ChemComm

Accepted Manuscript

Chemistry Communications

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Rational design of sulphur host materials for Li-S batteries: correlating lithium polysulphide adsorptivity and self-discharge capacity loss

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A versatile, cost-effective electrochemical analysis strategy is described that determines the specific S_n^{2-} adsorptivity of materials, and allows prediction of the long-term performance of sulphur composite electrodes in Li-S cells. Measurement of nine different materials with varying surface area, and hydrophobicity using this protocol determined optimum properties for capacity stabilization.

Sulphur is a low-cost, abundant earth element that has many applications. One is its use in rechargeable lithium-sulphur (Li-S) batteries, the latter having gained much interest in recent years due to their high theoretical capacity (1675 mAh/g) and energy density (2500 Wh/kg).[1] Upon discharge, elemental sulphur (S_8) is reduced at 2.3 V to form intermediate polysulphides (Li_2S_n, $2 \leq n \leq 8$) that are further reduced at approximately 2.0 V vs Li/Li^+ into lithium sulphide (Li_2S).[2]

There are several challenges with sulphur electrochemistry that hinder the commercialization of this energy storage system. Unquestionably, a main problem is the soluble nature of the polysulphide (S_n^{2-}) intermediates, allowing their diffusion into the electrolyte. Such undesired mass transport of electroactive species is at the origin of three major performance barriers. At open-circuit, the spontaneous reduction of S_n^{2-} on the surface of the negative electrode (known as self-discharge) can eventually result in Li_2S poisoning of the lithium electrode.[3] During charge, the oxidation of S_n^{2-} at the positive electrode is accompanied by their diffusion and reduction at the negative electrode in a similar fashion. This redox shuttle can proceed endlessly and therefore causes poor coulombic efficiency and capacity decay due to the loss of active material in the electrolyte or on the negative electrode.[3]

Previous work on mitigating the detrimental effects of S_n^{2-} solubility focused on two different aspects of the cell. Regarding the electrolyte, additives such as $LiNO_3$ that passivate the negative electrode prove effective to alleviate self-discharge over short rest times and improve coulombic efficiency, while S_n^{2-} dissolution can be decreased by using low polarity fluorinated ethers as co-solvents.[4] On the other hand, considerably more effort has been placed on the material used as the sulphur host, i.e. the positive electrode matrix. Materials such as mesoporous carbons[5] and semiconducting or metallic oxides[6,7] to name a few, with varying

surface area and polarity, have all been utilized in an attempt to limit S_n^{2-} diffusion out of the positive electrode.

The exhaustive search for a material that has a high electronic conductivity to facilitate charge transfer, substantial surface area and pore volume to allow high sulphur loading, and well-suited physical/chemical surface properties to inhibit S_n^{2-} diffusion into the electrolyte is still ongoing. It is vital to find a material with these characteristics so as to bring the Li-S battery one step closer to commercialization. Before spending valuable resources (money and time) on fabricating electrochemical cells to assess the long-term cyclability of a sulphur-based electrode composite, it is critical to ensure that the material envisaged as sulphur host meets all the criteria listed above. Herein, we report a facile yet rational method for screening sulphur host candidates, based on metrics: A quantitative electro-oxidation reaction provides the value for S_n^{2-} adsorptivity - which coupled with the surface area - is correlated to the extent of self-discharge at an intermediate state of discharge
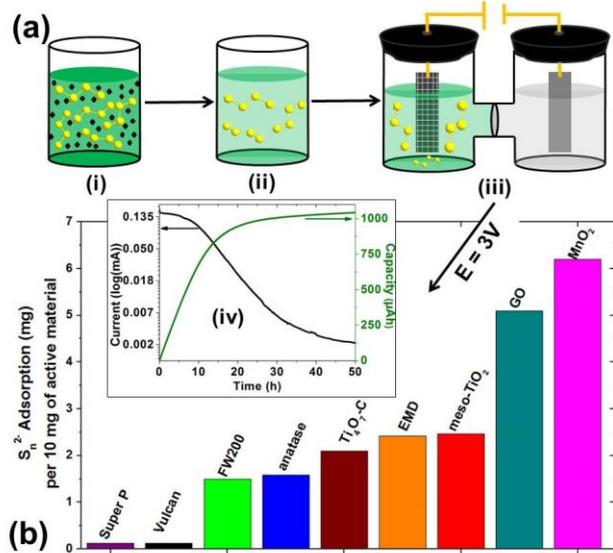
Fig. 1: (a) Schematic showing the method developed to determine polysulphide adsorptivity via electrochemical oxidation and (b) summary of calculated polysulphide adsorptivity per 10 mg of active material from experimental data

during a 5-day cycling protocol. The results prove more pertinent than 100 galvanostatic cycles to predict long-term cyclability.

