Supplementary Information

Unique Behaviour of Nonsolvents for Polysulphides in Lithium-Sulphur Batteries.

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Figure S1. The solubility of LiTFSI and Li_2S_6 in HFE was too low to be precisely titrated; therefore we report here physical-chemical metrics showing the absence of change in the density, viscosity and ionic conductivity of saturated solutions. Any measurable solubility would be expected to impact not any but all of these parameters.
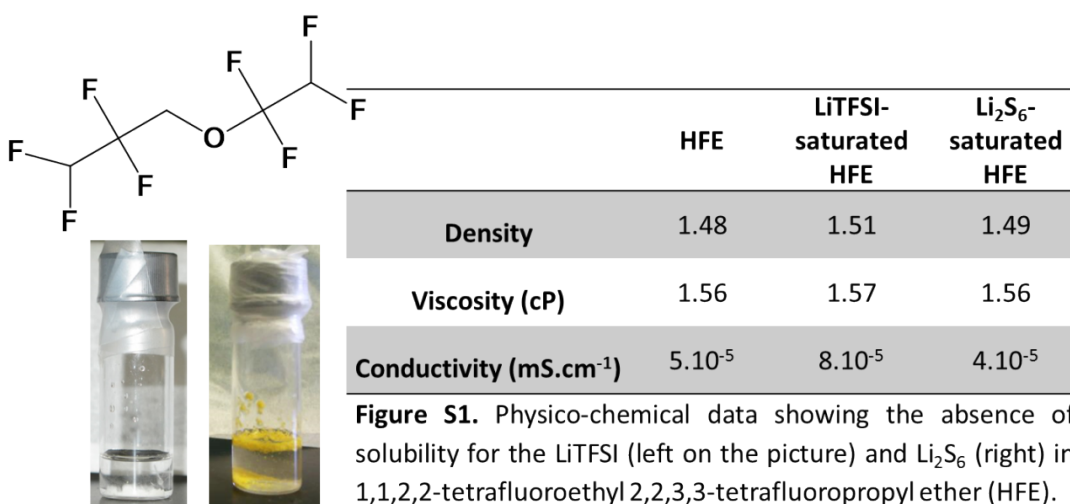

	HFE	LiTFSI-saturated HFE	Li_2S_6-saturated HFE
Density	1.48	1.51	1.49
Viscosity (cP)	1.56	1.57	1.56
Conductivity (mS.cm^{-1})	5.10^{-5}	8.10^{-5}	4.10^{-5}

Figure S1. Physico-chemical data showing the absence of solubility for the LiTFSI (left on the picture) and Li_2S_6 (right) in 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether (HFE).

Figure S2 . Physical properties of $(ACN)_2$:LiTFSI based electrolytes as a function of HFE volume fraction. **a.** viscosity compared to typical Li-S battery electrolytes and **b.** bulk (black) and molar (blue) ionic conductivities.
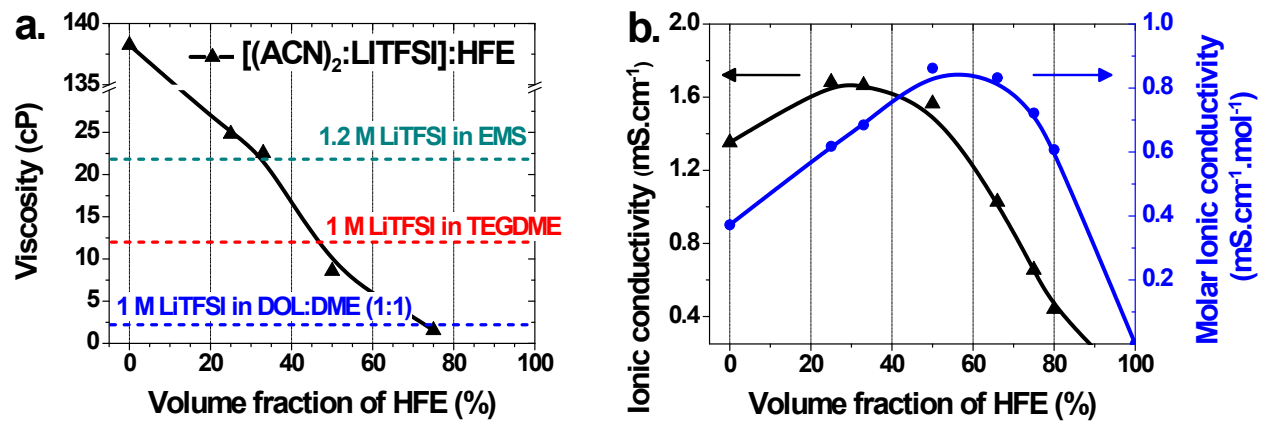
Figure S3a. Electrochemical impedance spectroscopy (EIS) Nyquist plots of Li-S full cells containing various ACN:HFE volume fractions at open circuit voltage.

