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#### Article

# Low-Cost LillSPAN Batteries Enabled by Sustained Additive Release

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the (GrAR) batteries have the potential to meet both of these goals, the integration of low-cost electrolytes that are simultaneously stable with both Li and SPAN limits their application. Herein, we present a scalable approach to remedy this issue. This approach utilizes  $LiNO_3$ as a solid additive to the cathode, which is specifically enabled by an electrolyte based on diethyl ether (DEE), having sparing solubility to  $LiNO_3$  and a Li metal cycling efficiency of 99.0%. The sustained release of  $LiNO_3$  into the electrolyte was found to produce a cathode electrolyte interphase (CEI) composed of S–O and F species that is correlated with a SPAN cycling retention of 85% after 200 cycles. This



interphase was characterized via X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), and scanning transmission electron spectroscopy (STEM). This endowed stability on the cathode side, in addition to the high Li metal reversibility, allowed for the assembly of a 40  $\mu$ m Lill3.5 mAh cm<sup>-2</sup> SPAN (2 wt % LiNO<sub>3</sub>) full-cell that exhibited stable cycling over 100 cycles. This study provides a viable method for the construction of LillSPAN batteries with a nonfluorinated electrolyte at a dilute salt concentration, allowing for the low intrinsic cost of SPAN to carry over to the system level.

**KEYWORDS:** *lithium metal, batteries, sulfur, electrolyte, electrode, additives* 

## INTRODUCTION

The ubiquity of fully electric transportation and the advent of advanced portable electronics require secondary batteries with energy densities beyond what is currently commercially available. As lithium-ion batteries (LIBs) are approaching their theoretical maximum energy density at the cell level, replacing the typically employed graphite anode (372 mAh g<sup>-1</sup>) with Li metal (3860 mAh g<sup>-1</sup>) is regarded as a central strategy for exceeding 300 Wh kg<sup>-1.1</sup> However, the high volume change and inherent reactivity of metallic Li inevitably yield low Coulombic efficiency (CE) during cycling, limiting the cyclability of practical Li metal batteries (LMBs) due to the repeated consumption of Li<sup>+.2-4</sup>

The recent improvement of the cycling behavior of LMBs in laboratory settings has generally been achieved through Li surface coatings,<sup>5–8</sup> three-dimensional (3D) porous hosts for volume change mitigation, improved plating morphology,<sup>9–11</sup> and improved electrolyte composition.<sup>12–18</sup> Among these, improving the electrolyte composition may represent the most promising strategy due to its intrinsic ability to reduce parasitic side reactions via solid electrolyte interphase (SEI) formation. As such, recent demonstrations of practical Li metal pouch cells have largely revolved around the improvement of the electrolyte.<sup>16,18</sup> Among the known electrolyte components, ether solvents paired with lithium bis(fluorosulfonyl)imide

(LiFSI) salt are leading candidates due to the inherent reductive stability of ethers, in addition to the fluorine-donating capability of LiFSI. $^{13-17}$ 

However, the inherent reductive stability of ether solvents comes at the expense of their oxidative stability; it is well documented that such electrolytes fail to support cathode chemistries > 4V vs Li/Li<sup>+</sup> at dilute salt concentrations.<sup>19,20</sup> While the employment of high concentration, highly fluorinated salts has been shown to extend the oxidative stability limit,<sup>13,14</sup> it is worth noting that due to the high cost of salt in relation to typical solvents, dilute electrolytes are preferred from an economic perspective. As such, sulfur chemistries are an ideal cathode match for ether systems, which compensate for a reduced relative redox potential with an extreme increase in specific capacity (1672 mAh g<sup>-1</sup>). Moreover, the low cost of sulfur is a tremendous financial advantage over that of the conventional transition-metal oxide

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Figure 1. Working schematic of the LiNO<sub>3</sub>/SPAN composite cathode and the impact of electrolyte composition on the cycling stability.

cathodes. However, Li–S batteries are known to suffer from a polysulfide "shuttling" process, in which soluble polysulfides migrate from a cathode to anode in the cell and react with Li and are generally associated with the poor cycling stability of elemental S.<sup>21–23</sup> While polysulfide dissolution is considered a primary mechanism for deterioration in elemental S cathodes, the same phenomenon is also relied on during normal operation, which has been noted to have an acute effect on the scaling of Li–S full-cells.<sup>24</sup>

