom, the methyl hydrogen atom at the C-2 position of the imidazolium ring appears to possess some acidic character [9]. It is conceivable that a benzyl-like compound forms first from a 2-methylimidazolium compound during the redox process, and then decomposes readily on the elec-

trode surface. In the case of **3b** and **3c**, however, there exists no such acidic hydrogen because the C-2 methylene group on the imidazolium ring is bonded to the electron-withdrawing ester group. In addition to enhancement of the electrochemical stability of the zwitterionic compounds, the ester group seems to play a role in facilitating lithium ion transport through an additional interaction with LiPF_6 .

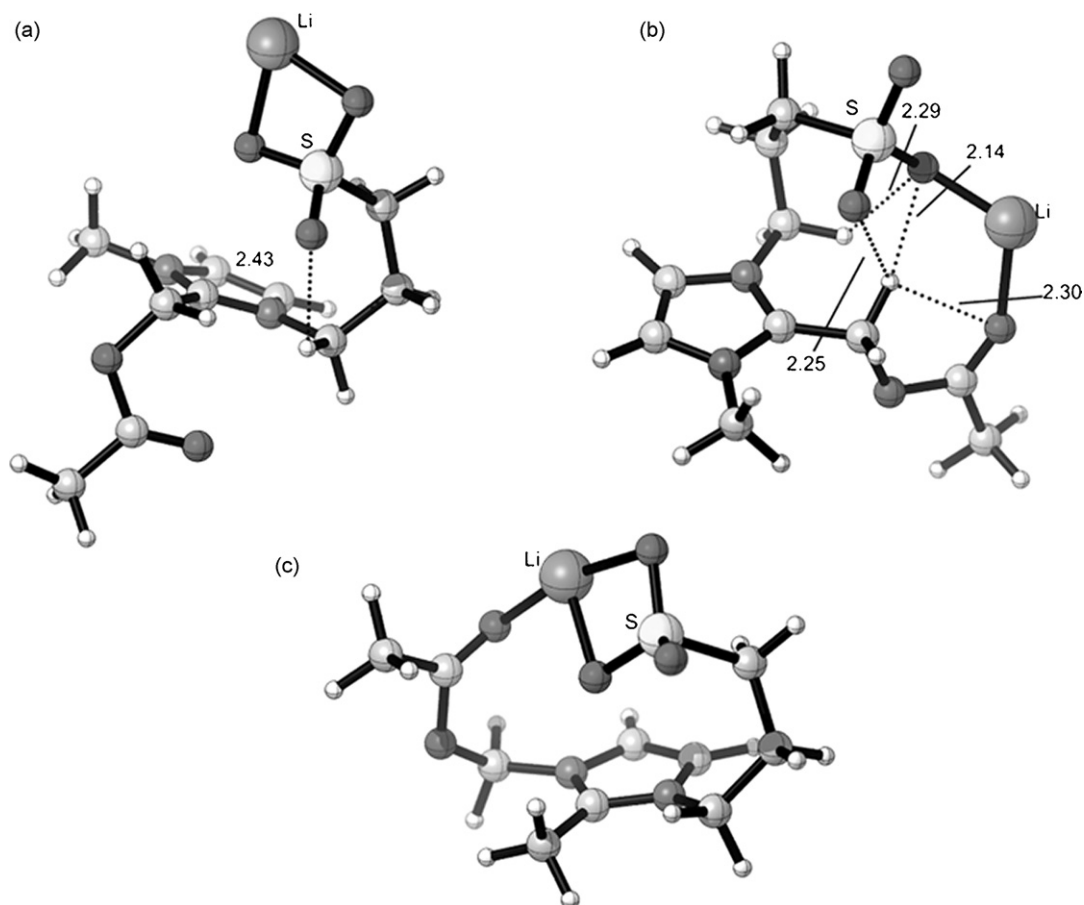


Fig. 7. Optimized structures of: (a) **3a**- Li^+ (molar ratio of $\text{Li}^+:\mathbf{3a}=1:1$), (b) **3a**- Li^+ (molar ratio of $\text{Li}^+:\mathbf{3a}=2:1$), and (c) **3d**- Li (molar ratio of $\text{Li}^+:\mathbf{3d}=1:1$).

3.4. FT-IR experiments

The interactions between LiPF_6 and zwitterionic compounds were investigated by means of FT-IR spectroscopy. As shown in Fig. 5, the peak at 1760 cm^{-1} , associated with the free carbonyl group of **3d** with the ester group at the 1-position, shifts to lower frequencies at 1757 and 1755 cm^{-1} upon interaction with one and two equivalents of LiPF_6 , respectively. The lower frequency shift for the carbonyl peak of **3d** is an indication that there is an additional interaction between the carbonyl group and the lithium ion bonded to sulfonate group.

