Electronic Supplementary Material (ESI) for Materials Advances.

Supplementary Information for "Sulfide Glass Solid-State Electrolyte Separators for Li Metal Batteries: Using an Interlayer to Increase Rate Performance and Reduce Stack Pressure"

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S1. Supplementary Section

S1.1 Raman Spectroscopy

Raman spectroscopy was utilized for two experiments in this study and a description of our methods will be separated accordingly. In the first experiment, Raman spectroscopy was used to characterize the composition of pristine glass samples based on short range order (SRO) structural units. And in the second experiment, Raman spectroscopy was used to identify and quantify dissolved glass species in solutions prepared by immersing glass samples into a DME:DOL solvent mixture.

S1.1.1 Raman Spectroscopy to Characterize Glass Composition

Spectra for each glass composition were normalized to the lowest common background. All spectra were fit using the gaussian function in the range of 330 to 450 cm^{-1}, with peaks being ascribed to the vibrational modes of $(Si_2S_5)^{2-}$, $(SiS_4)^{-}$, $(P_2S_6)^{4-}$, $(P_2S_7)^{4-}$, or $(PS_4)^{3-}$ short range order (SRO) structural units. The best fits were obtained when the peak location and full width half maximum (FWHM) were given ± 1% of constraint as reported in previous studies[1]. In case of the peak fitting out of 1% were regarded as peak shifts. For each glass composition, the relative abundance of each SRO structural unit was calculated with respect to the total area of the fitted peaks.

S1.1.2 Raman Spectroscopy to Characterize Dissolved Species

Spectra for each glass composition were normalized to the strong ν(C-O or C-C) mode of DOL at 940 cm^{-1} (data not shown).[2] All spectra were fit using the gaussian function in the range of 330 to 520 cm^{-1}, with peaks ascribed to the vibrational modes of dissolved $(P_2S_6)^{4-}$, $(P_2S_7)^{4-}$, $(PS_4)^{3-}$, or

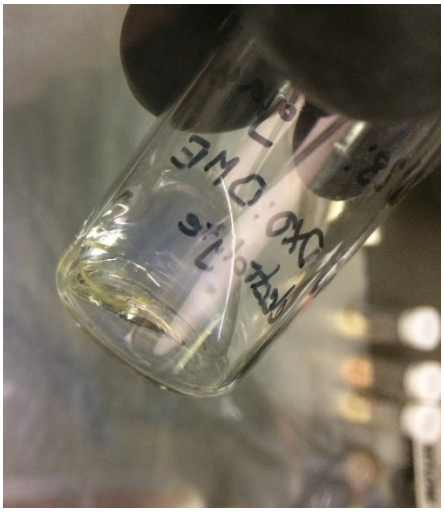
polysulfide species. In addition, two peaks at 365 and 396 cm^{-1} are ascribed to weak, unidentified vibrational modes of DME.[2] For each glass composition, the relative abundance of each glass species was calculated with respect to the total area of the fitted spectra. Because the fitted spectra includes contributions from DME peaks, the summation of dissolved species peak area does not equal 100%.

S2. Supplementary References

(1) Zhao, R.; Kmiec, S.; Hu, G.; Martin, S. W. Lithium Thiosilicophosphate Glassy Solid Electrolytes Synthesized by High-Energy Ball-Milling and Melt-Quenching: Improved Suppression of Lithium Dendrite Growth by Si Doping. *ACS Appl. Mater. Interfaces* **2020**, *12* (2), 2327–2337. https://doi.org/10.1021/acsami.9b16792.

