

Supporting information for
Beyond Fluorine:
Sustainable Ternary Polymer Electrolytes for Lithium Batteries

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Table S1: DSC procedure used for polymer electrolytes and ionic liquids.

STEP	START / °C	STOP / °C	RATE / °C MIN ⁻¹
1	20	-150	5
2	-150	60	5
3	60	60	Isotherm 10 min
4	60	-150	Quench
5	-150	80	5
6	80	-150	5
7	-150	80	5
8	80	RT	5

Table S2: Thermal behavior of DCTA and TFSI-based membranes with different PEO:salt:IL ratios during the first DSC cooling scan from RT to -150 °C (step 1).

Step 1, cooling scan (crystallization)			
Membrane	T(onset) / °C	T(peak) / °C	ΔHc / J g ⁻¹
DCTA 20:2:4	-19.9	-25.1	22.9
DCTA 20:2:2	n.a.	n.a.	n.a.
DCTA 20:1:2	n.a.	n.a.	n.a.
DCTA 20:1:1	n.a.	n.a.	n.a.
DCTA 20:1:0.5	n.a.	n.a.	n.a.
DCTA 20:1:0	n.a.	n.a.	n.a.
TFSI 20:2:2	n.a.	n.a.	n.a.
TFSI 20:1:2	n.a.	n.a.	n.a.
TFSI 20:1:1	n.a.	n.a.	n.a.
TFSI 20:1:0.5	n.a.	n.a.	n.a.
TFSI 20:1:0	n.a.	n.a.	n.a.

Table S3: Thermal behavior of DCTA and TFSI-based membranes with different PEO:salt:IL ratios during the first DSC heating scan from -150 to 60 °C (step 2).

Step 2, heating scan (melting)			
Membrane	T(onset) / °C	T(peak) / °C	ΔHm / J g⁻¹
DCTA 20:2:4	32.2	46.5	41.1
	1.8	9.7	19.0
DCTA 20:2:2	32.0	45.6	52.4
	-0.6	6.6	4.6
DCTA 20:1:2	31.3	50.4	31.3
DCTA 20:1:1	36.7	55.7	n.a.
DCTA 20:1:0.5	33.5	57.1	n.a.
DCTA 20:1:0	42.7	57.7	n.a.
TFSI 20:2:2	21.5	40.5	3.8
TFSI 20:1:2	39.4	51.9	28.3
TFSI 20:1:1	43.3	54.6	42.2
TFSI 20:1:0.5	46.1	56.5	50.7
TFSI 20:1:0	46.5	n.a.	n.a.

Table S4: Thermal behavior of DCTA and TFSI-based membranes with different PEO:salt:IL ratios during the first DSC cooling scan from 80 to -150 °C (step 6).

Step 6, cooling scan (crystallization)			
Membrane	T(onset) / °C	T(peak) / °C	ΔHc / J g⁻¹
DCTA 20:2:4	n.a.	n.a.	n.a.
DCTA 20:2:2	n.a.	n.a.	n.a.
DCTA 20:1:2	18.3	3.5	4.6
DCTA 20:1:1	23.6	12.1	44.3
DCTA 20:1:0.5	30.2	19.9	79.0
DCTA 20:1:0	39.5	34.9	83.6
TFSI 20:2:2			
TFSI 20:1:2	25.7	21.2	32.1
TFSI 20:1:1	32.1	29.2	42.1
TFSI 20:1:0.5	36.7	34.5	48.1
TFSI 20:1:0	43.2	37.7	63.8

Table S5: Thermal behavior of DCTA and TFSI-based membranes with different PEO:salt:IL ratios during the first DSC heating scan from -150 to 80 °C (step 7).

Membrane	Step 7, heating scan (cold crystallization)			Step 7, heating scan (melting)		
	T(onset) / °C	T(peak) / °C	ΔH_c / J g ⁻¹	T(onset) / °C	T(peak) / °C	ΔH_m / J g ⁻¹
DCTA 20:2:4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
DCTA 20:2:2	11.4	21.5	3.4	34.4	38.5	4.4
DCTA 20:1:2	-7.7	1.1	45.7	26.5	44.0	46.6
DCTA 20:1:1	-11.9	-0.1	21.9	34.3	49.5	57.9
DCTA 20:1:0.5	n.a.	n.a.	n.a.	39.7	54.4	69.7
DCTA 20:1:0	n.a.	n.a.	n.a.	49.8	59.6	90.8
TFSI 20:2:2	n.a.	n.a.	n.a.	26.5	32.4	0.6
TFSI 20:1:2	n.a.	n.a.	n.a.	35.7	48.8	28.0
TFSI 20:1:1	n.a.	n.a.	n.a.	39.7	52.0	38.3
TFSI 20:1:0.5	n.a.	n.a.	n.a.	42.6	54.7	49.1
TFSI 20:1:0	n.a.	n.a.	n.a.	50.6	66.0	59.4

