nature portfolio

Peer Review File

High Solubility Polysulfide Electrolytes for High Energy Density and Low-Cost K-Na/S Batteries

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

In this manuscript, the author used acetamide/ε-caprolactam (CPL) eutectic solvent in electrolyte for K-Na/S batteries. I think the characterizations of the reactions are insufficient and the practical application value is lacking. I do not recommend this paper for publication in Nature Communications. There are several issues that should be clarified.

1.The cost of the battery is not just the price of the components, the cost of the preparation and operation process should also be considered. For example, K and Na is much more active than that of Li, so the safety cost is much higher. Also, the operation temperature is 75℃, which is much more stringent than room-temperature Na/Li-S battery. Thus, the cost of the K-Na/S battery system should be more carefully instead of simply sum up the components price.

2.When the cell was tested in eutectic solvent electrolyte and TEGDME electrolyte, the capacity raised in the first few cycles. What exactly happened?

3.The eutectic solvent electrolyte did increase the capacity of the battery and the author indicated that the kinetics was boosted, however, the kinetics enhancement process should be more detailed. What reactions happened during the charge/discharge process? Which transformation steps were accelerated? More evidence should be provided.

4.In the cycling performance, the capacity in TEGDME electrolyte was lower than in eutectic solvent electrolyte, but showed a better capacity retention. Also, the capacities of 4 MS and 8 MS TEGDME are almost the same. Does it mean that the TEGDME electrolyte has better stability? How to balance the cell capacity and the cycle stability?

5.Rate performance of cells with 4 M sulfur in TEGDME electrolyte was lacked.

6.The author indicated that the eutectic solvent electrolyte enhanced the solubility of short-chain polysulfides, however, the high dissolution might lead to a more serious shuttle effect. This might be one of the main reasons that why the cell in eutectic solvent electrolyte showed worse cycle stability. What's the influence of the shuttle effect on the anode (such as dendrites) and how to balance the solubility and shuttle effect? Does higher solubility necessarily mean a better electrochemical performance?

7.The operation temperature of the cell is 75℃, which is much higher than the room-temperature. Recent years, there are so many reports of the room-temperature Na-S batteries, which have lower operation temperature, larger working current and higher safety than that of K-Na alloy. It is well-known of the high risk of K-Na alloy (especially at 75℃). Why the author chooses K-Na/S batteries? What's the superiority of the K-Na/S batteries?

8.During the cycle process, what's the reactions between S and K-Na? What's the priority between Na and K in these reactions?

9.The universality of the electrolyte should be provided. What's the performance of this electrolyte in Na-S batteries?

Reviewer #2 (Remarks to the Author):

The paper reports on a strategy to increase the kinetics and thereby the capacity/energy density by using a new electrolyte with an increased solubility of short chain polysulfides. In this way the slow kinetics of electrochemical reactions due to precipitation of short chain polysulfides at end of discharge can be avoided. This strategy is demonstrated mainly by comparing the performance of the new electrolyte to an electrolyte where the solubility of short chain polysulfides is low. With the new electrolyte the performance is enhanced showing high specific capacity. From this respect the paper has merits and could be of interest.

However, an actual understanding of the role of the new electrolyte is lacking and the results of the paper thus provide no general insight that could open new directions for design of electrolyte systems. The electrolyte is termed a deep eutectic solvent but the significance of this concept is not explained, neither is it in fact demonstrated that this electrolyte system is a deep eutectic system (note that also the added polysulfides should be part of this analysis). There, is an attempt to add some insight from molecular dynamics simulations but the relevance of this part is rather low. The simulations are done solely based on the solvents and the analysis is done on just on the RDF and interaction energy. In the electrolyte, which also contains KTFSI salt, the anion of the salt will for sure be part of the solvation of the cations and thus the conclusions now drawn are not necessarily correct.

The work does also not really show what the physical effect on the electrochemical processes really is of the new electrolyte. No precipitates are found at end of discharge, but this conclusion is drawn from an optical experiment which would not capture precipitates on the carbon paper supporting the electrochemical reaction if they are micron size or smaller (which is what one would indeed expect). Thus, insight into the actual mechanism behind the enhanced performance is not obtained.

With respect to the performance also raises significant questions. Capacity and cyclability is generally good. However, there are significant fluctuations in the coulombic efficiency which raises questions and there is significant capacity fade in the cell. In the manuscript it is suggested that it is due to evaporation of the electrolyte but why this would be the case in these types of cells is not clear. Also, the authors in fact claim that this electrolyte has a low vapour pressure which is in direct contradiction. Instead, a more likely explanation is some passivation in the system, e.g. continuous (but slow) build-up of insoluble products (e.g. MS_2) or continuous degradation of some component. Furthermore, while the capacity improves with the new electrolyte the rate capability is not impressive and could have been expected to be better if the kinetics is indeed faster with this system. Altogether, this shows that there is in fact very little understanding of what goes on in this system.

In addition, the claims of energy density in the article are not well justified. It is good that the details of the calculations are included but the analysis is based on an idealised cell not the actual cell used in the experiments. In these kind of systems the performance is strongly dependent on the ratio of the different components and one can not easily extrapolate results obtained from these experiments to an optimised cell.

Thus, the paper can not be recommended for publication in Nature Communications. It is rather suited (after revision addressing cur) for a more specialised journal in the field of batteries.

Table of Contents

Reviewer #1

In this manuscript, the author used acetamide/ε-caprolactam (CPL) eutectic solvent in electrolyte for K-Na/S batteries. I think the characterizations of the reactions are insufficient and the practical application value is lacking. I do not recommend this paper for publication in Nature Communications. There are several issues that should be clarified.

Question 1

The cost of the battery is not just the price of the components; the cost of the preparation and operation process should also be considered. For example, K and Na is much more active than that of Li, so the safety cost is much higher. Also, the operation temperature is 75℃, which is much more stringent than room-temperature Na/Li-S battery. Thus, the cost of the K-Na/S battery system should be more carefully instead of simply sum up the components price.

Response:

We thank the reviewer's comment. While room-temperature (RT) Na-S battery is attractive, we think a more reasonable baseline for this study is high-temperature (HT) Na-S batteries working at 300-350 ºC, since intermediate-temperature (IT) Na-S batteries and HT Na-S batteries both use β"-Al_2O_3 solid electrolytes and share similar configurations. HT Na-S has already been deployed at a scale of ~500 MWh[1], which indicates that costs on safety and manufacturing are within the reasonable range. On the other side, dendrite issues are more challenging for RT Na-S batteries, and RT Na-S batteries also require a more precise control of electrode uniformity, so the safety cost of RT Na-S batteries also remains to be evaluated.

Regarding system cost, we follow the protocol developed by Prof. Zheng Li, an expert on Na-S batteries, and the analysis includes costs of packaging[2]. We agree that manufacturing cost should be added. However, it should also be noted that IT Na-S batteries do not require complicated slurry-based coating and the removal of solvent, which is a major part of manufacturing cost in Li-ion batteries[3]. To caution readers about manufacturing, we add the following sentences in the manuscript on page 17.

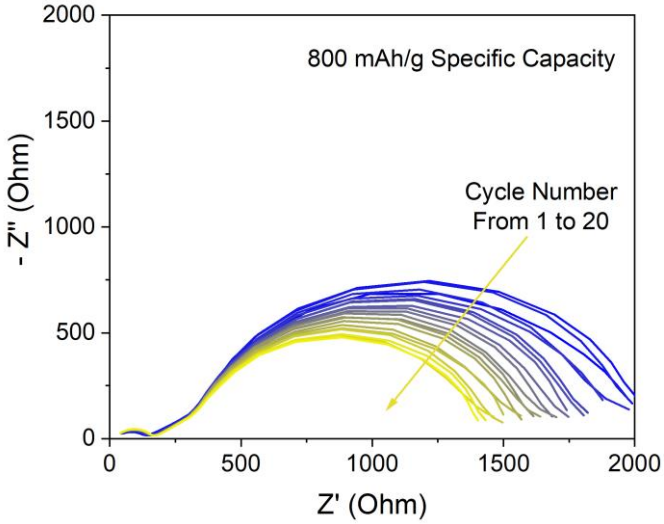
In addition, manufacturing cost should also be considered. Although this is difficult to evaluate, it is likely to be on pair with or less than Li-ion batteries[4]. This is because no slurry coating, drying and calendaring is needed for alkaline metal sulfur batteries, which count for the majority part of manufacturing cost in Li-ion batteries.[3] On the other side, Na and K need to be handled in an air-free environment.

Question 2

When the cell was tested in eutectic solvent electrolyte and TEGDME electrolyte, the capacity raised in the first few cycles. What exactly happened?

Response:

This is probably due to better wetting between the catholyte and the carbon substrate upon cycling, leading to fast kinetics and lower resistance. This is supported by electrochemical impedance spectroscopy (EIS) measured at a discharge capacity of 800 mAh/g in the CPL/acetamide eutectic solvent, which is close to 882 mAh/g, the maximum specific capacity of the cathode with 4 M [S]. We find that the charge transfer resistance of the cathode (the semi-circle at the lower frequency) decreases continuously upon cycling (Supplementary Fig. 8).



Supplementary Fig. 8. Impedance results in the first 20 cycles of 4M [S] K-S cells running at 75°C. All measurements are done at the same state of discharge (discharge to 800 mAh/g).

We add the following sentences in the manuscript (page 13):

The gradual capacity increase in CPL/acetamide upon cycling probably comes from better wetting between the catholyte and the carbon substrate, which is supported by decreasing charge transfer resistance upon cycling (Supplementary Fig. 8).

Question 3

The eutectic solvent electrolyte did increase the capacity of the battery and the author indicated that the kinetics was boosted, however, the kinetics enhancement process should be more detailed. What reactions happened during the charge/discharge process? Which transformation steps were accelerated? More evidence should be provided.

Response:

First, as we used K^+-conducting β"-Al_2O_3, the ions moving to the cathode are only K^+.[5]

In a conventional TEGDME electrolyte, the reaction is:

$2S_3^{2-}$ (l) + $2e^-$ + $6K^+$ → $3K_2S_2$ (s), and K_2S_2 (s) + $2e^-$ + $2K^+$ → $2K_2S$ (s)

Where l and s represent liquid and solid phases, respectively. K^+ diffuses very slowly in K_2S_2 and K_2S, as evidenced by the long diffusion tail in EIS in Fig. 3e, which corresponds to a diffusivity of 8×10^{-16} $cm^2\ s^{-1}$. This is the limiting step in the TEGDME electrolyte.

In contrast, as K_2S_2 and K_2S are soluble in the CPL/acetamide electrolyte, the reactions are:

$2S_3^{2-}$ (l) + $2e^-$ → $3S_2^{2-}$ (l), and S_2^{2-} (l) + $2e^-$ → $2S^{2-}$ (l)

As ion diffusion in liquid is very fast (about 3×10^{-7} $cm^2\ s^{-1}$ from Fig. 3e), this is no longer a limiting step and the kinetics is significantly boosted.

When [S] is higher than the solubility of K_2S_2 and K_2S, there are reactions of $2S_3^{2-}$ (l) + $2e^-$ + $6K^+$ → $3K_2S_2$ (s) and K_2S_2 (l) + $2e^-$ + $2K^+$ → $2K_2S$ (s), but these reactions are in parallel with $2S_3^{2-}$ (l) + $2e^-$ → $3S_2^{2-}$ (l) and S_2^{2-} (l) + $2e^-$ → $2S^{2-}$ (l), which just further contributes to the enhanced specific capacity.

We add the following sentences in the manuscript (page 5):

The cathode is polysulfides dissolved in a mixture of CPL and acetamide (1:1 molar ratio, Fig. 1a). Therefore, the cathode reaction in the range of S_3^{2-}/S^{2-} is $2S_3^{2-}$ (l) + $2e^-$ → $3S_2^{2-}$ (l) and S_2^{2-} (l) + $2e^-$ → $2S^{2-}$ (l) instead of $2S_3^{2-}$ (l) + $2e^-$ + $6K^+$ → $3K_2S_2$ (s) and K_2S_2 (s) + $2e^-$ + $2K^+$ → $2K_2S$ (s) in conventional ether electrolytes.

And the following sentence on page 13:

We further test samples with 4 M and 8 M [S] to enhance energy density of K/S batteries. As [S] is higher than the solubility of K_2S_2 and K_2S, the cathode reaction involves solid formation such as $2S_3^{2-}$ (l) + $2e^-$ + $6K^+$ → $3K_2S_2$ (s) and K_2S_2 (l) + $2e^-$ + $2K^+$ → $2K_2S$ (s), which further contributes to cell capacity in parallel with liquid/liquid transformation among $S_3^{2-}/S_2^{2-}/S^{2-}$.

