Supporting Information

Solid–Liquid Interfacial Properties Related to Ionic Conductivity of Mixtures of Metal Oxide Particles and Lithium Bis(fluorosulfonyl)amide-Sulfone Electrolytes

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Table S1. Median particle diameter (D50) and relative surface area of $\alpha-Al_2O_3$ and LLZ powder used in this study.

Material	D50 / μm	Relative surface area / m^2 g^{-1}
α-Al_2O_3	27.8	0.52
α-Al_2O_3	14.8	0.46
α-Al_2O_3	4.46	1.4
α-Al_2O_3	0.804	2.3
α-Al_2O_3	0.110	51
LLZ	18.6	0.39
LLZ	9.31	0.71
LLZ	5.05	1.2
LLZ	0.872	4.0

Table S2. NMR measurement conditions of T_1 and T_2.[a]

Samples	Nuclei	pulse sequence	x_pulse / µs	Tau interval T_1: exp / s, T_2: liner / ms			Relaxation delay / s
				Start	End	Points	
LiFSA:SL=1:3	^{1}H, T_1	inversion recovery	17.5	0.01	5	8	5
	^{1}H, T_2	CPMG	17.5	30	300	10	7
	^{7}Li, T_1	inversion recovery	9.4	0.01	5	8	5
	^{7}Li, T_2	CPMG	9.4	50	500	10	7
	^{19}F, T_1	inversion recovery	18.75	0.01	5	8	5
	^{19}F, T_2	CPMG	18.75	40	220	10	2
α-Al_2O_3 mixture[b]	^{1}H, T_1	inversion recovery	15.4	0.01	10	8	10
	^{1}H, T_2	CPMG	15.4	0.40	4	10	8
	^{7}Li, T_1	inversion recovery	7.8	0.01	10	8	10
	^{7}Li, T_2	CPMG	7.8	0.40	4	10	10
	^{19}F, T_1	inversion recovery	17.3	0.10	5	8	5
	^{19}F, T_2	CPMG	17.3	0.40	4	10	1

[a] Common conditions; 8 times scan, temperature of samples were 25 ˚C.

[b] (D50 0.11 um α-Al_2O_3):(LiFSA:SL = 1:3) = volume ratio 61:39, t_{liquid} = 3.1 nm.

Table S3. NMR measurement conditions of PFG stimulated echo method.

Samples	Diffusion time (Δ) / ms	PFG width (δ) / ms	PFG strength (G)[a] / T m^{-1}		Gradient recovery times (τ) / ms	Echo time (T_e) / ms	Pulse width / μs	Scans	Repetition time / s
			start	end					
LiFSA: SL=1:3	500	1.0	0.1	5.0	0.5	50	8.5	8	2.4
α-Al_2O_3 mixture[b]	12	1.2	0.1	13.5	0.2	20	8.5	1024	2.0

[a] log array (base number: 2), 8 points

[b] (D50 0.11 um α-Al_2O_3):(LiFSA:SL = 1:3) = volume ratio 61:39, t_{liquid} = 3.1 nm.

Table S4. NMR measurement conditions of ^{7}Li {^{1}H} HOESY and ^{7}Li {^{1}H} LGCP-HETCOR.

Samples	Method	Conditions					
LiFSA: SL=1:3	^{7}Li {^{1}H} HOESY	x Pulse / μs	y Pulse / μs	y Points	Mixing time / s	Scans	Repetition time / s
		10	15	128	1	16	2
α-Al_2O_3-(LiFSA: SL=1:3)[a]	^{7}Li {^{1}H} LGCP-HETCOR	Irradiation pulse width / μs	y Acquisition time / ms	y Points	Contact time / ms	Scans	Repetition time / s
		3.15	5.25	64	3	8	2

[a] (D50 0.11 um α-Al_2O_3):(LiFSA:SL=1:3) = volume ratio 61:39, t_{liquid} = 3.1 nm.

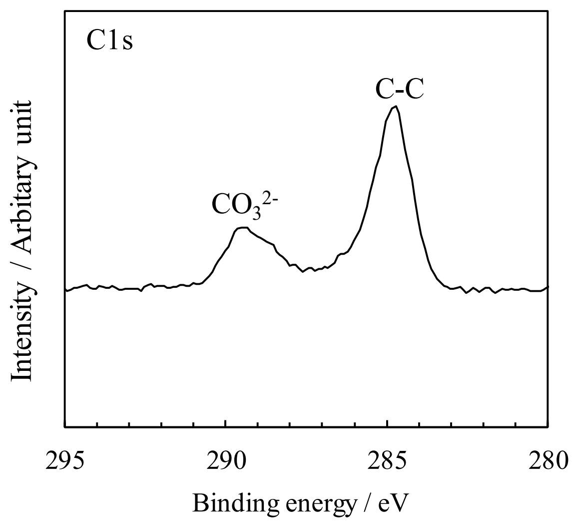

Figure S1. XPS (C1s) of LLZ particle surface.