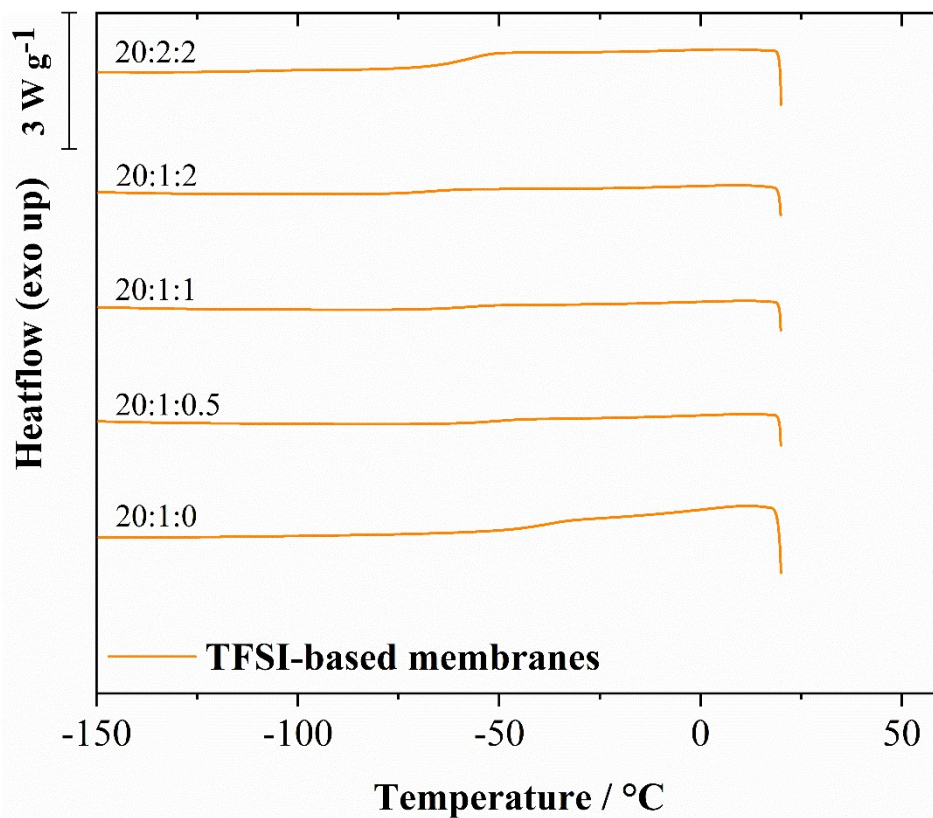


Figure S1: DSC thermograms of TFSI-based membranes with different PEO:salt:IL ratios, as indicated on the curves; scan rate: $5 \text{ }^{\circ}\text{C min}^{-1}$; cooling scan from RT to $-150 \text{ }^{\circ}\text{C}$ (step 1).

