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Ionic liquid enabling stable interface in solid state lithium sulfur batteries working at room temperature

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ABSTRACT

Power capability of solid state lithium sulfur (Li-S) batteries is severely weakened due to high impedance between electrodes and solid electrolyte. To solve this issue, herein we come up with a room temperature operating (20 °C) solid Li-S battery technology enabled by ionic liquid (IL) as interfacial modification. With IL, a significant decrease of interfacial resistance is observed from 3540 to 39 Ω cm^2 in symmetric cell, which can cycle well at a high current density of 0.5 mA cm^{-2} with a small over potential of 300 mV (20 °C). On this basis, solid state Li-S batteries are fabricated with IL modification, and performed an excellent electrochemical behavior at 0.2 mA cm^{-2} with the specific capacity of 340 mAh g^{-1}. Distinctly, the thin IL layer presents electrochemical and physical stability during the cycling and plays a flowable and seamless interfacial layer in solid state Li-S batteries.

Solid-state Li-S batteries have shown profound impact among next-generation energy storage technologies as its significantly high energy density (2600 kWh Kg^{-1}), low cost (cheap and abundant sulfur cathode), and high safety [1–4]. The employment of SE (solid electrolyte) can well solve the problem of polysulfide shuttling in sulfur part and dendrite growing in lithium metal part, which are two main obstacles in ether electrolyte based Li-S batteries [5–9]. However, the solid state Li-S batteries are still far from practice implementation as the huge interface resistance between SE and electrode materials (both Li metal and sulfur parts), which severely block the cell power capability and utilization of active materials, especially at room temperature operation [10–13].

Normally, due to the roughness of SE and solid electrodes (like Li metal foil and sulfur electrode coating on aluminum foil), gaps naturally form at the solid-solid interface when fabricating a solid state Li-S cell, which will largely reduce electrode-electrolyte contact area and lead to the high interfacial resistance as lithium ion cannot transport along these gaps. Limited by the contact area, the utilization of electrode capacity is also very low. Especially on the sulfur part, not only the insulating gaps, but also the ionic and electronic insulating sulfur active material hinder the lithium ion transportation. To eliminate the above insulating gaps and increase the utilization of sulfur, enormous efforts has been explored in recent years, like surface ALD modification of SE or composite electrolyte using [14–19]. However, the intricate technology and high operating temperature (above 60 °C) prevent the practical employment of solid state Li-S batteries. In addition, the hybrid electrolyte [20–27] also has attract much attention, consisting of solid-state electrolyte powder and the polymer components, such as PEO, PPC, PVDF. However, dendrite growth can not be suppressed because of the poor mechanic properties of the gel state hybrid electrolytes. From the point of interfacial engineering, a flowable liquid interfacial layer is superior than solid interfacial layer as it can accommodate the interfacial fluctuation and guarantee excellent adhesion. To make it more suitable for practical employment, the flowable liquid interfacial layer should also possess the following properties: 1) High stability with Li metal and good ion conductivity during cycling [28,29]. 2) Low vapor pressure and certain viscidity to increase the service life and decrease the usage amount [30]. 3) Anti-flammability to reduce the risk of fire at same extreme conditions as sulfur electrode and lithium metal are intrinsically flammable [31,32].

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Based on above principles, herein we come up with the method of simply using IL wetting at room temperature to form a sustainable and lithium ion conducting interface between SE and electrodes (both Li metal and sulfur parts). To verify the effective IL wetting, Li-S cells were fabricated using garnet-type $Li_{6.4}La_3Ta_{0.6}Zr_{1.4}O_{12}$ (LLZTO) ceramic electrolyte, Li metal foil anode and sulfur cathode coating on aluminum foil, where garnet SE has delivered much prospect [33–40]. After wetting the garnet electrolyte with trace room temperature IL (AMIMTFSI), a liquid intermediate was introduced, in which the initial solid–solid interface was substituted by the new solid-liquid-solid interfaces, simultaneously. The flowable IL layer constructs fast and stable lithium ion conduction channels throughout SE and solid electrodes, and can accommodate the interfacial fluctuation and guarantee excellent adhesion at all time. The new formed solid-liquid-solid interfaces can also provide homogeneous current distribution and a decrease of the area specific resistance (ASR) because of the better contact. The low vapor pressure, high lithium ion conductivity, appropriate viscidity and nonflammable properties of IL [41–45], in this work, guarantees the stability and safety of all solid-state Li-S batteries. On this basis, the fabricated solid state Li-S cells can perform well at room temperature. A remarkable electrochemical behavior was performed with a high capacity of 300 mAh g^{-1} at 0.2 mA/cm^2. A high Coulombic efficiency above 98.7% was as well remained in the 60 cycles.

