The effects of N-methyl-N-butylpyrrolidinium bis(trifluoromethylsulfonyl)imide–based electrolyte on the electrochemical performance of high capacity cathode material Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2

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1. Introduction

Searching for cheaper, but safer and higher capacity layered-cathode materials to substitute for LiCoO\(_2\) has been one of the most important subjects in the research of cathode materials for Li-ion batteries (LIB). Recently, the x Li\(_2\)MnO\(_3\) \((1-x)\) LiNi\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) series compounds have been intensively investigated because of their high specific capacities and good thermal stability [1]. The Li\(_2\)MnO\(_3\) component is presented to stabilize the electrode structure and enhance the discharge capacity of the electrode by extracting the lithium concomitant with release of oxygen (a net loss of Li\(_2\)O), typically at 4.6–4.8 V, to form a layered Mn\(_2\)O\(_3\) component [2]. As reported in our previous work [3], the cathode material Li[Li\(_{0.2}\)Mn\(_{0.54}\)Ni\(_{0.13}\)Co\(_{0.13}\)]O\(_2\) \((x=0.5)\) could deliver an initial discharge capacity of 250 mAh g\(^{-1}\), when discharged from 4.8 to 2.0 V at 18 mAg\(^{-1}\) at room temperature (RT). The reversible capacity of this cathode material is almost twice that of conventional layered/spinel cathode materials, such as LiCoO\(_2\) and LiMn\(_2\)O\(_4\).

However, in order to deliver high discharge capacity, these lithium-rich cathode materials have to be charged to high voltage of 4.6–4.8 V to activate Li\(_2\)MnO\(_3\) component. The upper cut-off voltage is beyond the electrochemical stability window of the organic carbonate-based electrolyte which are widely used nowadays, such as 1M LiPF\(_6\)/EC+DMC. The aggressive side reaction happening during charge up to 4.8 V leads to the formation of thick solid electrolyte interface (SEI) layer on the electrode surface, which is responsible for the high initial irreversible capacity loss (ICL) and damages the reversibility of lithium intercalation/de-intercalation process. The oxidation of the organic solvents at high voltage also produces gaseous reaction product and results in build-up of internal pressure of Li-ion battery. Meanwhile, the carbonate-based...
solvents of organic electrolyte are quite volatile and flammable, which poses a serious safety concern and reduces the battery operating temperature limit greatly.

From the safety point of view, room temperature ionic liquids (RTILs) have been investigated extensively as electrolytes for Li-ion batteries due to their desirable physicochemical properties such as extremely low vapour pressure, non-flammability and wide electrochemical stability window [4–8]. Amid the tested ILs, N-methyl-N-butylpyrrolidinium (Py14) bis(trifluoromethylsulfonyl)imide (TFSI) system provides a promising electrolyte candidate for Li-ion battery due to its good RT ionic conductivity of higher than 1 mS cm⁻¹, wide electrochemical stability window in excess of 5.5 V and a cathodic stability window extending below the lithium plating/stripping potential [9]. The electrochemical performances of Py14TFSI incorporated in polymer electrolyte systems, such as PEO-LiTFSI-Py14TFSI and polymeric ionic liquid (PIL)-LiTFSI-Py14TFSI polymer electrolytes, have been tested in lithium ion batteries [10–12]. However, lithium ion batteries with Py14TFSI electrolyte usually show poor rate capability due to the high viscosity of Py14TFSI. The poor rate performance makes cells using Py14TFSI-based electrolyte less attractive for high power density applications, such as electric vehicles (EVs) and hybrid electric vehicles (HEVs). Recently, to improve the electrochemical performance of electrode materials in the IL-based electrolyte, mixture electrolyte solutions containing Py14TFSI and other organic solvents have been prepared and investigated for lithium ion batteries [13,14]. As reported, the presence of Py14TFSI in the electrolyte is beneficial to the reduction of flammability of organic electrolyte and improvement of thermal stability of charged Li₁₋ₓCoO₂ in the electrolyte [13]. In IL-based electrolyte, LiTFSI is usually used as lithium salt because of its higher thermal stability than that of LiPF₆. However, LiTFSI is less stable in contact with aluminium current collector in the presence of organic solvents, such as EC and DMC [15]. Thus, alternative lithium salt like LiPF₆ has to be used instead of LiTFSI in mixture electrolyte containing IL and organic solvents when tested in a battery with high voltage (>4.5 V) cathode. To the best of our knowledge, the effects of adding IL into the organic electrolyte on the electrochemical performance of high voltage and high capacity lithium-rich cathode material Li[Li₂₀Mₐn₅₄Ni₀₁₃Co₀₁₃]O₂, especially the irreversible capacity loss and cycling stability, have seldom reported up to date.

In this work, with an aim to reduce the safety concern of lithium battery system using the high capacity lithium-rich cathode material Li[Li₂₀Mₐn₅₄Ni₀₁₃Co₀₁₃]O₂, we added IL (Py14TFSI) into the organic electrolyte system to prepare the Py14TFSI-added electrolytes, 1 M LiPF₆/Py14TFSI (1–δ) EC/DMC (1:1, v/v). The effects of Py14TFSI addition on the electrochemical performance and thermal stability of Li[Li₂₀Mₐn₅₄Ni₀₁₃Co₀₁₃]O₂ were investigated and discussed. The optimum composition of the Py14TFSI-added electrolytes has also been optimized based on the safety characteristics and electrochemical performances.

