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Role of perfluoropolyether-based electrolytes in lithium metal batteries: Implication for suppressed Al current collector corrosion and the stability of Li metal/electrolytes interfaces

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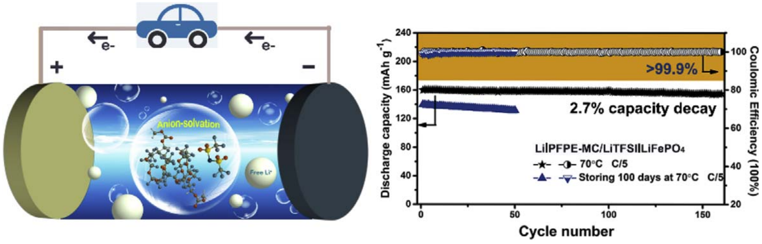
HIGHLIGHTS

- "Anion-solvation" interaction in PFPE-MC/LiTFSI was proven by Raman spectra.
- PFPE-MC effectively inhibited the Al foil corrosion induced by LiTFSI.
- PFPE-MC/LiTFSI electrolyte enabled the formation of dendrite-free Li anode.
- The composition of SEI layer on Li anode was identified by SR-XPS technique.
- Improved columbic efficiency and cyclability against EC + DMC/LiTFSI were achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

The development of safe and high performance lithium metal batteries represents a major technological challenge for this new century. Historically, intrinsic instabilities of conventional liquid organic electrolytes induced battery failures and safety issues that hinder the practical utilization of advanced rechargeable lithium metal batteries. Herein, we report a multifunctional perfluoropolyether-based liquid polymer electrolyte (PFPE-MC/LiTFSI), presenting a unique "anion-solvent" interaction. This interaction optimizes the interfacial chemistry of lithium metal batteries, which effectively inhibits the corrosion of aluminum current collectors, suppresses lithium dendrite growth, and also facilitates the formation of a thin and stable SEI layer on Li anode. Even at a high current density of 0.7 mA cm^{-2}, the lithium dendrites do not form after 1360 h of continuous operation. The $LiFePO_4$|PFPE-MC/LiTFSI|Li cell delivers a stable cycling performance with over 99.9% columbic efficiency either at ambient temperature or high temperature, which is significantly superior to those using traditional carbonate electrolytes. In addition, PFPE-MC/LiTFSI electrolyte also possesses eye-catching properties, such as being non-flammable, non-volatile, non-hygroscopic, and existing in the liquid state between −90 °C and 200 °C,

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which further ensures the high safety of the lithium metal batteries, making this electrolyte promising for the development of high energy lithium metal batteries.

1. Introduction

Rechargeable lithium-ion batteries, presently the most prevalent system for energy storage devices (ESDs), are considered for a wide variation of applications spanning from portable electronics, hybrid/electric vehicles to large-scale energy storage. However, even state-of-the-art lithium-ion technology cannot satisfy the ever-growing quest for energy density. Many kinds of strategies were implemented to enhance the energy density, while the basic and directly method is to adopt an electrode material with high specific capacity. For instance, the specific capacity of lithium metal (Li) as anode is 3900 $mAh{\cdot}g^{-1}$, which is as much as a tenfold improvement compared with the graphite anode (372 $mAh{\cdot}g^{-1}$) [1–3]. However, lithium metal batteries never developed appreciably, in contrast to the rapid development of the intercalation positive electrode concept after 1973 [4,5]. It is generally accepted that Li dendrites are formed at the anode side during the course of charging due to the non-uniform electric deposition of lithium, which result in "dead lithium" formation plus a thick cumulative solid electrolyte interphase (SEI) layer and short circuits, directly affecting the cycle life and the safety of the battery. [6,7].

Actually, these critical defects of Li metal batteries have for long been considered as incompatible with aprotic organic liquid electrolytes. The reasons have to be found in the composition of the commercial liquid electrolytes, namely lithium salt dissolved in organic liquids such as ethylene carbonate and dimethyl carbonate (EC + DMC) mixed solvents. In this system, the lithium ions (Li^+ ions) are solvated by coordinating EC molecules, which slows down the migration of Li^+ ions, decreasing the Li^+ transference number, and leads to the non-uniform deposition of lithium on the anode upon cycling, finally forming the lithium dendrites when locally salt depletion takes place [8]. Moreover, carbonates solvents, especially DMC with high vapour pressure can provoke fires and explosions in case of accidental battery shorts [8]. Also, the most common lithum hexafluorophosphate ($LiPF_6$) salts are easily decomposed to hydrofluoric acid (HF) in the moisture environment, and the electrolytes with commercial lithium bis trifluoromethane sulfonamide (LiTFSI) salts tend to corrode the aluminium (Al) current collector at high potential (> 4 V) [8–11]. Serious corrosion will also lead to crack extension and the detachment of the active materials, consequently result in the safety issue and short lifespan.