Our analytical method to determine the S_n^{2-} adsorptivity of an electrode matrix is depicted schematically in **Fig. 1a**.; details are provided in the Supplementary Information. Typically, in an argon filled glovebox, the sample is prepared by dispersing an accurately weighed specific host material into a stock solution of Li_2S_4 in tetraethylene glycol dimethyl ether (TEGDME) (**Fig. 1a (i)**). The suspension is allowed to stir and saturation of the material surface with S_n^{2-} is ensured by adding more of the Li_2S_4 stock solution until coloration persists after 18 hours. The suspension is then centrifuged and the supernatant collected for titration of the excess S_n^{2-} (**Fig. 1a (ii)**). As displayed in **Fig. 1a (iii)**, titration consists of the electrochemical oxidation of S_n^{2-} in a 1.0 M solution of $LiClO_4$/TEGDME, placed in the left hand compartment of an H-cell, utilizing a nickel foam current collector. The right hand compartment is filled with an electrolyte solution of 1.0 M $LiClO_4$ in TEGDME with 2 wt% $LiNO_3$, wetting a Li foil counter electrode. A constant voltage of 3.0 V is applied until the measured current reaches 0 mA (**Fig. 1a (iv)**). At this point, the total capacity resulting from oxidation of the excess Li_2S_4 to elemental sulphur is integrated over time.[†] A straightforward subtraction of the amount of S_n^{2-} titrated from the total amount initially added allows one to determine the amount of S_n^{2-} removed from solution via adsorption onto the matrix of interest (see **Figure S1**).

Nine different materials (acronyms defined in the SI) with varying surface area and hydrophobicity were tested to specifically probe the role of these properties. A summary of the experimentally determined S_n^{2-} adsorptivity of materials are displayed in **Fig. 1b**, where the effects of the physical and chemical properties can be assessed. As a general trend, non-polar materials (i.e. carbons such as Super P and Vulcan) adsorbed much less S_n^{2-} compared to polar materials (i.e. metallic oxides such as TiO_2 and MnO_2). These results are in agreement with recent publications, in which polar materials such as nanocrystalline Ti_4O_7 and MnO_2 nanosheets demonstrated the ability to readily bind polysulphides,[6,7] especially in comparison with still prevailing non-polar carbons.

Further correlations can be drawn between the S_n^{2-} adsorptivity of various samples and their respective surface area determined by the Brunauer-Emmett-Teller (BET) method (**Table S1**). Polarity is an intrinsic characteristic of a specific material, so that mesoporous and non-porous anatase TiO_2 have the same affinity for S_n^{2-}. In practice, mesoporous TiO_2 adsorbs 1.8 times more S_n^{2-} than the non-porous sample due to its higher surface area (indeed, more surface is available for adsorption), however the specific adsorptivity (i.e. per mass unit) does not scale linearly with the surface area. A similar comparison was drawn between EMD and MnO_2 nanosheets, indicating the surface accessed by S_n^{2-} in electrolyte solutions is not as high as gaseous N_2 adsorptivity which determines the BET surface area. For screening sulphur host candidates, polysulphide specific adsorptivity is a more relevant parameter: not only are
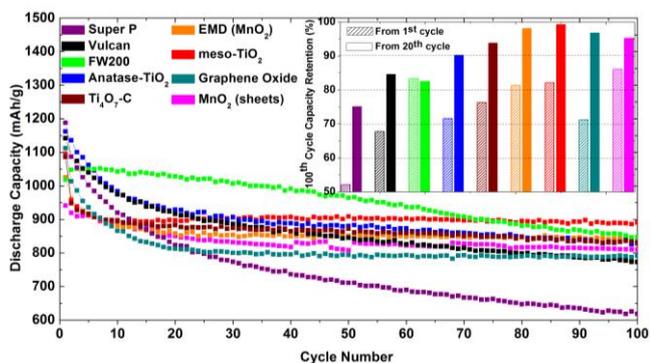
electrode composites typically formulated by weight, but the experimental conditions for its determination closely mimic those of actual Li-S cells.

