Can an inorganic coating serve as stable SEI for aqueous superconcentrated electrolytes?

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Supporting Information

-Solubility measurements details

-SEM observations

-GC-TCD/FID measurements in LP30 and WiSE-Al_2O_3 study by E-SEM

-Partial dissolution of LiF-coating layer when soaking in FEC, Li 1s and F 1s XPS measurements

-GC-TCD in WiSE

-Surface chemistry analysis after pre-soaking step, XPS meausurements

-Gas calculations

- Solubility measurements

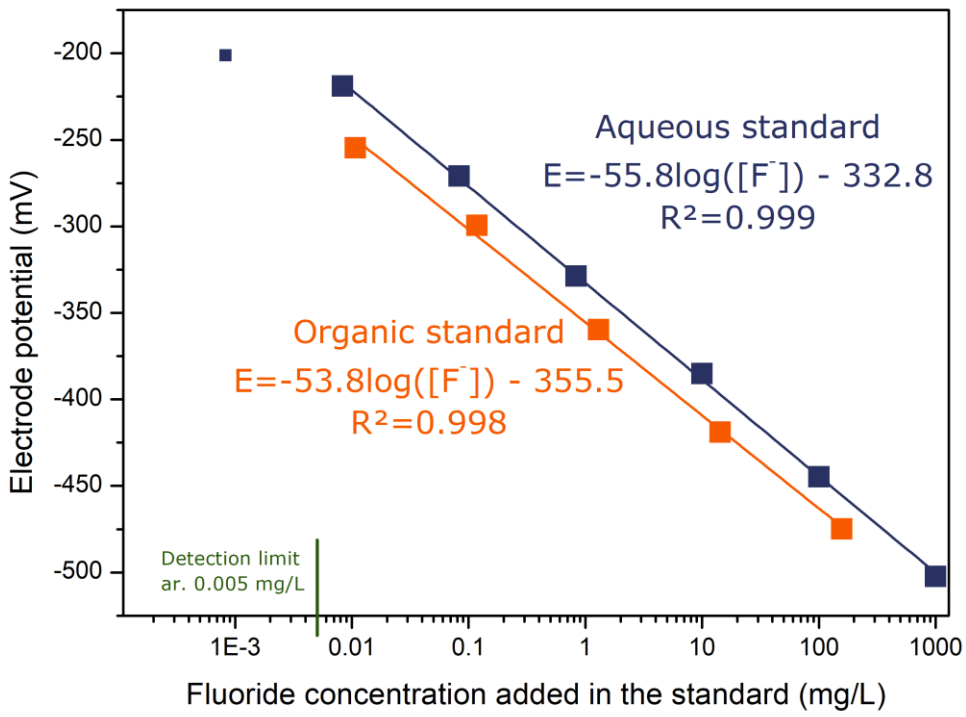

Figure S 1 Calibration curves obtained in aqueous and organic standards.

Table S 1 summarizes the solubility previously reported for LiF in pure solvents, either in alkylcarbonate ones or in water. The solubility of LiF was found to vary according to the solvent. Compared to the solubility of other SEI components such as lithium oxide (Li_2O) whose

solubility limit is found to be below 0.05 g / L [1], the solubility of LiF is relatively high in pure solvent.

Table S 1 LiF solubility limit found in literature in various solvents: water, EC, DMC, PC.

Solvent	LiF solubility at 25 °C (g / L)	LiF solubility at 40 °C (g / L)
H_2O	1.11 [2]	1.20 [2]
DMC	0.57 [2] $4 \cdot 10^{-3}$ [3]	
PC	0.14 [2]	0.21 [2]
EC		5.52 [2]

The difference in solubility limit of two orders of magnitude in dimethyl carbonate (DMC) between the two different report is explained by differences in the protocol, especially regarding the filtration technique leading to a colloidal or non-colloidal solution [1].

- *Solubility decrease with the initial increase of [Li^+]*

The constant of dissolution of LiF in an aqueous solution can be expressed following the equilibrium described in equation (1):

$$LiF(s) = Li^+\,(aq) + F^-(aq) \quad (1)$$

$$K_s = a_{Li+}a_{F-}$$

$$Ks = \gamma_{Li+}\,[Li^+] * \gamma_{F-}[F^-]$$

$$K_s = \gamma_{Li+}\gamma_{F-} * [Li^+][F^-]$$

Furthermore, knowing the following relationship regarding the activity coefficients of ions in solution:

$$\gamma_{Li+}\gamma_{F-} = {\gamma_{Li+F-}}^2$$

The expression for the constant of dissolution becomes:

$$K_s = {\gamma_{Li+F-}}^2 * [Li^+][F^-]$$

The fluoride and lithium ions concentration can be expressed as follow:

$$[Li^+] = [Li^+]_{electrolyte} + [Li^+]_{lim}$$

$$[F^-] = [F^-]_{lim}$$

$$\text{with } [Li^+]_{lim} = [F^-]_{lim}$$

Where $[Li^+]_{electrolyte}$ is the initial concentration of Li^+ cation due to the LiTFSI concentration in solution (i.e. 1 mol / kg, 3 m, 5 m, 7 m, 10 m, 15 m, 20 m), $[F^-]_{lim}$ is the solubility limit of fluoride measured by the ISE electrode and $[Li^+]_{lim}$ is the concentration of Li^+ cation added during the LiF dissolution in the electrolyte.

