



Novel dual-salts electrolyte solution for dendrite-free lithium-metal based rechargeable batteries with high cycle reversibility



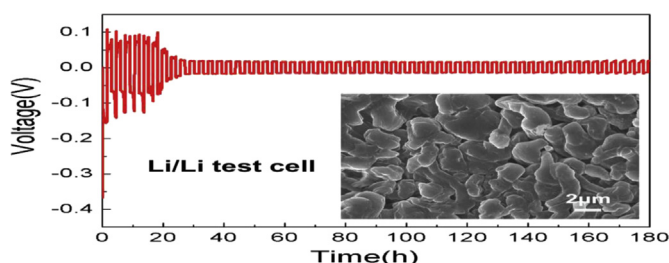
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HIGHLIGHTS

- A new dual-salts electrolyte solution has been explored for lithium metal anode.
- Excellent cycling performance and dendrite-free lithium deposit have been achieved.
- Low voltage polarization and favorable lithium morphology can be retained even at high current density of 10 mA cm^{-2} .

GRAPHICAL ABSTRACT



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ABSTRACT

Metallic lithium is the most promising negative electrode for high energy rechargeable batteries due to its extremely high specific capacity and the lowest redox potential. However, the low cycle efficiency and lithium dendrite formation during charge/discharge processes consistently hinder its practical application. Here a new dual-salts electrolyte composed of $\text{Li}[\text{N}(\text{SO}_2\text{F}_2)_2]$ and $\text{Li}[\text{N}(\text{SO}_2\text{CF}_3)_2]$ has been explored to simultaneously cope with these two problems. Under the unique protection of solid electrolyte interphase (SEI) film formed in this electrolyte solution and the improvement in Li crystal growth pattern, high cycle efficiency of ca. 99% and dendrite-free Li deposit have been achieved. Moreover, the excellent cycling performance and favorable lithium morphology can be retained even at high current density of 10 mA cm^{-2} . This study will greatly promote the development of Li-metal rechargeable batteries with high power and high energy density.

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1. Introduction

Although lithium-ion batteries are being widely used as power sources for portable devices and (hybrid) electric vehicles, the limited energy density of less than 200 Wh kg^{-1} by using conventional graphite anode material is still unable to meet the exigent demand for smaller and lighter devices and more powerful electric vehicles [1]. Driving by this challenge, more and more researchers pay attention to Li-metal-based rechargeable battery systems [2].

For instance, lithium–sulfur battery has been intensively investigated due to its high theoretical energy density of 2600 Wh kg^{-1} [3,4]. Moreover, a higher theoretical value is obtainable for lithium–air battery [5]. Both the systems use lithium metal as anode, which provides extremely high theoretical specific capacity (3800 mAh g^{-1}) and the lowest redox potential (-3 V vs. standard hydrogen electrode, SHE) [6]. Based on its unique advantage, metallic Li is becoming the most promising anode candidate for next generation energy storage systems. However, highly thermodynamic instability of lithium to organic solvents causes low cycle efficiency and lithium dendrite formation during discharge/charge processes, which are two major obstacles for its practical application [7,8]. The growth of lithium dendrites in continuous cycling

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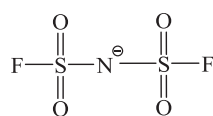
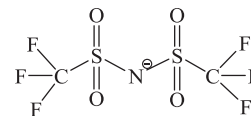
may lead to internal short circuit and further incur fire or other safety problems, while the low cycling efficiency will result in short cycle life and final battery failure [9,10].

Beginning in the early 1970s, various attempts from the Li surface protection to electrolyte selection have been made to solve these two key problems [11,12]. Although a great progress has been made to address these issues, few approaches are successful to solve all these problems at the same time. For example, some additives (e.g. CO₂ [13], SO₂ [14,15], 2-Meyhyfuran [16], etc.) in liquid electrolytes are helpful to gain relatively long cycle life, but lithium dendrite formation nature does not be changed. Compared with the liquid electrolyte, PEO-based one is advantageous for its elastic property and good compatibility with lithium, but the dendrite growth still could not be suppressed fundamentally and only the onset time of lithium dendrite formation can be prolonged to some extent [17–19]. In addition, its blocking to lithium dendrite growth seems to be invalid at elevated temperature due to losing mechanical strength of PEO [7,20]. A significant breakthrough has been achieved by Aurbach group [21]. The liquid electrolyte system containing 1,3-dioxolane (DOL), LiAsF₆ and tributylamine in trace amount as a stabilizer shows dendrite-free lithium morphology and almost 100% Li deposition–dissolution efficiency. Unfortunately, it still faces some application obstacles. At charging rate higher than 1.5 mA cm⁻², the cycle life is limited [22,23]. Moreover, the LiAsF₆ salt is toxic. Similarly, the newly proposed electrolyte with CsPF₆ as additive can effectively suppress lithium dendrite with a coulombic efficiency of more than 98% [24]. However, the additive can only be effective to prevent the dendrite growth at limited current densities. Too large a current density will induce a large voltage drop which may compel the additives to be co-deposited with Li and thereby diminish the effect of the additives [7]. In short, the up-to-date results are still unsatisfactory for practical application. It is necessary to design new electrolyte systems to cope with both the low coulombic efficiency and dendrite formation at adequate current rate.

