A novel boron-based ionic liquid electrolyte for high voltage lithium-ion batteries with outstanding cycling stability

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ABSTRACT

Advanced ionic liquid-based electrolyte is herein characterized for the application in high voltage lithium-ion batteries. The electrolyte based on N-propyl-N-methylpiperidinium difluoro(oxalate)borate (PP13DFOB), lithium bis(trifluoromethanesulfonyl)-imide (LiTFSI) and dimethyl carbonate (DMC) is fully characterized in terms of anodic corrosion behavior, electrochemical properties and cathode-electrolyte interphase stability. Experimental and computational results show that the preferential oxidation of PP13DFOB results in a stable and low impedance solid electrolyte interface (SEI) film on the surface of LiNi0.5Mn1.5O4 (LNMO) cathode and a passivation layer on Al foil, which suppress transition metal dissolution and Al corrosion at high voltage. As a result, the Li/LNMO and Li/graphite coin cells with ionic liquid-based electrolyte achieve excellent electrochemical performance, displaying a discharge capacity of 121.2 mAh g⁻¹ and 369.2 mAh g⁻¹ after 100 cycles at 0.5 C respectively and demonstrating no distinct capacitance attenuation during charge-discharge cycles.

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1. Introduction

Currently, the common Li salt which has been used in commercial Lithium-ion batteries (LIBs) is lithium hexafluorophosphate (LiPF6). However, LiPF6 is moisture sensitive and thermally unstable [1–4]. The thermal decomposition of LiPF6 generates PF₅ and LiF, which will react with cyclic carbonate solvent (e.g., ethylene carbonate, EC) and cause electrolyte solvents decomposition [5]. Moreover, the presence of trace water leads to the formation of HF from LiPF6 and will accelerate the dissolution of transition metal ions from the positive electrode and consequently deteriorate the overall electrochemical performances of LIBs, especially at high voltages and elevated temperatures [6–10].

To solve this problem, diversified functional additives and/or novel electrolyte solvents have been extensively investigated [11–17], while the improvements of electrochemical performances are still unsatisfactory. Additionally, plenty of efforts have been made to replace LiPF6 by more stable salts. Among various Li salts, lithium bis(trifluoromethanesulfonyl)-imide (LiTFSI) is a type of imide salt with the advantages of high thermal and moisture stability. However, one of the main obstacles that prevent the practical application of LiTFSI in LIBs or high voltage super capacitors is the severe aluminum corrosion problem when used in combination with carbonate-based solvents [18–20].

A vast amount of effort has been done to relief Al corrosion in LiTFSI containing electrolytes recently [21,22]. According to the previous reports, Al corrosion can be alleviated by increasing the concentration of LiTFSI. Mastumoto et al. proposed that Al dissolution can be inhibited in a concentrated (>1.8 M) LiTFSI electrolyte solution due to the formation of passivation film on Al current collector [23]. Dennis et al. reported that concentrated Ethylene carbonate (EC)–LiTFSI mixed electrolyte has a dramatically improved thermal and anodic stability compared to dilute electrolyte solution [24]. It was also claimed that the use of electrolyte additives has substantial effect on Al corrosion behavior [25–28].

Chen et al. proved that a stable passivation film containing B-O compound can be formed on the cathode materials through the decomposition of lithium bis(oxalato)borate (LiBOB) and LiTFSI [26]. Another excellent Li salt type additive is lithium difluoro(oxalate)borate (LiDFOB) [28]. Li et al. [29] improved the anodic stability of Al current collector and capacity retention of Li/
LiNi0.5Mn1.5O4 cell by using LiDFOB as an electrolyte additive. A detailed investigation from Kisung et al. revealed that LiDFOB has the best effect on protecting Al foil among various Li salt, such as LiBF4, LiDFOB, LiBOB and LiPF6 [30]. Although these additives can effectively alleviate the anodic Al corrosion, their practical applications are still limited by the poor electrochemical stability at high potentials.

Ionic liquids (ILs), which work as a viable alternative to traditional carbonate-based solvent, have many advantageous properties including negligible vapor pressures, non-flammability and high electrochemical stability window, etc [31–33]. Ruben et al. reported that ILs containing propylene carbonate (PC) and LiTFSI salt displayed excellent suppressed aluminum corrosion effect and rate performance in Li/LiFePO4 cells [34]. Very recently, Seitaro Yamaguchi proposed pyrrolidinium zwitterion based ionic liquid can work as corrosion inhibitor to enhance the anodic stability of Al current collector and LiCoO2 cathode [35]. To date, the ionic liquids functioned as electrolyte solvents for LIBs have been widely explored, but most of the operating voltages of the studied half-cells are still limited below 4.3 V, which is undesirable for practical applications.