Considering the high initial [Li^+] in the bulk electrolyte (>1 mol /kg i.e. 0.87 mol / L) and the measured fluoride solubility limit (< 1 g / L i.e. 0.05 mol / L) , [Li^+] can be simplified as follow:

$$[Li^+] = [Li^+]_{electrolyte}$$

Therefore,

$$[F^-]_{lim} = \frac{K_s}{\gamma^2_{Li+F-} * [Li^+]_{electrolyte,initial}} \quad (2)$$

- LiF coating characterization

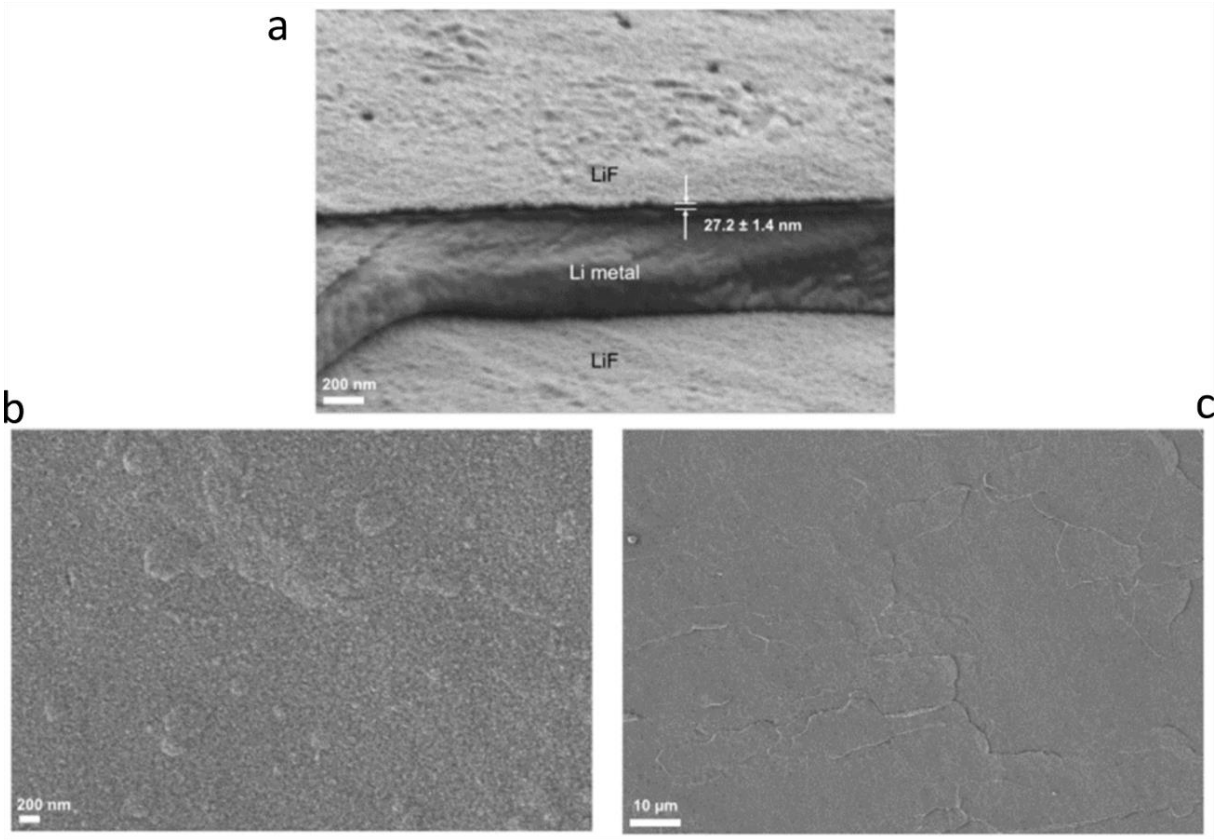

Figure S 2 Scanning electron microscopy (SEM) images (a)Cross section SEM image of a Li/LiF pristine sample. Top-view SEM images of a Li/LiF pristine sample, high magnification (b), low magnification (c).

The thickness of the coating is to be 27.2 +- 1.4 nm. Furthermore, He *et al.* [4] has shown by XRD measurements that Li/LiF films formed using a similar methodology, but with longer reaction times (which allows a thicker coating to grow), are crystalline. Thus, our artificial SEI has a nanoscopic polycrystalline SEI, with comparable thickness to native Li SEIs.

