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Linear and Crosslinked Ionic Liquid Polymers as Binders in Lithium-Sulfur Battery

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Abstract

A collection of different polymeric ionic liquids (PILs) were explored as cathode binders in lithium-sulfur batteries. The PIL molecular structure, polymer backbone, and polymer architecture were found to influence cell capacity, cyclability, and the morphology of the cathode itself. PILs with styrene backbones performed better than vinyl-based polymer, while crosslinked PILs imparted further improved capacities, cyclability, and reduced over-potentials. Unlike PVdF, PIL binders mixed with the sulfide species, resulting in more uniformly distributed sulfides in the cathode and better sulfide transport. These features helped to mitigate volume change-induced degradation that typically plagues Li-S batteries. The uptake of polysulfides by PILs also constrains the polysulfide shuttle during battery cycling, leading to better cycling stability. While traditionally binders are viewed only as a "glue" to hold active material together, PIL binders have additional functions and play an active role during Li-S working operation.

Introduction

High performance lithium-sulfur (Li-S) batteries that are lightweight and energy dense are contenders to replace current Li-ion technology.[1] While the potential energy storage of Li-S batteries is quite high, low cyclability arising from polysulfide migration to the anode, and/or volume changes at the cathode, significantly reduces the lifetime of such devices. For these reasons, researchers have sought to develop new electrolytes,[2–4] membranes,[5,6] cathodes,[7,8] and sulfur impregnation techniques[8] to overcome these persistent issues. In general, the role of binders in the operation of the battery has garnered less attention, despite comprising a significant portion of the total weight of the cell (5-10 wt%).[9–12] This is in light of the fact that the binder is responsible for "gluing" the components during large volume changes. Even small improvements to the overall performance of the battery can, on an industrial scale, lead to large energy savings. Polyvinylidene fluoride (PVdF) is currently the standard for lithium battery technology and is routinely used in lithium-ion and lithium-sulfur batteries for its chemical inertness and availability. Despite a number of its clear issues, such as delamination from the active components, it has thus far been sufficient for the development of new battery systems. One issue that PVdF does not address is the 80% volume expansion that occurs upon formation of Li_2S. This volume change disrupts electrical contacts within the cathode which in turn reduces cyclability.[13] An improved binder that can mitigate these issues could help to accelerate the development of Li-S batteries as a practical alternative to current technologies. One class of polymers that have recently garnered attention are polymeric ionic liquids (PILs), whose high electrochemical stability, conductivity, and good processability is well suited for electrochemical applications.[14] They have been incorporated in supercapacitors,[15] electrochemical sensors,[16,17] and a variety of energy devices[18,19] with good success. Recently it was found that their high stability was advantageous for use as a binder in lithium-ion batteries.[20,21] Linear PILs were capable of wrapping the powder components while still allowing for Li^+ to flow, thus improving cyclability.[20] Nanoparticle PILs were found to operate according to a different mechanism by allowing electrolyte to permeate between the free spaces.[21] During cycling, these nanoparticles would maintain contacts between the conductive components while permitting the flow of electrolyte. In comparison, only a few studies have been conducted for the use of PILs in lithium-sulfur batteries.[22–24] While molecular interactions between ionic-liquids and polysulfide species have been examined in great detail,[25–27] the role of a cationic polymer binder in similar environments is not well understood. There is strong evidence by Helms *et al.* for such polymers to facilitate lithium-ion transport and restrict sulfide diffusion simultaneously, which in turn leads to improved cyclability.[24] However, no study has been conducted to compare the effect of different cationic polymers or PILs. In this context, we examined five PIL binders, either as linear or crosslinked nanoparticles for their use in lithium-sulfur batteries. We found that in all cases, the PILs were generally better than PVdF with respect to cyclability, with some PILs displaying higher discharge capacities in extended cycling experiments. We found that this improvement is due to the compatibility between the PIL and the produced sulfides, which inhibits swelling-induced degradation and retention of the sulfides within the cathode. We postulate on the nature of the PIL in these batteries and demonstrate a potential route for further PIL binder exploration.

Experimental

Materials

Azobisisobutyronitrile (AIBN) was purchased from Wake Chemicals and used as received. Polyvinylidene fluoride (PVdF, average M_w 534000, CAS 24937-79-9, Sigma-Aldrich) and Printex XE2 (Degussa) were used for the electrode preparation. 1 M LiTFSI in TEGME:DOL (purity 99.9%, E057, Solvionic) was used as electrolyte. Lithium foil (FMC, 500 µm) was used as anode.