Question 4

In the cycling performance, the capacity in TEGDME electrolyte was lower than in eutectic solvent electrolyte but showed a better capacity retention. Also, the capacities of 4 MS and 8 MS TEGDME are almost the same. Does it mean that the TEGDME electrolyte has better stability? How to balance the cell capacity and the cycle stability?

Response:

Regarding better stability in TEGDME, there are three possible reasons:

1) Cycling time. As TEGDME and acetamide/CPL cells were cycled at the same current density (mA/g sulfur), the much higher specific capacity of acetamide/CPL cells means that the period of one cycle is 2-3 times that of TEGDME, which will result in more degradation.

2) Vapor pressure. TEGDME has a high boiling point of 275 °C, while acetamide and CPL have boiling point of 220 °C and 270 °C, respectively. The formation of eutectic solvent may further reduce the mixture's boiling point. The vapor pressure also shows the same trend. The vapor pressure of CPL/acetamide is much higher than TEGDME. While we cannot find data on CPL/acetamide itself, acetamide has a vapor pressure of 10.25 kPa at 100 °C [6], while TEGDME has a vapor pressure of 132 Pa at 100 °C[7]. Therefore, the evaporation of acetamide/CPL could be more significant than TEGDME.

3) Low K_2S_2 solubility in TEGDME. In TEGDME, although solid K_2S_2 is formed at the end of discharge, most specific capacity is attributed to soluble S/K_2S_3 redox, so there is very limited amount of solid precipitation, and thus degradation due to solid formation and volume change is very low.

We add the following sentences in the manuscript (page 15):

In contrast, the TEGDME cell only has an initial specific capacity of 378 mAh g^{-1} at 2 mA cm^{-2}, which remains at 343 mAh g^{-1} after 1000 cycles. The reason for better retention of TEGDME cells are discussed in Supplementary Note 6.

And we also add the discussions above as supplementary note 6.

Regarding the almost the same specific capacity of 4M [S] and 8M [S] cells in TEGDME, this is because most specific capacity is in the range of soluble S/K_2S_3, so the corresponding kinetics is very fast and thus concentration has a small effect on the discharge capacity. For example, 4 M [S] and 8 M [S] in TEGDME have ionic conductivities of 1.6 and 1.9 mS/cm at 75 °C, respectively, and the charge transfer resistance at 400 mAh/g are both ~200 Ohm (Fig. 5f).

To balance the cell capacity and cycle life, besides further enhancing the performance of CPL/acetamide by optimizing carbon substrate and concentration, and better sealing, another solution is to mix TEGDME and CPL/acetamide together. We are still working on optimizing the receipt of catholyte and that would be reported in our further research.

Question 5

Rate performance of cells with 4 M sulfur in TEGDME electrolyte was lacked.

Response:

The rate performance of cell with 4M sulfur in TEGDME electrolyte is provided and add to Fig. 5c in the main text (page 16).

The K/S cell with 4 M [S] in CPL/acetamide also shows reasonable power capability. At 0.5 mA cm^{-2} (0.09 C), the discharge capacity is 1025 mAh g^{-1}, and it remains at 895 and 765 mAh g^{-1} at 1.5 mA cm^{-2} (0.26 C) and 2.5 mA cm^{-2} (0.51 C), respectively (Fig. 5c and e). For comparison, the specific capacities of TEGDME catholyte counterparts are around 430 mAh g^{-1} between 0.5-2.5 mA cm^{-2}.

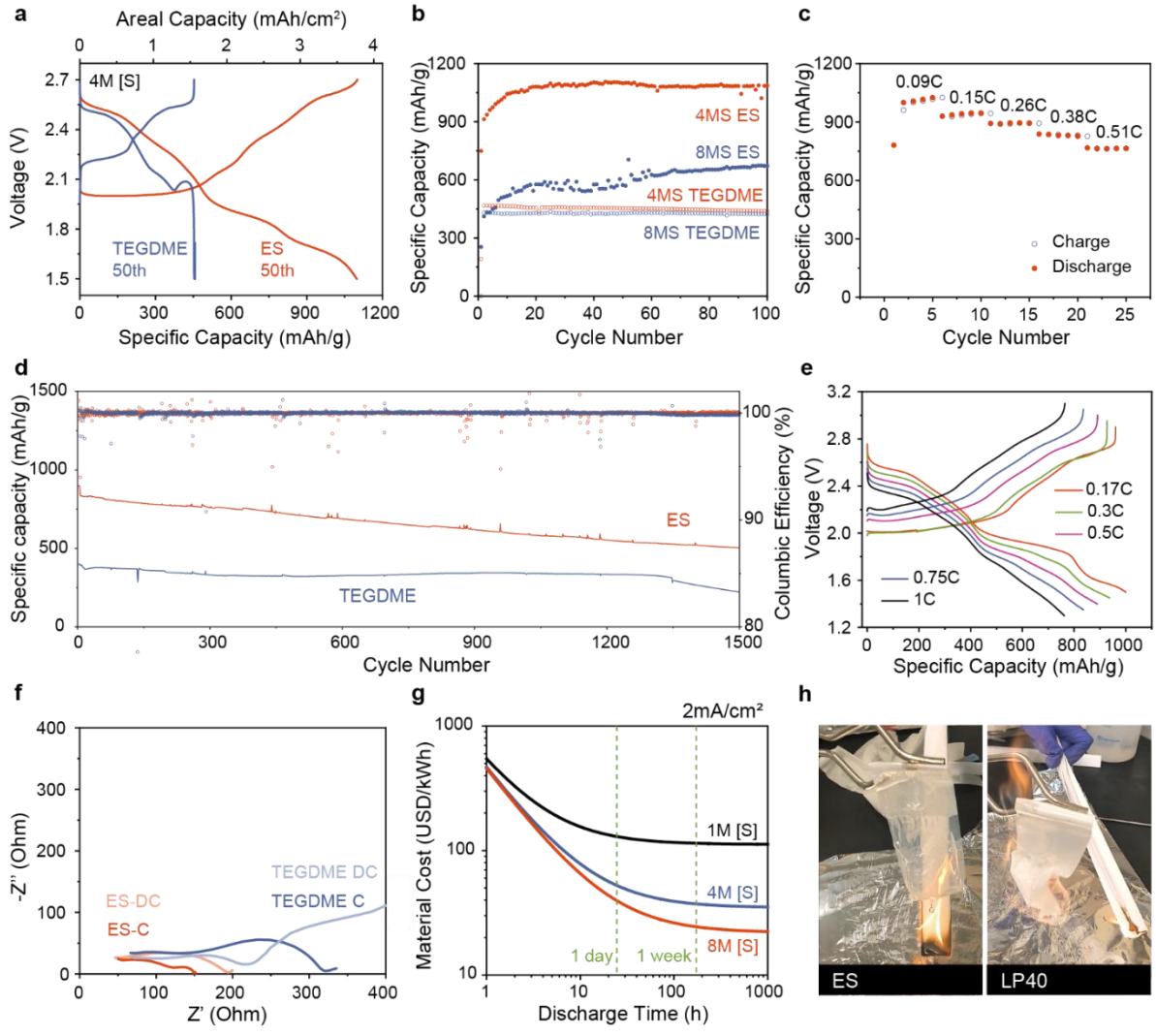


Fig. 5: Electrochemical performance of K/S batteries with 4 M and 8 M sulfur in catholytes

a, Charge/discharge voltage profiles of cells with 4 M sulfur in CPL/acetamide eutectic solvent (ES) and TEGDME catholyte. The current densities are 0.5 mA cm^{-2} (0.09 C). **b**, Cycling performance of cells with sulfur concentrations of 4 M and 8 M [S] in the cathode. The current densities are 0.5 mA cm^{-2}. **c**, Rate performance of cells with 4 M sulfur in ES electrolyte and TEGDME electrolyte. **d**, Cycling performances of

cells with 4 M sulfur in the cathode at 2 mA cm^{-2}. The first 5 cycles are at 0.5 mA cm^{-2}. **e**, Charge/discharge voltage profiles of cells with various C-rates. **f**, Electrochemical impedance spectroscopy of cells with 4 M sulfur in the cathode at the fully charged state (C) and at a discharge capacity of 460 mAh g^{-1} sulfur (DC). The electrolytes are ES and TEGDME, respectively. **g**, Eutectic solvent with separator (ES, left) and conventional Li-ion battery electrolyte with separator (LP40, right) on fire. Samples with polysulfides inside can be found in Supplementary Video 5.

Question 6

The author indicated that the eutectic solvent electrolyte enhanced the solubility of short-chain polysulfides, however, the high dissolution might lead to a more serious shuttle effect. This might be one of the main reasons that why the cell in eutectic solvent electrolyte showed worse cycle stability. What's the influence of the shuttle effect on the anode (such as dendrites) and how to balance the solubility and shuttle effect? Does higher solubility necessarily mean a better electrochemical performance?

Response:

We used a β″-Al_2O_3 solid electrolyte (BASE) as the solid electrolyte, which completely avoids the shuttle effect. This shares the same principle as high-temperature Na-S batteries. The elimination of shuttle effect is also supported by the nearly 100% Coulombic efficiency, as shown in Fig. 5d.

We also revised our article in page 4 to make the explanation clearer:

To address this issue and substantially enhance discharge capacity, here we propose a new family of amide electrolytes which have reasonable solubility of M_2S_2/M_2S (e.g., 1-2 M), which drastically enhances ionic diffusivity and reaction kinetics in the cathode. We apply this new design principle to IT K/S batteries in this work because 1) BASE can completely stop shuttle effect caused by such higher solubility.

Question 7

The operation temperature of the cell is 75°C, which is much higher than the room-temperature. Recent years, there are so many reports of the room-temperature Na-S batteries, which have lower operation temperature, larger working current and higher safety than that of K-Na alloy. It is well-known of the high risk of K-Na alloy (especially at 75°C). Why the author chooses K-Na/S batteries? What's the superiority of the K-Na/S batteries?

Response:

Room-temperature Na-S batteries have challenges in the following aspects.[8,9] (i) Formation of Na dendrites, which is even easier to form than lithium dendrites. (ii) Shuttle effects. (iii) Low specific

capacity of 400-500 mAh/g due to sluggish ionic diffusion in Na_2S_2 and Na_2S phases[10,11]. Although the low-capacity issues can be solved by using sulfur-polyacrylonitrile (SPAN)[12] or small molecule sulfur[13], the corresponding voltage decreases from 2.1 V to 1.6 V, which substantially reduces energy density.

Our intermediate temperature K-Na / S batteries successfully address these challenges by 1) No dendrites in liquid K-Na anode. 2) No shuttle effect due to the solid β"-Al_2O_3 electrolyte. 3) Substantially increased specific capacity (800-1500 mAh/g) and moderate voltage (2.1 V).

Supplementary Table 1. Reported works on RT Na-S/K-S batteries

Na-S battery	Design strategy	Current (mA cm^{-2} / mA g^{-1})	Average voltage (V)	Initial Capacity (mAh/g)	Cycle number	Normalized capacity decay (%/100 cycles)
12	SPAN	NA / 267	1.32	1510	100	6.5
14	Mo2N–W2N@PC	0.90 /1000	1.30	860	400	12.0
15	FeS2@ NCMS/S	NA /100	1.25	770	300	12.0
13	small sulfur molecules	1.68 / 1675	1.20	700	2000	0.3
16	3D-PNCV	NA / 5000	1.38	561	800	2.9
11	Co@PCNFs/S	1.64 / 830	1.45	530	600	4.6
10	S/MoS2/NCS	NA / 1000	1.40	427	2800	0.6
K-S battery	Design strategy	Current (mA/cm^2 / mA/g)	Average voltage (V)	Initial Capacity (mAh/g)	Cycle number	Normalized decay (%/100 cycles)
17	small sulfur molecules	0.02 / 20	1.00	1198	150	19.3
18	S–N–Cos–C	NA / 200	1.25	463	150	16.2
This work	**Amide electrolyte**	**2 / 600**	**2.10**	**830**	**1100**	**3.2**

Supplementary Table 2. Reported works on Intermediate Temperature (IT) Na-S/K-S batteries

Na-S battery	Design strategy	Current (mA/cm^2)	Average voltage (V)	Initial Capacity (mAh/g)	Cycles	Normalized capacity decay (%/100 cycles)	Operation Temperature (°C)
[19]	TEGDME catholyte	2.33	1.80	428	60	44.8	150
[20]	Na-Cs alloy	2.33	1.88	420	100	3.0	95
[21]	LAT heat-treating	4.67	1.92	339	1000	<0.1	120
K-S battery	Design strategy	Current (mA/cm^2)	Average voltage (V)	Initial Capacity (mAh/g)	Cycles	Normalized decay (%/100 cycles)	Operation Temperature (°C)
[5]	K-S battery	1.33	2.0	312	1000	<0.1	150
This work	**Dissolving K_2S and K_2S_2**	**2**	**2.10**	**830**	**1100**	**3.2**	**75**

Question 8

During the cycle process, what's the reactions between S and K-Na? What's the priority between Na and K in these reactions?