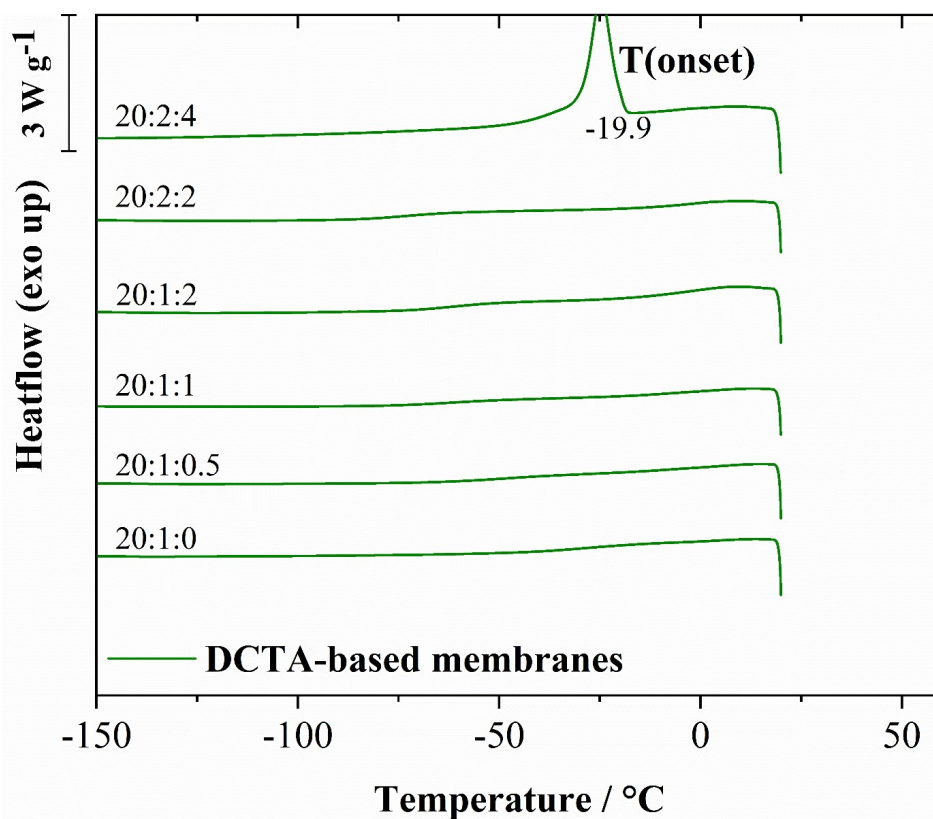


Figure S2: DSC thermograms of DCTA-based membranes with different PEO:salt:IL ratios, as indicated on the curves; scan rate: $5 \text{ }^{\circ}\text{C min}^{-1}$; cooling scan from RT to $-150 \text{ }^{\circ}\text{C}$ (step 1).

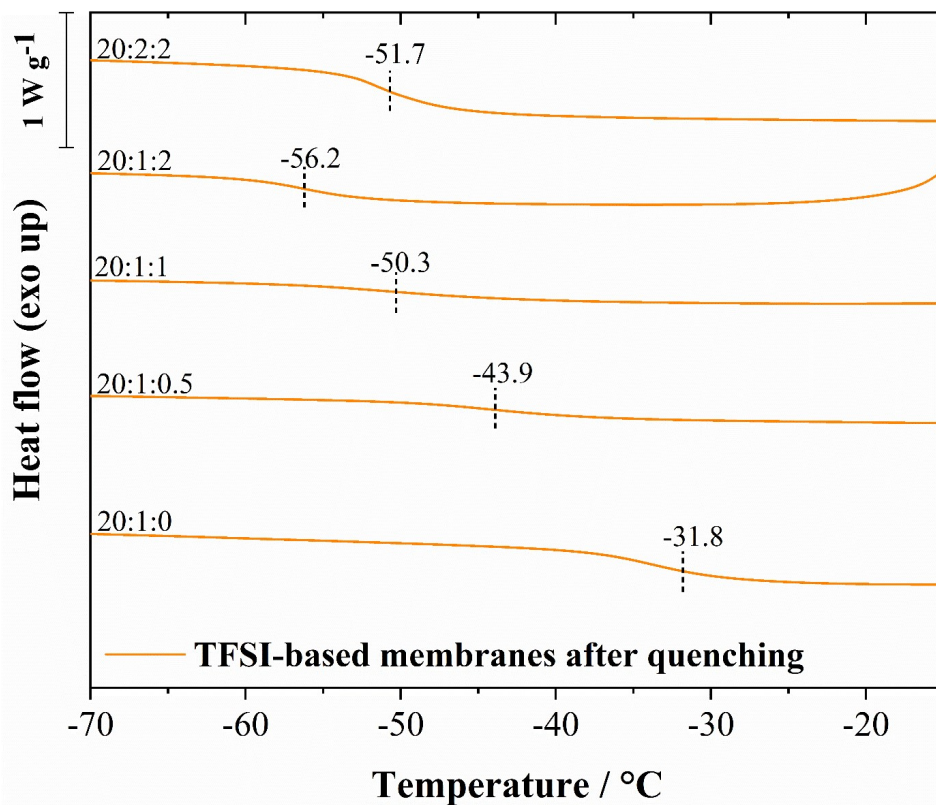


Figure S3: DSC thermograms of TFSI-based membranes with different PEO:salt:IL ratios, as indicated on the curves; scan rate: $5 \text{ }^{\circ}\text{C min}^{-1}$; heating scan after quenching (step 5); magnification of T_g .