In light of these limitations, there is a clear need for highcapacity, low-voltage, low-cost cathode chemistries with characteristics that are desirable for scale-up. The sulfurized polyacrylonitrile (SPAN) cathode does not rely on soluble intermediates, owing to the chemical confinement of S in a polymer network.<sup>25-28</sup> Hence, SPAN is considered a promising intermediate cathode chemistry to provide high energy densities while elemental S cathodes remain under development. SPAN is capable of providing a specific capacity of >600 mAh  $g^{-1}$  while maintaining a low cost due to the abundance of its raw materials. While the cycling stability of SPAN in carbonate-based electrolytes is exceptional due to the insolubility of polysulfides in the electrolyte, the poor reductive stability of such solvents presents a compatibility issue with Li metal, rendering practical Li-SPAN cells untenable in such electrolytes. As such, there has been a significant research effort to enhance the cycling performance of SPAN in ether systems to enable low-cost, high energy density Li-SPAN batteries. Of note, it has been demonstrated that increasing the salt concentration of ether electrolytes, in addition to doping the SPAN cathode with Se, both present viable methods of improving this cycling performance.<sup>29,30</sup> However, as the primary advantage of SPAN is its low materials cost, these methods are suboptimal, as they both serve to substantially increase the overall cost of the Li-SPAN cell.

Besides these strategies, previous studies have indicated that  $LiNO_3$  serves to suppress the polysulfide dissolution found in elemental S cathodes.<sup>31–33</sup> Additionally, we previously observed that a 0.5 M LiNO<sub>3</sub> additive in the bulk electrolyte has a similar effect on the SPAN cathode, which is largely attributed to the cathode electrolyte interphase (CEI).<sup>34</sup> While the prospect of LiNO<sub>3</sub> in the bulk electrolyte is ostensibly a

promising one, it is crucial to note that dissolved NO<sub>3</sub><sup>-</sup> is known to react with the Li anode, which is progressively consumed during cycling.<sup>31</sup> Hence, the benefits of LiNO<sub>3</sub>-based electrolytes are fleeting, particularly when the electrolyte loading in the cell is lowered, which is crucial to achieving a high energy density and is rarely explored in academic studies.<sup>1</sup> To address the limitations of LiNO<sub>3</sub> additives to the bulk electrolyte, we propose the addition of LiNO<sub>3</sub> to the cathode slurry itself, which when paired with an electrolyte of sparing LiNO<sub>3</sub> solubility, should in principle provide a long-lasting NO<sub>3</sub><sup>-</sup> reservoir that is not prematurely consumed by the anode.

Herein, we demonstrate the reversible cycling of SPAN cathodes in dilute concentration ether using the aforementioned LiNO<sub>3</sub>||SPAN composite electrode in concert with an electrolyte of sparing LiNO<sub>3</sub> solubility. It was found that the combination of this LiNO<sub>3</sub>||SPAN composite cathode and a diethyl ether (DEE) electrolyte creates the conditions required to form a robust CEI. Furthermore, we demonstrate that this cycling stability is dependent on the low LiNO<sub>3</sub> solubility offered by the DEE system, as such a strategy is not viable in typical ether electrolytes based on 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME), which readily dissolve LiNO<sub>3</sub>, and allow for its consumption by the Li anode. A working schematic for this strategy is shown in Figure 1. This  $LiNO_3/$ SPAN composite system was found to retain 85% of its capacity in 1 M LiFSI DEE after 200 cycles, while only retaining 35% in the DOL/DME control under the same conditions. Through the implementation of X-ray photoelectron spectroscopy (XPS) and scanning transmission electron microscopy (STEM), it was found that the cycling stability offered in the DEE system coincided with the existence of a F-rich CEI layer, which was not shared by the LiNO<sub>3</sub>/SPAN cathode cycled in the DOL/DME system. Lastly, the viability of this strategy was also demonstrated in Li metal full-cells with practical 3.5 mAh cm<sup>-2</sup> SPAN and  $1\times$ excess (lithiated cathode),  $2.35 \times$  excess (delithiated cathode) Li loading, which provided 100 cycles of stable performance. This work reveals a facile method of achieving practical Li-SPAN cells while maintaining the low-cost advantages of every system component.



**Figure 2.** Cycling performance of SPAN cathodes. (a) Cycling performance of 0 wt % LiNO<sub>3</sub>/SPAN. Charge/discharge profiles in (b) 1 M LiFSI DOL/DME and (c) 1 M LiFSI DEE. (d) Cycling performance of 2 wt % LiNO<sub>3</sub>/SPAN. Charge/discharge profiles in (e) 1 M LiFSI DOL/DME and (f) 1 M LiFSI DEE.

