A robust, water-based, functional binder framework for high energy lithium-sulfur batteries

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Abstract: We report here a water-based functional binder framework for the lithium-sulfur battery system, based on the general combination of a polyether and an amide-containing polymer. These binders are applied here to positive electrodes optimised towards high energy electrochemical performance based only on commercially available materials. Electrodes with up to 4 mAh cm^{-2} capacity and 97 – 98% coulombic efficiency are achievable in electrodes with a 65% total sulfur content and a poly(ethylene oxide):poly(vinylpyrrolidone) (PEO:PVP) binder system. Exchange of either binder component for a different polymer with similar functionality preserves the high capacity and coulombic efficiency. The improvement in coulombic efficiency from the inclusion of the coordinating amide group was also observed in electrodes where pyrrolidone moieties were covalently grafted to the carbon black, indicating the role of this functionality in facilitating polysulfide adsorption to the electrode surface. Mechanical properties of the electrodes appear not to significantly influence sulfur utilisation or coulombic efficiency in the short term but rather determine retention of these properties over extended cycling. These results demonstrate the robustness of this very straightforward approach, as well as the considerable scope for designing binder materials with targeted properties.

Introduction

The rechargeable lithium-sulfur (Li-S) battery is one of the most promising "post-Li-ion" technologies primarily because of a very high theoretical energy density of 2,600 Wh kg^{-1} (based on the free energy of formation of Li$_2$S) and the low cost of elemental sulfur. Cells with energy densities of up to 400 Wh kg^{-1}, which is almost twice as high as the state-of-the-art conventional Li-ion batteries, are already being produced on a commercial basis[1,2]. Cell-level energy densities of 500 – 600 Wh kg^{-1} are considered to be achievable[3,4], although this has been debated[5]. However, parasitic reactions at the Li negative electrode towards the electrolyte and the soluble intermediates of the cell reaction (polysulfides) result in severe drawbacks of short cycle life and a

high rate of self-discharge, which currently limit the Li-S system to relatively niche applications.

In recent years, there has been an intense research effort into tackling these drawbacks, with more than 2,000 research articles published on the topic since 2012[6] . Much of this effort has been directed to the development of a wide variety of host materials for sulfur[7]. An effective host material should foremost be highly porous: combining high surface area and pore volume to maximise utilisation and the weight fraction of active sulfur in the electrode respectively[8]. Most commonly, a material which can also confine polysulfides in the positive electrode is targeted, for example by physical trapping[9] or chemical adsorption[10–14] in the host, or by polysulfide-blocking layers external to the host[15–18]. Other notable complementary strategies include novel electrolytes with little or no solubility for polysulfides[19–23], or additives to stabilise the negative electrode against parasitic reactions[24–26].

A further approach of particular interest lies in the choice of the electrode binder. Electrodes for Li-ion batteries are produced industrially by coating a slurry of powdered active materials mixed with an inert polymeric binder (typically poly(vinylidene difluoride), PVdF) to ensure mechanical integrity. This approach is also typically used on the lab scale in research on most related battery chemistries, including Li-S. Because of the key role of soluble intermediates in the Li-S battery system, the choice of the binder is of key importance: we have recently demonstrated, for example, how PVdF can block pores in carbon hosts and severely limit discharge capacity[27]. Binders which swell and allow access to conductive surfaces, or the absence of binder together, can allow for much higher sulfur utilisation. Accordingly, there is significant current activity towards developing binder-free electrode structures[28–31]. However, there is also an increasing interest in identifying or developing new binder materials with properties which enable improved electrochemical performance through properties such as electronic conductivity or by interaction with polysulfides[32–40].

We have previously reported on the benefits of using poly(ethylene oxide) (PEO)[41] or a combination of PEO with poly(vinylpyrrolidone) (PVP)[42] as a binder for the sulfur electrode. Compared with a more conventional water-based binder of carboxymethylcellulose and styrene-butadiene rubber (CMC:SBR) – which has previously been determined by a number of groups as a good binder for sulfur electrodes[43] – we found that the use of PEO gave rise to improved sulfur utilisation and lower electrode impedance, which we attributed to the creation of an

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improved local electrolyte environment brought on by the swelling of the binder. The inclusion of PVP in the binder system effected improved capacity stability and reduced self-discharge, in line with previous reports on the same material[32]. We also found evidence of a cooperative effect of the two binders; the performance of the electrodes was better with a mixed binder system than with either of the individual components alone. The addition of PVP also facilitates easier coating of a PEO-based binder system from slurries in water, as the surfactant behaviour of the added PVP considerably decreases the slurry viscosity.

However, our previous investigations in this area were undertaken using positive electrodes of relatively low loading (< 1 mg_S cm^{-2}) and sulfur content (50%), as well as being based on a carbon host of relatively low porosity (Super P carbon black). At least two recent reviews have demonstrated that cell-level energy density will not significantly exceed that of Li-ion batteries if the electrode loading is below 2 mg_S cm^{-2}[5,44]. A higher weight fraction of sulfur in the electrode is also desirable for higher volumetric energy and for economic reasons, although this factor is less influential on the gravimetric energy density. It has to be accepted that high sulfur utilisation in a thin and dilute electrode with large excesses of electrolyte cannot be extrapolated to high loading electrodes with the specifications desired for high energy batteries; the electrochemical performance of the electrode depends very strongly on all aspects of electrode structure[4], as well as the electrolyte/sulfur (E/S) ratio[45].