Response:

There are two types of β"-Al_2O_3 solid electrolyte (BASE). Na-BASE only conducts Na^+ and passing K^+ will cause cracks of Na-BASE. K-BASE only conducts K+, even with the presence of Na in the Na-K anode. [5] So we are using K-BASE and only K+ passes BASE and moves to the cathode side. Therefore, the full cell reaction is $S + 2\ K \rightarrow K_2S$.

We have mentioned this reaction in the first paragraph in the Results part (line 9 on page 5).

Question 9

The universality of the electrolyte should be provided. What's the performance of this electrolyte in Na-S batteries?

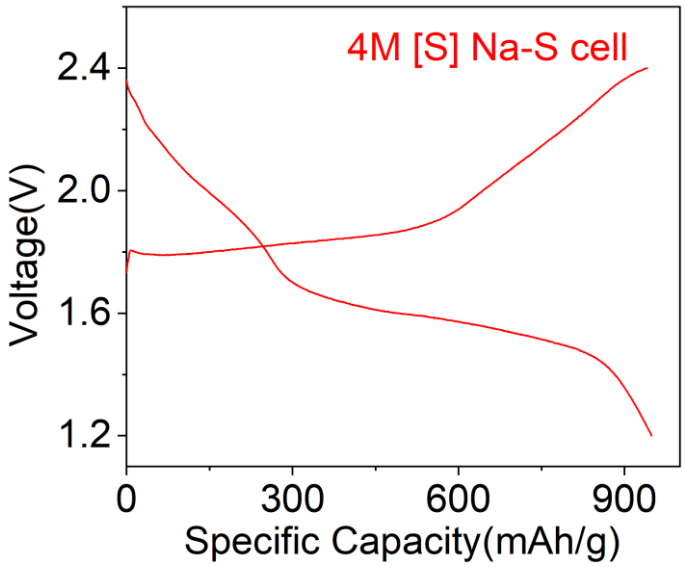
Response:

We demonstrated Na-Cs | Na-BASE | Na_2S_8 coin cells. Here the Cs is used to decrease the melting temperature of Na and increase the wetting between anode and BASE sheet[22].

In the manuscript, we add the following sentences in page 17,

Beside K/S batteries, the same design principle can also be applied to Na/S batteries as Na_2S and Na_2S_2 also have solubilities of 1.85 M and 2.80 M in CPL/acetamide at 75 °C, respectively. We also see a high discharge capacity of 940 mAh/g in the first cycle (Supplementary Fig. 11). The cycling performance needs to be improved due to poor interfaces between Na metal and BASE at 75 °C. We will report this in the future.

And the following figure as supplementary figure,



Supplementary Fig. 11. The voltage profile of the first cycling in 4M [S] Na-S cells running at 85 °C. 10% molar ratio of Cs metal is used as an additive to improve wetting towards Na-BASE sheet.

Reviewer #2

The paper reports on a strategy to increase the kinetics and thereby the capacity/energy density by using a new electrolyte with an increased solubility of short chain polysulfides. In this way the slow kinetics of electrochemical reactions due to precipitation of short chain polysulfides at end of discharge can be avoided. This strategy is demonstrated mainly by comparing the performance of the new electrolyte to an electrolyte where the solubility of short chain polysulfides is low. With the new electrolyte the performance is enhanced showing high specific capacity. From this respect the paper has merits and could be of interest.

Question 1

However, an actual understanding of the role of the new electrolyte is lacking and the results of the paper thus provide no general insight that could open new directions for design of electrolyte systems. The electrolyte is termed a deep eutectic solvent but the significance of this concept is not explained, neither is it in fact demonstrated that this electrolyte system is a deep eutectic system (note that also the added polysulfides should be part of this analysis).

Response:

We apologize for the confusion in our original submission. We have revised our paper to clarify these points, which are discussed below.

1) General insights on opening new direction.

The new insight is to develop electrolytes that can dissolve M_2S_2 and M_2S (M=K, Na) to enhance kinetics and increase capacity. This is distinct from conventional studies which tried to minimize the solubility of M_2S_x as they cause shuttle effect and uncontrollable precipitation. The reason why our new strategy works is the use of β"-Al_2O_3 solid electrolyte to completely eliminate shuttle effect, and β"-Al_2O_3 is well established in high-temperature Na-S batteries and it is made of only earth-abundant materials.

2) Eutectic Solvent

We mentioned eutectic solvent as this effect substantially reduces melting point of the solvent and thus decreases viscosity and increases conductivity. Fig. R1 shows the dependence of melting point on the composition of CPL/acetamide[23]. CPL and acetamide have melting point of 71 ºC and 82 ºC, respectively, and the melting point at CPL/acetamide = 1:1 (eutectic temperature) is -8 ºC. With 1.2 M K_2S inside, the solution remains liquid at 20 ºC (Fig. R1).

The reason why we use this CPL/acetamide eutectic solvent instead of only CPL or only acetamide is that the lower eutectic point not only decreases the operating temperature, but also reduces the viscosity of the solvent. The viscosity is CPL/acetamide is tested to be 6.9 mPa s at 75 ºC. On the other hand, CPL has a higher viscosity 10.8 mPa s at the same temperature and acetamide

is solid until 82 ºC. In addition, as polysulfides are corrosive and sensitive to air, we are not allowed to measure the viscosity of solution at our institution.

The decreased viscosity of solvents clearly justifies the use of CPL/acetamide mixture instead of each component. Such reduction in viscosity also leads to an attractive ionic conductivity. 1 M K_2S in CPL/acetamide eutectic solvent gives a conductivity of 1×10^{-3} S cm^{-1} at 75 ºC, which indicates that the solution has a low viscosity.

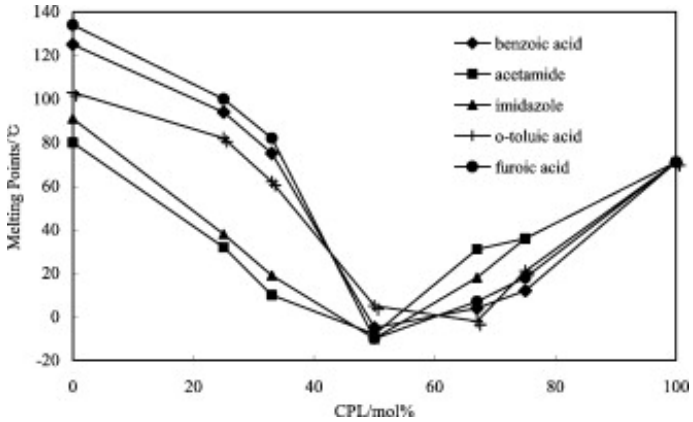


Figure R1. Melting points for CPL mixed with different organic chemicals.

Question 2

There, is an attempt to add some insight from molecular dynamics simulations but the relevance of this part is rather low. The simulations are done solely based on the solvents and the analysis is done on just on the RDF and interaction energy. In the electrolyte, which also contains KTFSI salt, the anion of the salt will for sure be part of the solvation of the cations and thus the conclusions now drawn are not necessarily correct.

Response:

The goal of simulation is to understand why K_2S_2 and K_2S have better solubility in CPL/acetamide than TEGDME, but not to simulate the real catholyte used in the cells. KTFSI does not affect the results since all solubility tests were done without KTFSI. Moreover, the concentration of KTFSI added is only 0.5 M, which is much less than the solubility.

Question 3

The work does also not really show what the physical effect on the electrochemical processes really is of the new electrolyte. No precipitates are found at end of discharge, but this conclusion is drawn from an optical experiment which would not capture precipitates on the carbon paper supporting the electrochemical reaction if they are micron size or smaller (which is what one would indeed expect). Thus, insight into the actual mechanism behind the enhanced performance is not obtained.

Response:

We further carry out SEM and synchrotron experiments. They are incorporated into the main article as Fig. 4a, b and Fig. 4c, d. The SEM images have spatial resolution of ~10 nm, which excludes the possibility of forming nanosized precipitates. The following sentences are added on page 11.

To verify the absence of solid precipitation in CPL/acetamide, several characterization methods were applied to elucidate the precipitation dynamics. First, ex-situ scanning electron microscope (SEM) images of cathode at 1.5 V revealed a smooth carbon surface without noticeable solid precipitates in CPL/acetamide (Fig. 4a). Moreover, S and K signals are very weak in Energy Dispersive Spectroscopy (EDS) spectrum and correspond to $K_2S_{1.0,}$ proving the full transformation from sulfur to K_2S. In contrast, in TEGDME cells, there is plenty of micron-sized particles, and EDS indicates that their compositions are $K_2S_{2.8}$ (Fig. 4b, Supplementary Fig. 7), corresponds to the discharge ending capacity of 562 mAh g^{-1} ($K_2S_{3.0}$). The same results are also observed by ex-situ Synchrotron-based X-ray Absorption. Near Edge Structure (XANES) mapping of sulfur, which shows that the intensities of sulfur signals in CPL/acetamide after 1 and 10 cycles are less than 1/10 of those in TEGDME, indicating no or very little solid precipitation (Fig. 4c).

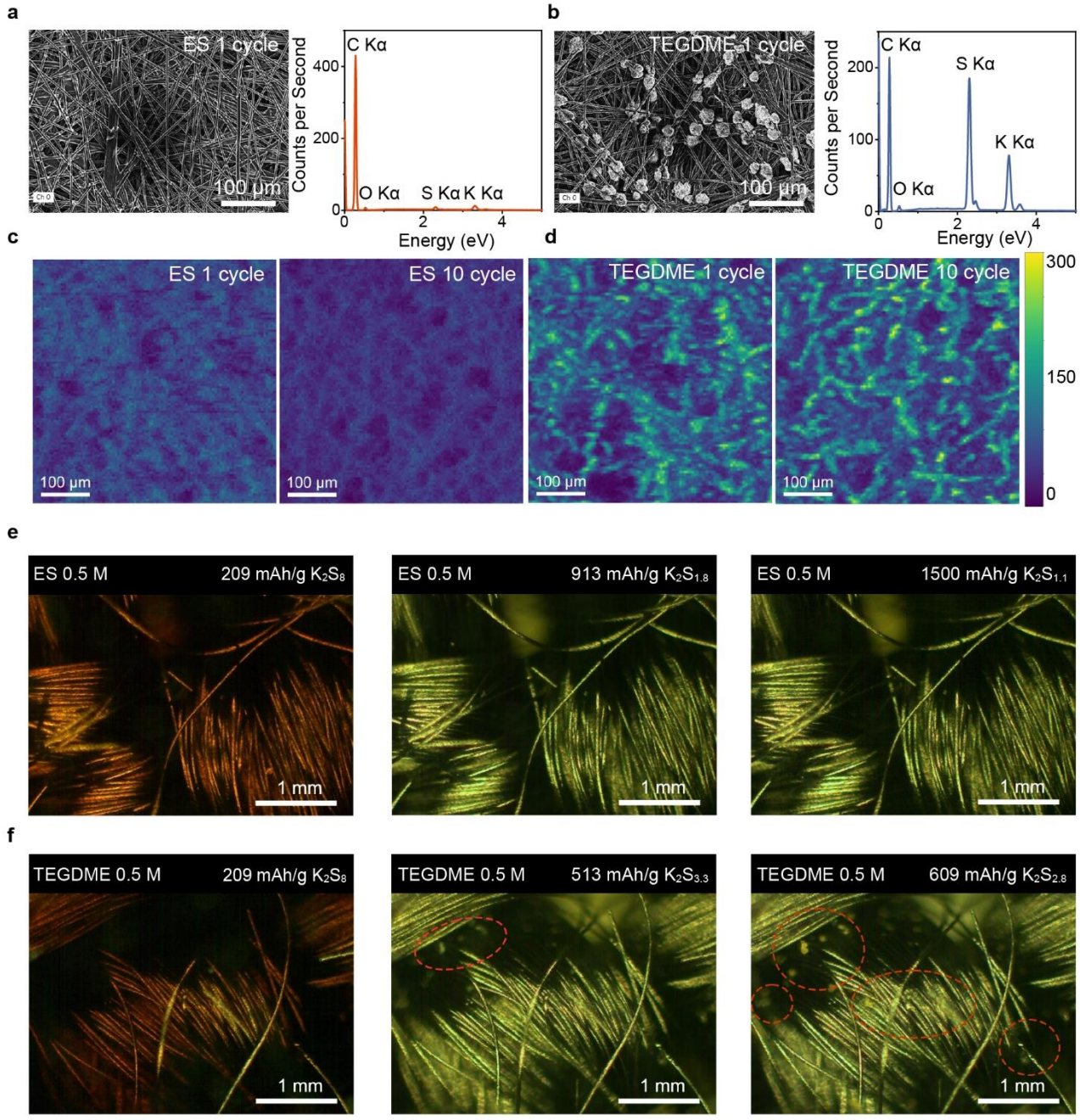


Fig. 4: Observation of K_2S_x particles in cathode side of K/S batteries

a, b Scanning Electron Microscope (SEM) imaging and Energy Dispersive Spectroscopy (EDS) spectrum results of carbon paper from cells after first cycle with 1M [S] CPL/acetamide eutectic solvent (ES) **(a)** and TEGDME **(b)**. **c, d** X-ray Absorption Near Edge Structure (XANES) mapping of sulfur element for carbon paper from cells after 1 or 10 cycles with ES **(c)** and TEGDME **(d). e, f** *Operando* optical microscope imaging of catholyte at room temperature in **e,** ES where no precipitation is observed even at the end of discharge and **f,** TEGDME where precipitation starts to appear in the middle of discharge. Precipitates are marked by red dashed circles. Specific capacities are counted from sulfur in **c-e** and Na_2S_8 in **f-g**. [S] in the catholyte and temperature are all 1 M and 75 °C in **a-d**, and 0.5 M and 25 °C in **e** and **f**.