#### RESULTS AND DISCUSSION

To determine the scientific viability of this proposed strategy, we select 2 wt % as a baseline  $NO_3$  amount; however, in principle, this value can be lowered as the electrolyte loading decreases and the cathode loading increases. The homogeneous distribution of the LiNO<sub>3</sub> in the slurry is facilitated by its solubility in *N*-methyl pyrrolidone (Figure S1a). Additionally, the selection of such an electrolyte that is simultaneously stable with Li metal and displays sparing solubility for LiNO<sub>3</sub> is crucial. As shown in Figure S1b, the DEE solvent serves the latter of these roles, where even 0.005 M salt was found to be insoluble. Furthermore, the Li cycling Coulombic efficiency was found to be 99.0% when paired with 1 M LiFSI (Figure S2).

To test the hypothesis laid out above, SPAN half-cells were then assembled with and without 2 wt % LiNO3 added to the cathode slurry and cycled in 1 M LiFSI DOL/DME (standard ether control) and 1 M LiFSI DEE. First, it is noteworthy that even with 0 wt % LiNO<sub>3</sub> in the slurry, the 1 M LiFSI DEE presents a substantial improvement compared with DOL/ DME (Figure 2a), where the cells were found to retain 376 and 259 mAh g<sup>-1</sup> after 100 cycles. Additionally, it was found that the DOL/DME electrolyte progressively dissolved the SPAN electrode, where the voltage profiles of the DOL/DME cell clearly display plateaus at ~2.05 V during discharge, as well as an activation process at  $\sim$ 2.2 V during charge, both of which are attributed to polysulfides (Figure 2b).<sup>29,34</sup> Furthermore, the DEE electrolyte was found to maintain Coulombic efficiency values > 99%, indicating that the shuttling of polysulfides is minimal (Figure 2c). The prevalence in this shuttling was also seen upon disassembly of the coin cells, where the DOL/DME electrolyte clearly exhibits a yellow color after 10 cycles, while the DEE does not (Figure S3). Despite this improvement, the 1 M LiFSI DEE system still fails to provide cyclability\_akin to that typically found from carbonate electrolytes.

This concern was found to be fully addressed with the addition of 2 wt % LiNO3 to the cathode slurry, specifically when this additive was paired with the 1 M LiFSI DEE electrolyte, retaining 596 and 541 mAh g<sup>-1</sup> after 100 and 200 cycles, respectively. While the performance substantially improved on the 0 wt % LiNO<sub>3</sub> cathode in 1 M LiFSI DEE, this was not the case in the 1 M LiFSI DOL/DME electrolyte (Figure 2d), where high LiNO<sub>3</sub> solubility would result in a 0.006 M LiNO<sub>3</sub> solution at 0.5 mAh cm<sup>-2</sup> cathode loading and 75  $\mu$ L of electrolyte. In fact, the capacity was found to fade at a rate comparable to that of the 0 wt % LiNO3 composite cathode, retaining 226 mAh g<sup>-1</sup> after 200 cycles. It was found that this poor cycling retention in addition to the lowered Coulombic efficiency was again attributed to a shuttling process, where the aforementioned polysulfide plateaus remain in the voltage curve of the DOL/DME cell (Figure 2e). The cell utilizing 1 M LiFSI DEE, on the other hand, exhibits no signs of such shuttling, with minimal changes in overpotential over the cycling period.

While the half-cell cycling results illustrate the viability of sustained additive release for the stabilization of the SPAN cathode, additional concerns regarding the practicality of the designed system should also be addressed. First, cycling stability endowed by the sparing dissolution of the 2 wt % LiNO<sub>3</sub> additive is also observed over long calendar times, where the same cell cycled in 1 M LiFSI DEE at C/10 was found to display a capacity fade from 610 to 607 mAh  $g^{-1}$ (99.5% retention) over 200 cycles (Figure S4). Hence, the advantages of this system design are not restricted to the relatively short calendar life of a typical high-rate half-cell testing. Furthermore, it is worth noting that the relatively low boiling point of DEE (~35 °C) raises a legitimate safety concern for scale-up. While this is indeed the case, it was also found that the same 2 wt % LiNO3 additive achieved a similar stabilizing effect in 1 M LiFSI di-n-propyl ether (DPE), whose solvent boiling point is ~90 °C (Figure S5).

