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Journal Name

ARTICLE

## Taming the polysulphide shuttle in Li–S batteries by plasma-induced asymmetric functionalisation of the separator

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A novel microporous separator for lithium–sulphur batteries, in the form of an asymmetric membrane with cation-exchange functional groups, was synthesised by a one-step plasma-induced graft co-polymerisation. This separator consisted of commercial porous polypropylene modified with styrene sulfonate at and near the surface of the material. Both successful grafting and membrane asymmetry were confirmed by attenuated total reflectance Fourier transform infrared spectroscopy. Morphological changes as a function of graft level were analysed using scanning electron microscopy. Additionally, the separators were tested for their ability to inhibit polysulphide diffusion, which showed a strong dependence on the amount of negatively charged  $\text{-SO}_3^-$  groups introduced to the hydrophobic substrate. Cycling tests in model Li-S cells with the modified separators showed improved coulombic efficiency.

### Introduction

The lithium–sulphur (Li–S) battery employs metallic lithium as the negative electrode and elemental sulphur as the active material in the positive electrode, a design that could significantly improve upon the specific energy of current battery technologies and lend itself to future applications in electric vehicles, grid-scale energy storage, and others.<sup>1</sup> This benefit largely comes from sulphur's theoretical specific charge of  $1672 \text{ mAh g}^{-1}$  and resulting specific energy of approximately  $2600 \text{ Wh g}^{-1}$ , a value much higher than the roughly  $800 \text{ Wh g}^{-1}$  found in current Li-ion batteries.<sup>2, 3</sup> While this new design is environmentally friendly and inexpensive, a number of challenges have hampered commercialisation thus far. Most importantly, sulphur is a poor conductor and generates soluble polysulphide intermediates ( $\text{Li}_2\text{S}_n$ ,  $4 < n < 8$ ) that contribute to undesirable cyclic electron transfer reactions, a process known as the polysulphide shuttle.<sup>4, 5</sup> Even if the insulating nature of sulphur can be mitigated by the incorporation of an appropriate conductive matrix composed of materials like carbon black,<sup>6</sup> carbon nanotubes,<sup>7</sup> carbon fibres,<sup>8</sup> or mesoporous carbon,<sup>9</sup> the suppression of the polysulphide shuttle remains a challenge. Previous research has focused on the development of electrolytes or electrolyte additives to minimise this effect, but results are still far from satisfactory.

An alternative approach involves the use of a functionalised separator that traps or repels the generated  $\text{S}_n^{2-}$  species. Zhang and Tran proposed to coat Celgard with a PEO– $\text{SiO}_2$  layer to obtain a composite gel polymer electrolyte (CGPE).<sup>10</sup> The presence of PEO– $\text{SiO}_2$  units was believed to effectively retard

the diffusion of polysulphides and improve the interface of the cathode and thus the cycling stability. Indeed, this composite coating significantly enhances the wettability of the separator. However, Li–S cells assembled with this separator showed average electrochemical performance comparable to that of cells with pristine separator (Celgard). A combination of high viscosity of CGPE with strong adsorption of  $\text{SiO}_2$  to polysulphides resulted in an inevitable polysulphide trap rather than ion selective shield. Recently the coating of Nafion on Celgard has been reported, which enables to build up an ion selective shield.<sup>11, 12</sup> This shield effectively reduces polysulphide mobility and leads to better rate capability. However, the thickness of the Nafion coating has a significant influence on both ionic conductivity and polysulphide repulsion, with lower Nafion loading leading to higher conductivity, yet to an increasing risk of defects in the film, impairing electrochemical performance.<sup>12</sup> One way to avoid these issues is to modify only the surface or the regions near the surface of the polyolefin separator. It can be achieved by activating the base film with subsequent introduction of ionic groups by graft co-polymerisation.

Plasma treatment is suitable in this regard since it utilises low energy electrons and thus affects only the surface and nearby regions.<sup>13</sup> Ciszewski *et al.*<sup>14, 15</sup> demonstrated that polypropylene based membranes grafted with acrylic acid (AAc) are promising candidates for inexpensive and safe nickel–cadmium battery separators. They additionally reported graft polymerisation of AAc onto plasma-activated porous polypropylene (PP) as a good way to enhance wettability. Even though the grafted functional acidic groups were observed not only on the surface but also within the pores of the membrane, the treatment, when optimised, can selectively modify the structure, which can be used to tune the properties of the separator.

