Journal of Power Sources 400 (2018) 225–231

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

$(CH_3)_3Si\text{-}N[(FSO_2)(n\text{-}C_4F_9SO_2)]$: An additive for dendrite-free lithium metal anode

Bo Tong[a,b], Jiawei Wang[b], Zhenjie Liu[b,c], Lipo Ma[b], Peng Wang[a], Wenfang Feng[a], Zhangquan Peng[b,*], Zhibin Zhou[a,**]

[a] *Key Laboratory of Material Chemistry for Energy Conversion and Storage (Ministry of Education), School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan 430074, China*

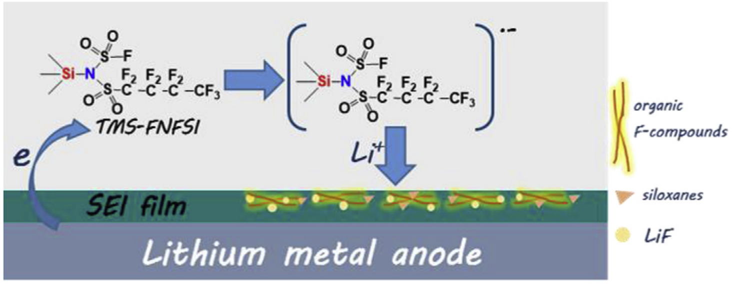
[b] *State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, China*

[c] *University of Science and Technology of China, Hefei 230026, China*

HIGHLIGHTS

- An additive, $(CH_3)_3Si\text{-}N[(FSO_2)(n\text{-}C_4F_9SO_2)]$, is reported for lithium metal anode.
- A LiF-rich, organic Si-/F-containing SEI film is formed on lithium metal anode.
- Growth of lithium dendrites is successfully suppressed.
- Li|$LiFePO_4$ cells with the additive show decent cycling performance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Lithium metal batteries
Lithium metal anode
Lithium dendrites
Additive
trimethylsilyl(fluorosulfonyl)(n-nonafluorobutanesulfonyl)imide

ABSTRACT

Formation of dendrite on lithium metal anode (LMA) poses a threat to commercial prospects of rechargeable lithium metal batteries (LMBs). Electrolyte engineering, including but not limited to using new solvents, salts and additives, is an effective remedy to surmounting this vexing problem. In this work, a novel additive, trimethylsilyl(fluorosulfonyl)(*n*-nonafluorobutanesulfonyl)imide {$(CH_3)_3Si\text{-}N[(FSO_2)(n\text{-}C_4F_9SO_2)]$, TMS-FNFSI}, is introduced to the ether-based electrolyte of $LiN[(CF_3SO_2)_2]$-1,3-dioxolane/dimethoxyethane (LiTFSI-DOL/DME) for LMBs. It preferentially reduces on LMA prior to the main electrolyte components (ethers and LiTFSI), resulting in a LiF-rich, organic F- and Si-containing solid electrolyte interphase (SEI) film, being validated by X-ray photoelectron spectroscopy (XPS). Thus, dendrite growth is effectively suppressed. Li|Cu cells, with 1.0 M LiTFSI-DOL/DME (1:1, v/v) containing 5 wt% TMS-FNFSI, exhibit an average coulombic efficiency up to 96.5% for ca. 100 cycles at the current density and areal capacity of 1 mA cm^{-2} and 2 mAh cm^{-2}, respectively. The Li|Li symmetric cells with TMS-FNFSI can run for more than 1200 h with a stable polarization voltage (ca. 25 mV) at 0.5 mA cm^{-2}. The Li|$LiFePO_4$ cells with TMS-FNFSI can operate steadily for 100 cycles with capacity retention of 92% at 0.2 C. The reduction decomposition mechanism of TMS-FNFSI is tentatively proposed.