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Figure 3. Ex situ XPS of delithiated 2 wt %  $LiNO_3$ /SPAN composite cathodes after 10 cycles in 1 M LiFSI DEE and DOL/DME: (a) S 2p and (b) F 1s spectra.



Figure 4. STEM analysis of 2 wt % LiNO<sub>3</sub>/SPAN composite cathodes after 10 cycles. (a) STEM image, (b) line scan EDS, and (c) the corresponding elemental analysis of SPAN cycled in 1 M LiFSI DOL/DME. (d) STEM image, (e) line scan EDS spectra, and (f) the corresponding elemental analysis of SPAN cycled in 1 M LiFSI DEE.

As our previous work has indicated that the role of  $LiNO_3$  in the improvement of the SPAN electrode is correlated with the presence of a robust CEI layer, we also investigated the interphase formed on the  $LiNO_3$ llSPAN composite electrodes after 10 cycles in 1 M LiFSI DEE and DOL/DME via XPS.<sup>34</sup> As shown in Figure 3a, it is first noteworthy that a substantial increase in the Li–S species is observed when cycling in the DOL/DME electrolyte, even when delithiated. As the electrode cycled in DEE presents a substantial reduction in this signature peak, these are ascribed to residual polysulfides. Additionally, it is seen that there is a substantial increase in  $SO_4/SO-F$  signal.  $SO_4$  species have been previously observed in elemental S electrodes in the presence of LiNO<sub>3</sub> and have been hypothesized to be advantageous in the suppression of the polysulfide shuttle.<sup>33</sup> Despite the change in cathode chemistry from elemental S to SPAN, its presence here, particularly with its high prevalence in the DEE electrolyte, is also correlated to the improved cycling performance. The F 1s spectra were subjected to a similar analysis, where it was found that the 2 wt % LiNO<sub>3</sub> llSPAN electrode cycled in DEE showed

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Figure 5. Demonstration of Li-SPAN full-cells utilizing 2 wt % LiNO<sub>3</sub>/SPAN composite cathodes. (a) Schematic of the cell design. (b) Cycling performance, voltage profiles in (c) 1 M LiFSI DEE and (d) 1 M LiFSI DOL/DME.

a substantially more intense Li–F signal than that cycled in DOL/DME (Figure 3b). Additionally, a new peak for S–O–F, which was not observed in the electrode cycled in DOL/DME at all was found in the DEE cycled electrode, which was determined due to the absence of the C–F peak in the C 1s spectra (Figure S6). The prevalence of S=O species in the composite electrode cycled in 1 M LIFSI DEE is also observed in the Fourier transform infrared spectra (FT-IR), which is shown in Figure S7. It is clear from the XPS analysis that these S–O species observed coincide with the improved cycling behavior of the 2 wt % LiNO<sub>3</sub>||SPAN electrode in 1 M LiFSI DEE, which is likely a result of the reduced polysulfide and LiNO<sub>3</sub> solubility of the DEE solvent.

The effect of the LiNO<sub>3</sub> cathode on the Li counter electrode was also investigated. As shown in Figure S8, there were negligible nitrogen-containing decomposition products found on the Li electrode when examined under XPS. While these species are commonly seen in LiNO<sub>3</sub>-based ether electrolytes, their absence here is likely due to the extremely reduced amount compared to these typical systems (0.006 M in the fully dissolved case). Additionally, scanning electron microscopy (SEM) studies revealed that while the DEE electrolyte was found to produce more uniform Li morphologies as compared to DOL/DME, the impact of the LiNO<sub>3</sub> cathode additive was not significant (Figure S9).

To further elucidate the CEI characteristics of the LiNO<sub>3</sub>|| SPAN composite electrode, STEM was also carried out on SPAN particles subject to the same cycling conditions as the XPS and FT-IR tests. Images of SPAN particles from the 2 wt % LiNO<sub>3</sub>||SPAN composite electrodes cycled in 1 M LiFSI DOL/DME and 1 M LiFSI DEE are shown in Figure 4a,d. It is worth mentioning that the SPAN material is amorphous and therefore not easily differentiated from its interphase from phase contrast. To probe the existence of the said interphase, line scan energy-dispersive X-ray spectroscopy (EDS) was carried out to track the atomic prevalence of different species in the SPAN particles at various locations. These locations are denoted as 1-5, 1 being the edge of the particle. As shown in Figure 4b,c, the SPAN cycled in 1 M LiFSI DOL/DME was found to have negligible contributions from fluoride at its interphase, as well as a relatively low prevalence of oxygen (~6%), which supports the XPS and IR results that indicate few SO<sub>4</sub>, SO<sub>x</sub>F, and LiF species were formed during cycling, contributing to the poor cycling stability. It is also important to note that the sulfur content is substantially lower than that of the pristine SPAN (~45%).

