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

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HIGHLIGHTS

- Simple cells of moderate sulfur loading exhibit capacities of over 1000 mAh g^{-1} with a PEO:PVP binder mixture.
- These capacities are over 200 mAh g^{-1} higher compared to our reference CMC:SBR system.
- High capacities of 800 mAh g^{-1} were retained at 1C.
- The increase is attributed to complementary functions of the binder with respect to their interactions with intermediates.
- Manipulation of binder functionality may be a promising strategy for improving capacity and stability in this system.

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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 1000 mAh g^{-1} at C/5 after 50 cycles and 800 mAh g^{-1} at 1C 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 2600 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].

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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 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; 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, 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 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 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].

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 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 Fig. 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 Fig. 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 h. Addition of the same polysulfide solution to an equivalent solution of PEO causes some precipitation