Interestingly, the peak at 1750 cm^{-1} , associated with the carbonyl group of **3a** bearing the ester group at the C-2 position, moves to higher frequencies at 1755 cm^{-1} when treated with 1.0 equiv. of LiPF_6 . This suggests that there is no direct interaction between the ester group and LiPF_6 . The higher frequency shift appears to originate from the increased electron density due to the strong interaction between the propylsulfonate group and LiPF_6 . It was initially expected that such an additional interaction would be stronger for **3a** than **3d** because the ester and sulfonate groups of **3a** are closely located with each other at the 2- and 3-positions. The carbonyl stretching frequency of **3a**, however, moves to a lower frequency at molar ratios of $\text{LiPF}_6/\mathbf{3a}=2$, which suggests that the excess lithium ions are able to interact with the ester group after the sulfonate group is fully bonded by the lithium ion.

3.5. Theoretical calculations

To discover out the reason for the discrepancy between our expectation and the spectroscopic results, theoretical calculations were made using the density functional theory method. The optimized structures of **3a** and **3d** are shown in Fig. 6. The aromatic imidazolium cation is found to have a planar energy minimum. Both the ester and the sulfonate groups in compound **3d** are located on the same side of the imidazolium ring. In contrast to **3d**, however, the two functional groups in **3a** are on the opposite sides of the imidazolium ring, possibly due to the steric crowding caused by the bulky ester group at the C-2 carbon. From the geometry of **3a**, the absence of an additional interaction between lithium ion bonded to sulfonate group and the ester group can be easily rationalized.

The determination of the molecular structures of the **3a**- Li^+ and **3d**- Li^+ complexes at the BP86 level of computation clearly demonstrates the interaction of Li^+ with the sulfonate and/or the ester group. All the structures are optimized with respect to the position of Li^+ ions above the plane of the imidazolium ring and are shown in Fig. 7. Intra-molecular interaction of the lithium ion bonded to sulfonate group with the ester group can be clearly seen in complex **3d**- Li^+ , whereas no interaction is observed in complex **3a**- Li^+ . At a higher molar ratio of $\text{Li}^+/\mathbf{3a}$, however, the excess Li^+ seems to interact with the ester group because the sulfonate group is fully occupied by Li^+ . Once coordinated to the carbonyl group, the Li^+ -coordinate ester group is likely to have a tendency to move towards the sulfonate group for the additional interaction, as can be seen in the geometry of **3a** in Fig. 7.

Contrary to the carbonyl groups, the stretching frequencies assigned to the $\text{S}=\text{O}$ double bond of the sulfonate group of **3a** and **3d** moved to higher frequencies, i.e., from 1037 and 1041 cm^{-1} to 1059 cm^{-1} , respectively, upon interaction with an equimolar amount of LiPF_6 (Fig. 5). In the absence of LiPF_6 , the negative charge on the sulfonate group is evenly distributed over three oxygen atoms. Once coordinated by Li^+ , however, the charge appears to be localized on two oxygen atoms, as can be seen from the geometries of **3a**- Li^+ and **3d**- Li^+ in Fig. 7, and thereby increase the bond order of the remaining uncoordinated $\text{S}=\text{O}$.

It should be mentioned here that the degree of $\text{S}=\text{O}$ peak shift to a higher frequency is larger for **3a** than for **3d**. This result implies that Li^+ interacts more strongly with the sulfonate group of **3a** than with that of **3d**. Given such a strong bond formation and the additional interaction with the ester group, the dissociation of LiPF_6 appears to be more facilitated.

4. Conclusions

The electrolytes containing a zwitterionic imidazolium compound with an ester group at the 2-position exhibits much improved cycling performance compared with those containing a zwitterionic compound bearing an ester group at the 1-position and a hydrogen or methyl group at the 2-position. The presence of an ester group at the 2-position significantly enhances the electrochemical stability of the zwitterionic imidazolium compounds, possibly by preventing decomposition of the electrolyte on the electrode surface.

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- [35] ^1H NMR (400 MHz, DMSO- d_6 , 25 °C): δ (ppm) = 7.85 (s, 1H, CH-Im), 7.77 (s, 1H, CH-Im), 5.40 (s, 2H, CH₂O), 4.37 (t, 2H, CH₂), 3.87 (s, 3H, NCH₃), 2.42 (t, 2H, CH₂), 2.08 (s, 3H, COCH₃), 2.07 (m, 2H, CH₂); calculated elemental analysis (%) for C₁₀H₁₆F₆LiN₂O₅PS: C 28.1, H 3.8, N 6.5, S 7.5; found: C 28.7, H 3.8, N 6.1, S 7.4.