Bearing all of this in mind, a novel IL-based electrolyte composed of (N-propyl-N-methylpyrrolidinium) difluorooxalate borate (PP13DFOB) and dimethyl carbonate (DMC) as co-solvent, LiTFSI as Li salt has been proposed in this work for a high voltage cathode material LiNi0.5Mn1.5O4 (LNMO). It has been proved that the addition of proper amount PP13DFOB in LiTFSI containing electrolyte can effectively suppress the aluminum corrosion and alleviate the dissolution of cathode transition metal ions in high voltage, resulting in outstanding electrochemical cycling stability.

2. Experimental

2.1. Electrolyte and battery preparation

Battery grade Li salt (LiPF6) and carbonate solvents (Ethylene carbonate (EC) and DMC) were provided by Shenzhen Optimum Nano Energy Co. Ltd. LiTFSI was purchased from Guangzhou Tinci Materials Technology Co. Ltd. PP13DFOB liquid ionic salt used in this study was obtained from Shanghai Chengjie Chemical Co. Ltd. LiTFSI-DMC/PP13DFOB-δ electrolytes with a composition of 0.5 M LiTFSI, δ vol% PP13DFOB and (100–δ) vol% DMC were prepared, with δ values ranging from 5 to 30. The molecular structures of the salt and solvents are illustrated in Fig. S1. The electrolyte consisted of 0.5 M LiTFSI and DMC was also prepared for comparison, marked as LiTFSI-DMC. Herein, chain carbonate is used instead of cyclic carbonate because: the low viscosity of chain carbonate can increase the conductivity of the electrolyte system; chain carbonate can avoid the side reactions between graphite and the solvent. Another reference electrolyte used in this study is composed of 1 M LiPF6 and a solvent mixture of EC and DMC in 1:2 vol ratio, marked as LiPF6-DMC. Herein, chain carbonate is used instead of cyclic carbonate because: the low viscosity of chain carbonate can increase the conductivity of the electrolyte system; chain carbonate can avoid the side reactions between graphite and the solvent. Another reference electrolyte used in this study is composed of 1 M LiPF6 and a solvent mixture of EC and DMC in 1:2 vol ratio, marked as LiPF6-DMC/EC.[19].

The LiNi0.5Mn1.5O4 cathode electrode was prepared by mixing graphite (Shenzhen BTR Co. Ltd.), Carboxymethyl Cellulose, carbon black and Polymerized Styrene Butadiene Rubber with a weight ratio of 93:3:1:3, followed by uniformly coating onto a Cu foil and dried at 110 °C under vacuum for 12 h.

Corrosion cells were composed of a high-grade Al foil disk working electrode and a lithium foil counter electrode. Electrochemical performance was tested by using LNMO or graphite as working electrode, lithium foil as counter electrode. Both configurations were assembled with CR2032 type-coin cells and Cegladr 2400 polypropylene membrane as separator in an Ar-filled glove box (Unilab, Mblaun).

2.2. Electrochemical characterizations and calculation methods

All the anodic aluminum corrosion experiments were carried out in corrosion cells using an electrochemical workstation test system (1470E Solartron). Cyclic voltammetry (CV) was scanned from an open circuit voltage (OCV) of 5.5 V (vs Li+/Li) to 2.5 V (vs Li+/Li). The scan rate was set at 10 mV s⁻¹. A total of 5 cycles were performed for each cell. Chronoamperometry (CA) was performed by applying a potential step from the OCV to 5.0 V (vs Li+/Li) with a sweep rate of 1 mV s⁻¹ and held for 12 h. The current was continuously monitored during voltage ramps and holds.

The galvanostatic charge/discharge (GCD) behavior of Li/LNMO and Li/graphite cells were explored on a Land battery test system (Land CT2001A, China) according to the following procedure: cells cycled at room temperature were first tested at a constant current of 0.1 C for three formation cycles followed by a constant current of 0.5 C for the next 100 cycles. The operation voltages were set at 4.5 V-3.5 V for the Li/LNMO cell and 3.0 V-0.01 V for Li/graphite cell. Electrochemical impedance spectroscopy (EIS) was carried out under discharged state using Solartron 1470E cell test system. The amplitude is 10 mV, and the frequency range is 10⁵ Hz–0.01 Hz. The quantum chemistry calculations were performed by Gaussian09 package. The solution molecule and ion structures were optimized and calculated by employing nonlocal DFT with B3LYP functional based on a DNP group.