- *LP30 GC-FID gas identification*

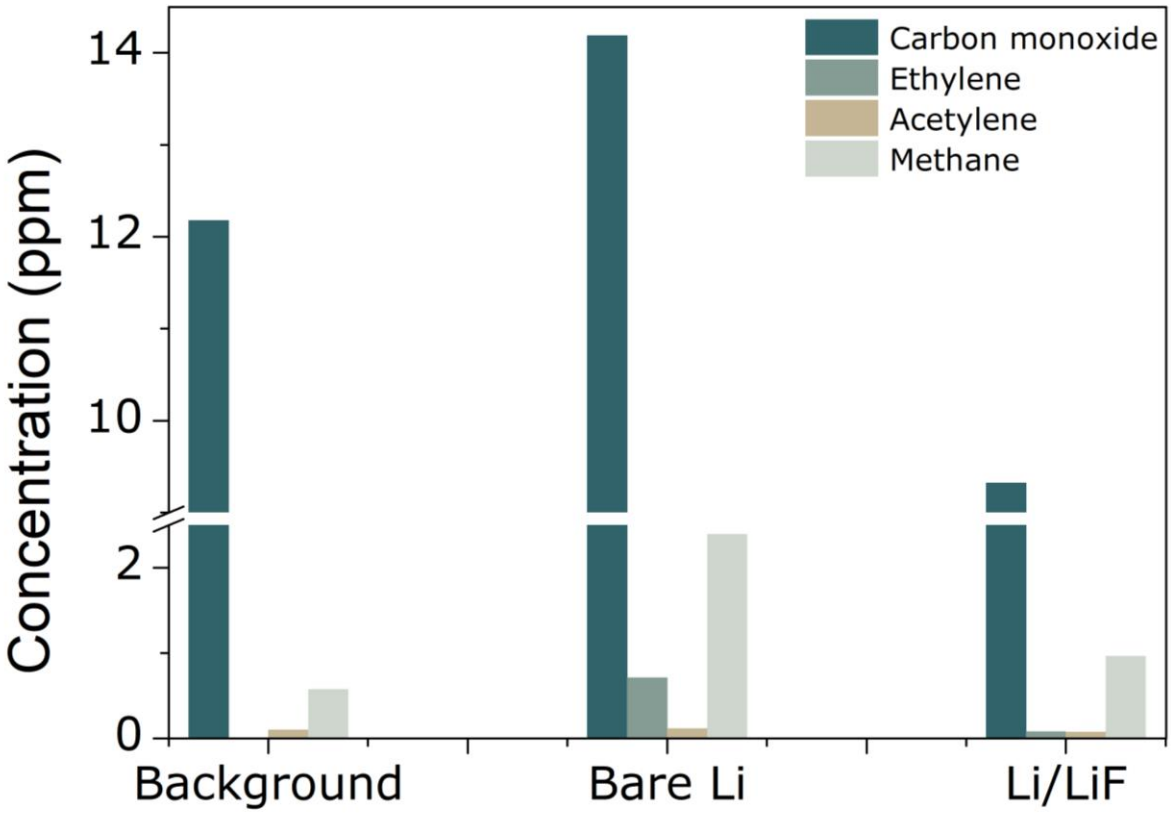

Figure S 3 Concentration in Carbon monoxide (dark blue), ethylene (light blue), acetylene (yellow) and methane (grey) when exposing Li-coated LiF or bare metallic Li samples to LP30 electrolyte during 15 min.

- *Al_2O_3 coating*

Having established that the major issue facing a native SEI relying on the formation of LiF is the lack of self-passivation observed in aqueous superconcentrated electrolytes rather than the LiF solubility, we explored the protective power of an artificial SEI composed of a conformal Al_2O_3 layer prepared by atomic layer deposition (ALD) onto metallic Li electrodes. Environmental SEM measurements were first performed on a 2 nm and a 10 nm thick Al_2O_3-coated metallic Li sample (Figure S 4a). As seen before exposure to moisture, Al_2O_3 coating prepared by ALD forms a granular and textured coating on the surface of Li, alike the

microstructure previously reported elsewhere for a similar coating[5]. Nevertheless, when gradually increasing the water partial pressure from 0 to 90 % RH, obvious degradations are observed starting at 30 % RH for the 2 nm thick coating (Figure S 4, top row). Bearing in mind that Al_2O_3 does not dissolve in pure water, this change in microstructure from granular to a cauliflower-like can arise from two effects. First, Al_2O_3 can gradually transform to $Al(OH)_3$, this phase transformation inducing a change in molar volume (from 403 mol/cm^3 for Al_2O_3 to 188.8 mol/cm^3 for $Al(OH)_3$, i.e. a contraction of 6 % in volume). Second, the granular morphology of the Al_2O_3 coating itself can induce reactivity of the underneath Li electrode. In other words, the granular morphology of the 2 nm Al_2O_3 coating prepared by ALD does not prevent water from accessing Li. Therefore, a thicker coating of 10 nm was then prepared, but similar degradation was observed, with a cauliflower-like structure being formed upon increased relative humidity (Figure S 4, bottom row), again associated with the formation of LiOH and $LiOH.H_2O$.

