

Functional, water-soluble binders for improved capacity and stability of lithium-sulfur batteries

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Note on changes to the manuscript: **additions are in red**, ~~deletions are struck through~~

Abstract

Binders based on mixtures of poly(ethylene oxide) (PEO) and poly(vinylpyrrolidone) (PVP) are here shown to significantly improve the reversible capacity and capacity retention of lithium-sulfur batteries compared to conventional binders. This mixed binder formulation combines the local improvement to the solvent system offered by PEO and the lithium (poly)sulfide-stabilising effect of PVP. Cells with cathodes made of simple mixtures of sulfur powder and carbon black with a binder of 4:1 PEO:PVP exhibited a reversible capacity of over 1,000 mAh g⁻¹ at C/5 after 50 cycles and 800 mAh g⁻¹ at 1 C after 200 cycles. Furthermore, these materials are water soluble, environmentally friendly and widely available, making them particularly interesting for large-scale production and applications in, for example, electric vehicles.

1. Introduction

The demand for ever-higher energy density in portable electrical storage is increasingly motivating research in systems beyond lithium-ion. Of these, the lithium-sulfur couple, with a theoretical energy density of 2,600 Wh kg⁻¹, is particularly promising, with the possibility of fully-assembled battery packs boasting an energy density two to three times larger than that of current Li-ion[1,2]. However, the Li-S system suffers from short cycle life and a high degree of self-discharge, attributable to the well-documented polysulfide redox shuttle[3].

Furthermore, the combination of poor electronic and ionic conductivity of the charge and discharge products with poor electrochemical reversibility limit sulfur utilization and make this a system of relatively low rate capability compared to Li-ion[4].

In the last few years, much of the research within this field has considered how cathode design can mitigate these drawbacks, with such varied strategies as templated carbon[5–7], nanotube- or graphene based[8–11] or even conducting polymer[12–14] host structures, control of sulfur distribution in the host and barriers to polysulfide dissolution[15–18]. However, the significance of such strategies is a matter of considerable debate: it has previously been demonstrated that a sophisticated host structure or even homogeneous mixing is not necessary for high capacity[19], and that complex syntheses of nanomaterials may not be sufficiently scalable for wider commercialisation[20]. The major electrochemical processes in the Li-S cell are the reactions of soluble polysulfide anions; the capacity and rate capability of the battery are therefore extremely dependent on the electrochemical kinetics and concentration of polysulfides in solution, and their access (diffusion) to the carbon surface[4,21]. Of course, the benefit of a higher concentration of polysulfides is offset by an enhancement of undesirable reactions at the anode, which contributes to self-discharge and irreversible loss of active mass to the anode[3].

While protection of the anode is clearly of great importance in extending cycle life[22,23], the electrolyte system is similarly important in ensuring a high capacity and rate capability; the latter of these must still merit attention considering the potential applications of the Li-S system, for example electric vehicles. A fact that is perhaps often overlooked is that, the cathode binder, as well as imparting mechanical stability to the cathode composite, can also be considered part of the *electrolyte* system in the Li-S cell. This is because polymers may swell or dissolve in the electrolyte and, unlike Li-ion systems, polysulfides in solution may interact with functional groups in the polymer. Furthermore, despite various articles on the performance of different binders in the Li-S system, such phenomena have not been widely

nor systematically investigated[1,24–28]. We have touched on this idea in a recent paper[29], in which we investigated the capacity improvement afforded by PEO when used as a binder, and concluded that PEO locally modifies the electrolyte system, suppressing passivation of the cathode and improving reaction kinetics. The observed performance improvement is
5 consistent with studies elsewhere in which improved capacity is observed with the use of short-chain PEG as a cathode coating[17] or as an electrolyte solvent[30]. Similarly, Seh *et al*[31] recently used DFT calculations to evaluate the strength of interaction between functional polymers and lithium sulfides. These calculations led to the identification of poly(vinylpyrrolidone) (PVP) as having a strong interaction with lithium (poly)sulfides;
10 subsequent experiments on cathodes using Li_2S as a starting material and PVP as the binder demonstrated remarkable cycling stability compared to cathodes using the conventional poly(vinylidene difluoride) (PVdF) binder. The authors suggested that the performance improvement from the inclusion of PVP could be attributed to the retention of polysulfide at the cathode as well as its good properties as a dispersant for cathode preparation. Interestingly,
15 similar calculations and a comparable performance improvement have recently been demonstrated for nitrogen-doped carbon host materials with related (e.g., pyrrolic N-C=O) surface functional groups[32].

