Development of Li/FeS₂ rechargeable batteries has been hampered by their short cycle life. In this paper, we start with the fundamental chemistry of FeS₂ in a non-aqueous liquid electrolyte to analyze the capacity fading mechanism of Li/FeS₂ batteries and propose three facile strategies for stabilizing capacity. It is repeatedly observed that the capacity fading of Li/FeS₂ cells follows a general mode consisting of a fast fading stage as Region 1, a slow fading stage as Region 2, and an accelerated fading stage as Region 3. We found that Region 1 is mainly attributed to the dissolution of lithium polysulfide leading to the loss of sulfur active material, and that Region 3 is mainly associated with the poor morphology of Li deposition resulting in the localized electric circuit shortening. The powder-like, small and loose Li particles not only react with electrolyte solvents drying-out the cell but also penetrate across the separator shortening the cell. Based on the above finding, the cycle life of Li/FeS₂ cells was improved by adding vinylene carbonate as the electrolyte additive, increasing mechanical pressure between two electrodes, and placing a carbon interlayer between the FeS₂ cathode and separator, respectively.

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The study on non-aqueous liquid electrolyte Li/FeS₂ rechargeable batteries has lasted for almost three decades, however, the advance toward commercialization is still very limited due to the poor cyclability of FeS₂ cathode material and poor understanding on the redox mechanism of FeS₂ in organic electrolytes. Most of previous efforts in improving the cyclability of Li/FeS₂ cells have been focused on either the FeS₂ material or electrolyte based on a redox mechanism consisting of a series of Li⁺ intercalation, conversion reaction, and disproportionation, as described by Eqs. 1–4.8–13

\[ \text{FeS}_2 + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Li}_2\text{FeS}_2 \]  

\[ \text{Li}_2\text{FeS}_2 + 2\text{Li}^+ + 2\text{e}^- \leftrightarrow \text{Fe} + 2\text{Li}_2\text{S} \]  

\[ \text{Li}_2\text{FeS}_2 - \text{xe}^- \leftrightarrow \text{Li}_{2-x}\text{FeS}_2 + x\text{Li}^+ \]  

\[ \text{Li}_{2-x}\text{FeS}_2 - (2 - x)\text{e}^- \rightarrow (2 - x)\text{Li}^+ + \text{FeS}_2 + (2 - x)\text{S} \quad x \geq 0.8 \]  

The first discharge of Li/FeS₂ cells has been intensively investigated and well understood. Under the thermodynamic equilibrium condition that is typically obtained by either reducing FeS₂ particle size or lowering the current density, the first discharge follows a Li⁺ intercalation (Eq. 1) and a conversion reaction (Eq. 2) in sequence, displaying two voltage plateaus with an equal capacity at 1.7 and 1.5 V, respectively.8,14 The recharge becomes much more complicated, first experiences a reversible conversion (Eq. 2) to form a Li₂FeS₂ intermediate, followed by a reversible Li⁺ deintercalation (Eq. 3) to form Li₂-xFeS₂ that undergoes an irreversible disproportionation (Eq. 4) producing nonstoichiometric FeS₂ and elemental sulfur as the x value in Li₂-xFeS₂ reaches and exceeds 0.8.8 After this, the resultant sulfur serves as an independent cathode material and hence induces the same problems as observed in the conventional Li/S cells, such as dissolution of lithium polysulfide (Li₂Sₙ with n > 2), redox shuttle, and other resultant parasitic reactions.15 Based on the above redox mechanism, the C-FeS₂ composites16–21 and carbon-modified/wrapped FeS₂ materials22–25 with various novel structures, such as nanocrystals, silica microspheres,26,27 and core-shell structures,28 have been widely synthesized to improve the cyclability and power capability of the Li/FeS₂ cells. On the other hand, the solid-state electrolyte,1,12–32 polymer composite electrolyte,6,11,29,30 and ionic liquid31,32 have been proposed to prevent the dissolution of Li₂Sₙ. More recently, the strong nucleophilic reactivity of polysulfide anions has come into attention, and it has been recognized that the carbonate-based electrolytes currently used in state-of-the-art Li-ion batteries are chemically incompatible with the Li/FeS₂ chemistry.1,27,34,35 All the strategies cited above were focused on either the FeS₂ cathode or the electrolyte with little attention to the Li anode.