Synthesis

Linear binders **PIL1**-**3** and crosslinked nanoparticle binder **PIL5** were synthesized according to literature procedures.[20,21] Crosslinked nanoparticle **PIL4** was synthesized from the TFSI based monomer[28] in methanol by precipitation polymerization. Briefly, monomer (7.32 g, 14.90 mmol) was dissolved in methanol (50 mL) containing 1.5 wt% AIBN (0.108 g, 0.657 mmol) and stirred for 18 h at 60 °C. The precipitate was then rinsed with methanol (4 x 100 mL) to remove excess monomer and dried *in-vacuo* (**Scheme S1**).

Electrochemistry

Carbon (Ensaco 350G, Imerys) was ball milled for 30 min at 300 rpm with sulfur in a mass ratio of 1:2. The mixture was heated to 155 °C with a heating ramp of 0.2 C min^{-1}, where it was kept for 5 h. The cooling down period to room temperature was performed at a rate of

0.5 C min^{-1}. The electrodes were prepared by mixing the sulfur/carbon composite (66 wt.% of sulfur), the binder (PVdF or **PIL1**-**5**), and conductive carbon black additive (Printex XE2, Degussa) in a mass ratio of 80:10:10. The slurry was prepared in N-methyl-2-pyrrolidine (NMP) and casted on a carbon coated aluminum foil. The typical sulfur loading on carbon coated aluminium foil was approximately 1.5 mgS cm^{-2}. A pouch type two electrode cell was prepared inside an argon filled glovebox. The sulfur cathode (2 cm^2 electrode) was separated from the metallic lithium anode with Celgard 2400 separator. The electrolyte 1 M LiTFSI in TEGDME:DOL (vol. 1:1) quantity was normalized to 15 µL mg^{-1} of sulfur. The batteries were cycled in the potential range between 1.5 V to 3.0 V by using Bio-logic VMP3 galvanostat/potentiostat at a current density of C/5 (334.4 mA g^{-1}).

X-ray photoelectron spectroscopy (XPS)

XPS measurements were performed using a Thermo Scientific K-Alpha+ X-ray Photoelectron Spectrometer. All samples were analyzed using a microfocused, monochromated Al Kα X-ray source (1486.68 eV; 400 µm spot size). The K-Alpha+ charge compensation system was employed during analysis to prevent any localized charge buildup. The samples were mounted on conductive carbon tape the resulting spectra analyzed using the Avantage software from Thermo Scientific.

Polysulfide uptake

Inside an argon filled glove box, 100 mg of each binder (PVdF and **PIL4**) were weight into two separate vial flask. 500 µL of 0.05 M Li_2S_2 in 1 M LiTFSI in TEGDME:DOL solution was added to each binder containing vial flask. The solution was left inside the glove box for 24 h.

Results and discussion

In order to determine the effect of different PIL binders on the performance of Li-S batteries, three different linear polymers (**PIL1**-**PIL3**) and two crosslinked polymers (**PIL4** and **PIL5**) were prepared (**Figure 1**). **PIL1** and **PIL2** possess a vinyl or styrenic backbone respectively, while **PIL3** is a styrenic PIL with a methyl protected substituent at its C2 position. We also examined two crosslinked nanoparticle systems, **PIL4** and **PIL5**, which possess both different molecular structures and a different number of polymerizable groups. These differences manifest in their size and morphology upon dispersion polymerization, with **PIL5** having an average diameter of 10-30 nm,[21] and **PIL4** a diameter of ~20 nm and comprised of smaller particles (~5 nm in diameter) (**Figure S1**).

