

Stable cycling of lithium sulfide cathodes through strong affinity with a bifunctional binder†

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Rechargeable lithium–sulfur batteries have attracted great interest in recent years because of their high theoretical specific energy, which is several times that of current lithium-ion batteries. Compared to sulfur, fully-lithiated Li_2S represents a more attractive cathode material because it enables pairing with safer, lithium metal-free anodes. Here, we demonstrate stable and high-performance Li_2S cathodes by using *ab initio* simulations to guide our rational selection of poly(vinylpyrrolidone) binder which exhibits strong affinity with both Li_2S and lithium polysulfides. A high discharge capacity of 760 mA h g^{-1} of Li_2S ($\sim 1090 \text{ mA h g}^{-1}$ of S) was achieved at 0.2 C with stable cycling over prolonged 500 charge/discharge cycles.

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Introduction

Over the past two decades, energy storage technologies based on lithium-ion batteries have proven successful and found widespread use in many present-day applications such as portable electronics and consumer devices.^{1–6} However, intercalation cathodes used in current lithium-ion batteries possess an inherent theoretical capacity limit of $\sim 300 \text{ mA h g}^{-1}$, which is a major factor limiting the specific energy of such batteries.^{1–6} These inherent theoretical constraints hinder the widespread use of lithium-ion batteries in many emerging applications such as vehicle electrification, thus impelling the pursuit of next-generation cathode materials with much higher specific capacities. Sulfur is a promising cathode material with a high theoretical capacity of 1673 mA h g^{-1} based on the electrochemical reaction: $\text{S}_8 + 16\text{Li} \leftrightarrow 8\text{Li}_2\text{S}$.^{7–9} There has been exciting progress in understanding and improving the electrochemical performance of sulfur cathodes.^{10–21} However, further progress is hindered by the need for pairing with a lithium metal anode which is prone to dendrite formation and other safety-related challenges.^{7–21}

Compared to sulfur, fully-lithiated Li_2S (theoretical capacity 1166 mA h g^{-1}) represents a more attractive cathode material because it enables pairing with high-capacity lithium metal-free anodes (such as silicon or tin), hence obviating dendrite formation and safety concerns associated with metallic lithium.^{22–28} Moreover, the high melting point of Li_2S (unlike that of sulfur) imparts greater ease of processing in the synthesis of carbon-based composite cathode materials.^{26,27} Despite the inherent promise, there have only been a handful of reports on Li_2S cathodes to date.^{22–28} Most efforts have been focused on the active material itself, in an attempt to improve the overall conductivity and limit polysulfide dissolution,^{22–28} with very little attention being placed on electrochemically-inactive components such as binders. Yet recent studies have shown that the use of effective binders can have a profound effect on the structural stability, kinetics and long-term cycling performance of electrode materials including silicon and sulfur.^{29–33} In the case of sulfur cathodes, the effect of different binders on their electrochemical performance has been well-studied,^{31–33} with the most commonly-used binder being poly(vinylidene fluoride) (PVDF).^{9–18} Developing an effective binder for Li_2S cathodes as opposed to sulfur requires a paradigm shift because Li_2S is ionic and highly-polar whereas sulfur is covalent and non-polar in nature. Because of this difference in bonding and chemical nature, binder materials that are known to interact strongly with sulfur particles to act as good dispersion agents might not be effective for Li_2S and *vice versa*. Besides strong interaction with Li_2S , it would be an added advantage if the proposed binder has a strong affinity for lithium polysulfides (Li_2S_n , $4 \leq n \leq 8$) as well. This would help to minimize loss of polysulfides into the electrolyte during cycling, which is a major reason for rapid capacity decay in Li_2S cathodes.^{22–28} Hence, advancing the performance of these cathodes requires a

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more thorough understanding of Li_2S -binder and Li_2S_n -binder interactions, both of which are relatively unexplored to date. While notable progress has been achieved in sulfur cathodes, the same cannot be said for Li_2S cathodes. The overall cycling performance and stability of Li_2S cathodes remain poor, with typical cycle life of less than 100 cycles demonstrated in the literature.^{22–28}

