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Diketopyrrolopyrroles Act as Redox Mediators in Lithium−Sulfur Batteries

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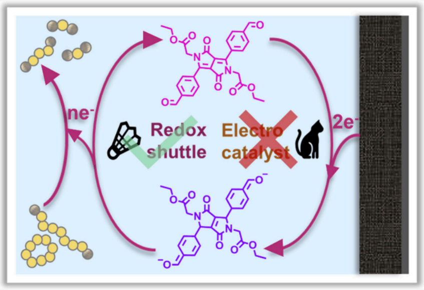
ABSTRACT: **Lithium−sulfur (Li−S) batteries are among the most promising next-generation energy storage technologies, offering gravimetric energy densities greater than those of state-of-the-art lithium-ion batteries. However, widespread commercialization of the technology is hindered by challenges related to the multistep redox chemistry of sulfur. The addition of diketopyrrollopyrroles (DPPs) to Li−S battery electrolytes can improve cell performance; however, their mechanism of action remains unclear. Here, we use a range of electrochemical methods to elucidate the mechanism through which DPPs affect the performance of the Li−S batteries. Electrochemical analysis demonstrates the importance of DPP redox potentials in enhancing the redox kinetics of polysulfide reduction, with analytical measurements confirming this is via a redox mediation process in which electrons are shuttled between polysulfide intermediates and the underlying current collector via the DPP molecule. We show that DPP derivatives that are not redox active at the potentials associated with the multi-step interconversion of sulfur and lithium sulfide in Li−S batteries do not show the same effect. Galvanostatic analysis confirms that the enhancement of the kinetics of polysulfide conversion translates to the operation of Li−S batteries, which show an improvement in the discharge capacity after the addition of the additives.**



Lithium−sulfur (Li−S) batteries are among the most promising of the “beyond Li-ion” battery technologies, owing to their high theoretical gravimetric capacity (1675 mA h g^{-1} S) and energy density (2500 Wh kg^{-1} S), which exceed those of Li-ion batteries (LIBs) significantly.[1−8] Li−S batteries benefit from the use of S as an earth-abundant, low-cost, and geographically widespread positive-electrode material.[9−13] They exploit the reversible 16-electron interconversion of S_8 and Li_2S at the positive electrode coupled with the plating and stripping of Li at the negative electrode. Cells typically contain mixtures of dioxolane (DOL) and dimethoxyethane (DME) as the electrolyte solvent.

Commercialization of Li−S batteries has been hindered by their poor rate performance, capacity retention, and cycle life.[14] The electrochemical interconversion of S_8 and Li_2S, in particular, is sluggish, limiting charge and discharge rates.[15] Furthermore, ether-soluble polysulfide intermediates that form at the positive electrode during discharge can reach the Li negative electrode where they react to form further reduced intermediates.[8] These intermediates can then in turn reach the positive electrode where they are reoxidized, giving rise to the so-called polysulfide shuttle phenomenon.[15−18] Irreversible reactions of the intermediates at the Li electrode result in a loss of active material, capacity fading, and an increased risk of the formation of Li dendrites that can potentially traverse the electrolyte, causing short circuits.[19−21]

Diketopyrrollopyrrole (DPP) derivatives consist of an electron-deficient core, comprising a planar π-conjugated dilactam structure, two aryl groups, and two *N*-substituted alkyl (R) groups.[22−24] The solubility of these systems can be altered by tuning the R-groups,[6] while modification of the aryl groups can influence the electron density of the DPP core, altering the redox properties of the molecule.[25] DPPs were commercialized in the 1980s as organic pigments for paints, plastics, *etc.*[26,27] and have since been used in dye-sensitized solar cells, organic light-emitting diodes (OLEDs), and sensors.[28−31] More recently, DPPs have been deployed in Li−S batteries, first by Niu and Zhang and co-workers who made coatings for the electrode separator, comprising DPPs in porous organic frameworks.[32] The team proposed that the coatings suppress polysulfide shuttling due to a strong interaction between DPP moieties and polysulfides. Niu, An,

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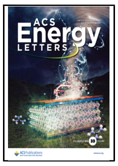

