Electrochemical performance of an ethylene carbonate-free electrolyte based on lithium bis(fluorosulfonyl)imide and sulfolane

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HIGHLIGHTS

- LiFSI/SL exhibits characteristics of a Walden electrolyte and crystallinity gap.
- LiFSI/SL enables reversible Li$^+$ intercalation into graphite without any additives.
- SEI derived from LiFSI contributes to stable Li$^+$ intercalation into graphite.
- A battery with LiFSI/SL shows excellent cycle stability at high temperature.

GRAPHICAL ABSTRACT
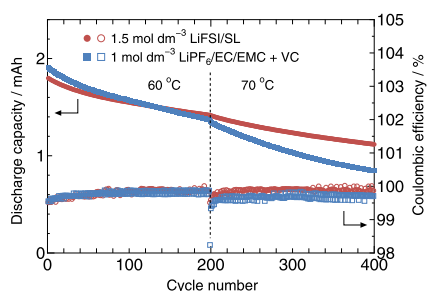
ARTICLE INFO

ABSTRACT

Lithium bis(fluorosulfonyl)imide (LiFSI) is one of the most promising lithium salts for use in lithium-ion batteries owing to its high ionic conductivity, high solubility in organic solvents, and excellent solid electrolyte interphase (SEI)-forming ability. In this study, we developed an ethylene carbonate (EC)-free electrolyte comprising LiFSI and sulfolane (SL) (LiFSI/SL). LiFSI/SL exhibits ideal Walden electrolyte behavior and crystallinity gap phenomena as well as reversible lithium intercalation into a graphite electrode. LiCoO$_2$/graphite full-cells containing the new electrolyte show superior cycle stabilities at room and high temperature compared to those with conventional LiPF$_6$/EC-based electrolytes. For example, after 200 cycles at 60 °C followed by 200 cycles at 70 °C, a cell with 1.5 mol dm^{-3} LiFSI/SL delivers a discharge capacity of 1.12 mAh, while that with 1.0 mol dm^{-3} LiPF$_6$/EC/EMC delivers a discharge capacity of only 0.84 mAh under the same conditions. The enhanced performance of batteries with LiFSI/SL can be attributed to the effective SEI derived from LiFSI.

1. Introduction

Lithium-ion batteries are essential power sources owing to their high energy densities and long operational lifetimes [1]. Accordingly, they are used in various portable electronic devices, such as laptop PCs, mobile phones, and smartphones. Their use has recently expanded to larger-energy-capacity applications such as electric vehicles (EVs), hybrid electric vehicles, and energy storage systems (ESSs). Since the

commercialization of lithium-ion batteries, nonaqueous electrolytes have been used in which lithium hexafluorophosphate (LiPF$_6$) is dissolved in a mixture of ethylene carbonate (EC) and acyclic carbonates. However, it has become widely accepted that EC and LiPF$_6$ cause several problems in the utilization of LiPF$_6$/EC-based electrolytes.

EC is currently regarded as an indispensable electrolyte component in the conventional lithium-ion batteries since its reductive decomposition on the surface of graphite negative electrodes, which are the

most commonly employed in such devices, allows for highly reversible lithium-ion intercalation into the graphite due to solid electrolyte interphase (SEI) formation [2]. However, EC-containing electrolytes frequently exhibit poor performance at low temperature since they freeze owing to the high melting point of EC [3]. Thus, acyclic carbonates such as dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC) are commonly mixed with EC to obtain liquid electrolyte at low temperature. However, these acyclic carbonates are highly flammable and present a considerable combustion risk [4].

$LiPF_6$ is also an important component for lithium-ion batteries owing to its balanced properties of high solubility in organic solvents and excellent ionic conductivity. The thermal instability and moisture sensitivity of $LiPF_6$, however, can induce degradation of battery performance. Despite these shortcomings, electrolyte formulations containing $LiPF_6$ and EC have become essential components of state-of-the-art lithium-ion batteries because there are currently no alternatives that exhibit comparable performance [5].

Accordingly, electrolytes free from $LiPF_6$ and EC have been explored in an effort to overcome the shortcomings of $LiPF_6$/EC-based electrolytes. As a lithium salt, lithium bis(fluorosulfonyl)imide (LiFSI) is one of the most promising alternatives (Fig. 1). It has been investigated as a conducting salt [6,7] and an additive [8] in $LiPF_6$/EC-based electrolytes since its invention by Armand in 1995 [9]. LiFSI exhibits thermal stability up to 200 °C and moisture stability, overcoming the problems associated with $LiPF_6$. Furthermore, LiFSI exhibits high ionic conductivity, high solubility in organic solvents, and excellent SEI-forming ability [10], leading to attractive properties such as long operational life and high-rate performance. Its excellent SEI-forming ability has enabled the development of EC-free electrolytes containing DMC [11], ionic liquids [12], or glyme [13] that show reversible lithium intercalation into graphite without any SEI-forming additives or co-solvents. Furthermore, LiFSI-based superconcentrated electrolytes in acetonitrile [14], 1,2-dimethoxyethane [15], or dimethyl carbonate [16] have been reported to exhibit stable cyclability and fast-charge capability. Thus, applying LiFSI to nonaqueous electrolytes presents the possibility of next-generation lithium-ion batteries with performance superior to conventional $LiPF_6$/EC-based electrolytes.