2. Experimental

2.1. Preparation of Py14TFSI-added electrolytes and the electrode material

The ionic liquid N-methyl-N-butylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Py14TFSI) (ρ = 1.4 g mL⁻¹) as shown in Scheme 1 was purchased from Merck company and dried for 24 h at 120 °C under vacuum prior to use. The viscosity of Py14TFSI detected by Brookfield programmable DV-III viscometer is 100.3 cp at 20 °C. Py14TFSI-added electrolytes, 1 M LiPF₆/Py14TFSI (1–δ) EC/DMC (1:1, v/v), were prepared with δ ranging from 0 to 1 in steps of 20 vol%. The IL free (δ = 0) electrolyte is indicated as reference electrolyte. Throughout this work, all the electrolyte solutions were prepared by volume and the volume ratio of EC to DMC is fixed at 1: 1. All the operations were carried out in the Argon-filled glove box (Labmaster100, Mbraun, Germany).

Cathode material Li[Li₂₀Mₐn₅₄Ni₀₁₃Co₀₁₃]O₂ was synthesized by a co-precipitation method [16]. The mixture of dried precipitate M(OH)₂ and required amount of LiOH·H₂O were pressed into pellets and precalcined at 480 °C for 10 h. Then the pellets were ground and made into new ones. The Li[Li₂₀Mₐn₅₄Ni₀₁₃Co₀₁₃]O₂ compound was finally obtained by sintering the new pellets at 900 °C for 15 h and then quenching them to room temperature.

2.2. Characterization

TG Analysis of the Py14TFSI-added electrolytes was measured with a Netzsch STA 409PC thermal analysis system (Netzsch, Germany) from RT to 600 °C at a heating rate of 10 °C min⁻¹ under Argon flow. The flammability of the electrolyte solutions was measured with a similar procedure used for self-extinguishing time (SET) test as reported in Refs. [17,18]. First, weighed electrolyte sample (ca. 0.1 g) absorbed in glass wool (ca. 0.3 mm in diameter) was exposed to fire for 10 s. If flame was observed, then the time for flame to extinguish was recorded. SET value was calculated by normalizing the flame burning time against the electrolyte weight. Ionic conductivity of the electrolyte solutions were measured by AC impedance spectroscopy with CHI608 workstation using a two Pt-electrode cell. Scanning electron microscopy (SEM) studies of pristine and cycled electrodes were performed on LEO1530 (Oxford company). XPS analysis of cycled electrodes (after 150 cycles at 1.0 C) was conducted using a Physical Electronics Quantum 2000 ESCA spectrometer (USA) with monochromatic Al Kα 1486.6 eV radiation operated at 23.2 W in a vacuum of <10⁻⁸ Torr. Thermal stability of Li[Li₂₀Mₐn₅₄Ni₀₁₃Co₀₁₃]O₂ electrodes at delithiated state of 4.6 V (ca. 320 mAh g⁻¹ of Li⁺ ions were extracted out of the electrodes) was examined by means of DSC with the Netzsch STA 409PC thermal analysis system (Netzsch, Germany) from 30 °C to 350 °C at a heating rate of 5 °C min⁻¹.

2.3. Electrochemical measurements

Electrochemical performances of the Py14TFSI-added electrolytes were tested in CR2025 coin-type cells. The Li[Li₂₀Mₐn₅₄Ni₀₁₃Co₀₁₃]O₂ electrodes were prepared by applying a mixture containing 80% active material, 10% acetylene black, 10% PVDF binder on circular Al current collector foils with a diameter of ca. 1.6 cm, followed by drying at 120 °C for 1 h. The electrode loading was controlled at about 3–5 mg. Then the Li[Li₂₀Mₐn₅₄Ni₀₁₃Co₀₁₃]O₂ cells were assembled with the electrodes as-prepared, metallic lithium foil (Φ 15.8 mm × 2 mm, China Energy Lithium Co., Ltd.) as counter electrode, Celgard 2300 as separator and the Py14TFSI-added electrolytes in Argon-filled glove box. The cells fabricated with electrolytes containing
Py$_{14}$TFSI volume fraction $\delta$ varying from 0 to 1 are indicated as Cell A (reference), Cell B (40% IL), Cell C (60% IL), Cell D (80% IL) and Cell E (pure IL), respectively. The charge–discharge experiments of Li/Li$_{10.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ cells were performed galvanostatically at 0.1 C (18 mA g$^{-1}$) and 1 C (180 mA g$^{-1}$) rates in the voltage range of 2.0−4.6 V on battery testers (Land CT2001A) at 27 $^\circ$C. The rate capability of the cells was tested by charging and discharging the cells from 0.1 C to 3 C. Capacities were calculated by only considering the active mass of the electrodes. All the potentials throughout the work are in reference to Li/Li$^+$ couple unless specified otherwise. Electrochemical impedance spectroscopy (EIS) of the cells during cycling (1.0 C) was measured at 4.3 V at frequency ranging from 100,000 Hz to 0.01 Hz with perturbation amplitude of 10 mV using a potentiogalvanostat PCSTAT 30 frequency response analyzer (Eco Chemie, Netherlands).