In this Edge Article, we present a rational design of stable and high-performance Li_2S cathodes by first using *ab initio* simulations to elucidate the interaction between Li_2S and lithium polysulfides with various functional groups found in macromolecular binders. In light of this understanding, poly(vinylpyrrolidone) was selected as a promising binder for experimental demonstration in Li_2S cathodes. This bifunctional binder was found to exhibit strong affinity with: (a) Li_2S to form a uniform dispersion of active material and carbon in the electrode slurry, and (b) lithium polysulfides to minimize their loss into the electrolyte during cycling. Using poly(vinylpyrrolidone) as a binder, an initial specific capacity of 760 mA h g^{-1} of Li_2S ($\sim 1090 \text{ mA h g}^{-1}$ of S) was achieved at 0.2 C, with unprecedented capacity retention of 94% in the first 100 cycles. Even after prolonged cycling over 500 charge/discharge cycles, the cells retained 69% of their initial capacity, which corresponds to a small capacity decay of 0.062% per cycle. To the best of our knowledge, this is the first time that a Li_2S cathode with this level of performance has been demonstrated.

Results and discussion

First, we sought to gain an understanding of Li_2S -binder interactions using *ab initio* simulations performed in the framework of density functional theory.^{34–38} To do so, we used a general structural framework based on vinyl polymers $-(\text{CH}_2-\text{CHR})_n-$ to represent the various functional groups (R) commonly found in macromolecular binders and studied the binding energies of these various groups with Li_2S . Common functional groups, including those that contain oxygen, nitrogen and halogen atoms, were included in these simulations. Strongly acidic and basic groups such as carboxyl, hydroxyl and amine groups were excluded due to their undesired reaction with Li_2S and sulfur, respectively.^{24,39} The results are summarized in Fig. 1 (see ESI† and Fig. S1 for details). We see that in general, the electron-rich groups with lone pairs on oxygen, nitrogen and halogen atoms are capable of binding with lithium in Li_2S through a coordination-like interaction (Fig. S1†). More importantly, the strongest interaction with Li_2S was observed in the case of binding with carbonyl ($>\text{C}=\text{O}$) groups such as those found in esters, ketones and amides, with binding energies of 1.10, 0.96 and 0.95 eV respectively (Fig. 1a). In all of these cases, the most stable configuration corresponds to lithium binding directly to the doubly-bonded oxygen atom in the $>\text{C}=\text{O}$ group, forming a strong lithium–oxygen (Li–O) interaction (Fig. 1b–e). This can be rationalized by considering the hard acid nature of Li^+ which renders strong interaction with the hard oxygen donor atoms in $>\text{C}=\text{O}$ groups.⁴⁰ In comparison, halogenated groups, which form the basis of many

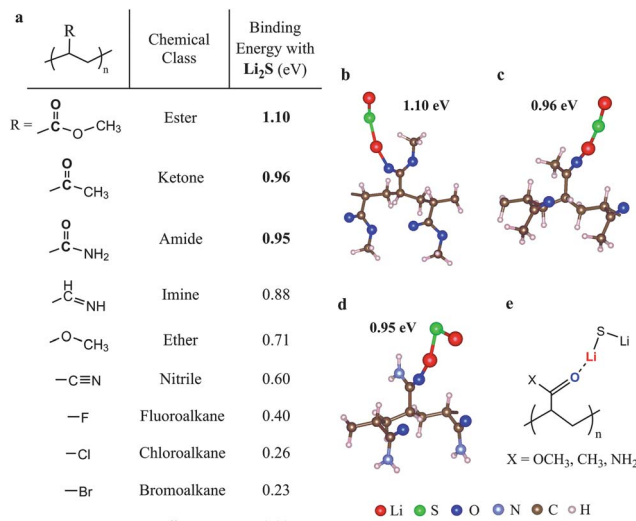


Fig. 1 (a) Table showing the calculated binding energy of Li_2S with various functional groups (R) based on the framework of vinyl polymers $-(\text{CH}_2-\text{CHR})_n-$. (b–d) *Ab initio* simulations showing the most stable configuration and calculated binding energy of Li_2S with (b) ester, (c) ketone and (d) amide R groups in vinyl polymers. (e) General schematic representing the Li–O interaction between Li_2S and $>\text{C}=\text{O}$ groups as shown in (b–d).

conventional binders including PVDF, possess much weaker interaction with Li_2S , with typical binding energies in the range of 0.23–0.40 eV (Fig. 1a). We see that the binding energy of Li_2S with halogenated groups follows the order: $-\text{F} > -\text{Cl} > -\text{Br}$ (Fig. 1a), which is in good agreement with the relative hardness of the donor atoms ($\text{F} > \text{Cl} > \text{Br}$).⁴⁰

