Covalent-Sulfur Polymer Positive Electrode for Enhanced Stability in Lithium-Sulfur Batteries

Roberto Manuel Torresi, Breno Luiz de Souza and Heloise M. Sintaku
Instituto de Química – Universidade de São Paulo
Av. Professor Lineu Prestes, 748 – Cidade Universitária, São Paulo/SP
rtorresi@iq.usp.br

The development of lithium-sulfur (Li-S) batteries has been extensively explored due to their potential to provide high energy density (2600 Wh kg^{-1}) and high theoretical specific capacity (1675 mAh g^{-1}) – nearly five times higher than conventional batteries – utilizing sulfur as the active material, a highly abundant and low-cost compound[1]. However, the practical application of these batteries is limited by intrinsic issues related to the dissolution of lithium polysulfide (LiPS) intermediates during the charge-discharge cycle[2]. This phenomenon, known as the shuttle effect, results in significant capacity loss and reduced coulombic efficiency. To mitigate these challenges, a practical strategy has been the synthesis of organosulfur polymers capable of covalently immobilizing sulfur species[3]. By heating sulfur (S_8) above 160 °C, ring-opening polymerization can be induced, leading to the formation of sulfur polymer chains. Copolymerizing these long sulfur polymers with crosslinking agents containing unsaturated C-C bonds enables the synthesis of polymers with high sulfur content[4]. These materials hold great potential for use as cathodes in lithium-sulfur batteries, as the molecular-level distribution and integration of sulfur within the polymer matrix enhances the stabilization of sulfur intermediates, thereby improving battery performance and durability. Considering this approach, we synthesized an organosulfur polymer, denominated S-TAIC, via a one-step process (Fig. 1a), followed by an extensive washing procedure to effectively remove residual and non-bonded sulfur, ensuring the purity of the material before its application as a positive electrode in Li-S batteries. Initial experiments suggest that disulfide bonds play a crucial role in modifying the reduction process observed in conventional sulfur cathodes (e.g., Carbon Black/S_8), leading to a reduced formation of long-chain polysulfides. This effect is evident in Fig. 1b and 1c, where the discharge curves show that the first plateau corresponding to long-chain polysulfides—is absent for S-TAIC (black solid line), whereas a distinct step is observed for the CB/S_8 electrode. Additionally, the derivative curves indicate a reduction in long-chain polysulfide conversion, with only 7% for S-TAIC compared to 29% for CB/S_8. These findings suggest that covalent S–S bonds act as anchoring sites, restricting sulfur species within the polymer matrix and mitigating the shuttle effect.

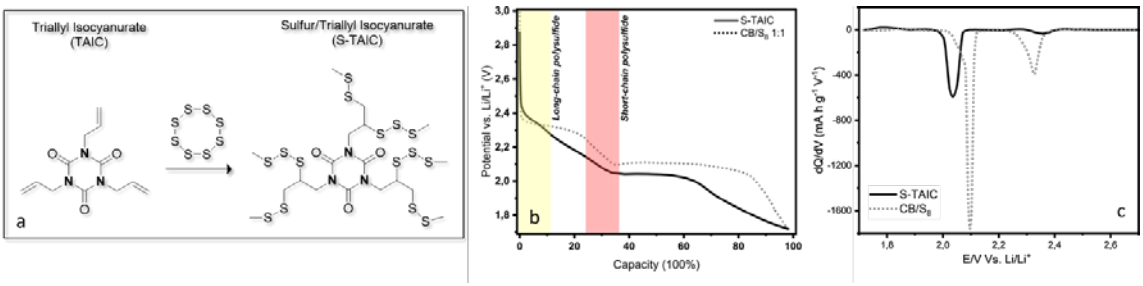

Fig. 1: a) Reaction scheme for the vulcanization of triallyl isocyanurate (TAIC) with elemental sulfur, forming S-TAIC. b) Discharge cycles of S-TAIC (solid black line) and CB/S_8 1:1 (dashed gray line) and c) Derivative curves of CDG. All tests were conducted between 1.7 and 3.0 V at 224.2 mA/g in 1M LiTFSI in DME:DOL (1:1, v/v) with 0.25 M $LiNO_3$.

[1] Shao Q, Zhu S, Chen J. A review on lithium-sulfur batteries: Challenge, development, and perspective. *Nano Research*, 2023, 16(6), 8097-8138.
[2] S. Chauque, B. L. Souza, H M. Sintaku, R. A. Ando, R. M. Torresi. Unveiling the polysulfide-PPY interaction for enhanced lithium–sulfur battery performance. *Electrochimica Acta*, 2024, V. 475, 0013-4686.
[3] S. Haldar, P. Bhauriyal, A. R. Ramuglia, A. H. Khan, S. De Kock, A. Hazra, V. Bon, D. L. Pastoetter, S. Kirchhoff, L. Shupletsov, A. De, M. A. Isaacs, X. Feng, M. Walter, E. Brunner, I. M. Weidinger, T. Heine, A. Schneemann, S. Kaskel, Sulfide-Bridged Covalent Quinoxaline Frameworks for Lithium–Organosulfide Batteries. *Adv. Mater*, 2023, 35, 2210-151.
[4] Xiang Li, Lixia Yuan, Dezhong Liu, Zhen Li, Jie Chen, Kai Yuan, Jingwei Xiang, Yunhui Huang. High sulfur-containing organosulfur polymer composite cathode embedded by monoclinic S for lithium sulfur batteries. *Energy Storage Materials*, 2020, V. 26, 2405-8297.