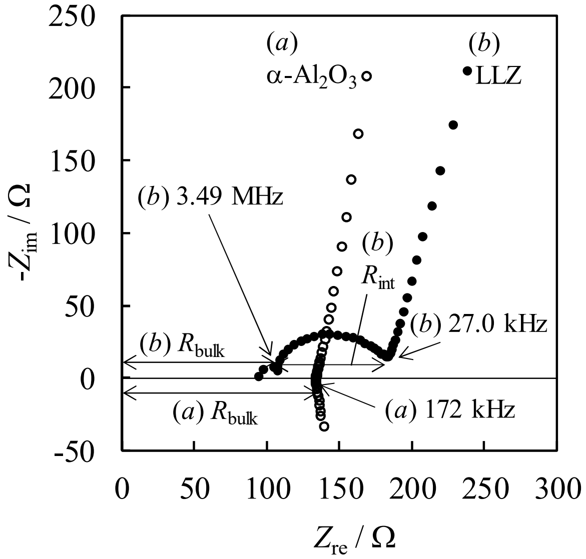

Figure S2. R_{bulk} and R_{int} evaluation of metal oxide mixture pellets (diameter: 10 mm).

(*a*) (D50 0.804 μm α-Al_2O_3):(LiFSA:SL = 1:3) = volume ratio 69:31,

t_{liquid} = 69 nm, pellet thickness: 0.53 mm, and

(*b*) (D50 0.872 μm LLZ):(LiFSA:SL = 1:3) = volume ratio 60:40,

t_{liquid} = 32 nm, pellet thickness: 0.54 mm.

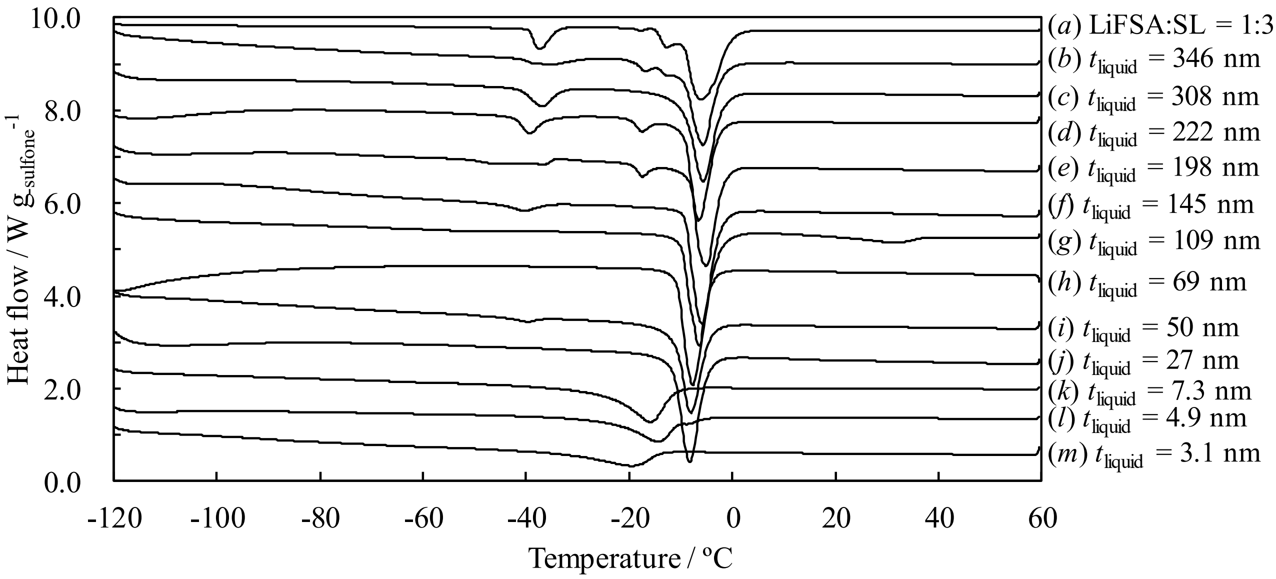

Figure S3. DSC curves of mixture of α-Al_2O_3 and (LiFSA:SL = 1:3) with different t_{liquid} samples.

(*a*) LiFSA:SL = 1:3 (without α-Al_2O_3),

(*b*) (D50 14.8 μm α-Al_2O_3):(LiFSA:SL = 1:3) = volume ratio 61:39, t_{liquid} = 346 nm,

(*c*) (D50 27.8 μm α-Al_2O_3):(LiFSA:SL = 1:3) = volume ratio 61:39, t_{liquid} = 308 nm,

(*d*) (D50 14.8 μm α-Al_2O_3):(LiFSA:SL = 1:3) = volume ratio 71:29, t_{liquid} = 222 nm,

(*e*) (D50 27.8 μm α-Al_2O_3):(LiFSA:SL = 1:3) = volume ratio 71:29, t_{liquid} = 198 nm,

(*f*) (D50 14.8 μm α-Al_2O_3):(LiFSA:SL = 1:3) = volume ratio 79:21, t_{liquid} = 145 nm,

(*g*) (D50 0.804 μm α-Al_2O_3):(LiFSA:SL = 1:3) = volume ratio 50:50, t_{liquid} = 109 nm,

(h) (D50 0.804 μm α-Al_2O_3):(LiFSA:SL = 1:3) = volume ratio 61:39, t_{liquid} = 69 nm,

(i) (D50 0.804 μm α-Al_2O_3):(LiFSA:SL = 1:3) = volume ratio 69:31, t_{liquid} = 50 nm,

(j) (D50 0.804 μm α-Al_2O_3):(LiFSA:SL = 1:3) = volume ratio 80:20, t_{liquid} = 27 nm,

(k) (D50 0.110 μm α-Al_2O_3):(LiFSA:SL = 1:3) = volume ratio 40:60, t_{liquid} = 7.3 nm,

(l) (D50 0.110 μm α-Al_2O_3):(LiFSA:SL = 1:3) = volume ratio 50:50, t_{liquid} = 4.9 nm,

and (m) (D50 0.110 μm α-Al_2O_3):(LiFSA:SL = 1:3) = volume ratio 61:39, t_{liquid} = 3.1 nm.

