



A new finding on the role of LiNO₃ in lithium-sulfur battery



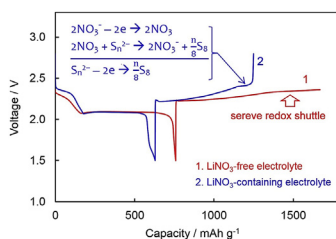
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HIGHLIGHTS

- Role of LiNO₃ in Li–S batteries is reinvestigated with focus on sulfur cathode.
- Nitrate anion catalyzes the conversion of polysulfide to elemental sulfur.
- A catalysis mechanism of nitrate anion on the Li₂S_n to S₈ conversion is proposed.
- Combination of a soluble nitrate and an insoluble nitrate leads to synergetic improvement.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium nitrate (LiNO₃) is the most studied additive and co-salt for the electrolyte of lithium-sulfur (Li–S) batteries, its known function is to suppress the redox shuttle of soluble lithium polysulfide (PS, Li₂S_n), which reflects as an increase in the battery's coulombic efficiency and cycling stability, as well as a reduced self-discharge rate. The current understanding on this function is that LiNO₃ reacts with Li to form a robust surface layer that consequently protects the Li anode from reacting with the dissolved PS. However, little is known on the sulfur cathode except that LiNO₃ reduces and adversely affects the battery's performance when the battery is discharged to lower than 1.7 V. In this paper we report a new finding on the role of LiNO₃ in enabling the stable cycling of the sulfur cathode. We show that LiNO₃ is capable of catalyzing the conversion of high soluble PS to slightly soluble elemental sulfur near the end of charging process, and that the combination of a soluble nitrate in the electrolyte and an insoluble nitrate in the sulfur cathode leads to synergetic improvement. In addition, a possible mechanism is proposed for the catalysis of LiNO₃ on the conversion of PS to elemental sulfur.

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1. Introduction

Lithium nitrate (LiNO₃) has been widely used as the electrolyte additive or co-salt in the electrolyte of rechargeable lithium-sulfur (Li–S) batteries since the first proposal by Mikhaylik in 2008 [1]. Main function of LiNO₃ in the Li–S batteries is to suppress the redox shuttle and self-discharge rate [2,3]. However, the mechanism for this improvement still has not been fully understood. The current

understanding is mainly limited to the Li anode, knowing that the presence of LiNO₃ increases the coulombic efficiency and cycle life of metallic Li in lithium polysulfide (PS, Li₂S_n) solutions [2,4,5]. These improvements are attributed to the fact that LiNO₃ reacts with metallic Li to form insoluble Li_xNO_y products, which constitute a robust surface layer on the Li anode and consequently protect the Li anode from reacting with the dissolved PS. The Li_xNO_y species on the Li surface have been identified not only by the spectroscopic analyses such as Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy, but also by the direct observation such as scanning electron microscope and scanning probe microscopy

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[4,6–9]. However, Xu et al. argued that the robust Li surface layer was not the only cause for the suppression of redox shuttle in the Li–S batteries [10]. They showed that the Li anode pre-cycled in a LiNO₃-containing electrolyte did not suppress the redox shuttle when being assembled with a pristine sulfur cathode and cycled in a LiNO₃-free electrolyte. On the other hand, we previously found that LiNO₃ was subject to irreversible reduction on the sulfur cathode when the battery was discharged to lower than 1.7 V, and that the reduction dramatically hurt the capacity and cyclability of Li–S batteries [11,12]. In addition to the discharge cutoff voltage, the binder and conductive carbon were also reported to affect the reduction of LiNO₃ [13,14]. For example, the binders containing oxygen functional groups, such as sodium alginate and sodium carboxymethyl cellulose, are shown to be favorable for the suppression of LiNO₃ reduction [13].

In order to further understand the function of LiNO₃ in the Li–S batteries, in the present work we conducted a comprehensive investigation with focus on the sulfur cathode. In this paper we show that LiNO₃ is responsible for catalyzing the conversion of highly soluble PS to slightly soluble elemental sulfur near the end of charging process (namely above 2.5 V vs. Li/Li⁺), and propose a possible mechanism for the catalytic effect. This finding will be very helpful for further development of the rechargeable Li–S batteries.

2. Experimental

All chemicals were purchased from Sigma-Aldrich. Prior to use, dimethyl ether (DME) and 1,3-dioxolane (DOL) were dried over 4 Å molecular sieves for a week; lithium bis(trifluoromethane-sulfonyl) imide (LiTFSI) and LiNO₃ were dried at 110 °C under vacuum for 10 h; elemental sulfur and Mg(NO₃)₂·6H₂O were used as received. Two sulfur cathodes were respectively coated onto a carbon-coated aluminum foil: one consisting by weight of 65% sulfur, 5% Mg(NO₃)₂·6H₂O, 10% Super-P carbon, 10% Ketjenblack EC-300JD carbon black and 10% poly(ethylene oxide) was coated by using deionized water as the solvent, and the other consisting of 77% sulfur, 10% Super-P carbon, 10% Ketjenblack EC-300JD carbon black and 3% poly(acrylonitrile-methyl methacrylate) (ANMMA, AN/MMA = 94:6, MW = 100, 000, Polysciences, Inc.) was coated by using *N*-methyl pyrrolidinone as the solvent. Resultant cathode was punched into 1.27 cm² circular disks (namely 0.5 inch in diameter) and dried at 60 °C under vacuum for 16 h. On average, the cathode had a 2 mg cm⁻² of sulfur loading. In an argon-filled glove-box, two electrolytes were prepared by using a 1:1 (wt.) DME/DOL mixed solvent: one with 0.5 mol kg⁻¹ LiTFSI was referred to as “LiNO₃-free electrolyte” and the other with 0.25 mol kg⁻¹ LiTFSI-0.25 mol kg⁻¹ LiNO₃ was referred to as “LiNO₃-containing electrolyte”.