### 3. Results and discussion

#### 3.1. Physicochemical properties of the Py$_{14}$TFSI-added electrolytes

##### 3.1.1. Thermogravimetric analysis (TGA)

To reduce the volatility of electrolyte is of great importance to the safety of Li-ion batteries. TG analysis of electrolyte solutions with various Py$_{14}$TFSI content is displayed in Fig. 1. The reference electrolyte (IL free) shows the most volatile, exhibiting 70% weight loss at 150 $^\circ$C and 95% weight loss at 234 $^\circ$C. The weight loss from 30 to 234 $^\circ$C is ascribed to the evaporation of organic solvents (EC/DMC) and decomposition of lithium salt (LiPF$_6$). By contrast, the pure IL electrolyte showed the lowest volatility and the best thermal stability, showing only 10% weight loss at temperature extending to 378 $^\circ$C. With the increase of Py$_{14}$TFSI in the electrolyte, volatility of the electrolyte is reduced gradually. When heated from 30 to 150 $^\circ$C, the 20%, 40%, 60% and 80% Py$_{14}$TFSI-added electrolytes show 32%, 22%, 15% and 8% weight losses, respectively. This suggests that the volatility of the electrolyte is strongly dependent on the content of IL. The result is in good agreement with the TG analysis for 0.5 M LiTFSI + Py$_{14}$TFSI + y PEGDME and 1 M LiPF$_6$ + EC/DEC/VC mixture electrolyte systems [5,19]. The higher Py$_{14}$TFSI content in the electrolyte, the lower volatility of the Py$_{14}$TFSI-added electrolyte would be.

![Fig. 1. TG analysis of the Py$_{14}$TFSI-added electrolytes.](image)

![Fig. 2. Temperature dependence of ionic conductivity of Py$_{14}$TFSI-added electrolyte solutions. The inset is the figure showing conductivity data that follow VTF equation.](image)

#### 3.1.2. Flammability

The result of SET test indicates that the reference electrolyte has the highest SET of ca. 250 s g$^{-1}$. As the Py$_{14}$TFSI content increases, the SET of the electrolyte decreases significantly. The SET of the electrolyte with 20% Py$_{14}$TFSI decreases sharply to 160 s g$^{-1}$. When Py$_{14}$TFSI content increases to 40%, no flame was observed under the testing condition. This indicates that Py$_{14}$TFSI could function as a flame-retardant additive and reduce the flammability of the electrolytes [20]. The recorded data are consistent with that obtained for 1 M LiPF$_6$/PP$_{13}$TFSI+(EC/DMC/EMC) [21] and 1 M LiPF$_6$/EMITFSI+(EC/DEC/VC) [19] electrolyte systems, which presented that electrolytes with ca. 40% of IL appeared to be nonflammable. Thus, to obtain an electrolyte system with good safety, the Py$_{14}$TFSI content should be about 40% or higher. With this regard, only the electrochemical performances of Li/Li$_{10.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ electrodes in electrolytes with ≥40% Py$_{14}$TFSI were investigated and discussed.

#### 3.1.3. Ionic conductivity

The TGA and SET results suggest that safety concern of the electrolyte is reduced with the addition of Py$_{14}$TFSI and that the safety of related Li-ion batteries could be enhanced as a consequence. However, the viscosity of neat IL (Py$_{14}$TFSI) is as high as 100.3 cp at 20 $^\circ$C. The increasing addition of Py$_{14}$TFSI would increase the viscosity and lower the conductivity of the electrolyte.

Fig. 2 shows the temperature dependence of ionic conductivity of electrolytes with different content of Py$_{14}$TFSI. The conductivity variation with temperature follows the Vogel-Tamman-Fulcher (VTF) behavior as shown in the inset figure of Fig. 2. The VTF equation is as follows: $\sigma = \sigma_0 \exp \left( \frac{-E_a}{RT} \right)$. In VTF equation, the parameter $\sigma_0$, $E_a$ and $R$ correspond to pre-exponential factor, activation energy and ideal gas constant, respectively. The fitted values of $\sigma_0$, $E_a$, $T_0$ and VTF equation fitting parameter ($R^2$) for the Py$_{14}$TFSI-added electrolytes are listed in Table 1. It is found that the

<table>
<thead>
<tr>
<th>IL content</th>
<th>$\sigma_0$/S cm$^{-1}$</th>
<th>$E_a$/kJ mol$^{-1}$</th>
<th>$T_0$/K</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% IL</td>
<td>0.046</td>
<td>0.66</td>
<td>237</td>
<td>0.998</td>
</tr>
<tr>
<td>20% IL</td>
<td>0.105</td>
<td>1.88</td>
<td>199</td>
<td>0.999</td>
</tr>
<tr>
<td>40% IL</td>
<td>0.176</td>
<td>2.97</td>
<td>184</td>
<td>0.999</td>
</tr>
<tr>
<td>60% IL</td>
<td>0.244</td>
<td>3.97</td>
<td>183</td>
<td>0.999</td>
</tr>
<tr>
<td>80% IL</td>
<td>0.676</td>
<td>6.96</td>
<td>163</td>
<td>0.999</td>
</tr>
<tr>
<td>100% IL</td>
<td>1.296</td>
<td>7.85</td>
<td>179</td>
<td>0.999</td>
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![Table 1. VTF equation parameters of ionic conductivity.](image)
activation energy $E_a$ of the electrolyte increases with the increasing content of Py14TFSI. In comparison, the fitted parameters ($\sigma_0$, $E_a$, $T_0$) for pure IL electrolyte are comparable to that reported for other IL electrolyte systems, such as LiTFSI-Py14TFSI [22] and LiTFSI-PP13TFSI [23]. As described in Fig. 2, with the increase of Py14TFSI content, the conductivity of the electrolyte decreases gradually. For example, at 30 °C, the reference electrolyte shows the highest conductivity of 13.85 mS cm$^{-1}$ while 60% and 80% Py14TFSI-added electrolytes show conductivity of only 4.57 and 1.89 mS cm$^{-1}$, respectively. The optimum Py14TFSI content should be screened by taking both safety property and electrochemical performance into consideration.