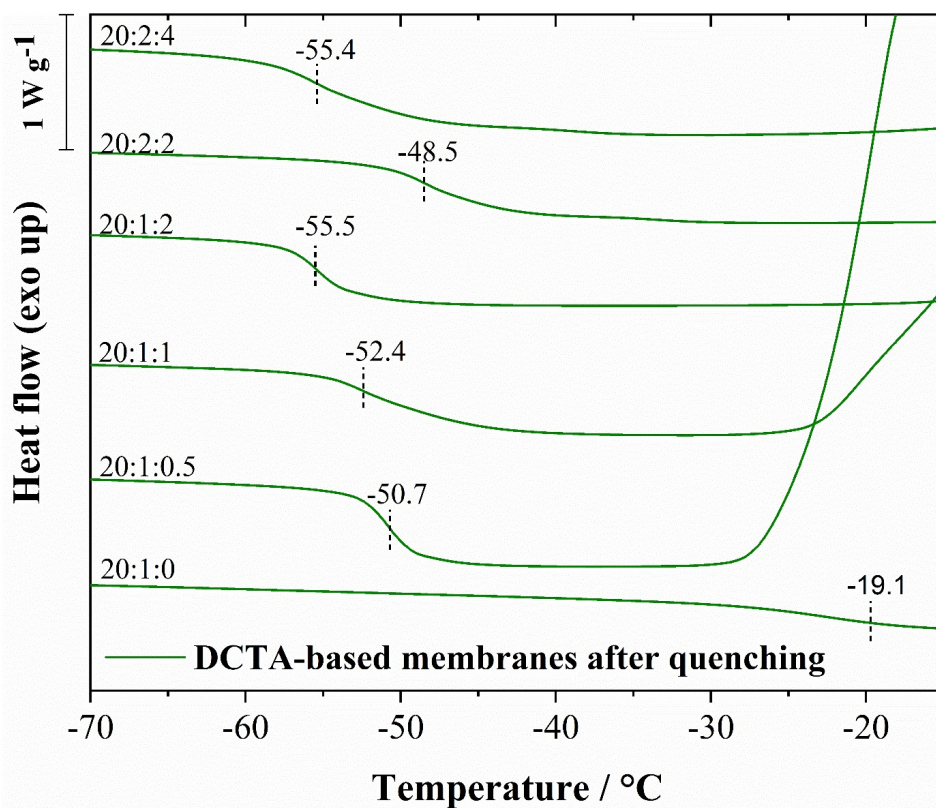


Figure S4: DSC thermograms of DCTA-based membranes with different PEO:salt:IL ratios, as indicated on the curves; scan rate: $5 \text{ }^{\circ}\text{C min}^{-1}$; heating scan after quenching (step 5); magnification of T_g .

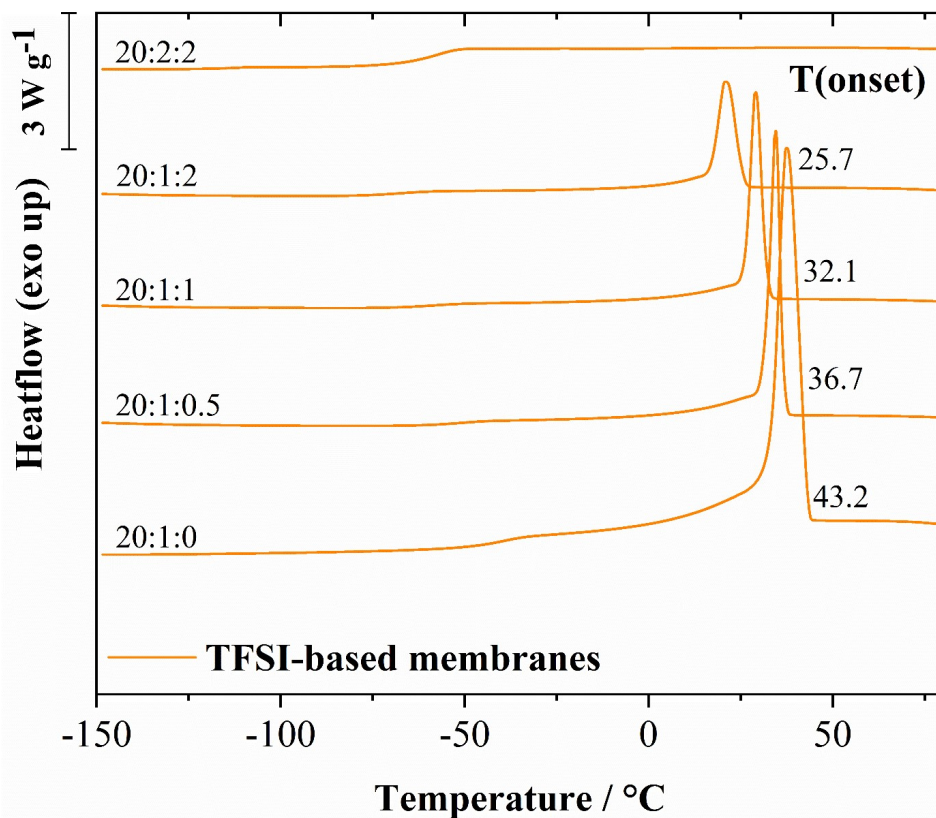


Figure S5: DSC thermograms of TFSI-based membranes with different PEO:salt:IL ratios, as indicated on the curves; scan rate: 5 °C min⁻¹; cooling scan from 80 to -150 °C (step 6).