Heat flow is based on SL weight ($g_{-sulfone}$), temperature scan rate: 10 °C min^{-1}.

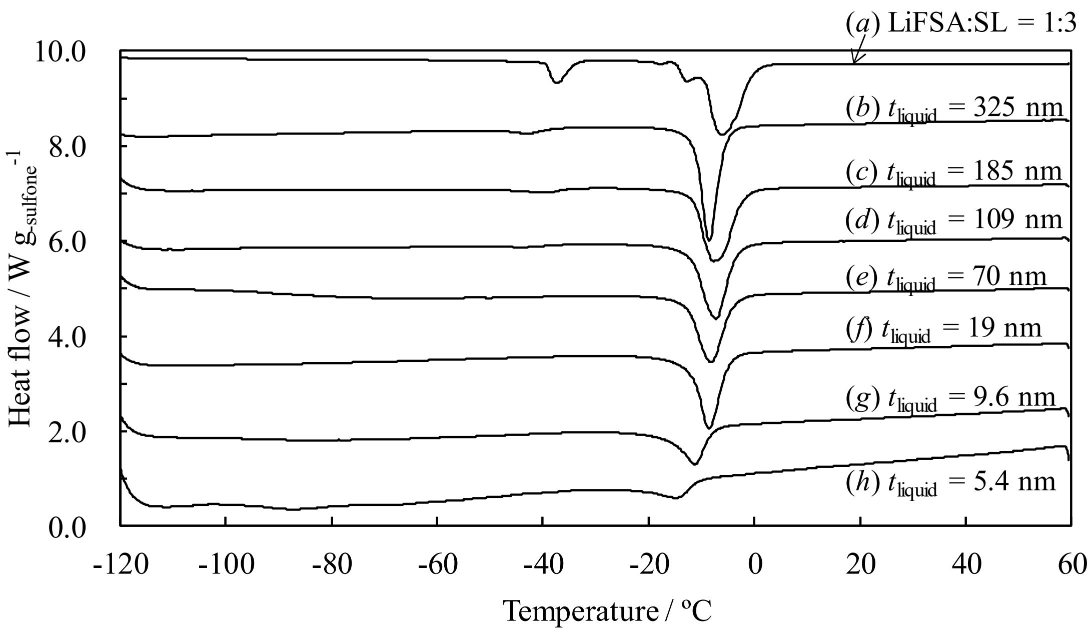

Figure S4. DSC curves of mixture of LLZ and (LiFSA:SL = 1:3) with different t_{liquid} samples.

(*a*) LiFSA:SL=1:3 (without LLZ),

(*b*) (D50 18.6 μm LLZ):(LiFSA:SL = 1:3) = volume ratio 61:39, t_{liquid} = 325 nm,

(*c*) (D50 9.31 μm LLZ):(LiFSA:SL = 1:3) = volume ratio 60:40, t_{liquid} = 185 nm,

(*d*) (D50 5.05 μm LLZ):(LiFSA:SL = 1:3) = volume ratio 60:40, t_{liquid} = 109 nm,

(*e*) (D50 5.05 μm LLZ):(LiFSA:SL = 1:3) = volume ratio 70:30, t_{liquid} = 70 nm,

(*f*) (D50 0.872 μm LLZ):(LiFSA:SL = 1:3) = volume ratio 72:28, t_{liquid} = 19 nm,

(*g*) (D50 0.872 μm LLZ):(LiFSA:SL = 1:3) = volume ratio 84:16, t_{liquid} = 9.6 nm,

and (*h*) (D50 0.872 μm LLZ):(LiFSA:SL = 1:3) = volume ratio 90:10, t_{liquid} = 5.4 nm.

Heat flow is based on SL weight ($g_{-sulfone}$), temperature scan rate: 10 °C min^{-1}.