3.2. Electrochemical performance of electrode material in Py14TFSI-added electrolytes

3.2.1. Charge/discharge performance at 0.1 C

The initial two charge/discharge profiles for Li[Li$_{1/3}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$]O$_2$ electrodes in the Py14TFSI-added electrolytes tested at 0.1 C are presented in Fig. 3. It is clearly shown that the first-cycle charge profile is characterized by an irreversible plateau where the potential is approximately constant at $-4.5$ V vs. Li/Li$^+$. The irreversible voltage plateau is obviously beyond the formal oxidation potential of Ni$^{2+}$ to Ni$^{4+}$ and Co$^{3+}$ to Co$^{4+}$. Similar plateaux are also observed for other lithium-rich electrodes with Li$_2$MnO$_3$-like character, such as Li[Li$_{0.67}$Li$_{0.33}$Mn$_{2/3}$Co$_{1/3}$]O$_2$ and x Li$_2$MnO$_3$·(1 − x) LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$.

To date, it is generally accepted that the dominant mechanism for the irreversible voltage plateau during first charge is an oxygen loss process [24,25]. Based on the results of in situ X-ray diffraction studies, Lu and Dahn firstly proposed that the irreversible voltage plateau could be ascribed to extraction of Li$^+$ accompanied with an irreversible loss of oxygen during the plateau (a net loss of Li$_2$O) [24]. Using differential electrochemical mass spectrometry (DEMS) technique, Armstrong et al. presented direct evidence for oxygen evolution associated with charging process at the irreversible plateau [25]. Moreover, Robertson and Bruce reported that the irreversible plateau was not only attributed to an oxygen loss but also ascribed to some Li$^+/H^+$ exchange, especially at high temperature of 50–55 °C, where the H$^+$ ions were generated from the oxidation of alkyl carbonates upon charging to high voltage [26,27]. As reported for Li[Ni$_{0.67}$Li$_{0.33}$Mn$_{2/3}$Co$_{1/3}$]O$_2$ (x = 0.15), the ratio of lithium removed via oxygen loss to that of Li$^+/H^+$ exchange was 4.4:1 when the material was charged at 30 °C. This ratio dropped to 3.06:1 when the material was charged at 55 °C, indicating that greater Li$^+/H^+$ exchange occurred at higher temperature [27]. Due to Li$^+/H^+$ exchange, hydrogen bonding formed between adjacent oxide ion layers and became the driving force for crystal structure to transform from layered (ABC) to CrOOH-type P3 structure (AABBC) [26,28].

Considering that the electrochemical performance evaluation of Li[Li$_{1/3}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$]O$_2$ electrode in Py14TFSI-added electrolyte was carried out at 27 °C, the irreversible voltage plateau at $-4.5$ V is dominantly due to the mechanism of oxygen loss. For pure IL electrolyte, it is electrochemically stable at voltage higher than 5.0 V [16] and not possible to be oxidized to generate H$^+$ ions, when even charged to high voltage of 4.6 V. Thus the possibility of Li$^+/H^+$ exchange could be eliminated for the electrode material charged in pure IL electrolyte. Without the existence of Li$^+/H^+$ exchange, the electrode structure would be more stable when cycled in the pure IL electrolyte because no hydrogen bonding between adjacent oxide ion layers is formed.

At the oxygen loss plateau, the Li$_2$MnO$_3$ component is activated to form MnO$_2$ component. Lithium ions can be re-inserted back into the MnO$_2$ component with the lowering of Mn oxidation state and thus the electrode material could deliver high discharge capacity during the subsequent discharge process. At low current rate of 0.1 C, Li[Li$_{1/3}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$]O$_2$ electrodes could deliver initial discharge capacities of up to 250 mAh g$^{-1}$ in Py14TFSI-added electrolytes, as described in Fig. 4(a). These discharge capacities
are equivalent to that of cells with the reference electrolyte [3,29]. Due to the high polarization caused by low ionic conductivity of pure IL electrolyte, less Li$_2$MnO$_3$ component of the electrode can be activated and thus the electrode exhibits a little lower discharge capacity of 237 mAh g$^{-1}$. The result means that even in electrolyte with high Py$_{14}$TFSI content, Li[Li$_0.2$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$]O$_2$ could still deliver high discharge capacity of ca. 250 mAh g$^{-1}$ for battery application. In comparison, with Py$_{14}$TFSI-added electrolyte, the discharge capacity of Li[Li$_0.2$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$]O$_2$ is almost twice that reported for Li/LiCoO$_2$ cell with 1 M LiTFSI/N$_{1116}$TFSI-EC-DEC mixture electrolyte at 0.05 C (140 mAh g$^{-1}$) [30], or Li/LiFePO$_4$ cell with LiF$_{13}$EMITFSI-EC-DEC-VC mixture electrolyte at 0.1 C (150 mAh g$^{-1}$) [19].