Garnet electrolyte is adopted as its high stability with Li metal and Li^+ conductivity. Fig. 1A schematically presents the original interface morphology between electrodes (Li metal and cathode disc) and garnet electrolyte in a Li-S cell. Here, the poor contact is obviously verified as the existing gaps, which indicates limited ion transport pathway for the garnet/Li interface. What is worse, the baleful corrosion section on Li anode will lead to a further deterioration, which is related to the nonuniform charge dispersion during Li metal cycling (stripping/platting procedures). After modified by IL intermediate, a perfect interface is achieved due to the good wettability between garnet electrolyte and electrodes (Li metal and cathode disc) in Fig. 1B. The new formed liquid-solid interphase contributes to the intimate contact without any gap, promoting effective local current distribution for the enhanced ion transport pathway. In addition, the flowable IL intermediate can quickly response to the interface fluctuation during Li metal cycling to meet a sustainable interface. Fig. 1C displayed the compared optical images of garnet electrolyte pellet with and without IL wetting. The amount of IL on one side of a ceramic pellet is trace (6 μL cm^{-2}) so as to wetting the surface without any effusion even though in the erected direction. The IL layer is ~2 μm which can be evaluated based on the grain radium (in Fig. S1).

AMIMTFSI (1-allyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide), a common room temperature ionic liquid, is used here. As the advanced liquid electrolyte solvent, it has received widely research due to the chemical stability, intrinsic nonvolatility and nonflammability [46–49]. In order to construct a stable interface, a wide stable electrochemical window (>4.5 V) is necessary to avoid the reaction with electrode materials, which was calculated in Fig. S5. The high ion conductivity (2.5×10^{-3} S cm^{-1}) was also calculated by the EIS (electrochemical impedance spectrum) measurement in Fig. S6 at room temperature (20 °C). Moreover, the excellent vapor pressure was assessed by fetching 15 μL AMIMTFSI and conventional liquid electrolyte (1 M LiTFSI in DOL and DME solvent) on two pieces of polished fresh lithium foil, respectively and restored in glovebox for three months at room temperature in Fig. S7. At the beginning, the room temperature IL well wetted the Li metal when dripped on the surface as like the organic electrolyte. Half an hour later, the distinct reduction for organic electrolyte was observed. The organic electrolyte completely evaporated in 1 h with solid salt left only. While, the IL is still retaining even after three months, which strongly exhibited its distinguished vapor pressure and nonvolatility.

The interface morphology was characterized by SEM (scanning electron microscope), as shown in Fig. 2 (A to D). For the original garnet/Li interface, the limited contact area could be found with the much void separating the Li metal and garnet ceramic (Fig. 2 A, B), even though the Li metal was melted on the garnet SE with a complicated heating procedure and cooled to room temperature

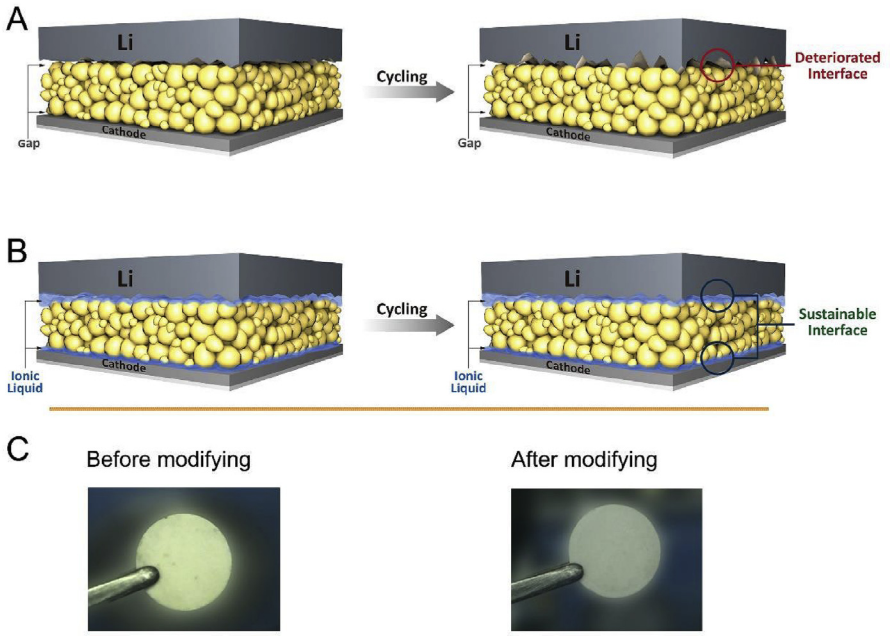

Fig. 1. Schematic diagram of the interface morphology between garnet electrolyte and Li metal in Li-S batteries. (A) The poor contact of the raw garnet/Li interface suffers from a deteriorated phenomenon during cycling. (B) A sustainable interface with excellent contact after IL wetting. (C) The optical images of garnet SE before/after with IL wetting.