In our recent review on a number of previous publications,1 we found that the initial FeS₂ cannot be recovered once it converts to metallic Fe and Li₂S in the first discharge. The subsequent charging and cycling are conducted through the conversion-type Li/FeS₂ and Li/Li₂S redox couples. In other words, upon the first discharge the Li/FeS₂ battery turns to the combination of a Li/FeS₂ cell and a Li/S cell.1,2,36 In addition, we noticed that the Li anode plays an even more important role in affecting the cycle life of Li/FeS₂ cells. Based on our new insight into the redox mechanism, in this paper we analyze the capacity fading mechanism of Li/FeS₂ cells and demonstrate three facile strategies for improving the cyclability of Li/FeS₂ cells.

**Experimental**

Commercial FeS₂ powder was purchased from Sigma-Aldrich and used as received. Using poly(acrylonitrile-methyl methacrylate) (AN-MMA, AN/MMA = 94:6, MW = 100,000, Polysciences, Inc.) as the binder and N-methyl pyrrolidone as the solvent, a slurry consisting of 75% FeS₂, 10% Super-P carbon, 10% Ketjenblack EC-300JD carbon black and 5% binder by weight was prepared and coated onto a carbon-coated aluminum foil. After drying in air, the FeS₂ cathode was punched into 1.27 cm² circular discs and further dried at 80°C under vacuum for 16 h. Resultant cathode had a FeS₂ loading of 2.2 ± 0.1 mg cm⁻². Using the same method, a slurry consisting of 45% Super-P carbon, 45% Ketjenblack EC-300JD carbon black and 10% ANMMA was coated onto a Celgard 3410 membrane, which gave a total 0.3 mg cm⁻² of carbon loading. A solution consisting of either a 1.0 m lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) or a 0.5 m LiI dissolved in a 1:1 (wt) mixture of dimethyl ether (DME) and 1,3-dioxolane (DOL) was used as the electrolyte. Using a Celgard 3410 membrane as the regular separator, the 2030-size Li/FeS₂ coin cell was assembled and filled with 15 ȝL electrolyte. The cell was cycled galvanostatically at 0.5 mA cm⁻² between 1.0 V and 2.6 V on a Maccor Series 4000 cycler. In consideration of the possible redox shuttle, a capacity equal to 110% of the last discharge capacity was applied as an additional limit to control the charging process.

Phase structure of the FeS₂ powder and the cycled cathode was analyzed by X-ray diffraction (XRD) using a Rigaku Ultima III diffractometer (Cu Kα radiation). The cathode was collected from a cycled cell and washed three times using a 1:1 DME/DOL mixed solvent in a dry room. Morphology of the FeS₂ powder and carbon interlayer

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**Mechanism and Solution for the Capacity Fading of Li/FeS₂ Battery**

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was observed and conducted Energy Dispersive X-Ray (EDX) analy-
sis on a Quanta 200F scanning electron microscope (SEM). For EDX
analysis, the carbon interlayer was collected without washing from
a Li/FeS$_2$ cell cycled to a certain state and then was transferred to
a carbon-based conductive tape for SEM observation. AC-impedance
of the Li/FeS$_2$ cell was measured at open-circuit potential over a
frequency range from 100 kHz to 0.01 Hz with a 10 mV oscilla-
tion by a Solartron SI 1287 Electrochemical Interface and a SI 1260
Impedance/Gain-Phase Analyzer.

