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Safe ionic liquid-sulfolane/LiDFOB electrolytes for high voltage $Li_{1.15}(Ni_{0.36}Mn_{0.64})_{0.85}O_2$ lithium ion battery at elevated temperatures

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ABSTRACT

In this study, 1-methyl-1-butylpiperidinium bis(trifluoromethanesulfonyl)-imide ($PP_{14}TFSI$)-sulfolane/lithium difluoro(oxalato)borate (LiDFOB) based electrolytes with inherent thermal stability and low flammability are investigated as promising alternatives of conventional $LiPF_6$/carbonate electrolyte in high voltage $Li/Li_{1.15}(Ni_{0.36}Mn_{0.64})_{0.85}O_2$ cells at elevated temperatures. The safe and stable electrolyte candidates are selected by optimizing relative composition and represent high oxidative stability (higher than 5.2 V vs Li/Li^+) above 55 °C. The $Li/Li_{1.15}(Ni_{0.36}Mn_{0.64})_{0.85}O_2$ cells with E60 electrolyte achieved 172.5 and 238.8 mAh g^{-1} after 50 cycles between 2.0 and 4.6 V at 0.5C at 55 and 70 °C. Moreover, the $Li/Li_{1.15}(Ni_{0.36}Mn_{0.64})_{0.85}O_2$ cell with E60 electrolyte obtains a superior discharge capacity of 97.9 mAh g^{-1} at high rate of 3C at 70 °C. At extremely high temperature of 85 °C, the cell with E60 electrolyte delivers 218.7 mAh g^{-1} after 50 cycles at 1C. The excellent cycling performance in high voltage $Li/Li_{1.15}(Ni_{0.36}Mn_{0.64})_{0.85}O_2$ cells at elevated temperatures is attributed to the intrinsic oxidative stability and the compact and stable cathode-electrolyte interface (CEI) film derived from E60 electrolyte. We believe it a promising candidate that can be safely used for high voltage Li-rich cells at elevated temperature.

1. Introduction

Rechargeable Lithium ion batteries (LIBs) have been widely utilized in electrical vehicles (EV), hybrid electrical vehicles (HEV) and consumer electronics owing to high specific energy, high rate capacity and long cycle life [1–3]. However, current development of LIBs still exist challenges such as higher energy density and stability under high voltage and temperature [4–6]. Recently, novel Li-rich materials, such as $Li_{1.15}(Ni_{0.36}Mn_{0.64})_{0.85}O_2$, has been attracted much attention because of its high operating voltage and discharge capacity, which is a direct method to achieve higher energy density in Li-ion battery at high temperatures [7–9]. Therefore, electrolytes with high operating voltage and temperature and compatibility with Li-rich materials are quite challenging [10–12].

Conventional electrolyte composed of $LiPF_6$ and carbonate solvent cannot meet the requirements of practical application to lithium ion batteries as a result of bad oxidation stability above 4.5 V vs. Li/Li^+ and thermal decomposition at elevated temperature (for instance, 55 °C), which may lead to undesired formation of unstable solid/electrolyte interface (SEI) film on the surface of cathode [13]. Moreover, the $LiPF_6$ salt is very sensitive to hydrolysis with even trace water in the electrolyte, and the hydrolysis product is HF [14]. This toxic product cause an acidic condition, in which the transition metal elements will be dissolved from the cathode materials and lead to poorer cell performance, especially at elevated temperature [15].

