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ARTICLE TYPE

Why PEO as a binder or polymer coating increases capacity in the Li-S system

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PEO, used either as a binder or a polymer coating, and PEGDME, used as an electrolyte additive, are shown to increase the reversible capacity of Li-S cells. The effect, in all three cases, is the same: an improved solvent system for the electrochemistry of sulfur species and suppression of cathode passivation on discharge. This constitutes a novel interpretation of the mechanistic behaviour of polyethers in the Li-S system, and sheds new light upon several previous studies.

The lithium-sulfur system has been the subject of renewed interest in recent years by virtue of its high theoretical energy density and low cost¹⁻³. However, many challenges remain, particularly with regards to extending cycle life beyond 100-200 cycles⁴. Many different strategies are being explored in the pursuit of long-term stability of this system, with the most effective approaches for performance improvement, for example concerning cathode design⁵⁻¹⁰ or electrolyte chemistry¹¹⁻¹⁴, still a matter of considerable debate.

In the last few years, poly(ethylene oxide) (PEO) and related materials such as derivatives of poly(ethylene glycol) (PEG) have been increasingly reported in the literature as materials for lithium-sulfur batteries; as a possible binder^{15,16}, as a coating for the cathode^{5,17-19} and, in the case of polyethers of shorter chain length, an electrolyte solvent. In each case, the polyether has been shown to improve the specific capacity of the cathode.

The second case, where PEG/PEO is employed as a polymer coating, is particularly interesting. The most prominent example of this strategy was reported by Nazar's group⁵, where the electrode capacity was significantly improved by covalently anchoring a short PEG chain to the surface of a carbon/sulfur composite. This behaviour was primarily ascribed to the hydrophilicity of the polymer, creating a preferential solubility for lithium polysulfide relative to the electrolyte. In this sense, the polymer coating acts as a barrier to polysulfide diffusion from the cathode into the bulk electrolyte. Restriction of active mass loss from – or confinement within – the cathode has been suggested as a possible approach to improving capacity retention in this system^{20,21}.

Similar strategies have been reported elsewhere, for example by direct deposition of PEG or PEO directly onto the surface of the cathode¹⁷⁻¹⁹. Although the specific capacity was also similarly improved by this approach, it must be noted that lower molecular weight polymers such as PEG-20000 are soluble and PEO ($M_w \leq 4,000,000$) at least readily swells in the common electrolytes. Especially in the former case, based on this observation, it seems unlikely that such a polymer coating could act as a barrier to polysulfide diffusion; yet, a similar effect resulted from these strategies.

Considering the effect of higher order polyether solvents such as poly(ethylene glycol) dimethyl ether (PEGDME) as electrolyte solvents leads us to an alternative interpretation. Barchasz *et al*²² demonstrated that increasing chain length in glyme solvents, from dimethoxyethane to PEGDME, leads to an associated increase in the discharge capacity. This improvement was attributed to a higher solubility for lower order polysulfides in the higher order glyme solvents, extending the lower discharge voltage plateau and delaying passivation of the cathode at end-of-discharge. Additionally, despite the higher polysulfide solubility, the SEI formed on the anode in these solvents suppresses the polysulfide redox shuttle. While solvents such as tetraglyme and PEGDME have high viscosities, the properties of the electrolytes derived from these can be optimised by mixing with appropriate co-solvents, such as 1,3-dioxolane²³⁻²⁶.

It is this same phenomenon which we hypothesise as the origin of the improved performance when higher molecular weight polymers are used as polymer coatings or as a binder: that the polymer in contact with the cathode surface dissolves or swells in the liquid electrolyte, modifying the solvent system at the interface. The improved solubility for polysulfide near the cathode surface delays precipitation of the insoluble discharge products, and in turn passivation of the cathode, thus affording an improvement in specific capacity.

We also believe that some evidence for this hypothesis is already present in the literature. In the aforementioned Nazar group article on PEG-functionalised carbon-sulfur composites, the authors propose that the effect of the PEG-functionalisation is as a “trap” for polysulfide and that this aids in curtailing the redox shuttle reaction of polysulfide at unprotected anode surfaces.

However, the authors also demonstrate both that cathode passivation is the practical major limit to discharge capacity and that the PEG-functionalisation “strongly inhibits” the deposition of insoluble discharge products on the cathode surface – without connecting these two observations. In addition, the capacity retention after 20 cycles – that is, the percentage difference between the capacity at the 20th cycle relative to the initial capacity – is minor. This is interesting to note since one might expect that if the major effect is to prevent mass loss into the bulk electrolyte, then the capacity retention, and not just the specific capacity, should be significantly improved. While we do not doubt the ability of such barrier layers to trap polysulfide, we suggest that this is not the primary origin of the improved specific capacity.