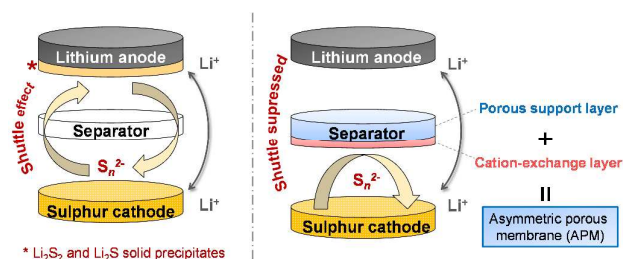
The concept of asymmetric porous membranes is used for separation applications in micro-, nano- and ultrafiltration.<sup>16</sup> In this case, size-selective separation is accomplished by a

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polymer top-layer less than 1  $\mu\text{m}$  in thickness (e.g., cation-exchange layer), whereas mechanical robustness is provided by the porous support layer.<sup>17</sup> This approach is advantageous, since both layers can be designed separately to facilitate cation passage while preventing anion transit through the Donnan exclusion effect.<sup>18</sup> Various design aspects of many of these kinds of membranes have been described by Ulbricht,<sup>19</sup> yet, to the best of our knowledge, this approach has not been applied to Li–S batteries.

Based on these approaches, we designed and synthesised an asymmetric porous membrane with  $S_n^{2-}$  ( $n = 5-8$ ) anion barrier functionality through a one-step plasma-induced graft copolymerisation of styrene sulfonate (SS) onto the surface of a commercial porous PP separator using two different post-treatment pathways. The synthesised membranes were characterised with attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and scanning electron microscopy (SEM). The Li-form was subsequently tested for polysulphide rejection and electrochemical performance. The presence of the  $-\text{SO}_3^-$  grafts in the membrane structure and their impact on separator properties are presented and discussed. The overall design and operating principle are shown in Scheme 1.



Scheme 1 Configuration of the Li–S cell assembly<sup>20</sup> with the concept of the asymmetric porous membrane shown on the right, comprising a cation-exchange layer as barrier for polysulphides. Sketch adapted and modified from reference

## Experimental part

### Chemicals

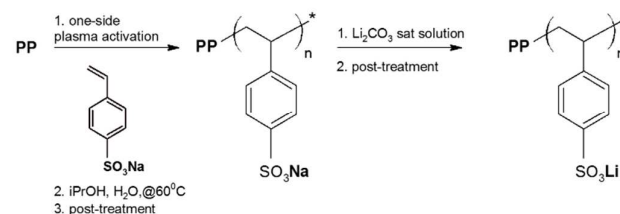
A PP porous substrate (TreoPore) with a thickness of  $25 \pm 5 \mu\text{m}$  and a pore size of  $0.05 \mu\text{m}$  was used as a support. 4-styrenesulphonic acid sodium salt hydrate (SSS, Sigma Aldrich) was used as a grafting monomer. Isopropanol (*i*PrOH, Prolabo VWR), ethanol (EtOH, Prolabo VWR), and *n*-pentane (Roth AG) were used in membrane synthesis.  $\text{Li}_2\text{CO}_3$  (Sigma Aldrich) was used for Na–Li ion exchange. Long-chain lithium polysulphides ( $\text{Li}_2S_n$ ;  $n \geq 5$ ) were kindly provided by Bosch. The denotation of polysulphides indicates the nominal composition calculated based on the stoichiometric ratio of sulphur and lithium. Additionally, 1 M lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) in dimethoxyethane:1,3-dioxolane (2:1 w/w) (BASF) was used as the electrolyte in the polysulphide diffusion experiments. Celgard 2400 (Celgard) and Nafion 211 (DuPont) were used as references. All solvents and materials were used as received.