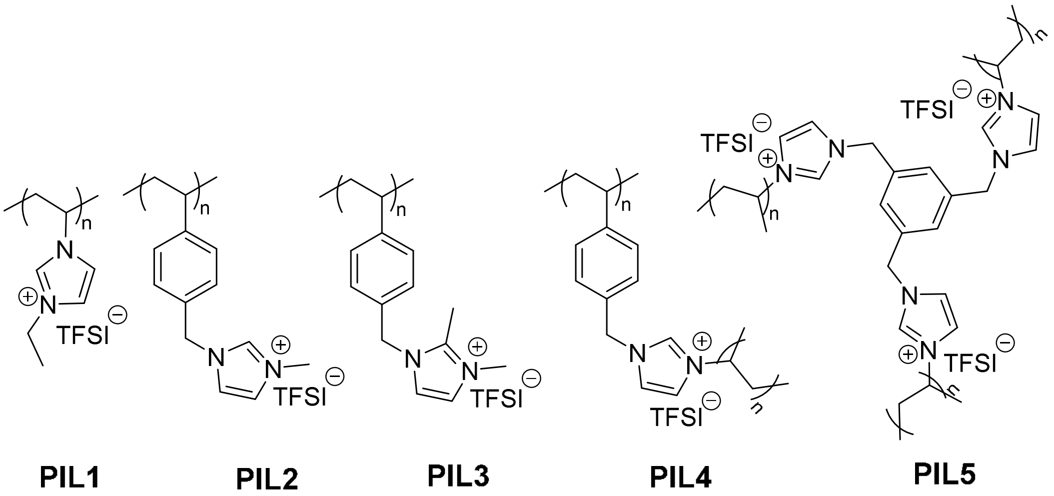

Figure 1: PIL binders examined for use in Li-S systems.

The electrochemical performance of the **PIL1**-**5** and PVdF as binders was tested in a Li-S battery at C/5 (334.4 mA g^{-1}) current density (**Figure 2**). PVdF is a well-known inert binder and possesses no electronic or ionic conductivity.[29] The cell with PVdF achieved an initial discharge of 847 mAh g^{-1}, which faded to 521 mAh g^{-1} and to 355 mAh g^{-1} after 200 and 500 cycles respectively, with a Coulombic efficiency of approximately 83%. **Figure 2** shows that PIL binders influence discharge capacities and the rate of capacity fading of the cell. **PIL1** exhibits a lower discharge capacity in comparison to PVdF, however after prolonged discharge-charge cycling, severe capacity degradation was observed. This is not surprising as similar instabilities for **PIL1** was observed in Li-ion battery[20] and is a result of side reactions on the ethyl substituent. Cells with **PIL2** had a lower initial capacity of 482 mAh g^{-1} and 494 mAh g^{-1} in the 1st and 50th cycle, respectively. However after 200 cycles, an increase of 16% of the initial capacity was observed (574 mAh g^{-1}), while after 500 cycles, a discharge capacity of 473 mAh g^{-1} was observed. The cells with binders **PIL3**-**5** showed an increase in capacities in the initial cycles, with cells containing binder **PIL3** reaching the highest discharge capacity after 11 cycles followed by cycling behaviour similar to PVdF. The similar performances of **PIL2** and **PIL3** indicates that methyl protection at the C2 position is not particularly important, unlike in Li-ion batteries which benefits from C2 protection.[20] This is likely due to the lower operating voltages in Li-S vs. Li-ion batteries and indicates that greater tolerances for PIL structures is possible, allowing for a greater number of PILs to be examined for these applications. The Li-S cell with **PIL4** attained the highest discharge capacity of 1015 mAh g^{-1} after 3 cycles and was the highest among the binders tested. The discharge capacity of the cell with **PIL4** slowly faded to 657 mAh g^{-1} and to 446 mAh g^{-1} after 200 and 500 cycles, respectively. The cell with **PIL5** had the lowest initial discharge capacity, however an increase of 10% was observed after 200 cycles with stable cycling.

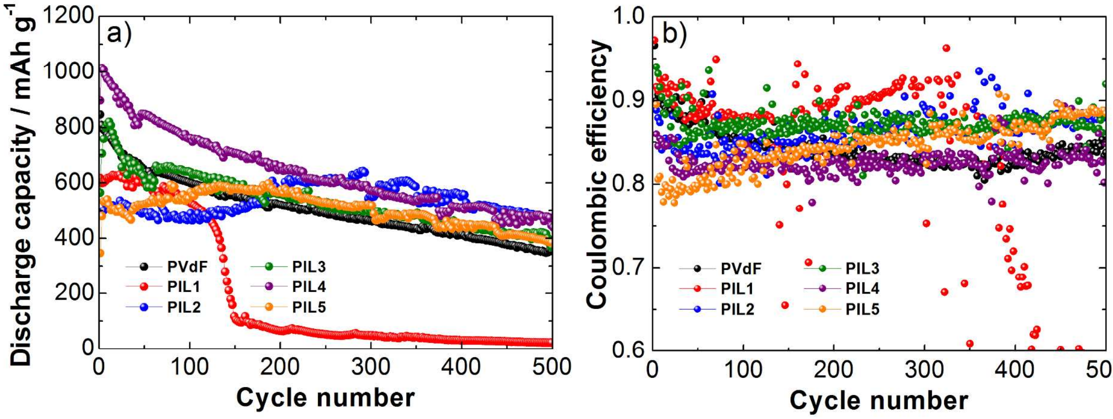

Figure 2: a) Discharge capacity and b) coulombic efficiency for PVdF and **PIL1-5** in Li-S battery at C/5 current density.

