

# Zeolitic Imidazole Framework-Based Materials by Mechanochemical Synthesis Applied as Positive Electrodes in Lithium-Sulfur Batteries

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## Highlights

Improve lithium-sulfur batteries' electrochemical performance with ZIF-based materials to mitigate the *shuttle* effect. Enhance and optimize mechanochemical synthesis for porous materials in LiBSs.

## Resumo/Abstract

The increasing energy demand, driven by the expansion of portable devices, has led to a search for more efficient energy storage solutions. Lithium-sulfur batteries (LiBSs) have emerged as a promising option, offering a high theoretical capacity ( $1675 \text{ mAh g}^{-1}$ ) and energy density ( $2600 \text{ Wh kg}^{-1}$ ), as well as the low cost of sulfur, its non-toxic nature and abundance. However, before LiBSs can be widely adopted, several challenges must be addressed, such as the *shuttle* effect caused by polysulfide dissolution, the expansion during lithiation, and sulfur's insulating property. Effective sulfur encapsulation and adsorption can be achieved by optimizing the positive electrode structure using metal-organic frameworks (MOFs) such as ZIF-S and conductive polymers, which are excellent sulfur hosts for Li-S batteries [1]. The synthesis of ZIF-S was performed in an MM400 ball mill. ZnO, 2-methylimidazole (2-MeIM), and 2-mercaptoimidazole (2-MerIM) were combined in a stainless-iron jar along with ethanol as liquid-assisted grinding solvent. Three varying ratios of 2-MeIM:2-MerIM were tested: (45:55); (40:60) and (25:75). These compounds were melted with sulfur at  $155^\circ\text{C}$  for 12h, then the composites (ZIF-S:S<sub>8</sub>) formed were mixed with CarbonBlack 65 and poly(vinylidene fluoride) in a ratio of 70:20:10 and coated in an Al-C current collector foil. Up to now, this study suggests that applying ZIF-S as positive electrodes in Li-S batteries catalyzes the formation process of long-chain polysulfides ( $\text{Li}_2\text{S}_x$ ,  $4 < x < 8$ ), commonly seen at 2.31 V, that results in irreversible loss of sulfur and rapid capacity degradation by the polysulfide dissolution in the electrolyte. It is interesting to note that the addition of a higher amount of 2-MerIM leads to greater suppression of the formation of soluble polysulfide, as demonstrated in Figure 1b. In addition, the formation of these intermediates is shifted to lower potentials in the case of proportions of 60 and 75 wt%, in comparison to the ZIF-8 metal-organic framework. This indicates that the amount of ligand added plays a crucial role in controlling polysulfide formation and even possibly catalyzing the reaction kinetics. [1] Susana Chauque, Breno L. Souza, Heloise M. Sintaku, Rômulo A. Ando, Roberto M. Torresi, Unveiling the polysulfide-PPY interaction for enhanced lithium-sulfur battery performance, *Electrochimica Acta*, V. 475 (2024).

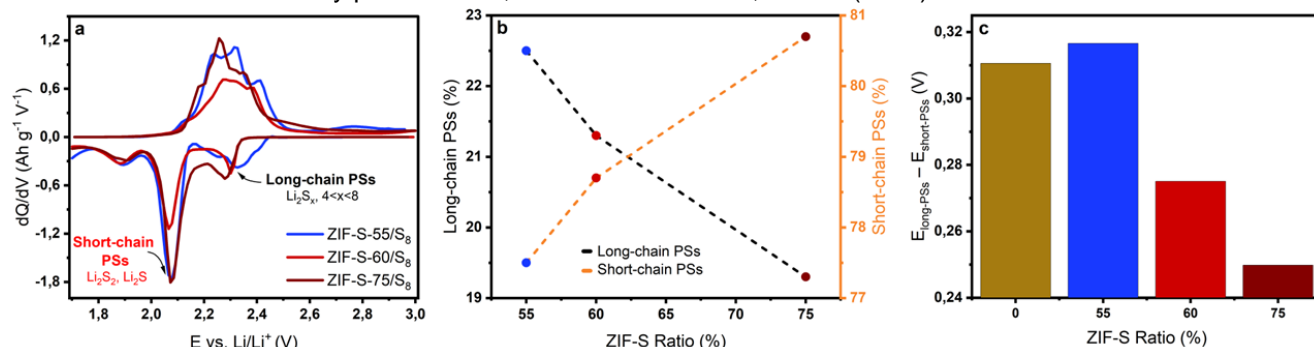


Figure 1. a) Derivate of galvanostatic curves versus potential. b) Polysulfide formation in function of ZIF-S ratio extracted from dQ/dV graph. c)  $\Delta E$  between long-chain and short-chain polysulfide. All the tests were performed between 3.0 and 1.7. V vs. Li/Li<sup>+</sup> in an electrolyte of  $1 \text{ mol L}^{-1}$  LiTFSI - DME/DOL containing 1% of LiNO<sub>3</sub> as additive.

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