However, the composite electrode cycled in 1 M LiFSI DEE does not share these characteristics. As shown in Figure 4e,f, the fluorine content was determined to be substantially higher, 21% at the edge of the particle, with a correspondingly high oxygen content of 19%, once again indicative of the presence of Li-F, S-O-F, and SO<sub>4</sub> species in the CEI. When crossexamined under XPS (Figure S10), it was found that these SO<sub>4</sub>/S-O-F species are distributed in the CEI disproportionately on the outside (position 1) and slowly decrease in prevalence when moving toward the SPAN particle. Additionally, it was observed that the nitrogen content in the interphase was 2.3% at position 1, which implies that the LiNO<sub>3</sub> additive does not incorporate itself into the interphase as a solid species. Although the inorganic species were found to be prevalent in the DEE cycled system, the sulfur content was found to slowly increase as the center of the SPAN particle was approached, from 18.8 to 40.5% from positions 1-5, respectively. These STEM results once again indicate that a protective interphase is formed when the LiNO<sub>3</sub>||SPAN composite electrode is cycled in the DEE electrolyte, while the DOL/DME system with high LiNO<sub>3</sub> solubility does not allow for this formation.

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Despite these trends, it is still important to note that there is no defined causal string that reveals the true role of LiNO<sub>3</sub> in the stabilization of this cathode chemistry. While LiNO<sub>3</sub> has previously been hypothesized to reduce the solubility of polysulfides in elemental S cathodes due to a catalytic effect,<sup>32</sup> conflicting reports also indicate that its role is to create a CEI layer that suppresses the diffusion of these species to the anode.<sup>33</sup> As the role of LiNO<sub>3</sub> is still up for debate in the elemental S space, it is also unclear whether the stabilization of the SPAN cathode observed here is a result of the elimination of these polysulfides, which may serve to react with species at the interphase that would otherwise form a CEI or the formation of the CEI itself. However, in terms of system design, either of these mechanisms results in a substantially improved cycling performance with the introduction of a minimal LiNO3 additive.

Lastly, to demonstrate the viability of this SPAN stabilization at a more practical level, Li metal full-cells were assembled with a 3.5 mAh cm<sup>-2</sup> 2 wt % LiNO<sub>3</sub>||SPAN composite electrode and a 40  $\mu$ m Li metal anode, which corresponds to a onefold excess when the SPAN is fully lithiated and 2.35× excess in the delithiated state (Figure 5a). These full-cells were then subjected to cycling in both electrolytes, where the cell employing 1 M LiFSI DEE exhibited substantially improved cycling compared to that of 1 M LiFSI DOL/DME, which retained 360 and 67 mAh  $g^{-1}$ , respectively. The voltage profiles for these cells are shown in Figure 5c,d, where it was observed that the deterioration of the DOL/DME cell was found to once again relate to polysulfide dissolution, whereas the DEE electrolyte maintained the character of the SPAN conversion profile. It is also noteworthy that the 1× LillSPAN (2 wt % LiNO<sub>3</sub>) cell cycled in 1 M LiFSI DEE was found to experience a coinciding increase in polarization as the cycle progressed, which may be related to the gradual exhaustion of the Li reservoir, where an increased porosity in plated Li is commonly observed.<sup>2</sup> These full-cell results not only indicate that the combination of the LiNO<sub>3</sub> composite electrode and the DEE electrolyte enables a reversible cathode and anode cycling in separate half-cells but also indicate that these separate results can be combined at practical electrode loadings in the same cell.

#### CONCLUSIONS

Through the combination of a 1 M LiFSI DEE electrolyte, which exhibits sparing LiNO3 solubility as well as reversible Li metal performance, and a LiNO<sub>3</sub>||SPAN composite electrode, the reversible cycling of the SPAN cathode in an economical ether electrolyte was demonstrated. Specifically, the sustained release of LiNO3 in the cathode enabled by the sparing solubility of LiNO3 in DEE resulted in the formation of a protective CEI that was largely composed of Li-F, SO<sub>4</sub>, and S-O-F species. This interphase was explored via XPS, FT-IR, and STEM, all of which indicated that the DEE electrolyte enables the formation of this interphase, while the DOL/DME electrolyte does not, which is likely due to the high solubility of LiNO<sub>3</sub>. Lastly, to provide a practical demonstration of the viability of this method, the stability of the composite electrode and DEE electrolyte was again confirmed in onefold Lill3.5 mAh cm<sup>-2</sup> full cells. Unlike previous approaches, which have sacrificed the intrinsically low system cost offered by SPAN, the scalable strategy demonstrated here represents a viable method for achieving stable LillSPAN full-cells at a low overall system cost.