The initial irreversible capacity losses (ICL) and coulombic efficiencies (CE) of Li[Li$_0.2$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$]O$_2$ electrodes in Py$_{14}$TFSI-added electrolytes at 0.1 C are compared in Fig. 4(b). In reference electrolyte, Li[Li$_0.2$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$]O$_2$ electrode exhibits the highest initial ICL of 67 mAh g$^{-1}$ with the lowest coulombic efficiency of 78.9%. With increasing Py$_{14}$TFSI content in the electrolyte, the initial ICL value decreases and the coulombic efficiency increases. In electrolyte containing 60% Py$_{14}$TFSI, not only could the electrode still deliver an initial discharge capacity as high as 250 mAh g$^{-1}$, but also the initial ICL of the electrode decreases to only 47 mAh g$^{-1}$ and the coulombic efficiency increases to 84.1%. Using pure IL electrolyte, the electrode material shows even lower initial ICL (39 mAh g$^{-1}$) and further improved initial coulombic efficiency (85.8%).

Although the lithium-rich material Li[Li$_0.2$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$]O$_2$ has much higher discharge capacity as compared to LiCoO$_2$, one drawback of this material is that the electrode suffers a large ICL in the first cycle. The large ICL is attributed to the irreversible extraction of Li$_2$O followed by an elimination of oxide ion vacancies and a condensation of crystal structure through the displacement of transition metal ions diffusing from the surface into bulk vacancies created by lithium ions [25]. Meanwhile, the aggressive side reaction between electrode material (evolved oxygen species, etc.) and the electrolyte is also responsible for the large ICL. However, it is difficult to differentiate the parasitic side reaction from the oxygen loss plateau (∼4.4–4.6 V) during first charge process and it is hard to know the contribution of side reaction to the total irreversible capacity loss.

Much effort has been directed to reduce the initial ICL and increase the initial coulombic efficiency [3,29,31,32] of lithium-rich cathode materials. Acid treatment is a useful approach to decrease the initial ICL of lithium rich cathode materials by leaching out Li$_2$O from Li$_2$MnO$_3$ component prior to charge/discharge measurements [32]. The initial coulombic efficiency of acid-treated materials could be even higher than 100%. However, due to the H$^+$/Li$^+$ exchange during chemical activation, acid treatment damages the cycling stability and rate performance of the electrode materials. Another effective strategy is to modify the surface of the electrode material with other inert materials, such as Al$_2$O$_3$ [29], TiO$_2$ [31], AlF$_3$ [3] and AlPO$_4$ [33,34]. For example, as reported by Wu et al. [29], after surface modification with Al$_2$O$_3$, the initial ICL of Li[Li$_0.2$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$]O$_2$ was reduced from 75 mAh g$^{-1}$ to 41 mAh g$^{-1}$ when the electrode was tested at C/20. This improvement was ascribed to the optimization of electrode/electrolyte interface and suppression of the side reaction between the electrode and the electrolyte.

In the present study, it is found that the addition of Py$_{14}$TFSI is another useful strategy to reduce the initial ICL of lithium-rich cathode material Li[Li$_0.2$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$]O$_2$, especially at high Py$_{14}$TFSI content. At Py$_{14}$TFSI content <80%, almost the same discharge capacity of ∼250 mAh g$^{-1}$ could be obtained, suggesting that almost the same amount of Li$_2$MnO$_3$ can be activated during the initial charge process [35]. The total charge capacity decreases with the increase of Py$_{14}$TFSI content in the electrolyte indicates that the side reaction between cathode and electrolyte is significantly suppressed. The main reason is that the IL (Py$_{14}$TFSI) is anodically stable at voltage in excess of 5.0 V [10], the addition of which can diminish the side reaction between the electrode and Py$_{14}$TFSI-added electrolyte at high operating voltage. Therefore, the cathode material Li[Li$_0.2$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$]O$_2$ in electrolyte with higher Py$_{14}$TFSI content shows less initial irreversible capacity loss and higher initial coulombic efficiency. Extremely, side reaction between electrode material and pure IL electrolyte would be negligible and the initial ICL of the electrode in pure IL electrolyte is reduced to only 39 mAh g$^{-1}$, which is even lower than that of Li[Li$_0.2$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$]O$_2$ electrodes modified with 2.5 mol% AlF$_3$ (47 mAh g$^{-1}$) [3] or with 3 wt% Al$_2$O$_3$ (41 mAh g$^{-1}$) [29]. It could also be tentatively proposed that the mechanism of surface coating in reducing the initial ICL is mainly via suppression of the aggressive side reaction between electrode and electrolyte.

### 3.2.2. Rate performance of the electrode material in Py$_{14}$TFSI-added electrolytes

The rate capability is an important factor for battery performance. High rate capability is more competitive in the occasion where high power supply is required.

