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Insight into the effect of lithium-dendrite suppression by lithium bis(fluorosulfony)imide/1,2-dimethoxyethane electrolytes

Peng Zhang*, Han Jin, Tong Wang, Miao Wang**

Department of Physics, Zhejiang University, Hangzhou 310027, PR China

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The highly concentrated lithium bis(fluorosulfonyl)imide/1,2–dimethoxyethane electrolyte is in the good graces of researchers due to its excellent electrochemical performance in lithium-metal batteries. However, our study reveals that the more concentrated electrolyte incurred more drastic lithium-dendrite growth. Minimum onset time (t_{sc}) of lithium-dendrite formation of only 7.4 and 18.6 h are observed in 4 M lithium bis(fluorosulfonyl)imide/1,2-dimethoxyethane electrolyte galvanostatically polarized at current densities of 1.0 and 0.5 mA cm^{-2}, respectively. In contrast, t_{sc} are as long as around 56 and > 190 h in 1 M electrolyte at 1.0 and 0.5 mA cm^{-2}, respectively. We found that 1 M electrolyte has comprehensive advantages in many respects, including Li^+ transference number (0.61), salt diffusion coefficient (1.47×10^{-5} cm^2 s^{-1}), ionic conductivity (1.52×10^{-2} S cm^{-1}), low polarization potential and solid electrolyte interphase protection, which collectively make contributions to outstanding lithium-dendrite suppression.

1. Introduction

Building high-powered rechargeable batteries is a crucial strategy to satisfy an ever-increasing demand for energy density [1,2]. Up to present, many novel battery systems beyond lithium–ion batteries have been proposed, e.g. lithium–oxygen [3,4] and lithium–sulfur rechargeable batteries [5,6], to significantly boost the specific energy density to as high as 3460 [7] and 2510 Wh kg^{-1} [8], respectively. It should be stressed that Li–O_2 and Li–S batteries are feasible only when lithium-based anode could be utilized with reliability. Frankly, lithium metal is regarded as an ideal anode in terms of its excellent theoretical capacity (3860 mAh g^{-1}), lowest electrochemical potential (−3.04 V vs. standard hydrogen electrode), and low density (0.534 g cm^{-3}). However, it is still difficult to meet the demands of the commercial lithium batteries on account of two formidable challenges with respect to low cycling efficiencies, and especially the dendritic lithium deposition. Much effort has been devoted to resolving these issues for over 40 years [9]. Most works focus on improving the stability and uniformity of the solid electrolyte interphase (SEI) on the surface of lithium metal by adjusting electrolyte compositions or optimizing functional additives [10–14]. However, it is very difficult to achieve sufficient passivation with lithium electrodes in the liquid electrolytes indicated by Aurbach [15]. The lithium metal alloy could avoid the formation of lithium dendrite since lithium exists as ions instead of simple substance [16]. However, a large internal stress caused by the sharp volume variation during alloying/dealloying processes destroyed the alloy structure [17]. Solid state ionic electrolytes including organic [18,19], inorganic [20], and their hybrid composite materials [21–23] were proposed to prevent the lithium-dendrite formation relying on their high mechanical strength, because the solid electrolyte with a Young's modulus higher than 6 GPa should be sufficient to inhibit dendritic deposition indicated by Newman and coworker [24]. However, such a hard electrolyte has a serious problem with respect to a high interfacial resistance between electrolyte and electrodes. Moreover, various artificial SEI layers have been developed in-situ or ex-situ by chemical pre-treatment to suppress dendritic Li deposition [25–29]. However, there is no conclusive evidence that the artificial SEI layers could withstand the drastic lithium volume variation without fracture upon repeated Li plating/stripping. In addition, the methods using structured Li anode [30] and hosts for dendrite-free lithium deposition [31,32] have already been reported. Significantly, a simple method that uses concentrated liquid electrolytes was recently proposed to suppress lithium-dendrite formation in

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* Corresponding author.
** Corresponding author.
E-mail addresses: zhangpengzju@zju.edu.cn (P. Zhang), miaowang@css.zju.edu.cn (M. Wang).

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parallel with improving the Coulombic efficiency (CE) for Li plating/stripping. Hu et al. reported that 7 mol L^{-1} lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1,3-dioxolane: 1,2-dimethoxyethane (1:1 by volume) could effectively prevent lithium-dendrite growth [33]. Unfortunately, the average CE was estimated to be as low as 71.4%. More recently, Qian et al. demonstrated a better result that a Li symmetrical cell using 4 M Lithium Bis(fluorosulfonyl)imide (LiFSI)–1,2-dimethoxyethane (DME) electrolyte was cycled for over 600 h at a current density of 10.0 mA cm^{-2} without short-circuit [34]. However, the cycling performance was merely examined at a small specific area capacity of 0.5 mAh cm^{-2}. For the practical use, the experiments should be performed at higher specific area capacities. In other words, there is a lack of conclusive evidence that lithium-dendrite formation could be prevented completely in the concentrated LiFSI–DME electrolytes polarized at a high current density (>1.0 mA cm^{-2}) with large specific area capacities. Note that lithium dendrite is usually difficult to pierce the Celgard separator due to its tiny pores (see later), which may mislead us into estimating the real onset-time of lithium dendrite formation (t_{sc}) to some extent. In this work, we are devoted to systematic examining and comparing the t_{sc} in the different concentrations of LiFSI–DME electrolytes, and discussing the influencing factors related to t_{sc} including the current density, Li^+ transference number (t_{Li}^+), bipolar diffusion coefficient (D_s), ionic conductivity (σ), structure and viscosity of electrolytes, SEI morphologies and compositions etc.