2.3. Material characterization

The cells were disassembled in Ar-filled glove box. The aluminum foils and LNMO electrode were rinsed with DMC for three times to remove the residual electrolytes followed by drying under vacuum at 40 °C for 6 h.

The morphology and chemical composition tests of Al foil were performed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopic (EDS) (SN3400, Hitachi). The surface morphology of cycled LNMO was observed by SEM. X-ray photoelectron spectroscopy system (XPS, Quantera-II, U1 vac-phi) was employed to identify the surface composition of the polarized Al foil and cycled LNMO cathode. XPS was tested with Al Kα line as an X-ray source and the spectra were calibrated by the hydrocarbon C₁s line at 284.6 eV. The transition metal deposited on the Li foil in the LiNi0.5Mn1.5O4/Li half cells after charge/discharge cycles were estimated by the following procedures: the cycled lithium foils were gingerly placed into sealed vials with 1 mL water in the fume hood. The mixtures were stirred at room temperature until a homogeneous and transparent liquid was formed and then stored at room temperature in vacuum for 2 days. The amount of the Mn and Ni ions in these electrodes were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES, Optima 7000DV, Perkin Elmer).

3. Results and discussion

3.1. Al corrosion

It is well known that LiTFSI can cause severe Al foil corrosion while it is used in combination with organic carbonates, e.g. DMC and EC [19]. In order to protect the Al current collectors from corrosion by imide-based electrolytes, ionic liquid, PP13DFOB, was...
used as a co-solvent in this study. Fig. 1 illustrates the CVs of the Al current collectors in different electrolytes. Apparent electrochemical responses can be observed in all the as-prepared electrolytes with the highest current density recorded in the first cycle. Al foil cycled in LiTFSI-DMC shows a counter-clockwise current response and the highest anodic current density among all the as-prepared electrolytes (Fig. 1a–f), implying severe Al corrosion [36,37]. From Fig. 1b–e, it can be seen that the obtained anodic current densities decrease with the increasing concentration of PP13DFOB in the electrolyte system. When the volume fraction of PP13DFOB is higher than 20%, the current densities are below 0.05 mA cm$^{-2}$ at the first cycle (Fig. 1d and e), which is comparable to the current density observed in the non-corrosive electrolyte (LiPF$_6$-DMC/EC, Fig. 1f), indicating that the addition of proper amount PP13DFOB can effectively relieve Al corrosion in LiTFSI-based electrolytes.

The superior inhibition ability of PP13DFOB was further confirmed by chronoamperometry test. Fig. 2a and b presents the chronoamperometric curves of Al electrodes recorded at 5.0 V vs Li/Li$^+$ in LiTFSI-DMC, LiPF$_6$-DMC/EC and LiTFSI-DMC/PP13DFOB-20 electrolytes. As shown in Fig. 2a and b, the anodic polarization current density of Al foil in LiPF$_6$-DMC/EC electrolyte decreases sharply at the first 10 min and remains nearly constant at an extremely low level after 12 h. In the case of LiTFSI-DMC electrolyte, the current density increases dramatically over time and reaches 0.22 mA cm$^{-2}$ after 12 h, implying the continuous dissolution of Al. With the addition of PP13DFOB, the LiTFSI-DMC/PP13DFOB-20 electrolyte shows similar electrochemical behavior to the non-corrosive electrolyte (LiPF$_6$-DMC/EC), demonstrating a stable and low current density of ca. 3 $\mu$A cm$^{-2}$ after 12 h, which is approximate two orders of magnitude lower than that in LiTFSI-DMC electrolyte. Based on the results of CV and CA experiments.

In order to further verify the Al corrosion phenomenon, SEM images of pristine Al foil and Al foils tested in different electrolytes after CA measurement are acquired. Pristine Al foil demonstrates a clean and smooth surface morphology (Fig. 2c). After CA test, the Al foil polarized in LiTFSI-DMC electrolyte suffers from serious corrosion, as indicated by the large pitting corrosion holes shown in Fig. 2d. However, no signs of corrosion can be observed on the Al surface tested in LiPF$_6$-DMC/EC and LiTFSI-DMC/PP13DFOB-20 electrolytes (Fig. 2e and f), which is in good agreement with the very low current densities recorded in the CA curves (Fig. 2b).