As a solvent, sulfolane (SL) is an excellent candidate for lithium-ion batteries (Fig. 1). SL has a high boiling point (T_b = 287 °C), a high flash point (T_f = 165 °C) [4], a high dielectric constant (ε = 43.4), and high oxidative stability up to 5.8 V [17]. Lithium-ion batteries containing $LiPF_6$-SL/EMC with $Li_4Ti_5O_{12}$ as the negative electrode material [18] or $LiPF_6$/SL + 10 wt% vinylene carbonate (VC) with graphite as the negative electrode material [19] have been reported to show good capacities.

Styrene-butadiene rubber/carboxymethylcellulose (SBR/CMC) as a binder in conjunction with a graphite negative electrode and $LiPF_6$-SL/DMC electrolyte enables to fabricate full-cells [20]. However, SL-based electrolytes contain flammable organic solvents such as DMC and DEC. Thus, they still present a risk of explosion by thermal runaway. Furthermore, SL-based electrolytes without flammable solvents and SEI-forming additives have not been reported because they are not stable with negative graphite electrodes.

Accordingly, in the present study, we propose an EC-free electrolyte composed of LiFSI and SL (LiFSI/SL) that contains no additives or co-solvents. LiFSI/SL behaves as a Walden electrolyte, and that with 1.5 mol dm^{-3} concentration exhibits crystallinity gap phenomena at low temperature. We demonstrate reversible lithium intercalation into

Fig. 1. Chemical structures of lithium bis(fluorosulfonyl)imide (LiFSI) and sulfolane (SL).

a graphite electrode using LiFSI/SL since the reductive decomposition product of LiFSI works as an effective SEI that suppresses further decomposition of the electrolyte. Furthermore, LiFSI/SL enables excellent cycle stability at high temperature as well as at room temperature.

2. Experimental

2.1. Materials

High-purity LiFSI (IONEL LF-101) was provided by Nippon Shokubai Co., Ltd. $LiPF_6$, LiTFSI, VC, SL, and a mixture of EC/EMC (3/7 by volume) were purchased from Kishida Chemical Co., Ltd. All materials were battery grade and used without further purification. Positive electrode sheets ($LiCoO_2$, 2.2 mAh cm^{-2}, polyvinylidene fluoride (PVdF) binder) and negative electrode sheets (natural graphite, 2.3 mAh cm^{-2}, PVdF binder) were purchased from Hosen Corp. and dried under vacuum overnight at 80 °C.

2.2. Electrolyte preparation

All electrolytes were prepared in a dry room (a dew point below −50 °C). SL-based electrolytes (1 mol dm^{-3} $LiPF_6$, 1 mol dm^{-3} LiTFSI, and 1, 1.5, and 2 mol dm^{-3} LiFSI in SL) were formulated by adding the lithium salt to SL heated to 60 °C. The corresponding electrolytes are abbreviated as $LiPF_6$/SL, LiTFSI/SL, and LiFSI/SL, respectively. For comparison, EC-based electrolytes (1 mol dm^{-3} $LiPF_6$, LiTFSI, or LiFSI in a mixture of EC/EMC) were prepared in a similar fashion. They are abbreviated as $LiPF_6$/EC/EMC, LiTFSI/EC/EMC, and LiFSI/EC/EMC, respectively. $LiPF_6$/EC/EMC with 2 wt% VC ($LiPF_6$/EC/EMC + VC) was prepared for cyclability evaluation.

2.3. Measurements

Ionic conductivities and viscosities were measured in a dry room using a conductance meter with an immersion type conductivity cell (DKK-TOA Corp., CM-25R, and CT-57101B) and a programmable rheometer (Brookfield, DV-III), respectively. The thermal stabilities of the electrolytes were studied using differential scanning calorimetry (DSC, Netzsch, DSC3500 Sirius). The sample was packed in a high-pressure crucible with a gold-plated surface, which was then sealed in a glove box filled with argon gas. The sample was then analyzed from 25 to 400 °C at a scan rate of 10 °C min^{-1}. The thermal characteristics of the electrolytes were also measured using DSC. The electrolyte sample was put into standard aluminum pan and sealed in a dry room. All samples were heated to 60 °C. The pans were then cooled to −100 °C and reheated to 100 °C (10 °C min^{-1}). Only the final heating traces are reported here.

2.4. Electrochemical properties

All battery evaluations were carried out using 2032-type coin cells. Coin cells were assembled in a dry room. A glass fiber filter (GC-50, ADVANTEC) that was dried at 80 °C overnight was used as a separator. Battery evaluation was conducted using a charge-discharge test device (Model ACD-M01-05N, ASKA Electronic Co., Ltd.).

To evaluate the graphite/lithium half-cells, positive cans made of stainless steel were used. Li metal (Honjo Metal Co., Ltd.) with a diameter of 14 mm as a negative electrode, natural graphite electrode with a diameter of 12 mm as a positive electrode, and 1 mol dm^{-3} SL-based electrolytes ($LiPF_6$/SL, LiTFSI/SL, or LiFSI/SL) were used. The tests were conducted by charging the cells at 25 °C to 0.01 V using a constant current (CC) protocol at 0.1C followed by discharge at 0.1C at constant current until 2.0 V was reached.

For the evaluation of the $LiCoO_2$/graphite full-cells, we used positive cans with aluminum-coated inner surfaces to prevent the corrosion of the stainless 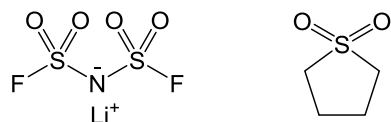steel by LiFSI. A natural graphite electrode with a