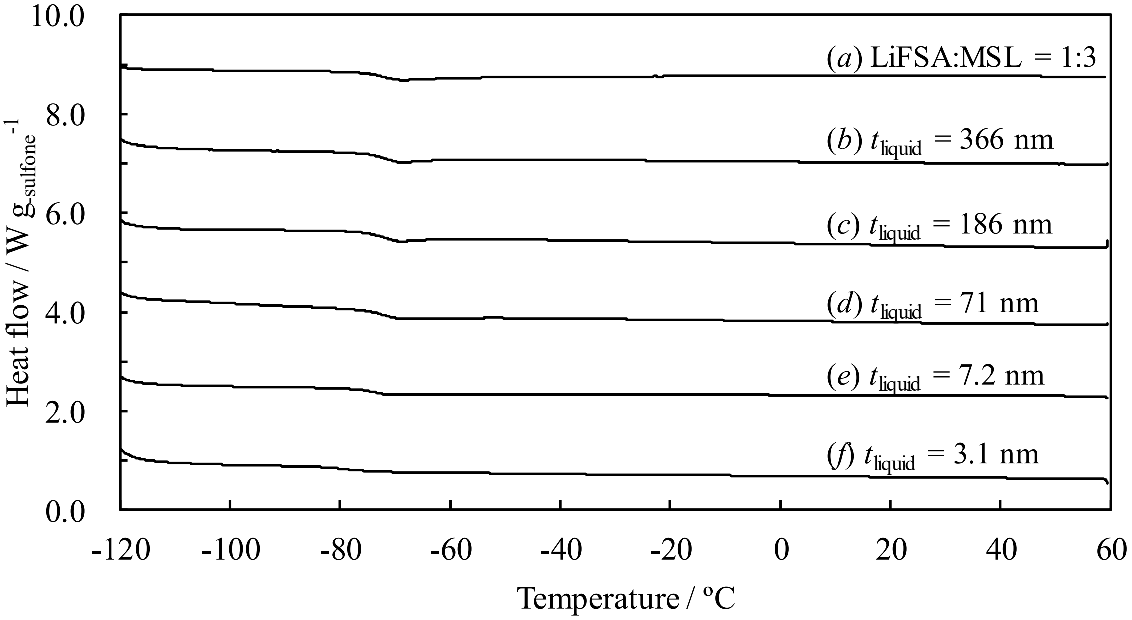

Figure S5. DSC curves of mixture of α-Al_2O_3 and (LiFSA:MSL = 1:3) with different t_{liquid} samples.

(*a*) LiFSA:MSL = 1:3 (without α-Al_2O_3),

(*b*) (D50 14.8 μm α-Al_2O_3):(LiFSA:MSL = 1:3) = volume ratio 60:40, t_{liquid} = 366 nm,

(*c*) (D50 14.8 μm α-Al_2O_3):(LiFSA:MSL = 1:3) = volume ratio 75:25, t_{liquid} = 186 nm,

(*d*) (D50 0.804 μm α-Al_2O_3):(LiFSA:MSL = 1:3) = volume ratio 61:39, t_{liquid} = 71 nm,

(*e*) (D50 0.110 μm α-Al_2O_3):(LiFSA:MSL = 1:3) = volume ratio 41:59, t_{liquid} = 7.2 nm,

and (*f*) (D50 0.110 μm α-Al_2O_3):(LiFSA:MSL = 1:3) = volume ratio 61:39, t_{liquid} = 3.1 nm.

Heat flow is based on MSL weight ($g_{-sulfone}$), temperature scan rate: 10 °C min^{-1}.

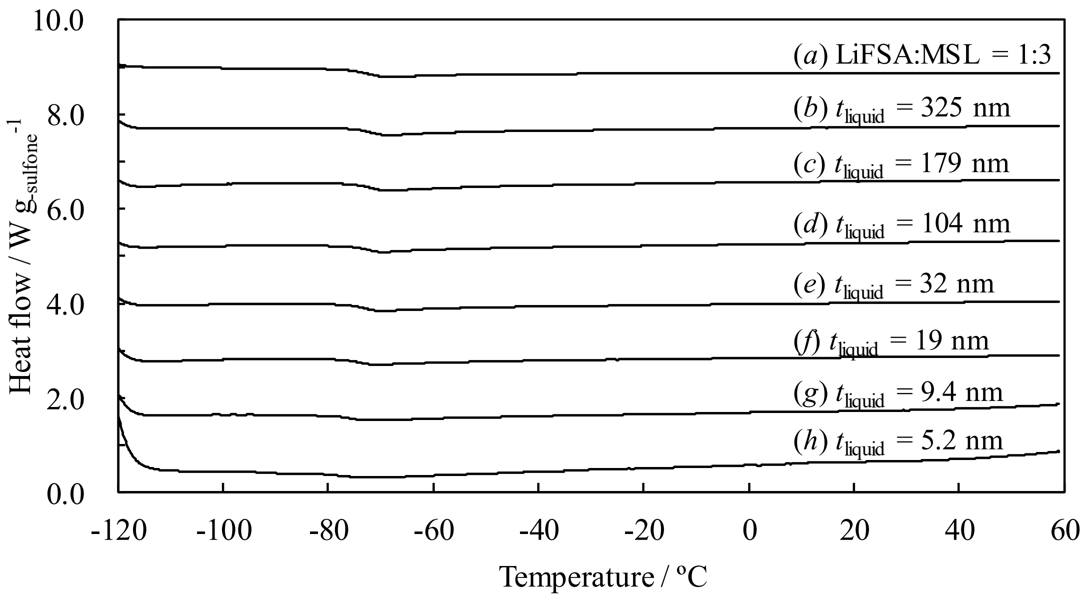

Figure S6. DSC curves of mixture of LLZ and (LiFSA:MSL = 1:3) with different t_{liquid} samples.