Results and Discussion

**Commercial FeS$_2$ material.**—Fig. 1 shows the XRD pattern and
SEM image of a commercial FeS$_2$ powder. It can be seen from Fig. 1a
that all XRD peaks are well indexed to the standard iron pyrite (FeS$_2$,
PDF card No. 9000594), featured by a Pa$_3$ space group consisting
of a Fe face-centered cubic sublattice, into which the S ions are em-
bodied. In the first bonding sphere, the Fe atoms are surrounded by
six S nearest atoms in a distorted octahedral arrangement, and the S
atoms have bonds with three Fe and one other S atom.$^{37}$ Mössbauer
spectroscopy$^{38}$ and Fe K-edge X-ray absorption fine structure$^{10}$ have
verified that the Fe ions are in a divalent (Fe$^{2+}$) state and the disulfide
(S−S)$^{2-}$ anions are in closed shell entities with each S bound to one
Fe and one other S atom.$^{35}$ The SEM image (Fig. 1b) shows that the FeS$_2$
particles are in shapes of irregular rock fragments and the size ranges
from a several to tens of micrometers. There are numerous tiny white
spots randomly distributed on the surfaces and edges of each particle.
These white spots, although not detected by XRD, are believed to be
the oxide and sulfate formed by the reaction of FeS$_2$ with water and
oxygen in air.$^{6,39}$

**Fundamental chemistry of Li/FeS$_2$ cell.**—Fig. 2 indicates voltage
profiles of the first three cycles for a typical Li/FeS$_2$ cell. The first
discharge consists of only a single voltage plateau at ∼1.5 V with
a 908 mAh g$^{-1}$ of specific capacity, which is slightly higher than
the theoretical value (894 mAh g$^{-1}$ based on a four-electron overall
reduction as expressed by Eq. 1 and Eq. 2) probably due to the reduc-
tion of small amount of oxidized products, such as Fe$_3$O$_4$, Fe$_2$O$_3$, and
FeS$_n$O$_x$ etc., on the surface of FeS$_2$ particles.$^{6,39,60}$ The single voltage
plateau is ascribed to the fact that the Li/FeS$_2$ cell was discharged
under a thermodynamic non-equilibrium condition because of rather
large FeS$_2$ particle size (up to tens of micrometers) and relatively
high discharge current density (0.5 mA cm$^{-2}$).$^{8,14}$ It is distinctly in-
dicated in Fig. 2 that the Li/FeS$_2$ cell no longer follows the voltage
profile of the first discharge once it is fully discharged to 1.0 V. Since
the 1$^{st}$ charge, the LiFeS$_2$ cell has presented two voltage plateaus at
∼2.1 V and ∼1.5 V in discharge; at ∼2.4 V and ∼1.8 V in charge,
which can be attributed to two reversible redox couples, as proposed by
Eq. 5 and Eq. 6.$^{1,21,35,36}$

\[
\text{Li}_2\text{Sn}^{2+} + (2n - 2) \text{Li}^+ + (2n - 2) \text{e}^- \leftrightarrow n\text{Li}_2\text{S} \quad [5]
\]

\[
\text{FeS} + 2\text{Li}^+ + 2\text{e}^- \leftrightarrow \text{Fe} + \text{Li}_2\text{S} \quad [6]
\]

There is a noticeable loss in the capacity from the 1$^{st}$ discharge
to the 1$^{st}$ charge mainly due to the dissolution of long-chain Li$_2$Sn
formed during recharge into an organic electrolyte. The absence of
the upper discharge voltage plateau at ∼2.3 V suggests that elemental
sulfur may not be formed in charging of a Li/FeS$_2$ cell. The above
redox mechanism is partially supported by the ex-situ XRD analysis
as indicated in Fig. 3. In all XRD patterns, there are two small peaks
of metallic Al, which are raised from the carbon-coated Al substrate
and taken as the background. The pristine cathode consists entirely
of characteristic peaks of pyrite FeS$_2$ (Fig. 3a). After discharging to
1.0 V (Fig. 3b), all these peaks disappear, instead, some weak and
broad peaks related to metallic Fe, Li$_2$S and S show up, in which the
diffraction peaks of Fe and Al are overlapped and elemental sulfur
may be formed by the oxidation of Li$_2$S during the preparation and

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Figure 1. A commercial FeS$_2$ powder. (a) XRD pattern, and (b) SEM image.