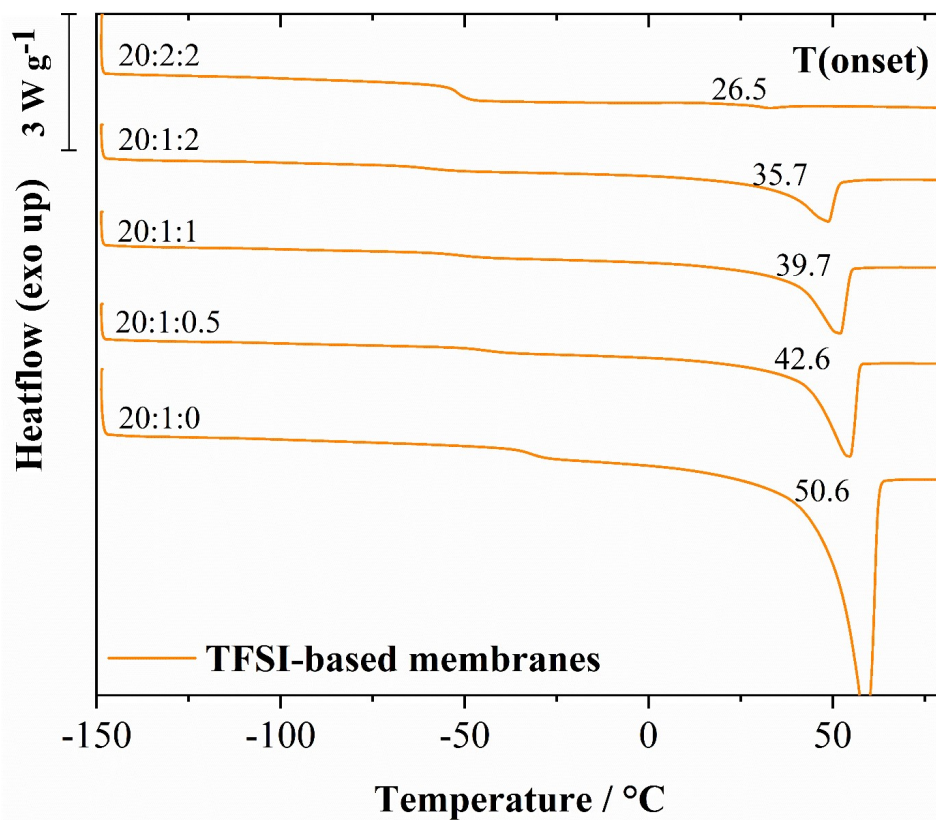


Figure S6: DSC thermograms of TFSI-based membranes with different PEO:salt:IL ratios, as indicated on the curves; scan rate: 5 °C min⁻¹; heating scan from -150 to 80 °C (step 7).