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**Fig. 1.** CV curves of Al electrodes in different electrolytes: (a) LiTFSI-DMC; (b) LiTFSI-DMC/PP$_{13}$DFOB-5; (c) LiTFSI-DMC/PP$_{13}$DFOB-10; (d) LiTFSI-DMC/PP$_{13}$DFOB-20; (e) LiTFSI-DMC/PP$_{13}$DFOB-30; (f) LiPF$_6$-DMC/EC.
Moreover, the stripes on Al foil become indistinct after polarized in LiPF6-DMC/EC and LiTFSI-DMC/PP13DFOB-20 electrolytes, indicating the formation of a passivation coating on Al surfaces. For the non-corrosive LiPF6-DMC/EC electrolyte, it is well known that LiPF6 can protect Al foil by reacting with Al ions to form Al-based compounds [38,39]. For the LiTFSI-DMC/PP13DFOB-20 electrolyte, it can be seen that Al passivation would be achieved in the LiTFSI-based electrolyte with the addition of appropriate amount of PP13DFOB.

To explore the surface composition of Al foils, EDS measurements of the pristine Al foil and Al foil polarized in three different electrolytes were performed and the results are given in Fig. S2 and Table S1. It can be seen that the fresh Al foil demonstrates a surface composition of 93.08% Al and 6.92% O. After the CA test, Al concentrations are decreased, especially for the sample tested in LiTFSI-DMC, showing only about 31.44%. The Al foil tested in LiTFSI-DMC/PP13DFOB-20 demonstrates the Al, F concentrations of 71.70% and 10.88%, which are comparable to the electrode polarized in LiTFSI-DMC/PP13DFOB-20 sample. These peaks are generally originated from the decomposition of electrolyte [40]. The Al 2p peak for the Al foil polarized in LiTFSI-DMC electrolyte exhibits three peaks at 77.1, 74.5 and 71.1 eV, which are assigned to Al-F, Al2O3 and bare Al metal, respectively (Fig. 3b) [41,42]. The newly generated Al-F peaks at 689.1 eV in Al 2p (Fig. 3b), C-F peak at 289.1 eV in C 1s (Fig. 3d) and C-F peak at 688.0 eV in F 1s (Fig. 3f) are strong evidences for the existence of the corrosion product \( \text{Al}([\text{SO}_2\text{CF}_3]_2)_x^{3-x} \) in the Al foil polarized in LiTFSI-DMC [22,38]. The possible reaction is given as following:

\[
\text{N}([\text{SO}_2\text{CF}_3]_2)_x + \text{Al}_2\text{O}_3 \rightarrow \{\text{Al}([\text{SO}_2\text{CF}_3]_2)_x\}^{3-x}
\]

Differently, the Al 2p peak for Al foil polarized in LiTFSI-DMC/PP13DFOB-20 electrolyte shows only two peaks assigned to Al2O3 and Al (Fig. 3c), with significantly increased Al2O3/Al peak ratio compared with pristine Al foil (Fig. 3a), demonstrating that a thick passivation film is formed on the surface of Al. Moreover, the C-F peak at 289.0 eV in C 1s (Fig. 3e) and B-F peak at 688.0 eV in F 1s (Fig. 3f) are strong evidences for the existence of the decomposition of DFOB. Besides, it should be noted that the characteristic B-O and B-F peaks at 192.2 eV and 193.4 eV

![Fig. 2.](image-url)

(a, b) Chronoamperograms of Al foil recorded from OVC to 5.0 V vs Li/Li+ in LiTFSI-DMC, LiPF6-DMC/EC and LiTFSI-DMC/PP13DFOB-20 electrolytes; the inset shows the enlarged view of the marked area in Fig. 2a. SEM images of (c) pristine Al foil and Al foil polarized in (d) LiTFSI-DMC, (e) LiPF6-DMC/EC and (f) LiTFSI-DMC/PP13DFOB-20; the insets show the enlarged view of the corresponding samples.
can be observed in the B 1s spectrum (Fig. 3j), which intensively prove the present of the byproducts from the decomposition of DFOB in the passivation film on the Al foil surface [42,43].

The high B concentration given by EDX test (Table S1) indicates that B-O/B-F compounds are the main component of the passivation film on the Al foil polarized in LiTFSI-DMC/PP13DFOB-20, which is responsible for the superior inhibition ability against Al corrosion in LiTFSI-based electrolyte. In addition, the intensity of LiF peak in the Al foil polarized in LiTFSI-DMC electrolyte (Fig. 3h) is remarkably stronger than that in the LiTFSI-DMC/PP13DFOB-20 electrolyte (Fig. 3i). Since LiF is insulated for electron and Li\(^{+}\), it can increase the interface film resistance and hinder the ionic migration between cathode and electrolyte, further reducing the electrochemical performance of the cells [44].