## ASSOCIATED CONTENT

### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.1c00257.

Materials and methods, characterization, and electrochemical testing details; optical photographs of LiNO<sub>3</sub> solutions; cycling performance of LillCu cells; optical photographs of disassembled half-cells; 0.1C rate cycling of 2 wt % LiNO<sub>3</sub> SPAN in 1 M LiFSI DEE; cycling of SPAN cathodes in 1 M LiFSI dipropyl ether; extended ex situ XPS of cycled SPAN cathodes; ex situ FT-IR of 2 wt % SPAN after 10 cycles; and ex situ SEM of cycled Li anodes (PDF)

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#### **Author Contributions**

J.H. and P.L. conceived the original idea. P.L. directed the project. J.H., Q.Y., H.L., and Z.W. carried out the experiments. Q.Y., X.X., H.Z., and Y.Y. assisted with characterization. J.H.,

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Z.C., and P.L. wrote the paper. All authors discussed the results and commented on the manuscript.

#### Notes

The authors declare no competing financial interest.

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## REFERENCES

(1) Liu, J.; Bao, Z.; Cui, Y.; Dufek, E. J.; Goodenough, J. B.; Khalifah, P.; Li, Q.; Liaw, B. Y.; Liu, P.; Manthiram, A.; Meng, Y. S.; Subramanian, V. R.; Toney, M. F.; Viswanathan, V. V.; Whittingham, M. S.; Xiao, J.; Xu, W.; Yang, J.; Yang, X.-Q.; Zhang, J.-G. Pathways for Practical High-Energy Long-Cycling Lithium Metal Batteries. *Nat. Energy* **2019**, *4*, 180–186.

(2) Xu, W.; Wang, J.; Ding, F.; Chen, X.; Nasybulin, E.; Zhang, Y.; Zhang, J.-G. Lithium Metal Anodes for Rechargeable Batteries. *Energy Environ. Sci.* **2014**, *7*, 513–537.

(3) Li, S.; Jiang, M.; Xie, Y.; Xu, H.; Jia, J.; Li, J. Developing High-Performance Lithium Metal Anode in Liquid Electrolytes: Challenges and Progress. *Adv. Mater.* **2018**, *30*, No. 1706375.

(4) Lin, D.; Liu, Y.; Cui, Y. Reviving the Lithium Metal Anode for High-Energy Batteries. *Nat. Nanotechnol.* **2017**, *12*, 194–206.

(5) Li, N.-W.; Yin, Y.-X.; Yang, C.-P.; Guo, Y.-G. An Artificial Solid Electrolyte Interphase Layer for Stable Lithium Metal Anodes. *Adv. Mater.* **2016**, *28*, 1853–1858.

(6) Liang, X.; Pang, Q.; Kochetkov, I. R.; Sempere, M. S.; Huang, H.; Sun, X.; Nazar, L. F. A Facile Surface Chemistry Route to a Stabilized Lithium Metal Anode. *Nat. Energy* **2017**, *2*, No. 652.

(7) Wang, G.; Xiong, X.; Xie, D.; Fu, X.; Lin, Z.; Yang, C.; Zhang, K.; Liu, M. A Scalable Approach for Dendrite-Free Alkali Metal Anodes via Room-Temperature Facile Surface Fluorination. *ACS Appl. Mater. Interfaces* **2019**, *11*, 4962–4968.

(8) Zhou, H.; Yu, S.; Liu, H.; Liu, P. Protective Coatings for Lithium Metal Anodes: Recent Progress and Future Perspectives. *J. Power Sources* **2020**, *450*, No. 227632.

(9) Ke, X.; Liang, Y.; Ou, L.; Liu, H.; Chen, Y.; Wu, W.; Cheng, Y.; Guo, Z.; Lai, Y.; Liu, P.; Shi, Z. Surface Engineering of Commercial Ni Foams for Stable Li Metal Anodes. *Energy Storage Mater.* **2019**, *23*, 547–555.