### Graft co-polymerisation

Functionalised separators were prepared by adapting a similar, previously reported one-step procedure.<sup>21</sup> Only one side of the porous PP films was exposed to low energy argon (Ar) plasma (90 W, gas flow rate of 72 ml/min) for 5 min. The lag time during which the activated films were exposed to ambient conditions before starting the grafting reaction was 30 min. The activated substrates were then immersed and reacted at  $60^\circ\text{C}$  in a monomer solution consisting of SSS (10% v/v), water (40% v/v), and *i*PrOH (50% v/v) that had been purged with nitrogen for 1 h. After predefined times, the grafted membranes (PP-*g*-PSSS) were removed from solution and extracted either in distilled water at  $60^\circ\text{C}$  overnight or using a multi-solvent exchange and evaporation method, adapted from the literature.<sup>22</sup> In the latter post-treatment method, the PP-*g*-PSSS separators were first immersed in *i*PrOH/ $\text{H}_2\text{O}$  for 30 min to remove water and unreacted SSS monomer. Subsequently, they were immersed in an excess of EtOH for 2 h, after which volatile *n*-pentane substituted EtOH (Scheme 2). The solvent, and any residual water, were evaporated under vacuum at  $60^\circ\text{C}$  for 24 h. The graft level (GL) of each film was determined by using the weights of the pristine PP film ( $W_0$ ) and the grafted film ( $W_g$ ) as follows:

$$\text{GL} = \frac{W_g - W_0}{W_0} \times 100\%$$

Possible dimensional changes induced by graft polymerisation were determined by measuring the thickness of the PP-*g*-PSSS samples and their size in the machining (MD) and transverse directions (TD). The former was measured using a thickness gauge (Heidenhain).



Scheme 2 Grafting process for the introduction of cation-exchange functionality onto a porous PP substrate.

### Cation exchange

In order to obtain  $\text{Li}^+$ -substituted PP-*g*-PSSS (PP-*g*-PLISS), the grafted membranes were immersed in a saturated aqueous solution of  $\text{Li}_2\text{CO}_3$  overnight. The resulting membranes were rinsed with water, subjected to multi-solvent exchange and evaporation, and vacuum dried at  $60^\circ\text{C}$  for 24 h. Nafion 211 membranes were converted to their  $-\text{SO}_3\text{Li}$  form using a similar approach, though without the multi-solvent exchange step.

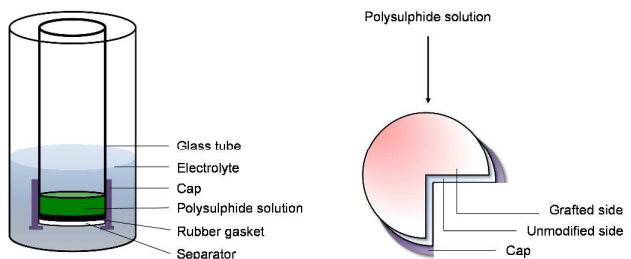
### Characterisation

All grafted films were characterised by FTIR using a System 2000 FTIR spectrophotometer (Perkin Elmer) and a horizontal ATR accessory equipped with a ZnSe crystal with a  $45^\circ$  angle of incidence (Specac). Spectra were acquired at  $4 \text{ cm}^{-1}$  resolution in the 600 to  $4000 \text{ cm}^{-1}$  region.

The morphology of the pristine porous substrates and of the PP-*g*-PSSS membranes was investigated using an SEM Ultra 55 (Carl Zeiss) at an acceleration voltage of 3 kV. All films were sputter-coated with chromium for SEM imaging.

### Polysulphide diffusion

The ability of the PP-*g*-PLiSS membranes to reject polysulphides was characterised in a setup adapted from the literature, in which samples were exposed to a dark, concentrated solution of  $Li_2S_n$  ( $n \geq 5$ ) on one side of the membrane, while the other side was exposed to a polysulphide-free electrolyte.<sup>12</sup> This solution was formed by mixing 0.5 ml each of  $Li_2S_5$ ,  $Li_2S_6$ , and  $Li_2S_7$  solutions in tetrahydrofuran and diluting them ten times with electrolyte. Next, 0.2 ml of the resulting solution was placed inside a glass tube, on top of which the separator was introduced. The glass tube was then turned upside-down and immersed in a vessel filled with pristine electrolyte (Scheme 3). All experiments were performed inside an Ar-filled glove box. The solutions were kept at rest to exclude external influence on the diffusion of the  $Li_2S_n$  species through the separator. Resulting colour changes were evaluated on the neat electrolyte side at predetermined times.