The amplitude of the high frequency semi-circle typically depends on the possible formation of a SEI layer, but also on how the electrolyte wets the positive and negative electrodes which is linked mostly to its viscosity, and to a lesser extent, to its hydrophobicity. In pristine Li-S cells, it is commonly agreed that most of the impedance in this frequency domain comes from the sulphur electrode as confirmed in **Figure S3c**).
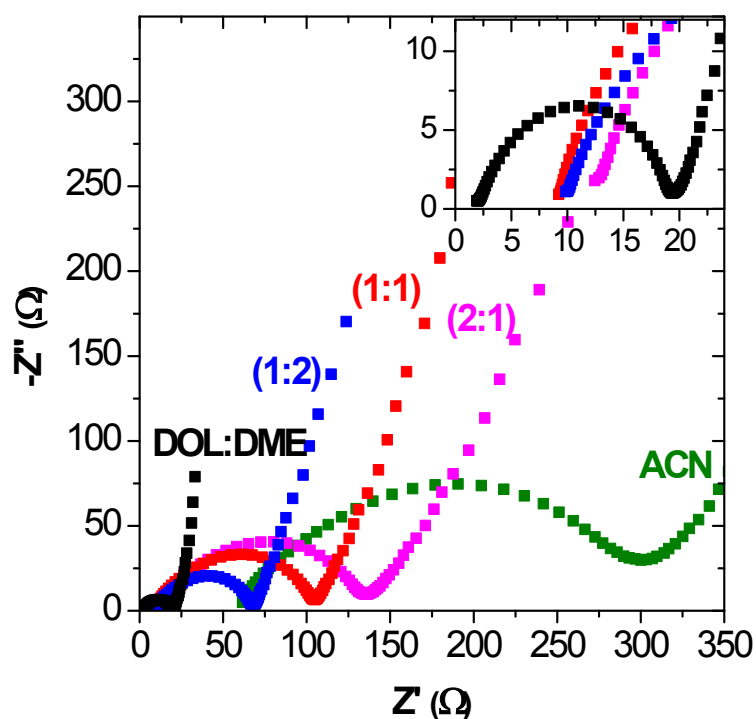
Figure S3b. Equivalent circuit used to fit the EIS diagrams, and the results of the fit for the electrolytes studied.
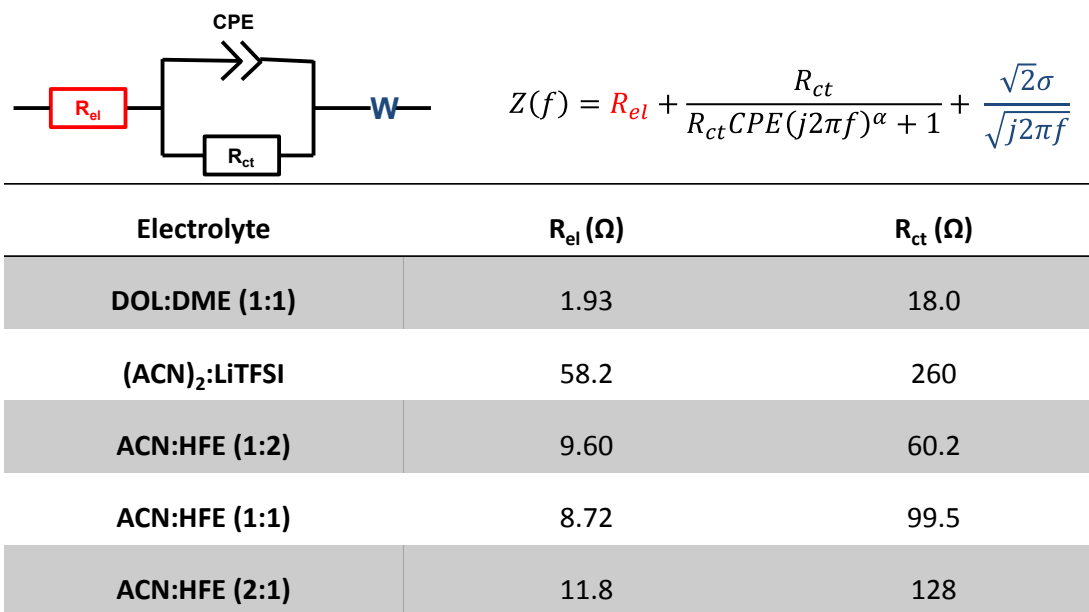