Figure 3 represents the discharge and charge voltage profiles of the Li-S batteries with PVdF and **PIL1**-**5**. In all tested samples, two Li-S characteristic plateaus were observed; the high and the low-voltage plateau.

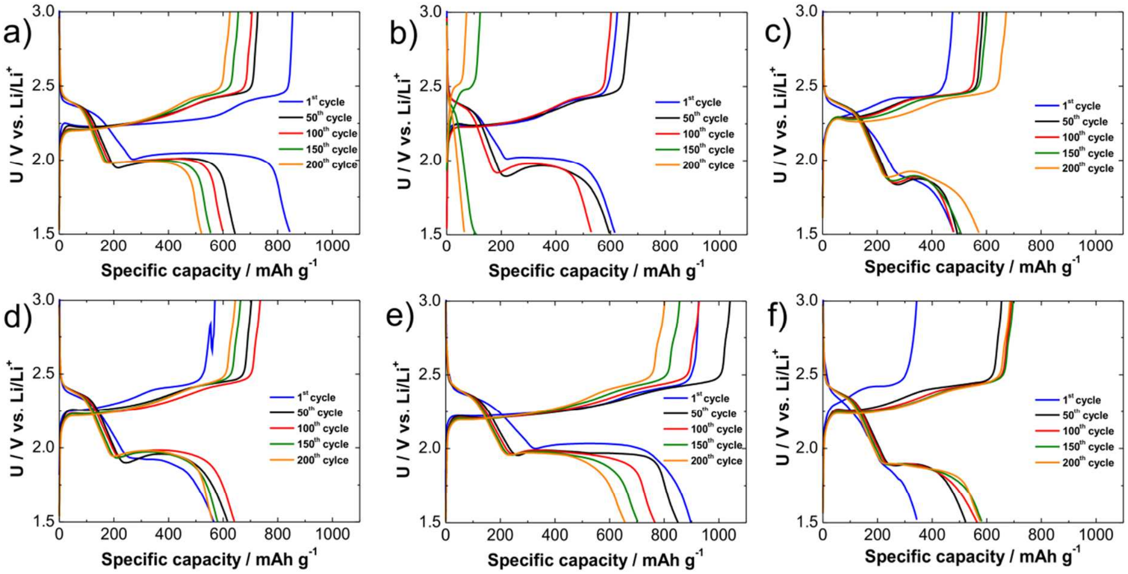

Figure 3. Galvanostatic discharge/charge voltage profiles for the Li-S cells with a) PVdF binder, b) **PIL1** binder, c) **PIL2** binder, d) **PIL3** binder, e) **PIL4** binder and f) **PIL5** binder at C/5 (334.4 mA g^{-1}) current density.

To facilitate the interpretation of the involved complex reactions, the voltage profile was divided into three sections, full discharge (denoted as Q_{disch}), high-voltage (Q_{high}) and low-voltage (Q_{low}) plateau. The high-voltage plateau (denoted as Q_{high}), from 2.5 V to 1.9 V correlates to a sulfur reduction into long- and mid-chain polysulfides. The low-voltage plateau (denoted as Q_{low}), from 1.9 V to 1.5 V correlates to the equilibrium between polysulfides and precipitated Li_2S.[29–31] Similar to what Peled et. al. have reported,[29] the binder influences both Q_{high}, Q_{low}, and the cell over-potential (**Table 1**). In the case of PVdF the Q_{high}/Q_{disch} ratio is approximately 30% and does not change from the 50th to the 200th cycle. The constant Q_{high}/Q_{disch} ratio shows that the capacity degradation is the same for the high-voltage and low-voltage plateau, which correlates with loss of sulfur. For **PIL4** the Q_{high}/Q_{disch} ratio increases from the 50th to 200th cycle. This may indicate that sulfur reduction to Li_2S_4 is more efficient with prolonged discharge-charge cycling. Interestingly, with **PIL2** and **PIL5**, the Q_{high}/Q_{disch} ratio is higher in comparison to the other binders, and is around half of Q_{disch}. However, from the 50th to the 200th cycle the Q_{high}/Q_{disch} ratio decreases to 40%. Similar behavior is observed in the obtained discharge capacities for **PIL2** and **PIL5** (**Figure 2**), where the capacity increases during prolonged cycling. The small initial Q_{low}/Q_{disch} ratio and its gradual increase with cycling is due to the less effective initial reduction from Li_2S_4 to Li_2S, which is an indication of an initial kinetics limitation. Furthermore, **PIL2** and **PIL5** have the highest over-potential. The similar capacity fading after 200 cycles between the PVdF and PILs binders indicates that similar degradation mechanisms occur. However, the fading with PILs is slower due to its favourable interaction with the polysulfide species.