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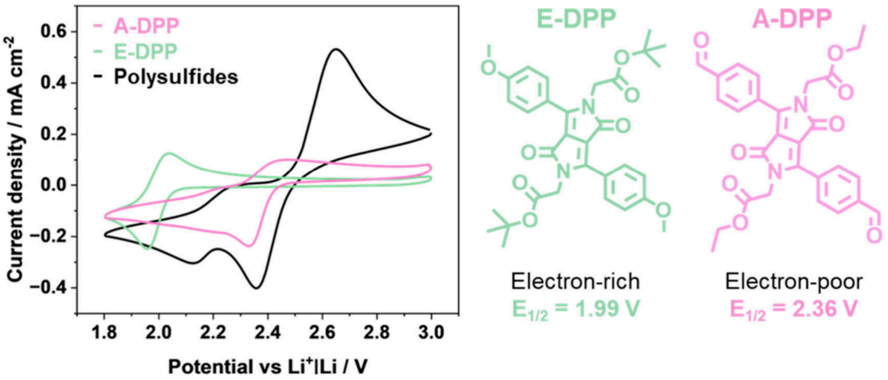

Figure 1. Cyclic voltammograms (CVs) of A-DPP (pink), E-DPP (green), and polysulfides (black). In each case, the concentration was 2 mM additive or polysulfide dissolved in DOL:DME 1:1 containing LiTFSI (1.0 M). The scan rate was 100 mV s^{-1}, all CVs were recorded under a N_2 atmosphere, and all potentials are reported relative to that of the $Li^+|Li$ couple.

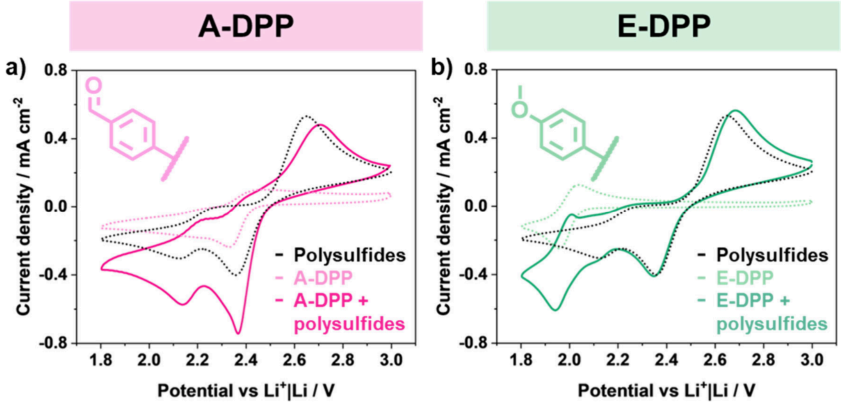

Figure 2. CVs of (a) A-DPP (pink) and (b) E-DPP (green), alongside the DPP-polysulfide mixtures (deeper colors) and polysulfides by themselves (black). The concentration of the additives and polysulfides were all 2 mM. All CVs were obtained in DOL:DME 1:1 ratio, containing LiTFSI (1.0 M) at a scan rate of 100 mV s^{-1} under an N_2 atmosphere, with all potentials plotted relative to that of the $Li^+|Li$ couple.

and Chen then used DPP-modified separators that they proposed mediated sulfur conversion reactions through interactions between DPP carbonyl groups and polysulfides, leading to improved cell cycling stability.[33] Caruso and Krishnamurthy recently used DPPs as positive electrode additives in Li−S batteries and proposed that they function as conventional electrocatalysts, interacting with polysulfides to lower the energy barrier for their conversion. The authors suggest that a pyridine functional group on their DPP molecule is key to controlling the efficiency of polysulfide binding.[34] In all examples, DPP was used to bind polysulfides, either limiting their movement inside the cell or lowering the energy barrier to their interconversion.

Another possible mode of action by which DPPs could potentially affect the operation of Li−S batteries, but has received no apparent attention, is related to their redox activity.[35] Some DPPs are redox active at the potentials experienced in Li−S batteries, and we propose that they may act as redox mediators (RMs). RMs are species that can be reduced or oxidized at an underlying current collector of a battery and then transfer charge to the active material, bypassing the direct electrochemical reactions between the battery material and the current collector.[36] RMs have successfully been implemented in a range of next-generation devices, including redox flow cells, lithium−air batteries, and Li−S batteries.[20,37] Some groups have optimized RMs to help improve discharge capacities, cycle life, and rate performance,[38−40] often at high mediator concentrations and/or in systems containing small amounts of cathode materials.