In this study, we first demonstrate the applicability of the PEO:PVP binder system as a water-based functional binder for the Li-S battery in test cells approaching practically relevant specifications. We here confirm that this binder system offers the same improvements to capacity, coulombic efficiency – an indicator of self-discharge rate – and capacity stability when applied to electrodes based on a highly porous carbon black host, with loadings in excess of 2 mg_S cm^{-2} and a total sulfur content of 65% in the electrode, with an E/S ratio set at a relatively low 6 µL mg_S^{-1}, when compared to an established reference system. New evidence for the mechanism of coulombic efficiency enhancement by PVP, namely that it facilitates adsorption of polysulfides at the electrode surface, is presented through the preparation of a carbon host material with pyrrolidone groups covalently grafted to the surface. Furthermore, and most significantly, we demonstrate that either PEO or PVP may be substituted for other polymer materials bearing the same polyether or amide functional groups, with almost complete preservation of the electrochemical properties of the electrode. Such alternative materials include those derived from monomers such as poly(ethylene glycol) derivatives, acrylates, acrylamides, or 2-oxazolines, which indicate a broad scope for future research into the design of new electrode binders with properties tailored to the application.

Results and Discussion

Optimisation of PEO:PVP-based electrodes

One of our principal aims in this study was to prepare sulfur electrodes of acceptably high loading based on a commercially available porous carbon black host, using a water-based slurry coating method with the optimised PEO:PVP binder system identified in our previous work.

Uniform coating of electrodes based on highly porous carbons or other nanomaterials is problematic for thicker electrodes, as a large volume shrinkage during drying can cause substantial cracking and/or loss of adhesion, especially at higher thicknesses. In the course of our experiments, we investigated a number of different commercially available carbon black materials and found that electrodes prepared with Ketjenblack EC-600JD (KB) consistently gave the highest reversible capacities. The high capacity is directly linked to the high porosity of the material (BET surface area of ~1400 m^2 g^{-1} and a pore volume of 2.7 cm^3 g^{-1}). However, preparation of electrodes with thicker loadings posed considerable difficulty. Our findings were very much in line with those already reported by Jozwiuk *et al.*[46], who similarly found that carbon blacks of higher porosity enabled higher capacities but gave brittle electrodes.

We were ultimately able to ensure acceptable electrode integrity by making a number of minor modifications to our electrode preparation procedure. Each of these modifications are either known in the Li-S battery field or well-established in the Li-ion battery industry. However, we include a description and motivation for these modifications here for the benefit of other researchers who may wish to conduct experiments with electrodes of similar specifications. The modifications are as follows:

- **Melt-infiltration of sulfur**. Melting sulfur into the pores of host materials is a very common approach to the fabrication of sulfur electrodes, but this procedure is often not well-motivated. In our experience, melt-infiltration does not appear to do much to improve sulfur utilisation where carbon blacks are used as the host material. This has also been discussed elsewhere[4]. However, pre-infiltration of sulfur into the KB carbon black used here in a sufficiently high S:KB ratio (at least 3:1) gives a composite with low enough porosity to give good quality electrode coatings without significant cracking. A further observation is that without melt infiltration, or with a low S:KB ratio, slurries were more viscous; our interpretation is that PVP, acting in part as a surfactant and ordinarily lowering the viscosity of the slurry, is in such cases absorbed by the KB.
- **Carbon nanofiber additive.** The addition of a small amount of carbon nanofibre (CNF, alternatively vapour-grown carbon fibre, VGCF) can act as an additional binder as well as a conducting additive. Electrodes prepared using CNF at a 3.5% w/w addition were observed to have significantly improved uniformity and mechanical integrity. An example is shown in Figure 1.
- **Graphite-coated aluminium substrate.** Primed current collectors are a well-established industrial

method for improving electrode-substrate contact[47,48]. The use of an Al substrate with a thin (~0.075 mg cm^{-2}) graphite coating was found to improve electrode adhesion and reduce electrode resistance. Although the coating adds weight to the electrode, it is insignificant – approximately 0.2% of the total electrode weight.

- **Super C65 carbon additive.** The addition of a small amount of the commonly-used conductive additive Super C65 was found to give considerably more uniform electrode coatings, with lower electrode resistances. Electrodes with either no additional carbon or with additional KB (without infiltrated sulfur) were typically highly prone to cracking above 2 mg$_S$ cm^{-2} and often showed high electrode resistance and short cycle life.

- **Ethanol/water-based slurry.** Lowering the surface tension of the slurry by the addition of a small amount of ethanol to the slurry (5 – 10 wt% relative to the amount of water) was found to give improved wetting properties compared to water alone and generally gave coatings with improved uniformity.
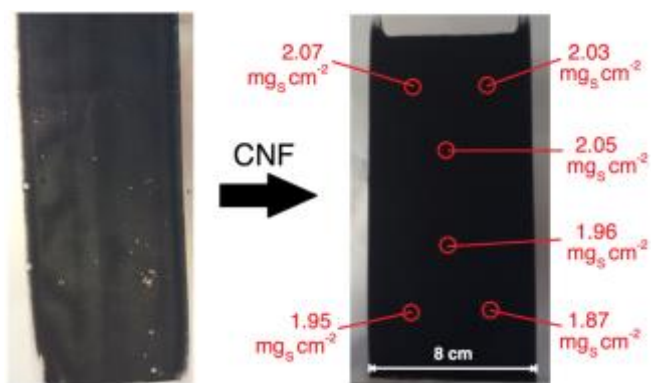
Figure 1. Photographs comparing the effect of a 3.5% w/w addition of carbon nanofibers to water-based slurries employing a PEO:PVP binder. Uniformity of sulfur loading is indicated for the coating with CNF.

With the above-described modifications, electrodes using the PEO:PVP binder system could be prepared with loadings of up to approximately 2.5 – 3 mg$_S$ cm^{-2} with good uniformity and no evidence of cracking. The loading could be controlled up to approximately 5 mg$_S$ cm^{-2} before electrode integrity became poor enough that electrodes could not be cut from the larger sheet without some delamination from the substrate. Typical electrode density was approximately 0.52 – 0.58 g cm^{-3} for electrodes in the range tested.