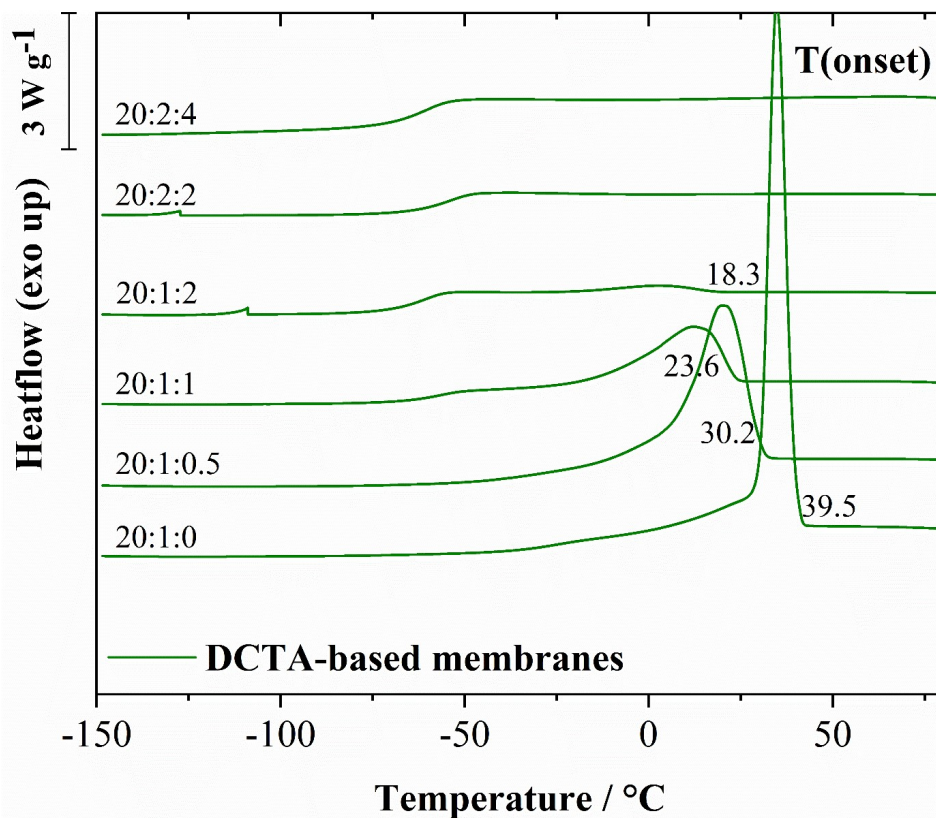


Figure S7: DSC thermograms of DCTA-based membranes with different PEO:salt:IL ratios, as indicated on the curves; scan rate: $5 \text{ }^{\circ}\text{C min}^{-1}$; cooling scan from 80 to $-150 \text{ }^{\circ}\text{C}$ (step 6).

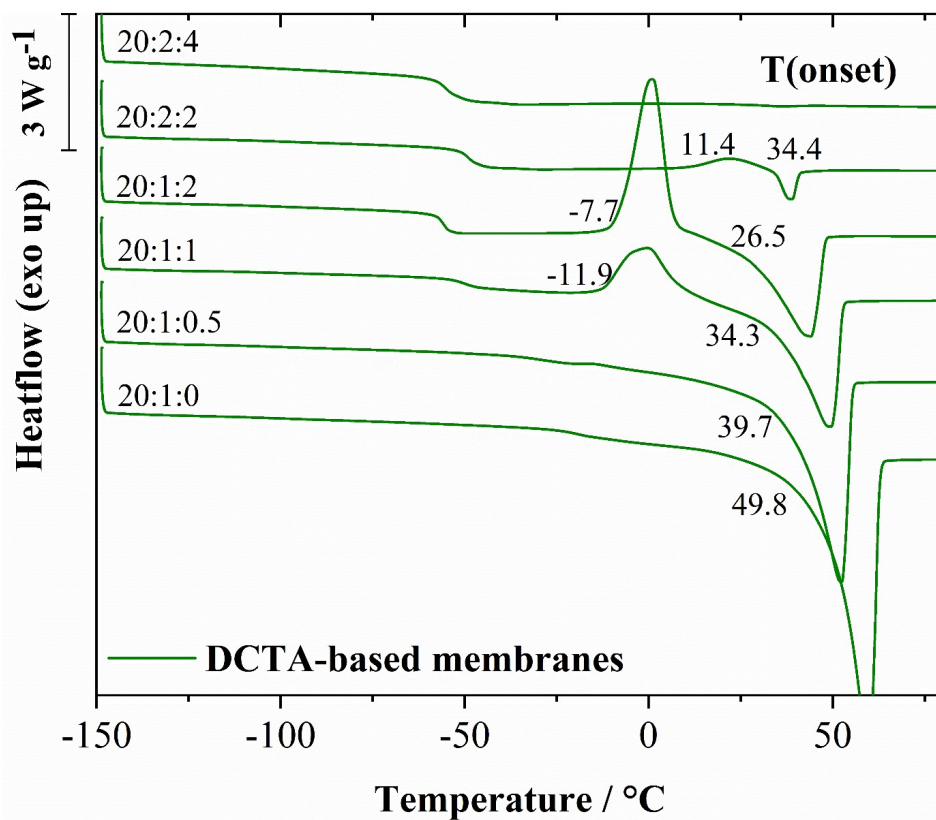


Figure S8: DSC thermograms of DCTA-based membranes with different PEO:salt:IL ratios, as indicated on the curves; scan rate: $5 \text{ }^{\circ}\text{C min}^{-1}$; heating scan from -150 to $80 \text{ }^{\circ}\text{C}$ (step 7).

Table S6: Ohmic drop and equivalent series resistance of selected cycles from LFP/Li metal cell with the DCTA 20:2:4 ternary polymer electrolyte.

DCTA 20:2:4			
Cycle number	C-rate	$\Delta V / V$	ESR / mΩ cm²
1	0.1	0.0381	1267
5	0.5	0.1956	1301
50	0.5	0.2452	1631
100	0.5	0.2693	1792
200	0.5	0.3074	2045
300	0.5	0.3177	2114

Table S7: Ohmic drop and equivalent series resistance of selected cycles from LFP/Li metal cell with the DCTA 20:2:4 ternary polymer electrolyte.

