Interfacial Tuning of Sulfohalide Electrolytes by $LiBF_4$ for Stable Lithium Metal Batteries

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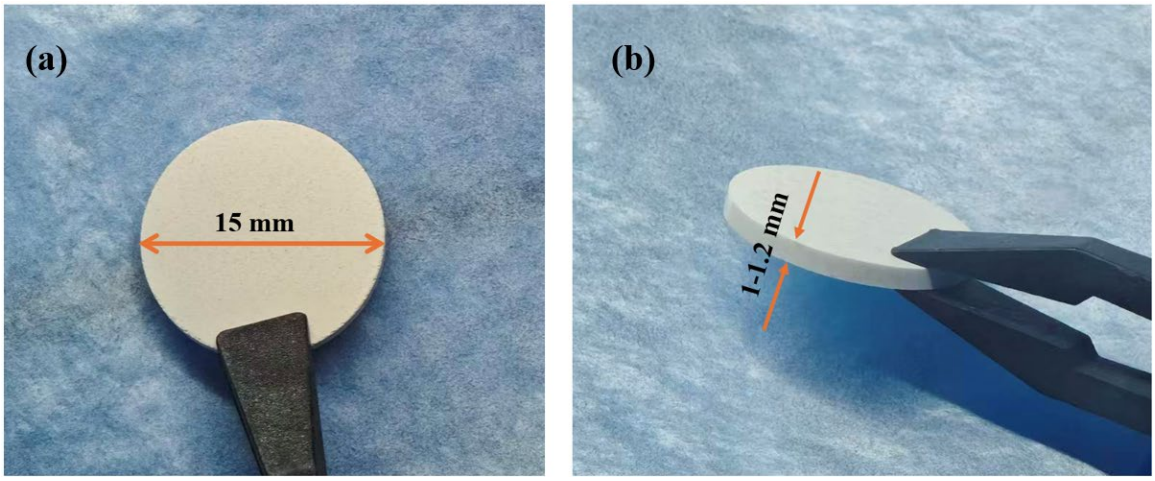

Figure S1. (a) Diameter and (b) thickness of the typical cold-pressed LSC@BF solid electrolyte pellet.

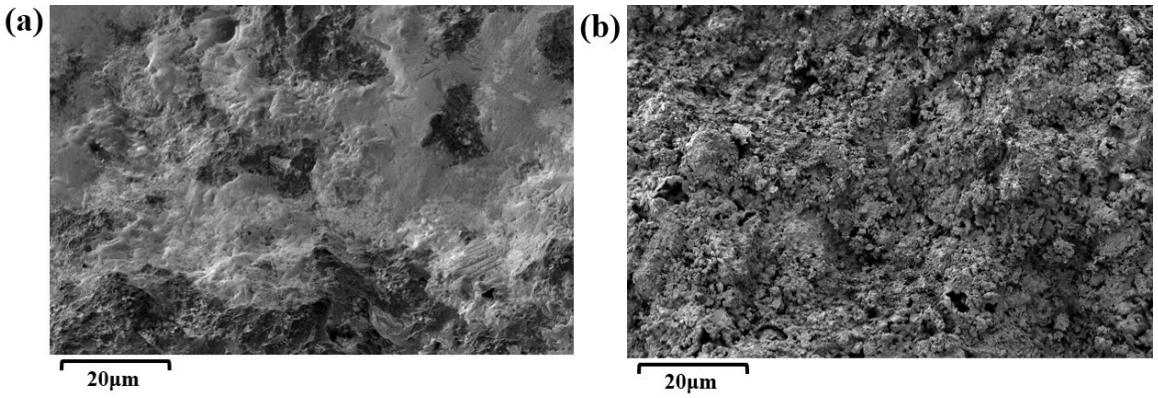

Figure S2. FESEM images of pelletized (a) LSC@BF and (b) LSC.