In this work, we aim to further investigate PEO and PVP as binders, as well as mixtures of the two materials. Aside from performance enhancement, these polymers are of interest since
20 they are water-soluble, safe, biodegradable and industrially important. The environmental friendliness and scalability of water-based cathode preparations with such commodity polymers is extremely relevant to this system, where the active material is potentially very cheap. To our knowledge, the PEO:PVP binder system has only been reported once, in a recent paper by researchers at Hydro-Québec[33], however, the choice of binder was not
25 discussed. There are other comparisons of different binders, including PEO[34] and PVP[9,25,35], in the literature, but these studies generally do not discuss the effect of these

binders on the chemistry or electrochemistry of polysulfides. Additionally, evaluation of the Li-S system is complex in that cell performance (i.e., sulfur utilisation and capacity retention) can differ dramatically, not just through different host structures, but also on factors including sulfur loading[21], mixing[19], choice of binder, electrolyte chemistry[30,36] and additives[4,37], electrolyte volume[38] and cycling limits[39]. Because of this, especially compared to Li-ion systems, it is difficult to compare the efficacy of one strategy with another. In this study we will attempt to investigate the effect of the binder by comparison with a simple, easily repeatable and well-performing reference system in which changes to other variables in the system are minimised as much as possible. Reaction kinetics will be studied by a combination of galvanostatic cycling and impedance spectroscopy (IS). Such electrochemical techniques are extremely useful for evaluating the overall behaviour of a cell in a system where the complexity of the reaction mechanism and thermodynamic instability of the reaction intermediates make precise characterisation by, e.g., spectroscopic methods, extremely challenging[40].

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2. Results and discussion

The effect of changing the binder composition was investigated initially by galvanostatic cycling of standardised test cells with varying cathode composition. The full experimental procedure is detailed in the experimental section. The cathodes in each case simply comprised composites of sulfur powder and Super P carbon black mixed by planetary ball milling with the chosen binder and water. The only exception to this procedure was the PEO binder, where acetonitrile was used; this is because water-based slurries containing only PEO as the binder are extremely viscous, and cathode coatings of acceptable quality were only obtained using acetonitrile. Cells were assembled using a precise amount of electrolyte relative to the mass of

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sulfur in order to minimise differences between cells due to active mass dissolution into the electrolyte. A binder composition of 2:3 carboxymethylcellulose sodium salt:styrene-butadiene rubber (CMC:SBR) was used as the reference material; CMC:SBR is frequently encountered as a water-soluble alternative to the commonly used PVdF, especially for Li-ion anode materials[41]. The moderate sulfur loading of the cathode of 50% and the relative excess of electrolyte ensures that the reference cell cycles with good capacity retention over a moderate number (50 – 200) of cycles and at moderate current densities.

2.1. Comparison of binders by galvanostatic cycling

The cycling behaviour of the Li-S cells at a moderate rate of C/5 is presented in Figure 1. For readability the data is presented as two plots: on the left, the reference CMC:SBR binder, the single component binders of PVP and PEO and the 4:1 PEO:PVP mixed binder, which was determined to have the best performance; the right-hand plot shows other PEO:PVP compositions tested. In agreement with our previous paper, PEO affords a capacity improvement of over 100 mAh g⁻¹ compared to the reference CMC:SBR system. While the use of PVP gives an initially smaller capacity increase (ca. 50 mAh g⁻¹) over CMC:SBR compared with PEO, the capacity is better retained. The capacity of the PVP-containing cathode matches that of the PEO cathode after 50 cycles. With a combination of PEO and PVP in a high PEO:PVP ratio (e.g., 4:1 and 9:1), the capacity is higher than either of the single-component binders – and more than 200 mAh g⁻¹ higher compared to CMC:SBR - with the same good capacity retention as for PVP. **These ratios are similar to the binder composition used in the previously-referenced paper by Hydro-Québec, i.e., 8:1 PEO:PVP[33].** The capacities after the first few cycles decreases with increasing PVP content, and the 1:1 mixture shows a lower capacity than either of the single component cathodes.