Question 4

With respect to the performance also raises significant questions. Capacity and cyclability is generally good. However, there are significant fluctuations in the coulombic efficiency which raises questions and there is significant capacity fade in the cell. In the manuscript it is suggested that it is due to evaporation of the electrolyte but why this would be the case in these types of cells is not clear.

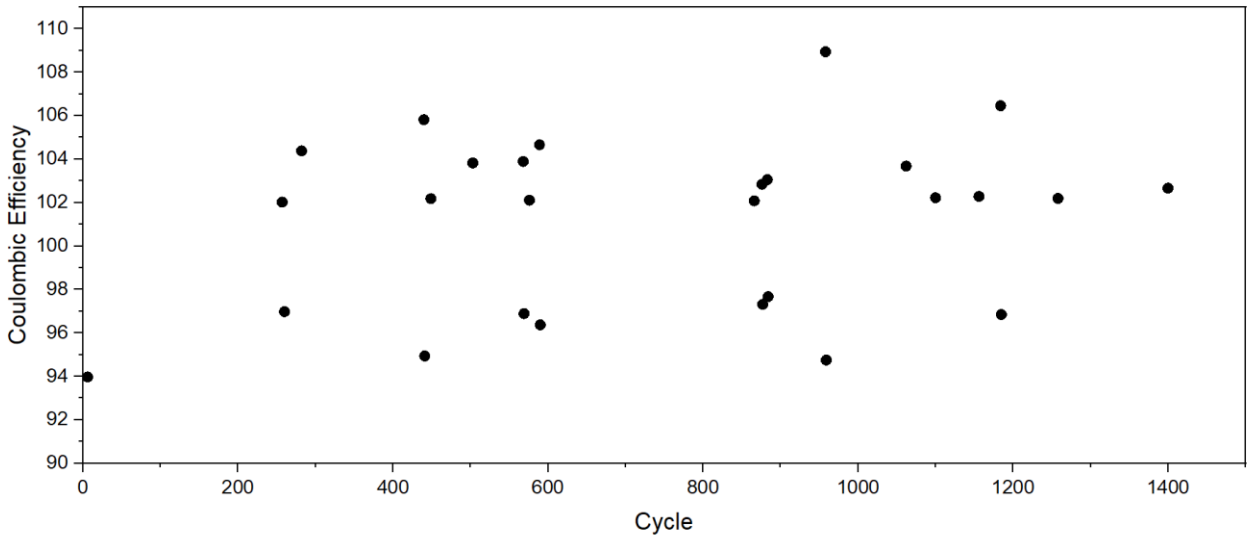
Response:

We check coulombic efficiencies (CE) of the cell with 1500 cycles in Fig. 5d. The "significant amount" of fluctuation in CE is an artifact caused by a high number of cycles in this figure. As shown in Supplementary Fig. 9, the frequency of "abnormal" CE (> 102% or < 98%) is about once every 50 cycles (roughly 10 days). And typically, a high CE > 102% is followed by a low CE < 98%, so the excessive discharge capacity and the deficient discharge capacity cancel out. Consequently, the fluctuation is unlikely to come from the system's intrinsic properties, and could come from the external perturbation (e.g., disruptions of connecting wires, sharp temperature change due to opening the oven).

We add the following sentence in the manuscript in page 15:

The variation in CE comes from environment disturbance, which happens averagely once every ~50 cycles (10 days, Supplementary Fig. 9).

We also add the figure below as Supplementary Fig. 9 in the supplementary information:



Supplementary Fig. 9 Irregular coulombic efficiency (<98% or >102%) for 4 M CPL/acetamide cells with the current density of 2 mA/cm^2 during 1500 cycle. The frequency of "abnormal" CE (> 102% or <98%) is actually about once every 50 cycles (roughly 10 days). And typically, a high CE > 102% is followed by a low CE < 98%, so the excessive discharge capacity and the deficient discharge capacity cancel out. As a consequence, the fluctuation is unlikely to come from the system's intrinsic properties, and could come from the external perturbation (e.g., disruptions of connecting wires, sharp temperature change due to opening the

oven).

Question 5

Also, the authors in fact claim that this electrolyte has a low vapor pressure which is in direct contradiction. Instead, a more likely explanation is some passivation in the system, e.g. continuous (but slow) build-up of insoluble products (e.g. MS2) or continuous degradation of some component.

Response:

The statement of low vapor pressure is to compare with conventional solvents[23] (e.g., FEC, DME). However, the vapor pressure of CPL/acetamide is much higher than TEGDME. While we cannot find data on CPL/acetamide itself, acetamide has a vapor pressure of 10.3 kPa at 100 ºC [6], while TEGDME has a vapor pressure of only 132 Pa at 100 ºC[7]. Such higher pressure may lead to more evaporation than TEGDME. Moreover, such evaporation could also result in passivation as the concentration of K_2S_x gradually increases upon solvent evaporation and finally precipitates out to some extent.

We add the following sentences on page 15 in the manuscript:

The reason for better retention of TEGDME cells are discussed in Supplementary Note 6.

And we also add a new section in Supporting Information as Supplementary note 6, which says:

Vapor pressure. The boiling points of the solvents show notable differences: TEGDME has a high boiling point of 275°C, while acetamide and CPL boil at 220°C and 270°C, respectively. The formation of a eutectic solvent in the mixture could further reduce its boiling point. Correspondingly, the vapor pressure trends align with boiling point data. CPL or acetamide exhibits higher vapor pressure compared to TEGDME. For instance, acetamide alone has a vapor pressure of 10.25 kPa at 100°C[6], whereas TEGDME's vapor pressure is substantially lower at 132 Pa[7] at the same temperature. This disparity suggests that evaporation could be more pronounced in eutectic solvent than in TEGDME.

Question 6

Furthermore, while the capacity improves with the new electrolyte the rate capability is not impressive and could have been expected to be better if the kinetics is indeed faster with this system. Altogether, this shows that there is in fact very little understanding of what goes on in this system.

Response:

The C rate seems not impressive since we have a high areal mass loading of ~ 4 mAh/cm^2, but actually 0.5 C corresponds to a relatively high current density of 2 mA/cm^2. Compared to room temperature Na-S batteries with typical current densities of 0.5 -1.5 mA/cm^2 (Table S1 on page 10 of this response), our current density is higher. Moreover, our current densities are also comparable to other intermediate Na-S batteries reported at a higher temperature of 100-150 ºC, as shown in Table S2 on page 11 of this response.

Question 7

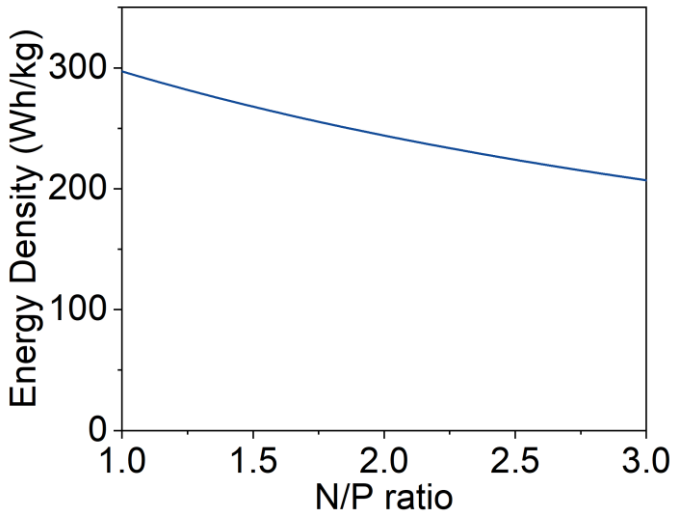
In addition, the claims of energy density in the article are not well justified. It is good that the details of the calculations are included but the analysis is based on an idealized cell not the actual cell used in the experiments. In this kind of systems, the performance is strongly dependent on the ratio of the different components and one cannot easily extrapolate results obtained from these experiments to an optimized cell.

Response:

We agree that claims on energy density of practical cells should be treated more carefully. Our calculations are based on N/P ratio of 1. In reality, more Na-K alloy is likely to be needed due to volume change. Supplementary Fig. 1 shows how energy density depends on N/P ratio. This should be carefully studied for practical studies. To caution readers on this, we revise the manuscripts as follows on page 17:

It should be noted that the calculation is only for materials only and the N/P ratio of 1, and the dependence of energy density on N/P ratio is shown in Supplementary Fig 1.

We also add the figure below as Supplementary Fig. 1 in the supplementary information:



Supplementary Fig. 1. The Negative electrode active material/Positive electrode active material molar ratio dependence of theoretical energy density for K/S battery with 4 M [S]. The mass of solvent and active material is considered in the calculation.

REFERENCE

1 Spoerke, E. D., Gross, M. M., Percival, S. J. & Small, L. J. in *Energy-Sustainable Advanced Materials* (eds Mark Alston & Timothy N. Lambert) 59-84 (Springer International Publishing, 2021).

2 Yang, F. C. *et al.* Sodium-Sulfur Flow Battery for Low-Cost Electrical Storage. *Advanced Energy Materials* **8** (2018). https://doi.org:10.1002/aenm.201701991

3 Liu, Y. T., Zhang, R. H., Wang, J. & Wang, Y. Current and future lithium-ion battery manufacturing. *Iscience* **24** (2021). https://doi.org:10.1016/j.isci.2021.102332

4 Duffner, F., Mauler, L., Wentker, M., Leker, J. & Winter, M. Large-scale automotive battery cell manufacturing: Analyzing strategic and operational effects on manufacturing costs. *Int J Prod Econ* **232** (2021). https://doi.org:10.1016/j.ijpe.2020.107982

5 Lu, X. C., Bowden, M. E., Sprenkle, V. L. & Liu, J. A Low Cost, High Energy Density, and Long Cycle Life Potassium-Sulfur Battery for Grid-Scale Energy Storage. *Advanced Materials* **27**, 5915-5922 (2015). https://doi.org:10.1002/adma.201502343

6 Vapor Pressure of Pure Substances - Inorganic Compounds. *Ind Eng Chem* **39**, 540-550 (1947).

7 Chaudhari, S. K., Patil, K. R., Allepus, J. & Coronas, A. Measurement of the Vapor-Pressure of 2,2,2-Trifluoroethanol and Tetraethylene Glycol Dimethyl Ether by Static Method. *Fluid Phase Equilibr* **108**, 159-165 (1995). https://doi.org:10.1016/0378-3812(95)02683-6

8 Wang, Y. *et al.* Revitalising sodium–sulfur batteries for non-high-temperature operation: a crucial review. *Energy & Environmental Science* **13**, 3848-3879 (2020). https://doi.org:10.1039/D0EE02203A

9 Yan, Z. C., Zhao, L. F., Wang, Y. X., Zhu, Z. Q. & Chou, S. L. The Future for Room-Temperature Sodium-Sulfur Batteries: From Persisting Issues to Promising Solutions and Practical Applications. *Advanced Functional Materials* **32** (2022). https://doi.org:10.1002/adfm.202205622

10 Wang, Y. *et al.* Tunable Electrocatalytic Behavior of Sodiated MoS2 Active Sites toward Efficient Sulfur Redox Reactions in Room-Temperature Na–S Batteries. *Advanced Materials* **33**, 2100229 (2021). https://doi.org:https://doi.org/10.1002/adma.202100229

