



Lithium dendrite suppression and cycling efficiency of lithium anode

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ABSTRACT

We propose a novel binary electrolyte of lithium bis(fluorosulfonyl)imide/1,3-dioxolane, that exhibits excellent performance for the suppression of lithium-dendrite growth and stability against lithium metal. With 2.5 M lithium bis(fluorosulfonyl)imide in 1,3-dioxolane, long short-circuit onset-times of 72.3 and > 190 h are observed in Li/Li cells polarized at galvanostatic current densities of 1.0 and 0.5 mA cm⁻², respectively. The coulombic efficiencies for the repeated Li plating/stripping in the 2.5 M electrolyte at 1.0 and 0.5 mA cm⁻² are as high as 99.0% and 99.5%, respectively. The electrolyte structure is changed with an increase in the concentration speculated from Raman spectra, which enables the reactivity toward lithium metal to be lowered.

1. Introduction

Lithium metal is regarded as an ideal anode for lithium batteries in terms of its high theoretical specific capacity (3860 mAh g⁻¹) and lowest electrochemical potential (-3.04 V vs. standard hydrogen electrode). However, to date, it is still difficult to meet the requirements of the commercial lithium batteries due to low faraday efficiencies, and especially hazardous dendritic deposition [1]. Much effort has been devoted to resolving these issues, such as the use of Li-alloy anodes [2], application of blocking solid-state ionic electrolytes [3–6], the exploitation of functional electrolyte additives [7,8], the formation of an artificial solid electrolyte interphase (SEI) on the lithium metal surface [9–14], and using structured Li anode [15,16] or lithium-deposition hosts [17]. Significantly, a simple method that uses a concentrated liquid electrolyte was recently proposed to suppress lithium-dendrite growth and improve cycling performance. Suo et al. reported that concentrated lithium bis(trifluoromethanesulfonyl)imide in 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME) (1:1 by volume) could effectively prevent lithium-dendrite growth [18]. However, the average coulombic efficiency (CE) for lithium plating/stripping was estimated to be as low as 71.4%. More recently, Qian et al. demonstrated a better result for a Li/Li symmetrical cell using an electrolyte of 4 M lithium bis(fluorosulfonyl)imide (LiFSI) in DME, which could be cycled for over 600 h at 10 mA cm⁻² [19]. However, the suppression of lithium-dendrite growth is ineffective in concentrated LiFSI-DME, as demonstrated in the results and discussion section.

Herein, we propose a novel electrolyte system that consists of LiFSI as the salt and DOL as the solvent, and systematically examine the effect

of lithium-dendrite suppression, CE, and cycling stability in various concentrations of LiFSI-DOL. Raman spectra and X-ray photoelectron spectroscopy (XPS) were performed to characterize the solution structures and SEI compositions on lithium metal, respectively. The morphology of Li deposition was analyzed using scanning electron microscopy (SEM).

2. Experimental

2.1. Materials

LiFSI (Central Glass Co. Ltd) was dried under vacuum conditions at 100 °C for 48 h, and anhydrous DOL (Aladdin) was dehydrated using activated 4 Å molecular sieves to eliminate trace water. The electrolyte was prepared by dissolving pre-weighed LiFSI in DOL in an Ar-filled glove box. Herein, 1 M LiFSI-DOL electrolyte, denotes 1 mol of LiFSI dissolved in 1 L of DOL. The water content in the electrolytes was below 20 ppm, as measured with a Karl-Fischer moisture meter.

2.2. Design of Li cells

Li symmetrical coin cells (CR2025) were composed of two 12 mm diameter lithium disks, each with a weight of ca. 28.1 mg (96.0 mAh cm⁻²), as the working and counter electrodes, respectively, and a circular separator (∅ 19 mm; Celgard 2400 film or Whatman GF/F glassfiber) soaked with electrolyte. The symmetrical cells were denoted as cell #1 (GF/F) and #2 (Celgard) for the different separator materials. A Li/Cu coin cell (cell #3) was fabricated using a lithium disk

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anode, a copper disk (\varnothing 16 mm) counter electrode, and a Celgard separator soaked with electrolyte.