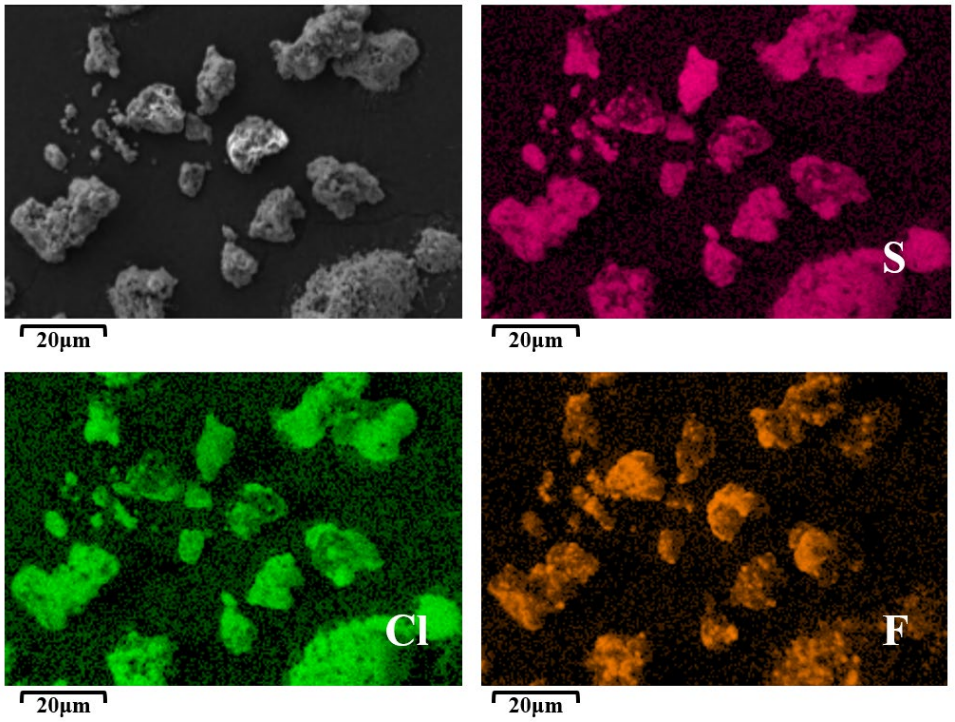

Figure S3. EDS elemental mapping images of LSC@BF SSE.

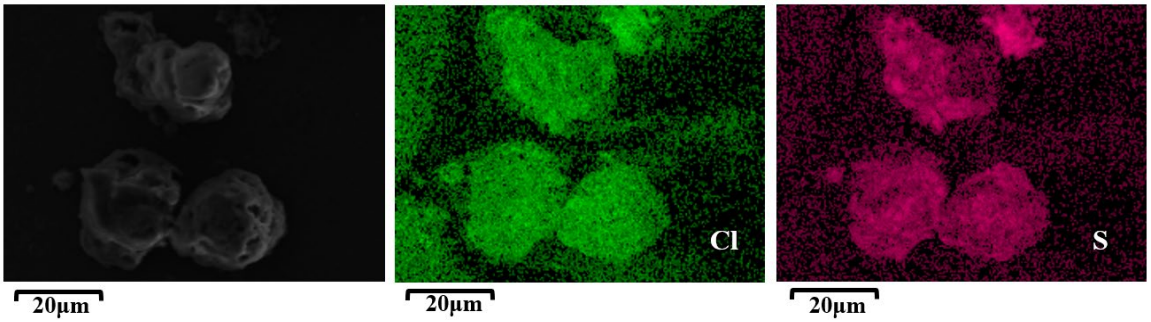

Figure S4. EDS elemental mapping images of LSC SSE.