Figure 2. Voltage profile of the first three cycles of a Li/FeS$_2$ cell.
has been repeatedly observed from a number of coin cells with small variation in the cycle number of each region. According to the capacity fading rate, the cycle life of a Li/FeS$_2$ cell can be divided into three regions: a fast fading stage from the 1$^{st}$ to $\sim$10$^{th}$ cycle as Region 1, a slow fading stage from $\sim$10$^{th}$ to 75$^{th}$ cycle as Region 2, and an accelerated fading stage from $\sim$75$^{th}$ cycle until cell’s death as Region 3. Except for the 1$^{st}$ cycle, Region 1 and Region 2 feature high coulombic efficiency ($\sim$99%), whereas Region 3 features low coulombic efficiency, in which most of charging processes were found to be terminated by the preset capacity limit (namely 110% of the last discharge capacity), instead by the charge cutoff voltage (2.6 V).

The capacity fading mode observed above can be attributed to the different roles of the Li$_2$Sn dissolution and Li deposits morphology in affecting the cycle life of Li/FeS$_2$ cells, which can be understood on the basis of Eq. 5 and Eq. 6.

Capacity fading in Region 1 is mainly attributed to the loss of sulfur active material, caused by the unavoidable dissolution of Li$_2$Sn in an organic electrolyte. Similarly to that observed in conventional Li/S cells, the first recharge loses a lot of capacity because Li$_2$Sn dissolves into a fresh electrolyte and some of dissolved Li$_2$Sn cannot diffuse back to the cathode in the subsequent discharge. This process (Region 1) lasts, although slows down with cycle number, until the concentration of Li$_2$Sn reaches equilibrium in the electrolyte throughout the cell (including the dead corner). In order to verify this hypothesis, we employed a sulfur-free electrolyte (i.e., a 0.5 m LiI 1:1 DME/DOL solution) and a carbon interlayer, as schematically illustrated in Fig. 5a, to trap the dissolved Li$_2$Sn in the 1$^{st}$ discharging and charging cycle. In this cell (Fig. 5a), the carbon interlayer is sandwiched between two separators without physical contact with the FeS$_2$ cathode. The SEM image and EDX analysis results of the carbon interlayer collected at the discharged state (1.0 V) and charged state (2.6 V), respectively, are compared Fig. 5b. In the discharged state (upper one in Fig. 5b), the carbon interlayer does not trap any sulfur species, agreeing with Eq. 1 and Eq. 2 that the FeS$_2$ converts to metallic Fe and Li$_2$S entirely through solid-to-solid phase transitions without forming any soluble Li$_2$Sn species. In the charged state (lower one in Fig. 5b), however, the carbon interlayer shows 0.93 wt% sulfur, indicating significant dissolution of Li$_2$Sn. Therefore, the same problems in relation to the dissolution of Li$_2$Sn as observed in the conventional Li/S cells are also present in the Li/FeS$_2$ cells. The loss of sulfur active material by the dissolution of Li$_2$Sn contributes the major to the capacity fading in Region 1.