Scheme 3 (Left) experimental setup for polysulphide diffusion tests adapted from the literature<sup>12</sup>; (right) a cross-sectional scheme of the separator assembly.

### Cell assembly

Standard Li-S composite electrodes were prepared by mixing 60 wt% sulphur, 30 wt% carbon black, and 10 wt% poly(ethylene oxide) (MW: 400'000, Fluka) binder in acetonitrile.<sup>6</sup> The resulting slurries were stirred and then doctor-bladed onto carbon-pre-coated aluminium foil. After 24 h of drying in air at room temperature, electrode discs were punched out and transferred to an Ar glove box. Coin-type test cells were then assembled by placing the separator between the composite sulphur electrode and the lithium counter electrode, and introducing the electrolyte. Celgard 2400 (unmodified reference separator) and PP-*g*-PLiSS with 5% GL and 30% GL were tested. Prior to cell assembly, each separator was soaked in electrolyte (100  $\mu$ l) for at least 30 min. Once the separator turned transparent, it was introduced into the cell with the grafted side facing the sulphur electrode, after which an additional 30  $\mu$ l of electrolyte was added to ensure proper wetting and good contact. Since the Celgard does not require additional time to be wetted, 50  $\mu$ l of electrolyte was introduced directly to the cell instead. On average, the positive electrode had sulphur loading of

$2.0 \pm 0.2 \text{ mg cm}^{-2}$  leading to an experimental electrolyte/sulphur ratio of 25 and approx.  $40 \text{ mL g}^{-1}$  for Celgard and the modified separators, respectively. All cells were galvanostatically cycled at a rate of 0.2 C (where 1 C is defined as  $j=1672 \text{ mA g}^{-1}$  of S) and at room temperature between 1.5 and 3.0 V vs.  $Li^+/Li$ .

## Results and discussion

### Grafting of SSS onto porous PP

SSS grafting and subsequent PP-*g*-PSSS extraction in hot water was found to induce not only gravimetric changes but also changes in geometry and appearance. These changes were more evident in the MD than in the TD (Fig. 1). In addition, washing PP-*g*-PSSS with water resulted in an inconsistent appearance, with randomly distributed opaque and transparent regions. The observed changes seemed to result from the drying step. Therefore, the post-grafting treatment was further investigated in order to reduce or to eliminate this effect.

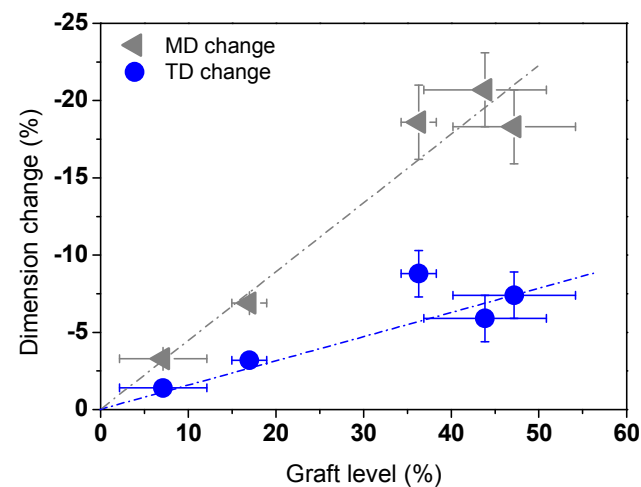


Fig. 1 The relationship between graft level and the associated dimensional changes of the grafted water-washed polymeric composites.

According to Davis and Overmann III,<sup>22</sup> it is possible to preserve asymmetry by avoiding drying in air. This prompted the development of the multi-stage solvent exchange and evaporation method. In this method, a water-miscible solvent, preferably a  $C_1$  to  $C_4$  alcohol, a  $C_1$  to  $C_6$  diethyl ether, or a miscible mixture of these, first replaces the water in the membrane. A second, volatile solvent such as a  $C_4$  to  $C_8$  alkane,  $C_4$  to  $C_8$  alicyclic compound or an isomer of octane, hexane, or heptane is used to drive out the first solvent and to reduce the capillary forces within the pores. The latter can be removed by evaporation without disrupting the porous sublayer or the cation-exchange layer.<sup>23</sup> This procedure resulted in an average GL of about 40% after 24 h of grafting. More importantly, no inhomogeneity was observed, and at the same time the sample shrunk significantly less, with MD and TD changes of less than 5.5% and 2.9%, respectively.