In an attempt to correlate the S_n^{2-} adsorptivity of materials to the long-term cycling ability of composite electrodes in Li-S cells, galvanostatic cycling was performed at a current density of C/2 (836 mA/g; corresponding to discharge or charge in two hours). The results are displayed in **Fig. 2**. As a general trend, samples with the highest S_n^{2-} adsorption achieved the highest capacity retention over 100 cycles. This was expected, as materials with a stronger affinity for S_n^{2-} can retard diffusion into the electrolyte, thus minimizing capacity fading. High surface area MnO_2 (nanosheets) and TiO_2 (mesoporous) exhibit slightly higher capacity retention than their lower surface area counterparts, but the difference is not as drastic as the S_n^{2-} adsorptivity would suggest. Again, the surface available for adsorption in the composite electrode is reduced compared with the previous experiment, owing to binder coverage for example.[9] This suggests that developing better cathode architecture to take advantage of the higher surface area is critical. Nonetheless, the trends drawn from **Fig. 1** are respected and the adsorptivity scale can be used to benchmark any new possible sulphur host. Comparing the 100th cycle capacity to the 20th cycle rather than the 1st cycle (inset, **Fig. 2**) is reasonable as time was allowed for full wetting of the positive electrode by the electrolyte. This enables better assessment of the long-term behaviour of cells; for example, graphene oxide (GO) which exhibits rapid fading followed by a steady capacity and FW200, an oxygen-rich carbon that shows slow but continuous decay. From the 20th to the 100th cycle, all cells based on polar sulphur hosts - transition metal oxides or oxidized carbons - have a capacity retention > 90%. This confirms that the S_n^{2-} adsorptivity indeed benefits prolonged cyclability. In contrast, sulphur electrodes using carbonaceous materials all exhibit poorer capacity retention (< 90%). Moreover, while graphene oxide[8] and MnO_2 nanosheets[7] both recently demonstrated cyclability up to 2000 cycles with record minimal fading rate of < 0.04% per cycle, the performance of Li-S cells incorporating non-polar carbon hosts keep steadily degrading even after 100 cycles (**Fig. 2**).
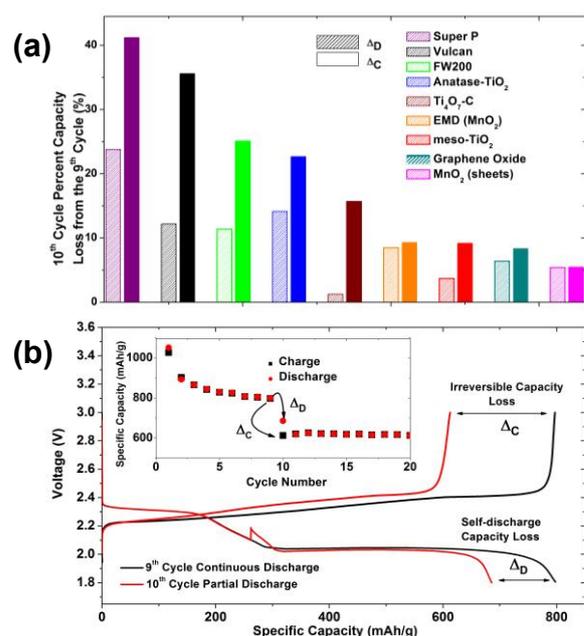
Fig. 3: (a) Voltage/capacity profile of 9th cycle (continuous discharge) and 10th cycle (3-day rest period during discharge). Inset: typical capacity/cycle index plot, illustrating Δ_D and Δ_C upon self-discharge; (b) summary of Δ_D and Δ_C for different materials.

Fig. 2: Galvanostatic cycling of all Li-S cells at a C/2 rate.