In this work, we show that DPPs act as RMs within the Li−S battery. We show this by exploiting the high degree of synthetic flexibility of DPPs, which allows tuning of their physicochemical properties,[27,41] to produce a DPP that is redox active at the potentials associated with sulfur interconversions at the positive electrode in Li−S cells and another DPP that is redox inactive at the relevant potentials. Based on previous reports of RMs in next-generation battery technologies,[42] we predict that only molecules that are redox active in the same potential window as sulfur will improve the performance of the cell. Using a combination of cyclic voltammetry, spectroscopic analysis, and galvanostatic cycling of full DPP-containing Li−S cells, we show that a redox-potential-matched DPP-based RM can intercept the redox cycling of polysulfides, shuttling electrons between the intermediates and the current collector. When incorporated into the electrolyte of Li−S cells, the DPP RM can increase the battery capacity by about 23% after 50 cycles. Our analysis also shows that a redox potential-mismatched DPP-based RM has a negligible impact on the electrochemistry of polysulfides and the capacity of Li−S batteries. This study demonstrates the specific role played by soluble DPP molecules in Li−S batteries

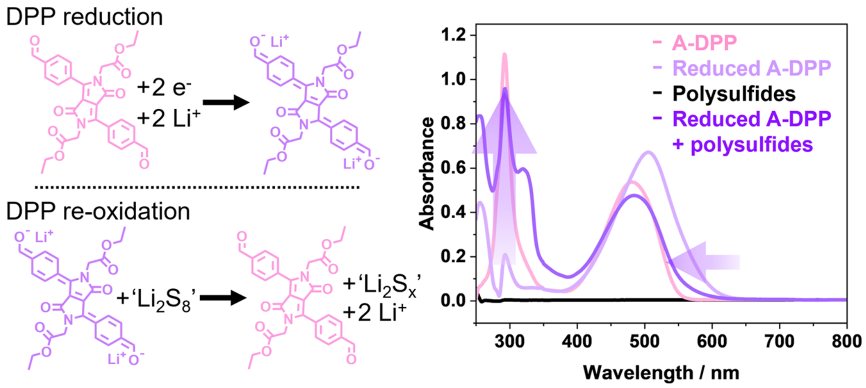

Figure 3. Scheme showing A-DPP (pink) reduction to A-DPP^{-2} (light purple), its subsequent reaction with polysulfides (Li_2S_8, black) to form A-DPP + lower order polysulfides (Li_2S_x where $x < 8$, deep purple) and the corresponding UV–vis spectrum for each stage of the reaction. A-DPP^{2-} was obtained via bulk electrolysis, using a carbon paper working electrode and $Li_{1-x}FePO_4$ reference and counter electrodes. Colored arrows indicate that important transformations are occurring. Spectra were obtained in DOL:DME 1:1 ratio, containing LiTFSI (1 M) under an N_2 atmosphere. The concentration of A-DPP and the polysulfides was 0.022 mM.