Interestingly, the GL values of the water-washed membranes were all slightly higher than the multi-solvent exchanged PP-*g*-PSSS (Fig. 2). This might be due to incomplete removal of the SSS homopolymer or unreacted SSS monomer from the grafted membrane. The SSS grafting kinetics, as well as thickness changes for the PP-*g*-PSSS as a function of grafting time, are presented in Fig. 2. Both sets of values gradually increase with grafting time regardless of the post-grafting treatment.

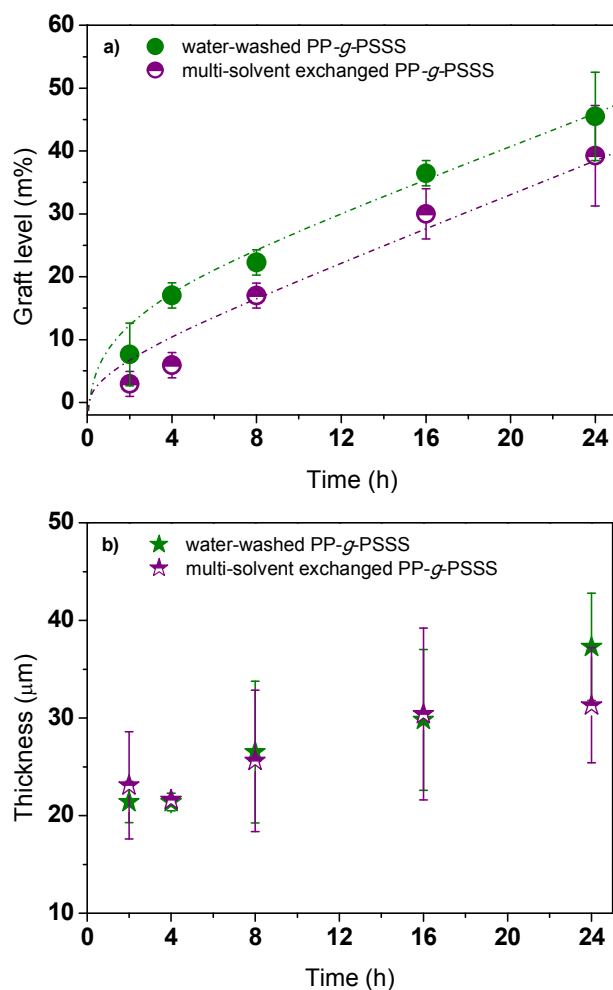


Fig. 2 (a) SSS grafting kinetics onto plasma-activated PP and (b) thickness changes in the resulting PP-*g*-PSSS as a function of grafting time.

The morphology of the grafted, multi-solvent-exchanged PP-based membranes was analysed by SEM. The PP-*g*-PSSS composites were measured from both sides in order to determine changes in porosity and morphology. The SEM images of the pristine material and of the PP-*g*-PSSS membranes with 5 and 40% GL are shown in Fig. 3. After 4 h of grafting when the GL reaches 5%, the morphology of the PP base film started to change, with the branch-like features gradually smoothing out and the pores becoming more closely spaced. While no differences were observed between the grafted and unmodified sides of 5% grafted PP-*g*-PSSS, it was

fairly easy to distinguish them in the case of the 40% grafted membrane, with the grafted side being non-porous and dense and the original porous structure mostly preserved on the other side. No significant changes in porosity and morphology were observed after Na-Li ion exchange.