The electrochemical behaviour of these electrodes was investigated for loadings between 2 and 5.3 mg$_S$ cm^{-2} in CR2025 coin cells. Electrodes with a reference binder system of carboxymethylcellulose sodium salt and styrene-butadiene rubber (CMC:SBR, in a 2:3 ratio) as used in our previous work[42] were also prepared. The discharge capacity, coulombic efficiency and energy efficiency over the first 50 cycles, and voltage profiles at the 10th cycle for these cells is presented in Figure 2.
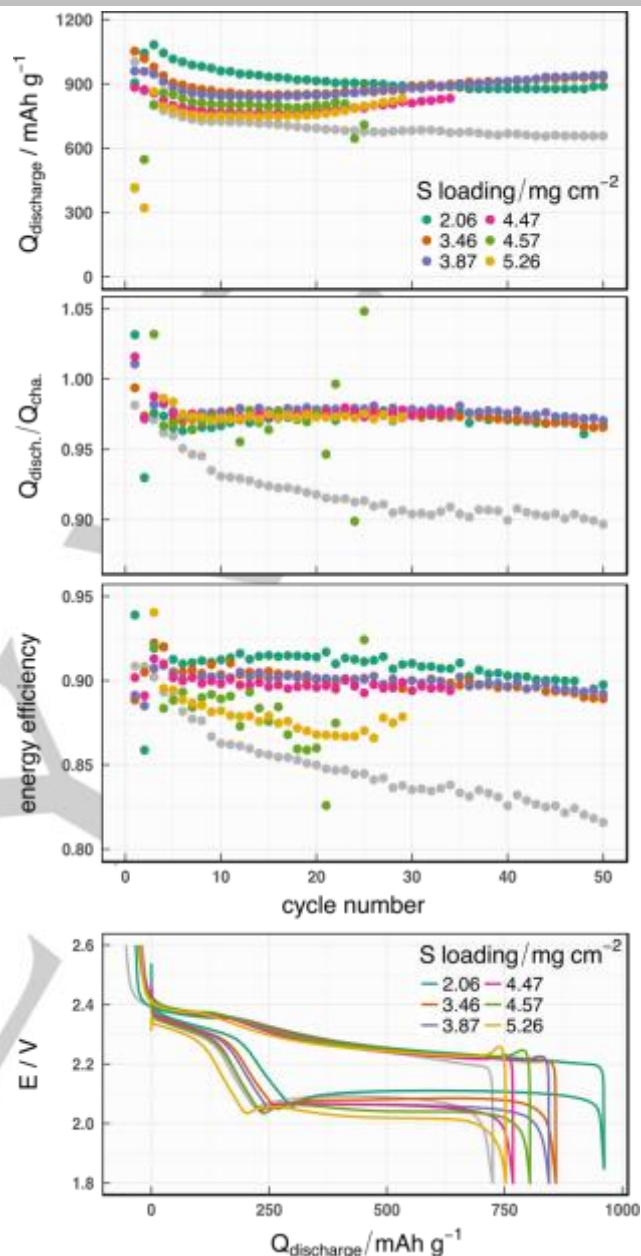
Figure 2. Galvanostatic cycling of electrodes containing a 4:1 PEO:PVP binder system at a constant current density of 167.2 mA g$_S$$^{-1}$. a) discharge capacity, b) coulombic efficiency, c) energy efficiency are given over 50 cycles. d) Voltage profiles for the 10[th] cycle. Grey data points/lines indicate the reference system with a 2:3 CMC:SBR binder at a loading of 1.95 mg$_S$ cm^{-2}.

Reversible capacities in the range of 900 mAh g$_S$$^{-1}$ were obtained for all investigated loadings with the PEO:PVP binder system. The discharge capacity over the first thirty cycles is higher for

electrodes of lower loading, but the capacity of the heavier electrodes begins to increase over time. The reason for this loading-dependent behaviour is unclear but may indicate differences in sulfur utilisation throughout the thickness of the electrode. Coulombic efficiency is almost identical for all cells at approximately 97 – 98%, and showing some evidence of a gradual decrease after forty cycles. The energy efficiency of the cells – defined as the ratio of discharge energy to charge energy and measured by the instrument directly – decreases with higher sulfur loading because of increased resistance in the electrode. This increased resistance is also evidenced by the voltage profiles, which show increased overpotential on discharge and a more prominent peak in the voltage at the beginning of charge for electrodes with high sulfur loading. Electrodes prepared with CMC:SBR under the same conditions showed lower capacities than all PEO:PVP electrodes at around 700 mAh g_S^{-1}, coulombic efficiencies decreasing to ~90% after 30 cycles, and energy efficiencies lower than all PEO:PVP electrodes and decreasing with cycle number, indicating increasing resistance in the electrode.

These results show that electrodes can be prepared with high sulfur content and high loadings, using the PEO:PVP binder system and commercially available carbon materials. The electrode capacities for all loadings reached approximately 600 mAh g^{-1}, based on the mass of the entire electrode coating, which is high relative to much of the existing literature and in line with figures reported for similar systems[4,44,46]. The highest capacity cells shown in Figure 2 correspond to areal capacities of approximately 4.5 mAh cm^{-2}, higher than for electrodes used in typical Li-ion batteries. However, all cells containing electrodes with sulfur loadings in excess of 4 mg_S cm^{-2} showed sudden cell failure within 25-35 cycles, consistent with a short circuit caused by the growth of lithium dendrites across the separator as a result of the relatively high current density.

In the course of this study we have prepared and tested a relatively large number of cells with electrodes of different loadings. A summary of the performance of 41 such cells is presented as a scatter plot of projected cell-level energy density against sulfur loading in Figure 3. Projected energy density is calculated as the discharge energy at the fiftieth cycle divided by the sum of the mass of all cell components: the positive electrode including current collector, separator, electrolyte at the volume used, and negative electrode at the thickness used in this work. Components of the test cell housing are not considered. Guide lines indicating capacities based on the mass of sulfur (i.e., sulfur utilization) and on the area of the electrode are given. The sulfur fraction in the electrode was 65% and the electrolyte/sulfur ratio was 6 μL mg_S^{-1} in all cases, and the sulfur loading was between 1.9 and 3.9 mg_S cm^{-2}.

