

# The synergetic interaction between $\text{LiNO}_3$ and lithium polysulfides for suppressing shuttle effect of lithium-sulfur batteries



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## ABSTRACT

$\text{LiNO}_3$  has been widely used as an effective electrolyte additive in lithium-sulfur (Li-S) batteries to suppress the polysulfide shuttle effect. To better understand the mechanism of suppressed shuttle effect by  $\text{LiNO}_3$ , herein we report a comprehensive investigation of the influence of  $\text{LiNO}_3$  additive on the formation process of the solid electrolyte interphase (SEI) layer on lithium anode of Li-S batteries by *operando* X-ray absorption spectroscopy (XAS). We observed that a compact and stable SEI layer composed of  $\text{Li}_2\text{SO}_3$  and  $\text{Li}_2\text{SO}_4$  on top of lithium anode is formed during the initial discharge process due to the synergetic effect of shuttled polysulfides and  $\text{LiNO}_3$ , which can effectively suppress the subsequent reaction between polysulfides in electrolyte and lithium metal and thus result in the alleviation of polysulfide shuttle effect. In contrast, when using electrolyte without  $\text{LiNO}_3$ , the shuttled polysulfides continuously react with lithium metal to form insulating  $\text{Li}_2\text{S}$  on lithium anode, leading to the irreversible capacity loss. Our present *operando* XAS study provides a valuable insight into the important role of  $\text{LiNO}_3$  for the protection of lithium anodes, which will be beneficial for the further development of new electrolyte additives for high-performance Li-S batteries.

## 1. Introduction

Lithium-sulfur (Li-S) batteries have attracted extensive attention for energy storage because they can yield rather high specific capacity of 1675 mA h/g ( $16\text{Li} + \text{S}_8 \rightarrow 8\text{Li}_2\text{S}$ ) and specific energy of 2600 W h/kg, indicating a superior energy storage capability [1–9]. In addition, sulfur has the features of light weight, high natural abundance, low cost and environmental benignity. Despite these advantages, the practical application of Li-S batteries is hindered by the rapid capacity degradation upon cycling and low Coulombic efficiency, mainly due to the notorious polysulfide shuttle effect [1,2]. The shuttle effect mainly arises from side reaction between the intermediate polysulfides formed throughout discharge/charge processes and the lithium anode.

$\text{LiNO}_3$  has been widely used as an effective electrolyte additive in Li-S batteries to suppress the polysulfide shuttle effect and thus to improve the cycling performance of Li-S batteries [10–19]. However, the mechanism of this improvement has not been fully understood yet. It is generally believed that  $\text{LiNO}_3$  participates in the formation of solid electrolyte interphase (SEI) film on the surface of lithium anode: it can

not only react with lithium to form a robust surface layer of insoluble  $\text{Li}_x\text{NO}_y$  but also oxidize polysulfides to form  $\text{Li}_x\text{SO}_y$ . Both surface species effectively passivate the lithium anode and therefore the internal redox reaction between soluble polysulfides and lithium anode is impeded [11,12,20–22]. However, Xu et al. claimed that the inhibition of shuttle effect by the  $\text{LiNO}_3$  additive is due to the continuous reaction of  $\text{LiNO}_3$  with lithium anode and/or reduced polysulfides rather than the formation of a stable passivation layer on lithium anode [23].

The reaction product of  $\text{LiNO}_3$  as well as its influence on the formation of SEI layer on lithium anode has been extensively investigated by *ex situ* microscopy (e.g., scanning electron microscope (SEM) and atomic force microscope (AFM)) and *ex situ* spectroscopy (e.g., X-ray photoemission spectroscopy (XPS) and Fourier transformed infrared spectroscopy (FTIR)) [13,20,21,24]. However, due to the highly reactive nature of lithium anode, *ex situ* analysis results may not always be reliable [25]. For instance, the lithium anode could react with the surrounding environment when it is removed from electrolyte solutions and washed by solvents. Therefore, *in situ* and *operando* experiments