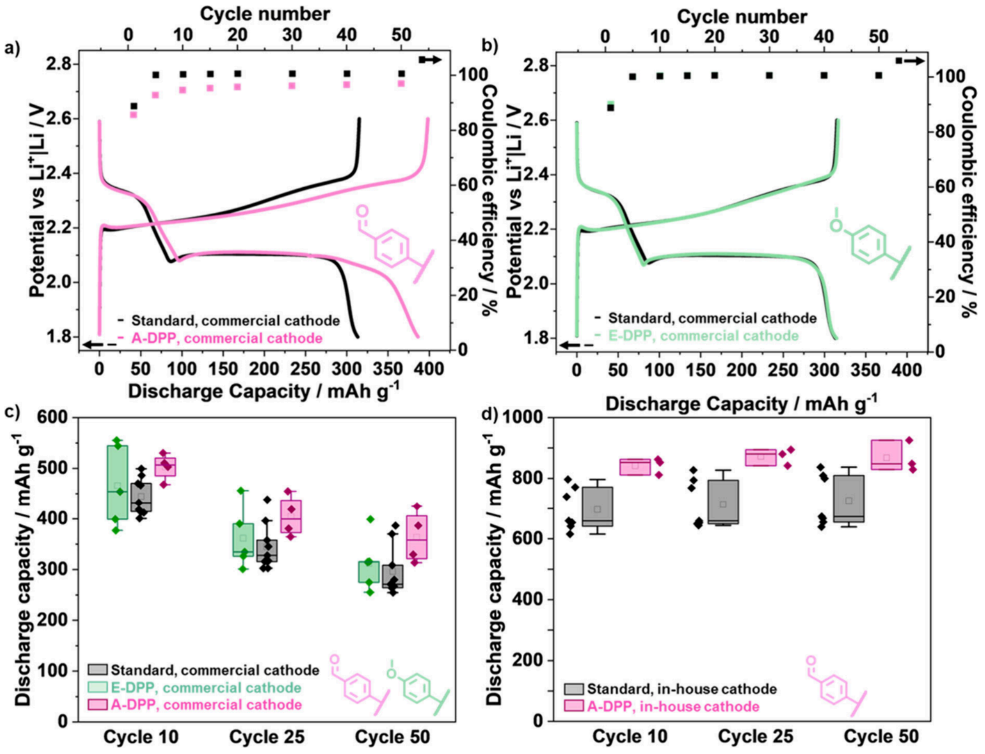

Figure 4. Cycling studies of Li–S cells with and without DPPs show that only A-DPP improves capacity retention. Charge–discharge curves (cycle 50) for cells using commercial S/C electrodes with (a) A-DPP and (b) E-DPP, alongside an additive-free cell. Cycle number vs Coulombic efficiency is also shown. Statistical box plots for Li–S cells using (c) commercial S/C electrodes and (d) in-house S/C electrodes with and without DPPs. All cells contained a DOL:DME 1:1 ratio electrolyte containing LiTFSI (1 M) and $LiNO_3$ (0.5 M) with 2 mM DPP when used. Three conditioning steps (0.05 C) were run prior to cycling at a rate of 0.1 at 40 °C.

and illustrates the need to match the redox potentials of RMs with those of battery materials.

Two derivatives were chosen for initial studies: a DPP derivative functionalized with an electron-withdrawing 4-benzaldehyde group (**A-DPP**) and one with an electron-donating 4-methoxybenzene group (**E-DPP**). The syntheses were performed following previously reported procedures (Schemes S1 and S2), and the corresponding NMR and IR spectra are shown in Figures S1–S11.[43,44] Figure 1 shows cyclic voltammograms (CVs) of A-DPP and E-DPP, alongside those of polysulfides. The synthesis and characterization of the polysulfide solution is given in the Supporting Information. The electrolyte in each case was lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 1.0 M) in 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) 1:1 vol %, which is the typical electrolyte used in Li–S batteries. The CV of A-DPP (Figure 1, pink line) shows an electrochemically irreversible redox couple, centered at 2.36 V vs $Li^+|Li$, as well as a less-pronounced redox couple centered at about 2.1 V. At lower voltammetric scan rates (Figure S12), the two redox couples were better resolved; scanning from positive to negative potential ultimately resulted in the formation of doubly reduced A-DPP^{2-}.[45] The reduction potential of A-DPP lies within the electrochemical window of the Li–S battery, suggesting that it may mediate sulfur redox reactions. In contrast, the CV of E-DPP displays one reduction process at 1.99 V vs $Li^+|Li$, which is negative of the potential range associated with sulfur interconversion processes.

To understand how DPPs impact sulfur redox reactions, voltammetry of lithium polysulfide solutions containing A-DPP and E-DPP was performed. The voltammogram of Li_2S_x showed two reduction peaks and one predominant oxidation peak (black trace in Figure 2a,b). Addition of A-DPP to the solution caused the first and second reduction peaks to increase in current. The enhancement was larger than the sum of the individual currents for Li_2S_x and A-DPP reduction, indicating that either (electro)catalysis or redox mediation occurred (comparing the voltammograms of the polysulfides and A-DPP alone, with that of the mixture in Figure 2a). In contrast, when E-DPP was added to the solution, the peak currents associated with the reduction of polysulfides remained unchanged compared to those of the solution with no E-DPP, indicating that E-DPP did not impact the rate of sulfur reduction in the CV experiment. Taken together, the two data sets indicate that the rate enhancement requires the redox potential of the DPP to be in the Li−S region of operation, consistent with them acting as redox mediators in the multistep sulfur reduction pathway. This conclusion appears to be contrary to recent suggestions that classical electrocatalysis could be driven by such systems.

To confirm that A-DPP acts as an RM, UV−visible absorption spectroscopy was used to study the reaction between 1:1 mixtures of A-DPP^{2-} and polysulfides in solution (Figure 3). Spectra of A-DPP and A-DPP^{2-} showed large absorbance bands centered at about 290 and 480 nm, with the $\pi-\pi^*$ transition of A-DPP^{2-} at 290 nm significantly smaller than that of A-DPP. After mixing A-DPP^{2-} with polysulfides, the spectrum returned toward that of the neutral A-DPP, consistent with reduction of the polysulfides by A-DPP^{2-} and its operation as a redox mediator. Note that the large absorption coefficients associated with the electronic transitions on DPP mean that the UV−vis absorption spectroscopy measurements were conducted by using 0.022 mM solutions. At this concentration the signals associated with polysulfides fall below detection limits (Figure S13). All changes in the UV−vis spectra can be ascribed to changes in the DPP structure.