The discharge capacities shown in Fig. 3 show reproducible performance in the range of 900 – 1000 mAh g^{-1}, which is consistent with the results presented in Fig. 2. On the basis of materials used in this work, cell energy density is calculated to be in the range 130 – 190 Wh kg^{-1}, which is roughly the range of

typical commercial Li-ion batteries. We wish to emphasise that this calculation takes into account the electrolyte excess – the electrolyte mass is approximately four times that of the electrode coating – in spite of the fact that the coin cells used in this work contain a relatively large amount of empty space. We estimate that ~ 300 Wh kg^{-1} with these electrodes is realistic if the electrolyte/sulfur ratio can be reduced to 3 μL mg_S^{-1} and if the negative electrode thickness can be reduced to the order of 30 μm; although it must be noted that both of these factors will impact negatively on the cycle life[46,49–51].
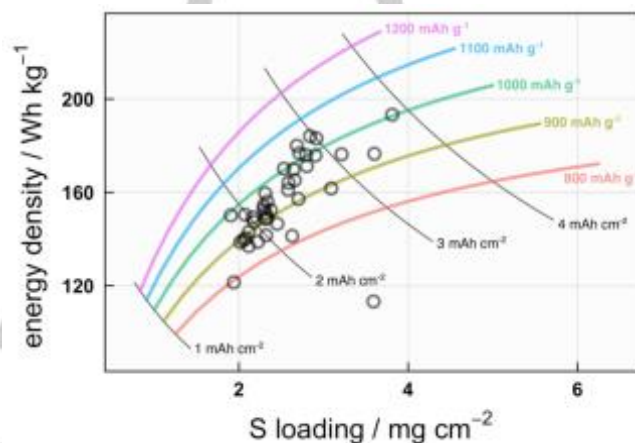
Figure 3. Projected cell-level energy densities for 41 CR2025 cells using electrodes of the type described in this work (black circles). Energy density is projected based on the 50th cycle discharge capacity, and on the electrolyte/sulfur ratio and lithium foil thickness used in this work. Coloured guide lines indicate constant sulfur utilisation, black guide lines indicate constant surface capacity.

Grafting of pyrrolidone groups onto KB

To provide evidence for the mechanism of coulombic efficiency enhancement by PVP in KB-based electrodes, we prepared a functionalised KB powder with pyrrolidone groups grafted to the carbon surface. The grafting was achieved by an oxidation of the carbon black with nitric acid, followed by a Steglich esterification protocol using DIC and DMAP with 1-(2-hydroxyethyl)-2-pyrrolidone (HEP). The reaction scheme is presented in Scheme 1.
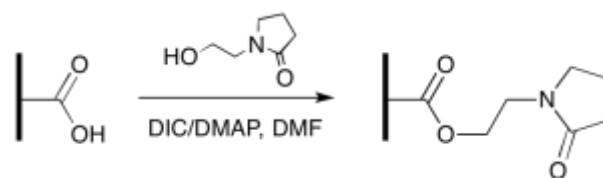
Scheme 1. Reaction scheme for the Steglich esterifaction of an oxidised KB surface with HEP.

The removal of any non-grafted HEP and other reactants was ensured by repeated sonication of the carbon in acetonitrile until no reactants could be detected in the washings by NMR. The presence of the grafted group was subsequently evidenced by XPS, and the HEP groups were determined by TGA to account for approximately 2% w/w of the carbon material (presented in the Supporting Information as Figures S1 and S2 respectively).

Electrodes were prepared using the HEP-functionalised KB with PEO alone as the binder. The electrode composition and preparation procedure was the same as in the previous experiments with the exception of the 155 °C melt-infiltration of sulfur: clear evidence of a chemical reaction between the molten sulfur and the functionalised carbon was observed with this process was attempted, and so for these electrodes the sulfur and carbon materials were simply mixed by hand. For this reason electrodes could only be prepared to a loading of approximately 1.2 mg_S cm^{-2}. Based on TGA, the weight fraction of pyrrolidone groups in the electrode is about 0.4%. For comparison, electrodes were also prepared with the "blank" KB carbon with both PEO and 4:1 PEO:PVP binders. The discharge capacities and coulombic efficiencies of these electrodes over the first 45 cycles are presented in Figure 4.
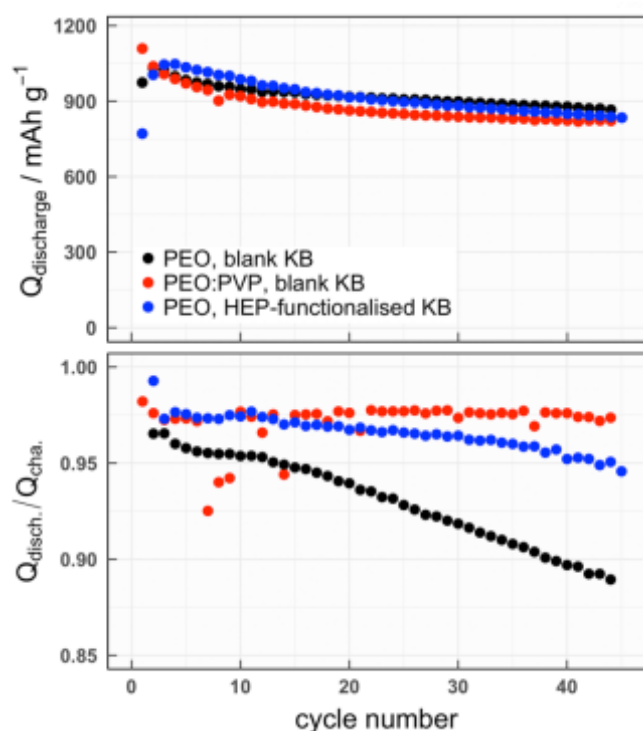
Figure 4. Discharge capacity and coulombic efficiency for HEP-functionalised KB electrodes with a PEO binder compared with "blank" KB electrodes with PEO and 4:1 PEO:PVP binders at a constant current density of 167.2 mA g_S^{-1}. Electrode loading ~ 1.2 mg_S cm^{-2}.