(*a*) LiFSA:MSL = 1:3 (without LLZ),

(*b*) (D50 18.6 μm LLZ):(LiFSA:MSL = 1:3) = volume ratio 61:39, t_{liquid} = 325 nm,

(*c*) (D50 9.31 μm LLZ):(LiFSA:MSL = 1:3) = volume ratio 61:39, t_{liquid} = 179 nm,

(*d*) (D50 5.05 μm LLZ):(LiFSA:MSL = 1:3) = volume ratio 61:39, t_{liquid} = 104 nm,

(*e*) (D50 0.872 μm LLZ):(LiFSA:MSL = 1:3) = volume ratio 61:39, t_{liquid} = 32 nm,

(*f*) (D50 0.872 μm LLZ):(LiFSA:MSL = 1:3) = volume ratio 72:28, t_{liquid} = 19 nm,

(*g*) (D50 0.872 μm LLZ):(LiFSA:MSL = 1:3) = volume ratio 84:16, t_{liquid} = 9.4 nm,

and (*h*) (D50 0.872 μm LLZ):(LiFSA:MSL = 1:3) = volume ratio 90:10, t_{liquid} = 5.2 nm.

Heat flow is based on MSL weight ($g_{-sulfone}$), temperature scan rate: 10 °C min^{-1}.

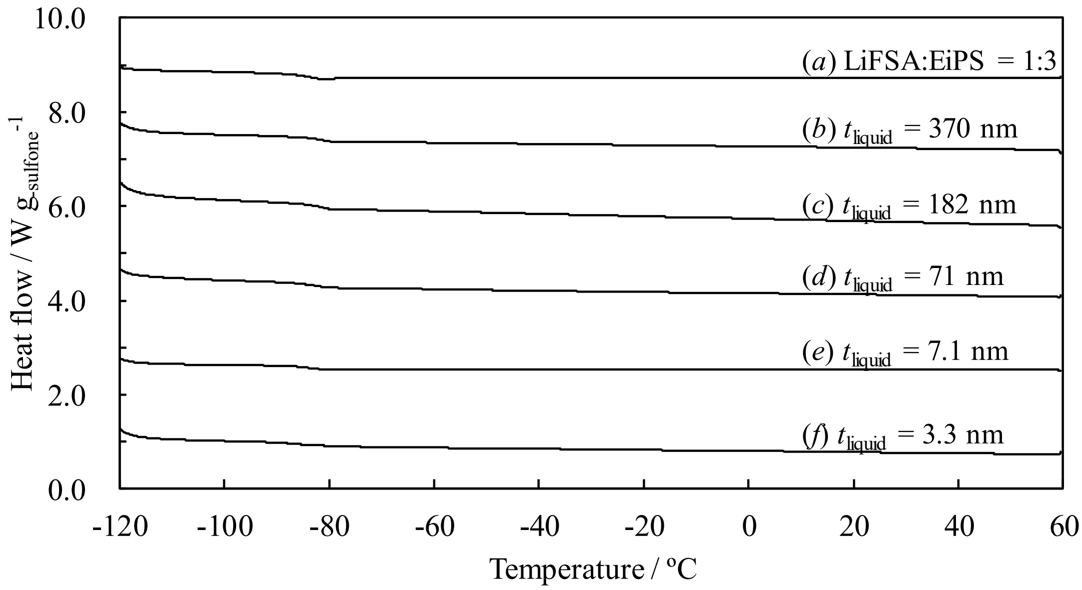

Figure S7. DSC curves of mixture of α-Al_2O_3 and (LiFSA:EiPS = 1:3) with different t_{liquid} samples.

(*a*) LiFSA:EiPS = 1:3 (without α-Al_2O_3),

(*b*) (D50 14.8 µm α-Al_2O_3):(LiFSA:EiPS = 1:3) = volume ratio 60:40, t_{liquid} = 370 nm,

(*c*) (D50 14.8 µm α-Al_2O_3):(LiFSA:EiPS = 1:3) = volume ratio 75:25, t_{liquid} = 182 nm,

(*d*) (D50 0.804 µm α-Al_2O_3):(LiFSA:EiPS = 1:3) = volume ratio 60:40, t_{liquid} = 71 nm,

(*e*) (D50 0.110 µm α-Al_2O_3):(LiFSA:EiPS = 1:3) = volume ratio 41:59, t_{liquid} = 7.1 nm,

and (*f*) (D50 0.110 µm α-Al_2O_3):(LiFSA:EiPS = 1:3) = volume ratio 60:40, t_{liquid} = 3.3 nm.
Heat flow is based on EiPS weight ($g_{-sulfone}$), temperature scan rate: 10 °C min^{-1}.