As discussed above, PP13DFOB can effectively suppress Al foil corrosion by forming a dense film on the surface of Al foil. Further evidence for this consequence is given by DFT calculations (Fig. 4a and Table 1). The energy of the highest occupied molecular orbital (HOMO) and lowest unoccupied orbital (LUMO) of different materials are listed in Table 1. Obviously, DFOB\(^{-}\) has the highest HOMO energy value, indicating that DFOB\(^{-}\) is a better electron donor than other molecules, resulting in preferential oxidation compared with TFSI\(^{-}\), PP13, and DMC. This is a strong supplement of the XPS and EDS results, revealing the outstanding anti-corrosion effect of PP13DFOB.

Based on the results mentioned above, the inhibition
mechanism in aluminum corrosion by the influence of PP13DFOB has been proposed. As shown in Fig. 4b, in the LiTFSI-based electrolyte, the TFSI\(^{-}\) anions will attack the Al\(_2\)O\(_3\)--native film on fresh Al foil to form \(\text{Al}[[\text{SO}_2\text{CF}_3]_2\text{Cl}]_x\)\(^{3-x}\) complex ions, which can be dissolved by carbonate solvents. With the destruction of Al\(_2\)O\(_3\), bare aluminum exposes to electrolyte and begins to dissolve at high potential continually. In contrast, with the addition of PP13DFOB, the preferential oxidation of DFOB\(^{-}\) on the surface of Al foil generates B-O/B-F compounds, which is stable enough to prevent the aluminum corrosion caused by LiTFSI. Additionally, the dielectric constant of the electrolyte is reduced by PP13DFOB, which can decrease the solubility of the solvent, leading to suppression of Al corrosion at some extent [45].

### 3.2. Compatibility with LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) cathode

The electrochemical performance of LiTFSI-DMC/PP\(_{13}\)DFOB-\(\delta\) electrolyte in high voltage Li/LNMO cell is studied in this part. Fig. 5 presents the cycling performance of Li/LNMO cells in different electrolytes at 0.5 C, where the first three formation cycles at 0.1C are not given. The cell with LiPF\(_6\)-DMC/EC electrolyte suffers a remarkable capacity fade from 122.7 mAh g\(^{-1}\) to 112.3 mAh g\(^{-1}\) after 100 cycles, corresponding to capacity retention of 91.5\%. For the cells with 5\% and 10\% PP\(_{13}\)DFOB based electrolytes (LiTFSI-DMC/PP\(_{13}\)DFOB-5, LiTFSI-DMC/PP\(_{13}\)DFOB-10), discharge capacities of 92.3 mAh g\(^{-1}\) and 106 mAh g\(^{-1}\) are delivered after 100 cycles respectively. The decreased capacities of the cells may be ascribed to the un-compact and incomplete SEI film formed on the cathode surface [16]. The cell with 20\% PP\(_{13}\)DFOB (LiTFSI-DMC/PP\(_{13}\)DFOB-20) shows the highest discharge capacity, which rises from 117 mAh g\(^{-1}\) at the first cycle to 122.0 mAh g\(^{-1}\) after 5 cycles and maintains almost constant for the subsequent cycles, indicating that sufficient concentration of PP\(_{13}\)DFOB is essential for excellent cycling performance. Interestingly, as the concentration of PP\(_{13}\)DFOB increased to 30\% (LiTFSI-DMC/PP\(_{13}\)DFOB-30), the discharge capacity exhibits dramatic decrease. This capacity fading may be due to the low ionic conductivity of the electrolyte. Therefore, appropriate amount of PP\(_{13}\)DFOB in the LiTFSI-DMC/PP\(_{13}\)DFOB-\(\delta\) electrolyte is necessary for achieving the best cycling performance of Li/LNMO cell.