The reversible capacities for each of the electrodes presented in Fig. 4 are approximately the same and of the order of 900 mAh g_S^{-1} over the first 45 cycles. This is consistent with the results presented in Fig. 2. However, there are clear differences in the coulombic efficiency. For the electrode with the "blank" KB and PEO binder (i.e., no pyrrolidone groups present in the electrode), the coulombic efficiency is initially in the range 95 – 96% and begins decreasing after around 10 cycles, at a rate of about 5% per 25 cycles. For the electrode with the 4:1 PEO:PVP binder system prepared with the same carbon material, a coulombic efficiency is maintained at an almost constant 97 – 98% over the first 45 cycles.

The electrode with the HEP-functionalised KB and PEO binder also shows a coulombic efficiency of approximately 97.5% in the initial cycles, which begins to decrease after around ten cycles. That the coulombic efficiency is identical in these initial cycles, where pyrrolidone groups are present either in the polymer binder or directly grafted to the surface, supports findings made elsewhere[52] that the effect of PVP is to adsorb onto the carbon surface and thereby facilitate adsorption of polysulfides on the surface of the conductive host.

The likely cause of the decreasing coulombic efficiency for the HEP-functionalised carbon electrode after ten cycles is weak mechanical integrity of the electrodes. This was observed qualitatively in the process of preparing and handling these electrodes, but is also supported by inspection of the voltage profiles for the HEP-functionalised electrode in particular (Supporting Information, Figure S3); the higher polarization for these electrodes is likely a reflection of poorer particle-particle contact and electrode-substrate contact. Expansion of the electrode on cycling can plausibly increase the flux of polysulfides to the negative electrode; the dissolution of the PEO binder may further contribute to this. This may also point to a key role for PVP as a binder in the conventional sense; that is, retention of capacity by maintaining mechanical stability.

Alternative binders

We have demonstrated in the first section that electrodes of commercially acceptable specification and preparation methods can be achieved with the PEO:PVP binder system coated from a water-based slurry. However, despite the compatibility of this binder system for the electrochemistry of the Li-S system, some disadvantages remain. As previously noted, electrodes we have prepared coated to a loading above 3 mg_S cm^{-2} (corresponding to a thickness of approximately 80 µm) show a tendency to crack significantly on drying. Even higher loadings are preferable[5,44], although thinner electrodes may also suffice if the sulfur utilisation is sufficiently high. In any event, there is a clear motivation for continuing to identify and develop new materials with beneficial functionality but which also provide the mechanical strength needed for thick or highly porous electrodes.

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A further potential consideration arises from the nature of the PEO:PVP binder system. As we observed in our previous publication[42], PVP forms an insoluble complex with lithium polysulfides, whereas PEO tends to gel significantly with the electrolyte. An inter-polymer complex between the two polymers in the presence of Li+ ions might be expected, although since we have not observed the interaction of PEO and PVP *in situ* we cannot exclude the possibility of a phase separation of the two binder components over time, which may impact on cycling stability. As we also observed in the previous section, the rheology of the slurries appears to be influenced by the preferential absorption of one of the binders by the carbon black host. Such an effect would be avoided by the use of co-polymers with mixed functionality. Since co-polymers are also interesting for the development of single materials with targeted properties, we present here an investigation of several polymers with similar functionality to PEO and PVP but which also belong to materials classes which are of potential interest for future co-polymer synthesis. The principal aim here is to explore how the substitution of either binder for a structurally different material but bearing the same functional groups affects electrochemical performance.

The structures of the alternative candidate binders investigated in this work are given in Figure 5. A polymer bearing polyether functionality, poly(poly(ethylene glycol methyl ether methacrylate)) (PPEGMA), was synthesised by a free radical polymerisation reaction to be studied as an alternative to PEO. PPEGMA can be considered itself as a graft copolymer of poly(ethylene glycol) chains grafted to an acrylate backbone. As alternatives to PVP, poly(N,N-dimethylacrylamide) (PDMA) and poly(N-isopropylacrylamide) (PNIPAM) were also synthesised by free radical methods, and poly(2-ethyl-2-oxazoline) (POZ) was purchased. These three polymers all bear repeating amide functional groups, and were observed to show the same evidence of complexation to polysulfides in solution (i.e., formation of an insoluble precipitate) as PVP.

PPEGMA, PDMA and PNIPAM are also acrylic monomers and so are potential candidates for co-polymerisation by virtue of the similar reactivity of the monomers. POZ is a poly(2-oxazoline), a class of polymers synthesised by the cationic ring-opening polymerisation of 2-oxazoline monomers and currently of considerable interest to chemists, especially for biomedical applications[53]. The monomers themselves can be synthesised with various side groups under a wide range of conditions, most conveniently from the reaction of a carboxylic acid or a nitrile with 2-aminoethanol[54]. POZ is also a structural isomer of PDMA.

Electrodes were prepared with binder systems of 4:1 w/w PEO:[amide] where [amide] was either PVP, POZ, PDMA, or PNIPAM. Electrodes were also produced with a 4:1 PPEGMA:PVP binder system. The loading of all electrodes was approximately 2 mg$_S$ cm^{-2} and the weight fraction of all other materials was identical to those described in the previous section. The densities of the electrodes was calculated to be in the range 0.54 – 0.62 g cm^{-3} for all compositions. A comparison of the cycling behaviour of these electrodes is presented in Figure 6.