The slow capacity fading in Region 2 is ascribed to the continued, but much slowed down, loss of sulfur species by the dissolution of Li$_2$Sn and the progressive growth of resistive surface layer on the Li anode by the chemical or electrochemical reduction of the dissolved Li$_2$Sn to insoluble Li$_2$S or Li$_2$S on the Li surface.$^{15,41}$ Although the loss of sulfur species from the FeS$_2$ cathode and the growth of surface layer on the Li anode accompany with the entire life of a Li/FeS$_2$ cell, the accelerated capacity fading in Region 3 is more associated with the localized electric circuit shortening, which can be evidenced by comparing the voltage profiles in Region 2 and Region 3, as indicated by Fig. 6. In Region 2 (Fig. 6a), coulombic efficiency for all cycles retained $\sim$99% although capacity declines due to the progressive loss of sulfur species. We are interested in finding that the discharge voltage profile gradually splits into multiple plateaus from the normal two plateaus with an increase in the cycle number. This is probably due to the drying-out of liquid electrolyte as a result of the parasitic reactions between the metallic Li and electrolyte solvent.$^{42}$ Because of a solubility issue, the multiple-stage reduction of Li$_2$Sn to Li$_2$S is partially transitioned to solid-to-solid reactions, which hence leads to multiple discharge voltage plateaus. On the other hand, in Region 3 (Fig. 6b), the coulombic efficiency dramatically decreases with the cycle number until reaching a constant of 91% (i.e., a number determined by the preset charging capacity equal to 110% of the last discharge capacity). Since the charging voltage has never reached a constant, the observed decrease in the coulombic efficiency is unlikely to be the redox shuttle of the dissolved Li$_2$Sn, instead the localized electric circuit shortening.

Figure 3. Ex-situ XRD pattern of FeS$_2$ cathode at different cycling state. (a) Pristine cathode, (b) after 1$^{st}$ discharging to 1.0 V, (c) after 1$^{st}$ recharging to 2.6 V, and (d) after 200 cycles at charged state (2.6 V).

Figure 4. Typical capacity fading mode of Li/FeS$_2$ cells.
The localized electric circuit shortening is verified indirectly by changing the charging current density. Fig. 7 compares the cycling voltage profiles of a Li/FeS₂ cell in Region 3. It is shown that the cell discharges almost same capacity (∼310 mAh g⁻¹) when charged at 0.5 mA cm⁻² and at 1.0 mA cm⁻², respectively. Importantly, the high charging current density (1.0 mA cm⁻²) results in lower polarization and much higher irreversibility compared with 0.5 mA cm⁻², which provides excellent evidence of an increased electric circuit shortening caused by the Li metal under a high charging current density. In order to further confirm our judgment, morphologies of the Li anode in different cycling regions of the Li/FeS₂ cells are compared in Fig. 8. It is shown that all Li deposits are powder-like with large surface area. With an increase in cycle number, the Li deposits become darker and thicker because on one hand the powder-like Li particles become smaller and on the other hand its reaction products with the organic solvent progressively build up. Worse, the Li deposits become very small and very loose with an increase in the cycle number. For example, many Li deposits in Region 3 are automatically peeled off the Li anode.

Figure 5. (a) Schematic configuration of a carbon interlayer placed for collecting dissolved Li₂Sn, and (b) EDX spectrum of the carbon interlayer harvested after 1st discharge and 1st recharge, respectively.

Figure 6. Selected voltage profiles of a Li/FeS₂ cell in (a) Region 2, and (b) Region 3.

Figure 7. Effect of charging current density on cell’s performance in Region 3.
surface even very care was given in the process of cell disassembly (see Fig. 8d). These small and loose Li deposits are easy to penetrate across the porous separator, leading to localized electric circuit shortening.