Presently, researches on addressing this problem have been extensively investigated. Mainly researches were focusing on adopting Li salts, functional solvents or additives to suppress the side reaction of electrolyte at high voltage and temperature. However, the investigations on good cell performance at high voltage and high temperature are still lacking. Wang et al. [16] reported a Li salt lithium trifluoromethyl benzimidazole (LITFB) used as electrolyte additive that Li-rich/Li cell achieved high discharge capacity with a scan rate of 0.1C after 20 cycles at 60 °C without obvious decay. Shi et al. [17] improved the capacity retention of graphite/$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ full cells from 69% to 82.3% after 100 cycles at 60 °C by using electrolyte mixing F-EPE with LiBOB and GBL due to the good thermal stability of the LiBOB salt and protective SEI film on the graphite anode. Li et al. [18] formulated a desired ternary solvent system (EC–PC–EMC) with $LiPF_6$ and achieved a reasonable cycling stability at room temperature and

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elevated temperatures up to 60 °C. As can be seen from recent report, electrolyte composed of high thermal tolerance solvents with film forming Li salts or additives is an effective strategy for better electrochemical performance at high voltage and temperature. Nevertheless, articles reporting good cell performance above 60 °C are scarce.

In recent years, room temperature ionic liquids (RTILs) are widely used in high voltage and temperature electrolytes. Compared with organic solvents, RTILs possess advantages of non-flammability, negligible vapor pressure, wide electrochemical window and high thermal stability. Cao et al. [19] reported LiTFSI/RTIL based electrolytes outperform the $LiPF_6$/organic carbonate-based electrolyte in terms of cycling performance in LNMO/LTO full-cells at elevated temperatures. Ababtain et al. [20] employed ionic liquid/propylene carbonate (PC)/LiTFSI electrolytes to enhance the cycling performance of Si electrode at high temperature, even at 100 °C. Plylahan et al. [21] showed Pyr_{13}TFSI/FEC hybrid solvent with dissolved LiTFSI salt as electrolytes for high temperature LIBs, and this hybrid electrolyte exhibits 300 cycles at 80 °C with only a 4.7% capacity loss. It seems that ionic liquid (IL) can enhance the electrochemical and thermal stability of electrolyte at high voltage and temperature due to its properties, but its high viscosity and moderate conductivity hinder the cycling performance [22]. The electrolyte combination containing IL with high electrochemical stability, organic solvent with high thermal stability, Li salts with good film forming stability can be designed to satisfy the demand of high voltage and temperature.

Considering these issues, piperidium-based ionic liquid 1-methyl-1-butylpiperidinium bis(trifluoromethanesulfonyl)-imide (PP_{14}TFSI) is introduced to this electrolyte system as main component, and sulfolane with high electrochemical stability, non-flammability, high boiling point and high dielectric constants is used as co-solvent. Lithium difluoro(oxalato)borate (LiDFOB) is adopted as Li salt because of its good thermal stability and excellent film forming ability on surface of electrodes. In this work, we formulated the electrolytes by adjusting relative composition of PP_{14}TFSI, sulfolane, and Li salt to investigate viability of PP_{14}TFSI/sulfolane based electrolytes with inherent non-flammability at elevated temperature in high voltage $Li/Li_{1.15}(Ni_{0.36}Mn_{0.64})_{0.85}O_2$ half cells, and the chemical structures of PP_{14}TFSI, sulfolane and LiDFOB are depicted in Fig. 1.

