Enabling reliable lithium metal batteries by a bifunctional anionic electrolyte additive

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ABSTRACT

Lithium metal has been considered as an attractive anode for high energy density lithium battery because of high specific capacity and the lowest redox potential. However, the growth of Li dendrites during cycling has hindered the practical application of Li metal battery (LMB). Herein, TTFEB is adopted as a bifunctional electrolyte additive to improve the performance of Li metal anode, which is beneficial for the surface chemistry of anode and the property of the electrolyte. A LiF-rich SEI layer and enhanced Li^+ migration in electrolyte can be achieved with 2% TTFEB, which result in uniform Li deposition without uncontrollable Li dendrites. With controlled Li deposition in TTFEB-containing electrolyte, a significantly improved Coulombic efficiency (~ 96%) in Li|Cu cell, long lifetime (over 1000 h), and weak polarization in Li|Li cell can be obtained. Moreover, excellent cycling performance and rate capability of Li|LiFePO$_4$ cells with TTFEB are also presented in this work. Our strategy provides new insights on the diverse function of electrolyte additives for rechargeable LMB.

1. Introduction

Lithium ion batteries (LIBs) have achieved great success for applications in portable electronic devices, electric vehicles and grid energy storage [1]. However, the requirement of increasing energy density of LiBs forces the development of high capacity materials [2]. Lithium metal anode has been strongly regarded as an ideal anode for rechargeable batteries due to its extremely high theoretical specific capacity (3860 mA h g^{-1}), low density (0.59 g cm^{-3}), and the lowest redox potential (−3.04 V vs. standard hydrogen electrode) [3]. However, two main barriers, the undesirable Li dendrite growth during repeated depositing/stripping process and low Coulombic efficiency of these processes, restrict the practical application of Li metal anode [3,4]. The random growth of Li dendrites is mainly initiated by several non-uniform factors, such as inhomogeneous distributions of the current density on the electrode surface and the concentration gradient of Li ions at the electrolyte/electrode interface. Moreover, the uneven and instable solid-electrolyte interphase (SEI) layer will crack during repeated charge/discharge process, which accelerate Li dendrite growth at these so-called "hot spots" [5–7]. The resulting Li dendrite may penetrate through the separator, causing internal short circuiting and safety hazards [7–9]. In addition, the side reactions between the Li metal with electrolyte are more serious due to the high surface area of Li dendrite and repeated breakage/repair of the instable SEI layer, which results in low Coulombic efficiency and consumption of active lithium as well as the electrolyte [10,11].

Over the years, tremendous effort has been devoted to settle the issues of lithium metal anode mentioned above, varieties of strategies have been proposed [4,12–14]. Among these approaches, it is long recognized that electrolyte configuration is an effective and economical route to stabilize SEI on the surface of Li metal anode, thus preventing uncontrolled Li dendrite growth and enhancing the cycle stability of Li metal anode [6,15,16]. In particular, the adoption of electrolyte additive, from which the in-situ formed SEI layer improved the brittle and non-uniform nature of the original SEI layer, has been widely investigated owing to its advantages in industrial applications [17,18]. Various electrolyte additives, with different molecular structure, such as HF [19], fluoroethylene carbonate (FEC) [17], vinylene carbonate (VC) [20], LiNO$_3$ [21], trace-amount water [22], lithium polysulfide [9], and copper acetate [23], have been investigated to improve the performance of Li metal anode. Among the numerous additives, the electrolyte additives capable of forming LiF-rich SEI layer are particularly favored according to its dense and uniform properties of the SEI layer and therefore induced uniform Li deposit, resulting in superior cycling performance of Li metal anode [17,19,22,24]. The beneficial impact of LiF on the Li deposition and dissolution process has been

well understood [24–26]. However, mostly introduced electrolyte additives for Li metal anode are merely serve to stabilize the SEI layer [12], few studies mention the effect of additives on the properties of the electrolyte and its influences on the performance of lithium metal batteries.

In fact, the lithium ion transference number of the electrolyte is a crucial factor for the Li dendrite formation and growth, as it's closely connected with the Li ion concentration gradient at the electrolyte/electrode interface [27,28]. Previous studies have demonstrated that the ionic distribution near the anode dramatically affects the morphology of Li deposits, and high Li-ion transference number electrolytes, in which promoting preferential transport of Li$^+$, are believed to reduce the tendency to form ion concentration gradients and therefore enhancing the electrochemical efficiency and suppressing the uneven morphology of Li metal anode [29–31]. Models of Li dendrites highlight the significance of Li$^+$ migration, which directly affect uniformity of spatial distribution of Li$^+$ during Li deposition process [3]. Several approaches have been proposed to increased Li-ion transference numbers such as single-ion electrolytes [32], and "soggy sand" electrolytes [33]. Lu et al. reported a single-ion Li$^+$ conducting electrolyte with the tethered anions, presenting high Li-ion transference number, exhibits superior ability for inducing uniform Li deposit and increasing the cell lifetime of 40-fold in symmetric Li|Li cells [30]. Nevertheless, electrolyte additives have not been explored to employ in the high Li-ion transference number electrolytes for Li metal batteries.

Combined the electrolyte performance and SEI layer, we propose a fluoride boron-based anion receptor, Tris (2, 2, 2-trifluoroethyl) borate (TTFEB), as a bifunctional electrolyte additive for enhancing the performance of lithium metal anode. Based on the previous work, most anion receptors can increase t_{Li}^+ value caused by tethering the anions in the electrolyte [34–36]. In addition, groups containing fluorine in TTFEB may promote the formation of LiF-rich SEI layer, which benefit to stabilize the Li metal anode/electrolyte interface. Indeed, the Coulombic efficiency and cycle stability of lithium metal anode, as well as the cycling and rate performance of Li|LiFePO$_4$ full-cell, are significantly improved after the adoption of TTFEB. The morphology of Li deposition and the composition of SEI layer are further investigated for the description of the working mechanism of TTFEB.