For all cells the coulombic efficiency is relatively similar and reaches a high and stable value of almost 99% after the first 20 cycles. This data is plotted in Figure 2. The high coulombic efficiency can be attributed to the efficient passivation of the Li anode by LiNO_3 [22,39]. We can attempt to rationalise the effect of the PVP content of the cathode on the cycling performance by consideration of its chemical interaction with polysulfides, as previously predicted by Seh *et al*[31]. Addition of 0.3 mL of a saturated solution of Li_2S_6 in the electrolyte solvent to 1 mL of a solution of PVP in the same solvent affords a red precipitate which subsequently remains in a stable suspension over at least 48 hours. Addition of the same polysulfide solution to an equivalent solution of PEO causes some precipitation of a brown solid which decomposed completely within 48 hours, leaving what appeared to be sulfur powder beneath a layer of PEO gel. The products of these reactions are shown in Figure 3. This observation is consistent with the strong interaction between PVP and lithium polysulfide as predicted by Seh *et al*. It would therefore be expected that, on the first discharge of the cell, dissolution of sulfur from the cathode in the form of lithium polysulfide leads to the formation of a similar PVP: Li_2S_x complex at the binder. Such a complex might be analogous to complexes of PVP and iodine currently used as antiseptics[42], or other polymer-ion crosslinked materials as reported in the literature[43,44]. Unfortunately, at the time of writing, we have not been unable to isolate this material as a stable solid for characterisation. Nonetheless, this interaction has a clear effect on the stability of the cell through the improved capacity retention, possibly through improved retention of polysulfide in the vicinity of the cathode as previously suggested. A possible explanation for the poorer specific capacity for cathodes with mixed binders and higher PVP content (i.e., 1:1, 7:3 PEO:PVP; see Figure 1) may be that a larger proportion of active mass is complexed into an insoluble form which is then rendered inactive by phase separation of the two binder components.

Measuring the relaxation of cells under open circuit conditions following cycling, as shown in Figure 4, gives the clearest indication of the improved stability afforded by the inclusion of PVP in the binder. Cells were assembled with cathodes containing CMC:SBR, PEO and 4:1 PEO:PVP binders, respectively. After 5 charge-discharge cycles at $C/5$, the cells were left to rest at open circuit for exactly 1 week. At the end of the week, the open circuit voltage (OCV) for the cell containing the 4:1 PEO:PVP binder was 174 mV higher (2.334 V) than the cell with PEO (2.170 V) and 183 mV higher than the cell with CMC:SBR binder (2.161 V). The shape of the voltage profile, especially for the cells containing PEO and CMC:SBR binders, appears similar to the voltage profile for the Li-S cell during charge and discharge, with two major plateaus with average voltages of approximately 2.3 V and 2.15 V. The decreasing voltage of cells over time at open circuit likely indicates a change in the stoichiometry of lithium sulfides at the electrode surface towards shorter chain polysulfides, which is a possible indicator of self-discharge due to the redox shuttle. The inclusion of even a small proportion of PVP therefore effects a dramatic improvement in the stability of the system, possibly aiding to resist self-discharge, for example through retaining polysulfides near the cathode as suggested by Seh *et al.* For the best-performing mixed binder of 4:1 PEO:PVP, the high reversible capacity of over 1000 mAh g^{-1} , retained over more than 50 cycles, is competitive with the state-of-the-art Li-S research, as outlined in a recent review[24]. Furthermore, this result is also an important demonstration that the role of the binder extends beyond ensuring efficient utilisation of the active surface area of the cathode.