Representative photographs of electrodes prepared with these different binder systems is presented in the Supporting Information as Figure S4. Electrodes with acceptable quality and uniformity could be prepared with all of the binder systems. Electrodes prepared with alternative PEO:[amide] binders were seen to be somewhat more brittle, as observed by an occasional tendency for parts of the electrode to flake off the substrate when cutting into discs. In particular, PEO:PDMA electrodes were noticeably poorer in this regard, and electrodes tended to have a comparably high amount of large agglomerates of carbon materials on the surface of the coating (this can be observed in the photographs presented in the Supporting Information.
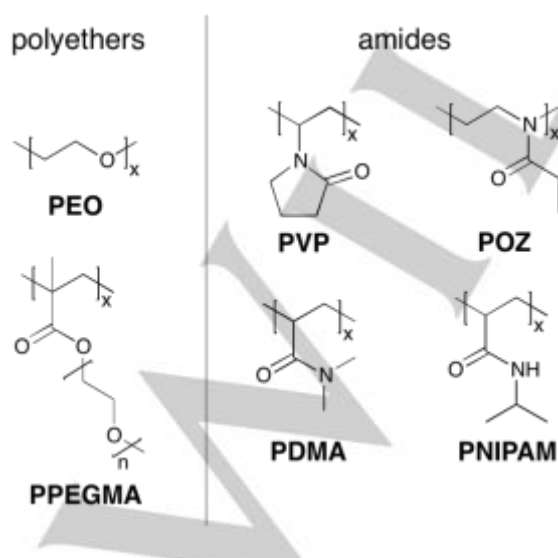
Figure 5. Structures of the candidate binders investigated in this work.
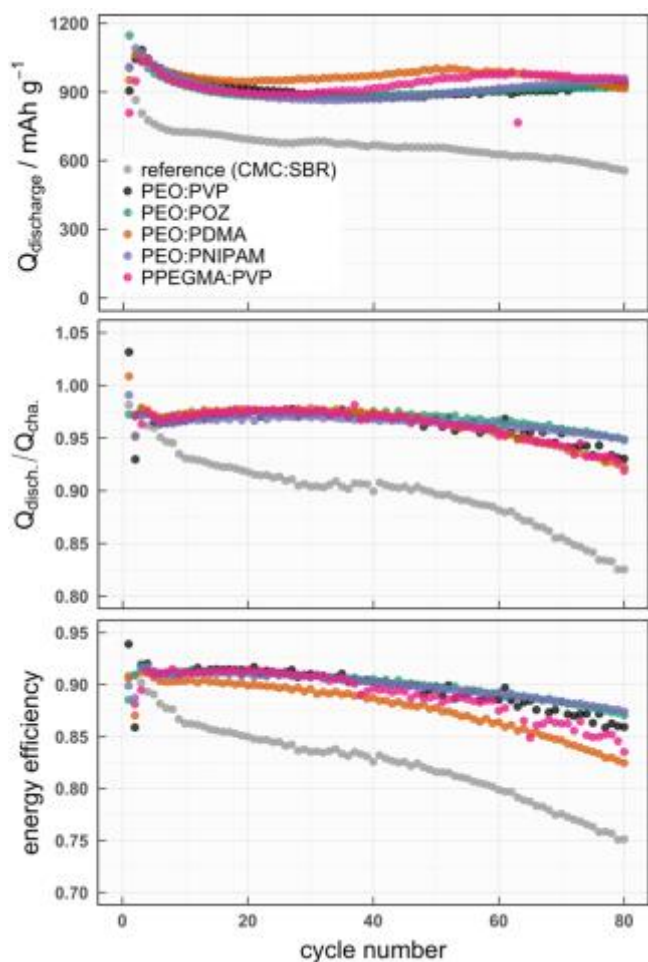
Figure 6. Comparison of electrodes with a 4:1 PEO:[amide] or PPEGMA:PVP binder system with the 2:3 CMC:SBR and 4:1 PEO:PVP reference binder systems by galvanostatic cycling at a constant current density of 167.2 mA g_S^{-1}. a) discharge capacity, b) coulombic efficiency, c) energy efficiency are given over the first 80 cycles.

The cycling behaviour over the first 80 cycles is similar in both reversible discharge capacity and coulombic efficiency for all of the alternative binder systems compared to PEO:PVP. Electrodes prepared with the reference CMC:SBR binder system shows approximately 200 mAh g_S^{-1} lower capacity and considerably lower coulombic efficiency – 90% compared to 97 – 98% at the 40th cycle – than electrodes with any of the alternative PEO:[amide] binder systems.

The surprising similarity of the cycling performance for the electrodes containing functional binders despite the different amide-containing binders support our previous observations that the performance improvement associated with these binders is derived from the chemical functionality of the polymer and its interactions with the electrolyte system. That the differences in

cycling performance between the different PEO:[amide] electrodes are relatively small indicates that the electrochemistry of the electrodes is rather insensitive to the mechanical properties or macrostructure of the electrode, at least in the short term. The substitution of PEO for PPEGMA in the binder system further supports our conclusion that the chemical functionality of the polymer binder is of primary importance. PPEGMA is a highly viscous, sticky liquid: although this is far from the desired properties in an electrode binder, electrodes containing the PPEGMA:PVP binder system show very similar cycling performance compared to PEO:PVP electrodes.

However, as with the HEP-functionalised carbon black discussed in the previous section, we observe some evidence for faster fade in coulombic efficiency and energy efficiency in both PEO:PDMA and PPEGMA:PVP electrodes, as well as changes in discharge capacity similar to those observed for higher-loading electrodes in Fig. 2. These observations indicate that maintaining mechanical integrity of the electrodes is of greater significance for capacity and coulombic efficiency retention in the long term. This is in line with other reports elsewhere, for example in the investigations of electrode calendering on capacity retention by Kim *et al*[55]. We have made similar observations in initial investigations of calendered electrodes which showed some improvement in coulombic efficiency retention at the expense of a small reduction in sulfur utilisation. We wish, however, to caution against drawing conclusions about the effect of the alternative binders on cycle life, since we have not optimised the electrode preparation for each individual binder system. Furthermore, we have demonstrated in other work that coulombic efficiency and capacity retention are also heavily dependent on the decomposition of the electrolyte by the negative electrode, and the cycle life in cells of the type presented here is typically 100 – 120 cycles[50,56]. It is readily apparent that the cycle life of the cells investigated here depend on the interplay of a number of different factors, which we consider a topic for much future research.