Full Li−S cells in which the electrolyte contained A-DPP or E-DPP (2 mM DPP in 1:1 DOL:DME, 1.0 M LiTFSI, and 0.5 M $LiNO_3$) were electrochemically tested, and the cell cycling performance was compared to those of cells containing no additive. Each cell was subject to three 0.05 C conditioning cycles before cycling at 0.1 C for 50 cycles. Commercial NANOMYTE BE-70E S/C electrodes (NEI corporation, Somerset, NJ, USA) were used in the first instance to provide a universal comparison and to act as a reproducible screening tool (Figure 4a−c). Galvanostatic analysis of the cells containing commercial S/C electrodes with no additive displayed two plateaus at 2.34 and 2.10 V vs $Li^+|Li$ on reduction and a single plateau at ∼2.3 V vs $Li^+|Li$ on the return charge, as expected for a conventional Li−S cell.[8,46] Upon addition of A-DPP to the electrolyte, the discharge capacity was 23% higher than that of the standard cell after 50 cycles, suggesting enhanced active material utilization. This enhancement agrees with the previous CV data that demonstrate an increase in polysulfide reduction current. Interestingly, the Coulombic efficiency (CE) was shown to drop to 96% upon addition of A-DPP, which we believe is attributed to mediator shuttling within the cell. It was shown by Tsao et al. that overcharge is commonly observed when using solution-phase redox mediators and is not necessarily related to electrolyte degradation or loss of active material.[36] Unsurprisingly (based on the electroanalytical data), addition of E-DPP to the cell did not show any notable enhancement of capacity during cell cycling, exhibiting a discharge curve similar to that of the standard cell (Figure 4b).

A statistical analysis of the cell capacity during cycling is shown in Figure 4c, demonstrating the improvement in performance with A-DPP. Each diamond in Figure 4c corresponds to the discharge capacity of a single cell at the specified cycle number. The boxes encompass the interquartile range, while the line and square inside indicate the median and mean, respectively. The whiskers encapsulate the data within 1.5 times the interquartile range. A-DPP cycling studies were repeated with in-house fabricated C/S electrodes, which can reliably achieve ca. 700 mAh g^{-1}, which is closer to state-of-the-art in terms of specific capacity (Figure 4d).[11] Again, A-DPP provided a statistical improvement in cell performance with a mean capacity of 850 mAh g^{-1} at cycle 50 and a high capacity retention. These data support the observation from voltammetric analysis that A-DPP acts as a redox mediator, shuttling electrons from the electrode to S_8 and polysulfides during cell discharge. Voltammetric analysis of E-DPP, in contrast, showed no evidence of redox mediator activity and accordingly cell testing demonstrates that it does not improve cell performance.

We successfully demonstrated that DPP additives in the Li−S battery do not act as a catalyst or electrocatalyst for sulfur-based redox reactions. Rather, their improvement in cell performance stems from their ability to act as redox mediators, overcoming the intrinsic limitation and poor conductivities of the active components within the Li−S battery. We have confirmed that A-DPP, which possesses the correct redox potential to act as a redox mediator for sulfur reduction and Li_2S oxidation, provides a statistically significant enhancement of cell capacity and capacity retention. We have demonstrated the capacity of this mediator to operate in the presence of both commercially available and in-house high-performance C/S electrodes. Finally, we highlight the importance of taking a statistical approach to Li−S cell data analysis to both demonstrate reproducibility, facilitating verification of performance data by other researchers, and statistically validate improvements in multiple cells.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.5c01262.

Synthesis and characterization (^1H NMR, ^{13}C NMR, and ATR-IR) of A-DPP and E-DPP and additional supporting voltammetry (PDF)

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Author Contributions

J.S.S. wrote the manuscript and performed the electrochemical, galvanostatic and analytical experiments with support from BMGD. F.M. designed, synthesized, and characterized the DPP molecules. A.J.K. supported in the planning and interpretation of the analytical experiments. D.A.W. and L.R.J. contributed to the electrochemical and galvanostatic analysis and interpretation. D.B.A. and G.N.N. devised and supervised the project. All authors contributed to the writing of the manuscript.

Author Contributions

#J.S.S. and F.M. contributed equally to the study.

Notes

The authors declare no competing financial interest.

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