(10) Liu, H.; Yue, X.; Xing, X.; Yan, Q.; Huang, J.; Petrova, V.; Zhou, H.; Liu, P. A Scalable 3D Lithium Metal Anode. *Energy Storage Mater.* **2019**, *16*, 505–511.

(11) Niu, C.; Pan, H.; Xu, W.; Xiao, J.; Zhang, J.-G.; Luo, L.; Wang, C.; Mei, D.; Meng, J.; Wang, X.; Liu, Z.; Mai, L.; Liu, J. Self-Smoothing Anode for Achieving High-Energy Lithium Metal Batteries under Realistic Conditions. *Nat. Nanotechnol.* **2019**, *14*, 594–601.

(12) Chen, S.; Zheng, J.; Mei, D.; Han, K. S.; Engelhard, M. H.; Zhao, W.; Xu, W.; Liu, J.; Zhang, J.-G. High-Voltage Lithium-Metal Batteries Enabled by Localized High-Concentration Electrolytes. *Adv. Mater.* **2018**, *30*, No. 1706102. (13) Qian, J.; Henderson, W. A.; Xu, W.; Bhattacharya, P.; Engelhard, M.; Borodin, O.; Zhang, J.-G. High Rate and Stable Cycling of Lithium Metal Anode. *Nat. Commun.* **2015**, *6*, No. 6362. (14) Alvarado, J.; Schroeder, M. A.; Pollard, T. P.; Wang, X.; Lee, J. Z.; Zhang, M.; Wynn, T.; Ding, M.; Borodin, O.; Meng, Y. S.; Xu, K. Bisalt Ether Electrolytes: A Pathway towards Lithium Metal Batteries with Ni-Rich Cathodes. *Energy Environ. Sci.* **2019**, *12*, 780–794.

(15) Cao, X.; Ren, X.; Zou, L.; Engelhard, M. H.; Huang, W.; Wang, H.; Matthews, B. E.; Lee, H.; Niu, C.; Arey, B. W.; Cui, Y.; Wang, C.; Xiao, J.; Liu, J.; Xu, W.; Zhang, J.-G. Monolithic Solid–Electrolyte Interphases Formed in Fluorinated Orthoformate-Based Electrolytes Minimize Li Depletion and Pulverization. *Nat. Energy* **2019**, *4*, 796–805.

(16) Niu, C.; Lee, H.; Chen, S.; Li, Q.; Du, J.; Xu, W.; Zhang, J.-G.; Whittingham, M. S.; Xiao, J.; Liu, J. High-Energy Lithium Metal Pouch Cells with Limited Anode Swelling and Long Stable Cycles. *Nat. Energy* **2019**, *4*, 551–559.

(17) Ren, X.; Zou, L.; Cao, X.; Engelhard, M. H.; Liu, W.; Burton, S. D.; Lee, H.; Niu, C.; Matthews, B. E.; Zhu, Z.; Wang, C.; Arey, B. W.; Xiao, J.; Liu, J.; Zhang, J.-G.; Xu, W. Enabling High-Voltage Lithium-Metal Batteries under Practical Conditions. *Joule* **2019**, *3*, 1662–1676.

(18) Weber, R.; Genovese, M.; Louli, A. J.; Hames, S.; Martin, C.; Hill, I. G.; Dahn, J. R. Long Cycle Life and Dendrite-Free Lithium Morphology in Anode-Free Lithium Pouch Cells Enabled by a Dual-Salt Liquid Electrolyte. *Nat. Energy* **2019**, *4*, 683–689.

(19) Jiao, S.; Ren, X.; Cao, R.; Engelhard, M. H.; Liu, Y.; Hu, D.; Mei, D.; Zheng, J.; Zhao, W.; Li, Q.; Liu, N.; Adams, B. D.; Ma, C.; Liu, J.; Zhang, J.-G.; Xu, W. Stable Cycling of High-Voltage Lithium Metal Batteries in Ether Electrolytes. *Nat. Energy* **2018**, *3*, 739–746.

(20) Ren, X.; Zou, L.; Jiao, S.; Mei, D.; Engelhard, M. H.; Li, Q.; Lee, H.; Niu, C.; Adams, B. D.; Wang, C.; Liu, J.; Zhang, J.-G.; Xu, W. High-Concentration Ether Electrolytes for Stable High-Voltage Lithium Metal Batteries. *ACS Energy Lett.* **2019**, *4*, 896–902.