The GCD profiles of Li/LNMO cell with LiTFSI-DMC/PP\(_{13}\)DFOB-20 and LiPF\(_6\)-DMC/EC electrolytes are presented in Fig. 6a and b. In the first cycle, the cell with LiPF\(_6\)-DMC/EC electrolyte delivers a comparative higher initial discharge capacity than LiTFSI-DMC/PP\(_{13}\)DFOB-20. In the following cycles, the discharge capacity of the cell with LiPF\(_6\)-DMC/EC electrolyte continues to decrease while the discharge capacity of the cell with LiTFSI-DMC/PP\(_{13}\)DFOB-20 electrolyte continues to increase. As a result, after 100 cycles, the cell with LiTFSI-DMC/PP\(_{13}\)DFOB-20 electrolyte demonstrates a discharge capacity of 125 mAh g\(^{-1}\), which is much higher than that of LiPF\(_6\)-DMC/EC (112 mAh g\(^{-1}\)). Furthermore, the cells with LiTFSI-DMC/PP\(_{13}\)DFOB-20 electrolyte shows a relative lower charge plateau and a higher discharge plateau compared to LiPF\(_6\)-DMC/EC electrolyte (Fig. 6a and b), indicating that the electrode polarization in LiTFSI-DMC/PP\(_{13}\)DFOB-20 electrolyte is weaker than that in LiPF\(_6\)-DMC/EC electrolyte. The high capacity retention and low polarization of the cell with LiTFSI-DMC/PP\(_{13}\)DFOB-20 electrolyte indicates the excellent compatibility between the electrolyte and the LNMO cathode.

The effect of PP\(_{13}\)DFOB on the cycling stability of Li/LNMO cells was further confirmed by the results of EIS tests. The spectra were fitted with the equivalent circuit model inserted in Fig. 6c and the values of R\(_{f}\) and R\(_{ct}\) are listed Table 2. Generally, R\(_{f}\) represents the resistance contribution from the surface film and R\(_{ct}\) is related to the resistance of charge transfer process. The impedance of the cell with LiTFSI-DMC/PP\(_{13}\)DFOB-20 electrolyte increases after 3 cycles, attributing to the formation of SEI film on the cathode surface, which delivers a larger R\(_{f}\). This result is consistent with the lower discharge capacity in the first 5 cycles (Fig. 5). In the following cycles, the R\(_{f}\) and R\(_{ct}\) of the cells with LiPF\(_6\)-DMC/EC and LiTFSI-

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**Table 1**
The frontier molecular orbital energy of DFOB\(^{-}\), TFSI\(^{-}\), DMC and PP\(_13\).

<table>
<thead>
<tr>
<th>Material</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFOB(^{-})</td>
<td>3.5941</td>
<td>2.1744</td>
</tr>
<tr>
<td>TFSI(^{-})</td>
<td>4.2414</td>
<td>3.0185</td>
</tr>
<tr>
<td>DMC</td>
<td>3.5941</td>
<td>2.1744</td>
</tr>
<tr>
<td>PP(_13)</td>
<td>9.5811</td>
<td>8.4405</td>
</tr>
</tbody>
</table>

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**Fig. 4.** (a) The energy level diagram of the frontier molecular orbitals relative to the energy in a vacuum (E\(_{vac}\)) and the HOMO and LUMO plots of DFOB\(^{-}\), TFSI\(^{-}\), DMC, PP\(_{13}\). (b) The inhibition mechanism in aluminum corrosion by the influence of PP\(_{13}\)DFOB.

**Fig. 5.** The cycling performance of Li/LNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) cell in different electrolytes under the voltage range of 3.5--4.9 V at 0.5C.
DMC/PP13DFOB-20 electrolytes increase with cycle number. As for the cell conducted 100 cycles in LiPF6-DMC/EC electrolyte, $R_f$ and $R_{ct}$ greatly increase from 12.32 $\Omega$ to 68.93 $\Omega$ and from 96.94 $\Omega$ to 180.21 $\Omega$ respectively. In contrast, $R_f$ and $R_{ct}$ of the cell cycled with LiTFSI-DMC/PP13DFOB-20 electrolyte show a smaller increment, indicating that PP13DFOB creates a less impedance SEI film on the surface of LNMO cathode. This SEI film with low resistance can also facilitate Li$^+$ transfer between SEI film and LNMO bulk, leading to good cycling performance.

The GCD profiles of Li/LNMO cell with (a) LiPF6-DMC/EC and (b) LiTFSI-DMC/PP13DFOB-20 electrolytes. The EIS curves of Li/LNMO cell with (c) LiPF6-DMC/EC and (d) LiTFSI-DMC/PP13DFOB-20 electrolytes; the inset in (c) shows the equivalent circuit.