---

[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: zqpeng@ciac.ac.cn (Z. Peng), zb-zhou@mail.hust.edu.cn (Z. Zhou).

https://doi.org/10.1016/j.jpowsour.2018.08.007
Received 22 May 2018; Received in revised form 13 July 2018; Accepted 5 August 2018

1. Introduction

In the past decades, one of the research directions of electrochemical energy systems is centered around promoting the energy and power density [1,2]. Lithium metal anode (LMA) is being considered as the 'holy grail' of all battery materials, because of its high theoretical specific capacity (3860 mAh g^{-1}), which is nearly ten times higher than that of traditional graphite (372 mAh g^{-1}) [1,2]. Therefore, attempts have been made to utilize LMA in post-lithium-ion batteries, such as lithium–sulphur (Li–S) and lithium–oxygen (Li–O_2) batteries [3–5]. However, the future of all these endeavours hinges on the prospect to control the unwanted but ubiquitous growth of lithium dendrites and boost the poor coulombic efficiency (CE) [1–3].

The metallic lithium is, thermodynamically, unstable towards any kind of organic solvents (e.g., ethers, carbonates, and sulfones) [6]. Fortunately, the formation of a functionalized solid electrolyte interphase (SEI) film between LMA and organic electrolyte can remarkably stabilize the LMA and suppress dendrite growth via facilitating uniform lithium deposition [5,7]. The SEI film is generally formed through the reductive decompositions of electrolytes on the LMA, owing to its most negative electrochemical potential (-3.04 V *vs.* standard hydrogen) [1]. Obviously, a delicate balancing act of the electrolyte recipe is indispensable for the formation of a high-quality SEI film [5,7]. Nowadays, the solution of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)-based 1, 3-dioxolane (DOL)/dimethoxyethane (DME) (1:1, by volume) is one of the intensively studied electrolytes for lithium metal batteries (LMBs) using intercalation/conversion type cathodes, such as Li|$LiFePO_4$ and Li–S batteries [8,9]. This is majorly attributable to the excellent stability of LiTFSI and polymerizability of DOL, forming a relatively stable SEI film through their reductions on LMA [6–8]. However, it is proved to be incompetent for effectively suppressing the growth of lithium dendrites with prolonged cycling [2,8,9].

Generally, a bifurcated strategy has been employed to address the concern of the growth of lithium dendrites. The first is to design an artificial SEI film, composed of polymers (e.g., poly(vinylene carbonate-co-acrylonitrile) (P(VC-co-AN)) [10] and poly(dimethylsiloxane) (PDMS) [11]) and inorganics (e.g., Li_3N [12–15] and Li_3PO_4 [16]) on LMA. The poor and unstable physical and/or electric contact between the LMA and these artificial SEI films is the major deficiency of this approach. The other is to develop novel electrolyte additives for *in-situ* forming SEI films on LMA [17]. For examples, certain Si-containing compounds (e.g., tetraethoxysilane) [18–20] and fluoroethylene carbonate (FEC) [17,21] have been suggested as electrolyte additives to dictate the SEI formation, considering their abilities to form high flexible polymers (poly(fluoroethylene) and siloxane) on LMA via their reduction reactions. These additives indeed show promising potentials to suppress lithium dendrites formation to some extent, but the unsatisfactory CE remains a challenge [11,18–20].

Herein, a novel compound, namely, trimethylsilyl(fluorosulfonyl)(*n*-nonafluorobutanesulfonyl)imide {$(CH_3)_3Si\text{-}N[(FSO_2)(n\text{-}C_4F_9SO_2)]$, hereinafter abbreviated as TMS-FNFSI, Scheme 1a}, containing both organosilicon (–TMS) and fluorinated sulfonimide (–FSO_2 and –$C_4F_9SO_2$) moieties, is designed, synthesized (See Fig. 1) and explored as an SEI-forming additive in LMBs. Our strategy of design and utilization of TMS-FNFSI for LMA is largely based on our continuous interest in new fluorinated sulfonimide conducting salts for LMBs: (1) imide salts containing –FSO_2 group [22–27] are prone to be reduced to form LiF, which is helpful to facilitate Li-ion diffusion through SEI film; (2) organic silicon (e.g., TMS-OR) and F-containing compounds, originating from –TMS [18–20] and –$C_4F_9SO_2$ groups [5,9,27,28], can significantly enhance the flexibility of SEI, which is required to accommodate the surface and volume change of LMA during Li plating/stripping; and (3) moreover, protic contaminants (H_2O, alcohols and HF) in electrolyte, probed to be high active towards metallic lithium [6], can be chemically scavenged via cleaving the Si–N bond [29,30] in TMS-FNFSI. Through combining electrochemical tools with several advanced characterization technologies, e.g., scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS), we provide compelling evidence that a LiF-rich, organic F- and Si-containing SEI film can be effectively formed via the favourable reductions of TMS-FNFSI on LMA. Given this, the growth of lithium dendrites can be suppressed and the cycle life of the LMBs (Li|Cu and Li|$LiFePO_4$ cells) is remarkably enhanced.