To further understand the reactivity of Al_2O_3-coated metallic Li in contact with superconcentrated aqueous electrolytes, GC-TCD measurements were performed alike the ones carried out for the LiF-protected samples. Upon exposure to 20 m LiTFSI, a constant evolution of H_2 is observed during 2 hours with a concentration of ar. 0.15 % of H_2 in the headspace (Figure S 4b). While this concentration is much smaller than the one observed previously with the LiF-protected Li electrode (Figure 3b), once normalized by the amount of Li taking into account the surface and the thickness of the metallic Li electrode, one can estimate that 18 % of the metallic Li was consumed by the reaction. Thus, as observed by operando SEM and postmortem XRD, the conformal coating of Al_2O_3 does not prevent metallic Li from reacting with WiSE aqueous electrolyte but slows down the reaction. Finally, alike for LiF-protected samples, upon exposure to 20 m LiTFSI : 8 m LiBETI electrolyte, the

concentration of H_2 measured by GC-TCD is 2 to 3 times lower than that measured in 20 m LiTFSI electrolyte. Nevertheless, the concentration of gas keeps increasing upon measurement, indicating a continuous degradation of the coating and a greater reactivity of the underneath Li electrode. Eventually, 6.4 % of Li is estimated to be consumed after 2 hours.

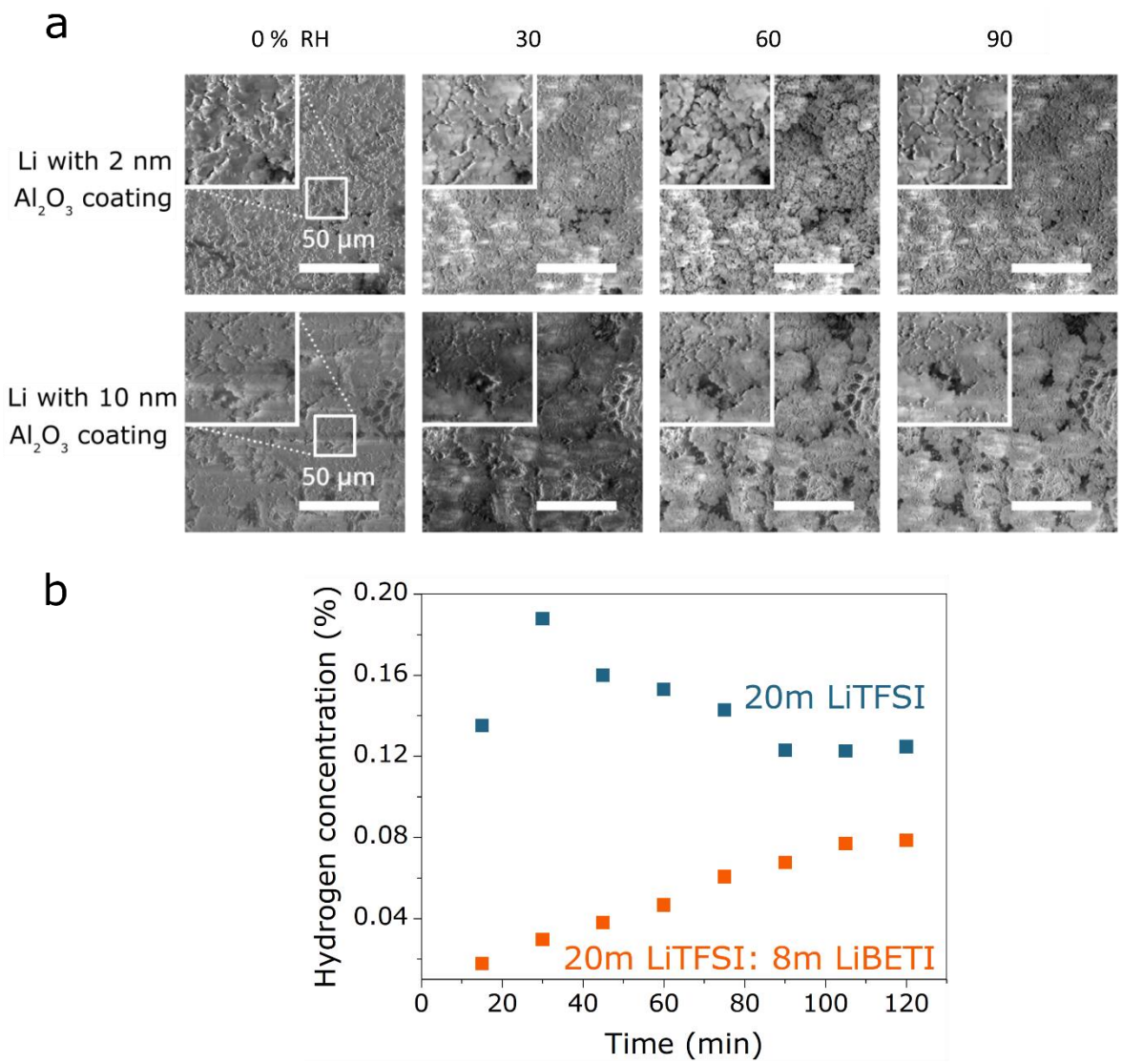

Figure S 4 (a) SEM images for 2 nm (top) and 10 nm (bottom) Al_2O_3 coated metallic Li taken successively at 0, 30, 60 and 90 % RH with zoom-ins. (b) Gas evolution as a function of time for 10 nm Al_2O_3-coated metallic Li samples after exposure to 20 m LiTFSI (*blue*) and 20 m LiTFSI : 8 m LiBETI (*orange*) aqueous superconcentrated electrolytes.

- Partial dissolution of LiF-coating layer when soaking in FEC, Li 1s and F 1s XPS measurements

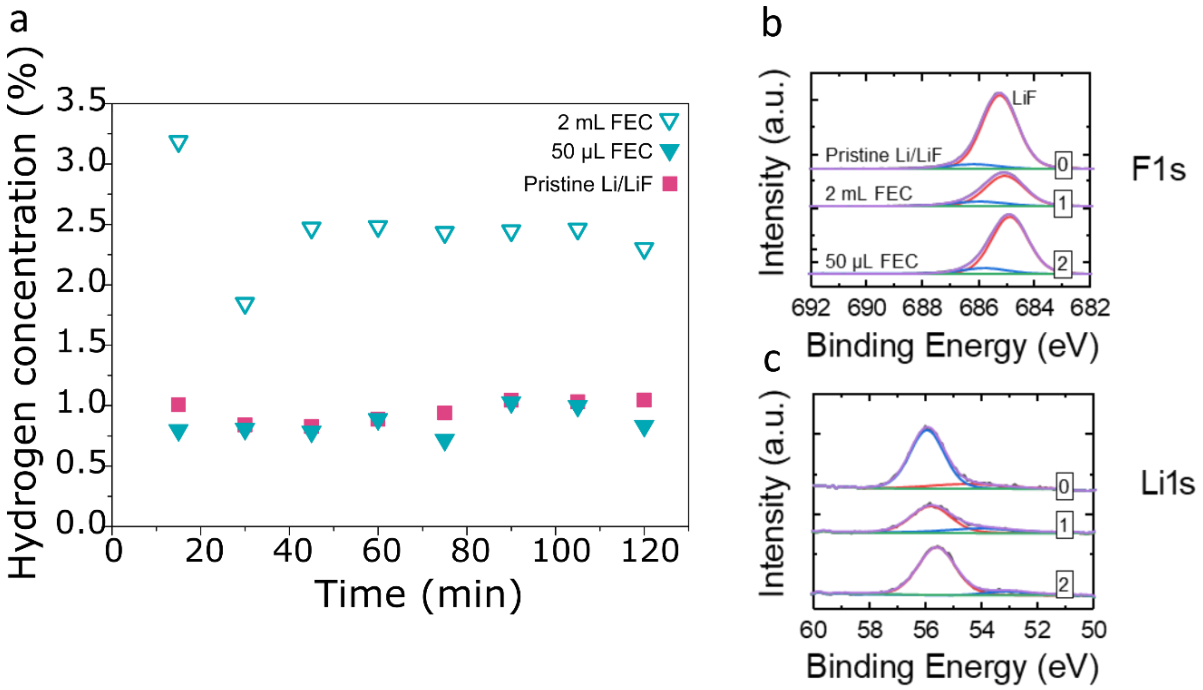

Figure S 5 (a) Hydrogen evolution as function of time for pristine Li/LiF sample (pink), pre-soaked in 2 mL FEC (light blue, empty triangle), pre-soaked in 50 µL FEC (light blue, full triangle) prior to exposure to 20 m LiTFSI : 8 m LiBETI aqueous superconcentrated electrolyte electrolyte (WiBS). X-ray photoelectron spectroscopy (XPS) spectrum of (b) F 1s and c. Li 1s of pristine Li/LiF (0), pre-soaked Li/LiF sample in 2 mL FEC (1), pre-soaked Li/LiF sample in 50 µL FEC (2).