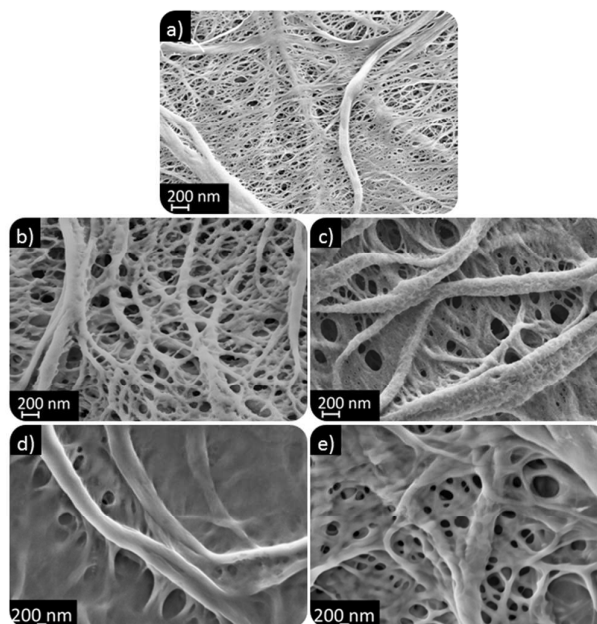


Fig. 3 SEM micrographs of (a) the pristine PP substrate and the multi-solvent-exchanged PP-*g*-PSSS with a GL of (b, c) 5% and (d, e) 40%. Micrographs (b) and (d) show the grafted side of the membrane, whereas the micrographs of the unmodified side are shown in (c) and (e).

#### PP-*g*-PLiSS spectroscopic analysis

ATR-FTIR spectroscopy was employed to study the chemical functionalisation of the region within 5  $\mu\text{m}$  of the surface of the multi-solvent-exchanged PP-*g*-PLiSS separators. The spectral region between 950 and 1025  $\text{cm}^{-1}$  contains information about both the PP base polymer (bands at 973 and 997  $\text{cm}^{-1}$ ) and the grafted functional groups (band at 1011  $\text{cm}^{-1}$ ).<sup>24</sup> It was possible to monitor the temporal evolution of the grafting by normalising all spectra to the intensity of the PP band at 1376  $\text{cm}^{-1}$  (see Supporting Information for details on the normalisation procedure); the collected data for the grafted and unmodified sides are provided in Fig. 4a and b, respectively. On the grafted side, a strong, gradual increase in absorbance with increasing GL is observed at 1011  $\text{cm}^{-1}$ . On the unmodified side, this increase is substantially less pronounced, indicating that grafting is indeed highly asymmetrical and dependent on the grafting time. When the GL exceeds 30%, the SS signal is visible on both sides of the membrane, indicating functionalisation throughout the separator.

As reported by Yamaguchi *et al.*,<sup>25, 26</sup> there are three possible mechanisms that can explain this observation. First, plasma treatment forms free radicals on the surface of the porous substrate, and while the graft co-polymerisation proceeds,

grafted polymer chains grow into the pores. Additionally, radicals formed on the surface of the substrate migrate through the PP structure, leading to polymer growth from within the pores. Finally, some plasma excited species can penetrate the substrate pores, forming radicals directly on the pore surface and prompting graft chain growth at the corresponding sites.

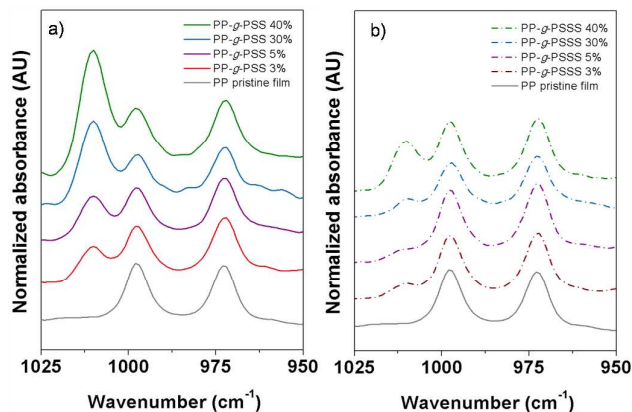


Fig. 4 ATR-FTIR spectra of the (a) grafted and (b) unmodified sides of the multi-solvent-exchanged PP-*g*-PLiSS and pristine PP, normalised to the height of the PP peak at 1376 cm<sup>-1</sup>.