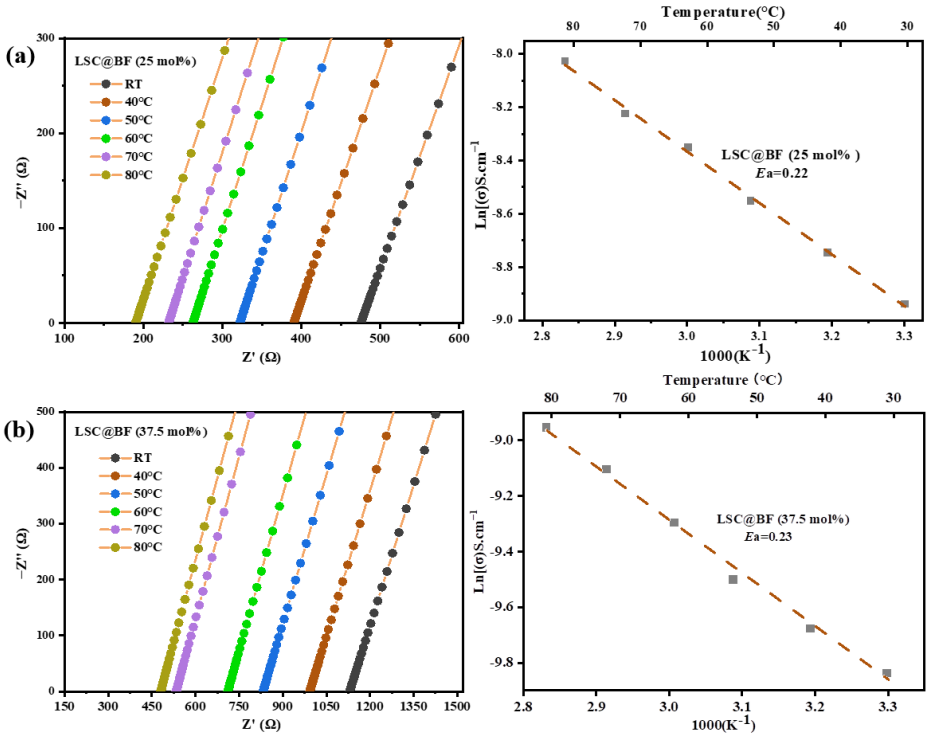

Figure S5. (a) EIS Nyquist plots of LSC@BF SSE at higher $LiBF_4$ content, and their corresponding Arrhenius plots.

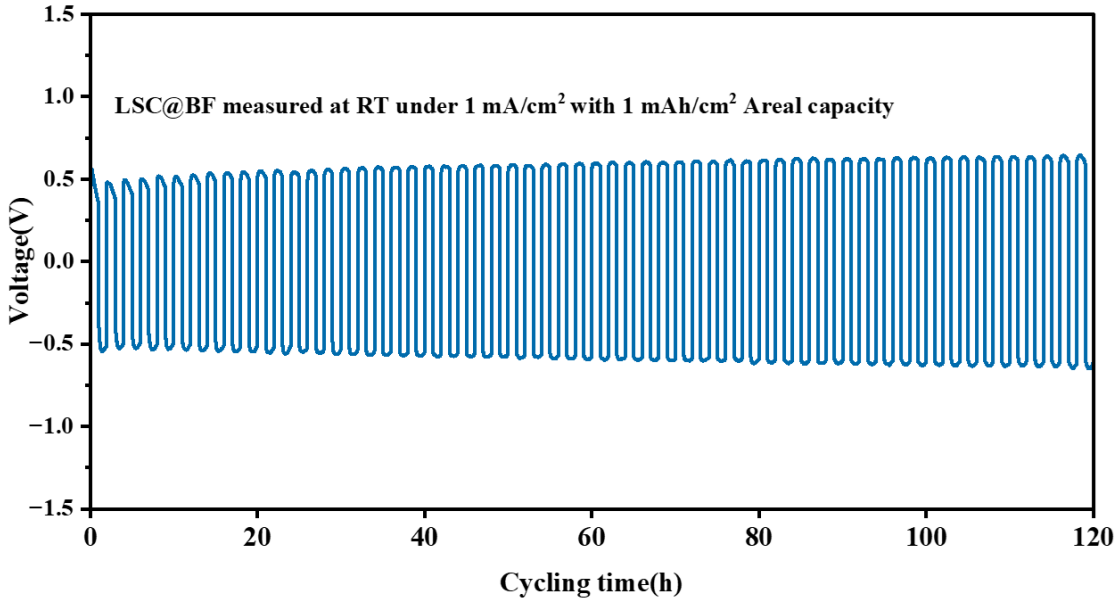

Figure S6. Li plating/stripping of LSC@BF in Li symmetric cells cycled at 1 mA cm^{-2}.