The rate performance for Li[Li$_0.2$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$]O$_2$ cells with the Py$_{14}$TFSI-added electrolytes is shown in Fig. 5. As can be predicted, the rate capability of the cells decreases in the trend: Cell A (reference) > Cell B (40 IL%) > Cell C (60 IL%) > Cell D (80 IL%) > Cell E (pure IL). The reference electrolyte cell shows the best rate capability while the pure IL electrolyte cell exhibits the poorest rate capability. The discharge capacity of cell with pure IL electrolyte (Cell E) decreases rapidly to only 35 mAh g$^{-1}$ at 1.0 C, which is only about 15% of the discharge capacity at 0.1 C. Li-ion batteries with pure IL electrolyte usually show poor rate capability due to the high viscosity of IL electrolyte. Similar poor rate performance was reported for Li/LiCoO$_2$ cell with Py$_{14}$TFSI at 1.0 C, which showed only 23% of capacity retention versus to the discharge capacity at 0.1 C [36].

Cell B (40 IL%) and Cell C (60 IL%) exhibit comparable discharge capacities up to 1.0 C rate, that is, 167 and 169 mAh g$^{-1}$, compared to 182 mAh g$^{-1}$ for Cell A (reference). At current rates higher than 1.0 C, the discharge capacities of Cell B and Cell C both start to deviate from that of Cell A. However, the rate performance of the cathode electrodes in 40–60% Py$_{14}$TFSI-added electrolytes is still attractive for many applications.
Cell D (80% IL) shows discharge capacities equivalent to that of reference electrolyte cell up to 0.5 V. However, at 1.0 V rate, the performance of Cell D starts to deviate from that of Cell A, showing only 48% of capacity retention of the discharge capacity at 0.1 C. The poor rate performance of cells using Py14TFSI-added electrolyte is attributed to the lower concentration of organic solvent molecules that are available for ion solvation [19]. With the increase of Py14TFSI content, the ionic conductivity of the electrolyte decreases and the battery polarization for charge and discharge process would become large. This means that less Li$_2$MnO$_3$ component of the electrode could be activated during initial charge process and thus lower discharge capacity could be achieved in Py14TFSI-added electrolyte, especially at high Py14TFSI content and/or tested at high current rates. In order to achieve desirable rate capability of the electrode, the Py14TFSI content is recommended to be lower than 80%.

3.2.3. Cycling performance of the electrode material at 1.0 C

The cycling performance and normalized capacity versus cycle number for Li/Li[$\text{Li}_{0.3}\text{MnO}_0.8\text{NiO}_{0.15}\text{Co}_{0.13}]$O$_2$ cells with Py14TFSI-added electrolytes at 1.0 C rate are presented in Fig. 6(a) and (b). As shown in Fig. 6(a), with the increasing addition of Py14TFSI into the electrolyte, the discharge capacities of the fabricated cells decrease gradually. As discussed above, this is due to the increasing battery polarization caused by the decrease of ionic conductivity of Py14TFSI-added electrolyte and, consequently, less Li$_2$MnO$_3$ component of the electrode material could be activated within the charge voltage limit. The initial discharge capacities for Cell B (40% IL), Cell C (60% IL) and Cell D (80% IL) are 158, 151 and 124 mAh g$^{-1}$, respectively. With pure IL electrolyte, the discharge capacity of Cell E is quite low (only ca. 25 mAh g$^{-1}$) at 1.0 C rate due to the high viscosity and low ionic conductivity of pure IL electrolyte. Although the initial discharge capacities of Cell B, C and D are a little lower than that of cell with reference electrolyte, cells with Py14TFSI-added electrolytes show superior capacity retentions during extended charge/discharge cycling in comparison with that of cell A, as shown in Fig. 6(b). To be specific, the capacity retentions for Cell B, C and D after 150 cycles are 81.0%, 84.4% and 80.0%，respectively, which are higher than that of 54.0% for Cell A.

Two possible reasons could be responsible for the better cycling stability achieved for Li/Li[$\text{Li}_{0.3}\text{MnO}_0.8\text{NiO}_{0.15}\text{Co}_{0.13}]$O$_2$ cells with Py14TFSI-added electrolyte than that for cell with reference electrolyte. The addition of Py14TFSI reduces the ionic conductivity of the electrolyte, which decreases the lithium ion transportation in the electrolyte and increases the polarization of the battery system. Less amount of Li$_2$MnO$_3$ component could be activated and lower discharge capacity could be obtained for electrode in electrolyte with higher Py14TFSI content. Nevertheless, the un-activated Li$_2$MnO$_3$ component left in the electrode plays an important role in stabilizing the electrode structure during the subsequent cycles [1]. On the other hand, ascribed to the high anodic stability of Py14TFSI, less side reaction occurs between electrode and Py14TFSI-added electrolyte and thus the electrode/electrolyte interface would be much more stable during cycling. SEM, XPS and EIS measurements have been performed to explore why Li/Li[$\text{Li}_{0.3}\text{MnO}_0.8\text{NiO}_{0.15}\text{Co}_{0.13}]$O$_2$ electrolyte shows superior cycling stability in Py14TFSI-added electrolyte.

3.2.4. The evidence of different interfacial behavior of the Li-rich electrode material in Py14TFSI-added electrolytes

SEM images of pristine electrode and electrodes cycled in reference electrolyte and Py14TFSI-added electrolyte at 1.0 C for 300 cycles are shown in Fig. 7. As can be seen from Fig. 7(a), pristine electrode shows a uniform distribution of cathode material Li[$\text{Li}_{0.2}\text{MnO}_0.8\text{NiO}_{0.13}\text{Co}_{0.13}]$O$_2$, acetylene black (AB) and binder (PVDF). After cycling in reference electrolyte for 300 cycles, the surface of the electrode is covered by a thick SEI layer and is difficult to discern the active material and other component of the electrode, as can be observed from Fig. 7(b). That is because in reference electrolyte, aggressive side reaction takes place between electrode material and the electrolyte when charged to high voltage (4.6 V) and the side products form on the surface of the electrode (SEI layer). The SEI layer becomes thicker with the accumulation of side reaction with the increase of cycle number. This would influence the reversibility of lithium ion intercalation/de-intercalation process and thus results in capacity fading during extended cycling, especially from 80th to 150th cycle.