$$Z(f) = R_{el} + \frac{R_{ct}}{R_{ct}CPE(j2\pi f)^{\alpha} + 1} + \frac{\sqrt{2}\sigma}{\sqrt{j2\pi f}}$$

Electrolyte	R_{el} (Ω)	R_{ct} (Ω)
DOL:DME (1:1)	1.93	18.0
(ACN)$_2$:LiTFSI	58.2	260
ACN:HFE (1:2)	9.60	60.2
ACN:HFE (1:1)	8.72	99.5
ACN:HFE (2:1)	11.8	128

Figure S3c. Electrochemical impedance measured in a 3-electrode configuration after one full cycle in $(ACN)_2$:LiTFSI. Between 200 kHz and 20 mHz, the total impedance (black) is a good approximation of the impedance of the sulfur working electrode (red) and a pure resistance for the electrolyte (R_{el} = 82 Ω). Contribution from the lithium counter electrode (blue) is only significant at higher frequencies (not shown), so that the semi-circle measured on a full cell describes interfacial processes at the positive electrode (shifted red curve).
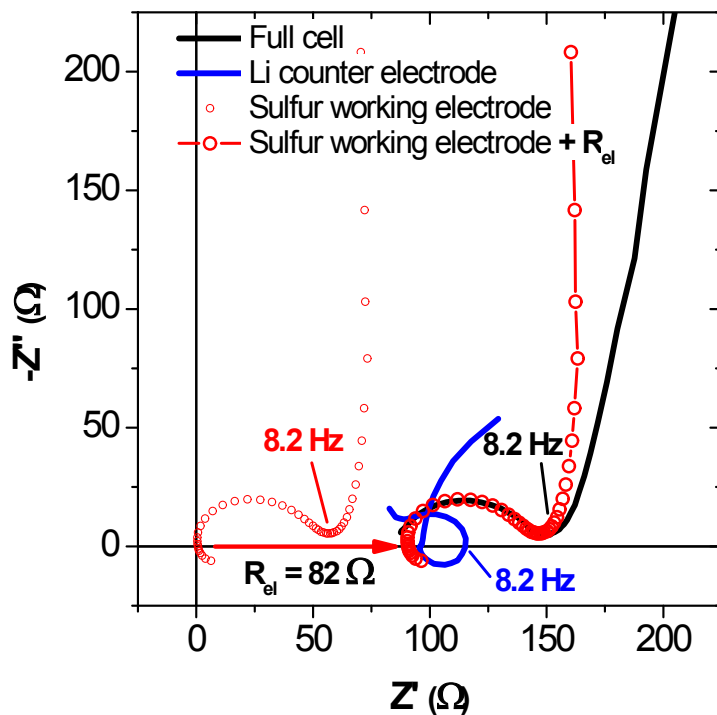
Figure S4. Photographs of separators from Li-S coin cells employing a DOL:DME **(a., black)** **or** an ACN:HFE **(b., red)** ACN:HFE electrolyte; arrows indicate the state of discharge where the cells were recovered. The absence of coloration in the ACN:HFE-containing cells supports the conclusion of negligible solubility/mobility of lithium polysulfides in such electrolytes.