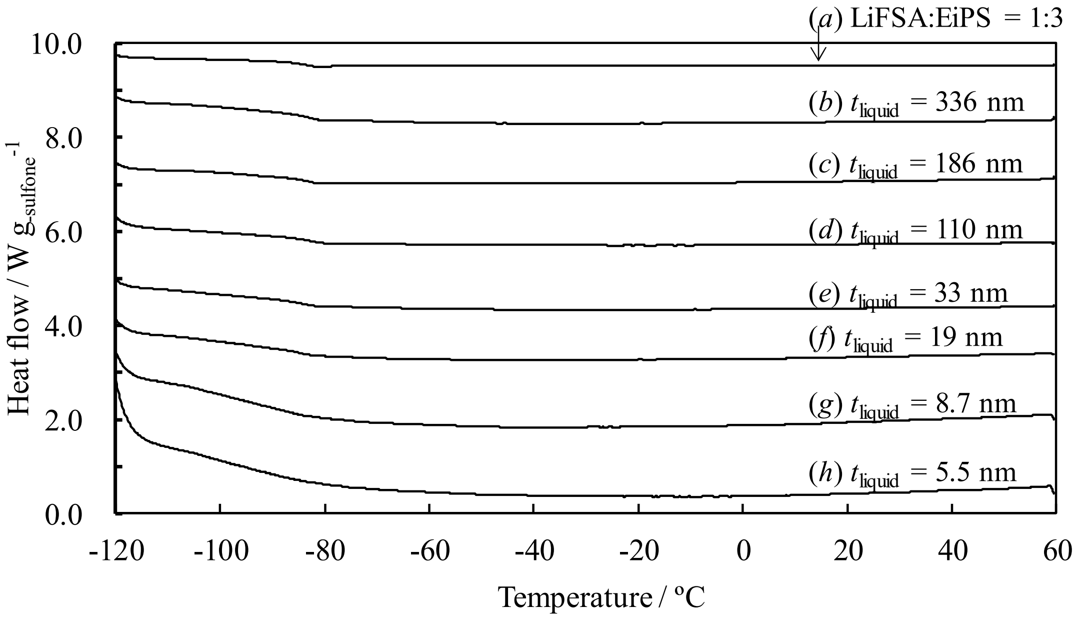

Figure S8. DSC curves of mixture of LLZ and (LiFSA:EiPS = 1:3) with different t_{liquid} samples.

(*a*) LiFSA:EiPS = 1:3 (without LLZ),

(*b*) (D50 18.6 μm LLZ):(LiFSA:EiPS = 1:3) = volume ratio 60:40, t_{liquid} = 336 nm,

(*c*) (D50 9.31 μm LLZ):(LiFSA:EiPS = 1:3) = volume ratio 60:40, t_{liquid} = 186 nm,

(*d*) (D50 5.05 μm LLZ):(LiFSA:EiPS = 1:3) = volume ratio 60:40, t_{liquid} = 110 nm,

(*e*) (D50 0.872 μm LLZ):(LiFSA:EiPS = 1:3) = volume ratio 60:40, t_{liquid} = 33 nm,

(*f*) (D50 0.872 μm LLZ):(LiFSA:EiPS = 1:3) = volume ratio 72:28, t_{liquid} = 19 nm,

(*g*) (D50 0.872 μm LLZ):(LiFSA:EiPS = 1:3) = volume ratio 85:15, t_{liquid} = 8.7 nm,

and (*h*) (D50 0.872 μm LLZ):(LiFSA:EiPS = 1:3) = volume ratio 90:10, t_{liquid} = 5.5 nm.

Heat flow is based on EiPS weight ($g_{-sulfone}$), temperature scan rate: 10 °C min^{-1}.

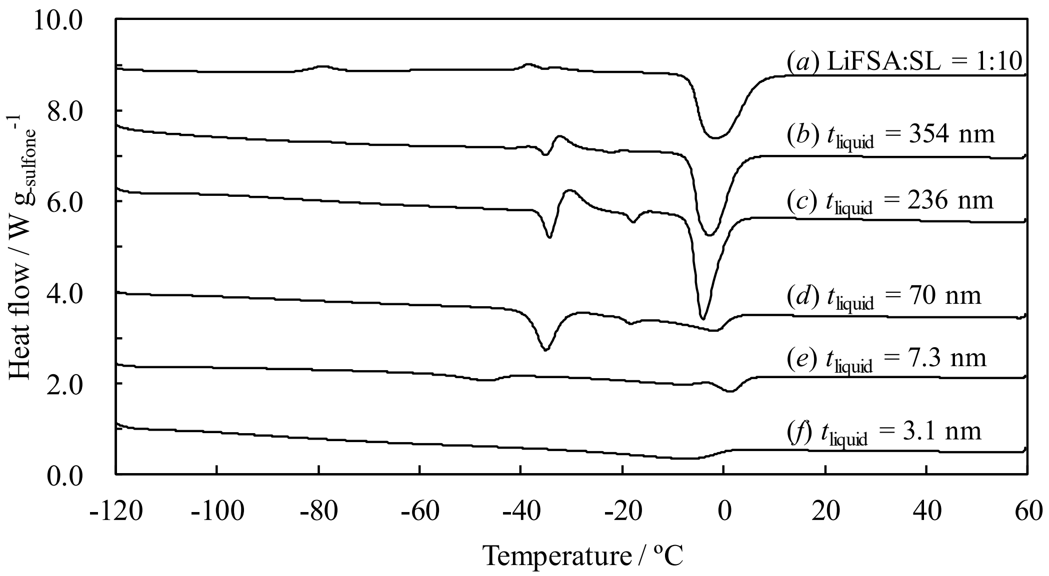

Figure S9. DSC curve of mixture of α-Al_2O_3 and (LiFSA:SL = 1:10) with different t_{liquid} samples.