2.3. Electrochemical tests

The CE for lithium plating/stripping was measured using the method proposed by Aurbach et al. [20]. The Li^+ transference number (t_{Li^+}) and salt diffusion coefficient (D_s) of the LiFSI-DOL were measured with a combination of AC impedance spectroscopy and DC polarization according to the methods by Abraham et al. [21] and Ma et al. [22], respectively, using an electrochemical workstation (CH Instruments, China, CHI660D). These measurements, including ionic conductivity of LiFSI-DOL, were performed as previously reported [23]. The onset-time of short-circuit (t_{sc}) by lithium-dendrite growth was measured by galvanostatic deposition on the Li substrate using cell #1 because it is difficult for a glassfiber separator to effectively block lithium dendrite growth due to its large average pore size (ca. 0.7 μm). Electrochemical cycling tests for Li plating/stripping were conducted using cells #2 and #3 with a battery test system (Neware, China, BTS-5V 20 mA) at 25 $^\circ\text{C}$.

2.4. Material characterization

The viscosity of the electrolytes was measured using a digital rheometer (BrookField, R/S-CC+). Raman spectra were recorded with a confocal Raman microscope system (Horiba, LabRAM HR Evolution, resolution ca. 2 cm^{-1}). The surface and cross-sectional morphologies of the lithium deposition were investigated using SEM (FEI, SIRION-100). XPS measurements were performed using a spectrometer (Kratos Analytical, Axis Ultra DLD) equipped with a monochromatized aluminum X-ray source. The lithium electrodes were washed with dimethyl carbonate, dried and then transferred into the XPS chamber using an in-house transfer holder without exposure to air. The binding energies were calculated with respect to the C-(C,H) component (BE = 284.8 eV) of the C 1s peak.

3. Results and discussion

Cell #3 was designed to evaluate the cycling stability and efficiency for lithium plating/stripping in different concentrations of LiFSI-DOL at a current density of 1.0 mA cm^{-2} and in 2.5 M LiFSI-DOL at 0.5 mA cm^{-2} . The measurements were performed with the following conditions: lithium equivalent to an areal capacity of 2 mAh cm^{-2} was deposited on the copper substrate at a specific current density, and the current direction was reversed until the cutoff voltage reached 1.0 V vs. Li. In addition, the saturated LiFSI-DOL could be as high as ca. 6.8 M at 25 $^\circ\text{C}$. The cell with 2.5 M LiFSI-DOL demonstrated better cycling performance than those using other concentrations of LiFSI-DOL, and could be cycled for 500 cycles with a stable and high average CE of 98.8%. Moreover, the average CE of the initial 350 cycles (2800 h) even reached 99.5% at 0.5 mA cm^{-2} , which is better than the performance of most previously reported cells using other electrolytes [8,19,23–25]. As depicted in Fig. 1b, the CE of Li/2.5 M LiFSI-DOL/Cu at current densities of 1.0 and 5.0 mA cm^{-2} can reach ca. 99.0% and 98.5%, respectively, measured using Aurbach's method. Fig. 1c compares the long-period cycling stability of the Li anode in different concentrations of LiFSI-DOL using cell #2, where specific currents was passed for 2 h (1.0 mA cm^{-2}) or 4 h (0.5 mA cm^{-2}) and the current direction was reversed for the same time. The cycle stability of the cells was improved with an increase in the electrolyte concentration. As expected, the cell with the 2.5 M LiFSI-DOL achieved excellent Li plating/stripping durability for more than 2000 h. When the current density was decreased to 0.5 mA cm^{-2} , the cell could be cycled for 2700 h and maintained extremely steady polarization voltage, which indicates lower reactivity with respect to lithium metal for 2.5 M LiFSI-DOL compared with the other LiFSI-DOL concentrations. Fig. 1d shows the changes in the polarization potential of cell #1 with different concentrations of LiFSI-

DOL and 4 M LiFSI-DME at a current density of 1.0 mA cm^{-2} to measure t_{sc} . The cell potential increased abruptly to 0 V, which indicates short-circuit ascribed to lithium-dendrite growth piercing through the glassfiber separator. t_{sc} was extended with an increase in the LiFSI-DOL concentration from 0.25 M to 2.5 M, and a peak at ca.72.3 h (72.3 mAh cm^{-2}) was observed in 2.5 M LiFSI-DOL. To the best of our knowledge, no electrolyte has yet demonstrated similar ability against lithium-dendrite growth, and this is even longer than that with a solid-state polymer electrolyte [26]. In the case of polarization at a current density of 0.5 mA cm^{-2} , the lithium electrode can deliver a specific areal capacity of more than 95 mAh cm^{-2} (> 190 h), which is close to that of the entire lithium metal disk without short-circuit. In contrast, a t_{sc} of only 7.4 h was observed for 4 M LiFSI-DME, as shown in Fig. 1d.