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>LiPF6-DMC/EC ($\Omega$)</th>
<th>LiTFSI-DMC/PP13DFOB-20 ($\Omega$)</th>
</tr>
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<tbody>
<tr>
<td>Before cycling</td>
<td>$R_f + R_{ct}$</td>
<td>76</td>
</tr>
<tr>
<td>After 3 cycles</td>
<td>$R_f$</td>
<td>12.32</td>
</tr>
<tr>
<td></td>
<td>$R_{ct}$</td>
<td>96.94</td>
</tr>
<tr>
<td>After 50 cycles</td>
<td>$R_f$</td>
<td>36.71</td>
</tr>
<tr>
<td></td>
<td>$R_{ct}$</td>
<td>116.52</td>
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<tr>
<td>After 100 cycles</td>
<td>$R_f$</td>
<td>68.93 $\Omega$</td>
</tr>
<tr>
<td></td>
<td>$R_{ct}$</td>
<td>180.21 $\Omega$</td>
</tr>
</tbody>
</table>

Table 2: Fitted $R_f$ and $R_{ct}$ values of the Li/LNMO cells cycled in LiPF6-DMC/EC and LiTFSI-DMC/PP13DFOB-20 electrolytes.

DMC/PP13DFOB-20 electrolytes increase with cycle number. As for the cell conducted 100 cycles in LiPF6-DMC/EC electrolyte, $R_f$ and $R_{ct}$ greatly increase from 12.32 $\Omega$ to 68.93 $\Omega$ and from 96.94 $\Omega$ to 180.21 $\Omega$ respectively. In contrast, $R_f$ and $R_{ct}$ of the cell cycled with LiTFSI-DMC/PP13DFOB-20 electrolyte show a smaller increment, indicating that PP13DFOB creates a less impedance SEI film on the surface of LNMO cathode. This SEI film with low resistance can also facilitate Li$^+$ transfer between SEI film and LNMO bulk, leading to good cycling performance.

Fig. 7 a–c shows the morphologies of the LNMO cathode before and after 100 cycles with different electrolytes. The clean and smooth spinel structure of the fresh LNMO electrode can be observed in Fig. 7a. After cycled in LiTFSI-DMC/PP13DFOB-20 electrolyte, the particle of LNMO electrode maintains its structure integrity and a compact film can be observed on its surface, which is due to the positive effect of PP13DFOB (Fig. 7b). Differently, in the LiPF6-DMC/EC electrolyte, a thick and rough film is attached on the cathode surface (Fig. 7c), indicating severe electrolyte decomposition. Fig. 7d illustrates the optical images of the Li foil electrodes after 100 cycles. The contents of transition metal ions deposited on the Li foils detected with ICP-AES are marked in the corresponding images. The Li foil cycled in LiTFSI-DMC/PP13DFOB-20 exhibits a low concentration of Mn and Ni on the surface (1.311 and 0.402 ppm). However, after cycling with LiPF6-DMC/EC electrolyte, the concentrations of Mn and Ni on Li foil are dramatically increased to 7.243 and 1.527 ppm, respectively. Besides, the gloss on the Li foil in the LiTFSI-DMC/PP13DFOB-20 electrolyte is bright, which provides indirect evidence for the effective inhibition of transition metal dissolution and electrolyte decomposition. Generally, the transition metal dissolution is mainly ascribed to the attack of HF to the unprotected LiNi0.5Mn1.5O4 cathode [16,44]. The dissolution of transition metal ions and the decomposition of electrolyte are the main reasons of the poor cycling stability of the cell with the LiPF6-DMC/EC electrolyte in high potential batteries.

The participation of PP13DFOB in the formation of protective SEI film is further confirmed by XPS (Fig. 8). From the survey spectrum, S, B, C, N, O and F can be detected on the LNMO cycled with LiTFSI-DMC/PP13DFOB-20 (Fig. S3). Deconvolutions of the C 1s, F 1s and B 1s are presented in Fig. 8a–c. Characteristic peaks of C-C/C-H (284.8 eV), C-O (268.3 eV), C=O (289.0 eV), C-F (290.8 eV), and the
salts (293.0 eV) in C 1s spectra (Fig. 8b) and C-F (688.7 eV) in F 1s spectra (Fig. 8c) are ascribed to the conductive additive and binders in the electrode and the decomposition of LiTFSI, DMC. Additionally, two peaks at 193.6 eV (B-F) and 191.0 eV (B-O) in B 1s (Fig. 8d) indicate the presence of B-O/B-F compounds on the LNMO cathode surface, which is consistent with the above discussion for the Al corrosion in LiTFSI-DMC/PP13DFOB-20 (Fig. 3j). Combined with XPS, SEM and EIS results, it can be concluded that a stable and low impedance SEI film has been formed on the surface of LNMO cathode by the addition of PP13DFOB, which can effectively protect the electrode and enhance the cycling stability of high voltage LIBs.