#### Polysulphide-rejection ability

Lithiated Nafion 211 and Celgard 2400 were chosen as reference materials to mimic the cation-exchange layer and porous support layer, respectively. The results of the polysulphide rejection diffusion experiments for the reference materials and several PP-*g*-PLiSS membranes are summarised in Fig. 5. As expected, Celgard 2400, a monolayer PP separator, does not suppress the diffusion of polysulphides. After 30 min of immersion (1a), the electrolyte began to turn green. The colour intensified after another 60 min (2a), while a green-brownish solution was obtained after 150 min (3a). In contrast, no change in colour was observed when a lithiated Nafion 211 membrane is used as a separator (1d-3d), indicating that the diffusion of the long-chain polysulphides is prevented. These observations are in good agreement with recently published results from Bauer *et al.*<sup>12</sup>

Membranes with three different GLs (5, 30, and 40%) were investigated where the grafted side was facing the polysulphide solution. No colour change was observed with the 5% grafted membrane after 90 min of exposure to the electrolyte (2b). However, a faint green coloration was observed after 150 min (3b), suggesting that diffusion was not completely prevented. The low GL and, consequently, low negative charge concentration might account for this. Alternatively, the 30% sample (1c - 3c) showed no colour change, even after 150 min, a result that was also observed with the 40% grafted sample.

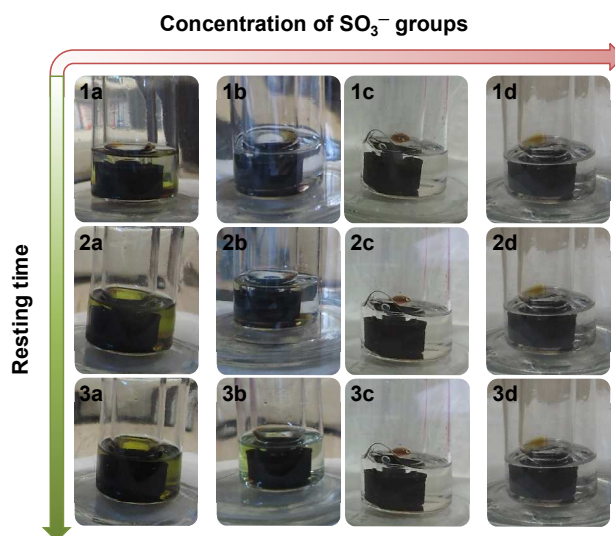


Fig. 5 Polysulphide diffusion tests of Celgard (1a-3a), PP-*g*-PLiSS with a GL of 5% (1b-3b) and 30% (1c-3c), and lithiated Nafion 211 (1d-3d) for resting times of 30 min (row 1), 90 min (row 2), and 150 min (row 3).

#### Preliminary cell cycling tests

Preliminary galvanostatic cycling tests were performed as a proof of concept to demonstrate the ability of the asymmetrically functionalised separator to reduce the polysulphide shuttle in the Li-S battery. Fig. 6a shows the specific charge and the coulombic efficiency as a function of the number of cycles for Li-S cells containing the modified porous separator. The cycling performance of the cell with Celgard as reference separator is plotted for comparison.

It is found that the specific charge is dependent on the degree of functionalisation. The use of a highly-grafted separator (PP-*g*-PLiSS 30%) resulted in much lower specific charge (Fig. 6a), owing to a high overpotential already observable in the first cycle (Fig. 6b), apparently caused by excessive grafting. This notable much lower specific charge might be a consequence of much slower Li ion transfer through this highly-grafted asymmetric porous membrane. The cell containing the separator with low graft level (PP-*g*-PLiSS 5%) shows specific charge (Fig. 6a) and first cycle voltage profile (Fig. 6b) similar to that of the Celgard reference. However, after twenty cycles (Fig. 6c) a slightly increased overpotential is observed, yet without compromising the cell's specific charge.

The cycling results show that both grafted separators demonstrate a coulombic efficiency improved by more than 15% compared to that obtained with Celgard, indicating significant polysulphide shuttle suppression. In the case of the highly-grafted separator the average efficiency is nearly 100%. With the lower grafted sample, however, the average efficiency is around 95%. These few percent of efficiency loss may be a result of the shuttle effect, which still exists to limited extent in the cell with 5% modified PP-*g*-PLiSS. The remaining open porous structure on the grafted side of this PP-*g*-PLiSS allows the diffusion of polysulphides and thus the follow-up parasitic reactions. Presumably the amount of SO<sub>3</sub><sup>-</sup> groups at or near the surface of the separator is not yet sufficient to completely eliminate the polysulphide shuttle.