Fig. 2a and b show SEM images of Li deposition on the copper substrate after 70 h at 1.0 mA cm^{-2} in 1 M and 2.5 M LiFSI-DOL, respectively. Very homogeneous granule-like Li deposition without dendrites was observed in 2.5 M LiFSI-DOL, which confirms its outstanding capability for lithium-dendrite suppression. In contrast, lithium deposition in the dilute electrolyte (1 M) could be categorized as heterogeneous morphology, and numerous thin needle-like lithium deposits scattered across the deposition were observed in the surface and cross-sectional SEM images. The needle-like lithium deposition may be more prone to lithium-dendrite growth, which could explain the small t_{sc} (ca. 45 h) in 1 M LiFSI-DOL.

The physicochemical and electrochemical properties of LiFSI-DOL including viscosity, t_{Li^+} , D_s , ionic conductivity were measured. At first, t_{Li^+} was improved with an increase in the concentration from 0.48 for 0.25 M LiFSI-DOL to the peak of 0.67 for 2.5 M LiFSI-DOL, due to an increase in mobile Li^+ number density [18]. However, t_{Li^+} decreased to 0.61 for 4 M LiFSI-DOL, which may be ascribed to a decrease in the Li^+ diffusion coefficient with the increase in the radius of Li diffusing complexes [27]. The calculated t_{sc} according to Sand's time equation [28], at 1.0 mA cm^{-2} , using the data of t_{Li^+} , D_s and revised salt concentration, are 5.7, 22.7, 67.2, 136.7, 149, and 107.4 h for 0.25, 0.5, 1, 2, 2.5, and 4 M LiFSI-DOL, respectively. The salt concentrations must be revised based on the change in the volume of as-prepared LiFSI-DOL mixtures according to Sand's time equation. Note that the longest theoretical t_{sc} was obtained for 2.5 M LiFSI-DOL. However, the practical t_{sc} in different concentrations of LiFSI-DOL were much lower than the calculated Sand's times, which may be attributed to the local inhomogeneity on the surface of lithium metal [29]. The viscosity and ionic conductivity of 2.5 M LiFSI-DOL were 3.7 $\text{mPa}\cdot\text{s}$ and $1.12 \times 10^{-2} \text{Scm}^{-1}$, which are comparable to a commercial organic electrolyte. To characterize the solution structures, Raman spectra were obtained in a pure Ar atmosphere, and peak deconvolution of the spectra was performed with the Voigt function [30]. As shown in Fig. 2c, the band at 721 cm^{-1} in pure DOL was assigned to the CH_2 in-plane rocking mode of free DOL molecules [31,32]. An anticipated band at 717 cm^{-1} assigned to free FSI $^-$ [33] was absent in the spectra, which may be due to the influence of free solvent molecules. The bands at 730, 743, and 746 cm^{-1} are supposed to arise from solvent-separated ion pairs, contact ion pairs, and multiple ion aggregates respectively, due to the different local environments of the FSI $^-$ anions [34,35]. The intensity of the free solvent band decreased with an increase in the LiFSI concentration, and then disappeared completely in 2.5 M LiFSI-DOL, which indicates that most solvent molecules had coordinated to FSI $^-$ and Li^+ . Jeong et al. suggested that the lack of free solvent in concentrated electrolytes is beneficial for a decrease in the SEI layer thickness [25] that results in an increase in the CE. Qian et al. speculated that concentrated electrolyte is less prone to reaction with Li metal, and produces an SEI with lower resistance [19]. XPS measurements of the lithium electrode surface of cell #2 with various concentrations at 1 mA cm^{-2} after cycling were performed, and F 1s spectra attributed to FSI $^-$ reduction are shown in Fig. 2d. Two peaks in the spectra at 684.8 and 688.0 eV are assigned to Li–F and S–F, respectively [36]. The peak intensity of Li–F decreased with an increase

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