11 Yang, H. *et al.* Architecting Freestanding Sulfur Cathodes for Superior Room-Temperature Na–S Batteries. *Advanced Functional Materials* **31**, 2102280 (2021). https://doi.org:10.1002/adfm.202102280

12 Kim, H. *et al.* Enhanced reversible capacity of sulfurized polyacrylonitrile cathode for room-temperature Na/S batteries by electrochemical activation. *Chem Eng J* **426** (2021). https://doi.org:10.1016/j.cej.2021.130787

13 Guo, Q. B. *et al.* Ultrastable Sodium-Sulfur Batteries without Polysulfides Formation Using Slit Ultramicropore Carbon Carrier. *Advanced Science* **7** (2020). https://doi.org:10.1002/advs.201903246

14 Zhang, S. *et al.* Mo2N–W2N Heterostructures Embedded in Spherical Carbon Superstructure as Highly Efficient Polysulfide Electrocatalysts for Stable Room-Temperature Na–S Batteries. *Advanced Materials* **33**, 2103846 (2021). https://doi.org:https://doi.org/10.1002/adma.202103846

15 Yan, Z. *et al.* A High-Kinetics Sulfur Cathode with a Highly Efficient Mechanism for Superior Room-Temperature Na–S Batteries. *Advanced Materials* **32**, 1906700 (2020). https://doi.org:https://doi.org/10.1002/adma.201906700

16 Jiang, Y. *et al.* Single-Atom Vanadium Catalyst Boosting Reaction Kinetics of Polysulfides in Na–S Batteries. *Advanced Materials* **35**, 2208873 (2023). https://doi.org:https://doi.org/10.1002/adma.202208873

17 Xiong, P. *et al.* Room-Temperature Potassium–Sulfur Batteries Enabled by Microporous Carbon Stabilized Small-Molecule Sulfur Cathodes. *ACS Nano* **13**, 2536-2543 (2019). https://doi.org:10.1021/acsnano.8b09503

18 Ge, X. *et al.* Metal–Organic Framework-Derived Nitrogen-Doped Cobalt Nanocluster Inlaid Porous Carbon as High-Efficiency Catalyst for Advanced Potassium–Sulfur Batteries. *ACS Nano* **14**, 16022-16035 (2020). https://doi.org:10.1021/acsnano.0c07658

19 Lu, X. *et al.* Advanced intermediate-temperature Na–S battery. *Energy & Environmental Science* **6**, 299-306 (2013). https://doi.org:10.1039/C2EE23606K

20 Lu, X. *et al.* Liquid-metal electrode to enable ultra-low temperature sodium–beta alumina batteries for renewable energy storage. *Nature Communications* **5**, 4578 (2014). https://doi.org:10.1038/ncomms5578

21 Tai, Z. *et al.* Novel Quasi-Liquid K-Na Alloy as a Promising Dendrite-Free Anode for Rechargeable Potassium Metal Batteries. *Advanced Science* **8**, 2101866 (2021). https://doi.org:10.1002/advs.202101866

22 Lu, X. C. *et al.* Liquid-metal electrode to enable ultra-low temperature sodium-beta alumina batteries for renewable energy storage. *Nature Communications* **5** (2014). https://doi.org:10.1038/ncomms5578

23 Liu, B. Y., Zhao, J. J. & Wei, F. X. Characterization of caprolactam based eutectic ionic liquids and their application in SO2 absorption. *J Mol Liq* **180**, 19-25 (2013). https://doi.org:10.1016/j.molliq.2012.12.024

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The revised form of manuscript has addressed the comments from the reviewers, and I therefore recommend it be published in its present form.

Reviewer #3 (Remarks to the Author):

The authors showed a K-Na/S battery with higher capacity due to the use of the an acetamide/CPL electrolyte that has higher solubility of KxS. The authors have answered some of the reviewers' comments, but a few areas of the paper that is still confusing, including the calculation of the energy density and cost. In addition, some additional evidence are needed. Please see detailed comments below

Detailed comments:
1. What is meant by 1M [S] and 4M [S] in the abstract? Please elaborate
2. Explain why IT K/S battery has higher average voltage than RT K/S batteries? What is the difference in reaction mechanism?
3. Fig. R1 in the rebuttal should be added to the manuscript to explain why acetamide/CPL = 1:1 is used in this experiment
4. How much electrolyte do you need? What is the maximum solubility of S in the electrolyte? Elaborate on how the solubility of S and K2Sx changes with acetamide and CPL ratio
5. What is the ionic conductivity of BASE?
6. For the theoretical capacity of S, is it calculated based on S going to S2-? Please specify clearly

7. How do the authors know that the K-BASE separator does not conduct Na+? What is the reason for the ionic selectivity of K-BASE if it is still alumina-based?

8. For Fig. 1b, what is the current rate? What is the concentration of the KxS in the electrolyte after 1 day or 1 week discharge?

9. Describe how is the solubility test of K2Sx in the electrolyte conducted.

10. For SEM and XANES tests, if the electrodes were washed by solvents, then wouldn't the solid, if there are any, be washed away as well?

11. In Fig. 3b, the authors attribute the low capacity to solid K2S2/K2S formed in TEGDME. If there is limited solubility in TEGDME, then would increasing the amount of electrolyte allows higher capacity? Please show.

12. For 4M [S] and 8M [S] tests, the capacity seems to be limited by the formation of solid phases. If that is the case, show how the capacity changes with electrolyte amount

13. Elaborate on what is the cause of capacity fading of the cells with CPL/acetamide?
14. The energy and cost calculations are confusing and need clarification. First of all, why the discharge time is 24 h? In addition, clear calculation of the amount of S and K should be shown, and if the authors increase the discharge time to one week, how the actual amount of S and K changes.

15. K/Na alloy should be a liquid at room temperature. Comment on the performance of your battery

at room temperature.
16. Elaborate if Super C65 is suspended in the catholyte?
17. Why is Na2S added into the catholyte, as written in the materials preparation section?
18. What is the actual thickness of the K-BASE separator? Please add to experimental section.
19. Please state clearly the test temperature during electrochemical measurements.
20. Please add vendor of K2S8
21. What is the role of KTFSI and why it is not added for the SEM/EDS tests?
22. In some cases, the author refers to K/S and other cases K-Na/S. Since the anode contains Na, the authors should standardize to K-Na/S for consistency.

Question 1:

What is meant by 1M [S] and 4M [S] in the abstract? Please elaborate

Response:

We appreciate the reviewer's comment. [S] is defined as the overall concentration of sulfur atoms in the solution in the unit of mol/L (M). It counts sulfur from all polysulfides and sulfides. For example, if there are 1 mol K_2S and 1 mol K_2S_2 in a 1-liter solution, the concentration of sulfur is $1 \times 1 + 1 \times 2 = 3$ M.

We have added the definition to the manuscript as follows (line 22 on page 4):

Note that [S] counts sulfur from all polysulfides and sulfides inside the solution.

Question 2:

Explain why IT K/S battery has higher average voltage than RT K/S batteries? What is the difference in reaction mechanism?

Response:

Thank the reviewer for pointing out this issue. We assume that the reviewer refers to references 3 and 4 in Supplementary Table 1, which is copied below. In these two references of RT K/S batteries, the average voltages are 1.00 and 1.25 V, respectively, which are much lower than IT K/S batteries (2.10 V in our report and 2.00 V in reference 7). This arises from that they use small molecule sulfur, where sulfur exists as S_x (x = 1-4), which is known to have a lower voltage than S_8, the common form of S cathode (e.g., ~1.7 V vs. 2.1 V), in Li-S batteries[1,2]. When S_8 is used, the voltage of RT K/S batteries is also around 2.0 V, as shown in references 5 and 6, which is similar to our IT K-Na/S batteries. These two references are also added in the updated Supplementary Table 1.

We also add voltage profiles from reference 3 (small molecule sulfur) and reference 5 (S_8) in K-S batteries as Fig. R1a and Fig. R1b below, respectively. Clearly, when S_8 is used, the voltage is ~2.0 V.

To remind readers about this, the discussion above is added after Supplementary Table 1 in the supplementary information.

Supplementary Table 1.
Reported works on RT Na/S and K/S batteries

K/S battery	Design strategy	Current (mA/cm^2 / mA/g)	Average voltage (V)	Initial capacity (mAh/g)	Cycle number	Normalized decay (%/100 cycles)
[3]	Small sulfur molecules	0.02 / 20	1.00	1198	150	19.3

[4]	S–N–Cos–C	NA / 200	1.25	463	150	16.2
[5]	Homogeneous catalyst	NA/800	1.93	650	200	8.4
[6]	Concentrated electrolyte	NA/10	2.10	606	NA	NA
This work	**Amide electrolyte**	**2 / 600**	**2.10**	**830**	**1100**	**3.2**

Supplementary Table 2.
Reported works on Intermediate Temperature (IT) Na/S and K/S batteries

K/S battery	Design strategy	Current (mA/cm^2)	Average voltage (V)	Initial capacity (mAh/g)	Cycle number	Normalized decay (%/100 cycles)	Operation temperature (°C)
[7]	TEGDME catholyte	1.33	2.00	312	1000	<0.1	150
This work	**Dissolving K_2S and K_2S_2**	**2**	**2.10**	**830**	**1100**	**3.2**	**75**

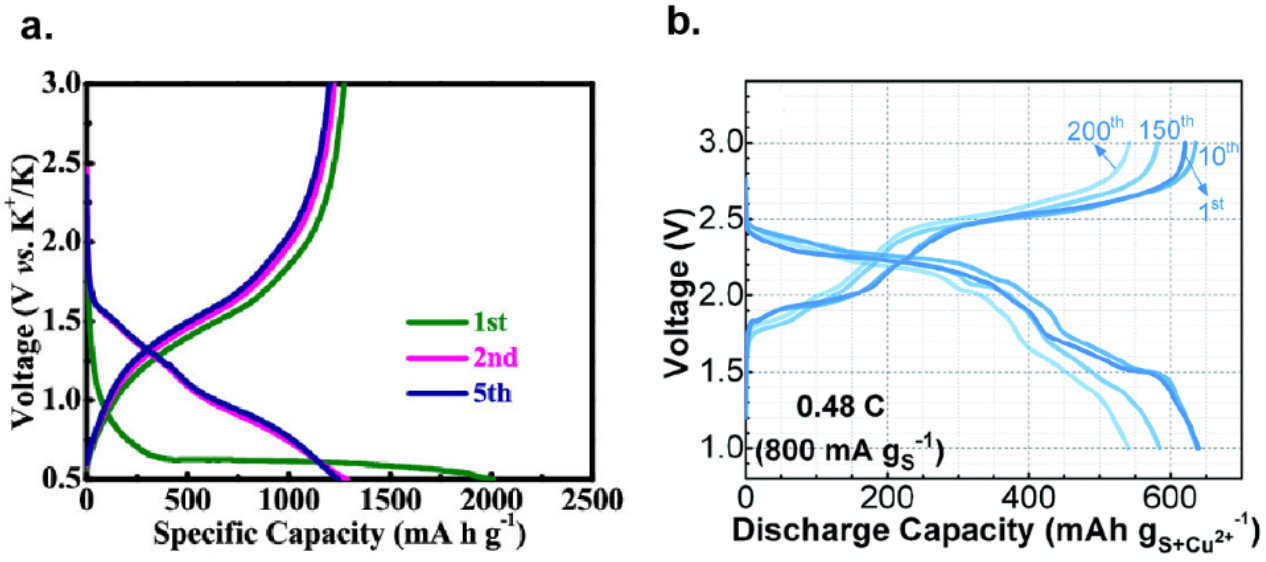


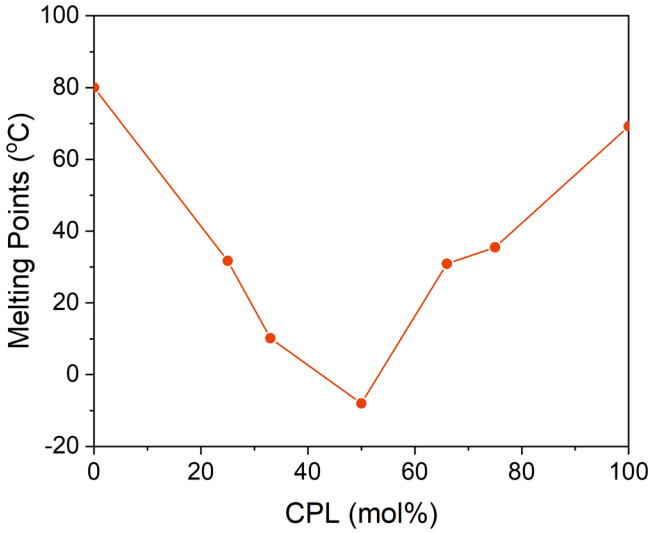
Fig R1. a) Galvanostatic charge-discharge profiles of microporous C/S composite 20 mA g^{-1} in K-S batteries[3], where S should exist in small molecule sulfur status (S_1-S_4) b) The selected galvanostatic discharge and charge curves at 0.48C for the first 200 cycles for K/S cells with metal catalyst at room temperature[5], where sulfur is S_8.

