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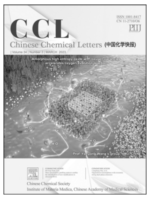

Editorial

Encapsulating-polysulfide electrolyte: An answer to practical lithium–sulfur batteries

Endowed with high theoretical specific energy (2600 Wh/kg) and low material cost, lithium–sulfur (Li–S) battery emerges as a promising candidate for the next-generation energy storage system. A working Li–S battery is in fact a liquid electrochemical system where the reaction of solid S/lithium sulfide (Li_2S) proceeds via dissolved lithium polysulfides (LiPSs) intermediates [1]. The effective solvation of LiPSs is essential for S utilization and reaction kinetics but also induces severe challenges for stable Li metal anodes. The parasitic reactions between active Li and high-concentration LiPSs become rather detrimental under practical conditions with high S loading (>4 mg_s/cm^2), low electrolyte/S (E/S) ratio (<3 μL/mg_s), and limited Li anode (<50 μm), further hindering the cell lifespans. It is therefore imperative to protect the Li metal anode from its parasitic reactions with LiPSs for practical Li–S batteries [2,3].

Among the various research efforts, regulating the electrolyte compositions stands out as a direct means to tune the status, solvation, and reactivity of LiPSs [4]. The electrolyte solutions can be classified into moderately, sparingly, and highly solvating solutions by their distinctive solvation power. Moderately solvating electrolytes confer arguably the best rate capability but cause severe Li corrosion; highly solvating electrolytes promote Li_2S deposition but suffer from serious parasitic reactions with Li; and sparingly solvating electrolytes stabilize the Li anode but induce sluggish reaction kinetics of the S cathode [5]. Current electrolytes are therefore far from ideal in terms of balancing the requirements from both electrodes, and the selection rationale of solvating polysulfides remains controversial [6,7].

Recently, Qiang Zhang's group proposed a novel concept of encapsulating-polysulfide electrolytes (EPSEs) to suppress the parasitic reactions with Li while maintaining satisfactory conversion kinetics of S redox reactions [8]. The EPSEs were featured with two distinctive solvent shells encapsulating a LiPS molecule. The inner solvent shell consists of 1,3 dioxolane/ dimethoxyethane (DOL/DME), the same as the solvents of conventional moderately solvating electrolyte, *i.e.*, 1.0 mol/L bis(trifluoromethanesulphonyl)imide (LiTFSI) in DOL/DME (1:1, v/v, denoted as PSE), to ensure the moderate dissolution of LiPSs and sufficient S conversion reaction kinetics. On the other hand, isopropyl ether (DIPE) is introduced to the outer solvent shell due to its poor solvating power. And the high stability of DIPE against reductive decomposition can mitigate the side reactions with Li as there is a preferential contact between the Li anode and the outer shell. This desirable electrolyte structure was verified by a combination of molecular dynamics (MD) simulations and experimental measurements (Fig. 1). The high stability of EPSE and the mitigated parasitic reaction with LiPSs were directly proved by an intact Li foil after immersing in EPSE with dissolved Li_2S_8. The DIPE-EPSE enables Li–S coin cells with high S loading (4 mg_s/cm^2), lean electrolytes (7.5 μL/mg_s), and thin Li thickness (50 μm) to maintain a capacity retention of above 60% for 120 cycles, which is predominantly superior to traditional PSE. In addition, the specific energy of the pouch cell reaches 300 Wh/kg and can be maintained with a capacity retention of 81% and an average CE of 96.4% after 23 cycles.

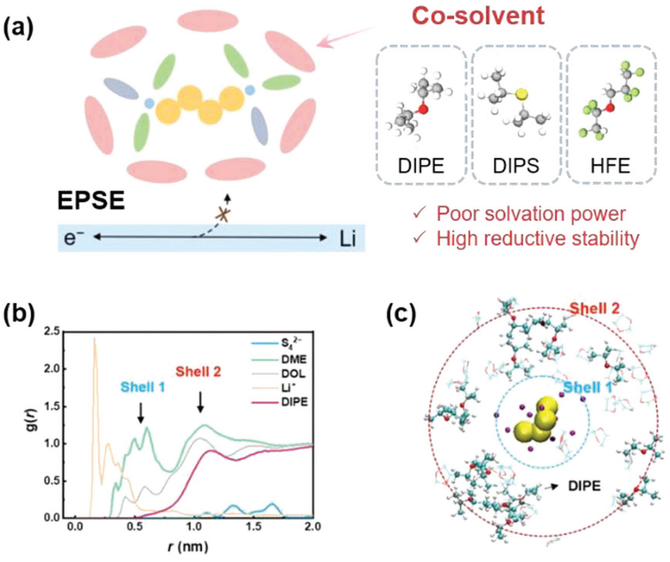

Fig. 1. (a) Schematic illustration of electrolyte structure of LiPSs in EPSE. Li^+ and S_4^{2-} are marked in blue and yellow. The right panel shows typical co-solvents in the outer shell, including DIPE, DIPS, and HFE. The balls in white, gray, red, light green, and yellow refer to H, C, O, F and S atoms, respectively. (b) The radial distribution functions, g(r), around S_4^{2-} in EPSE, obtained from MD simulations. (c) Snapshots of the molecular distributions around S_4^{2-} in EPSE obtained from MD simulations. DME and $TFSI^-$ are omitted here. Reproduced and adapted with permission [8]. Copyright 2021, Wiley-VCH.

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More recently, the concept of EPSEs was further elaborated with di-isopropyl sulfide (DIPS) and 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (HFE) as the outer shell solvents [9,10]. Two crucial criteria were proposed for constructing the EPSEs, that is, poor solvating power and high reductive stability of the outer shell solvent. Among the three solvents, the solvating power of HFE is much weaker than DIPS and DIPE, leading to dramatically improved cycling stabilities of Li–S batteries under practical conditions. Ideally, the solvating power of the outer solvent should be weaker than the inner one to prevent the crosstalk between inner and outer solvation shells and thus maintain the well-encapsulating nature of EPSEs.

In summary, the concept of EPSEs highlights the effectiveness to regulate the solvation structure of LiPSs through the delicate design of hierarchical solvation shells. Such a design breaks the limitations of conventional electrolytes featuring a simpler solvation structure. While the multilayer solvation shells encapsulating LiPSs are beneficial for the cycling stability, several side effects remain. For instance, the larger solvation structure of LiPSs in EPSEs and the incorporation of inert solvents might slow down the transport and reaction kinetics compared to traditional PSE. Addressing these side effects through balancing the solvating power and anti-reductive ability of co-solvents would likely be the next step. Adopting polysulfide-redox catalysts in the sulfur cathode will also be a viable strategy as it only introduces interference to the solvation structure of EPSEs at the cathode side. Nevertheless, we believe that EPSEs have shown a huge potential to be a satisfactory answer to practical Li–S batteries, although the path towards the finish line is still winding and further efforts are required.

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