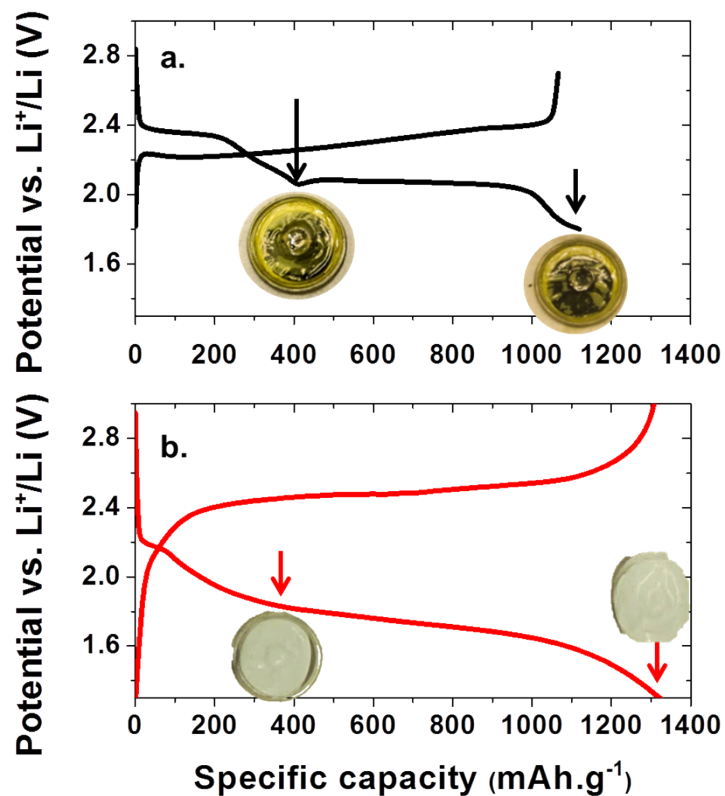
Figure S5. *Operando* XANES spectra showing the correction applied to the full cell (black) by subtraction of the electrolyte contribution (blue) in order to obtain quantitative spectra of the sulfur electrode upon discharge (red) in the **a.** initial state and **b.** fully discharged state. To optimize the signal/noise ratio in the energy range of interest (2465 – 2477 eV), the step size and integration time were varied during the scan (see Table below). XANES spectra were acquired every 1110 seconds so that the composition change between two spectra is about 50 mAh g^{-1}sulfur (i.e. 3% of the total capacity) at a cycling rate of C/10. Owing to carbon dilution, the density of sulfur in the 80 µm-thick electrode is only 50 mg cm^{-3} so that the absorption length at the S K-edge is increased from 2.4 µm (pure sulfur) to 60 µm in the carbon-rich composite electrode (i.e. half the thickness).

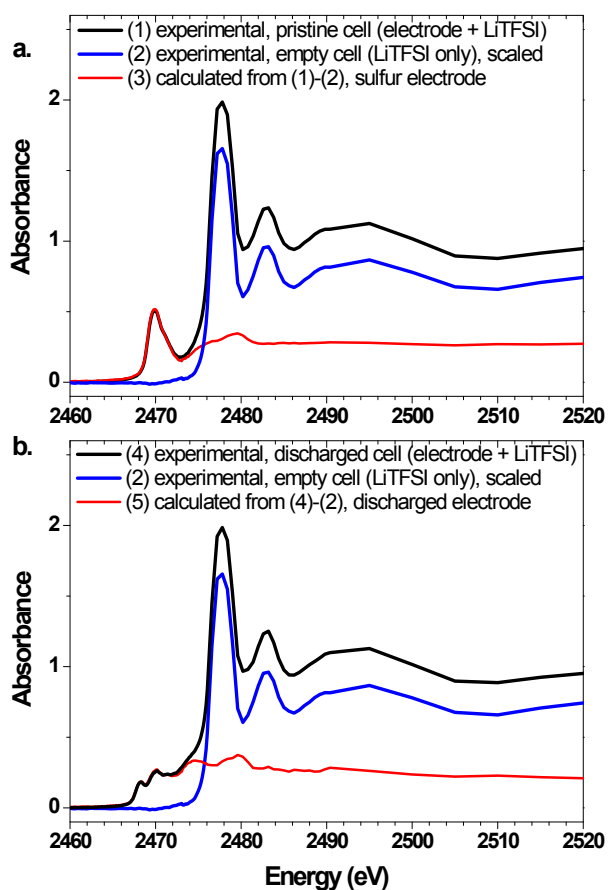| Start (eV)	Stop (eV)	Inc. (eV)	Time (s)
2430.00	2465.00	1.0	1
2465.00	2477.00	0.15	5
2477.00	2490.00	0.6	1
2490.00	2550.00	5.0	1