Extensive efforts have been devoted to improving the lithium metal battery life and safety, including protecting the Li interface via interlayers or artificial SEI layers [12–16], constructing rational Li host materials [17–20], optimizing the organic electrolytes [21–23] and exploring the new electrolytes systems [24–28]. Very recently, solid polymer electrolytes (SPEs) are regarded as a promising candidates for next-generation lithium metal batteries (LMBs) because of their non-leakage and non-combustion. Besides, solid polymer-based batteries can be packed more densely in a flexible configuration, increasing the volumetric energy densities [29]. However, the full development of SPEs has been hampered by some intrinsic properties, such as low ionic conductivity, large interfacial impedance and inferior mechanical strength. Till now, several approaches, such as composite polymer electrolytes (with nanoparticles [30–35], nanofibers [36–39], nanosheets [40] and others [41–43]), block/grafted co-polymer/homo-polymer electrolytes [44–51] and cross-linked polymer matrix [52–54] have been developed to boost the performance of SPEs. Nevertheless, despite the rapid progress in the chemistry of SPEs that we have reviewed recently, none of them satisfies simultaneously the requirements of high room temperature ionic conductivity, high Li^+ transference number, superior mechanical properties and good interfacial compatibility with electrode, which would make the lithium metal battery competitive with respect to the lithium-ion battery. [5].

Previous works of Wong. et al. demonstrate that perfluoropolyether-based liquid polymer possess nonflammable characteristics, low glass transition temperature and acceptable ionic conductivity, which have made a significant step toward eliminating key security hazard in the Li-ion batteries [55,56]. Nevertheless, a serials of questions remain to be explored: dose the perfluoropolyether liquid polymer show any reactivity with the Li metal anode? Will the SEI film grow on Li anode surface and if any, how will it be formed and stabilized? Another concern is the perfluoropolyether's chemical compatibility with the current collector. In the present work, we address these questions by investigating the effect of PFPE-MC/LiTFSI polymer electrolyte, aiming to obtain a valuable reference for designing future electrolytes of high energy density and high safety LMBs.

In the first step, the anodic behaviour of Al current collectors in PFPE-MC/LiTFSI was investigated. Utilizing Surface enhance Raman technique, a unique anion-solvation interaction was confirmed in those polymer electrolytes and the inhibition mechanism of Al current collector corrosion was proposed. We further demonstrate that this anion-solvation interaction plays a key role in suppression of Li dendrite growth and SEI formation process on Li anode and therefore has the significant implications for the cycling performance of batteries employing metallic Li anode.

2. Experimental

2.1. Materials

Fluorolink D10-H (PFPE-diol; Mn = 1400 g/mol was purchased from the Solvay Solexis (Shanghai). Triethylamine, 1, 1, 1, 3, 3-pentafluorobutane and methyl chloroformate were purchased from the Alfa Aesar. Lithium bis trifluoromethane sulphonamide (LiTFSI, battery grade), ethylene carbonate and dimethyl carbonate solvate were obtained from Suzhou Novolyte. All materials were stored and used as received in an argon filled Mbraun glovebox.

The methyl carbonate-capped perfluoropolyethers (PFPE-MC) was prepared by esterifying reaction, as described in detail in appendix data. Chemical characterizations include ^1H NMR (600 MHz, $CDCl_3$): $\delta = 3.805$ (s 6H), 4.466 (m 4H) (Fig. S1).

2.2. Electrolyte and battery preparation

Electrolytes with various molarities of LiTFSI in PFPE-MC and ethylene/dimethyl carbonate (EC + DMC, 1:1, v/v) were prepared in an Ar-filled glovebox (H_2O, $O_2 < 0.1$ ppm). Quantification of water content in the resulting electrolyte solutions was less than 20 ppm, determined by Karl–Fischer titration. CR2025 cells (Li‖Li, Li‖Cu and Li‖$LiFePO_4$ (80% of active materials + 10% of super P + 10% of PVDF binder)) were assembled in an Ar-filled glove box, using a polymeric membrane of Celgard 2400 (diameter: 19 mm) as separator and a given concentration of LiTFSI in PFPE-MC and EC + DMC as electrolyte. The galvanostatic charge/discharge tests were conducted on a LANHE battery test system at various temperatures in a temperature-controlled box (ZKMEIQI MQ-DT50). As shown in Fig. S12, the electrochemical tests shown that the Li‖$LiFePO_4$ battery with PFPE-MC/0.7 M LiTFSI displays the optimal electrochemical performance compared to other molarities of LiTFSI. Thus, PFPE-MC and EC + DMC solvents containing 0.7 M LiTFSI salts were chosen to further explore their interfacial