Question 3:

Fig. R1 in the rebuttal should be added to the manuscript to explain why acetamide/CPL = 1:1 is used in this experiment

Response:

Fig. R1 in the previous rebuttal is redrawn and added in the supplementary information as Supplementary Fig. 1.



Supplementary Fig. 1. Melting points for CPL/acetamide with different mixing ratios. The figure is redrawn from Liu et al.[8]

We also adapted the manuscripts as follows (line 7 on page 5):

The cathode is polysulfide dissolved in a mixture of CPL and acetamide (1:1 molar ratio, Fig. 1a), which has the lowest melting point among CPL/acetamide mixtures (Supplementary Fig 1).

Question 4:

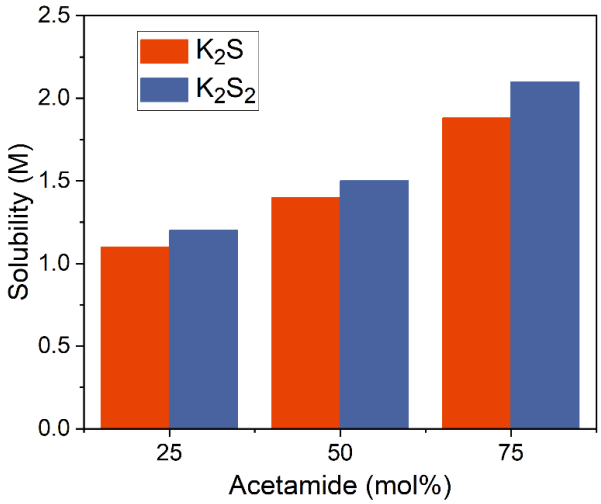
How much electrolyte do you need? What is the maximum solubility of S in the electrolyte? Elaborate on how the solubility of S and K2Sx changes with acetamide and CPL ratio.

Response:

We appreciate that you brought up this concern. 13.4 µL catholyte was used in our coin cell configuration. Sulfur is almost insoluble (<0.1M) in the CPL/acetamide catholyte since sulfur is nonpolar. However, once it is slightly reduced (e.g., the sulfur particles in contact with the current collector), sulfur is converted to K_2S_8, which is highly soluble, so the kinetics of sulfur is not a limiting factor. This is similar to the case of conventional DOL/DME electrolytes, where sulfur also has a solubility much lower than polysulfides[9].

We measured the solubility of K_2S and K_2S_2 in CPL/Acetamide mixtures with different mixing

ratios. It is clear that the solubilities of K_2S_2 and K_2S increase along with the increasing amount of acetamide, indicating that there is a stronger interaction between acetamide and K_2S_x. The figure is added in the supplementary information as Supplementary Fig. 3.



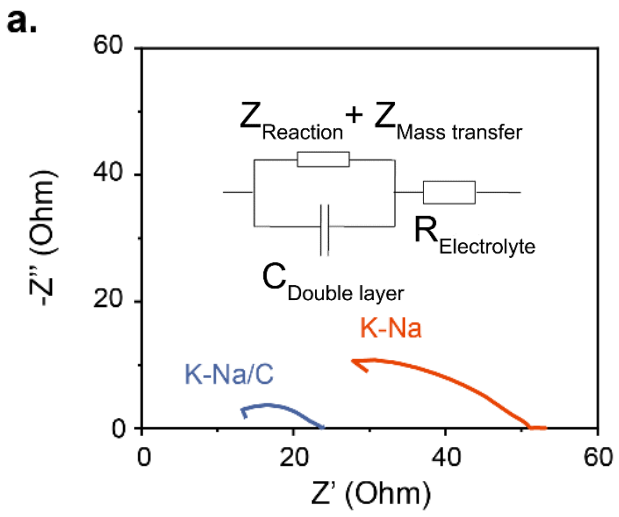
Supplementary Fig. 3. Solubility of K_2S and K_2S_2 for CPL/acetamide mixtures with different acetamide fractions.

Question 5

What is the ionic conductivity of BASE?

Response:

Based on our K-Na/K-BASE/K-Na symmetry cell results (Supplementary Fig. 6), the resistance of BASE is ~10 ohm, and thus the conductivity of K-BASE is 16 mS/cm at 75 ºC. Such a high conductivity enables long cycling and low overpotential due to electrolyte resistance. The BASE resistance is obtained by using the equivalent circuit shown below.



Supplementary Fig. 8a Impedance results of symmetry cell with K-Na/C or K-Na alloy as

electrode in both sides.

Question 6

For the theoretical capacity of S, is it calculated based on S going to S^{2-}? Please specify clearly

Response:

Yes, the theoretical capacity of S is based on S to S^{2-} (S + 2e- → S^{2-}), which corresponds to 1675 mAh/g sulfur.

Question 7

How do the authors know that the K-BASE separator does not conduct Na+? What is the reason for the ionic selectivity of K-BASE if it is still alumina-based?

Response:

Your vigilance on this matter is greatly appreciated. The fact that K-BASE does not conduct Na^+ is validated by both thermodynamic simulations and experimental results in the literature.

In thermodynamic simulations, K^+ in K-BASE has a Gibbs free energy of 65 kJ mol^{-1} lower than Na^+ in K-BASE[10], so K^+ prefers to stay in K^+ - BASE than Na^+.

Experimentally, Baclig et al[11] used two experiments to show that Na^+ cannot replace K^+ in K-BASE. First, electron microprobe analysis (EPMA) is used to detect the polished surface of K-BASE after exposure to K-Na alloy at 300 ºC for 140 hours. The results show that the exchange of K^+ and Na^+ in K-BASE is less than 1.5%. Since we only run cells at 75 ºC, the exchange of ions would be minimal. Second, they used inductively coupled plasma optical emission spectrometry (ICP-OES) to measure the Na ion concentration in a cell with K-Na alloy anode, K-BASE separator, and a catholyte of 0.1 M $K_3[Fe(CN)_6]$, 0.1 M $K_4[Fe(CN)_6]$, and 1 M KOH. After 75 mAh discharging, the concentration of sodium ion in the cathode side is still at the same level as the baseline, and the calculated transference number of potassium is >0.99.

β"-Alumina is actually just a popular name for this material, but it is not pure Al_2O_3. The exact composition is Na_2O-nAl_2O_3 (n=5~11) for Na-BASE, and it is K_2O-nAl_2O_3 (n=5~11) for K-BASE[12]. Therefore, it contains the ions to transport.

Question 8

For Fig. 1b, what is the current rate? What is the concentration of the K_xS in the electrolyte after 1 day or 1 week discharge?

Response:

Thank you for spotlighting this concern. In Fig. 1b, the current rates are 2 mA cm^{-2} for both 1-

day-discharge and 1-week-discharge curves. The concentrations of [S] are always the same during charging and discharging, which equals the values on the x-axis. Only the valence of S is changed. For example, it is always 4 M [S] for the case with an x-axis value of 4 M. What is changed between the two curves is the capacity per area (mAh/cm^2). The amount of catholyte for the 1-week case is seven times that for the 1-day case.

For example, there is 1 M K_2S_8 (8 M in S) before discharge. After discharging, it will transform into 1.6 M K_2S+3.2 M K_2S_2 (8M in S), which corresponds to 1000 mAh g^{-1} specific capacity (the value used in calculating specific energy).

Question 9

Describe how is the solubility test of K_2S_x in the electrolyte conducted.

Response:

Your attention to this detail is highly appreciated. Take K_2S_2 as an example. Firstly, K_2S is mixed with sulfur with a 1:1 molar ratio in a glass vial with 500 μL solvent. Then the mixture is stirred on a hot plate at the set temperature. If the solution becomes clear, then we will add some extra K_2S and sulfur (with a 1:1 molar ratio). Otherwise, we will add a certain amount of extra solvent. After repeating this process, if we find that a certain concentration of C_0 of K_2S_2 is soluble, which is defined as no solid inside the vial after 2 hours of sediment and C_0 + 0.05 M is not soluble, which is defined as the existence of solid precipitates after 2 hours, then we can say that the solubility of K_2S_2 is C_0 at this temperature.

We have added the above description to the experiment section in the main text (line 2 on page 19).

Question 10

For SEM and XANES tests, if the electrodes were washed by solvents, then wouldn't the solid, if there are any, be washed away as well?

Response:

We are grateful for your careful consideration of this issue. In SEM, the washing procedure aims to remove the original catholyte along with K_2S_x dissolved in the solvent so we can get a clear image of insoluble residues (i.e., insoluble K_2S_x) on the carbon substrate. If we only evaporate the solvent, then both soluble and insoluble K_2S_x (if any) will remain on the surface of carbon paper, and we cannot distinguish them.

To dispel the misgiving on this problem, we further do a SEM test with no solvent washing, but using Kimwipes paper to absorb and remove the catholyte on carbon paper. The SEM results show that there is no particle left on the carbon substrate when the CPL/acetamide catholyte is used. We

have replaced the original SEM results of CPL/acetamide in Fig. 4 by the new image below.

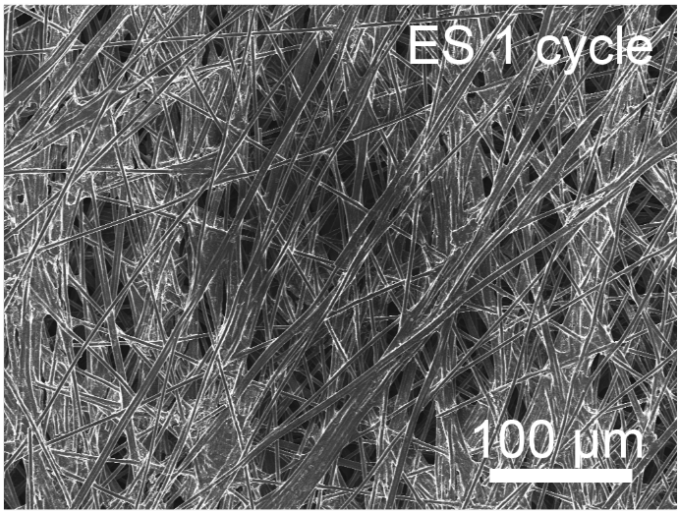


Fig. 4a Scanning Electron Microscope (SEM) imaging results of carbon paper from cells after the first cycle with 1M [S] CPL/acetamide eutectic solvent (ES).

In XANES tests, we did not wash away the solvents. The carbon paper was retrieved from coin cells and sealed in a plastic bag directly, so the carbon paper was immersed in the catholyte, and there was no issue caused by washing away.

Question 11

In Fig. 3b, the authors attribute the low capacity to solid K_2S_2/K_2S formed in TEGDME. If there is limited solubility in TEGDME, then would increasing the amount of electrolyte allows higher capacity? Please show.

Response:

We are grateful for your meticulous feedback. First, we assume that the reviewer means adding more solvent but not more catholyte, since adding more catholyte will not reduce the amount of solid K_2S_2/K_2S formed. If so, as shown in Fig. 2d in the main text, K_2S, K_2S_2, and K_2S_3 all have solubilities less than 0.1 M (based on S) in TEGDME. As a consequence, adding extra TEGDME will not help increase the dissolution of K_2S/K_2S_2/K_2S_3 substantially and thus the specific capacity of the sulfur cathode.

Moreover, increasing the amount of solvent is equivalent to reducing the concentration of sulfur in the electrolyte. In the paper, we measured the electrochemical performance for 1 M / 4 M / 8 M in TEGDME in Fig. 3 and Fig. 5. Here, we overlapped them together as Fig. R3. The specific capacities of 4 M and 8 M cells do not differ much, but when [S] is reduced to 1 M, the specific capacity indeed increases to 603 mAh/g. However, such specific capacity is still less than that for 8 M S in CPL/acetamide (672 mAh/g). Moreover, with 1 M [S], the specific energy at the cell level is

only 37 Wh/kg for 603 mAh/g, which is too low for practical applications.

If the reviewer means adding more catholytes (solvent and polysulfides), please let us know, and we will be happy to run the experiments, although we think more catholytes will only increase the mass of active materials per area and the transport distance, which lead to lower specific capacity.