2.2. High rate cycling and kinetic effects

The performance of the four binders of principal interest in this study, i.e., CMC:SBR, PEO, PVP and 4:1 PEO:PVP, was studied further by a combination of higher rate galvanostatic cycling with impedance spectroscopy. The full electrochemical experiment is detailed in the

experimental section. The program essentially comprised sequences of galvanostatic cycling at a rate of 1C (1,672 mA g⁻¹) with periodic rest intervals, during which impedance spectra were obtained with the cell in a fully charged or discharged state. The cycling data over 200 cycles is presented in Figure 5, with selected Nyquist plots showing cell impedance in the charged and discharged states after 10, 100 and 200 cycles presented in Figure 6. At this relatively high cycling rate, the cell containing the 4:1 PEO:PVP binder combination still retains the best capacity compared to the other compositions tested, with a reversible capacity of over 800 mAh g⁻¹ after 200 cycles. Observing that the cells using 4:1 PEO:PVP and PEO alone as binders exhibit the same initial discharge capacity of 1170 mAh g⁻¹, this result is further evidence for the ability of PVP to effect an improvement in capacity retention despite a slightly increased cell impedance for the mixed binder system.

The PEO-containing cells show significantly higher capacities than the CMC:SBR-containing reference cell in agreement with the previous result at moderate cycling rates. Interestingly, while showing superior capacity when cycled at C/5 compared to the CMC:SBR reference, the cell containing PVP alone as the binder performs considerably worse when cycled at 1C. This is an indicator of slower reaction kinetics compared to other cells. Such effects are easily seen by examination of the voltage profiles, which are presented for the first and 197th cycles (the latter being the last full cycle in the loop of 10 cycles before the 200th cycle) for these cells in Figures 7 and 8 respectively. The voltage profiles show generally decreased hysteresis for PEO-containing cells with an elongation of the lower discharge plateau and suppression of the voltage peak seen at the beginning of the charge cycle, as we have previously reported. By comparison, the cell containing PVP alone as the binder shows a very large hysteresis, despite good performance at lower charge-discharge rates. However, an interesting feature of note is the suppression of the voltage peak at the beginning of the discharge cycle for PVP-containing cells, compared to CMC:SBR and PEO. This feature may be related to initial complexation of polysulfide to PVP in the binder as suggested above. After 197 cycles, the

trends are broadly the same; reduced hysteresis, especially for the upper plateau, and better retention of both major plateaus for the cells with PEO-containing cathodes. The voltage profiles of the PEO and 4:1 PEO:PVP cells appear to be essentially the same apart from proportional increases in the length of the major plateaus in the latter case. This could be an indication of higher availability of active sulfur in the 4:1 PEO:PVP cell, supporting the argument for improved sulfur retention near the cathode.

Further insight into the effect of the binders on reaction kinetics can be gained by study of the impedance response of the cells (Figure 6). In all cases the major features of the Nyquist plot are a major semi-circle, which can be interpreted as representing the reactions of polysulfide at the cathode, and low-frequency diffusional impedance. Coupled with this at higher frequency is the porosity. There is an additional high-frequency semicircle representing dissolution and plating of Li at the anode. This feature has a small charge transfer resistance (R_{ct}) for all binders except for PVP; this higher resistance may indicate an effect on the composition of the solid-electrolyte interface (SEI) due to PVP, perhaps as a result of PVP dissolution in the electrolyte contributing to a more resistive layer, but also possibly reflecting a lower content of sulfur species in the SEI.

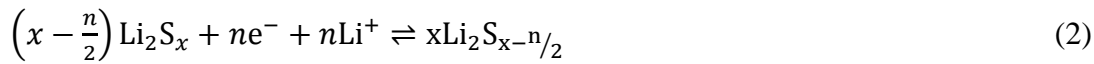
Analysis of the major semi-circle provides information about the electron transfer kinetics of polysulfide independent of processes on other timescales, for example, diffusion. Such analysis by measuring R_{ct} from the diameter of this semi-circle alone may be misleading since the actual electrochemical surface area of the cathode is unknown and may change continuously throughout operation of the cell. It is also further complicated in view of the fact that R_{ct} is also in series with the porosity of the cathode, and so the true R_{ct} may be obscured. This therefore makes it difficult to distinguish kinetic effects from changes in porosity. However, for these cells, we believe that the true R_{ct} is the dominant element in the semi-circle under consideration, for three reasons: first, that the major semi-circle and Warburg features fit the Randles circuit relatively well in most cases, and we were unable to obtain a

sensible fit when taking into account the porosity; secondly, that these cathodes are thin and Super P carbon is relatively non-porous, and thirdly; that we have previously demonstrated that the addition of PEO as a cathode coating or PEGDME as an electrolyte additive effected a similar improvement in performance when compared with the use of PEO as a binder, and
5 that these strategies would not be expected to influence cathode porosity[29].

