



A compatible carbonate electrolyte with lithium anode for high performance lithium sulfur battery



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ABSTRACT

We report a new carbonate electrolyte of 1 M LiFSI dissolved in the EMC/FEC (70/30, v/v) solvent for lithium metal based batteries. Favorable LiF-rich SEI layer is formed on Li anode to suppress side reactions under the synergistic effect of LiFSI and FEC. Thus, the dendrite-free Li morphology and high Coulombic efficiency for Li plating/stripping can be obtained with improved cycle stability compared with conventional LiPF₆/EC-DMC electrolyte. Li | S@pPAN cell assembled with the new electrolyte shows quite low lithium ion transfer resistance, excellent long cycle stability and rate performance. A high discharge capacity of 1270 mAh g⁻¹ remains after 1000 cycles at 2 C, with an inappreciable capacity decay of 0.0015% per cycle. Due to the low interface impedance and high Li⁺ diffusion coefficient, a capacity of 1210 mAh g⁻¹ even at 10 C can be maintained. This deliberately designed electrolyte offers new insights into the understanding of interfacial stability between electrolyte and Li anode. Furthermore, our work offers a new approach towards high energy-density and high rate Li-S battery.

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1. Introduction

The rapid development of electric vehicles, unmanned aerial vehicles and others urgently demands rechargeable batteries with high energy density. Nevertheless, the state-of-the-art lithium (Li)-ion batteries (LIBs) can only offer volumetric and gravimetric energy densities up to 770 Wh L⁻¹ and 260 Wh kg⁻¹ respectively [1], which hardly fulfill the requirements. So far, Li metal batteries (LMBs) are considered as the promising choice due to Li anode's ultra-high theoretical specific capacity (3860 mAh g⁻¹), and very low potential (−3.040 V vs. SHE) [2]. Among the LMBs, Li-sulfur (Li-S) and Li-oxygen (Li-O₂) batteries with high theoretical energy density of 2600 and 3500 Wh kg⁻¹ have been widely explored [3–5]. Unfortunately, dendrite growth and limited cycle efficiency of the Li electrode lead to the safety hazard and short cell cycle life, which hinder its practical application [6,7].

Great efforts have been made to tackle these problems, including the use of solid-state electrolytes [8,9], the Li surface modification [10,11], electrolyte optimization via special additives [6,12], high concentration salt [13,14] and ionic liquid [15]. Among these strategies, *in-situ* protection of lithium metal electrode by the improved electrolyte systems makes continuous progresses. Lu et al. reported the stability of lithium electrodeposition in common liquid electrolytes reinforced with halogenated lithium salts [16]. Yang et al. used a new dual-salts ether-based electrolyte composed of LiTFSI and LiFSI to stabilize Li surface with high cycle efficiency of ca. 99% and dendrite-free Li deposit [17]. Zhang et al. reported that the use of 4 M LiFSI in 1,2-dimethoxyethane enables the high-rate cycling of a lithium metal anode at high Coulombic efficiency (up to 99.1%) without dendrite growth [13]. Although impressive progresses have been made in recent years, it should be noted that most of improvements of cycling stability for Li metal anode are aimed at ether-based electrolytes. Their actual application in LMBs is restricted by the safety risk arising from their low boiling and flash points.

With regard to Li-sulfur (Li-S) batteries, ether-based electrolytes are considered to be a compromised choice to accommodate the paradox originating from sulfur cathode and Li anode [18]. As mentioned above, ether solvents show better compatibility with Li

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metal anode than carbonate solvents. However, the dissolution of intermediate polysulfides in ether-based electrolytes and their reaction with Li anode would generate a so-called “polysulfides-shuttle” for elemental sulfur based cathode [19]. This leads to continuous loss of active material into the electrolyte and results in low discharge capacities and rapid capacity decay during cycling [20]. In order to overcome the dilemma, small sulfur molecule-based composite cathode materials, such as pyrolyzed polyacrylonitrile sulfur (S@pPAN) [21,22] have been proposed, which could undergo reversible lithiation and delithiation processes in carbonate based electrolytes. With regard to lithium salt, though LiPF₆ has been employed as the main lithium salt in Li-ion batteries, it shows unsatisfied performance for Li metal anode [17]. Based on the researches about ether-based electrolytes for LMBs, lithium bis(fluorosulfonyl)imide, Li[N(SO₂F)₂] (LiFSI) is a promising alternative lithium salt for its good compatibility with Li metal [13,23,24]. In particular, it possesses high ionic conductivity which benefiting from the sufficient disassociation of Li⁺ and FSI⁻ for their quite weak interaction [25,26]. As for the solvents, the ability to form favorable SEI layer on Li anode surface is critical, which is directly related to Li metal's safety and stability [7]. FEC has been extensively studied as an effective electrolyte additive to facilitate the formation of a stable SEI layer on Li metal and silicon-containing anodes [6,27–29]. Furthermore, FEC-based organic carbonate solution with LiPF₆ was studied in the Li | Li cells and Li | LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ (NMC) cells to be compared with conventional EC-based electrolyte [30]. It is demonstrated that a stable and efficient solid electrolyte interphase (SEI) was formed on the surface of Li metal anode. Nevertheless, as its high viscosity and relatively high melting point of FEC, linear carbonates such as dimethyl carbonate (DMC), diethyl carbonate (DEC) or ethyl methyl carbonate (EMC) need to be added as co-solvents to compensate the deficiencies [31]. Though electrolyte with FEC as additives in Li-S cell have been investigated, the electrolytes reported in the papers are LiPF₆ [32] or LiODFB [33].