In our attempts to unify these observations from the literature, we studied the effect of PEO and PEG in three different environments: as a binder, as a coating, and as an electrolyte additive. The aim was to demonstrate a common performance-enhancing effect for all three approaches relative to a simple reference cathode of ball-milled sulfur and carbon black with CMC/SBR used as the binder.

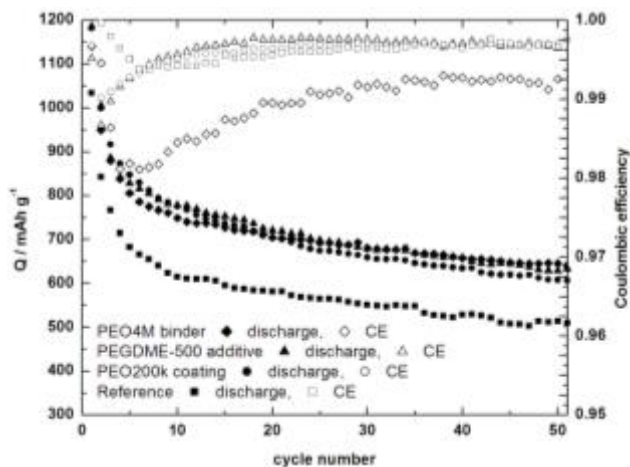


Figure 1: discharge capacity (solid) and coulombic efficiency (hollow) for the reference and PEG/PEO-modified cells at C/5.

Fig. 1 shows us that the specific capacity is improved to more or less the same extent by the effect of PEG/PEO in these three different approaches. The capacity is improved in all cases by approximately 150 mAh g⁻¹ over the first fifty cycles relative to the reference cathode. Similar sustained increases in capacity were reported for PEG-coated cathodes in the literature. However, the same sustained increase in capacity is seen where PEGDME-500 is used to partially dilute the electrolyte, in a 1:9 ratio of PEGDME:reference electrolyte. From this observation alone we contend that the mechanism of the improvement in capacity in the PEO binder and coated cathode cases is unlikely to be due to a barrier or polysulfide trapping effect.

Inspection of the voltage profiles of the cells, as shown in Fig. 2, clarifies the effect further. In all PEG/PEO-modified cells, the voltage profile of the first cycle reveals a reduced hysteresis for both of the charge/discharge plateaux with respect to the reference cathode, in spite of the expected increase in viscosity of

the electrolyte. This reduced hysteresis is therefore strongly indicative of improved electron transfer kinetics for the sulfur

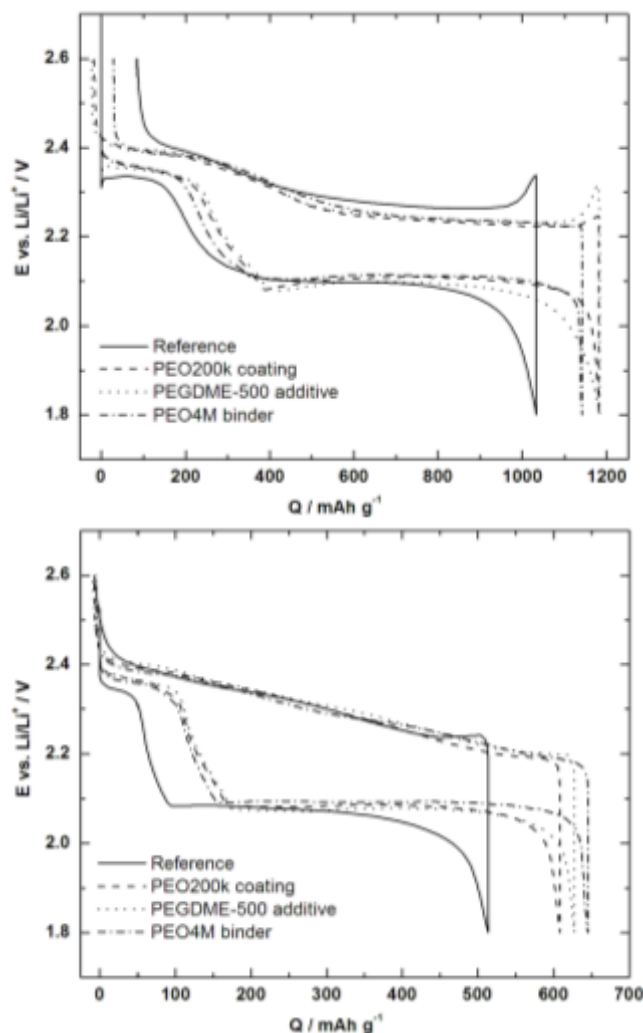


Figure 2: voltage profiles for the reference and PEG/PEO-modified cells at C/5 for the top) 1st cycle and bottom) 50th cycle.