Table 1. Effect of the cycling and binders on Q_{disch}, Q_{high}/Q_{disch}, Q_{low}/Q_{disch} ratio and cell over-potential.

	Cycle 50				**Cycle 200**			
Binder	**Q_{disch} [mAhg^{-1}]**	**Q_{high}/Q_{disch} [%]**	**Q_{low}/Q_{disch} [%]**	**Pol. [mV]**	**Q_{disch} [mAhg^{-1}]**	**Q_{high}/Q_{disch} [%]**	**Q_{low}/Q_{disch} [%]**	**η_{tot} [mV]**
PVdF	644	34	66	146	521	35	65	152

PIL1	597	37	63	171	64	100	/	/
PIL2	494	55	45	274	574	42	58	212
PIL3	616	40	60	184	562	36	64	163
PIL4	851	31	69	122	657	38	64	140
PIL5	523	47	53	242	578	39	61	219

To study the effect of the binders on the cathode morphology, *post mortem* SEM analysis was performed on disassembled cathodes (**Figure S2**). SEM images of freshly discharged (1.5 V) and charged (3 V) cathodes containing PVdF, **PIL2,** and **PIL4** are shown in **Figure 4**. In the case of the fresh cathode with PVdF binder, a porous cathode structure was observed with interconnected sulfur-impregnated carbon particles. The discharged cathode with PVdF shows that the pores are blocked due to the crystallization of Li_2S on the cathode surface. When charged, the open porosity is re-established due to Li_2S consumption and the reformation of sulfur. The fresh electrode with binder **PIL2** is similar to the cathode with PVdF binder, while the fresh cathode containing binder **PIL4** possessed a polymeric film of interconnected sulfur-impregnated carbon particles on the surface. SEM images of the discharged cathodes with **PIL2** and **PIL4** were similar to each other with a “swelled particle” structure containing open pores. This is in stark contrast to the discharged cathode containing PVdF binder, which appears to have filled pores and no “swelling”. This indicates that the growth of Li_2S is likely different in the presence of PIL vs PVdF and that the improved cycling is derived from this interaction. According to Welton *et al.*,[32] dissolution of ionic solutes in ILs takes place *via* metathesis reactions, thus resulting in an intimate mixing of the two ionic components. The observed differences in the SEM between the discharged PVdF and PIL samples can be explained by the uniform mixing and retention of sulfide species with PIL binder (in the form of ion-exchange reactions), which then influences Li_2S growth and battery cycling. The fluorophilic character of PVdF does not allow any of these processes to occur and thus leads to poorer cycling stability.

