

Designing Host Materials for Sulfur Cathodes: From Physical Confinement to Surface Chemistry

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The development of lithium–sulfur batteries has become an important area of research to meet the growing demand of modern society for energy-storage devices.^[1] The batteries demonstrate the multi-electron redox chemistry of the earth-abundant, cost-effective, eco-friendly element sulfur, which has an excellent theoretical specific energy of 2600 Wh kg^{−1}.^[1] However, the formation of electrolyte-soluble polysulfide intermediates give rise to the so-called polysulfide-shuttle effect, leading to a loss of active material at the cathode and causing poor Coulombic efficiency and cycling life as well as capacity loss.^[2] Unlike conventional insertion-type cathode materials in lithium-ion batteries, sulfur and its lithiated derivatives (Li₂S_x, *x* = 1–8) that suffer from complicated phase evolution are innately without a host in aprotic electrolytes. Therefore, the rational design and engineering of artificial host materials is of significant importance for the development of high-performance sulfur cathodes.

The shuttle phenomenon stems from the dissolution of heteropolar polysulfide intermediates, composed of covalent chains of different numbers of S atoms capped with two terminal lithium atoms. Historically, physical confinement is the most common strategy employed in the design of host materials for the sulfur cathode. This strategy aims to minimize the leakage of solvated polysulfides by either physical absorption to inherently porous hosts or by coating of an external physical barrier (Figure 1a).^[3] In this regard carbon materials have gained popularity because of their superior conductivities.^[4] However, the usually nonpolar C–C bonding can only provide polar polysulfide intermediates with a “sulfiphobic” surface.^[5] Once polysulfides are solvated, they detach from the electrode surface as a result of poor affinity for the surface and diffuse away. Subsequent reduction of polysulfides to form insoluble lithium sulfides is thus rendered more difficult because of the repulsion between the polar reactants and the nonpolar conductive surface. As a result, the concentration of polysulfides within the cathode increases. In principle, physical confinement can only slow down the diffusion process. The diffusion of polysulfide intermediates leads to a) the increased viscosity of electrolytes, b) retarded ion transportation, c) a loss of active

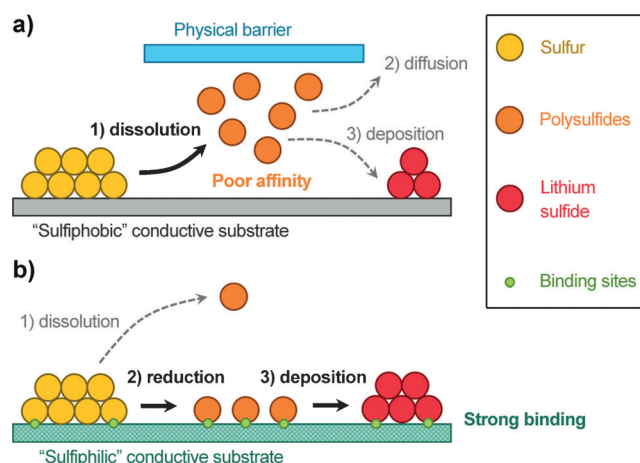


Figure 1. The two principles employed in the design of host materials for sulfur cathodes: a) Physical confinement of polysulfides by introducing an external barrier with a sulfiphobic conductive surface (for example, carbonaceous materials); and b) enhancing the affinity of the polysulfide intermediates for the surface by using polar adsorbents as sulfiphilic conductive substrates.

materials, and d) the passivation of anode interfaces. Ultramicroporous carbon was employed to maximize the physical confinement but this method sacrifices the sulfur content.^[6] Therefore, employing physical confinement alone is both insufficient and kinetically unfavorable to tackle the polysulfide-shuttle issue.

To address the issue of the poor interaction between polar sulfur species with cathode hosts, another promising approach is to adopt “sulfiphilic” surface chemistry to host lithium (poly)sulfides (Figure 1b). Some polar adsorbents have already been employed for use in sulfur cathodes.^[7] However, these materials are usually electrical insulators and the adsorbed polysulfides cannot be reduced when bound directly to the surface. Therefore, the host material must be both sulfiphilic and conductive to anchor mobile redox centers and to use directly the adsorbed polysulfide species.^[8] This two-in-one approach gives rise to the required interaction between polysulfide adsorbates and conductive adsorbents, with subsequent rapid surface redox chemistry and homogeneous nucleation/growth of Li₂S. Thus the redox kinetics of the system are accelerated, synergistically suppressing the shuttle effect and benefiting the spatial distribution of sulfur compounds. Recently, Nazar et al. and Wang et al. demon-

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strated superior electrochemical behavior of sulfur host materials for lithium–sulfur batteries by employing this surface-chemistry strategy.^[9, 10]

The surface properties of porous carbon hosts can be modified by functionalization, for example, by nitrogen doping. Given that nitrogen is more electronegative than carbon, the enhanced electronegativity of the surface after doping could facilitate chemical adsorption of polysulfides.^[11] Considering both electrical transport and surface affinity, Wang and co-workers synthesized carbon-nanotube-interpenetrated mesoporous nitrogen-doped carbon spheres (MNCS/CNT) to serve as the cathode host material for sulfur.^[9] The ability of the MNCS material to adsorb polysulfides was investigated by UV/Vis absorption spectroscopy (Figure 2a). It was found that of the materials studied, MNCS adsorbed the largest amount of polysulfide species. The relative adsorption amounts of MNCS (and MNCS/CNT) were significantly (4–10 times) larger than for other adsorb-