Based on this assumption, kinetic information can be obtained by examining the relaxation frequency, f^* , which is the maximum of the semi-circle in the imaginary part of the impedance, $-Z''$. This relaxation frequency relates to a time constant given by:

$$\tau = R_{ct}C_{dl} = \frac{1}{2\pi f^*} \quad (1)$$

10 Where C_{dl} is the double layer capacitance. We can also assume that, on the time scale of these processes (< 1 second), the fastest reactions (i.e., the process of lowest impedance) are that of polysulfides in solution, and that insoluble discharge products (S_8 , Li_2S) are effectively inactive. There are several such reactions but the overall equilibrium can be expressed as:



15 This can be considered as a simple electrochemical reaction with slow electron transfer kinetics, especially for cells in the discharged state. For such reactions at low overpotentials the Butler-Volmer equation approximates to a linear relationship:

$$R_{ct} = \frac{\partial \eta}{\partial I} = \frac{RT}{nFI_0} \quad (3)$$

While the AC perturbation of 50 mV used in this experiment, in order to ensure good quality
20 data, would ordinarily be considered high for this approximation, the result should not deviate significantly from the relationship expressed in Equation 3. We can further express the exchange current density I_0 as:

$$I_0 = nFAc_{\infty}k_s \quad (4)$$

Where A is the electrochemical surface area, c_{∞} is the bulk concentration of polysulfide and k_s
25 is a pseudo-rate constant representing the heterogeneous rate constant for the reaction

described in Equation 2. By combination of Equation 1, 3 and 4 we arrive at an expression for the relaxation time constant τ :

$$\tau = \left(\frac{RT}{n^2 F^2} \right) \left(\frac{C_{dl}}{A} \right) \frac{1}{c_{\infty} k_s} \quad (5)$$

- Since the ratio C_{dl}/A is assumed to be a constant, the relaxation time constant is approximately inversely proportional to the product of the polysulfide concentration and the pseudo-rate constant k_s . While accurate values for c_{∞} and k_s are unmeasurable by this technique, the time constant τ at least gives an indication of polysulfide reaction kinetics. Average values for τ have been determined for these cells in the charged and discharged states and are tabulated in Table 1.
- The estimated time constants for CMC:SBR and PEO-containing cathodes are higher (i.e., slower kinetics) in the discharged state. The average relaxation times indicate $c_{\infty} k_s$ products approximately 2 times larger in the discharged state and approximately 3 to 5 times higher in the charged state for PEO-containing cathodes compared with CMC:SBR. These observations are consistent with the previous interpretation of the voltage profiles. Similarly, the estimated time constant for the PVP cathode in the charged state is significantly higher than for the other cathodes, further reflecting the poor performance as a result of this binder. However, the PVP cathode is unique in that the time constant in the discharged state is lower than that for the charged state. This unusual trend could be interpreted as evidence of stabilisation of lithium sulfides by PVP.
- It is interesting to note that the addition of PVP, which, as a single binder, performs relatively poorly at high rate, still effects an improvement in capacity when combined with PEO. As previously stated, a possible interpretation is that the effect of PVP is to improve the retention of polysulfides in the vicinity of the cathode. Another interpretation might be that PVP could partially dissolve from the cathode and aid in the formation of a more efficient SEI layer, curtailing the redox shuttle. However, while such an effect cannot be ruled out, based on our

results and the previous work of Seh *et al* on this binder, it is more plausible that the major effect of PVP involves stabilisation of the cathode environment.

A further unusual trend in the impedance spectra which should be addressed is that R_{ct} for CMC:SBR and PEO-containing cathodes in the discharged state decreases on cycling. Such
5 behaviour is unexpected and difficult to explain since it would appear to indicate an increase in the rate of the reaction. Based on Equation 3 and 4, a relatively unchanged $c_{\infty}k_s$ product would appear to imply an increasing electrochemical surface area, which could be a result of dissolution of passivating solids (e.g., binder or Li_2S) out of the cathode over time. However, such a phenomenon is not supported by a significant stabilisation of capacity and has not, to
10 our knowledge, been reported in the literature. The origin of this trend in the impedance could be a basis for a future study.