Figure S6. a. incremental capacity and **b.** voltage-composition discharge profile obtained by staircase voltammetry using DOL:DME (1:1) or ACN:HFE (1:1) electrolytes with a potential step of 5 mV/h.. Inserts in panel **a** show the raw chrono-amperograms normalized by the sulfur loading in the positive electrode. They were shifted in time to display the maxima in current response. In the case of ACN:HFE (1:1), two different limiting currents were used, namely C/50 (black) and C/100 (red).
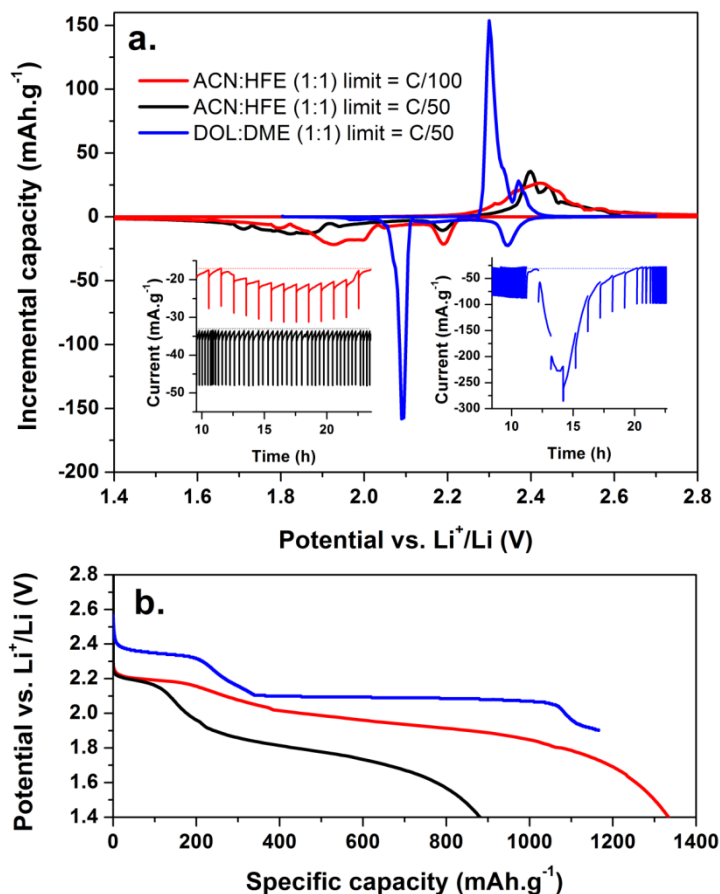
Figure S7. Galvanostatic intermittent titration (GITT) experiment in ACN:HFE (1:1) performed in a 3-electrode cell. The curve in black shows the potential of the sulfur working electrode (WE), while the blue curve shows the potential of the lithium counter electrode (CE), both *vs.* a lithium metal reference. The cycling protocol consists in C/10 current pulses for 20 min alternated with 60 min OCV periods. In the upper insert, the red curve corresponds to E(WE) – E(CE), i.e. the voltage measured in a standard 2-electrode coin cell as plotted in **Figure 8**. The lower insert shows E(CE) with an expanded scale. From the given example, it is clear that the polarization – or overpotential – is attributed to the sulfur/electrolyte interface (0.23 V, i.e. 95%) while the contribution of the lithium/electrolyte interface is minimal (0.012 V, i.e. 5%).