On the contrary, as shown in Fig. 7(c) and (d), when electrodes are cycled in 40% and 60% Py14TFSI-added electrolytes for 300 cycles, the surface morphology of the electrodes does not show an obvious difference in comparison with the pristine one. That is because Py14TFSI has higher anodic stability, less side reaction takes place between electrode material and the Py14TFSI-added electrolyte during charge to high voltage. As a result, the morphology of electrode cycled in Py14TFSI-added electrolyte does not change much even after extended cycling.

XPS experiments were performed to investigate the SEI layer composition of cycled electrode. The S 2p and N 1s region XPS spectra of electrode cycled in 60% Py14TFSI-added electrolyte at 1.0 C for 150 cycles are shown in Fig. 8(a) and (b). The results of the S 2p region spectra indicate the presence of SO$_2$CF$_3$ species at 169.0 and 170.2 eV (doublet) and a small amount of oxidized sulfur species at 167.0 eV (ca. 3% calculated from peak area) [37], as described in Fig. 8(a). The SO$_2$CF$_3$ species mainly exist on the surface of the electrode because the intensity of S 2p spectra for SO$_2$CF$_3$ moiety decreases rapidly with etching depth. Similarly, the intensity of N 1s peak also decreases rapidly with the etching depth, as shown.
in Fig. 8(b). The result suggests that only a thin SEI layer (about 10 nm) formed on the cathode electrode surface upon charge and discharge for 150 cycles. The N 1s region spectra could be resolved into two peaks, quaternary ammonium cations Py14+ at 402.0 eV [37] and amide type product at 399.6 eV [38,39]. The amide type product is associated with existence of TFSI− in the solid electrolyte interface (SEI layer). This demonstrates that the TFSI− anions and Py14+ cations of Py14TFSI is stable within the voltage range (2.0–4.6 V) and mainly present as precipitated salt of the SEI layer components.

Considering that the Py14TFSI is anodically stable at voltage in excess of 5.0 V [10], the addition of Py14TFSI would increase the anodic stability of the reference electrolyte. It is proposed that the cations (Py14+) and anions (TFSI−) of Py14TFSI are inclined to be absorbed on the surface of the electrode through electrostatic force. During charge process, cations and anions of Py14TFSI existing on the surface of the electrode prevent the direct contact between electrode and electrolyte and thus delay and suppress the side reaction between them. The result of cyclic voltammetry (CV) experiments verifies that the oxidation current for 60% Py14TFSI-added electrolyte on stainless steel (SS) working electrode is less aggressive and occurs at higher voltage (vs. Li/Li+) than that for reference electrolyte (data not shown). Thus, in the presence of Py14TFSI, less side products form on the surface of the electrode and the electrode/electrolyte interface would be much more stable. This would be the reason that cathode electrode cycled in IL-added electrolyte exhibits good cycling stability. During the formation of SEI layer, some cations and anions of the Py14TFSI are trapped in the SEI layer and become the components of it. However, the SEI layer composition differences between electrodes cycled in reference electrolyte and Py14TFSI-added electrolyte are still unknown.

In the future work, more effort will be devoted to getting insight to SEI layer composition differences, with the complementary results of FTIR and Raman measurements.

Electrochemical impedance spectroscopy (EIS) has also been performed to understand more about the origin of the good electrochemical performance of cell with Py14TFSI-added electrolyte. The measurements were carried out at charged state of 4.3 V at 50th, 100th and 150th cycles when cycled at 1.0 C. The measured impedance spectra of Cell A (reference) and Cell C (60% IL) are presented in Fig. 9(a) and (b), respectively. As shown, a high-frequency semicircle, an intermediate-frequency semicircle and low-frequency tail are observed in the measured impedance spectrum. The high frequency semicircle is related to the SEI resistance (Rsei). The intermediate frequency semicircle is ascribed to the charge transfer resistance (Rct) in the cathode/electrolyte interface. The low frequency tail is associated with the Li+ ion diffusion process in the solid phase of the electrode [3,40]. The measured impedance spectra were simulated with the equivalent circuit inserted in Fig. 9(a). In the equivalent circuit, Re is the component associated with electrolyte resistance, Rsei and CPEsei are impedance and related capacitive element of the SEI layer, Rct and CPEct are charge transfer resistance and double layer capacitance at the electrode/electrolyte interface, and W1 and C1 are Warburg impedance and capacitive elements related to accumulation of Li+ ions in the active mass [41]. The fitted results are shown as lines in Fig. 9(a) and (b), which correspond well with the measured spectra. The fitted result of the evolution of Re, Rsei and Rct resistances is summarized in Table 2. Due to the difficulty in fitting the electrolyte resistance (Re) and SEI resistance (Rsei) for reference electrolyte cell, the Re (relatively small) and Rsei resistances are calculated together.
It can be found from the data provided in Table 2, as the charge/discharge cycling proceeds, all kinds of resistances increase for both Cell A and Cell C. Obviously, the resistances, especially the charge transfer resistance, for Cell A increase at a faster rate. In detail, the total resistances of Cell A at 100th and 150th cycles are about 1.5 and 2.5 times of that at 50th cycle, respectively. The fast increase of charge transfer resistance and the total resistance is the reason for the rapid capacity fading of the reference electrolyte cell. Due to the high viscosity of the component of Py14TFSI, the $R_t$ resistance of Cell C ($\sim$5 $\Omega$) is relatively high in comparison with that of reference electrolyte cell. Nevertheless, Cell C (60% IL) shows very stable charge transfer resistance ($R_t$) and SEI layer resistance during cycling, exhibiting only 15% increase of total resistance from 50th to 150th cycle. The stable charge transfer resistance and total resistance of Cell C would be ascribed to the effective suppression of side reaction on the electrode surface and the formation of stable electrode/electrolyte interface during cycling in the presence of Py14TFSI. The obtained EIS result, which is in good agreement with SEM morphology observations and XPS spectra analysis, could explain the good extended cycling stability of Cell C.