Conclusions

Positive electrodes for lithium-sulfur batteries with relatively high sulfur contents of 65% w/w and controllable loadings of up to 5.2 mg_S cm^{-2} have been prepared by a simple melt-infiltration process using commercially available carbon materials and a water-based coating process using the 4:1 PEO:PVP functional binder system. The previously-determined[42] benefits of using this binder system relative to an established reference – improved reversible capacity, coulombic efficiency and energy efficiency – are retained for these thick, high-sulfur content electrodes, demonstrating the commercial applicability of this binder system. Intrinsic weaknesses in electrode adhesion and mechanical integrity, and difficulties in controlling slurry rheology, can be largely mitigated with careful choice of slurry composition and substrate.

The exchange of either PEO or PVP in the binder system for a different polymer bearing the same functional groups preserves

the improved electrochemical performance. Direct covalent grafting of pyrrolidone groups to the carbon surface in place of an amide-containing functional binder also afforded a similar increase in capacity, providing strong evidence for the role of PVP and other functionally similar polymers for facilitating adsorption of polysulfides. The presence of the functional groups in all of the alternative polymers tested appear to be of greater importance than the effect of those polymers on the mechanical properties of the electrodes. These results demonstrate the potential for designing functional co-polymer materials for applications as binders in this battery system based on acrylates, acrylamides and 2-oxazolines. With the acrylic systems in particular, there is a vast number of readily available monomers and a considerable scope for designing polymers with targeted properties.

We have additionally made some observations that point to the influence of mechanical integrity in retaining capacity and coulombic efficiency on extended cycling, but only in electrodes where poorer mechanical properties were easily apparent during preparation. As noted in the discussion above, however, this observation has to be considered against the known effect of electrolyte decomposition by the negative electrode. The various mechanisms contributing to capacity fade are not trivial to distinguish, and so we believe this question remains a topic for further research.

Experimental Section

Materials

Lithium bis(trifluoromethyl)sulfonimide (LiTFSI, Novolyte) and lithium nitrate (LiNO$_3$) were dried at 120 °C prior to use. Ketjenblack carbon black (KB, EC-600JD, Akzo Nobel), sulfur powder (Aldrich), Super C65 carbon black (Imerys), carbon nanofibers (CNF, 20-200 nm x 100 µm, Aldrich), carboxymethyl cellulose (CMC, Leclanché), styrene-butadiene rubber (SBR, Targray PSBR-100), poly(ethylene oxide) (PEO, M$_w$ ~ 4,000,000, Aldrich), poly(2-ethyloxazoline) (POZ, M$_w$ ~ 500,000, Aldrich), poly(vinylpyrrolidone) (PVP, M$_w$ ~ 360,000, Aldrich), 1,2-dimethoxyethane (DME, Novolyte) and 1,3-dioxolane (DOL, anhydrous, Aldrich) were used as received. Azobisisobutyronitrile (AIBN, Aldrich) was recrystallized from methanol before use. N,N-dimethylacrylamide (DMA, Aldrich) and poly(ethylene glycol methyl ether methacrylate) (PEGMA, M$_n$ ~ 500) were filtered over activated, basic aluminium oxide (Brockmann grade I, Alfa Aesar) before use. N-isopropylacrylamide (NIPAM, Aldrich), 4-dimethylaminopyridine (DMAP, Aldrich), diisopropylcarbodiimide (DIC, Aldrich) and 1-(2-hydroxyethyl)-2-pyrrolidone (HEP, Aldrich) were used as received.

^{1}H NMR spectra were obtained at 25 °C with a JEOL Eclipse+ 400 MHz NMR spectrometer. Polymer molecular weight and polydispersity index (PDI) was determined by gel permeation chromatography (GPC), using an Agilent 1260 Infinity GPC with PolyPore columns. The system solvent was dimethylformamide (DMF) containing 40 mM LiBr, and operating at 1 mL/min and 80 °C. Poly(methyl methacrylate) (PMMA) standards were used to calibrate the system.

Polymer synthesis and characterisation

Synthesis of poly(N,N-dimethylacrylamide) (PDMA): 2.7 mg AIBN (0.016 mmol) was dissolved into a solution of 5 mL DMA (0.0485 mmol) in 10 mL tetrahydrofuran (THF). The reaction was carried out at 70 °C under an Ar atmosphere. The reaction was quenched with EtOH and the solvent removed under reduced pressure. The resulting viscous liquid was added dropwise into cold Et$_2$O to precipitate the polymer as a white powder. The product was filtered, washed three times with Et$_2$O (20 mL) and dried for at least three days under vacuum. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 3.17 – 2.73 ppm (6H), 2.72 – 2.22 ppm (1H), 1.84 – 1.40 & 1.35-1.11 ppm (2H), consistent with atactic PDMA[57]. GPC: M$_n$ = 47,700 g mol^{-1}, M$_w$ = 83,500 g mol^{-1}, PDI = 1.75.

Synthesis of poly(N-isopropylacrylamide) (PNIPAM): 1.32 mg AIBN (0.008 mmol) was dissolved into a solution of 2.75 g NIPAM (0.0237 mmol) in 10 mL THF. The reaction was carried out at 70 °C under an Ar atmosphere. The reaction was quenched with EtOH and the solvent removed under reduced pressure. The resulting viscous liquid was added dropwise into a 1:1 mixture of Et$_2$O and cyclohexane to precipitate the polymer as a white powder. The product was filtered, washed three times with diethyl ether (20 mL) and dried for at least three days under vacuum. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 3.97 ppm (1H), 2.30 – 1.44 ppm (3H), 1.10 ppm (6H). GPC: M$_n$ = 16,900 g mol^{-1}, M$_w$ = 35,000 g mol^{-1}, PDI = 2.07.