Herein, we report a new electrolyte of 1 M LiFSI dissolved in the carbonate solvents EMC/FEC (70/30, v/v) for LMBs. The co-effect of FEC and LiFSI in carbonate electrolyte systems for preventing Li dendrite formation and remarkably improving the cyclability of Li anode and cycle/rate performance of Li-S cells has been demonstrated. It is confirmed that the new electrolyte can suppress the lithium dendrites and improve Coulombic efficiency effectively. Furthermore, S@pPAN composite cathode has been coupled with the proposed electrolyte to construct a full cell, which exhibits impressive high cycling stability and rate performance.

2. Experimental section

2.1. Preparation of S@pPAN materials

The S@pPAN materials were prepared as the reported method [34,35]. Sublimed sulfur powder and PAN (Mw = 150,000) were mixed intensively in a mass ration of 8:1 and heat treated at 300 °C for 8 h or 4 h under argon atmosphere. The sulfur content is as determined to be 45 wt% and 55 wt% by elemental analysis (Perkin Elmer PE 2400 II).

2.2. Electrochemical characterization

Lithium hexafluorophosphate (LiPF₆), lithium bis(fluorosulfonyl)imide Li[N(SO₂F)₂] (LiFSI), ethyl methyl carbonate (EMC), and fluoroethylene carbonate (FEC) were purchased in battery grade from BASF Battery Materials and were used as received. The standard electrolyte 1 M LiPF₆ in 1:1 EC/DMC (v/v), 1 M LiPF₆ in EMC/FEC (7:3, v/v) and 1 M LiFSI in EMC/FEC (5:5, 7:3

and 9:1, v/v) were prepared in an argon filled glove box. Carbonyl-β-cyclodextrin was obtained via a previous published method [34]. 2 g of β-cyclodextrin was added to a vial with 5 ml of H₂O₂ aqueous solution (30 wt%), and heated to 80 °C under seal condition. After 24 h, the production was then dried under vacuum to get the brown solid. To fabricate working electrodes, S@pPAN, Super-P, and carbonyl-β-cyclodextrin with a weight ratio of 80:10:10 were mixed to form homogeneous slurry, which was coated on aluminum foil and then dried in a vacuum oven at 60 °C for 8 h. The typical sulfur loading was about 1.0 mg cm⁻² and 3.0 mg cm⁻² for 45 wt% and 55 wt% S@pPAN cathodes, respectively. Electrochemical experiments were carried out using CR2016 coin cells, which were assembled in an argon-filled glove box (H₂O, O₂ < 0.1 ppm, Mbraun) with Celgard 2400 (Celgard, USA) separator and pure Li foil (Alfa Aesar, 99.9%, 200 μm in thickness) anode. The electrolyte volumes are ca. 25 and 75 μL in assembling the 2016 type coin cells for S loading of 1 and 3 mg cm⁻², respectively. The electrolyte-to-sulfur ratio is ca. 25. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were obtained on a PARSTAT 4000 electrochemical workstation. EIS was measured in the frequency range from 100 kHz to 0.1 Hz. Galvanostatic charge/discharge was conducted using a Land CT2001A multi-channel battery testing system in the fixed voltage range of 1.0–3.0 V (vs. Li/Li⁺) at room temperature. The cells were tested with different C-rates at 1 C, 2 C, 3 C, 5 C, 8 C and 10 C for each 5 cycles and then back to 1 C. The durability test was conducted at 2 C. The current rate was calculated based on the theoretical capacity of S (1 C = 1672 mA g⁻¹) and the specific discharge/charge capacities were based on the sulfur weight. Lithium plating/dissolution efficiency and voltage polarization of Li anode in LiPF₆/EC-DMC, LiPF₆/EMC-FEC and LiFSI/EMC-FEC were tested by Li | Cu and Li | Li cells, respectively. For the Coulombic efficiency test, a constant plating current density of 0.25 mA cm⁻² was passed through the cell for 2.5 h, and then the same dissolution current density was applied until the cut-off voltage of 1.0 V vs. Li/Li⁺. Symmetric Li | Li metal plating/stripping test was conducted at current density of 0.5 mA cm⁻² and specific areal capacity of 1.0 mA h cm⁻².

2.3. 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 three times with anhydrous DMC 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 an X-ray photoelectron spectrometer (AXIS ULTRA DLD, Kratos Analytical Ltd., UK) with a monochromatic Al Kα 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 × 300 μm and analysis chamber pressure was less than 5 × 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.

3. Results and discussion

Coulombic efficiency (CE) of Li plating/stripping processes with different electrolytes were evaluated through galvanostatic cycling experiments by Li | Cu cells. As shown in Fig. 1a, the initial CE of the LiFSI/EMC-FEC (7:3) electrolyte is 92.5%, which may be attributed to the decomposition of the electrolyte to form SEI. The CE becomes

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