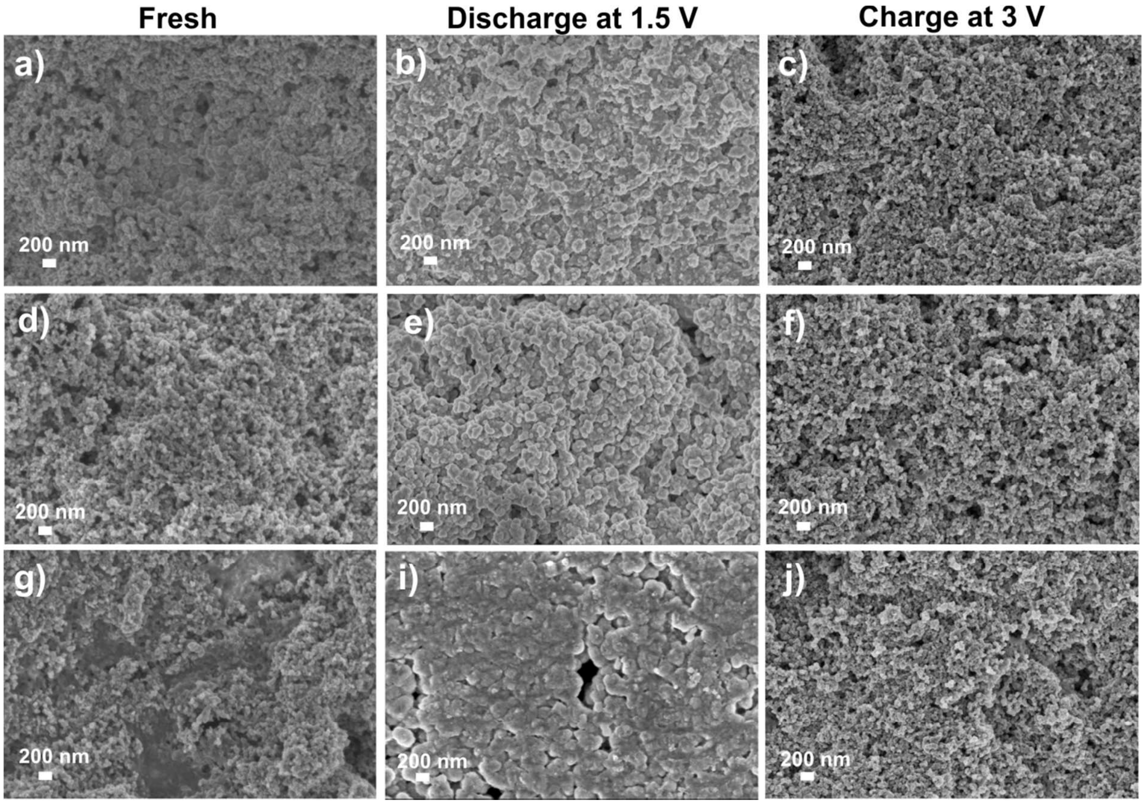

Figure 4: SEM micrographs higher magnification top-view for fresh, discharged at 1.5 V and charged at 3.0 V sulfur cathodes with a) to c) PVdF binder, d) to f) **PIL2** and g) to j) **PIL4**.

Analysis of the cathodes by X-ray photoelectron spectroscopy (XPS) S 2*p* spectra (**Figure 5**) revealed that the morphology differences observed in the SEM are not met by differences in their surface chemical composition.