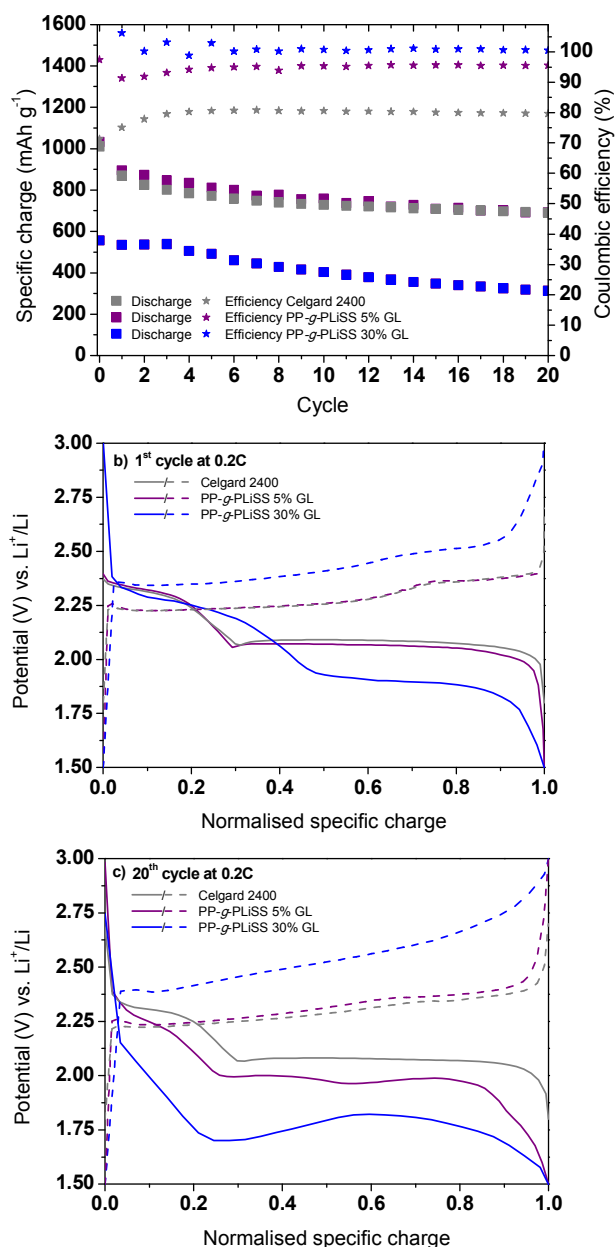


Fig. 6 (a) Cycling performance of Li-S cells with Celgard 2400 and 5 and 30% grafted PP-g-PLISS; corresponding normalised galvanostatic curves for the (b) first and (c) twentieth lithiation and delithiation.

## Conclusions

Styrene sulfonate was successfully grafted onto a plasma-activated porous PP substrate. In addition, inhomogeneities in the grafted membranes were minimised and shrinkage was significantly reduced by using a multi-solvent exchange and evaporation post-treatment. The graft level (GL) increased with grafting time, from about 3% after 2 h up to about 40% after 24 h. Asymmetry in the grafted separators was confirmed by ATR-FTIR and found to be inversely related to the GL,

regardless of the post-treatment method. The polysulphide rejection ability of the functionalised separators was demonstrated, using Celgard 2400, an unmodified porous separator, as a standard for comparison. Electrochemical tests confirmed the applicability of these materials in Li-S batteries, as cycling experiments with functionalised separators resulted in much higher coulombic efficiencies than those obtained with the standard separator.

## Acknowledgements

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## Abstract

A novel polymer separator in the form of an asymmetric porous membrane with  $S_n^{2-}$  anion barrier functionality was synthesised by plasma-induced graft co-polymerisation. It shows superior polysulphide rejection ability and improved coulombic efficiency in comparison to the standard separator.

