

Duplex component additive of tris(trimethylsilyl) phosphite-vinylene carbonate for lithium sulfur batteries



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ABSTRACT

The practical application of lithium–sulfur battery, one of the most promising batteries close to market, is hindered by its poor cyclability. Herein, Tris(trimethylsilyl) phosphite-Vinylene carbonate (TMSP-VC) is firstly investigated as a duplex-component additives to prolong the cycle life and enhance the rate performance of Li-S batteries. TMSP and VC function synergistically to modify the interfacial film of sulfur cathode and Li anode, and accelerate the lithium ion diffusion. Using traditional carbonate electrolyte with 1 wt%TMSP-2 wt%VC additives, S@pPAN cathode delivers a reversible capacity of 1243 mA h g⁻¹ over 800 cycles at 1 C, and a discharge capacity of 990 mA h g⁻¹ at the extremely high rate of 20 C.

1. Introduction

Due to high energy density, low cost and long cycle life, lithium ion batteries (LIBs) have been successfully commercialized in electric portable devices and electrical vehicles. However, the state-of-the-art Li-ion battery cannot satisfy society's demands for batteries with longer cycle life and higher energy density [1–3]. Accordingly, for a remarkably high theoretical capacity of 1675 mA h g⁻¹ for sulfur cathode, high specific energy density of 2600 W h kg⁻¹ and low cost, lithium-sulfur (Li-S) batteries show great potential for the next generation of “beyond lithium ion battery” and have recently attracted intense interest [4–7]. Li-S batteries greatly reduce overcharge dangers compared with conventional LIBs through utilizing “integration chemistry” instead of insertion chemistry [8]. Nonetheless, the practical application of Li-S batteries is hindered by several critical problems to be resolved, including the poor electronic/ionic conductivity of sulfur and its discharge products, the expansion/shrinkage of sulfur during cycling (i.e., ~ 76%), and the shuttling phenomenon resulted from the solubility and diffusivity of polysulfide intermediates. These lead to low sulfur utilization, low Coulombic efficiency and poor cycle stability of Li-S batteries [9–11].

Therefore, continuous efforts have been conducted to enhance the electrochemical performances of Li-S batteries via optimizing the conductive sulfur composites, anode or electrolyte composition to solve aforementioned problems. In particular, through the syntheses of nano sulfur composite material with unique conductive framework including carbon, graphene, conductive polymer and metal oxide, the electrochemical performances of Li-S cells have been significantly improved

[12–14]. In previous research, Wang et al. first synthesized molecular-level composite materials S@pPAN, in which single molecular sulfur S_n (1 ≤ n ≤ 8) was mono-dispersed and encapsulated in pyrolyzed polyacrylonitrile (PAN) matrix to be a semiconductor, possessing an electrical conductivity of ca. 10⁻⁴ S cm⁻¹ [15,16]. The composite S@pPAN effectively prevented the polysulfide from dissolving and obtained up to 95% sulfur utilization, showing excellent compatibility with common carbonate electrolyte without obvious discharge/charge plateau. Moreover, the S@pPAN cathode delivered high electrochemical activity and nearly 100% Coulombic efficiencies except the first cycle in common carbonate electrolyte. Compared with the frequently used ether electrolytes in Li-S batteries, carbonate electrolytes shows relatively lower vapor pressure, which is another advantage of S@pPAN composites [17–19]. However, the common carbonate solvents with LiPF₆ impede the robust electrochemical performances of S@pPAN composite materials after about 200 cycles due to the side-reaction of electrolyte and the continuous growing cathode electrode interface. To achieve long-term cycle stability and excellent rate performance, various strategies have been reported to stabilize the interface between electrodes and electrolyte.

So far, plenty of functional additives [20–23], binary lithium salts [24,25] and new liquid electrolyte [26,27] are employed in Li-S battery to improve its electrochemical properties. As one of the most facile and economic solution, introducing functional additive into common electrolyte systems could effectively inhibit the electrolyte decomposition and participate in the formation of SEI [28–32]. For common elemental sulfur cathodes, LiNO₃ was widely adopted to form a passivation layer on lithium anode surface to alleviate the shuttle

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phenomenon of polysulfide [33,34]. Based on S@pPAN cathodes, some novel electrolytes and additives have been proposed to improve the performance of Li-S batteries. A dual-functional inflammable electrolyte additive (TTFP) were reported to enhance the cyclic stability and rate capability by modifying the interfacial film on the S@pPAN cathode [35]. Furthermore, Yang et al. proposed a novel electrolyte system (1 m LiODFB/EC-DMC-FEC) to suppress the lithium dendrites, which simultaneously shows highly compatibility with sulfur cathode [36]. Besides, some other organic phosphates, like TPPi [36] and DMMP [37], have been reported to be introduced into standard electrolytes to enhance the safety of the battery without sacrificing electrochemical performance. Also, Tris(trimethylsilyl) borate(TMSB), the common film forming additive in LIBs, was also effective in Li-S battery systems with S@pPAN cathode [38]. Generally, the electrolyte additives adjusted the interfacial reactions and led to prolonged cycle life and enhanced rate performances for sulfur-based composite materials.

In earlier studies, Tris(trimethylsilyl) phosphite (TMSP) has been applied as an efficient electrolyte additive for several cathodes [39–41], for example $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The improved capacity retention and longer cycle life were attributed to the stable passive film derived from TMSP oxidation before carbonate solvents. Moreover, Vinylene Carbonate (VC) was reported as a highly promising additive for Li metal anode [42–44]. Herein, to the best of our knowledge, TMSP and VC were adopted for the first time to modify S@pPAN cathode and Li metal anode respectively. We assume that TMSP and VC could function synergistically in Li-S batteries.