(21) Pang, Q.; Liang, X.; Kwok, C. Y.; Nazar, L. F. Advances in Lithium–Sulfur Batteries Based on Multifunctional Cathodes and Electrolytes. *Nat. Energy* **2016**, *1*, 1–11.

(22) Kang, N.; Lin, Y.; Yang, L.; Lu, D.; Xiao, J.; Qi, Y.; Cai, M. Cathode Porosity Is a Missing Key Parameter to Optimize Lithium-Sulfur Battery Energy Density. *Nat. Commun.* **2019**, *10*, No. 4597.

(23) Dörfler, S.; Althues, H.; Härtel, P.; Abendroth, T.; Schumm, B.; Kaskel, S. Challenges and Key Parameters of Lithium-Sulfur Batteries on Pouch Cell Level. *Joule* **2020**, *4*, 539–554.

(24) Shi, L.; Bak, S.-M.; Shadike, Z.; Wang, C.; Niu, C.; Northrup, P.; Lee, H.; Baranovskiy, A. Y.; Anderson, C. S.; Qin, J.; Feng, S.; Ren, X.; Liu, D.; Yang, X.-Q.; Gao, F.; Lu, D.; Xiao, J.; Liu, J. Reaction Heterogeneity in Practical High-Energy Lithium–Sulfur Pouch Cells. *Energy Environ. Sci.* **2020**, *13*, 3620–3632.

(25) Wei, S.; Ma, L.; Hendrickson, K. E.; Tu, Z.; Archer, L. A. Metal–Sulfur Battery Cathodes Based on PAN–Sulfur Composites. J. Am. Chem. Soc. 2015, 137, 12143–12152.

(26) Liu, H.; Holoubek, J.; Zhou, H.; Chen, A.; Chang, N.; Wu, Z.; Yu, S.; Yan, Q.; Xing, X.; Li, Y.; Pascal, T. A.; Liu, P. Ultrahigh Coulombic Efficiency Electrolyte Enables LillSPAN Batteries with Superior Cycling Performance. *Mater. Today* **2021**, *42*, 17–28.

(27) Yang, H.; Chen, J.; Yang, J.; Wang, J. Prospect of Sulfurized Pyrolyzed Poly(Acrylonitrile) (S@pPAN) Cathode Materials for Rechargeable Lithium Batteries. *Angew. Chem., Int. Ed.* **2020**, *59*, 7306–7318.

(28) Zhao, M.; Li, B.-Q.; Peng, H.-J.; Yuan, H.; Wei, J.-Y.; Huang, J.-Q. Lithium–Sulfur Batteries under Lean Electrolyte Conditions: Challenges and Opportunities. *Angew. Chem., Int. Ed.* **2020**, *59*, 12636–12652.

(29) Zhou, J.; Guo, Y.; Liang, C.; Cao, L.; Pan, H.; Yang, J.; Wang, J. A New Ether-Based Electrolyte for Lithium Sulfur Batteries Using a S@pPAN Cathode. *Chem. Commun.* **2018**, *54*, 5478–5481.

(30) Chen, X.; Peng, L.; Wang, L.; Yang, J.; Hao, Z.; Xiang, J.; Yuan, K.; Huang, Y.; Shan, B.; Yuan, L.; Xie, J. Ether-Compatible Sulfurized Polyacrylonitrile Cathode with Excellent Performance Enabled by

Fast Kinetics via Selenium Doping. Nat. Commun. 2019, 10, No. 1021.

(31) Li, W.; Yao, H.; Yan, K.; Zheng, G.; Liang, Z.; Chiang, Y.-M.; Cui, Y. The Synergetic Effect of Lithium Polysulfide and Lithium Nitrate to Prevent Lithium Dendrite Growth. *Nat. Commun.* **2015**, *6*, No. 7436.

(32) Zhang, S. S. A New Finding on the Role of LiNO3 in Lithium-Sulfur Battery. J. Power Sources 2016, 322, 99–105.

(33) Zhang, L.; Ling, M.; Feng, J.; Mai, L.; Liu, G.; Guo, J. The Synergetic Interaction between LiNO3 and Lithium Polysulfides for Suppressing Shuttle Effect of Lithium-Sulfur Batteries. *Energy Storage Mater.* **2018**, *11*, 24–29.

(34) Xing, X.; Li, Y.; Wang, X.; Petrova, V.; Liu, H.; Liu, P. Cathode Electrolyte Interface Enabling Stable Li–S Batteries. *Energy Storage Mater.* **2019**, *21*, 474–480.