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are highly desired to gain a better mechanistic understanding of the role of  $\text{LiNO}_3$  in the surface chemistry of lithium anode [26]. Although a few *in situ* and *operando* SEM and optical microscopy studies to investigate the passivation of lithium metal using  $\text{Li}_2\text{S}_8$  and  $\text{LiNO}_3$  as co-additives in the electrolyte have been reported [13,27], the formation process of the SEI layer on lithium anode in a working Li-S battery with and without  $\text{LiNO}_3$  additive has seldom been studied [28]. In this work, we have systematically investigated the formation process of the SEI layer on lithium anode with and without  $\text{LiNO}_3$  additive in electrolyte for Li-S cells by *operando* S K-edge X-ray absorption spectroscopy (XAS) throughout the first discharge process. The advantage of XAS is that it is element-resolved and sensitive to the local chemical bonding environment and solvent environment [29]. *Operando* XAS method has been widely used to investigate the reaction mechanism of sulfur cathode during the charge/discharge processes previously [24,30–35]. For example, we have investigated the electrochemical charging mechanism of  $\text{Li}_2\text{S}$  by using *operando* S K-edge XAS in our previous report [35]. In contrast, the present study explores the sulfur speciation in electrolyte and lithium anode by using a specially designed coin cell (Figure S1 in Supporting information) to characterize the role of  $\text{LiNO}_3$  in the formation process of the SEI layer on lithium anodes. By using electrochemistry investigation, morphology characterization and *operando* XAS, we have found that  $\text{LiNO}_3$  and intermediate polysulfides formed during the discharge process enable a synergetic effect and lead to the formation of a stable SEI layer with  $\text{Li}_2\text{SO}_3$  and  $\text{Li}_2\text{SO}_4$  on top, which can effectively alleviate the shuttle effect and thus improve the cycling performance of Li-S cells.

## 2. Results and discussion

Fig. 1a shows the galvanostatic cycling performances of Li-S cells with and without 2 wt%  $\text{LiNO}_3$  additive in the electrolyte. An initial discharge capacity of 1026.7 mA h/g is achieved when using  $\text{LiNO}_3$  as the additive in the electrolyte, which is much higher than that without  $\text{LiNO}_3$  (829.9 mA h/g). In addition, the capacity of Li-S cell with  $\text{LiNO}_3$  is maintained at 531.5 mA h/g after 19 cycles, equaling to 51.8% of the initial capacity; while the capacity of Li-S cell free of  $\text{LiNO}_3$  is retained at only 162.8 mA h/g (19.6% of its initial capacity). These results clearly demonstrate that  $\text{LiNO}_3$  is an effective additive to improve the cycling performance of Li-S cells.

Fig. 1b and c show the representative discharge/charge voltage profiles of Li-S cells using the electrolyte with and without  $\text{LiNO}_3$  in the voltage window of 1.8–2.6 V at 0.05 C (1 C = 1675 mA/g), respectively. The cell using the electrolyte with  $\text{LiNO}_3$  exhibits two typical discharge plateaus at 2.3 V and 2.1 V, indicating the formation of long chain polysulfides and short chain polysulfides during the discharge process [1,2,36]. The charge voltage profiles also show the plateau at 2.3 V, followed by a steep rise of voltage to the cutoff voltage (2.8 V) [1,2,36]. In contrast, when using the electrolyte without  $\text{LiNO}_3$ , the voltage

profiles show only indistinguishable plateaus, which is probably due to the distorted discharge/charge processes [37]. Overall, these results clearly indicate that the use of  $\text{LiNO}_3$  as additive makes the electrochemical reaction of sulfur reversible during the discharge/charge processes and results in a higher specific capacity, which is consistent with previous reports [11,14,16–18,21,23]. According to the conventional understanding,  $\text{LiNO}_3$  can oxidize the polysulfides and be reduced itself to form a protective  $\text{Li}_x\text{SO}_y/\text{Li}_x\text{NO}_y$  SEI layer between the electrolyte and the lithium anode to suppress the polysulfide shuttle effect and the decomposition of electrolyte [14,21,24].

To better understand the influence of  $\text{LiNO}_3$  on the formation of the SEI layer on lithium anodes, scanning electron microscope (SEM) was employed to obtain the morphology of lithium anodes cycled with and without  $\text{LiNO}_3$  additive. Fig. 2 shows the SEM images of lithium anodes using the electrolyte with the addition of  $\text{LiNO}_3$  after 1st discharge (Figs. 2a and 2b) and 1st charge (Figs. 2c and 2d) and the electrolyte without  $\text{LiNO}_3$  after 1st discharge (Figs. 2e and 2f) and 1st charge (Figs. 2g and 2h), respectively.