Additional *ab initio* simulations were performed to elucidate the interaction of various functional groups with $\text{Li-S}\cdot$ species, which can be used to represent the relevant end groups in the general class of lithium polysulfides ($\text{Li-S-S}_{n-2}-\text{S-Li}$; Li_2S_n in short, $4 \leq n \leq 8$). The results are summarized in Fig. 2 (see ESI† and Fig. S2 for details). We see that $\text{Li-S}\cdot$ species exhibit the strongest binding with $>\text{C}=\text{O}$ groups as well, with typical binding energies in the range of 1.20–1.26 eV (Fig. 2a). This is contrasted with the much lower binding energy of $\text{Li-S}\cdot$ with halogenated groups, such as 0.62 eV in the case of binding with $-\text{F}$ groups (Fig. 2a). For the interaction of $\text{Li-S}\cdot$ with $>\text{C}=\text{O}$ groups, we also find that the most stable configuration corresponds to lithium binding directly to the doubly-bonded oxygen atom, forming a strong Li–O interaction as shown in Fig. 2b–e.

In light of this understanding of Li_2S -binder and $\text{Li-S}\cdot$ -binder interactions, we selected poly(vinylpyrrolidone) (PVP), a commonly-available polymer rich in $>\text{C}=\text{O}$ groups, as a promising binder in Li_2S cathodes. Our *ab initio* simulation results show that the $>\text{C}=\text{O}$ groups in PVP exhibit high binding energies of 1.14 and 1.30 eV with Li_2S and $\text{Li-S}\cdot$ species, respectively (Li–O interaction; Fig. 3a). In comparison, conventionally used PVDF binder (rich in $-\text{F}$ groups) was found to possess weaker interaction with Li_2S and $\text{Li-S}\cdot$ species, with lower binding energies of 0.64 and 0.83 eV, respectively (Fig. 3b). To compare the effectiveness of PVP and PVDF binders as dispersion agents for Li_2S cathodes, electrode slurries were prepared by mixing ball-milled commercial Li_2S particles with conductive carbon

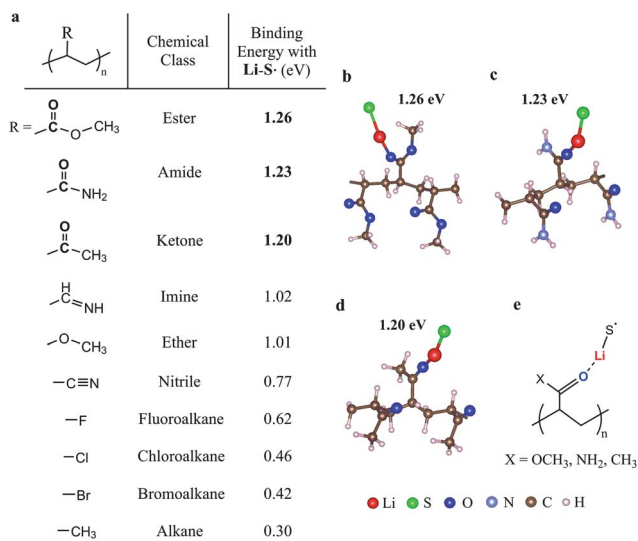


Fig. 2 (a) Table showing the calculated binding energy of Li-S[•] species with various functional groups (R) based on the framework of vinyl polymers $-(CH_2-CHR)_n-$. (b–d) *Ab initio* simulations showing the most stable configuration and calculated binding energy of Li-S[•] with (b) ester, (c) amide and (d) ketone R groups in vinyl polymers. (e) General schematic representing the Li-O interaction between Li-S[•] and $>C=O$ groups as shown in (b–d).

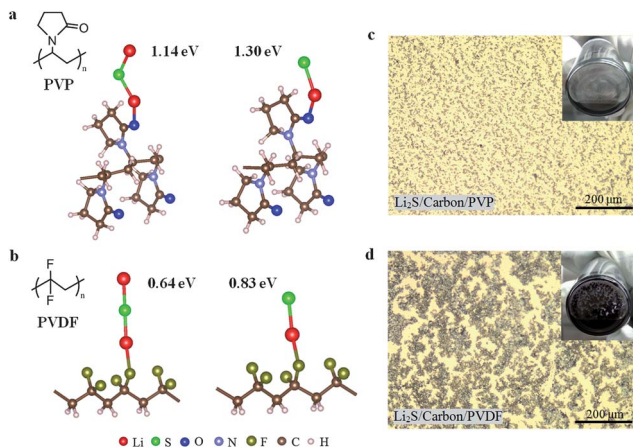


Fig. 3 (a, b) *Ab initio* simulations showing the most stable configuration and calculated binding energies of Li₂S and Li-S[•] species with (a) PVP and (b) PVDF binders. (c and d) Optical microscopy and digital camera images (inset) showing the electrode slurry of (c) Li₂S/carbon black/PVP binder and (d) Li₂S/carbon black/PVDF binder in *N*-methyl-2-pyrrolidinone (60 : 35 : 5 by weight in both cases).