2. Experimental

2.1. Materials preparation

Anhydrous DME (Aladdin) was dehydrated using activated 4 Å molecular sieves (Aladdin) to eliminate the trace water. Lithium bis(fluorosulfonyl)imide (LiFSI) (Central Glass Co., Ltd.) and Lithium trifluoromethanesulfonate ($LiCF_3SO_3$) (Aladdin) were dried under vacuum condition at 100 °C and 130 °C for 48 h, respectively.

2.2. Synthesis of binary electrolyte

The electrolytes were prepared by dissolving the desired amount of lithium salt in DME solvent in an Ar-filled glove box ($H_2O < 1$ ppm, $O_2 < 1$ ppm). The final water content in all electrolytes was under 20 ppm measured by a Karl–Fischer moisture meter (KEM, MKC–510). In this article, 1 M LiFSI–DME electrolyte, denotes 1 mol of LiFSI dissolved in 1 L of DME.

2.3. Battery assembling Li symmetrical coin cell (CR2025) was composed of two 12 mm diameter lithium disks, each with a weight of ca

28.1 mg, 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 lithium disk anode, a copper disk (⌀16 mm) counter electrode, and a Celgard separator soaked with electrolyte.

2.4. Electrochemical measurement

The measurements of onset-time of lithium dendrite formation (t_{sc}) were conducted by galvanostatic deposition on the Li substrate using cell #1 and cell #2 with different concentrations of LiFSI–DME electrolytes. The average CE for lithium plating/stripping at 1.0 mA cm^{-2} was measured using cell #3 on the basis of the method proposed by Aurbach [35]. An initial amount of lithium corresponding to 5 coulombs per cm^2 was deposited on a copper substrate, and then the deposited lithium of 1.25 coulombs per cm^2 was periodically plated/stripped at 1.0 mA cm^{-2} for 20 circles, followed by dissolving the residual plated lithium thoroughly (the charge cutoff potential was 1 V vs. Li reference). All the measurements including t_{sc} and CE were conducted on a battery test system (Neware Technology Co., Ltd., BTS-5 V 20 mA) at 25 °C.

The Li^+ transference number (t_{Li}^+) of LiFSI–DME electrolytes were measured with a combination of AC impedance spectroscopy and DC polarization using an electrochemical workstation (CH Instruments, Inc., CHI660D) according to a method outlined by Abraham et al. [36]. First, the measurement of initial impedance of the cell #2 was carried out, and then the cell was polarized at 5 mV for several hours to obtain the steady-state currents. At last, the cell impedance was measured once more without delay.

$$t_{Li^+} = \frac{I_s R_f}{I_0 R_1}\left[\frac{\Delta V - I_o R_1^o}{\Delta V - I_s R_1^s}\right] \tag{1}$$

Where I_o and I_s are the initial and steady-state currents, R_1^o and R_1^s are the initial and steady-state resistances of the passivating layers on the Li anodes, respectively. R_1 and R_f represent the initial and final bulk resistances of the electrolytes, respectively.

The bipolar diffusion coefficient (D_s) was calculated from the slope of a plot of lnΔ ϕ vs. time proposed by Ma et al. [37].

$$\text{slope} = -\frac{\pi^2 D_s}{L^2} \tag{2}$$

Where L is the thickness of the LiFSI–DME electrolytes. We fabricated a Li symmetrical coin-type cell using a glassfiber separator (ϕ12 mm) in a concentric ring (thickness 200 μm) using a PTFE concentric-ring as a gasket with an internal diameter of 12 mm and an external diameter of 19 mm. Then it was supposed that the thickness of electrolyte was approximate to that of the concentric ring. The cell was polarized at a constant potential of 5 mV for several hours to reach a steady-state, and then the potential was interrupted and monitored without delay. AC impedance spectroscopy of the LiFSI–DME electrolytes were measured by fabricating a symmetrical cell with two platinum blocking electrodes using a self-designed device, in order to calculate their ionic conductivities.

2.5. Material characterization

The viscosity of electrolytes were measured using a digital rheometer (BrookField, R/S-CC+) at 25 °C. Raman spectra of LiFSI–DME electrolytes were recorded with a Horiba confocal Raman microscope system excited by a 532 nm laser (Horiba, LabRAM HR evolution, resolution ca. 2 cm^{-1}). The solutions were placed in the capillary tubes sealed by vacuum silicone grease, which was operated in an Ar-filled glove box to avoid air exposure. For band-fitting the Labspec 6 software for windows (HORIBA, Ltd.) was used. The surface morphologies of lithium deposits were investigated using Scanning Electron Microscope (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 energy with respect to the C–(C,H) component (BE = 284.8 eV) of the C 1s peak was used as the reference for calibration.