(*a*) LiFSA:SL = 1:10 (without α-Al_2O_3),

(*b*) (D50 14.8 μm α-Al_2O_3):(LiFSA:SL = 1:10) = volume ratio 61:39, t_{liquid} = 354 nm,

(*c*) (D50 14.8 μm α-Al_2O_3):(LiFSA:SL = 1:10) = volume ratio 70:30, t_{liquid} = 236 nm,

(*d*) (D50 0.804 μm α-Al_2O_3):(LiFSA:SL = 1:10) = volume ratio 61:39, t_{liquid} = 70 nm,

(*e*) (D50 0.110 μm α-Al_2O_3):(LiFSA:SL = 1:10) = volume ratio 40:60, t_{liquid} = 7.3 nm,

and (*f*) (D50 0.110 μm α-Al_2O_3):(LiFSA:SL = 1:10) = volume ratio 61:39, t_{liquid} = 3.1 nm.

Heat flow is based on SL weight ($g_{-sulfone}$), temperature scan rate: 10 °C min^{-1}.

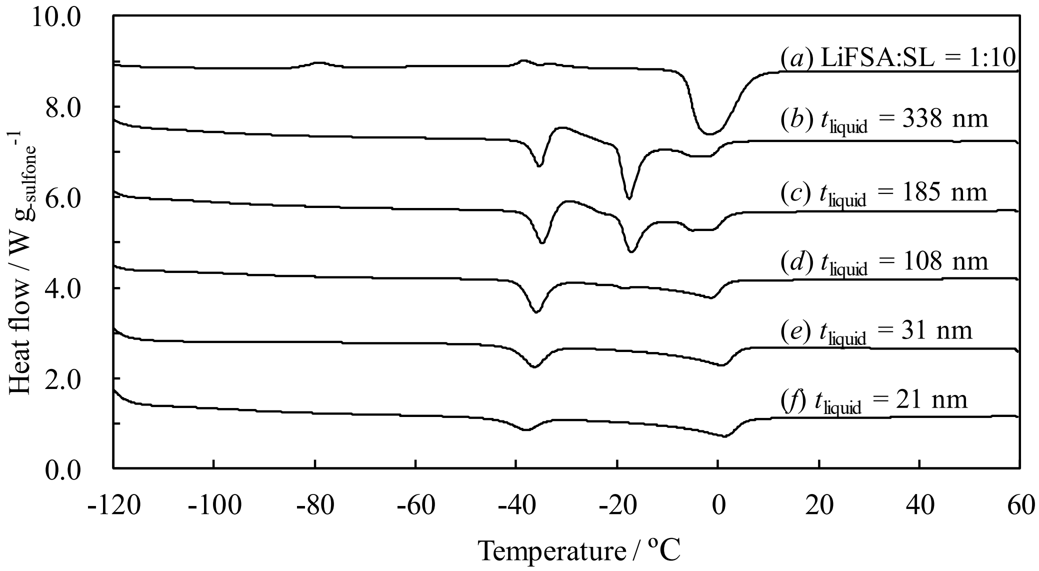

Figure S10. DSC curve of mixture of LLZ and (LiFSA:SL = 1:10) with different t_{liquid} samples.

(*a*) LiFSA:SL = 1:10 (without LLZ),

(*b*) (D50 18.6 μm LLZ):(LiFSA:SL = 1:10) = volume ratio 60:40, t_{liquid} = 338 nm,

(*c*) (D50 9.31 μm LLZ):(LiFSA:SL = 1:10) = volume ratio 60:40, t_{liquid} = 185 nm,

(*d*) (D50 5.05 μm LLZ):(LiFSA:SL = 1:10) = volume ratio 60:40, t_{liquid} = 108 nm,

(*e*) (D50 0.872 μm LLZ):(LiFSA:SL = 1:10) = volume ratio 61:39, t_{liquid} = 31 nm,

and (*f*) (D50 0.872 μm LLZ):(LiFSA:SL = 1:10) = volume ratio 70:30, t_{liquid} = 21 nm.

Heat flow is based on SL weight ($g_{\text{-sulfone}}$), temperature scan rate: 10 °C min^{-1}.