Besides shortening the electric circuit, the small and loose Li deposits are also responsible for the drying-out of liquid electrolyte because of the large surface area that greatly enhances their reactivity with the electrolyte solvent. In order to verify this, the ac-impedance spectra of an alive cell in Region 2 and a dead cell in Region 3 are compared in Fig. 9. The impedance spectrum of an electrochemical cell typically consists of two semicircles followed by a straight sloping line at low frequencies. In many cases, two semicircles are overlapped into one, and the resultant impedance spectrum is explained using an equivalent circuit shown in the inset of Fig. 9, where $R_b$ is the bulk resistance reflecting the ohmic resistance of cell’s hardware, two electrodes and electrolyte/separator, $R_{er}$ refers to as the cell’s reaction resistance that reflects a combined effect of the ohmic surface layer resistance ($R_\text{s}$) and faradaic charge-transfer resistance ($R_{\text{ct}}$), and $W$ is the Warburg impedance corresponding to the adsorption and diffusion of Li$^+$ ions on the electrode surface.\textsuperscript{36,43} As we can observe in Fig. 9, the alive cell has very similar $R_b$ and $R_{er}$ at the discharged and charged states, whereas the dead cell shows much less $R_{er}$ at the charged state than at the discharged state. The much less $R_{er}$ would be another symptom of the localized electric circuit shortening at the charged state of the dead cell. In particular, the dead cell has much higher $R_b$ and $R_{er}$ compared with the alive cell. Since the $R_b$ is directly affected by the ionic conductivity of electrolyte and electrolyte-wetted separator, the significantly higher $R_b$ of the dead cell than the alive cell suggests the drying-out of liquid electrolyte. The causes for higher $R_{er}$ of the dead cell than the alive cell are more complicated, which are associated with not only the drying-out of liquid electrolyte but also the increased $R_b$ on the Li anode as a result of the enhanced reactions of the powder-like Li particles with electrolyte solvent and dissolved Li$_2$Sn. Based on the analyses above, the accelerated capacity fading in Region 3 can be mainly attributed to the poor morphology of Li deposition in charging process, which leads to powder-like, small and loose Li particles that not only penetrate across the porous separator to shorten the cell but also react with electrolyte solvent to dry out the cell. Finally, it should be pointed out that all the factors discussed above last for the entire life of Li/FeS$_2$ cells, however, their role in affecting the cycle life of Li/FeS$_2$ cells varies with the cycle number. From the viewpoints of cycling performance, the loss of sulfur active material results in capacity fading whereas the localized electric circuit shortening kills the cell.

**Strategy for improving Li/FeS$_2$ cell.**—As analyzed above, the poor morphology of Li deposition in charging process essentially affects the cycle life of Li/FeS$_2$ cells. Therefore, our priority was first to improve the morphology of Li plating and then to minimize the loss of sulfur active material. For this purpose, we here demonstrate three facile strategies for improving the cycle life of Li/FeS$_2$ cells: (1) using vinylene carbonate (VC) as the electrolyte additive to form robust solid electrolyte interphase (SEI) on the Li surface, (2) applying a carbon interlayer between the FeS$_2$ cathode and solid electrolyte interphase (SEI) on the Li surface, (2) applying a carbon interlayer between the FeS$_2$ cathode and separator to confine the dissolved Li$_2$Sn from out-diffusion. Fig. 10 compares the effect of these three strategies on the cycle life of Li/FeS$_2$ cells, in which all cells were assembled and cycled in very similar conditions, including the loading of FeS$_2$ and the volume of liquid electrolyte. By defining the total cycle number in Region 1 and Region 2 as the cycle life, the control cell only lasted for 85 cycles (curve-a). With an addition of 2 wt% VC into the electrolyte, the cycle life increased to 103 cycles (curve-b), ascribing to the formation of an improved SEI on the Li anode surface.\textsuperscript{46,48} The cycle life was further increased to 127 cycles (curve-c) when two pieces of Li foils were used as the anode to increase the mechanical pressure between two electrodes, which has been reported to be effective in promoting the dense and uniform deposition of Li and enhancing the coulombic efficiency of Li plating and stripping cycling.\textsuperscript{46,48} The most significant improvement was found to be the use of a carbon interlayer, which was applied by employing a carbon-coated separator with the carbon
layer facing the FeS$_2$ cathode. As indicated by curve-d, the carbon interlayer extended the cycle life up to about 200 cycles, which can be attributed to the bi-function of the carbon interlayer.49–51 (1) confining the dissolved Li$_2$S$_n$ from out-diffusion on the cathode, and (2) reducing the parasitic reactions with the dissolved Li$_2$S$_n$ on the anode. Even with the improvement of three strategies above, the capacity of these Li/FeS$_2$ cells was still poorly remained due to the continuous loss of sulfur active material and the progressive growth of resistive Li surface layer, caused by the unavoidable dissolution of Li$_2$S$_n$ in an organic electrolyte and the irreversible reduction of the dissolved Li$_2$S$_n$ to insoluble Li$_2$S$_2$/Li$_2$S on the Li anode.15