In fact, as reported by Urbonaite *et al.*,[10] capacity retention after 100 cycles may be misleading, since physical confinement will eventually be breached. After 500 cycles, typical meso-structured carbons (i.e. FW200) behaved as poor sulphur hosts, equivalent to carbon blacks, and a novel cell testing protocol was necessary. Self-discharge experiments were therefore conducted at an intermediate state of discharge (SOD) on Li-S cells incorporating each of our nine materials (see SI for details).[11] **Fig. 3a** displays the typical voltage profile exhibited by all materials. After 9 formation cycles, the 10th discharge was interrupted at 2.1 V, where the fraction of sulphur under the form of soluble S_n^{2-} is maximal.[12] After resting for 3 days, discharge was resumed and resulted in a lower capacity compared the 9th discharge (Δ_D), while the subsequent 10th charge suffered even a further capacity drop when compared to the 9th charge (Δ_C). As displayed in the inset of **Fig. 3a**, the specific capacity remained stable during the subsequent cycles ($11 - 20$), and therefore Δ_C was irreversibly lost for any of the materials. This is explained more fully below.

Fig. 3b compiles Δ_D and Δ_C for all the different materials studied. To assess internal chemical reactions at open-circuit, self-discharge in batteries is typically measured as Δ_D, and in the case of Li-S batteries, one would attribute it to polysulphide diffusion. Although there is no direct correlation here between Δ_D and specific S_n^{2-} adsorptivity of each host material, Δ_C clearly scales inversely with the amount of S_n^{2-} retained in the positive electrode by adsorption onto the host matrix. Simply, materials with a large S_n^{2-} adsorptivity (as seen in **Fig. 1b**) have the lowest irreversible capacity loss (Δ_C) compared to those materials with a lower S_n^{2-} adsorptivity. Although such a trend was anticipated, the quantification makes it quite clear: Super P based sulphur electrodes lose more than 40% of their capacity after only 3 days shelving at intermediate SOD. In contrast, hosts such as graphene oxide or MnO_2 nanosheets retain 91% and 94% of their active sulphur content, respectively. Therefore, chemisorption of S_n^{2-}, as seen in the case for MnO_2 and GO[7], is advantageous for inhibiting the irreversible capacity loss, over physisorbed S_n^{2-} as seen in TiO_2 and Ti_4O_7.[6]

The origin of the irreversible capacity loss that varies between different materials is explained using a simple mechanism in **Fig. 4**. In the first scenario, a non-polar host (black circles) is coated with sulphur (yellow, A) which upon discharge to 2.1 V is reduced to soluble S_n^{2-} (green, B). Since non-polar surfaces interact poorly with
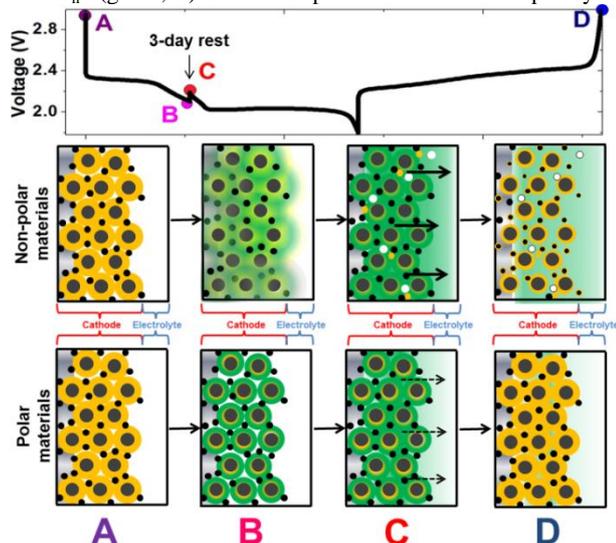
ions, S_n^{2-} readily diffuses into the electrolyte during the 3 day rest (C). In open-circuit mode, polysulphides can form Li_2S via dismutation, which could precipitate anywhere: the positive electrode, the separator or the negative electrode. Upon subsequent charge (D) the active material lost from the positive electrode - either in the form of S_n^{2-} in the separator or electrochemically inaccessible Li_2S - is not reoxidized to sulphur and as such, the reversible storage capacity of the Li-S cell is irreparably diminished. Polar host materials inherently mitigate irreversible capacity loss by binding S_n^{2-}. In this second scenario, the S_n^{2-} remains in close interaction with the host material upon discharge to 2.1 V (B) and over the 3 day rest minimal S_n^{2-} diffuse into the electrolyte (C). Upon full charge, electrochemically accessible Li_2S or S_n^{2-} oxidize to sulphur, leaving a marginal concentration of S_n^{2-} in the electrolyte which results in the small irreversible capacity loss observed with these polar host materials (**Fig. 3b**). As mentioned earlier, while the exact chemistry of host-S_n^{2-} binding varies with the nature of the host (see ref. 6 and 7 for details), increasing the specific surface area available for adsorption (Table S1) maximizes S_n^{2-} adsorptivity (**Fig. 1b**). Hence the retention of polysulphides in the positive electrode composite is enabled under closed and open-circuit conditions.