To demonstrate the Al corrosion in the Li/LNMO cell, the Al 2p spectra for LNMO electrode cycled in LiTFSI-DMC/PP13DFOB-20, LiPF6-DMC/EC and LiTFSI-DMC.

Fig. 7. SEM images of LNMO cathode (a) before cycling and after 100 cycles with (b) LiTFSI-DMC/PP13DFOB-20 and (c) LiPF6-DMC/EC. (d) Optical images of the Li foil electrodes after 100 cycles in different electrolytes.

Fig. 8. High resolution XPS spectra of (a) C1s, (b) F1s and (c) B1s for LNMO cathode cycled with LiTFSI-DMC/PP13DFOB-20. (d) Comparison of Al 2p for LNMO cathode cycled with LiTFSI-DMC/PP13DFOB-20, LiPF6-DMC/EC, and LiTFSI-DMC.
for comparison. An obvious Al 2p peak can be seen in the curve for LNMO cycled in corrosive LiTFSI-DMC electrolyte, indicating the existence of Al corrosion product in the electrolyte. While in the curve for LiTFSI-DMC/PP13DFOB-20 and LiPF6-DMC/EC samples, no peaks can be observed at the binding energy for characteristic Al 2p, verifying that there is no Al compounds in the electrolytes, which indirectly proves the non-corrosive nature of our LiTFSI-DMC/PP13DFOB-20 electrolyte.

3.3. Compatibility with graphite anode

Li/graphite cells were assembled with LiTFSI-DMC/PP13DFOB-20 electrolyte to verify its compatibility with graphite anode. Fig. 9a shows that the initial charge and discharge capacities are 421.0 and 368.7 mAh g\(^{-1}\), and the corresponding coulomb efficiency is 87.03%. Besides, it can be seen that two discharge voltage plateaus appear during the first discharge (lithium insertion) of the battery. The first voltage plateau appears at 1.6 V and disappears in the second cycle, which is attributed to the irreversible reductive decomposition of DFOB\(^{-}\) and the SEI film formation [46]. The other plateau located in 0.05–0.3 V is originated from the reversible Li\(^{+}\) intercalation and de-intercalation process. The CV curves given in the inset of Fig. 9a are in good consistent with the GCD curves. After the first two SEI formation cycles, the long cycling stability of LiTFSI-DMC/PP13DFOB-20 electrolyte gradually decrease with cycling. After 100 cycles, the value decrease to 354.3 and 355.6 mAh g\(^{-1}\) for LiPF6-DMC/EC and 368.1 and 369.2 mAh g\(^{-1}\) for LiTFSI-DMC/PP13DFOB-20, corresponding the capacity retentions of 94.27% and 98.46% respectively. The high capacity retention obtained for the LiTFSI-DMC/PP13DFOB-20, corresponding the capacity retentions of 94.27% and 98.46% respectively. The high capacity retention obtained for the LiTFSI-DMC/PP13DFOB-20 electrolyte identifies the excellent compatibility of the electrolyte to graphite anode.

4. Conclusion

In this work, we presented a comprehensive study on the aluminum corrosion behavior and electrochemical properties of the high voltage LNMO cathode and graphite anode in the novel Li-based electrolyte LiTFSI-DMC/PP13DFOB-20. According to the DFT calculation results, the DFOB\(^{-}\) anion exhibits high HOMO energy value, which makes it a promising candidate for participating in the SEI film formation. As a result, B-O-B-F species that generated from the decomposition of PP13DFOB have been detected on the surface of Al foil and high voltage LNMO cathode, resulting in superior inhibition ability against aluminum corrosion and transition metal ions dissolution. The cells with LNMO cathode exhibit outstanding cycling performance in LiTFSI-DMC/PP13DFOB-20 electrolyte. After 100 cycles at 0.5 C, Li/LNMO cell with LiTFSI-DMC/PP13DFOB-20 delivers a discharge capacity of 121.2 mAh g\(^{-1}\) with a coulomb efficiency of 97.6%. This electrolyte also shows positive effect toward graphite anode, delivering a higher discharge capacity than that in LiPF6-DMC/EC electrolyte. This study presents a promising strategy to alleviate Al corrosion in LiTFSI-based electrolyte and further improve the cycling performance of LIBs at high cut-off voltages.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.electacta.2018.06.170.

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