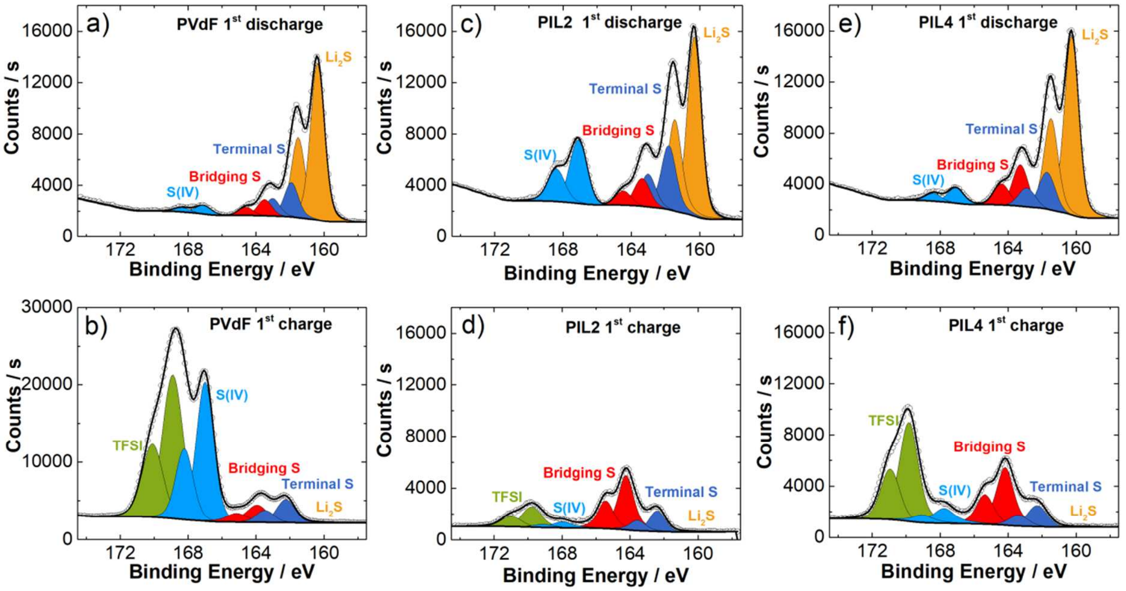

Figure 5: XPS S 2*p* spectra of the composite cathode with a) PVdF in the 1st discharge, b) PVdF in the 1st charge, c) PIL2 in the 1st discharge, d) PIL2 in the 1st charge, e) PIL4 in the 1st discharge and f) PIL4 in the 1st charge.

In all cases, four different components were observed in the discharged samples. They include Li_2S (around 160.5 eV), terminal (around 162 eV) and bridging (around 163.6 eV) sulfur, and the decomposition products S(IV) from TFSI salts.[6] As well, the TFSI anion was only observed in the charged cathodes. Thus, the stark differences between PVdF vs PIL in the charged cathodes is a result of how the respective binders affect the growth of the produced sulfides. The perfluorinated structure of PVdF prefers not to mix with the sulfide salts, resulting in sulfide precipitation on top and in between the binder/carbon interstitial spaces (**Figure 6**). This is supported by the dramatically low solubility of lithium sulfides in fluorinated solvents, which applies to the interaction between PVdF and the lithium sulfides.[24,33,34] PILs however have shown the ability to uptake a variety of anions, direct the growth of crystalline compounds like bismuth sulfide, and generally promote the stabilization of interfaces for nanoparticle dispersions.[35–38] The more favourable interactions between the produced lithium sulfides and PIL results in a mixing of these two components, a more even distribution and volume expansion within the cathode, and thus more stable cyclability (**Figure 6**, bottom right). This is supported by the XPS S2*p* spectra (**Figure 5**) of the cathodes in charge state. On the surface of the cathode with PVdF binder, mostly LiTFSI salts and a mixture of short- and mid-chain polysulfides are present, due to dissolution and shuttling of long-chain polysulfides. On the surface of the cathode with PILs binders, mostly long-chain polysulfides are found. These results support the interaction and uptake of polysulfides by PILs. Furthermore, we assume it is for this reason that the carbon particles appear more swelled in the SEM images for **PIL2** and **PIL4** in comparison to PVdF. It was also noticed that lithium sulfide sublimation occurred in the SEM vacuum chamber for the discharged cathode containing PVdF and not for PIL, indicating that the lithium sulfides are strongly bound within/around the PIL[24]. This effect does not appear to be different for **PIL2** and **PIL4** despite the former being a soluble homopolymer and the latter a nanoparticle binder. In contrast to this, high over-potentials were observed for **PIL2** and **PIL5** and not for **PIL4**. In the case for **PIL2**, easier transport of electrolyte between the interstitial spaces for the particle system which is not possible for the linear homopolymers (**Figure 6**, left).[21] For **PIL5** the kinetics of Li_2S growth was hampered (**Figure 3**) and may stem from the more crosslinked and unswellable structure, preventing mixing with produced sulfides.