species. Also on the first cycle, the reference cathode shows a significant voltage peak at the beginning of the charge cycle. This has previously been attributed to polarisation as a result of the deposition of insoluble products on the cathode. This peak is reduced with the addition of PEGDME to the electrolyte, suppressed further with the PEG200k coating and is eliminated entirely with the use of the PEO binder. After 50 cycles the lower discharge plateau for each of the PEG/PEO-modified cells remains flatter for longer discharge times with a sharper endpoint at the end of discharge. The upper discharge plateau is also significantly better retained due to the effect of the polyether with respect to the reference cathode, a further observation which agrees with the behaviour of the PEG-coated cathodes reported by Nazar’s group. In both the polyether-modified cases and the reference cathode, the 50th charge cycle shows largely the same sloping voltage profile.

The best performance, with the largest reduction in polarisation

and the highest retention of capacity after 50 cycles, is seen for the cell with the PEO binder. The PEO200k cathode coating also showed low polarisation but with slightly poorer capacity retention. In this case, the PEO200k loading was approximately 5% of the weight of the cathode. It is thought that during the coating process at least some of the PEO can penetrate to the cathode surface where it can effect the performance improvement. By comparison, we expect that PEO used as a binder will coat the cathode to a greater extent than a cathode coating and that this is a likely reason for the improved performance of the PEO binder relative to the cathode coating.

To summarise these observations, the electrochemistry of all PEG/PEO-modified cells can be interpreted as a common improvement in the electrochemical reversibility of the sulfur species and a suppression of passivation of the cathode at the end-of-discharge as a result of the presence of PEG/PEO. These observations strongly support our hypothesis that PEO binders or cathode coatings dissolve or swell in the liquid electrolyte, modifying the electrolyte system in a similar fashion to using shorter chain PEGDME as an electrolyte co-solvent. We furthermore argue that such a capacity improvement mechanism agrees with all observations made in the literature so far on the benefit of PEG/PEO in all the approaches discussed in this work.

These results demonstrate the considerable benefit of PEO and PEG derivatives – and in relatively small proportions – to the lithium-sulfur system, and that the proposed effect can be accessed by several different strategies, including those demonstrated in this work.

Notes and references

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[‡] Experimental information: Lithium bis(trifluoromethyl)sulfonimide (LiTFSI, Novolyte) and LiNO₃ (Aldrich) were dried at 120 °C overnight prior to use. All other chemicals were used as received. The ‘reference’ cathode coatings were prepared by mixing of sulfur powder with Super P carbon black, Targray PSBR-100 and carboxymethylcellulose sodium salt (CMC, Leclanché) in a 50:40:6:4 ratio respectively in deionised water by planetary ball-milling for 2 hours. The slurry was 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 – 2 mg (approx. 0.3 – 0.6 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 3x3 cm glass-fibre filter separator soaked with 100 μL per mg of sulfur of the electrolyte. The reference electrolyte was composed of 1 M LiTFSI, 0.25 M LiNO₃ in 1:1 1,2-dimethoxyethane/1,3-dioxolane (DME/DOL). The cells were galvanostatically cycled at C/5 (based on a theoretical capacity of sulfur of 1,672 mAh g⁻¹) between 2.6 and 1.8 V vs Li/Li⁺ with an Arbin battery cyclers.

The effect of PEO/PEG derivatives was investigated by modifying the reference system with PEO/PEG in different forms:

- a) Cathodes with poly(ethylene oxide) (PEO4M, M_w = 4,000,000, Aldrich) as a binder were prepared according to the

same procedure as the reference cathode with a composition of 50:40:10 S:C:PEO in acetonitrile.

- b) Poly(ethylene oxide) (PEO200k, M_w = 200,000, Aldrich) was deposited onto the reference cathodes from a 1 wt% solution of PEO200k in 3:1:1 EtOH:H₂O:BuOAc by spin-coating at 1000 rpm for 30 seconds. The PEO loading was 0.12 mg (ca. 0.04 mg cm⁻²).
- c) The reference electrolyte was directly diluted with poly(ethylene glycol) dimethyl ether (PEGDME, M_w = 500, Aldrich) in a 9:1 electrolyte:PEGDME ratio, i.e., 10 mg PEGDME per mg sulfur.

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