



Highlight

One stone two birds: Dual-effect kinetic regulation strategy for practical lithium–sulfur batteries

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Lithium–sulfur (Li–S) batteries are deemed as one of the most promising energy storage systems due to their ultrahigh theoretical energy density of 2600 Wh kg⁻¹ far beyond the current lithium-ion battery technique [1]. Generally, the sulfur redox reactions undergo complex conversion processes between solid sulfur (S₈), soluble lithium polysulfides (LiPSs, Li₂S_n, 4 ≤ n ≤ 8), and solid lithium sulfide (Li₂S) to afford high specific capacity of 1672 mAh g⁻¹ [2,3]. However, the sluggish kinetics of the above-mentioned multi-electron and multi-phase sulfur redox reactions [4,5] seriously hinder the actual battery performances regarding poor rate responses, low Coulombic efficiency, and limited cycling lifespan [6,7]. Worse still, the formation of LiPS clusters under practical working conditions such as under lean electrolyte or varied temperatures further aggravates the sulfur redox kinetics severely [8,9]. Hence, approaches to regulate the properties of LiPSs are essential for high performance Li–S batteries.

To address above issue, Manthiram and co-workers very recently proposed a strategy by adopting methyl trifluoroacetate (CH₃TFA) as the electrolyte additive to accelerate the sulfur redox kinetics and simultaneously prevent the formation of LiPS clusters [10] (Fig. 1a). Specifically, according to density functional theory (DFT) calculation, CH₃TFA can react with LiPSs spontaneously to generate LiTFA and (CH₃)₂S_n products (Fig. 1b). The high donor number (DN) anion TFA⁻ competes with polysulfide anions (S_n²⁻) in binding with Li⁺ and therefore breaks the large-scale clustering networks of Li⁺–S_n²⁻ linkages to enhance the solubility of LiPSs. Meanwhile, (CH₃)₂S_n species regulates the sulfur conversion pathway and accelerates the sulfur redox kinetics. To probe above *in situ* reactions, ¹³C-nuclear magnetic resonance (NMR) spectroscopies of CH₃TFA and CH₃TFA + Li₂S₆ samples were conducted (Fig. 1c). The signal representing methyl group downshifted from

55 ppm to 22 and 25 ppm, demonstrating the weakened electron shielding effect consistent with the expectation that the pendant group of methyl had moved from –OCO– to –S_n– after the spontaneous reaction.

Consequently, with the addition of CH₃TFA, the peak currents in both the reduction and the oxidation processes increased accompanied with decreased polarization between charge and discharge procedures in cyclic voltammetry (CV) profiles, illustrating the enhanced full-range sulfur redox kinetics as expected (Fig. 1d). Li–S full cells were further evaluated with high areal sulfur loading of 4.6 mg_S cm⁻². As a result, under the current densities from C/20 to C/3, the specific capacity can be facilitated by *c.a.* 200 mAh g⁻¹ and the retention rate was boosted as well (Fig. 1e). Furthermore, the CH₃TFA-containing pouch cells with high-areal-sulfur-loading cathodes of 4.8 mg_S cm⁻² and lean electrolyte to sulfur (E/S) ratio of 4.5 μL mg⁻¹ were tested at 0.05C. The pouch cells afforded much higher discharge capacity than that of the controlled pouch cell along 40 cycles (Fig. 1f). Overall, this work demonstrates an effective electrolyte additive as the kinetics promoter by combining the virtues of high DN anions and organosulfur species through a spontaneous *in-situ* reaction. The success of the dual-effect homogeneous promoter in constructing high-performance practical Li–S batteries inspires deeper exploration of molecular design of kinetic promoters and enables further discovery into the complex multi-electron energy storage system of Li–S batteries.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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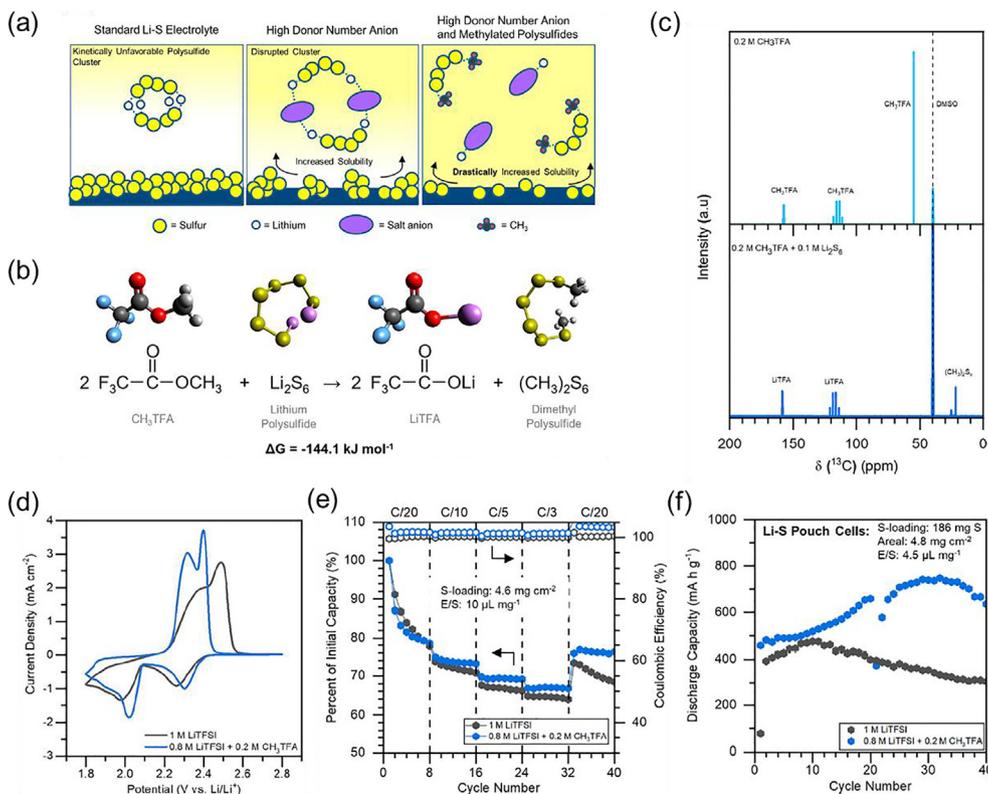


Fig. 1. (a) Mechanism illustration of sulfur redox kinetics in standard electrolyte, with high-donor-number salts, and regulated with both high-donor-number salts and organosulfur species. (b) Computational evaluation of the energetics of the reaction between CH₃TFA and LiPSs (taking Li₂S₆ as an example) (c) ¹³C NMR spectra of 0.2 M CH₃TFA and 0.2 M CH₃TFA + 0.1 M Li₂S₆. (d) CV profiles of Li-S cells with or without CH₃TFA. (e) Rate capability with or without CH₃TFA in Li-S coin cells. (f) Cycling performances of Li-S pouch cells operating at 0.05 C under lean E/S ratio of 4.5 $\mu\text{L mg}^{-1}$. Copyright 2021, American Chemical Society.

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