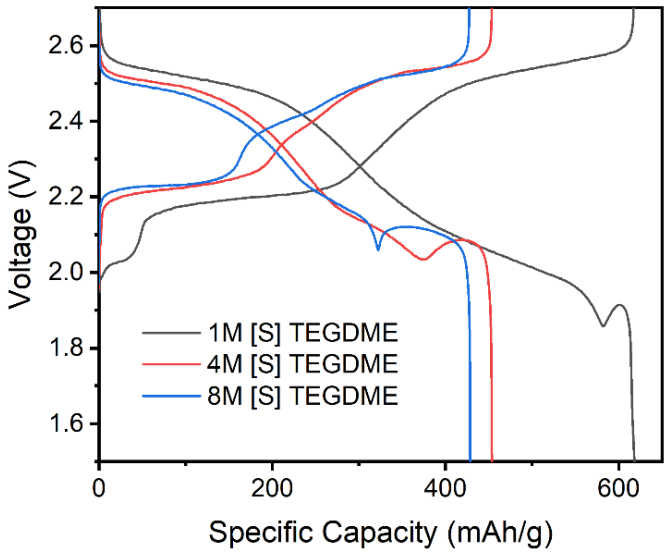


Fig. R3a Discharge-charge curves for TEGDME K-Na/S cells at the 50th cycle, which has similar or higher capacity than the first cycle, adapted from Fig. 3 and 5 in the main text.

Question 12

For 4M [S] and 8M [S] tests, the capacity seems to be limited by the formation of solid phases. If that is the case, show how the capacity changes with electrolyte amount.

Response:

Similar to the answer to question 11, increasing the amount of solvent is equivalent to reducing the concentration of sulfur in the electrolyte. Therefore, 1 M [S] is the same as increasing the electrolyte amount in the 4 M case by 4 times. To answer this question quantitatively, Fig R3b shows the overlap of the voltage profile of 1 M / 4 M / 8 M [S] at cycle 50. We can see that a lower concentration of [S] indeed increases the specific discharge capacity significantly, from 604 mAh/g at 8 M to 1100 mAh/g at 4 M, and 1584 mAh/g at 1 M. Therefore, the dilution with electrolyte indeed increases the discharge capacity since more K_2S_2 and K_2S can be dissolved in acetamide/CPL.

Again, If the reviewer means adding more electrolytes (both salt and solvent), please let us know, and we will be happy to run the experiments, although we think more electrolytes will only increase the mass of active materials per area and the transport distance, which lead to lower specific capacity.

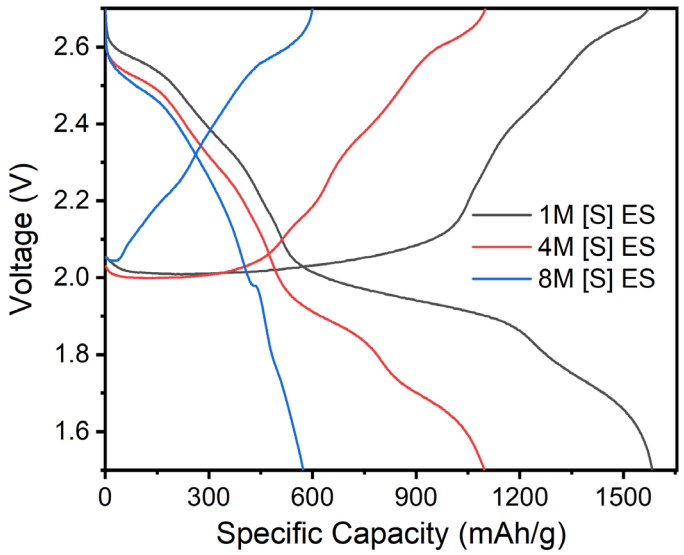


Fig. R3b Discharge-charge curves for K-Na/S cells in acetamide/CPL electrolyte at the 50th cycles, adapted from Fig. 3 and 5 in the main text.

Question 13

Elaborate on what is the cause of capacity fading of the cells with CPL/acetamide?

Response:

Thank you for drawing our attention to this issue. We think that the capacity fading in CPL/acetamide is mainly caused by the evaporation of this solvent since CPL/acetamide has a much higher vapor pressure than TEGDME. This is elaborated in the Supplementary Note 6.

Vapor pressure. The boiling points of the solvents show notable differences: TEGDME has a high boiling point of 275 °C, while acetamide and CPL boil at 220 °C and 270 °C, respectively. The formation of a eutectic solvent in the mixture could further reduce its boiling point. Correspondingly, the vapor pressure trends align with boiling point data. CPL or acetamide exhibits higher vapor pressure compared to TEGDME. For instance, acetamide alone has a vapor pressure of 10.25 kPa at 100 °C, whereas TEGDME's vapor pressure is substantially lower at 132 Pa at 100 °C. This disparity suggests that evaporation could be more pronounced in CPL/acetamide than in TEGDME.

Besides vapor pressure, there are two other possible reasons why CPL/acetamide has worse cycling than TEGDME, which is also discussed in Supplementary Note 6:

1. *Cycling duration time. TEGDME and acetamide/CPL cells are cycled at an identical current*

density. However, due to the significantly higher specific capacity of acetamide/CPL cells, the duration of one cycle is approximately 2 to 3 times longer than that of TEGDME. This extended cycling period likely contributes to greater degradation in the acetamide/CPL cells (e.g. aging of coin cell gaskets and PTFE sealing O rings).

2. *Solubility of K_2S_2. During the discharge process, solid K_2S_2 is formed. However, the majority of the specific capacity is attributed to the soluble S/K_2S_3 redox reaction. Since the transformation mostly happens from S to K_2S_3, a small amount of solid precipitation will not lead to the irreversibility of reaction.*

Question 14

The energy and cost calculations are confusing and need clarification. First of all, why the discharge time is 24 h? In addition, clear calculation of the amount of S and K should be shown, and if the authors increase the discharge time to one week, how the actual amount of S and K changes.

Response:

We appreciate you highlighting the area of energy and cost calculation. For the discharge time problem, since the purpose of IT Na/S or K/S batteries is large-scale energy storage for the grid, 24 hours and 7 days are reasonable time scales. This is mentioned in the introduction part (line 4 on page 3):

Long-duration energy storage (LDES) with an operational period over one day is of particular importance as it enables stable power output at extreme conditions and leverages seasonal variations. However, LDES is highly challenging due to the demanding requirement on low cost, since it is operated for a limited number of cycles, ***such as ~1,500 times for weekly operation and ~400 times for monthly operation in 30 years, much less than short-term energy storage with everyday cycling and thus ~10,000 cycles in 30 years.***

Besides, we have rewritten the calculation of energy density and cost (Supplementary Note 2 and Supplementary Note 7) as follows to make it clearer. For example, we add more tables to clarify the values of each component.

Supplementary Note 2. Calculation of specific energy

The theoretical specific energy is calculated based on the stoichiometric ratio of sulfur and K, and the theoretical capacity of sulfur (1675 mAh g^{-1}) and K (687 mAh g^{-1}). Only the mass of sulfur, K, and CPL/acetamides are considered. Therefore, as shown in Table S3 below, for 1 Ah cell, the mass of sulfur and K are 0.597 g and 1.46 g, respectively (Supplementary Table 3). The mass of

CPL/acetamide depends on [S], and it is calculated to be 18.6 g, 4.66 g, and 2.33 g for 1 M, 4 M, and 8 M, respectively. Hence the total mass for 1 Ah cell is 20.7 g, 6.71 g, and 4.38 g, respectively. Given that the average voltage of K-Na/S cells is 1.98 V, the theoretical specific energy of K-Na/S batteries is 95.8, 295, and 452 Wh/kg for 1, 4, and 8 M [S]. The specific energy of other concentrations is calculated with the same procedure.

Supplementary Table 3.

Calculation of theoretical energy density for K-Na/S cells

[S] (M)	Capacity (Ah)	Average voltage (V)	Sulfur mass (g)	Potassium mass (g)	CPL/acetamide (g)	Total mass (g)	Specific energy (Wh/kg)
1	1	1.98	0.597	1.46	18.6	20.7	95.8
4	1	1.98	0.597	1.46	4.66	6.71	295
8	1	1.98	0.597	1.46	2.33	4.38	452

The calculation of practical specific energy at the cell level is shown in Supplementary Table 4, we use the practical capacity of electrodes (e.g., 1000 mAh g^{-1} sulfur and 600 mAh g^{-1} for K). Moreover, the masses of BASE and packaging are taken into account.

For BASE, we assume that its thickness is 0.5 mm and its density is 3.31 g cm^{-3} [13] so its mass is 1.66 kg m^{-2}. The electrode mass per area depends on the current density and discharge time. Take 2 mA cm^{-2} and 24-hour discharge as an example, the areal capacity is 48 mAh cm^{-2}, so the mass of sulfur is 48 mAh cm^{-2} / 1000 mAh g^{-1} = 0.48 kg m^{-2}. Similarly, the mass of K is 0.80 kg m^{-2}. The mass of CPL/acetamide is 15, 3.75, and 1.88 kg m^{-2} for 1 M, 4 M, and 8 M [S] respectively. For packaging, we assume that the packaging is Al with a thickness of 0.05 mm, so the mass of Al on the two sides together is 0.27 kg m^{-2}.

Take a footprint area of 100 cm^2, 4 M sulfur and a discharge time of 24 hours as an example, the total energy is 48 mAh cm^{-2} × 1.98 V × 100 cm^2 = 9.50 Wh. The total mass is 4.80 g + 8.00 g + 37.5 g + 16.6 g + 2.7 g = 69.6 g, and thus the specific energy is 136 Wh kg^{-1}.

When the discharge time increases to one week, the mass of each component above can be calculated similarly, and we summarize the data in Supplementary Table 5 below.

Supplementary Table 4.

Calculation of practical energy density for 24-hour discharge at 2 mA cm^{-2} and 100 cm^2 area

[S] (M)	Capacity (Ah)	Average voltage (V)	Sulfur mass (g)	Potassium mass (g)	CPL/acetamide mass (g)	BASE mass (g)	Packaging mass (g)	Total mass (g)	Specific energy (Wh/kg)
1	4.80	1.98	4.80	8.00	150	16.6	2.70	182	52.1

4	4.80	1.98	4.80	8.00	37.5	16.6	2.70	69.6	136
8	4.80	1.98	4.80	8.00	18.8	16.6	2.70	50.9	186

Supplementary Table 5.

Calculation of practical energy density for one-week discharge at 2 mA cm^{-2} and 100 cm^2 area

[S] (M)	Capacity (Ah)	Average voltage (V)	Sulfur mass (g)	Potassium mass (g)	CPL/acetamide mass (g)	BASE mass (g)	Packaging mass (g)	Total mass (g)	Specific energy (Wh/kg)
1	33.6	1.98	33.6	56.00	1050	16.6	2.70	1160	57.3
4	33.6	1.98	33.6	56.00	263	16.6	2.70	372	179
8	33.6	1.98	33.6	56.00	132	16.6	2.70	241	276

Supplementary Note 7. Material Cost estimation of K-Na/S battery system

In material cost estimation, we take the cost of sulfur, K, CPL/acetamide, BASE and packaging into account, and we use the practical specific capacities for generating the 1-day discharge and 1-week discharge curves in Fig. 1b (see Supplementary Note 2). The cost of these materials per weight is listed in Supplementary Table S13.

Supplementary Table 13. Reactor Components Cost per Area

Components	Price ($ kg^{-1})
Sulfur	0.2
CPL/acetamide	6.5
K metal	12.1
BASE	10
Aluminum	2.3

Based on these prices, we can calculate the cost of each component in K-Na/S batteries for the same configurations in Fig. 1b. Here we use 1-day discharge as an example, and the results are

shown in Supplementary Table 14. Again, we assume the current density is 2 mA cm^{-2} and the footprint area is 1 m^2.

Supplementary Table 14.
Calculation of cost of K-Na/S batteries for 1-day discharge at 2 mA cm^{-2} and 1 m^2 area

[S] (M)	Capacity (Ah)	Average voltage (V)	Sulfur cost ($)	Potassium cost ($)	CPL/acetamide cost ($)	BASE cost ($)	Packaging cost ($)	Total cost ($)	Cost per energy ($/kWh)
1	480	1.98	0.096	9.68	97.5	16.6	0.621	124.5	131
4	480	1.98	0.096	9.68	24.4	16.6	0.621	51.4	54.1
8	480	1.98	0.096	9.68	12.2	16.6	0.621	39.2	41.2

Question 15

K/Na alloy should be a liquid at room temperature. Comment on the performance of your battery at room temperature.

