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Synthesis and evaluation of a novel pyrrolidinium-based zwitterionic additive with an ether side chain for ionic liquid electrolytes in high-voltage lithium-ion batteries

Shunsuke Horiuchi[a], Haijin Zhu[b], Maria Forsyth[b], Yuko Takeoka[a], Masahiro Rikukawa[a], Masahiro Yoshizawa-Fujita[a,*]

[a] *Department of Materials and Life Sciences, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan*
[b] *Institute for Frontier Materials and the ARC Centre of Excellence for Electromaterials Science, Deakin University, Geelong, VIC 3216, Australia*

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ABSTRACT

Ionic liquids (ILs) containing zwitterions were studied as electrolytes for lithium-ion batteries. The effect of a pyrrolidinium zwitterion with a long ether side chain on the thermal and electrochemical properties of an IL and the charge/discharge properties of Li/$LiCoO_2$, Li/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC), and graphite/Li cells with IL/zwitterion electrolytes was investigated. The melting temperature of the IL-based electrolyte composed of *N*-methyl-*N*-methoxymethylpyrrolidinium bis(fluorosulfonyl)amide ([$Pyr_{1,1O1}$][FSA]) and lithium bis(fluorosulfonyl)amide (LiFSA) with 3-(1-(2-(2-methoxyethoxy)ethyl)pyrrolidin-1-ium-1-yl)propane-1-sulfonate (OE2pyps) as the zwitterionic additive was about −18 °C. The electrochemical window of [$Pyr_{1,1O1}$][FSA]/LiFSA/OE2pyps was over 5 V vs. Li/Li^+. Li|electrolyte|$LiCoO_2$ cells containing the [$Pyr_{1,1O1}$][FSA]/LiFSA/OE2pyps electrolyte system exhibited high capacity values in the cut-off voltage range of 3.0–4.3 V, even after 50 cycles. Moreover, increases of interfacial resistance between the electrolyte and cathode during cycling were suppressed. Li|electrolyte|NMC cells containing this electrolyte system also exhibited high capacities in a wide cut-off voltage range of 3.0–4.6 V, even after 50 cycles. In the cyclic voltammograms of cells employing a graphite electrode, the intercalation/deintercalation of lithium ions was observed between 0 and + 0.4 V vs. Li/Li^+. Further, graphite|electrolyte|Li cells containing [$Pyr_{1,1O1}$][FSA]/LiFSA/OE2pyps exhibited stable charge/discharge cycle behavior over 5 cycles.

1. Introduction

Lithium-ion battery (LIB) technology has seen rapid development over the past three decades, and consequently, LIBs are now widely used to power laptops, mobile phones, electric vehicles, etc. [1]. However, before further expanding the use of LIBs, their safety and energy density must be improved. Currently, LIBs employ organic liquid electrolytes such as ethylene carbonate and diethyl carbonate. Although these conventional electrolytes show good cycling stability, they pose inevitable risks, including volatility and low ignition temperatures. Ionic liquids (ILs) are considered safer electrolyte candidates because they exhibit many attractive properties, such as low volatility, flame retardancy, high ionic conductivities, and wide electrochemical windows [2]. Sakaebe et al. reported that ILs composed of various quaternary cations with the bis(trifluoromethylsulfonyl)amide ([TFSA]) anion exhibit good cycle stabilities in Li/$LiCoO_2$ cells [3,4]. Garcia et al. reported that 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([C_2mim][TFSA]) exhibits much higher cycle stability than either 1-ethyl-3-methylimidazolium tetrafluoroborate ([C_2mim][BF_4]) or conventional organic liquid electrolytes in $LiTi_5O_{12}$/$LiCoO_2$ cells [5]. Although such ILs show good cycle stabilities, lithium ion intercalation from IL electrolytes into the graphite anode is difficult owing to competitive intercalation of the organic cations present in the ILs. The addition of vinylene carbonate to the ILs prevents the intercalation of organic cations [6], likely by decomposing to form a large-cation-blocking film on the graphite anode. On the other hand, Ishikawa et al. reported the intercalation of lithium ions into a graphite electrode in *N*-methyl-*N*-propylpyrrolidinium bis(fluorosulfonyl)amide ([Pyr_{13}][FSA]) without additives [7]. The formation of a capacitive layer composed of FSA anions and lithium cations is believed to prevent the

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[*] Corresponding author.
E-mail address: masahi-f@sophia.ac.jp (M. Yoshizawa-Fujita).

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intercalation of organic cations into the graphite anode [8]. Rapid charge/discharge processes have also been achieved in cells containing ILs with a high concentration of LiFSA [9]. These results suggest that ILs containing the FSA anion are attractive electrolyte components for LIBs. Recently, we proposed a novel electrolyte system composed of *N*-methyl-*N*-methoxymethylpyrrolidinium bis(fluorosulfonyl)amide ([$Pyr_{1,1O1}$][FSA]) and LiTFSA ([$Pyr_{1,1O1}$][FSA]/LiTFSA), which has higher ionic conductivity, lower viscosity, and a lower melting temperature than [Pyr_{13}][FSA]/LiTFSA [10].

For practical applications, improvements in the energy density of LIBs employing ILs are required, and the cut-off voltage needs to be increased. However, high voltages induce a significant decrease in the cycle stability of LIBs owing to decomposition of the electrolyte, which results in the formation of a passivation layer on the electrode, even when ILs are used as electrolytes [11]. This decomposition reaction must be suppressed at high cut-off voltages to allow the use of high-voltage cathode materials [12,13]. In the case of conventional liquid electrolytes, various types of additives (e.g., fluoroethylene carbonate) have been used to improve anodic stability [14,15].