TFSI 20:2:2			
Cycle number	C-rate	$\Delta V / V$	ESR / mΩ cm²
1	0.1	0.0160	532
5	0.5	0.0822	547
50	0.5	0.0917	610
100	0.5	0.1001	666
200	0.5	0.1120	745
300	0.5	0.1243	827

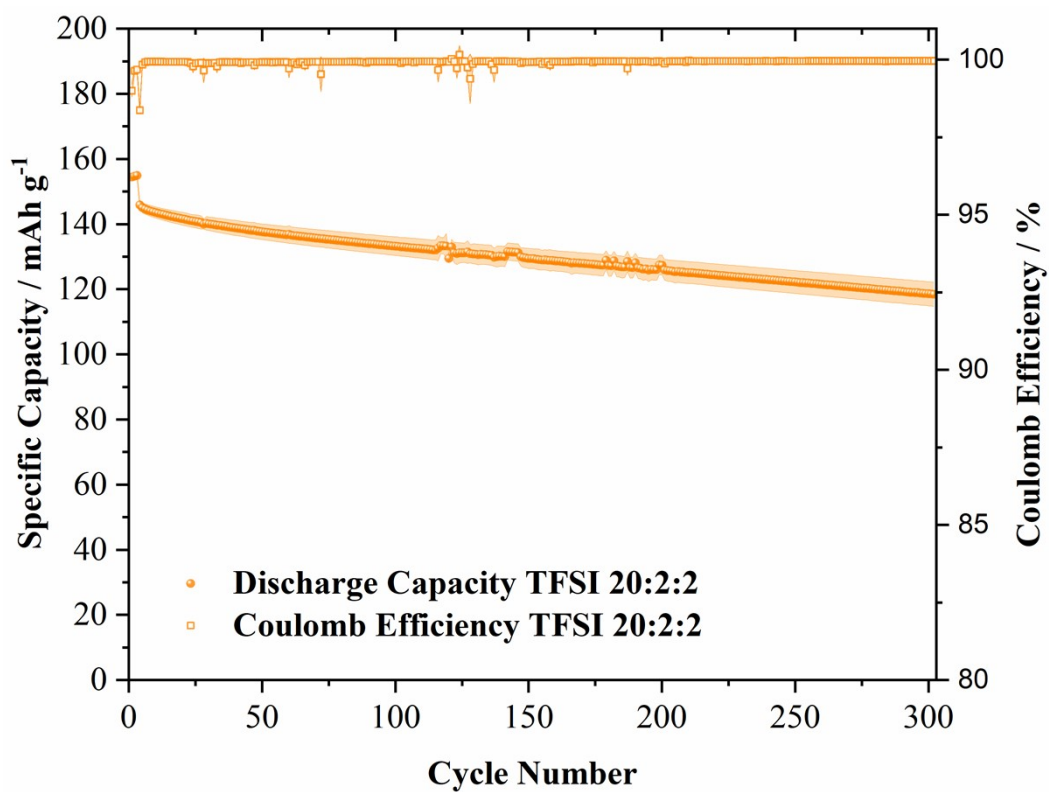


Figure S9: Galvanostatic cycling (300 cycles) of LFP|Li metal cells with a TFSI 20:2:2 TSPE between 2.5 and 3.8 V vs. Li⁺|Li; 3 formation cycles: C/10, then C/2; mass loading: 1.1 mg cm⁻².