3. Conclusion

By the use of a mixed binder composed of 4:1 PEO:PVP we have demonstrated relatively stable cycling of our Li-S test cells which retain a capacity of over 1000 mAh g⁻¹ at C/5 after 5 50 cycles and over 800 mAh g⁻¹ at 1C after 200 cycles, without the use of a sophisticated carbon host structure. Such performance is, to our knowledge, considerably improved compared to any other reported binder for this system and is competitive with the performance of any Li-S cells in the literature to date.

Based on analysis of cycling behaviour and impedance spectroscopy we conclude that this 10 binder system combines the complementary benefits of faster reactions of polysulfides and enhanced capacity due to the inclusion of PEO and an improvement in capacity retention from PVP. These observations are strong evidence that the binder should be considered as a chemically active component of the electrolyte system in a Li-S cell, and that manipulation of the functionality of such materials is a potentially significant strategy in the search for 15 improved cycle life of these cells. Differences in electrochemical kinetics may also allow for improved rate capability as we have touched upon in this work; however, the structure of the host composite is still likely to have the largest influence on capacity and rate capability, and it is not clear that the trends observed for the simplified system described here will remain when using different carbon hosts with very different properties.

20 It is also worth stressing that a considerable benefit of this binder system is that it allows for dispersion of carbon-sulfur composites in water. The addition of PVP, even in the small amounts used in this work, significantly reduces the viscosity of water-based slurries containing PEO as a binder. While PEO and PVP are just two examples of possible functional binders, both of these materials are produced on a large scale and are environmentally 25 compatible. Considering the key advantage of the low cost of sulfur and that perhaps the biggest markets for Li-S in decades to come could be in large-scale applications, it is surely

important to investigate simple and scalable strategies such as these. Such strategies are compatible with efforts made elsewhere to optimise the structure of the carbon host and further stabilize the anode, and may bring the Li-S system considerably closer to wider commercialisation.

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4. Experimental Section

Materials: Lithium bis(trifluoromethyl)sulfonimide (LiTFSI, Novolyte) and LiNO₃ (Aldrich) were dried at 120 °C overnight prior to use. 1,2-dimethoxyethane (DME, Novolyte), CMC binder (Leclanché) were used as received. 1,3-dioxolane (DOL, anhydrous), poly(ethylene oxide (PEO, M_w = 4,000,000), poly(vinyl pyrrolidone (PVP, M_w = 360,000) and lithium sulfide (Li₂S) were used as received from Aldrich. A sample of SBR binder (Targray PSBR-100) was kindly provided by Fraunhofer IWS, Dresden, Germany.

Cathode preparation: Cathode coatings were prepared by mixing of sulfur powder, Super P carbon black and binder in a 50:40:10 ratio respectively in the appropriate solvent by planetary ball-milling for two hours. The solvent used for PEO as the binder was acetonitrile, water was used for all other slurry compositions. The slurries were bar-coated onto Al foil and allowed to dry at ambient conditions. Cathodes were cut into 2 cm diameter discs with an average sulfur loading of approx. 1.5 – 2.5 mg (approx. 0.5 – 0.8 mg cm⁻²). The cathodes were transferred to an argon-filled glove box and dried under vacuum at ambient temperature overnight. Vacuum-sealed pouch cells were prepared using Li foil (125 μm, Cyprus Foote Minerals) as the counter-reference electrode separated with a 2.5 mm diameter glass-fibre filter separator soaked with 100 μL per mg of sulfur of the electrolyte. The electrolyte was composed of 1 M LiTFSI, 0.25 M LiNO₃ in 1:1 DME:DOL. The cells were cycled under galvanostatic conditions at C/5 (334 mA g⁻¹, based on a theoretical capacity of sulfur of 1,672 mAh g⁻¹) between 2.6 V and 1.8 V vs Li/Li⁺ with an Arbin battery cycler.