- Surface chemistry analysis after pre-soaking step, XPS measurements

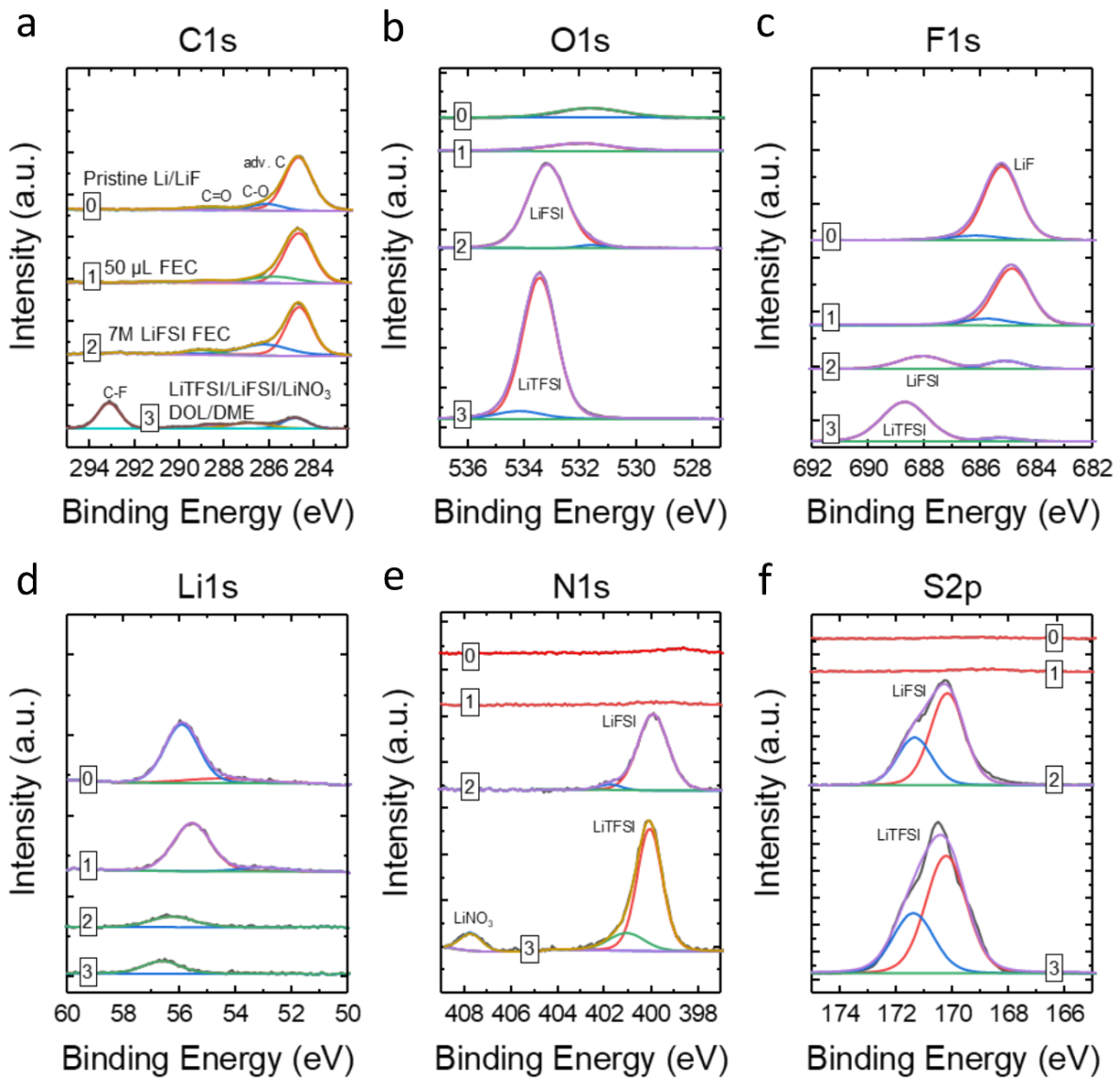

Figure S 6 X-ray photoelectron spectroscopy (XPS) spectrum of (a) C 1s, (b) O 1s, (c) F 1s, (d) Li 1s, (e) N 1s, (f) S 2p of pristine Li/LiF (0), pre-soaked in 50 µL FEC (1), pre-soaked in 7 M LiFSI (2) and pre-soaked in 2 M LiFSI : 1 M LITFSI in DOL/DME, 3 % $LiNO_3$ (3).