black and PVP/PVDF binder (60 : 35 : 5 by weight) in *N*-methyl-2-pyrrolidinone. Using PVP as the binder, a uniform dispersion of Li₂S and conductive carbon was obtained as evidenced by optical microscopy (Fig. 3c), with no large aggregates observed at the bottom of the slurry (Fig. 3c inset). On the other hand, large aggregates were clearly visible in the electrode slurry containing PVDF as the binder (Fig. 3d; the inset shows particle sedimentation at the bottom of the slurry). The good dispersion properties of PVP binder can be attributed to its strong affinity for Li₂S, which enables strong adsorption of PVP onto the surface of Li₂S particles to stabilize the dispersion, consistent with *ab initio* simulation results.

To evaluate the electrochemical performance of Li₂S cathodes using PVP binders, 2032-type coin cells were assembled. An electrode slurry was first prepared by mixing ball-milled commercial Li₂S particles with conductive carbon black and PVP binder (60 : 35 : 5 by weight) in *N*-methyl-2-pyrrolidinone to obtain a uniform dispersion, followed by drop-casting onto carbon fiber paper to form the working electrode. Carbon fiber paper was used as the current collector (instead of aluminum foil) because it not only enables a higher mass loading of Li₂S (~ 2 mg cm⁻²), but also provides a larger surface area for deposition of Li₂S during cycling. 2032-type coin cells were then assembled with lithium foil as the counter electrode. The electrolyte used was lithium bis(trifluoromethanesulfonyl)imide in 1 : 1 v/v 1,2-dimethoxyethane and 1,3-dioxolane, with LiNO₃ (1 wt%) as an additive to help passivate the surface of the lithium anode and reduce the shuttle effect.⁹ The Li₂S cathodes were first activated at C/20 (1 C = 1166 mA g⁻¹), by charging to a high cutoff voltage of 3.8 V vs. Li⁺/Li for complete delithiation followed by discharge to 1.8 V, as described in previous work.²⁴ Galvanostatic cycling was then carried out at the specified C-rate from 1.8 to 2.6 V vs. Li⁺/Li. Specific capacity values were calculated based on the mass of Li₂S or the corresponding mass of S in the samples.

Using PVP as the binder, the Li₂S cathodes exhibited stable cycling performance with a high initial capacity of 760 mA h g⁻¹ of Li₂S (~ 1090 mA h g⁻¹ of S) at 0.2 C as displayed in Fig. 4a. Relative to the initial cycle, the capacity retention achieved at the end of 100 cycles was as high as 94%. The average Coulombic efficiency over 100 cycles was calculated to be 97%. Most importantly, even after prolonged cycling over 500 charge/discharge cycles at 0.2 C, the cells retained 69% of their initial capacity (Fig. 4c), which corresponds to a small capacity decay of 0.062% per cycle. For comparison, cells were also assembled based on conventional PVDF binder which shows poorer dispersion ability and weaker binding with Li₂S and lithium polysulfides (Fig. 3b and d). Li₂S cathodes using PVDF exhibited lower specific capacity and faster capacity decay under identical testing conditions (Fig. 4a). The capacity retention using PVDF binder was only 72% after 100 cycles (compared to 94% for PVP binder), indicating a greater degree of polysulfide dissolution into the electrolyte in the former case. This is supported by testing for sulfur content in the electrolyte after discharge using inductively coupled plasma-optical emission spectroscopy (ICP-OES; see ESI† for details).¹⁷ ICP-OES analysis showed a consistently higher percentage loss of sulfur into the electrolyte at various stages of cycling (1, 5, 10 and 20 cycles) for cells using PVDF compared to PVP as the binder (Fig. 4b). For instance, in the case of cells using PVDF binder, 27% of the total sulfur mass on the electrode was found to be dissolved in the electrolyte after 20 cycles, compared to 13% in the case of PVP binder (Fig. 4b). This indicates stronger affinity of PVP binder with lithium polysulfides to minimize their loss into the electrolyte, consistent with *ab initio* simulation results.