3.3. Thermal property of charged electrodes – differential scanning calorimetry (DSC)

Thermal stability of cathode material, especially at delithiated state, is greatly important related with battery safety. Differential scanning calorimetry (DSC) is a useful technique to record the thermal reaction between charged electrode and electrolyte [3,36,42]. The DSC profiles for Li[Li$_{0.2}$Mn$_{0.52}$Ni$_{0.13}$Co$_{0.13}$]O$_2$ electrodes at charged state in Py14TFSI-added electrolytes are shown in Fig. 10(a). As shown, the peak temperature for thermal reaction between charged electrode and the residual electrolyte is increased with the increase of Py14TFSI content, from 207.3 °C for reference electrolyte to 230.0 °C for pure IL electrolyte. Meanwhile, with the increasing Py14TFSI content in the electrolyte, the charged electrode produces less amount of heat, as shown obviously in Fig. 10(b). The charged electrodes with 40%, 60%, 80% and 100% Py14TFSI-added electrolytes produce 656, 629, 589 and 407 J g$^{-1}$ of heat, respectively. Particularly, the heat produced from charged electrode with pure IL electrolyte is less than half of that produced from charged electrode with reference electrolyte, which is 860 J g$^{-1}$. The results suggest that the component of the Py14TFSI plays a key role in reducing the thermal reaction between charged electrode and the residual Py14TFSI-added electrolyte. Similarly, Xiang et al. also observed that the area of exothermic peak associated with thermal reaction between charged Li$_{0.5}$CoO$_2$ and electrolyte LiTFSI([Py$_3$TFSI + xDEC]) decreased dramatically with the increase of IL content [36].

<table>
<thead>
<tr>
<th>Table 2</th>
<th>The fitted results of EIS spectra of Cell A (reference) and Cell C (60% IL) during cycling.</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Cell A (reference)</td>
</tr>
<tr>
<td>50th cycle</td>
<td>$R_t /\Omega$</td>
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<td></td>
<td>$R_{ct}/\Omega$</td>
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<td>$R_{ct}/\Omega$</td>
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FIG. 8. (a) S 2p and (b) N 1s region spectra for electrode cycled in 60% Py14TFSI-added electrolyte for 150 cycles at 1.0 C.

FIG. 9. Nyquist plots of EIS spectra for Cell A (reference) and Cell C (60% IL) at 50th, 100th and 150th cycles at 1.0 C.
Fig. 10. (a) DSC profiles of the electrodes at charged state of 4.6 V and (b) the amount of heat produced by charged electrodes with residual Py14TFSI-added electrolytes.

4. Conclusions

In summary, we have demonstrated some beneficial effects of ionic liquid Py14TFSI-added electrolytes for Li-rich cathode materials with high capacity. For example, Li[Li0.2Mn0.804Ni0.13Co0.13]O2 electrode material could deliver high discharge capacity of ca. 250 mAh g\(^{-1}\) in electrolyte with Py14TFSI content up to 80% at 0.1 C. The added Py14TFSI with high anodic stability could effectively suppress the side reaction between electrode material and Py14TFSI-added electrolyte. As a result, the initial irreversible capacity loss of Li[Li0.2Mn0.804Ni0.13Co0.13]O2 electrode decreased and the initial coulombic efficiency increased with the increase of Py14TFSI content. In pure IL electrolyte, the electrode exhibited the lowest ICL of 39 mAh g\(^{-1}\) and the highest CE of 85.8%. For the cycling performance, Li[Li0.2Mn0.804Ni0.13Co0.13]O2 exhibited superior extended cycling stability at 1 C in Py14TFSI-added electrolyte to that in reference electrolyte. The cathode electrode exhibited the highest capacity retention of 84.4% after 150 cycles in 60% Py14TFSI-added electrolyte, which is higher than that of only 54% for electrode in reference electrolyte. The superior cycling performance of the electrode material in Py14TFSI-added electrolyte was mainly ascribed to the suppression of side reaction between electrode and electrolyte and the formation of stable electrode/electrolyte interface during charge/discharge cycling. The thermal reaction between charged electrode and the residual electrolyte was also significantly suppressed with the addition of Py14TFSI.

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References