- *Li/LiF coating exposure to WiSE, GC-TCD experiment*

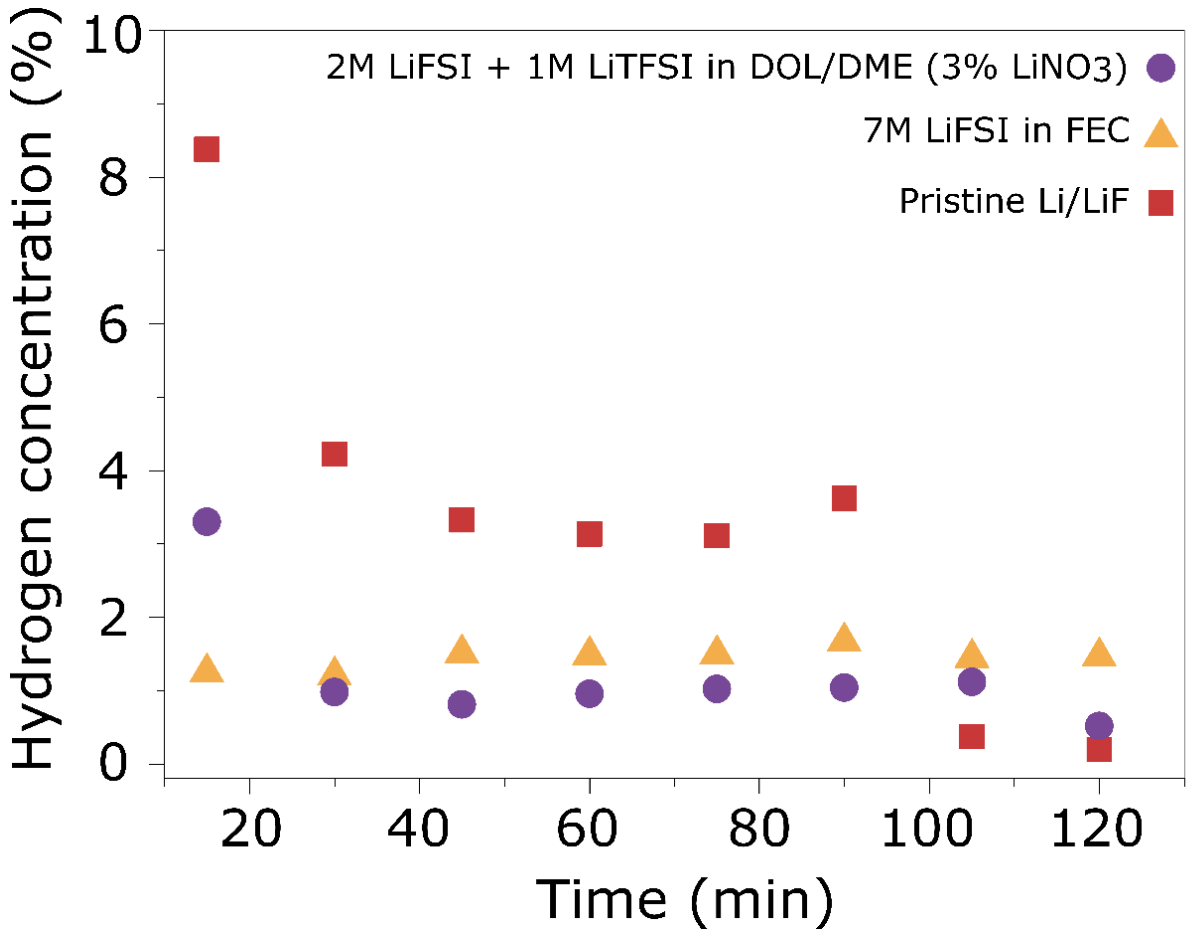

Figure S 7 Hydrogen evolution as function of time for pristine Li/LiF sample (red), pre-soaked in 7 M LiFSI in FEC (yellow), pre-soaked in 2 M LiFSI : 1 M LiTFSI in DOL/DME (purple) prior to exposure to 20 m LiTFSI aqueous superconcentrated electrolyte (WiSE).

The Li consumption of LiF-coated Li samples exposed to WiSE fades from 74 % for the pristine sample to 27 % in 1 M LiTFSI : 2 M LiFSI in DOL/DME and 33 % in 7 M LiFSI in FEC, respectively. Furthermore, trends observed for both organic electrolytes are similar than in WiBS. In details, after 15 min exposure to WiSE, the hydrogen concentration measured for the sample soaked in 1 M LiTFSI : 2 M LiFSI in DOL/DME increases to ar. 3 % then stabilizes at ar. 1 % while it is mostly constant during the two hours experiment after soaking in 7 M LiFSI in FEC. However, one can notice that although the decrease of Li consumption is significant, the differences recorded between these two soaking steps is less remarkable than in WiBS and the Li

consumption is still greater than the one of the Li/LiF sample exposed to WiBS. One possible explanation would be the difference of kinetics for such electrolyte penetration being dependent on its viscosity and the mass transport across the microporosity and/or cracks leading to a faster access of water in the case of WiSE and preventing from greater performances.

- Gas calculation

Based on the GC-TCD results, one can assess the consumption of Li after the sample had been exposed 120 min to WiSE or WiBS.