Synthesis of poly(poly(ethylene glycol methyl ether methacrylate)) (PPEGMA): 15 mg AIBN (0.09 mmol) was dissolved into a solution of PEGMA (15 mL) in 30 mL *i*PrOH and degassed with N$_2$ for 15 min. The reaction was carried out at 80 °C for 2 hours. The reaction mixture was quenched with 10 – 15 mL of acetone, and slowly poured into a 1:1 mixture of Et$_2$O and cyclohexane to precipitate the polymer as a highly viscous liquid. The excess solvent was decanted off, the product was washed with Et$_2$O and dried under vacuum. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 4.07 ppm (2H), 3.7 – 3.58 ppm (PEG backbone), 3.54 ppm (2H), 3.37 ppm (3H, *s*), 2.0 – 1.65 ppm (2H), 1.1 – 0.8 ppm (3H). GPC: M$_n$ = 87,790 g mol^{-1}, M$_w$ = 300,000 g mol^{-1}, PDI = 3.42.

Functionalisation of Ketjenblack carbon (KB)

Preparation of oxidised KB: KB (3.0 g) was dispersed into 50 mL concentrated HNO$_3$ in a round-bottomed flask. The flask was fitted with a condenser and heated to 110 °C with constant stirring for 30 min. Evolution of NO$_2$ from the reaction mixture was observed during this time. On cooling, 50 mL of water was added to the mixture, the carbon was recovered by vacuum filtration and washed several times with water. The carbon was re-dispersed into water and sonicated for 15 minutes to remove any traces of acid, and then filtered again. This process was performed three times. The carbon was then dried at 80 °C under vacuum overnight.

HEP grafting onto KB: Oxidised KB (1.0 g) was dispersed into 50 mL of DMF with DMAP (0.207 g, 1.694 mmol) under vigorous stirring. The dispersion was cooled to 0 °C and HEP (7.7 mL, 68 mmol) and DIC (2.9 mL, 19 mmol) were added to the solution. After five minutes, the ice bath was removed and the reaction was left to warm to room temperature for three hours. The carbon was recovered by vacuum filtration, and washed with H$_2$O and then EtOH. The carbon was then three times re-dispersed into CH$_3$CN, sonicated for 15 min and filtered to remove any remaining reactants. The product was then dried at 70 °C under vacuum overnight. The presence of the HEP group on the carbon surface was evidenced by X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA), the results of which are presented in the Supporting Information (Figs. S1 and S2).

Cell preparation and electrochemical testing

Sulfur powder and KB were first mixed manually in a 65:21 w/w ratio and heated to 155 °C for 20-25 minutes to melt S into the carbon. For electrodes prepared with the HEP-functionalised KB, the 155 °C heating step was not performed. Slurries were then prepared by dispersing the composite into H_2O, or H_2O containing 5 – 10% v/v EtOH, along with the other solid components, to give a final composite of 65% S, 21% KB, 3.5% Super C65, 3.5% CNF, 7% binder. The solid content of the slurries was typically 15 – 20%. The binders used in this work were either a 2:3 mixture of CMC:SBR, used as the reference system, or a 4:1 mixture of a polyether component (PEO or PPEGMA) and an amide-containing component (PVP, POZ, PDMA or PNIPAM) respectively. The slurries were mixed by planetary ball-milling for 2 hours and cast onto graphite-coated Al foil (graphite loading approx. 0.075 mg cm^{-2}) by doctor-blading to a typical loading of 1.9 – 2.2 mg$_S$ cm^{-2}. The loading could be easily varied between 1 and 5 mg$_S$ cm^{-2} by varying the separation between the blade and the substrate. The electrodes were allowed to dry in air, cut into 13 mm diameter discs, dried at 55 °C overnight and transferred to an Ar-filled glove box.

CR2025 coin cells were prepared comprising the previously described positive electrodes, a porous polyethylene separator (SOLUPOR, Lydall Performance Materials) and 125 μm-thick Li foil (25.8 mAh cm^{-2}, Cyprus Foote Mineral) as the negative electrode. The electrolyte was 1 M LiTFSI, 0.25 M LiNO$_3$ in 1:1 v/v DME:DOL, at a fixed electrolyte:sulfur ratio of 6 μL mg$_S^{-1}$ (C/10 based on the theoretical capacity of sulfur, and between 0.3 and 0.9 mA cm^{-2} depending on loading) between voltage limits of 1.8 and 2.6 V using an Arbin BT-2043 battery cycler.

Acknowledgements

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Entry for the Table of Contents

FULL PAPER

Function over form: functional binders based on a general combination of polyether- and amide-containing polymers enable high-capacity electrodes for lithium-sulfur batteries – using only commercially available materials and a simple water-based preparation procedure.
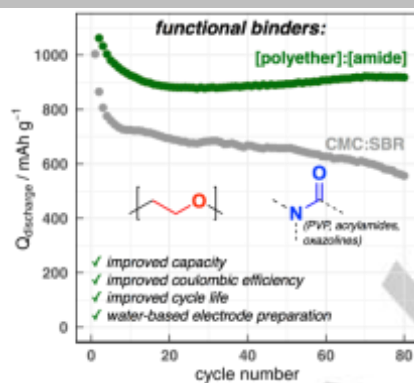
Matthew J. Lacey*, Viking Österlund, Andreas Bergfelt, Fabian Jeschull, Tim Bowden and Daniel Brandell

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A robust, water-based, functional binder framework for high-energy lithium-sulfur batteries