Zwitterions, in which positive and negative charges are connected by covalent bonds, have been studied as novel electrolyte materials with the goal of suppressing migration of the component ions along the potential gradient [16–19]. Zwitterions are nonvolatile and exhibit thermal and electrochemical stabilities that are comparable to those of ILs [17,20,21]. Several researchers have shown that zwitterions can be successfully utilized as ion-dissociation promoters in gel electrolytes [22]. Recently, we found that the oxidation limit of oligo-ether electrolytes is improved with the addition of 5.5 wt% of zwitterions [23,24]. The addition of zwitterions also improved the charge/discharge cycle stability of Li/$LiCoO_2$ cells containing oligo-ether electrolytes by preventing an increase in the charge transfer resistance between the electrolyte and cathode [24]. Moreover, the addition of zwitterions had positive effects on the dissociation of lithium salts in the ILs and the formation of a solid-electrolyte interface (SEI) [25]. We also reported that the charge/discharge capacity and coulombic efficiency of [Pyr_{13}][FSA]/LiTFSA composites are improved with the addition of a small amount (5 wt%) of pyrrolidinium-based zwitterion 3-(1-butylpyrrolidinium)propane-1-sulfonate (Bpyps) [26].

Although zwitterions are interesting materials as additives in LIBs, there are few reports on the charge/discharge properties of such rechargeable cells. To extend the practical use of zwitterions as additives in LIBs, in this work, we examined the charge/discharge properties of an IL electrolyte containing a zwitterion in Li/$LiCoO_2$, Li/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC), and graphite/Li cells. We used the [$Pyr_{1,1O1}$][FSA]/lithium bis(fluorosulfonyl)amide (LiFSA) composite as an IL with 3-(1-(2-(2-methoxyethoxy)ethyl)pyrrolidin-1-ium-1-yl)propane-1- sulfonate (OE2pyps) added as a zwitterion. The chemical structures of the electrolyte components are shown in Fig. 1. It is well known that the thermal and electrochemical stabilities of pyrrolidinium cations are superior to those of other organic cations; therefore, we adopted the pyrrolidinium cation motif in both the IL and zwitterion structures. As zwitterions containing pyrrolidinium cations tend to have poor solubility in ILs, we introduced a functional ether side chain to improve the solubility of the pyrrolidinium-based zwitterions. To examine the stability of the electrolyte at high voltages, charge/discharge tests for Li|[$Pyr_{1,1O1}$][FSA]/LiFSA/OE2pyps|NMC cells were carried out at high cut-off voltage ranges. To investigate the intercalation/deintercalation of lithium cations, we also conducted charge/discharge tests using graphite|[$Pyr_{1,1O1}$][FSA]/LiFSA/OE2pyps|Li cells.

2. Experimental

2.1. Materials

Pyrrolidine (Wako Pure Chemical Industries, Ltd., 95.0%) was distilled under atmospheric pressure before use. Sodium hydride (50%–72% in oil), acetonitrile (99.8%, dehydrated), and tetrahydrofuran (THF, 99.5%, dehydrated) were purchased from Wako Pure Chemical Industries, Ltd. 1-Bromo-2-(2-methoxyethoxy)ethane (Sigma-Aldrich, 90%) and 1,3-propanesultone (Tokyo Chemical Industry Co., Ltd., 99.0%) were distilled *in vacuo* prior to use. [$Pyr_{1,1O1}$][FSA] was synthesized according to the literature procedure [10]. LiFSA (Kishida Chemical Co., Ltd., 99.0%) was dried at 120 °C *in vacuo* before use. Lithium foils (thickness: 0.4 mm, diameter: 16 mm) were purchased from Honjo Metal Co., Ltd. Poly(vinylidene difluoride) (PVDF) (#1120) was purchased from Kureha Battery Materials Japan Co., Ltd. Acetylene black was purchased from Denki Kagaku Kogyo Co., Ltd. Lithium cobalt oxide (average particle diameter: 1.02 μm) and lithium nickel manganese cobalt oxide (average particle diameter: 0.81 μm) were purchased from Kusaka Rare Metal Products Co., Ltd.

2.2. Synthesis of 1-(2-(2-methoxyethoxy)ethyl)pyrrolidine (OE2py)

Under an argon atmosphere, sodium hydride (2.41 g, 100 mmol) was suspended in THF (20 mL). Pyrrolidine (3.50 g, 50 mmol) dissolved in 30 mL of THF was added dropwise to the solution. The mixture was stirred at 25 °C for 15 h, then 1-bromo-2-(2-methoxyethoxy)ethane (9.15 g, 50 mmol) was added to the solution. After stirring at 70 °C for 15 h, the resulting suspension was filtered to remove the white precipitate. The solvent was removed from the filtrate by rotary evaporation to give the yellow crude product. The crude product was purified by distillation under reduced pressure. The fraction collected at 120 °C under a

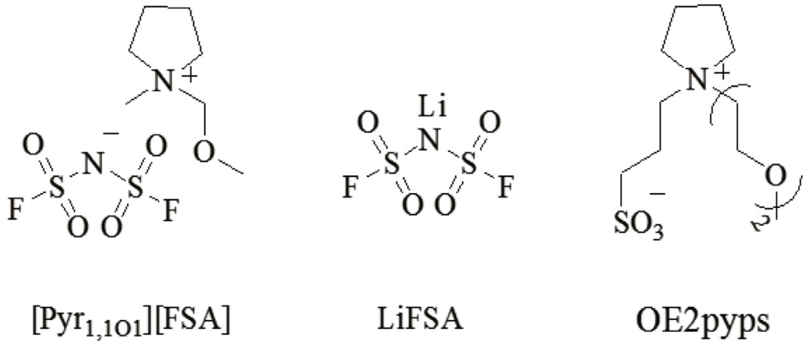

Fig. 1. Chemical structures of electrolyte components.