After the 1st discharge, the lithium anode cycled with  $\text{LiNO}_3$  shows a relatively smoother and more compact surface compared with that cycled without  $\text{LiNO}_3$  (Figs. 2a and 2b vs. Figs. 2e and 2f), indicating that the reaction between intermediate polysulfides and lithium anodes is alleviated by adding  $\text{LiNO}_3$  in electrolyte [13,21]. The holes observed on the surface of lithium anodes could be induced by the nonuniform extraction of lithium during the discharge process. While after the 1st charge, the surface of the lithium anode cycled with  $\text{LiNO}_3$  still exhibits a relatively smooth morphology with a few protuberances (Figs. 2c and 2d), indicative of the formation of a dense and stable SEI layer due to the complex reaction between lithium metal,  $\text{LiNO}_3$ , and polysulfides [15,21,24]. In contrast, uneven growth of mossy lithium accompanied with apparent cracks in the SEI layer can be clearly observed when using the electrolyte without  $\text{LiNO}_3$  (Figs. 2g and 2h). As a consequence, fresh lithium metal is continuously exposed to the electrolyte during cycling, resulting in the electrolyte decomposition and rapid loss of lithium metal and electrolyte [13]. This finding is consistent with previous reports showing that the reaction products ( $\text{Li}_2\text{S}$ ) of polysulfides and lithium metal can induce heterogeneities of the lithium metal surface and thus aggravate electrolyte decomposition and lithium dendrite formation [13,38]. Overall, the SEM results provide a direct evidence that  $\text{LiNO}_3$  strongly affects the morphology and thus the surface chemistry of the SEI layer on lithium anodes, which can greatly influence the cycling performance of Li-S cells.

In order to further understand the influence of  $\text{LiNO}_3$  on the surface chemistry of SEI layer formed on lithium anodes, *operando* S K-edge XAS experiments were performed throughout the first discharge process of Li-S cells using the electrolyte with and without  $\text{LiNO}_3$  additive. Figs. 3a and 3b show the *operando* S K-edge XAS spectra of Li-S cells using electrolyte with and without  $\text{LiNO}_3$  throughout the first discharge process, respectively. For convenience of

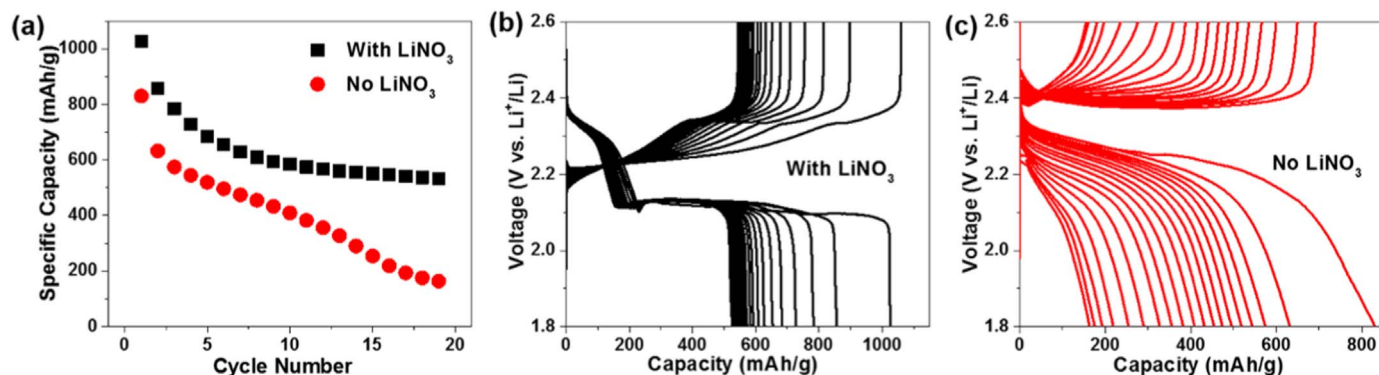


Fig. 1. (a) Cycling performance of Li-S cells with  $\text{LiNO}_3$ -containing and  $\text{LiNO}_3$ -free electrolyte. (b, c) Voltage profiles of Li-S cells with  $\text{LiNO}_3$ -containing and  $\text{LiNO}_3$ -free electrolyte for the first 19 cycles.

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