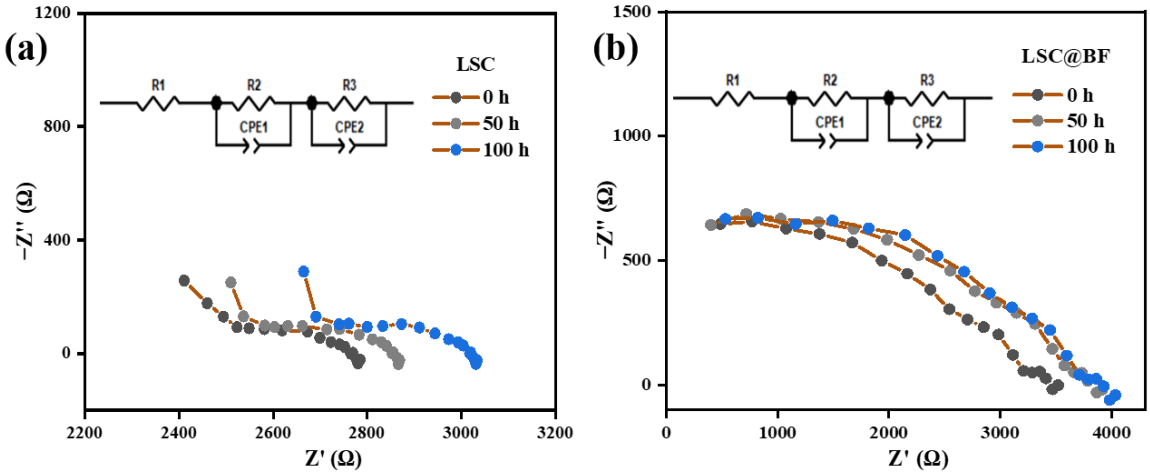

Figure S7. Nyquist plot before and after cycling for 100 h in a cell using (a)LSC and (b)LSC@BF.

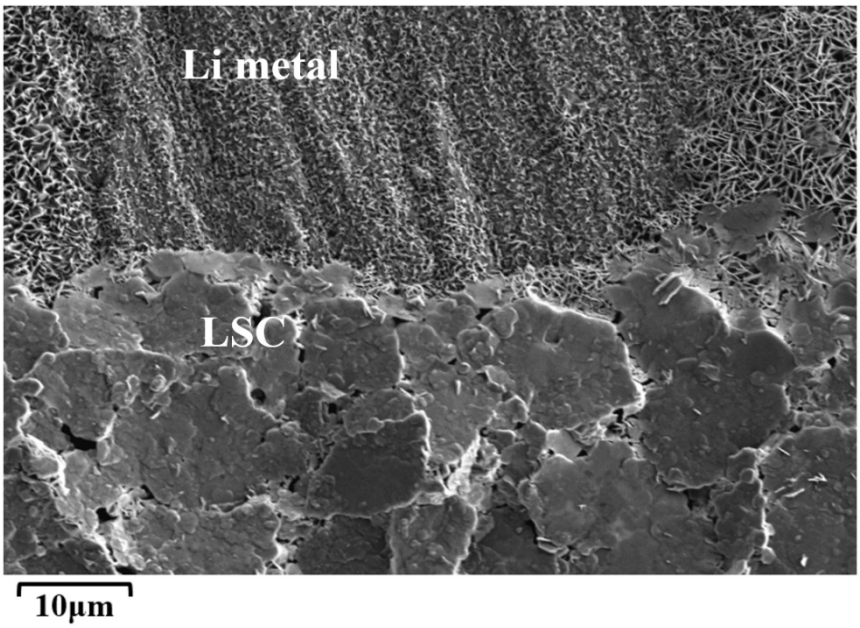

Figure S8. The cross-section FESEM image of the Li|LSC interface after cycling for 100 h at 0.1 mA cm^{-2}.