2. Experimental

2.1. Electrolyte and electrode preparation

The synthesis process of PP_{14}TFSI was based on the methods reported in our previous paper [23], and the resultant product is colorless liquid. After vacuum dying at 80 °C for 48 h, the water content was less than 10 ppm detected by Karl Fisher titration. The ionic liquid was characterized by nuclear magnetic resonance (NMR) on Varian VNMRS 400 spectrometer: ^{1}H NMR δ 0.97−1.01 (t, 3H), 1.38−1.49 (m, 2H), 1.66−1.76 (m, 2 × 2H), 1.88 (brs, 2 × 2H), 3.02 (s, 3H), 3.25−3.56 (m, 3 × 2H); ^{13}C NMR δ 12.96, 19.15, 19.56, 20.3 20.25, 47.01, 60.96, 63,9, 118.01; ^{19}F NMR δ −85.36; No impurities were found. The investigated electrolytes were prepared by dissolving LiDFOB (Suzhou Fosai Inc.) in binary solvents containing PP_{14}TFSI and sulfolane (Alfa Aesar). The compositions are shown in Table 1 and the obtained electrolytes were non-flammable which is discussed in our precious paper [23]. A conventional electrolyte containing 1 M $LiPF_6$ dissolved in a solvent mixture of EC, DEC and EMC in 3:2:5 wt ratio was used for comparison (expressed as $LiPF_6$/org). The Li-rich electrode (Jiangte Lidian Co. Ltd) was mixed with 10 wt% carbon black, 10 wt% polyvinylidene fluoride (PVDF) binder in N-methylpyrrolidone and 80 wt% $Li_{1.15}(Ni_{0.36}Mn_{0.64})_{0.85}O_2$ material, the resulting slurry was cast on the aluminum foil and dried at 70 °C for 6 h. Then the film was punched into round discs of 14 mm diameter and dried at vacuum environment at 80 °C for 24 h. The active material of each disc is about 1.8 mg. Graphite electrode was prepared with the same method as Li-rich electrode. CR2032 type cells were assembled with Li-rich cathode, a Celgard 2400 polypropylene separator, Li foil as counter electrode and prepared electrolytes. All the electrolytes preparation and cells assembling works were operating in glove box (Unilab, Mbraun, $O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm).

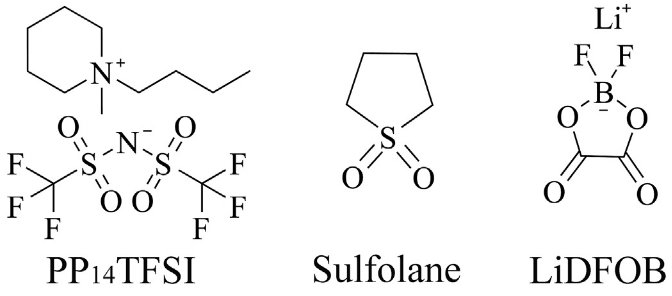

Fig. 1. Chemical structures of 1-methyl-1-butylpiperidinium bis(trifluoromethanesulfonyl)-imide (PP_{14}TFSI), sulfolane and lithium difluoro(oxalato)borate (LiDFOB).

2.2. Electrochemical measurements

The conductivity of electrolytes was measured in a conductivity cell by the AC impedance method in the frequency range of 10^6 to 0.1 Hz, the cell constant was determined with a standard KCl solution (0.01 M) at 30 °C. The temperature of the conductivity cell was controlled with a temperature-controlled chamber (EA1888, FUYIDA). The electrochemical windows were measured on CHI660E (Chenhua, Shanghai) by using linear sweep voltammetry measurement (LSV) on platinum electrode and Li foil as counter and reference electrode at a scan rate of 0.1 mv/s. Cycling charge-discharge measurements of Li/Li-rich cells were cycled for 3 cycles at 0.1C between 2 and 4.6 V on LAND battery test system (Wuhan Land Electronics Co. Ltd) at room temperature. After three formation cycles, the cells were transferred to temperature-controlled chamber for next step of tests. Electrochemical impedance spectra were recorded on a potentiostat (1470E, Solartron) paired with a frequency response analyzer (FRA 1260, Solartron) in frequency range from 100 kHz to 10 mHz with an amplitude of 10 mV. The cells tested were at fully discharged state.

2.3. Materials characterization

The cells after cycling were disassembled in glove box, the cathode were removed carefully from the cells and rinsed with anhydrous dimethyl carbonate (DMC) two times. After drying, morphology of Li-rich electrodes was observed by field emission scanning electron microscopy (FE-SEM, JEOL). The composition of CEI film was analyzed by means of X-ray photoelectron

Table 1
The composition of the electrolytes investigated in this work.

Electrolyte	PP_{14}TFSI (wt%)	Sulfolane (wt%)	LiDFOB
E50	50	50	0.5 mol kg^{-1}
E60	60	40	0.5 mol kg^{-1}
E70	70	30	0.4 mol kg^{-1}