2. Experimental section

2.1. Preparation of sulfur cathode

16 g elemental sulfur and 2 g polyacrylonitrile (PAN, Aldrich) was homogeneously mixed by ball milling and then heat-treated at 300 °C in nitrogen for 450 min, resulting in S@pPAN black powder. The sulfur cathodes were fabricated by mixing S@pPAN with 41.3 wt% S, Super P and carbonyl- β -cyclodextrin (C- β -CD) binder [45] in the ratio of 8:1:1 to form slurry. After stirring for 6 h, the slurry was uniformly coated onto carbon coated aluminum foil and dried at for 70 °C under vacuum overnight. The cathode was cut into circular discs area of 1.13 cm² with the average composites mass loading of about 1 mg cm⁻¹.

2.2. Preparation of electrolyte

Lithium hexafluorophosphate (LiPF_6) in ethylene carbonate (EC) and dimethylcarbonate (DMC) (1:1, v/v) was used as basic electrolyte. The experimental functional electrolyte was obtained by adding adequate amounts of Tris(trimethylsilyl) phosphite (TMSP) and Vinylene carbonate (VC) into the common electrolyte, and further stirring for 12 h at room temperature. It is noted that the electrolyte was prepared and stored in an argon-filled dry glove box (MB-10 compact, MBRAUN) containing less than 1 ppm water and O₂.

2.3. Physical characterizations

Ionic conductivity tests of the electrolyte were carried out with a DDS-307A conductivity meter at ambient temperature. The morphology of the sulfur cathode and Li anode were observed using SEM (FEI Nova Nano-scanning electron microscope). Before examination, the Li-S coin cells in the full-charged state after 100 cycles were disassembled in an argon-filled glove box and then obtained electrodes were rinsed with dimethylcarbonate (DMC) thoroughly. It is noted that the dried Li anode must be sealed in a Ar-filled container and transferred quickly into the SEM equipment to avoid oxidation. Surface composition of the electrode after 100 cycles in electrolyte with and without additives was analyzed by the X-ray photoelectron spectroscopy (XPS), using a

Kratos Axis UltraDLD spectrometer (Kratos Analytical-A Shimadzu Group Company) with monochromatic Al K α source (1486.6 eV) under ultra-high vacuum. Also, the samples should be thoroughly washed with DMC to remove any electrolyte salt residuals. The obtained spectra after calibration were fitted via using XPS peak software (version 4.1).

2.4. Electrochemical measurements

The testing CR2016-type Li-S coin cells were assembled in an argon-filled glove box, using the as-prepared sulfur electrode as cathode, pure lithium foil as anode, and Celgard2300 film as separator. Also, to evaluate the effects of TMSP and VC in Li-S batteries, electrolytes with and without additive were employed, respectively. The galvanostatic discharge/charge tests were carried out on a LAND-CT 2001A Cell Test System (Wuhan, China) in the voltage range of 1.0–3.0 V (vs. Li/Li⁺). The rate performance of cells was evaluated using the same equipment at the discharged current density of 0.5 C, 1 C, 3 C, 5 C, 7 C, 9 C, 10 C, 12 C, 15 C, 20 C, 30 C, respectively, and charged at 0.5 C (1 C equal to 1672 mA g⁻¹ for sulfur). Alternative current impedance spectroscopy of Li-S cells with different electrolyte were measured using AUTOLAB PGSTAT302N (Metrohm) at full-charged state over a frequency range from 100 kHz to 0.01 Hz with an amplitude of 5 mV. Cyclic voltammograms (CVs) were performed on a CHI760E Electrochemical Workstation (Shanghai, China) with the three-electrode cell equipment between 1 V and 3 V. The working electrode was a sulfur-based electrode (area: 1.13 cm²), the counter and the reference electrodes were lithium metal anodes.

3. Results and discussion

To evaluate the effect of TMSP on Li-S batteries, a comparison of the cycling performance of S@pPAN cathode with various contents of TMSP additive at 1 C is demonstrated in Fig. 1. It is clear that the cycle stability of the cells was remarkably improved with the addition of TMSP, especially with 1 wt% TMSP. The S@pPAN composites in blank electrolyte showed gradually continuous capacity decrease before 150 cycles but suffered a fast decay later. After 400 cycles, the capacity retention was only 57.7%, as calculated against the 2nd cycle. On the contrary, the cell using electrolytes with 1 wt% TMSP maintained a reversible discharge capacity of 1250.1 mA h g⁻¹ in 400th cycle with a fading rate of 0.036% per cycle, indicating that the capacity retention was up to 85.6%. However, when the concentration of TMSP additive increased to 10 wt%, the capacity decreased to 455.5 mA h g⁻¹ which was partially ascribed to the decreasing ionic conductivity of 8.42 S cm⁻¹ (Fig. S1) and mainly possible destroyed interface because of too much TMSP. Apparently, TMSP showed remarkable effect on the cyclability of S@pPAN composite cathode, and the introduction of 1 wt % TMSP into electrolyte significantly prolonged its cycle life.

It was reported that the addition of VC benefit the cyclability of lithium ion batteries by effectively improving anode [42–44]. The electrochemical performances of Li-S batteries with TMSP and VC

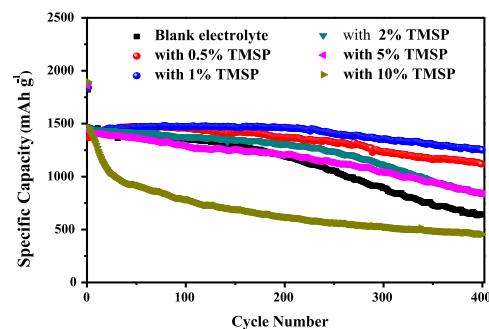


Fig. 1. Cyclic performance at the current rate of 1 C at 25 °C.

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