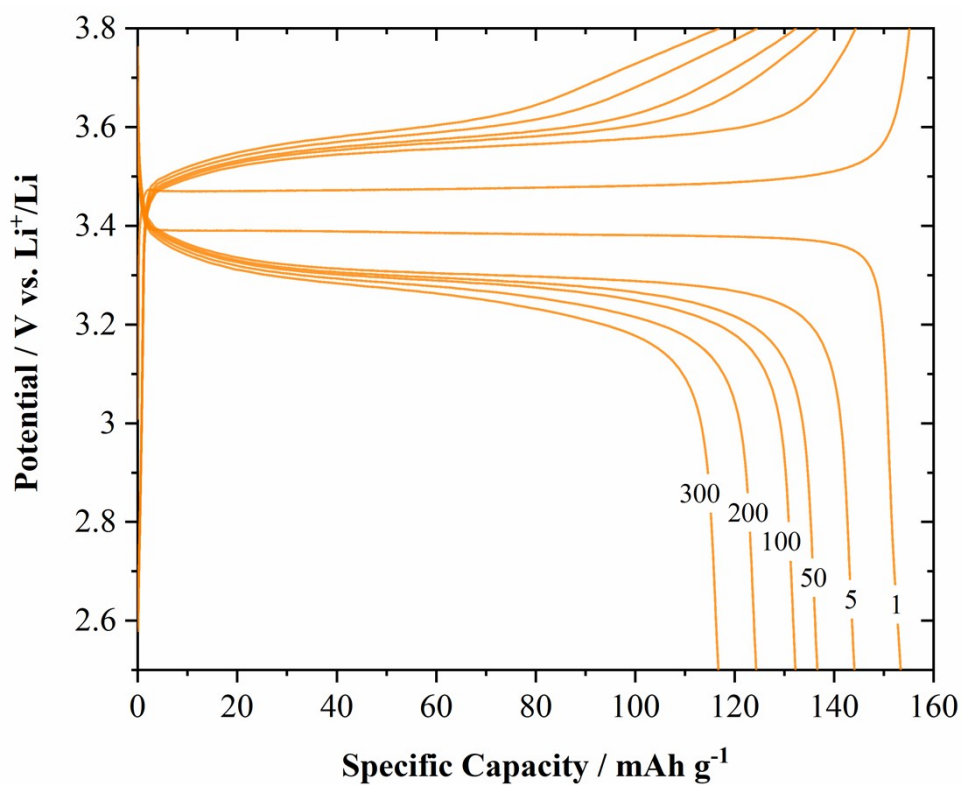


Figure S10: Potential profiles of selected charge and discharge curves of the long-term cycling (300 cycles) with TFSI 20:2:2 shown in figure S9.

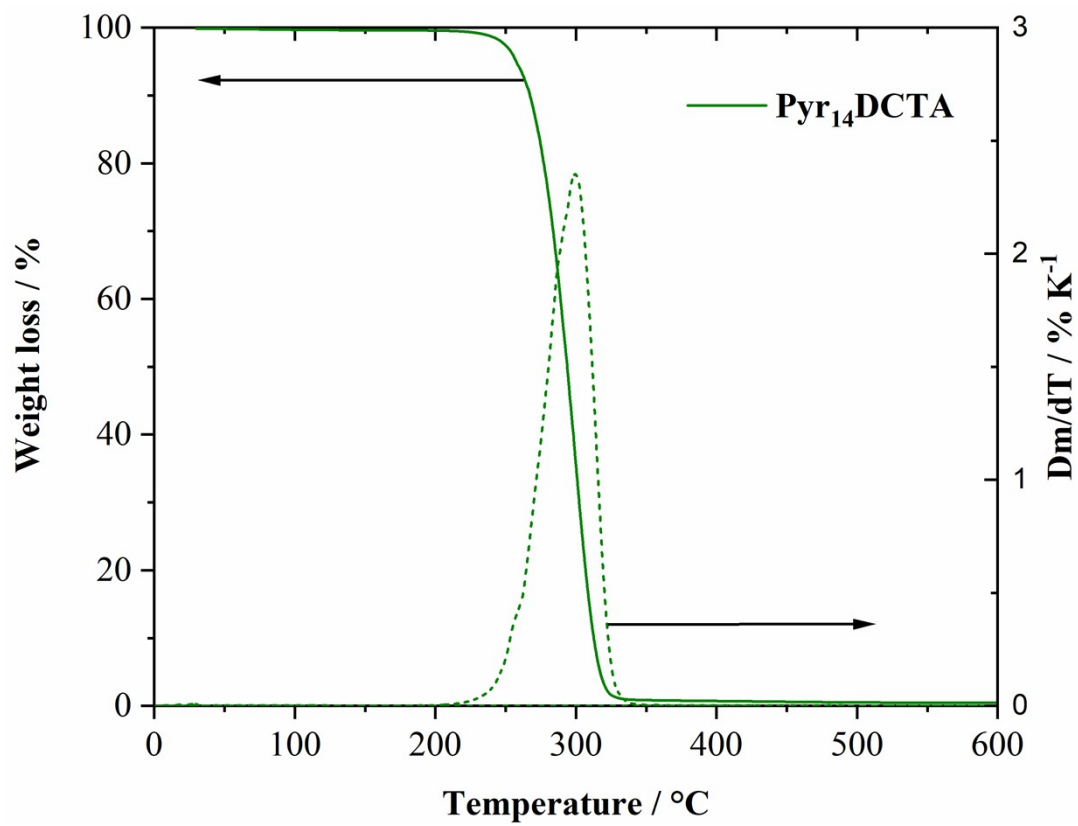


Figure S11: Thermogravimetric Analysis of Pyr₁₄DCTA und N₂ atmosphere; scan rate: 10 K min⁻¹.