2. Experimental

2.1. General remarks

(fluorosulfonyl)(*n*-nonafluorobutanesulfonyl)imide acid {$H[(FSO_2)(n\text{-}C_4F_9SO_2)N]$, HFNFSI, 99.5%, Suzhou Fluolyte Co., Ltd., China}, and LiTFSI (battery degree, TCI, Japan) were used without further treatment. Anhydrous dichloromethane (CH_2Cl_2, Aladdin, 99.5%), hexamethyl disilylamine (HMDS, Aladdin, 99.5%), anhydrous 1, 3-dioxolane (DOL, Aladdin, 99.5%) and dimethoxyethane (DME, Aladdin, 99.5%) were dried with freshly activated 4 Å molecular sieve for at least 3 days before use. All the procedures related to handling moisture and oxygen sensitive reagents were performed under dry argon atmosphere, or in a glove box (MBraun, H_2O and $O_2 < 0.1$ ppm).

The spectra of ^{1}H- (399.65 MHz), and ^{19}F- (376.05 MHz) nuclear magnetic resonance (NMR) were recorded on a Bruker AV400 spectrometer. Chemical shift values (δ) were reported in ppm, and tetramethylsilane and CCl_3F were used as an internal and external reference for ^{1}H- and ^{19}F NMR, respectively.

2.2. Preparation of TMS-FNFSI

HFNFSI (15.00 g, 0.0394 mol) was dissolved in anhydrous CH_2Cl_2 (50 mL) at 25 °C under stirring conditions, and then HMDS (2.54 g, 0.01576 mol) was added dropwise under an argon atmosphere (Scheme 1c). The mixture was stirred at 25 °C for 5 h. The crude product was isolated by filtration and then the filtrate was evaporated under high vacuum conditions (0.5 mmHg) at 50 °C for 24 h to remove the solvent and any volatile residuals. The liquid substances obtained were further purified by re-dissolving in anhydrous CH_2Cl_2 and refluxed over anhydrous active carbon for 30 min. The solvent was evaporated under reduced pressure, offering a transparent and colorless liquid product (10.82 g, yield 91%) (Scheme 1b).

2.3. Preparation of electrolytes and electrode

The electrolytes were prepared by dissolving 1.0 M LiTFSI in DOL/DME (1:1, by volume) in an argon-filled glove box (MBraun, H_2O and $O_2 < 0.1$ ppm) without and with 1, 2, 5, and 10 wt% TMS-FNFSI (by weight) as an additive. The water content in the as-prepared electrolytes was < 20 ppm, as determined by Karl-Fischer coulometric titration (Metrohm KF 831).

The $LiFePO_4$ cathode sheet was fabricated by dispersing the composite materials, comprised by $LiFePO_4$ powder: Super P: polyvinylidene fluoride (PVDF) = 90:3:7 (by weight) in N-methyl-2- pyrrolidinone (NMP), and spread onto Al foil (Φ12 mm) and then vacuum-dried at 120 °C for 24 h before use. The loading of $LiFePO_4$ (170 mAh g^{-1}) in the as-prepared cathode sheet is ca. 4 mg cm^{-2}.

2.4. Evaluation of lithium metal batteries

All the cells were assembled by standard 2032 coin-type configuration in an Ar-filled glove-box (MBraun, H_2O and $O_2 < 0.1$ ppm). The Li|Cu (and Li|$LiFePO_4$) cells were assembled with a Li foil (Φ12 mm), a Celgard 2400 (polypropylene membrane) separator, the as-prepared electrolyte (110 μL) and corresponding cathodes (Φ12 mm). The Li|Li cells were assembled using lithium foils as both working and counter electrodes, respectively.