As is generally known, SEI layer on lithium metal strongly affects Li deposit morphology and cycling performance [25]. As the main source of organic composition in SEI film, the choice of solvents in electrolytes is very important for lithium anode. The commonly used liquid electrolyte solutions adopt three families of solvents, namely, ethers, esters, and alkyl carbonates. It is already known from previous studies that lithium is not passivated in ester or alkyl carbonate (e.g. BL, PC, DMC, etc) based electrolytes for lack of stable or flexible solid surface films on lithium [26–28]. With regard to the compatibility to highly reactive Li metal, ethers seem to be a good choice for its relatively low oxidation state [29,30]. Particularly, the cyclic ether solvents are superior to stabilize the surface of Li metal by forming an elastic surface layer through the ring-opening reaction [31]. For example, the electrolyte with 1,3-dioxolane (DOL) as solvent and LiAsF₆ as lithium salt shows the distinct superiority in cycling stability because of the formation of flexible and insoluble polydioxolane oligomers on the lithium surface, which could accommodate the morphological change of the Li-metal during cycling [21,22]. Based on the above results, we choose DOL as main solvent. On the other hand, lithium salts also play a critical role for forming a thin, compact and uniform SEI film. However, compared to the variety of solvents, the Li salts suitable for lithium metal-based systems are very limited [13]. Li [N(SO₂CF₃)₂] (LiTFSI) is often used in Li–S batteries and also ionic liquids containing TFSI⁻ anion have proven helpful for improving lithium metal cycling efficiency, but the tolerance of large current density of Li anode is still limited [13,32,33]. In view of that another sulfonyl imide salt Li[N(SO₂F)₂] (LiFSI) possesses high ionic conductivity and good compatibility with lithium [34–36], we conceive the combination of LiFSI and DOL for a new electrolyte to

match Li metal anode. However, it has been found in our experiment that the solubility of LiFSI is very low in DOL solvent and open-ring polymerization of DOL is easily induced. Although adding dimethoxymethane (DME) as co-solvent can improve the solubility of LiFSI greatly, its stability in DOL–DME co-solvent is still poor.

In the present work, combined with the high stability of LiTFSI in DOL solvent system, a novel dual-salts electrolyte solution mating organic LiTFSI to inorganic LiFSI is designed and prepared, in which LiFSI not only provides high conductivity, but also dominates the interfacial behavior, while LiTFSI acts as stabilizer and conducting agent. Both the anion structures are given in the followed (I) and (II). This simple but effective dual-salts electrolyte system shows steady and high coulombic efficiency and dendrite-free lithium deposition even at high current density. The possible function mechanism is explored and discussed.

(I) FSI⁻ anion(II) TFSI⁻ anion

2. Experimental

2.1. Preparation of dual-salts electrolyte solution

All the raw materials used in experiments are Li battery grade. LiTFSI and LiFSI were obtained from Capchem. Co. Ltd. and Suzhou Fluolyte. Co. Ltd, respectively. Anhydrous 1,3-dioxolane (DOL) and dimethoxymethane (DME) were obtained from Aldrich, Inc. The experimental work was carried out in an Ar-filled dry glove box (MB-10 compact, MBRAUN) containing less than 1 ppm water and O₂. Firstly, anhydrous DOL was mixed with anhydrous DME in 2:1 volume ratio, then 0.5 M LiTFSI was dissolved in the mixed solvent. Finally, 0.5 M LiFSI was slowly added to the above solution and further stirred for 12 h at room temperature in the glove box to form the electrolyte solution. The mole ratio of Li⁺ from these two kinds of salts was 1:1. The total concentration of dual-salts was 1 mol L⁻¹ and the water content in the final electrolyte is 30.8 ppm measured by coulometric KF titrator (C30, Mettler Toledo).

2.2. Electrode characterization

The morphologies of lithium metal electrodes were observed by FEI Nova Nano-scanning electron microscope (SEM). Firstly, cells were disassembled in the glove box and then the obtained electrodes were thoroughly washed by anhydrous DME to remove any electrolyte salt residuals. To avoid exposure to air, the dried samples were sealed in an air-isolating container and transferred quickly into the SEM equipment under the protection of Ar flow.

The X-ray photoelectron spectroscopy (XPS) analysis was performed using a Kratos Axis UltraDLD spectrometer (Kratos Analytical-A Shimadzu Group Company) with monochromatic Al K α source (1486.6 eV). Before transferring the samples to the equipment, an air-isolating container with protective Ar flow was used to avoid moisture/air exposure. Under slot mode, the analysis area was 700 \times 300 μ m and analysis chamber pressure was less than 5 \times 10⁻⁹ Torr. The binding energy was calibrated according to the C 1s peak (284.8 eV) of adventitious carbon on the analyzed sample surface.

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