Next, the Li₂S cathodes with PVP binders were subject to cycling at various C-rates to evaluate their electrode kinetics and stability (Fig. 4d and e). When the C-rate was increased from 0.2

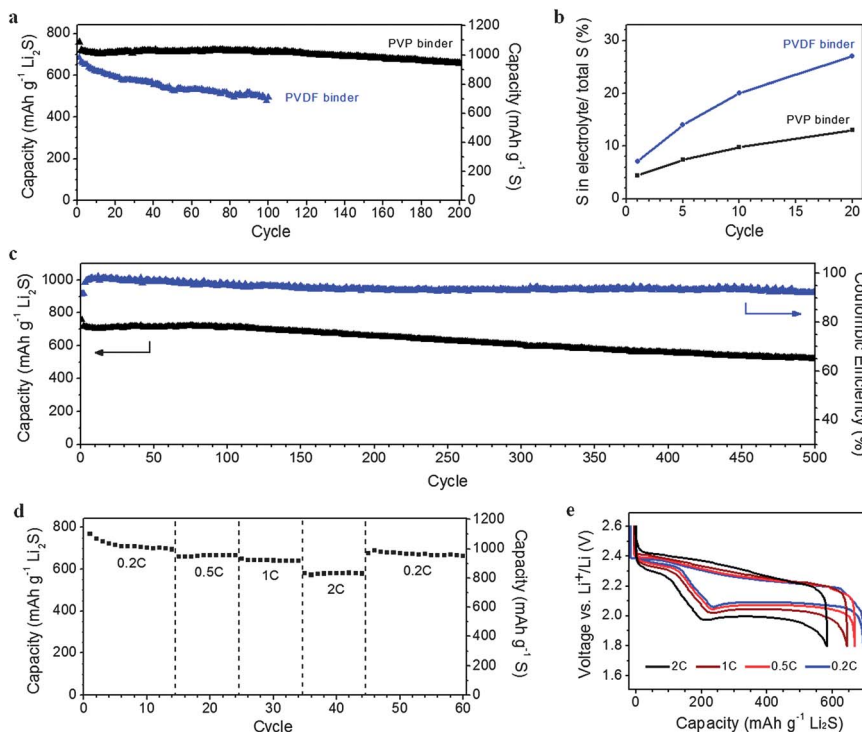


Fig. 4 (a) Specific capacity of Li_2S cathodes using PVP binder cycled over 200 cycles at 0.2 C, in comparison with PVDF binder. (b) Percentage of sulfur in the electrolyte relative to the total sulfur mass on the electrode after cycling at 0.2 C using PVP binder in comparison with PVDF binder. (c) Specific capacity and Coulombic efficiency of Li_2S cathodes using PVP binder upon prolonged cycling over 500 cycles at 0.2 C. (d) Specific capacity and (e) voltage profiles of Li_2S cathodes using PVP binder cycled at various C-rates from 0.2 C to 2 C. Specific capacity values were calculated based on the mass of Li_2S or the corresponding mass of S in the samples.

to 0.5 to 1 C, the cells delivered high stabilized capacities of 695, 670 and 645 mA h g⁻¹ of Li_2S (~997, 961 and 925 mA h g⁻¹ of S respectively), as shown in Fig. 4d. The respective capacities achieved at 0.5 C and 1 C correspond to 96% and 93% of the capacity that was attained at 0.2 C, indicating fast reaction kinetics in the cathodes. This is supported by the little change in voltage hysteresis between the charge and discharge curves at 0.2, 0.5 and 1 C (Fig. 4e). Even at a C-rate of 2 C, a high reversible capacity of 580 mA h g⁻¹ of Li_2S (~832 mA h g⁻¹ of S) could still be attained (Fig. 4d). When the C-rate was switched abruptly from 2 C to 0.2 C again, the original capacity was largely recovered (Fig. 4d), indicating robustness and stability of the cathode material.

Conclusions

In summary, we have demonstrated stable cycling performance in Li_2S cathodes through the rational use of bifunctional PVP binders that possess strong Li-O interaction with both Li_2S and lithium polysulfides. Given the simplicity of our strategy, the appropriate choice of binder can be combined with more elaborate cathode structures such as Li_2S -carbon nanocomposites^{26,27} to further mitigate polysulfide dissolution and capacity decay. Insight gained from this work, particularly through *ab initio* simulations, can be extended to other promising high-capacity electrode materials for the future development of novel binders with precisely-tailored functionalities.

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