Polysulfide:polymer reactions: PVP was dried under vacuum at 80 °C prior to use. A saturated solution of lithium polysulfide with a nominal stoichiometry of Li_2S_6 was prepared by mixing the appropriate ratios of Li_2S and sulfur powder in DME:DOL over 24 hours.

Polymer solutions of PEO, PVP and were prepared by dissolving approximately 15 mg of polymer in 1 mL DME:DOL. The reactions of lithium polysulfide were observed by addition of 0.3 mL of the saturated polysulfide solution to each of the polymer solutions.

Impedance spectroscopy: Impedance spectroscopy combined with galvanostatic cycling was performed with a VMP2 (Princeton Applied Research – Bio-Logic Science Instruments).

Cells were cycled according to a program of 11 discharges and 10 charges within the aforementioned cycling limits at 1 C. Following the 11th discharge, the cell was allowed to relax at OCV for 1 hour. The impedance spectrum was obtained with the cell in the same two-electrode configuration at open circuit ($E_{oc} \sim 2.4$ V in the charged state, ~ 2.15 V in the discharged state) over the range 200 kHz – 10 mHz with $V_{pp} = 50$ mV. The cell was then charged to 2.6 V at C/5, allowed to relax for 1 hour and the impedance spectrum again measured. The experiment was continued in this fashion for at least 20 loops.

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References

- [1] X.L. Ji, L.F. Nazar, *J. Mater. Chem.* 20 (2010) 9821.
- [2] P.G. Bruce, S.A. Freunberger, L.J. Hardwick, J.M. Tarascon, *Nat. Mater.* 11 (2012) 19.
- [3] Y. V Mikhaylik, J.R. Akridge, *J. Electrochem. Soc.* 151 (2004) A1969.
- [4] S.S. Zhang, *J. Power Sources* 231 (2013) 153.
- [5] X. Ji, K.T. Lee, L.F. Nazar, *Nat. Mater.* 8 (2009) 500.

- [6] N. Jayaprakash, J. Shen, S.S. Moganty, A. Corona, L.A. Archer, *Angew. Chem. Int. Ed. Eng.* 50 (2011) 5904.
- [7] C. Liang, N.J. Dudney, J.Y. Howe, *Chem. Mater.* 21 (2009) 4724.
- 5 [8] S.M. Zhang, Q. Zhang, J.Q. Huang, X.F. Liu, W.C. Zhu, M.Q. Zhao, W.Z. Qian, F. Wei, *Part. Part. Syst. Charact.* 30 (2013) 158.
- [9] Y.-J. Choi, K.-W. Kim, H.-J. Ahn, J.-H. Ahn, *J. Alloy. Compd.* 449 (2008) 313.
- [10] H.L. Wang, Y. Yang, Y.Y. Liang, J.T. Robinson, Y.G. Li, A. Jackson, Y. Cui, H.J. Dai, *Nano Lett.* 11 (2011) 2644.
- [11] S. Evers, L.F. Nazar, *Chem. Commun.* 48 (2012) 1233.
- 10 [12] J. Wang, J. Yang, J. Xie, N. Xu, *Adv. Mater.* 14 (2002) 963.
- [13] Y. Zhang, Z. Bakenov, Y. Zhao, A. Konarov, T.N.L. Doan, M. Malik, T. Paron, P. Chen, *J. Power Sources* 208 (2012) 1.
- [14] X. Yu, J. Xie, J. Yang, H. Huang, K. Wang, Z. Wen, *J. Electroanal. Chem* 573 (2004) 121.
- 15 [15] Y.S. Su, A. Manthiram, *Nat. Commun.* 3 (2012) 1166.
- [16] X. Wang, Z. Wang, L. Chen, *J. Power Sources* 242 (2013) 65.
- [17] J.-Q. Huang, Q. Zhang, S.-M. Zhang, X.-F. Liu, W. Zhu, W.-Z. Qian, F. Wei, *Carbon N. Y.* (2013) 1.
- 20 [18] Y.-J. Choi, Y.-D. Chung, C.-Y. Baek, K.-W. Kim, H.-J. Ahn, J.-H. Ahn, *J. Power Sources* 184 (2008) 548.
- [19] S.S. Zhang, *Electrochem. Comm.* 31 (2013) 10.
- [20] A. Manthiram, Y. Fu, Y.-S. Su, *Acc. Chem. Res.* 46 (2013) 1125.
- [21] X.L. Li, Y.L. Cao, W. Qi, L. V Saraf, J. Xiao, Z.M. Nie, J. Mietek, J.G. Zhang, B. Schwenzer, J. Liu, *J. Mater. Chem.* 21 (2011) 16603.
- 25 [22] Y. V. Mikhaylik, I. Kovalev, R. Schock, K. Kumaresan, J. Xu, J. Affinito, in: *ECS Trans.*, The Electrochemical Society, 2010, pp. 23–34.
- [23] D. Aurbach, E. Pollak, R. Elazari, G. Salitra, C.S. Kelley, J. Affinito, *J. Electrochem. Soc.* 156 (2009) A694.
- [24] D. Bresser, S. Passerini, B. Scrosati, *Chem. Commun.* 49 (2013) 10545.
- 30 [25] Y. Jung, S. Kim, *Electrochem. Comm.* 9 (2007) 249.