Comparison with a previously reported, 4-electrode Swagelok™ cell[12] designed to estimate S_n^{2-} concentration in the electrolyte shows the versatility of our approach. The Swagelok™ cell, although able to detect S_n^{2-} concentration *in situ*, required a complex assembly procedure and four electrodes, whereas the strategy developed herein is a versatile, cost-effective method that determines the specific S_n^{2-} adsorptivity of materials prior to cell development. This method can be extended to any new candidate for use as a sulphur host in a Li-S cell prior to fabricating expensive electrochemical full cells. Second, a vital 5-day cycling protocol allows prediction of the long-term performance of sulphur composite electrodes by measuring the ability of the host to retain the active sulphur mass under real operating conditions. In **Fig. 5**, the parameters relevant for a sulphur host material (surface area and S_n^{2-} adsorptivity), are put in perspective together with the capacity retention following a self-discharge experiment. From this forward-looking plot, one easily visualizes how critical is S_n^{2-} adsorptivity and surface area in the capacity retention after self-discharge.

Fig. 4: Schematic displaying a typical electrochemical half-cell undergoing self-discharge using either non-polar or polar sulphur host materials.
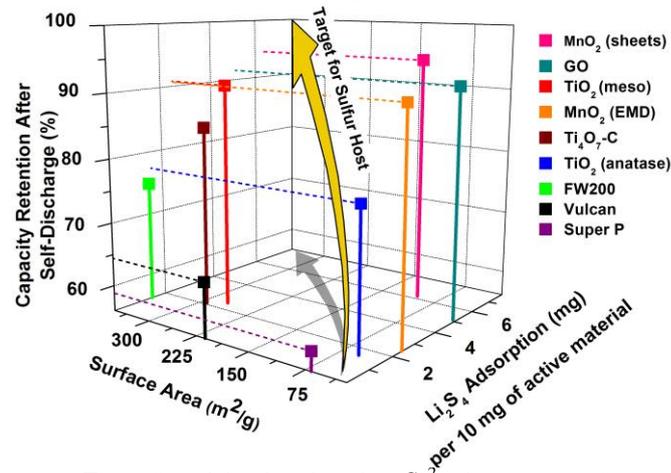
Fig. 5: Target for sulphur host based on S_n^{2-} adsorption, surface area and capacity retention following a self-discharge experiment.

The fact that the Li-S cell operates at about 2.2 V particularly allows it to benefit from optimization of both factors, which would not be the case for a conventional Li-ion (or Li-O_2) cell because of the aggravated reactivity of electrolytes (or intermediate species) at higher potentials. However, clever and efficient electrode

architecture is equally important in order to take advantage of these properties. Although this is also key for conventional Li-ion cells, for the chemical transformation chemistry underlying the Li-S cell, it is paramount. The search for novel sulphur hosts should therefore first focus on tailoring their surface for maximum interaction before engineering such materials with expanded surface area, in order to achieve even higher capacity retention upon cycling.

Acknowledgements

Notes and references

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Electronic Supplementary Information (ESI) available:

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[† Additional information pertaining to the method, and method validation are presented in the Supplementary Information section].

See DOI: 10.1039/c000000x/

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