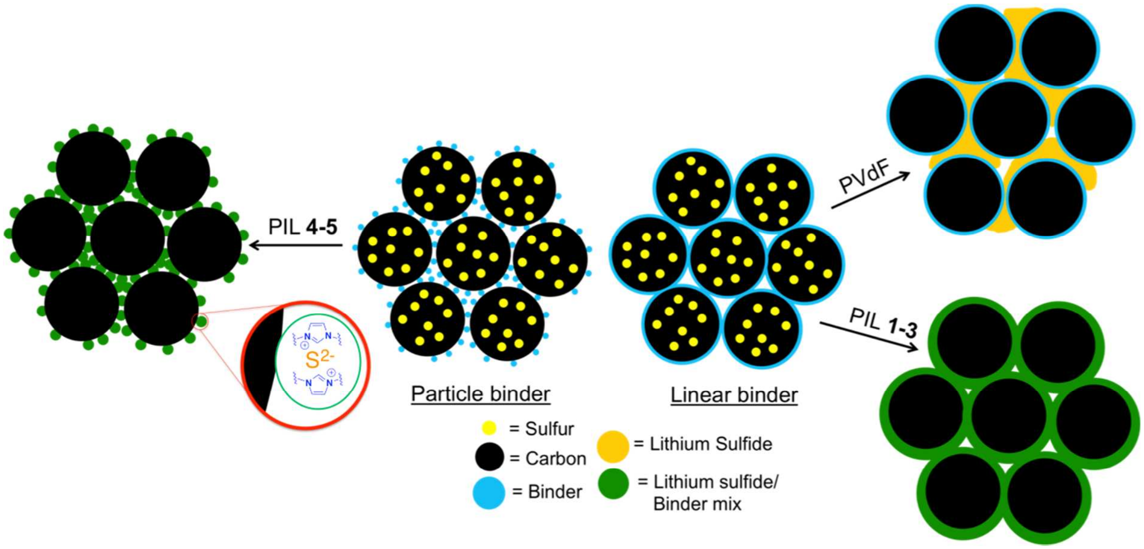

Figure 6: Schematic representation of the sulfide precipitation around and in between the binder/carbon for PVdF and PIL binders.

To test the swelling and the polysulfide uptake of the polymers, TEGDME:DOL solutions containing 0.05 M Li_2S_2 and 1 M LiTFSI TEGDME:DOL were mixed with PVdF and **PIL4** (**Figure S3**).[39] When the green solution was mixed with the PVdF dispersion, the colour of the solution remained unchanged after 24 hr (**Figure S3a**). When the polysulfide solution was mixed with a dispersion of **PIL4**, the PIL noticeably swelled and the colour of the solution changed from green to orange (**Figure S3b**). The change of colour from green to orange suggests a chemical reaction between the **PIL4** and the Li_2S_2, meaning **PIL4** acts as a catalyst for the disproportionation reaction of Li_2S_2[40,41] as presented on the followed reaction:

$$3S_2^{2-} \leftrightarrow S_4^{2-} + 2S^{2-}$$

After 24 hr **PIL4** was swelled and absorbed the polysulfide solution, forming a white gel. The ability for the particles to reversibly swell and deswell allows for their use as “sulfide reservoirs” during cycling. This feature combined with their effective electrolyte transport demonstrates an improved approach for PIL utilization in lithium-sulfur battery systems.

In Li-S batteries, the role of the PIL binder is not only to “glue” the active material together, but to also play an active role during the cycling. They efficiently improve the reduction of sulfur into lithium polysulfides and improve the Li_2S redistribution over the carbon surface. Furthermore, PIL-based binders can reduce volume change-induced stress by uptaking/releasing lithium polysulfides during swelling and deswelling cycles.

Conclusions

In conclusion, five different PILs were used as binders in lithium-sulfur batteries and compared to conventional PVdF. The PIL binders possessed different chemical structures, polymer backbones, and different polymeric architectures, including linear homopolymers and nanoparticles. We found that in all cases, PILs were equal to or superior than PVdF with respect to cyclability, with some PILs displaying higher discharge capacities across the tested lifetime. The PIL binders improved the reduction of sulfur into Li_2S_4 more efficiently while simultaneously improved Li_2S redistribution in the cathode, which boosted battery cyclability. We can conclude that the key to this increased performance is a result of the favourable interactions between the PIL and the produced lithium sulfide species, resulting in mixing of the two and a more even volume expansion during discharge. This is in contrast to PVdF, which does not mix with the lithium sulfide species, resulting in uneven volume expansion between the carbon particles. Such added stress within the cathode results in shorter lifetime with respect to their PIL counterparts. Finally, we show that PIL nanoparticles lower the resistance of the cell in comparison to PIL homopolymers by promoting electrolyte flow between the carbon particles during cycling. This is a result of their small size, high surface area, swellability for the produced lithium-sulfide species, and improved electrolyte transport through the interstitial spaces. Furthermore, the PIL nanoparticles promoted the disproportionation reaction of the low soluble short-chain polysulfides into long-chain polysulfides, which has a beneficial influence on the achieved capacities. These findings illustrate the positive effects of using PILs in lithium-sulfur batteries and will aid the search for optimized binder designs. Future work will also examine how Li_2S crystal growth is influenced by the presence of PIL.

ASSOCIATED CONTENT

Supporting information

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXXX

Contains a synthetic scheme, SEM images, and comparison photos of the swelled binders.

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