

Full paper

# Nucleophilic substitution between polysulfides and binders unexpectedly stabilizing lithium sulfur battery



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## ABSTRACT

Polysulfide shuttling has been the primary cause of failure in lithium-sulfur (Li-S) battery cycling. Here, we demonstrate a nucleophilic substitution reaction between polysulfides and binder functional groups can unexpectedly immobilizes the polysulfides. The substitution reaction is verified by UV–visible spectra and X-ray photoelectron spectra. The immobilization of polysulfide is *in situ* monitored by synchrotron based sulfur K-edge X-ray absorption spectra. The resulting electrodes exhibit initial capacity up to 20.4 mAh/cm<sup>2</sup>, corresponding to 1199.1 mAh/g based on a micron-sulfur mass loading of 17.0 mg/cm<sup>2</sup>. The micron size sulfur transformed into nano layer coating on the cathode binder during cycling. Directly usage of nano-size sulfur promotes higher capacity of 33.7 mAh/cm<sup>2</sup>, which is the highest areal capacity reported in Li-S battery. This enhance performance is due to the reduced shuttle effect by covalently binding of the polysulfide with the polymer binder.

## 1. Introduction

Over the past decades, a strong demand for low-cost and high-energy-density rechargeable batteries has spurred lithium-sulfur (Li-S) rechargeable battery research. Rechargeable Li-S batteries have great commercial potential for two reasons. First, sulfur is an abundant and low-cost material. Second, the Gibbs energy of the lithium (Li) and S reaction is approximately 2600 Wh/kg, assuming the complete reaction of Li with sulfur to form Li<sub>2</sub>S, more than five times the theoretical energy of transition metal oxide cathode materials and graphite coupling. With these advantages, Li-S batteries could be both high energy density and low cost, satisfying demand in both stationary energy storage and transportation application [1,2]. Despite its advantages, the use of rechargeable Li-S batteries is still very limited. Obstacles include the low conductivity of sulfur and the loss of sulfur cathode material as a result of polysulfide dissolution, which causes a shuttle effect and significant capacity fading [3,4]. Theoretically, the octasulfur (cyclo-S<sub>8</sub>) is reduced by steps to solid Li<sub>2</sub>S during lithiation in the sulfur cathode. During this process, electrolyte soluble Li<sub>2</sub>S<sub>x</sub> are generated when the x value ranges from 8 to 4. The soluble lithium polysulfides diffuse through the electrolyte and further reduced at the lithium metal side to form low-order of polysulfide. The partially

reduced and soluble polysulfides can diffuse back to the sulfur electrode side, which are oxidized to higher-order of polysulfides at the cathode side during the delithiation process [5]. This shuttle effect, together with low conductivity, leads to poor sulfur utilization and fast-capacity fade, which have hindered widespread use of rechargeable Li-S batteries [6,7].

Efforts to trap the shuttling polysulfides have mainly focused on meso/nano-carbon matrix as summarized by Liu et al. [8–20] formation of sulfur composites initiated by Wang et al. [21–23] and metal oxide/sulfide hosts reviewed by Mai et al. [24] Since divinylolxyhydroxyolysulphides was first developed by T.A. Skotheim et al. as an alternative binder solution for Li-S batteries [25], polymers including gelatin [26–28], polyethylene oxide [29], polyacrylic acid [30], carboxyl methyl cellulose [31], polyvinylpyrrolidone [32], gum arabic binder [33], carbonyl-β-cyclodextrin [23] and polyamidoamine dendrimer [34] were identified as promising binders to address the issue. Besides the better dispersion and distribution properties of the emerging binders, as revealed by Cui et al. [32] the existence of carbonyl groups in the emerging binders play a pivotal role in the improved cycle performance. The electron-rich oxygen with lone pairs is favourable to form lithium-oxygen (Li-O) bond with lithium polysulfides. The contribution of carbonyl groups and surface modification

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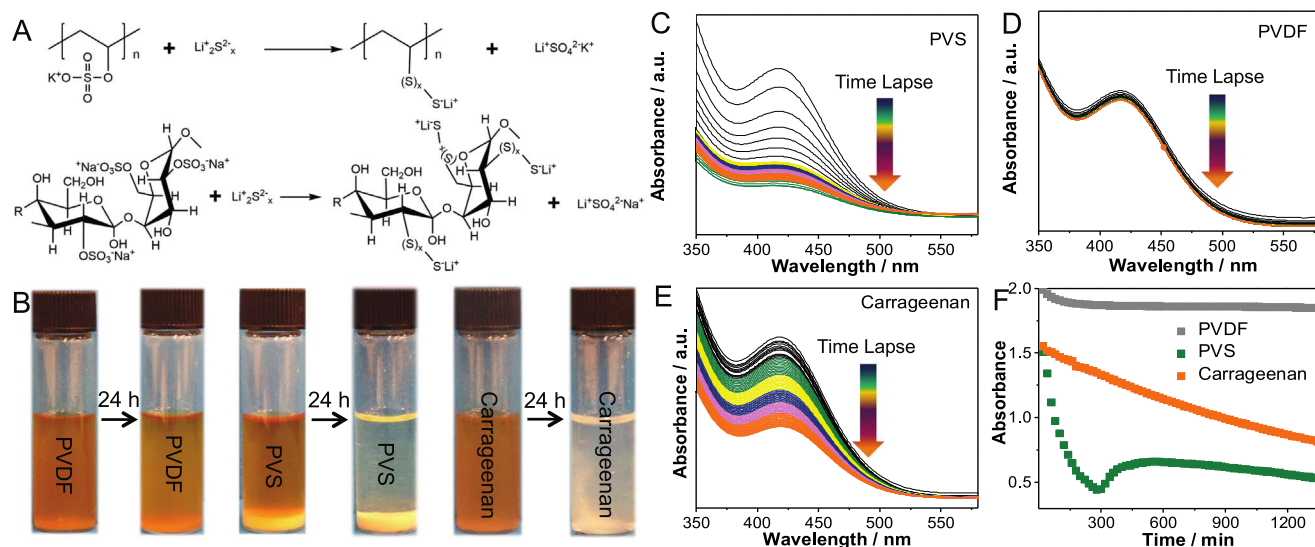
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**Fig. 1.** The polymers with chemical leaving groups can react with polysulfide. (A) Molecular structures of PVS and natural product of carrageenan and their replacement reactions with polysulfide to form immobilized polysulfides on the polymer backbones. (B) Visual effects of the polysulfide solution exposed to different binders over 24 h. (C,D,E) The time-lapsed UV-vis absorbance of *in situ* UV-vis spectra of PVS, PVDF and carrageenan in 3 mmol/L Li polysulfide in DOL/DME solution. (F) UV-vis absorbance changes with time of the three polymer binders.