Response:

We are grateful for your insight in identifying this potential application. We only discharged one cell at room temperature for the *operando* optical observation where ~1200 mAh g^{-1} is obtained (Fig. 4e), but the cell is with only 0.5 M [S] and 0.25 mA/cm^2. Reasonable long-term cycling of K-Na/S cells is difficult to achieve at RT due to the significantly larger impedance at RT (~ 1700 ohm) than that at 75 ºC (~160 ohm, Fig. R4). Such higher impedance arises from:

1) The RT conductivity of catholyte is only ~10% of that at 75 ºC. For example, the ionic conductivity of 4 M [S] in CPL/acetamide is 1.5 mS/cm at 75 ºC, but only 0.14 mS/cm at 25 ºC.
2) The catholyte is very viscous at RT, which also leads to sluggish reaction kinetics. As shown in Fig R4, the charge transfer resistance (part II) increases from ~ 80 ohm at 75 ºC to ~ 1400 ohm at 25 ºC, indicating bad kinetics at RT. We identify the semicircle at low frequency represents the charge transfer process at the cathode side.
3) The wetting between K-Na alloy and K-BASE sheet becomes a problem at RT. Although K-Na alloy is a liquid at RT, its high surface energy leads to poor contact with K-BASE. The corresponding charge transfer resistance (semicircle at higher frequency in Fig. R4) increases from ~40 ohm at 75 ºC to 400 ohm at RT.

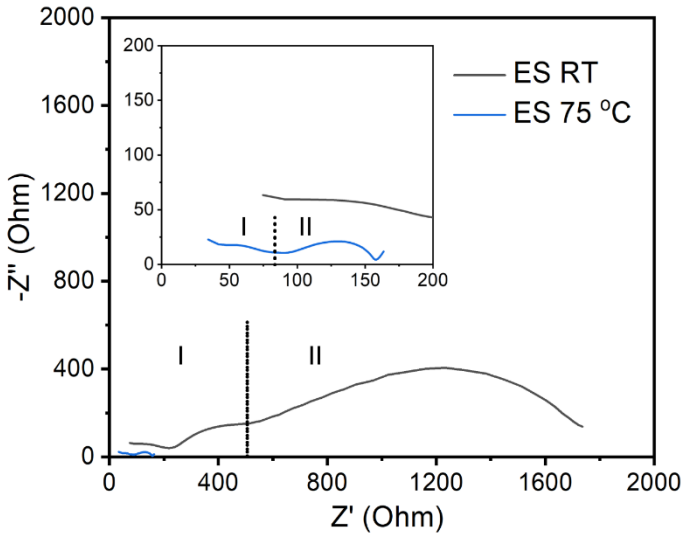


Fig. R4. EIS of 1M [S] in CPL/acetamide cells at 75 °C and RT. Part 1 corresponds to charge transfer at the K-Na/BASE interface, and part 2 corresponds to the catholyte.

Question 16

Elaborate if Super C65 is suspended in the catholyte?

Response:

We appreciate the reviewer's comment. Super C65 is nanopowder (~30 nm in diameter) and will suspend in catholyte after a long time of stirring. Then the mixture is added to the carbon paper.

We have revised the description in the experimental parts (line 17 on page 18) as follows:

To form a catholyte, 0.125 M/0.5 M/1 M of anhydrous Na_2S (98%, Sigma Aldrich), 0.5 M potassium bis(trifluoromethanesulfonyl)imide (KTFSI, 97%, Sigma Aldrich), and 1.25 wt% (of solvent) Super C65 carbon black were mixed with CPL/acetamide and stirred at 80 °C until a homogeneous mixture is formed.

Question 17

Why is Na_2S added into the catholyte, as written in the materials preparation section?

Response:

We appreciate your careful reading in pointing out this concern. At the beginning, we tried to prepare K_2S_8 in the catholyte so [S] is homogeneous in the catholyte. K_2S_8 in catholyte can be prepared by adding K_2S and S in the solvent through the reaction $K_2S + 7\ S \rightarrow K_2S_8$. However, unfortunately we could not purchase K_2S with a high purity during most time of our research, so we used Na_2S instead, and thus the starting material is Na_2S_8. Therefore, the corresponding [Na^+] in the

electrolyte was 0.25 M, 1 M, and 2 M for cells with 1 M, 4 M, and 8 M [S]. In our electrolyte, we also have 0.5 M KTFSI to enhance ionic conductivity, as discussed in the answer to question 21.

During the discharge, since only K^+ can pass K-BASE as shown in the answer to question 7, the sulfur redox is accompanied by the addition of K^+ in the electrolyte. So, the final discharge product is M_2S, where M is a mixture of ~85-95% of K and 5-15% of Na.

Towards the end of the manuscript preparation, we find a vendor that can provide K_2S with a high purity. Therefore, all the characterization tests (including SEM, synchrotron, solubility, Raman etc.) were performed with K_2S_8 (K_2S + 7 S) as the starting material.

We are sorry for such confusion. The method section accurately describes what has been done in our experiments so others can easily repeat our experiments. On the other hand, as shown in Fig. R5, there is almost no difference in discharge/charge curves when starting with K_2S_8 or Na_2S_8.

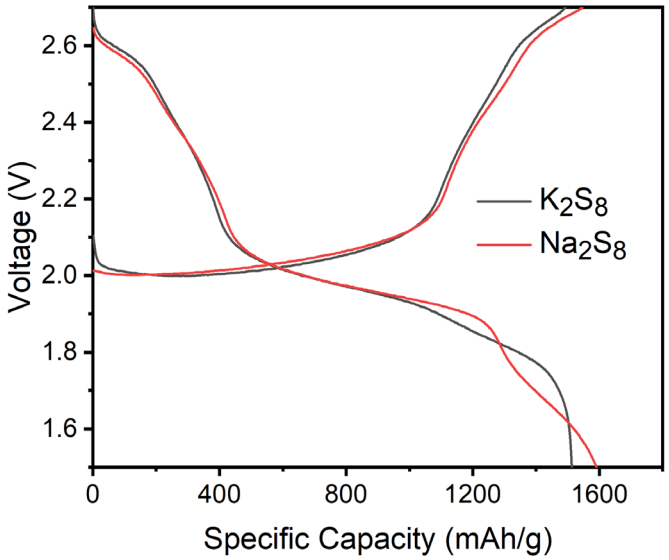


Fig. R5. Discharge-charge curves in the first cycle with K_2S_8 or Na_2S_8 as the starting material in the cathode side.

Question 18

What is the actual thickness of the K-BASE separator? Please add to experimental section.

Response:

We are thankful for your keen observation of this detail. The thickness of K-BASE sheet is 1 mm. We added it into the experimental section as follows (line 15 on page 19):

Potassium-β''-alumina (K-BASE) with 1 mm thickness was purchased from Ionotec Inc. and cut into disks with 15 mm diameter.

Question 19

Please state clearly the test temperature during electrochemical measurements.

Response:

All electrochemical tests were done at 75 ºC in an oven. The only outlier is the cell for *operando* optical imaging, which was done at room temperature since the heating element is not compatible with our optical microscopes.

We added the testing temperature in Method parts as follows (line 9 on page 20):

All cells were kept at 75 ºC in convection drying ovens (MTI Corp.).

We also added the testing temperature into figure captions to make it clearer:

All tests are done in a 75 ºC oven. ((Fig. 3, line 10 on page 10)

[S] in the catholyte and temperature are 1 M and 75 ºC, respectively, for ***a-d****, and 0.5 M and 25 ºC, respectively, in* ***e*** *and* ***f****.* (Fig. 4, line 5 on page 13)

All electrochemical tests for ***a-f*** *are done at 75 ºC in an oven.* (Fig. 5, line 10 on page 15)

Question 20

Please add vendor of K_2S_8

Response:

Thanks for pointing this out. We added the vendor in the method part of the main text (line 9 on page 21):

K_2S_8 catholyte is formed by mixing K_2S (Thermal Fisher Scientific) and S (Sigma Aldrich) with the stoichiometric ratio in either CPL/acetamide or TEGDME and stirred at a 75 ºC heat plate overnight.

Question 21

What is the role of KTFSI and why it is not added for the SEM/EDS tests?

Response:

Thanks for asking this question. KTFSI acts as a salt additive in the catholyte to increase the ionic conductivity of the catholyte. For example, without KTFSI, then at the fully charged state, all K^+ ions in the catholyte move to the anode and get reduced, so there is no ion left in the catholyte,

and the catholyte conductivity will be very low. The addition of KTFSI can solve this problem.

For the SEM/EDS test, we want to observe K_2S_x particles as precipitation on the carbon paper substrate. For this target, only discharging is needed so there is no worry of K ion depletion. Besides, since K and S both exist in KTFSI, it is not added to avoid interference with K and S signals from K_2S_x.

Question 22

In some cases, the author refers to K/S and other cases K-Na/S. Since the anode contains Na, the authors should standardize to K-Na/S for consistency.

Response:

We appreciate the reviewer's note that the expression might be confusing. To avoid such confusion, we change K/S to K-Na/S when we discuss our experiments and cells. When we talk about K/S and Na/S batteries in general, we keep them as K/S and Na/S for accuracy.

REFERENCE

1 Xin, S. *et al.* Smaller Sulfur Molecules Promise Better Lithium-Sulfur Batteries. *Journal of the American Chemical Society* **134**, 18510-18513 (2012). https://doi.org/10.1021/ja308170k

2 Guo, J. C., Xu, Y. H. & Wang, C. S. Sulfur-Impregnated Disordered Carbon Nanotubes Cathode for Lithium-Sulfur Batteries. *Nano Lett* **11**, 4288-4294 (2011). https://doi.org/10.1021/nl202297p

3 Xiong, P. X. *et al.* Room-Temperature Potassium-Sulfur Batteries Enabled by Microporous Carbon Stabilized Small-Molecule Sulfur Cathodes. *Acs Nano* **13**, 2536-2543 (2019). https://doi.org/10.1021/acsnano.8b09503

4 Ge, X. *et al.* Metal–Organic Framework-Derived Nitrogen-Doped Cobalt Nanocluster Inlaid Porous Carbon as High-Efficiency Catalyst for Advanced Potassium–Sulfur Batteries. *ACS Nano* **14**, 16022-16035 (2020). https://doi.org/10.1021/acsnano.0c07658

5 Lai, N. C., Cong, G. T. & Lu, Y. C. A high-energy potassium-sulfur battery enabled by facile and effective imidazole-solvated copper catalysts. *J Mater Chem A* **7**, 20584-20589 (2019). https://doi.org/10.1039/c9ta06906b

6 Wang, L., Bao, J. Z., Liu, Q. & Sun, C. F. Concentrated electrolytes unlock the full energy potential of potassium-sulfur battery chemistry. *Energy Storage Mater* **18**, 470-475 (2019). https://doi.org/10.1016/j.ensm.2018.10.004

7 Lu, X. C., Bowden, M. E., Sprenkle, V. L. & Liu, J. A Low Cost, High Energy Density, and Long Cycle Life Potassium-Sulfur Battery for Grid-Scale Energy Storage. *Advanced Materials* **27**, 5915-5922 (2015). https://doi.org/10.1002/adma.201502343

8 Liu, B. Y., Zhao, J. J. & Wei, F. X. Characterization of caprolactam based eutectic ionic liquids and their application in SO2 absorption. *J Mol Liq* **180**, 19-25 (2013). https://doi.org/10.1016/j.molliq.2012.12.024

9 Adeoye, H. A., Dent, M., Watts, J. F., Tennison, S. & Lekakou, C. Solubility and dissolution kinetics of sulfur and sulfides in electrolyte solvents for lithium-sulfur and sodium-sulfur batteries. *J Chem Phys* **158** (2023). https://doi.org/Artn 06470210.1063/5.0132068

10 Tan, A., Singh, G., Tsurumi, T. & Nicholson, P. S. Ion-Exchange and Thermodynamic Studies on (Na-K) Beta"-Alumina. *Solid State Ionics* **21**, 67-72 (1986). https://doi.org/Doi 10.1016/0167-2738(86)90010-X

11 Baclig, A. C. *et al.* High-Voltage, Room-Temperature Liquid Metal Flow Battery Enabled by Na-K|K-β"-Alumina Stability. *Joule* **2**, 1287-1296 (2018). https://doi.org/10.1016/j.joule.2018.04.008

12 Yang, K. S., Liu, D. Y., Qian, Z. F., Jiang, D. T. & Wang, R. H. Computational Auxiliary for the Progress of Sodium-Ion Solid-State Electrolytes. *Acs Nano* **15**, 17232-17246 (2021). https://doi.org/10.1021/acsnano.1c07476

13 β-alumina (NaAl11O17) Crystal Structure: Datasheet from "PAULING FILE Multinaries Edition – 2022" in SpringerMaterials (https://materials.springer.com/isp/crystallographic/docs/sd_1410950) (Springer-Verlag Berlin Heidelberg & Material Phases Data System (MPDS), Switzerland & National Institute for Materials Science (NIMS), Japan).

REVIEWERS' COMMENTS

Reviewer #3 (Remarks to the Author):

The authors have answered all the enquiries satisfactorily