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Pyrrole as a promising electrolyte additive to trap polysulfides for lithium-sulfur batteries

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HIGHLIGHTS

- The effect of Py additive in Li-S batteries is investigated for the first time.
- A surface protect layer on cathode through electrochemical oxidation polymerization.
- PPy can act as a conductive/absorbing agent or barrier layer to trap polysulfides.
- An appropriate amount of pyrrole additive leads to improving performance.

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ABSTRACT

Lithium–sulfur batteries are a promising energy storage devices beyond conventional lithium ion batteries. However, the “shuttle effect” of soluble polysulfides is a major barrier between electrodes, resulting in rapid capacity fading. To address above issue, pyrrole has been investigated as an electrolyte additive to trap polysulfides. When pyrrole is added into electrolyte, a surface protective layer of polypyrrole can be formed on the sulfur cathode, which not only acts as a conductive agent to provide an effective electron conduction path but also acts as an absorbing agent and barrier layer suppressing the diffusion of polysulfide intermediates. The results demonstrate that an appropriate amount of pyrrole added into the electrolyte leads to excellent cycling stability and rate capability. Apparently, pyrrole is an effective additive for the entrapment of polysulfides of lithium-sulfur batteries.

1. Introduction

Rechargeable batteries with long cycle life and high energy density are highly desired to satisfy the growing demand for a multitude of emerging applications, ranging from portable electronics devices to electric vehicles [1,2]. Lithium–sulfur batteries (LSB) have widely recognized as one of the most promising candidates for next generation energy storage devices (2600 Wh kg^{-1}), which ascribes to the natural abundance, low cost, non-toxicity and high theoretical specific capacity (1675 mAh g^{-1}) of elemental sulfur [3–5]. Despite these considerable advantages, the practical application of LSB is still hindered by a set of shortcomings, including poor cycle life, tremendous capacity fading and rate capability loss [6,7]. Specifically, there exists several inevitable obstacles [6–9]:the insulating nature of elemental sulfur (5×10^{-30} S cm^{-1} at 25 °C) and the final discharge products (Li_2S and Li_2S_2), which lead to low electronic conductivity within sulfur electrodes; severe volume changes in the active electrode materials during the lithiation/delithiation processes; the “shuttle effect” caused by a series of parasitic reactions between the cathode and anode through the migration of soluble polysulfide intermediates in organic electrolytes, resulting in capacity loss and poor cycle life.

The rapid capacity decay in LSB is closely related to the “shuttle effect” of soluble polysulfide intermediates. Aiming to address above issues, continuous efforts have been devoted to trapping soluble polysulfide intermediates far from lithium metal anode through physical/chemical absorption or physical barrier. Nanostructured cathodes [6,10–13], modified separators or interlayers [8,14–17], protected anodes [18–22], and advanced electrolyte [7,23,24], could limit soluble polysulfide intermediates in their specific structures, thus, to some extent, these advanced measures

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could effectively restrain the “shuttle effect”. Nevertheless, the excessive use of non active material and the alleviating transportation of Li^+ would sharply sacrifice energy density of the battery, since the dissolution of polysulfide intermediates in organic electrolytes is inevitable. Therefore, a useful approach is to build a solid electrolyte interphase (SEI) with good electrochemical stability on the cathode or anode.

For that reason, electrolyte additives are commonly used to alleviate the “shuttle effect” in ether-based electrolyte. For instance, lithium nitrate ($LiNO_3$) was widely used as the additive in ether-based electrolyte for LSB because it reacts with metallic lithium to form a surface passivating film that functions as a physical shielding to protect the lithium anode [25–28]. Consequently, improved coulombic efficiency and cycling performance were observed in LSB with $LiNO_3$ additive [25,26]. However, $LiNO_3$ can be reduced irreversibly on the carbon surface at potentials lower than 1.6 V, and the stabilized SEI formed infinitely with the continuous consumption of $LiNO_3$ [27,28]. Furthermore, Zhang et al. [29] further investigated the function of $LiNO_3$ focusing on the sulfur cathode and showed that $LiNO_3$ can catalyze the conversion of polysulfide to elemental sulfur. Indeed, $LiNO_3$ as a strong oxidizing agent would be faced with the contradiction between consumption mechanism and safety concerns. Recently, phosphorus pentasulfide (P_2S_5) and lithium iodide (LiI) were reported to induce a formation of an effective protective SEI [20,30]. P_2S_5 assists in the formation of a more favorable SEI of Li_3PS_4 on the surface of lithium metal anode, which not only prevents polysulfide intermediates from reacting with the lithium metal, but also helps to convert insoluble lithium polysulfide into more soluble products. The formed protective film contained iodine in LiI added electrolyte can prevent the dissolution of polysulfides on the cathode side and the reduction of polysulfides on the anode side. However, such approaches still could not provide satisfactory performance improvements due to the presence of defects within the protective layers. Therefore, researchers are seeking alternative electrolyte additives for LSB.