Conclusions

In summary, we analyzed the capacity fading mechanism of Li/FeS$_2$ cells from the viewpoint of fundamental chemistry of FeS$_2$ in a non-aqueous liquid electrolyte. According to capacity fading rate, the cycle life of Li/FeS$_2$ cells can be divided into three regions, namely fast fading Region 1, slow fading Region 2, and accelerated fading Region 3. A number of factors are known to affect the cycling performance and accompany with the entire life of Li/FeS$_2$ cells, including the loss of sulfur active material by the unavoidable dissolution of Li$_2$S$_n$, the poor morphology of Li deposition, the drying-out of liquid electrolyte, and the progressive growth of resistive surface layer on the Li anode. The role of these factors in affecting the cycle life varies with the cycle number. Roughly, Region 1 is mainly attributed to the dissolution of Li$_2$S$_n$ leading to the loss of sulfur active material, and Region 3 is mainly associated with the poor morphology of Li deposition resulting in the localized electric circuit shortening. We show that the cycle life of Li/FeS$_2$ cells can be significantly extended by adding vinylene carbonate as the electrolyte additive, increasing mechanical pressure between two electrodes, or placing a carbon interlayer between the FeS$_2$ cathode and separator. However, the capacity retention is still poor because of the progressive loss of sulfur active material and resultant reactions with the Li anode. More effective strategy in confining the dissolved Li$_2$S$_n$ from diffusing out of the cathode is urgently needed for future development of the Li/FeS$_2$ rechargeable batteries with low cost and high energy density.