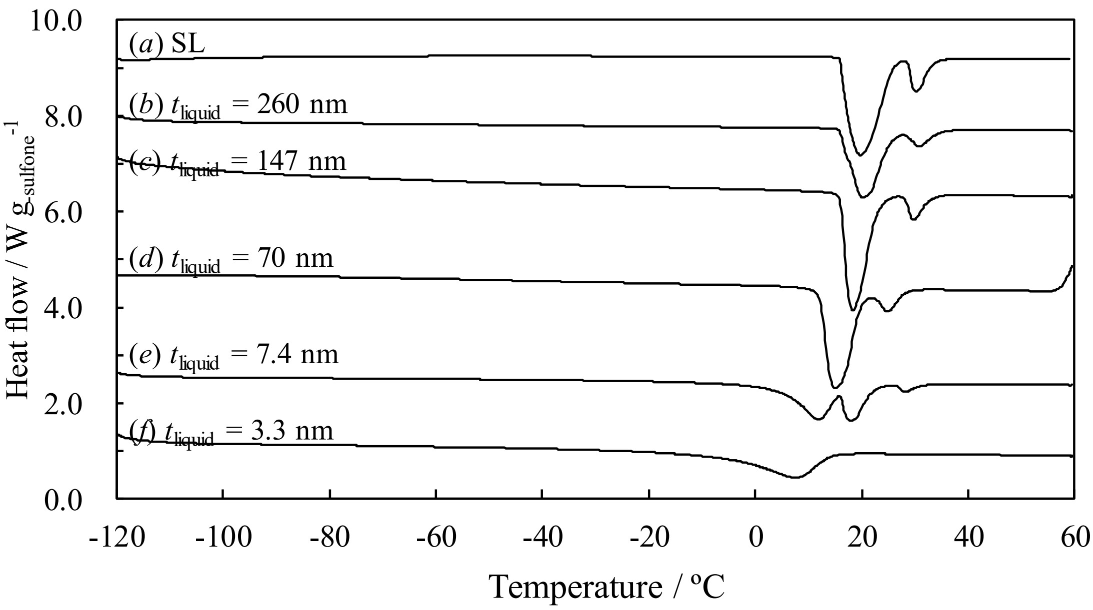

Figure S11. DSC curve of mixture of α-Al_2O_3 and SL with different t_{liquid} samples.

(*a*) SL (without α-Al_2O_3),

(*b*) (D50 14.8 μm α-Al_2O_3):SL = volume ratio 68:32, t_{liquid} = 260 nm,

(*c*) (D50 14.8 μm α-Al_2O_3):SL = volume ratio 79:21, t_{liquid} = 147 nm,

(*d*) (D50 0.804 μm α-Al_2O_3):SL = volume ratio 61:39, t_{liquid} = 70 nm,

(*e*) (D50 0.110 μm α-Al_2O_3):SL = volume ratio 40:60, t_{liquid} = 7.4 nm,

and (*f*) (D50 0.110 μm α-Al_2O_3):SL = volume ratio 60:40, t_{liquid} = 3.3 nm.

Heat flow is based on SL weight ($g_{-sulfone}$), temperature scan rate: 10 °C min^{-1}.

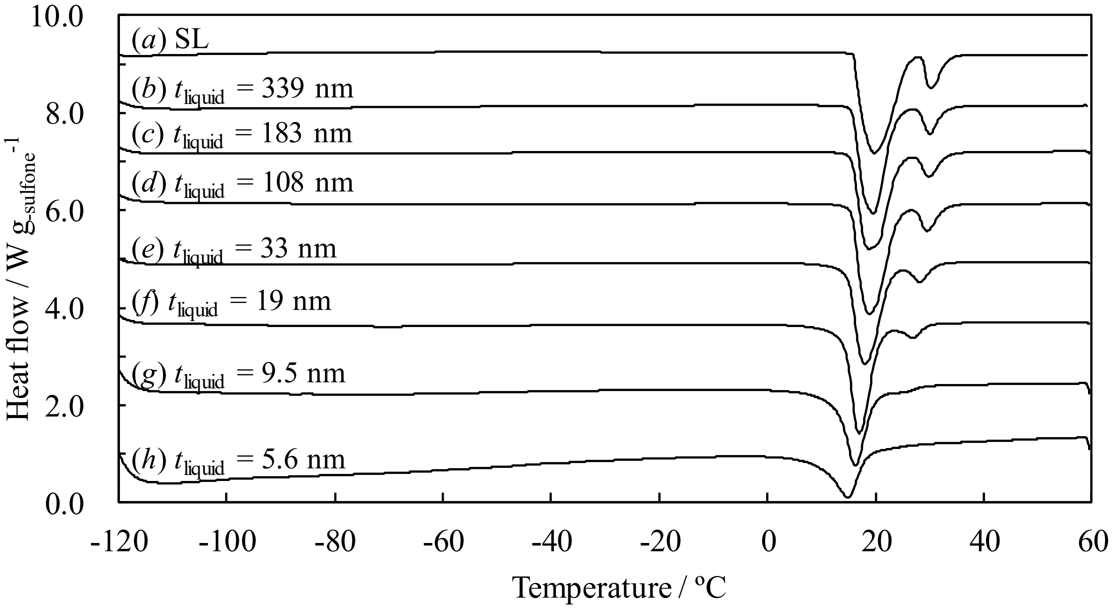

Figure S12. DSC curve of mixture of LLZ and SL with different t_{liquid} samples.

(*a*) SL (without LLZ),

(*b*) (D50 18.6 μm LLZ):SL = volume ratio 60:40, t_{liquid} = 339 nm,

(*c*) (D50 9.31 μm LLZ):SL = volume ratio 60:40, t_{liquid} = 183 nm,

(*d*) (D50 5.05 μm LLZ):SL = volume ratio 60:40, t_{liquid} = 108 nm,

(*e*) (D50 0.872 μm LLZ):SL = volume ratio 60:40, t_{liquid} = 33 nm,

(*f*) (D50 0.872 μm LLZ):SL = volume ratio 72:28, t_{liquid} = 19 nm,

(*g*) (D50 0.872 μm LLZ):SL = volume ratio 84:16, t_{liquid} = 9.5 nm,

and (*h*) (D50 0.872 μm LLZ):SL = volume ratio 90:10, t_{liquid} = 5.6 nm.

Heat flow is based on SL weight ($g_{-sulfone}$), temperature scan rate: 10 °C min^{-1}.