Using the cathode and electrolyte prepared above and a Celgard 3401 membrane as the separator, BR2335-type Li–S coin cells were assembled and filled with 30 μL electrolyte unless specified otherwise. It should be noted that in the present work, excess amount of liquid electrolyte was used for the purpose to highlight the effect of LiNO₃ in spite of the fact that the excess liquid electrolyte leads to large loss of sulfur active material due to the dissolution of PS. The Li–S cell was galvanostatically cycled on a Maccor Series 4000 cycler under the conditions noted in either the caption or the inset of figure. Electrochemical characterization was conducted using a Solartron SI 1287 Electrochemical Interface and a SI 1260 Impedance/Gain-Phase Analyzer. For a three-electrode electrochemical cell, a platinum (Pt) wire with 0.762 mm in diameter and 8 mm in length exposing to the solution was used as the working electrode, and two Li foils were used as the reference electrode and counter electrode, respectively. Cyclic voltammetry was performed at 20 °C by first scanning from open-circuit voltage to the low voltage end for the two-electrode Li–S cell, and by first

scanning from open-circuit potential to the high potential end for the three-electrode electrochemical cell, respectively. The potential scanning rate was at 0.1 mV s⁻¹. Ac impedance of the Li–S cell was measured at open-circuit voltage in the frequency range from 0.01 to 100 kHz with an ac oscillation of 10 mV amplitude.

3. Results and discussion

3.1. General benefit of LiNO₃ to Li–S battery

General benefits of LiNO₃ to the Li–S batteries are well reflected in the voltage profile of the discharging and charging. Fig. 1a shows the voltage profile of a Li–S cell with a LiNO₃-free electrolyte, which was discharged and charged by starting with a fresh cell and a 2.1 V discharge cutoff voltage and then in sequence lowering the discharge cutoff voltage to 1.0 V through 1.8 V, 1.5 V and 1.2 V, respectively. It can be seen that none of the charging process can reach the pre-set charge cutoff voltage (2.8 V), instead all charging constantly stayed at 2.5 V until the capacity limit (i.e., a capacity equaling to 120% of the last discharge capacity), indicating severe redox shuttle (Fig. 1a). On contrary, all charging processes for the cell with a LiNO₃-containing electrolyte reached 2.8 V regardless of the discharge cutoff voltage, indicating substantial suppression of the redox shuttle (Fig. 1b). Consistently, the capacity of these two cells was unexpectedly decreased with a decline in the discharge cutoff voltage, and the initial voltage bump (i.e., the small voltage peak) of the charging gradually becomes significant with lowering of the discharge cutoff voltage, especially when the cutoff voltage was at 1.2 V and 1.0 V. The former is due to the accumulated loss of sulfur active material, which does not stop until the concentration of sulfur species reaches the equilibrium throughout the cell, and the latter can be attributed to the increased polarization of a solid-to-solid phase transition from Li₂S to Li₂S₂ as a result of an increase in the amount of insulating Li₂S when the discharge cutoff voltage is lowered [15,16]. Fig. 1c exhibits a typical cycling performance of the cells with a LiNO₃-containing electrolyte. Without exception, the coulombic efficiency (CE) gradually declined after tens of normal cycles with CEs ranging between 99% and 100%. This phenomenon is known to be the progressive depletion of LiNO₃, caused by the irreversible reduction of NO₃⁻ anions on the Li anode and sulfur cathode [11,12].

In order to observe how LiNO₃ affects the Li anode and sulfur cathode, respectively, a Li–S cell with LiNO₃-containing electrolyte was cycled for 5 times to ensure the formation of matured surface layer on two electrodes and then disassembled at the end of the 5th charging, as shown by Fig. 2a and Fig. 2b. The harvested Li anode and sulfur cathode were carefully washed using a 1:1 DME/DOL mixed solvent to remove lithium salts and soluble PS species, followed by reassembling with a pristine sulfur cathode and a pristine Li anode, respectively, and activating with 30 μL LiNO₃-free electrolyte. For the cell consisting of the cycled Li and a pristine sulfur cathode, all charging processes repeatedly reached 2.8 V (Fig. 2c), however, the CEs were somewhat low, stabilizing at ~90% (Fig. 2d). These results reveal that the surface layer on the cycled Li anode can greatly suppress redox shuttle, but the redox shuttle is still present to some extent. On the other hand, for the cell consisting of a pristine Li and the cycled sulfur cathode, not only the cell could be charged to 2.8 V (Fig. 2e), but also the CEs achieved higher than 99% (Fig. 2f). By comparison of the CEs in Fig. 2d and Fig. 2f, we conclude that the surface layer formed on the sulfur cathode with the incorporation of LiNO₃ may play a more important role than that on the Li anode in suppressing the redox shuttle of dissolved PS. It should be noted that the specific capacity in Fig. 2f was much lower than those in Fig. 2b and Fig. 2d. This is because in the cell of Fig. 2f, all soluble PS species were already removed in the processes

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