2. Experimental section

2.1. Preparation of electrolytes, electrodes, and cells

Tris (2, 2, 2-trifluoroethyl) borate (TTFEB, 98%) was purchased from Sigma-Aldrich Co., Ltd. and adopted without further purification. Battery-grade solvents ethylene carbonate (EC), dimethyl carbonate (DMC) and lithium salt LiPF$_6$ were purchased from Guangzhou Tianci Materials Technology Co., Ltd. The mixture of EC/DMC solvents (1:2, volume ratio), which were further purified by 4A type molecular sieve, with 1 mol/L LiPF$_6$ was prepared as the blank electrolyte. A certain amount of TTFEB was added to the blank electrolyte as the functional electrolyte.

LiFePO$_4$ material was provided by Harbin Coslight Power Co., Ltd and LiFePO$_4$ electrode ($\sim$ 3 mg cm^{-2}) was prepared by coating the slurry of LiFePO$_4$, Super-P and polyvinylidene fluoride (PVDF) binder (8:1:1, weight ratio) in N-methylpyrrolidone (NMP) solvent onto Al foil current collector and dried under vacuum at 120 °C for 12 h. The battery-grade Li foil used as the anode was obtained from China Energy Lithium Co., Ltd. The CR2025-type coin cells (Li|Cu, Li|Li, and Li|LiFePO$_4$) with different kinds of electrodes, separator (Celgard2500), and as-prepared electrolytes were assembled in the argon-filled glove box (< 1 ppm H$_2$O, < 10 ppm O$_2$).

2.2. Electrochemical measurements

The Li-ion transference number (t_{Li}^+) was measured by combining AC impedance and DC polarization (10 mV) measurements with a symmetric Li|electrolyte|Li cell at room temperature. The Li|Cu cells were galvanostatically tested at a current density of 0.1 and 0.5 mA cm^{-2} using Neware BTS Test Control. In each cycle, 0.5 mA h cm^{-2} metallic Li was deposited onto the Cu substrate during discharging, then the cells were charged to the cutoff voltage of 0.5 V (vs. Li$^+$/Li) at the same current. The symmetric Li|Li cells were galvanostatically tested at a current density of 1 and 2 mA cm^{-2} with time controlled charge and discharge cycles. In each cycle, 4 mA h cm^{-2} metallic Li was deposited and striped. The Li|LiFePO$_4$ cells were also galvanostatically tested over the range of 2.5−4.2 V at room temperature. The Li|LiFePO$_4$ cells were first cycled at 0.1 C (1 C = 170 mA g^{-1}, based on LiFePO$_4$ materials) for three formation cycles and the cycled at 1 C in the cycling performance test. The rate performance of cells were evaluated at various rates of 0.2 C, 0.5 C, 1 C, 2 C, 5 C, 10 C, and 0.2 C for 5 cycles, respectively. Electrochemical impedance spectroscopy (EIS) measurement of cells after different cycles were performed in a frequency ranging from 100 kHz to 100 mHz with an amplitude of 10 mV on PARSTAT-2273 electrochemical workstation.

2.3. Characterizations and computation

The cycled Li|Cu cells and Li|LiFePO$_4$ cells in different electrolytes were disassembled in the argon-filled glove box and Cu foils or Li electrodes were taken out and rinsed with anhydrous DMC for three times to remove away residual solvents and salts. The morphologies of depositing Li on the Cu foils and Li metal electrodes were observed with scanning electron microscope (SEM, VEGA 3 SBH). Cross section polisher (IB-09020CP) and SEM were used for Cross-section SEM images of the Cu substrates after depositing Li. The compositions of surface film on the Li anode were measured by X-ray photoelectron spectroscope (XPS, PHI 5700 ESCA system) using Al Kα radiation (hν = 1486.6 eV) as the X-ray source. During the transfer process, all the samples were protected with Ar$^+$ to avoid contact with air. The in-situ DEMS measurements were performed in a "one-dot" system described elsewhere [37,38]. DEMS system consists of a MS system, measuring pinhole, homemade microspur-controlled system, video camera, and the electrochemical cell. The mass spectrometer is a Qulee BGM-202 mass spectrometer for the DEMS measurements. The battery with a hole in one side is connected to the instrument by a self-made glass tube and the connections are sealed with glue and vacuum ester to ensure sealing.

The energy levels of the highest occupied molecule orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the solvents EC, DMC and additive TTFEB were calculated with Gaussian 09 programs package. The equilibrium and transition structures were fully optimized by B3LYP method at 6−31 + G (d, p) basis set.

3. Results and discussion

3.1. Properties and electrochemical stability of the electrolyte

The majority of electrolyte additives for modifying SEI layer on the surface of the anode are based on its preferential reduction compared to the base electrolyte [20−22,39]. Therefore, the reduction potential is a very important parameter to determine whether the additive can consummate the surface chemistry of the anode. The energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) reflects the capability to gain or lose electrons, which are expected to evaluate the electrochemical stability of the electrolyte [40,41]. Fig. S1 and Table 1 show the frontier molecular orbitals and corresponding calculated energies of EC, DMC, and TTFEB additive, respectively. As shown in Table 1, TTFEB