- [26] Y.Q. Huang, J. Sun, W.K. Wang, Y. Wang, Z.B. Yu, H. Zhang, A.B. Wang, K.G. Yuan, *J. Electrochem. Soc.* 155 (2008) A764.
- [27] J. Sun, Y.Q. Huang, W.K. Wang, Z.B. Yu, A.B. Wang, K.G. Yuan, *Electrochim. Acta* 53 (2008) 7084.
- 5 [28] J. Sun, Y.Q. Huang, W.K. Wang, Z.B. Yu, A.B. Wang, K.G. Yuan, *Electrochem. Comm.* 10 (2008) 930.
- [29] M.J. Lacey, F. Jeschull, K. Edström, D. Brandell, *Chem. Commun.* 49 (2013) 8531.
- [30] C. Barchasz, J.-C. Leprêtre, S. Patoux, F. Alloin, *Electrochim. Acta* 89 (2013) 737.
- [31] Z.W. Seh, Q. Zhang, W. Li, G. Zheng, H. Yao, Y. Cui, *Chem. Sci.* 4 (2013) 3673.
- 10 [32] J. Song, T. Xu, M.L. Gordin, P. Zhu, D. Lv, Y.-B. Jiang, Y. Chen, Y. Duan, D. Wang, *Adv. Func. Mater.* (2013) n/a.
- [33] C.-S. Kim, A. Guerfi, P. Hovington, J. Trottier, C. Gagnon, F. Barray, A. Vijh, M. Armand, K. Zaghbi, *J. Power Sources* 241 (2013) 554.
- 15 [34] S.E. Cheon, J.H. Cho, K.S. Ko, C.W. Kwon, D.R. Chang, H.T. Kim, S.W. Kim, *J. Electrochem. Soc.* 149 (2002) A1437.
- [35] N.-I. Kim, C.-B. Lee, J.-M. Seo, W.-J. Lee, Y.-B. Roh, *J. Power Sources* 132 (2004) 209.
- [36] C. Barchasz, J.-C. Leprêtre, S. Patoux, F. Alloin, *J. Electrochem. Soc.* 160 (2013) A430.
- 20 [37] S.S. Zhang, *Electrochim. Acta* 97 (2013) 226.
- [38] S. Urbonaite, P. Novák, *J. Power Sources* 249 (2014) 497.
- [39] S.S. Zhang, *Electrochim. Acta* 70 (2012) 344.
- [40] S. Wenzel, H. Metelmann, C. Reiß, A.K. Dürr, J. Janek, P. Adelhelm, *J. Power Sources* 243 (2013) 758.
- 25 [41] W.-R. Liu, M.-H. Yang, H.-C. Wu, S.M. Chiao, N.-L. Wu, *Electrochem. Solid-State Lett.* 8 (2005) A100.
- [42] F. Haaf, A. Sanner, F. Straub, *Polym. J.* 17 (1985) 143.
- [43] S. Ghosh, J. Rasmusson, O. Inganäs, *Adv. Mater.* 10 (1998) 1097.
- [44] I. Iliopoulos, R. Audebert, *Macromolecules* 24 (1991) 2566.