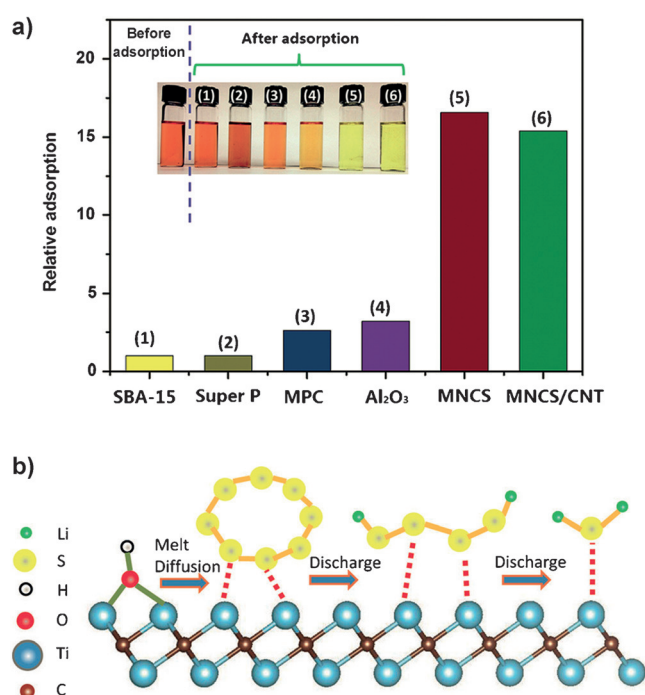


Figure 2. a) The relative adsorption amounts (normalized to the value of Super P carbon black) of MNCS compared with other adsorbents. Inset: Photographs of polysulfide solutions before and after adsorption.^[9] b) Representation of S–Ti–C bond formation on the MXene (Ti₂C) surface.^[10] SBA-15 is a form of mesoporous silica. MPC = mesoporous carbon.

ents. This difference in adsorptivity is evident from the strong decoloration of the polysulfide solution after exposure to MNCS (Figure 2a, inset).

Employing a material with a lower carbon content, Nazar et al. reported a delaminated MXene-phase Ti₂C (d-Ti₂C) material demonstrating high conductivity and an active 2D surface that can bind polysulfide intermediates by strong metal–sulfur interactions.^[10] MXenes are a family of 2D metal carbides or carbonitrides, first reported by Gogotsi et al. in 2011, which combine unusual metallic conductivity with

hydrophilicity.^[12] As a result of the high activity, the exposed Ti–OH bond can be easily replaced with a S–Ti–C bond after heat treatment with sulfur, inducing a switch in the nature of the MXene phases from hydrophilic to sulfiphilic (Figure 2b). The initially adsorbed polysulfides are converted into Li₂S to form nucleation sites on the surface, inducing further deposition through epitaxy on the existing Li₂S nuclei. All sulfur species were bound to the sulfiphilic metallic surface under dynamic control. Employing this technique, polysulfide loss is minimized, the surface redox chemistry is fast, and solid products are homogeneously deposited. Given that the properties of a MXene phase can be easily tuned, MXene and other 2D materials hold great promise as sulfur host materials for lithium–sulfur batteries.^[13] Additionally, Gogotsi and co-workers have developed a selective electrochemical extraction method to fabricate new laminated materials, filling the gap in material composition between pure inorganic materials and carbon materials.^[14]

Compared to systems employing the physical-confinement technique, the above highlighted MNCS/CNT and MXene systems exhibited remarkable enhancements of both capacity and cycling stability. A high initial capacity of 1438 mAhg^{−1} was obtained at a current density of 0.84 mA cm^{−2} for MNCS/CNT composites with 70 % of sulfur. The system also demonstrated excellent cycling stability as after 200 cycles a specific capacity of approximately 1200 mAhg^{−1} was retained at a current density of 1.68 mA cm^{−2}. Furthermore, the system exhibits a high sulfur loading of 5 mg cm^{−2}.^[15] Considering the MXene d-Ti₂C hosts, their composites with 70 % of sulfur demonstrated a discharge capacity of 1090 mAhg^{−1} at current density 0.84 Ag^{−1} and a low decay rate of 0.05 % per cycle over the course of 650 cycles.

To build on the success reported in the highlighted articles on the design of host materials for sulfur cathodes, the next step will be to understand mechanistically the intrinsic interfacial properties of sulfur/sulfiphilic conductive substrates. With this information, we may gain more insight into the heterogeneous electrocatalytic process, which also involves charge transfer and multiple phases. For example, the electronic structures and surface defects of the host materials can be investigated and an analysis of the microkinetics can also be undertaken. Such a fundamental understanding will lead to new advances in material design and should improve the screening process in the search for new host materials. Moreover, these insights are important for other analogous electrochemical energy-storage systems where redox centers are mobile or metastable and the phase transformation is complicated.

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