Table S 2 Experimental parameters

Volume of the cell Vcell (mL)	Total pressure Ptot (bar)	Temperature T (°C)	Ideal gas constant R (J/(mol.K))	Thickness of Li foil* e (µm)		Diameter of Li foil Ø (mm)		Li density ρ (g/cm³)	Molar mass of Li M (g/mol)
5.5	3.06	20	8.314	LiF	Al_2O_3	LiF	Al_2O_3	0.534	6.941
				100	30.5	9	7		

*based on SEM observation

$$n_{cell}^{gas} = \frac{Ptot * Vcell}{R * T} = 689.8\ \mu mol$$

$$n_{Li\ foil} = \frac{\rho * \pi * Ø^2 * e}{4 * M} = 489\ \mu mol\ (LiF)\ or\ 90\ \mu mol\ (Al_2O_3)$$

$$n_{Hydrogen} = n_{cell}^{gas} * x_{Hydrogen}$$

$$Ratio\ of\ Li\ consumed = \frac{2 * n_{Hydrogen}}{n_{Li\ foil}}$$

*The molar ratio of hydrogen ($x_{Hydrogen}$) is obtained from the sum of the amount of H_2 measured after each 15min interval.

$$2H_2O + 2e^- \rightarrow 2HO^- + H_2$$
$$Li \rightarrow Li^+ + e^-$$
$$H_2O + Li \rightarrow LiOH + \frac{1}{2}H_2$$

Table S 3 Aqueous superconcentrated electrolytes properties

	WiSE	WiBS
Density (g/mL)	1.696	1.783[2]
Mass ratio of water (W_{H2O})	0.148	0.10
Amount of water in 250 µL of electrolyte (mmol)	3.49	2.48

LiF sample:

$$n_{Li\ foil} = 489\ \mu mol$$

Table S 4 Consumption of Li after exposure to 20 m LiTFSI (WiSE) for the Li/LiF-coated samples: pristine, pre-soaked in 7 M LiFSI in FEC or 2 M LiFSI : 1 M LiTFSI in DOL:DME, 3 % $LiNO_3$ assuming HER as sole source for hydrogen evolution in Li consumption ratio calculation.

Exposure to 20 m LiTFSI	Molar ratio of H_2 (after 120 min) $x_{Hydrogen}$(%)	Amount of H_2 released (after 120 min) $n_{Hygrogen}$ (µmol)	Ratio of Li consumed (after 120 min) (%)
Li/LiF pristine	26.35	182	74
Li/LiF pre-soaked in 7 M LiFSI in FEC	11.53	80	33
Li/LiF pre-soaked in 2 M LiFSI : 1 M LITFSI in DOL/DME, 3% $LiNO_3$	7.94	67	27

Table S 5 Consumption of Li after *exposure* to 20 m LiTFSI : 8 m LIBETI (WiBS) for the Li/LiF – coated pristine Li/LiF, pre-soaked in 2 mL FEC, pre-soaked in 50 µL FEC, pre-soaked in 7 M LiFSI in FEC or 2 M LiFSI : 1 M LiTFSI in DOL:DME, 3 % $LiNO_3$ assuming hydrogen evolution only caused by HER in Li consumption ratio calculation.

Exposure to 20 m LiTFSI : 8 m LiBETI	Molar ratio of H_2 (after 120min) $x_{Hydrogen}$(%)	Amount of H_2 released (after 120min) $n_{Hygrogen}$ (µmol)	Ratio of Li consumed (after 120min) (%)
Li/LiF pristine	7.63	53	22
Li/LiF pre-soaked in 2 mL pure FEC	19.6	135	55
Li/LiF pre-soaked in 50 µL pure FEC	6.85	47	19
Li/LiF pre-soaked in 50 µL of 7 M LiFSI in FEC	1.41	10	4
Li/LiF pre-soaked in50 µL of 2 M LiFSI + 1 M LITFSI in DOL/DME, 3% $LiNO_3$	6.44	44	18

Al_2O_3 sample:

$$n_{Li\,foil} = 90\ \mu mol$$

Table S 6 Consumption of Li after exposure to 20 m LiTFSI (WiSE) or 20m LiTFSI : 8 m LiBETI (WiBS)

	Molar ratio of H_2 (after 120min) $x_{Hydrogen}$(%)	Amount of H_2 released (after 120min) $n_{Hygrogen}$ (µmol)	Ratio of Li consumed (after 120min) (%)
Li/LiF exposed to 20m LiTFSI	1.15	7.933	18
Li/LiF exposed to 20m LiTFSI : 8m LiBETI	0.416	2.867	6.4

- **Estimation of cycle life considering the water consumption assess by GC-TCD**

Table S 7 Estimation of water and Li consumption according to the gassing measured by GC-TCD

Case	LiF-coated Li, cracks filled with 7M LiFSI in FEC, exposure to WiSE	LiF-coated Li cracks filled with 7M LiFSI in FEC, exposure to WiBS	Mo_6S_8 electrode used in WiSE
Water consumption ($\mu mol_{H_20}/h$)	80	10	0.1
Water amount in 250 µL of electrolyte (mmol)	3.49	2.48	3.49
Time (h) needed to consume water	44	248	35 000
Number of cycle considering 1C C-rate (1 Li^+ inserted / h)	<50	<250	8750
Li amount used in the study (µmol)	489	489	/
Time (h) needed to consume Li	6.1	48.9	/

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