



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-methylpiperidiniumdifluoro(oxalate)borate ($\text{PP}_{13}\text{DFOB}$), 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 $\text{PP}_{13}\text{DFOB}$ results in a stable and low impedance solid electrolyte interface (SEI) film on the surface of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (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 (LiPF_6). However, LiPF_6 is moisture sensitive and thermally unstable [1–4]. The thermal decomposition of LiPF_6 generates PF_5 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 LiPF_6 , which 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 LiPF_6 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 ($>1.8 \text{ M}$) 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/

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LiNi_{0.5}Mn_{1.5}O₄ 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, Seitara 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-methylpiperidinium)difluoro(oxalato)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 LiNi_{0.5}Mn_{1.5}O₄ (LNMO). It has been proved that the addition of proper amount PP₁₃DFOB in the 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 ionic liquid 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/EC. The water contents in the electrolytes are less than 20 ppm, measured by an automatic Karl Fisher titrant.

The LiNi_{0.5}Mn_{1.5}O₄ based cathode electrode (LNMO) was prepared by mixing LiNi_{0.5}Mn_{1.5}O₄ with acetylene, carbon black and polyvinylidene fluoride binder in N-methyl pyrrolidone. The resulted slurry was coated on Al foil with a diameter of 14 mm, and then dried at 110 °C in vacuum for 12 h. The mass loading of LiNi_{0.5}Mn_{1.5}O₄ is 1.6 mg cm⁻². The graphite anode was fabricated 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 Ceglard 2400 polypropylene membrane as separator in an Ar-filled glove box (Unilab, Mblau).

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 4.9 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, UI vac-phi) was employed to identify the surface composition of the polarized Al foil and cycled LNMO cathode. XPS was tested with Al K α line as an X-ray source and the spectra were calibrated by the hydrocarbon C_{1s} line at 284.6 eV. The transition metal deposited on the Li foil in the LiNi_{0.5}Mn_{1.5}O₄/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

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