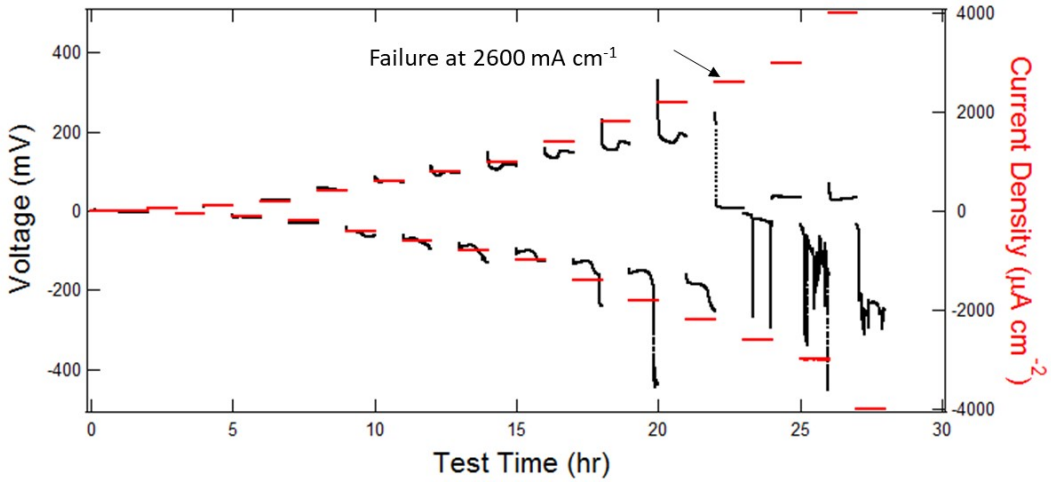
(2) Suo, L.; Zheng, F.; Hu, Y.-S.; Chen, L. FT-Raman Spectroscopy Study of Solvent-in-Salt Electrolytes. *Chinese Phys. B* **2015**, *25* (1), 16101.

S3. Supplementary Figures

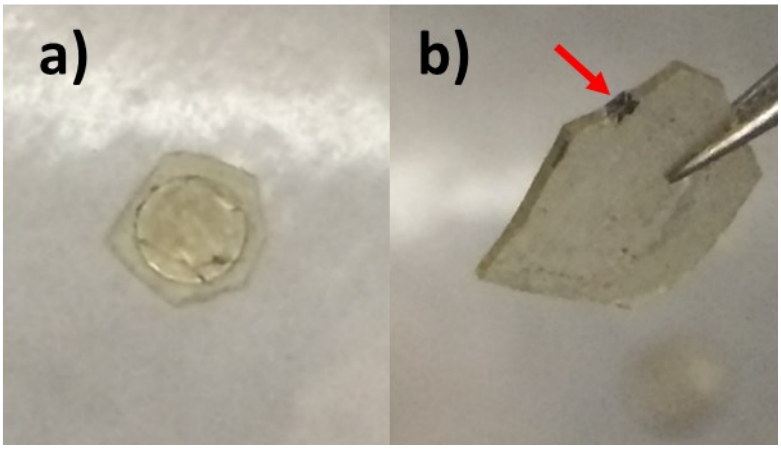


SFigure 1. Liquid electrolyte salts LiTFSI and $LiNO_3$ do not influence the insolubility of the $(Li_2S)_{60}(SiS_2)_{28}(P_2S_5)_{12}$ glass in 1:1 (v/v) DME:DOL. A glass sample immersed in liquid electrolyte for 2 years shows no sign of dissolution.

SFigure 2. The $(Li_2S)_{50}(GeS_2)_{45}(GeO_2)_5$ glass (second from left) is also insoluble in glass in 1:1 (v/v) DME:DOL after two weeks just like the $(Li_2S)_{60}(SiS_2)_{28}(P_2S_5)_{12}$ glass (first from left). As expected, a variety of $(Li_2S)_x(P_2S_5)_{100-x}$ glasses (right group) are soluble in DME:DOL as evidenced by the solution's yellow color and turbidity.



SFigure 3. Additional CCD experiment with a hybrid Li/LE/SSE/LE/Li test cell confirming the repeatability of our result.



SFigure 4. a) Picture of the Li/LE/SSE/LE/Li hybrid symmetric test cell after completion of CCD experiment. Failure was attributed to cracking a short circuiting. b) Picture of the $(Li_2S)_{60}(SiS_2)_{28}(P_2S_5)_{12}$ glass wafer with the Li metal electrodes removed. The red arrow points to the Li metal short (gray).