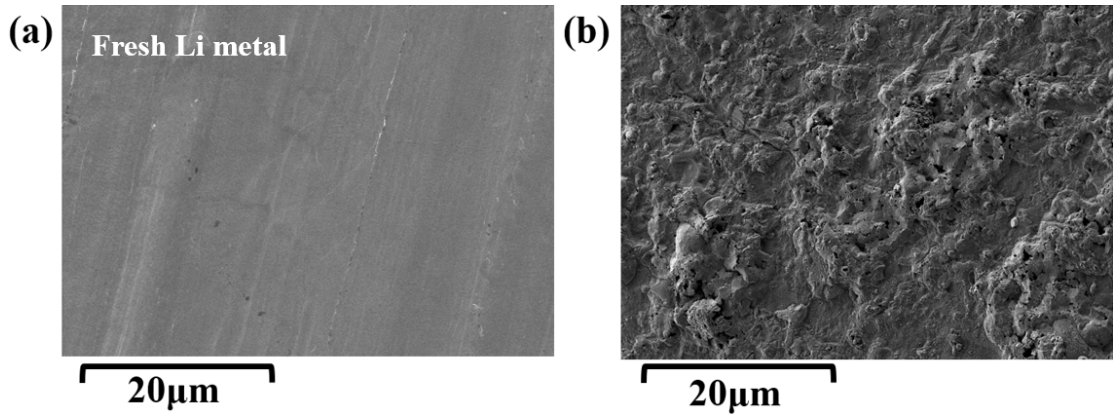

Figure S9. FESEM images of (a) fresh Li metal surface morphology, (b) Li metal surface morphology after cycling for 100 h with LSC at 0.1 mA cm^{-2}.

Table S1. Ionic transport comparison of our SSEs with other thio-halides and other fluorinated SSEs at room temperature.

SSEs	Bulk ionic conductivity (S cm^{-1})	Activation energy (eV)	References
LSC	4.44×10^{-4}	0.21	This work
Li_6PS_5Cl	4.96×10^{-3}	0.34	Ref. [1]
Li_4SnS_4	7.0×10^{-5}	0.41	Ref. [2]
$Li_7Ge_3PS_{12}$	1.1×10^{-4}	0.26	Ref. [3]
LSC@BF	4.32×10^{-4}	0.22	This Work
$LSCF_{0.25}$	3.38×10^{-4}	0.23	Ref [4]
$LiBH_4$@$LiBF_4$	0.9×10^{-5}	No report	Ref. [5]
LAGP@$LiBF_4$	3.21×10^{-4}	0.37	Ref. [6]
LATP@$LiBF_4$	8.5×10^{-4}	No report	Ref. [7]
$Li_4(BH_4)_3I$@SBA-15	2.5×10^{-4}	0.46	Ref. [8]
$LiBF_4$@Li_2S@LiCl	1.19×10^{-6}	0.28	Ref. [9]

Table S2. Ionic conductivity and activation energy values comparison of LSC@BF SSEs with different $LiBF_4$ content tested at room temperature (RT), 50℃ and 70℃.

$LiBF_4$ in LSC@BF (mol%)	Ionic conductivity (S cm^{-1})		Activation Energy (eV)
0	RT	1.28×10^{-5}	0.21
	50℃	1.95×10^{-5}	
	70℃	2.22×10^{-5}	
12.5	RT	3.87×10^{-5}	0.22
	50℃	5.70×10^{-5}	
	70℃	8.89×10^{-5}	
25	RT	7.61×10^{-5}	0.22
	50℃	9.67×10^{-5}	
	70℃	1.15×10^{-4}	
37.5	RT	2.62×10^{-4}	0.23
	50℃	5.88×10^{-4}	
	70℃	9.30×10^{-4}	

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