effect was also evidenced by our group through poly(9, 9-dioctylfluorene-co-fluorenone-co-methylbenzoic ester) (PFM) binder [35].

An alternative method to provide strong binding with polysulfide is through a covalent bond between the electrode and sulfur species. A nucleophilic substitution reaction between the dissolved polysulfides and leaving groups on the polymer binder can fix the polysulfides on to the electrode *via* the newly formed C-S covalent bond. A number of factors govern reactivity in a nucleophilic reaction: the ability of both the nucleophile and the leaving group to polarize, the stability of the leaving group, and the interaction between the nucleophile and leaving group [36]. To capture the polysulfide in a timely manner, the choice of leaving group is critical. A good leaving group must be able to stabilize a large negative charge in both the transition state and the product stage. A good measure of anion stability is the  $\text{p}K_a$  of an anion's conjugate acid, with the lower  $\text{p}K_a$  being associated with a better leaving group [36]. Considering the unique requirements of the Li-S batteries, the leaving group also must not introduce reactive species into the system. Based on these requirements, the sulfate leaving group is adopted. (Fig. 1A) [34]. Synthetic poly(vinyl sulfate) potassium salt (PVS), a commonly used synthetic polymer, has a sulfate rich chemical structure that can be well controlled and would be an ideal polymer to form a composite. However, the binding strength of PVS is inadequate when used as a binder to form a composite electrode. In contrast, carrageenan, a material derived from polysaccharides in seaweed [37], has desirable features for binders such as aqueous solubility, high adhesiveness, variable concentrations of sulfate leaving groups, biodegradability, and nontoxicity. The density of sulfate groups on carrageenan controls the gelation process [38] and the extended hydroxyl groups are indigent to the polysaccharide structure, providing an extended interaction with the surrounding polar aqueous environments. Nature has inadvertently designed carrageenan to be an ideal material for sulfur electrode binder applications. It not only possesses the sulfate leaving groups to capture sulfides, but also has rich hydroxyl groups for adhesion to form stable conductive networks with carbon black conductive additives and interaction with polar electrolyte. Carrageenan has much greater adhesion and sulfate functionality as a leaving group. Carrageenan should have an even better chemical reactivity with polysulfide than PVS, due to some of the sulfate groups on the primary carbon sites.

## 2. Results and discussion

### 2.1. Nucleophilic substitution reaction in the electrode

In this research, initial efforts are focused on PVS with a sulfate leaving group and polyethylene type backbone [39]. Ultraviolet-visible spectroscopy (UV-vis) is conducted to confirm the polysulfide immobilization capability of the polymers as shown in Fig. 1. The 0.1 g polymer is soaked in the 1-mL 3-mmol/L long-chain lithium polysulfide (average formula  $\text{Li}_2\text{S}_6$ ) in 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME) solution for 24 h to track the polysulfide substitution evolution. This design allows polysulfide to continuously be captured by the electrode *via* a chemical substitution reaction. Li polysulfide is a strong nucleophile [40], which can attack active carbon (C) sites attached to good leaving groups. This nucleophilic substitution reaction results in the formation of a new C-S bond with the departure of the leaving group. PVS is a liner polymer with sulfate functional groups, which is a very good leaving group during a nucleophilic substitution reaction with polysulfide [41,42] (Fig. 1A). The *in situ* spectra indicate that  $\text{Li}_2\text{S}_6$  species produce characteristic peaks in around 430 nm. Fig. 1 (C-E) [43]. The full spectra and reaction kinetics are demonstrated in Fig. S3. A significant polysulfide concentration decrease is recorded for the solution exposed to PVS polymer within 3 h. In contrast, the absorption signals for polysulfide solution exposed to PVDF hold constant, indicating limited substitution of PVDF with polysulfide over 24 h. When the PVS polymer is exposed to the electrolyte with polysulfide, the nucleophilic attack of the polysulfide to the PVS causes the instant formation of the oligosulfide crosslink PVS network structure, leading to the rapid depletion of polysulfide in the electrolyte phase. Fig. 1B and C show the rapid removal of polysulfide in the electrolyte, as the UV visible spectra of the electrolyte solution show rapid dwindling of the polysulfide absorption peak when exposed to the PVS polymer. In comparison, PVDF does not have good leaving group [44–46], therefore polysulfide stays in the electrolyte as shown in Fig. 1B and D. Fig. 1B shows the visual color changes after the introduction of PVS into the polysulfide-containing electrolyte. The reaction between polysulfide and the functional PVS polymer is confirmed not only by the decrease of polysulfide concentration in the presence of PVS, but also by the formation of S-S and C-S bonds in the PVS polymer through the appearing peak located at 2472.7 and 2473.7 respectively, in the synchrotron-based sulfur K-edge X-ray

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