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References

1. S. S. Zhang, J. Mater. Chem. A, 3, 7689 (2015).
2. D. Zhang, J. P. Tu, J. Y. Xiang, Y. Q. Qiao, X. X. Xia, X. L. Wang, and C. D. Gu, Electrochim. Acta, 56, 9980 (2011).
3. T. Takeuchi, H. Kageyama, K. Nakaniishi, Y. Inada, M. Katayama, T. Ohba, H. Senoh, H. Sakaee, T. Sakai, K. Tatsumi, and H. Kobayashi, J. Electrochem. Soc., 159, A75 (2012).
4. M. Walter, T. Zund, and M. V. Kovalenko, Nanoscale, 7, 9158 (2015).
5. L. A. Montoro and J. M. Rosolen, Solid State Ionics, 159, 233 (2003).
6. L. A. Montoro, J. M. Rosolen, J. H. Shin, and S. Passerini, Electrochim. Acta, 49, 3419 (2004).
7. J. W. Choi, G. Cheruvally, J. H. Ahn, K. W. Kim, and J. H. Ahn, J. Power Sources, 163, 158 (2006).
8. R. Feng, J. R. Dahn, and C. H. W. Jones, J. Electrochem. Soc., 136, 3206 (1989).
9. T. B. Kim, J. W. Choi, H. S. Ryu, G. B. Cho, K. W. Kim, J. H. Ahn, K. K. Cho, and H. J. Ahn, J. Power Sources, 174, 1275 (2007).
10. A. Kitajou, J. Yamaguchi, S. Hara, and S. Okada, J. Power Sources, 247, 391 (2014).
11. Y. Shao-Horn, S. Osniowska, and Q. C. Horn, J. Electrochem. Soc., 149, A1499 (2002).
12. S. S. Zhang, J. Power Sources, 231, 153 (2013).
13. D. Zhang, Y. J. Mai, J. Y. Xiang, X. H. Xia, Y. Q. Qiao, and J. P. Tu, J. Power Sources, 217, 229 (2012).
14. L. Liu, Z. Yuan, C. Qiu, and J. Liu, Solid State Ionics, 241, 25 (2013).
15. S. B. Son, T. A. Yersak, D. M. Piper, S. C. Kim, C. S. Kang, J. S. Cho, S. S. Suh, Y. U. Kim, K. H. Oh, and S. H. Lee, Adv. Energy Mater., 4, 1300961 (2014).
16. J. Liu, Y. Wen, Y. Wang, A. P. A. van, J. Maier, and Y. Yu, Adv. Mater., 26, 6025 (2014).
17. W. Qiu, J. Xia, H. Zhong, S. He, S. Lai, and L. Chen, Electrochim. Acta, 137, 197 (2011).
18. D. T. Tran, H. Dong, S. D. Walck, and S. S. Zhang, RSC Adv., 5, 87487 (2015).
19. X. Wen, X. Wei, L. Yang, and P. K. Shen, J. Mater. Chem. A, 3, 2090 (2015).
20. H. Xue, D. Y. W. Yu, J. Qing, X. Yang, J. Xu, Z. Li, M. Sun, W. Kang, Y. Tang, and C. S. Lee, J. Mater. Chem. A, 3, 7945 (2015).
21. T. S. Yoder, M. Tussing, J. E. Cloud, and Y. Yang, J. Power Sources, 274, 685 (2015).
22. F. Jin and Y. Wang, J. Mater. Chem. A, 3, 14741 (2015).
23. D. Zhang, G. Wu, J. Xiang, J. Yin, C. Gai, and G. Li, Mater. Sci. Eng. B, 178, 483 (2013).
24. H. Xue, D. Y. W. Yu, J. Qing, X. Yang, J. Xu, Z. Li, M. Sun, W. Kang, Y. Tang, and C. S. Lee, J. Mater. Chem. A, 3, 7945 (2015).
25. T. Evans, D. M. Piper, S. C. Kim, S. S. Han, V. Bhat, K. H. Oh, and S. H. Lee, Adv. Mater., 26, 7386 (2014).
26. Y. Zhu, L. Suo, T. Gao, X. Fan, F. Han, and C. Wang, Electrochim. Acta, 54, 18 (2015).
27. D. T. Tran and S. S. Zhang, J. Mater. Chem. A, 3, 12240 (2015).
28. S. S. Zhang and D. T. Tran, Electrochim. Acta, 176, 784 (2015).
29. G. Brostigen and A. Kjekshus, Acta Chem. Scand., 23, 2186 (1969).
30. E. A. Ferrow and A. B. Sjoeberg, Hyperfine Interact., 163, 95 (2006).
31. D. Golodnitsky and E. Peled, Electrochim. Acta, 45, 335 (1999).
32. R. Murphy and D. R. Strongin, Surf. Sci. Rep., 64, 1 (2009).
33. S. S. Zhang and J. A. Read, J. Power Sources, 200, 77 (2012).
34. J. Kulisch, H. Sommer, T. Brezesinski, and J. Janek, Phys. Chem. Chem. Phys., 16, 18765 (2014).
35. S. S. Zhang, D. Foster, and J. Read, J. Power Sources, 191, 648 (2009).
36. R. Mogi, M. Inaba, S. K. Jeong, Y. Iriyama, T. Abe, and Z. Ogumi, J. Electrochem. Soc., 149, A1578 (2002).
37. H. Otta, K. Shima, M. Ue, and J. I. Yamaki, Electrochim. Acta, 49, 565 (2004).
38. D. P. Wilkinson, H. Bloom, K. Brantl, and D. Wainwright, J. Power Sources, 36, 517 (1991).
39. T. Hiari, I. Yoshimatsu, and J. Yamaki, J. Electrochem. Soc., 141, 611 (1994).
40. L. Gireaud, S. Grugeon, S. Laruelle, B. Yrieix, and J. M. Tarascon, Electrochem. Commun., 8, 1639 (2006).
41. S. S. Zhang and J. Read, US Pat. Appl., US20130309572 (2013).
42. S. H. Chung and A. Manthiram, Adv. Funct. Mater., 24, 5299 (2014).
43. J. Balbach, T. Jaumann, M. Klose, S. Oswald, J. Eckert, and L. Giebeler, Adv. Funct. Mater., 25, 5285 (2015).