Herein, we investigated pyrrole (Py) as an electrolyte additive in LSB for the first time. Polypyrrole (PPy) were formed as a surface protective layer on the sulfur cathode through electrochemical oxidative polymerization method during the charge/discharge process. Since PPy possess good conductivity and stability, which can act as a conductive agent, absorbing agent or barrier layer on the surface of cathode, the electrochemical performance of LSB with different amounts of Py additive was greatly improved. The results indicate that the addition of an appropriate amount of Py to the electrolyte significantly inhibits the diffusion of polysulfide intermediates and exhibits excellent cycling stability and rate capability.

2. Experimental section

2.1. Preparations of sulfur cathode and electrolytes

Porous carbon (PC) was synthesized by template-free method described in our previous work [31]. Sulfur/porous carbon (S/PC) composite was prepared by a simple melt-diffusion approach. Typically, the carbon hosts were mixed with sublimed sulfur (the weights of carbon and sulfur were in the ratio 1:3) in a Teflon container. The mixture was then heated in an Ar atmosphere at a temperature of 155 °C for 20 h to form the S/PC composite. Subsequently, the S/PC composite was combined with acetylene black and polyvinylidene fluoride binder with a mass ratio of 80:10:10 in N-methyl-2-pyrrolidene (NMP). The slurry was then blade cast onto an aluminum foil and dried at 60 °C for 12 h under vacuum. The mass loading of the sulfur active material on the electrode was about 1.0 mg cm^{-2}.

Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 1.0 mol L^{-1}) salt in a solvent of 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) (volume ratio of 1:1), containing 0.4 mol L^{-1} lithium nitrate ($LiNO_3$) as an electrolyte additive was used as the basic electrolyte. Different amounts (1%, 5%, and 10%, by weight) of Py were added to the basic electrolyte labeled as the experimental electrolyte.

2.2. Performance characterization

The lithium ion diffusion coefficient (D_{Li+}, cm^2 S^{-1}) was evaluated by AC impedance measurement and calculated according to the following (1) and (2) equations:

$$DLi^+ = \frac{R^2T^2}{2n^4F^4S^2C^2\sigma^2} \tag{1}$$

$$Z' = Rs + Rct + \sigma\omega^{-0.5} \tag{2}$$

where R is the gas constant, T is the absolute temperature, n represents the number of electrons in the reaction (for LSB, $n = 2$), F is Faraday's constant, S is the apparent surface area of the cathode, C is the concentration of Li ions in the electrolyte, σ is the Warburg coefficient, Z' is the real axis resistance in the low frequency region, and ω is the angular frequency in the low frequency region.

The lithium polysulfide (Li_2S_6) was prepared by chemically reacting sublimed sulfur (99.95%) and an appropriate amount of lithium sulfide (Li_2S, Alfa Aesar, 99.9%). Typically, the stoichiometric amounts of S and Li_2S with a molar ratio of 5:1 were dissolved in DOL/DME (volume ratio of 1:1) by magnetically stirring at 70 °C in an argon-filled glove box for 10 h. Afterwards, 10 mg of PPy was placed in 8 mL of lithium polysulfde solution (5 mM) for the polysulfide capture test.

2.3. Electrochemical measurements

Two-electrode coin cells (CR2025) with lithium metal as the anode were assembled in an argon-filled glove box for electrochemical experiments and the amount of electrolytes were about 35 μL. The galvanostatic charge/discharge measurements were conducted at different rates between 1.7 and 2.8 V on a LAND-CT2001A battery testing system (Wuhan, China). The specific capacity values were calculated based on the mass of sulfur in the cathode. Both cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed on a CHI660E electrochemical workstation (Shanghai, China). CV tests were performed at a scanning rate of 0.1 mV s^{-1} in the potential range of 1.5–3.0 V to characterize the redox behavior and kinetic reversibility of the cells. EIS measurements were carried out in the frequency range between 100 KHz and 10 mHz by applying a 5 mV AC oscillation. All the electrochemical tests were performed at ambient temperature and all potentials cited in this paper were referred to Li/Li^+.

2.4. Characterization of the lithium anode surface, sulfur cathode surface before and after cycling

The CR2025 coin cells after 100 charge/discharge cycles transferred into the glove box and dissembled for further examination. The cycled anodes and cathodes were repeatedly rinsed with DME and drying in the glove box to remove the residual solvent. Morphology and elemental mapping were examined by field emission scanning electron microscopy (FESEM, Hitachi-S4800, Japan) and energy dispersive X-ray spectroscopy (EDS). The X-ray diffraction (XRD) patterns were characterized on a Rigaku Smart