Electronic Supplementary Material (ESI) for RSC Advances.

Free-standing Li^+-conductive films based on PEO-PVDF blends

Supplementary materials

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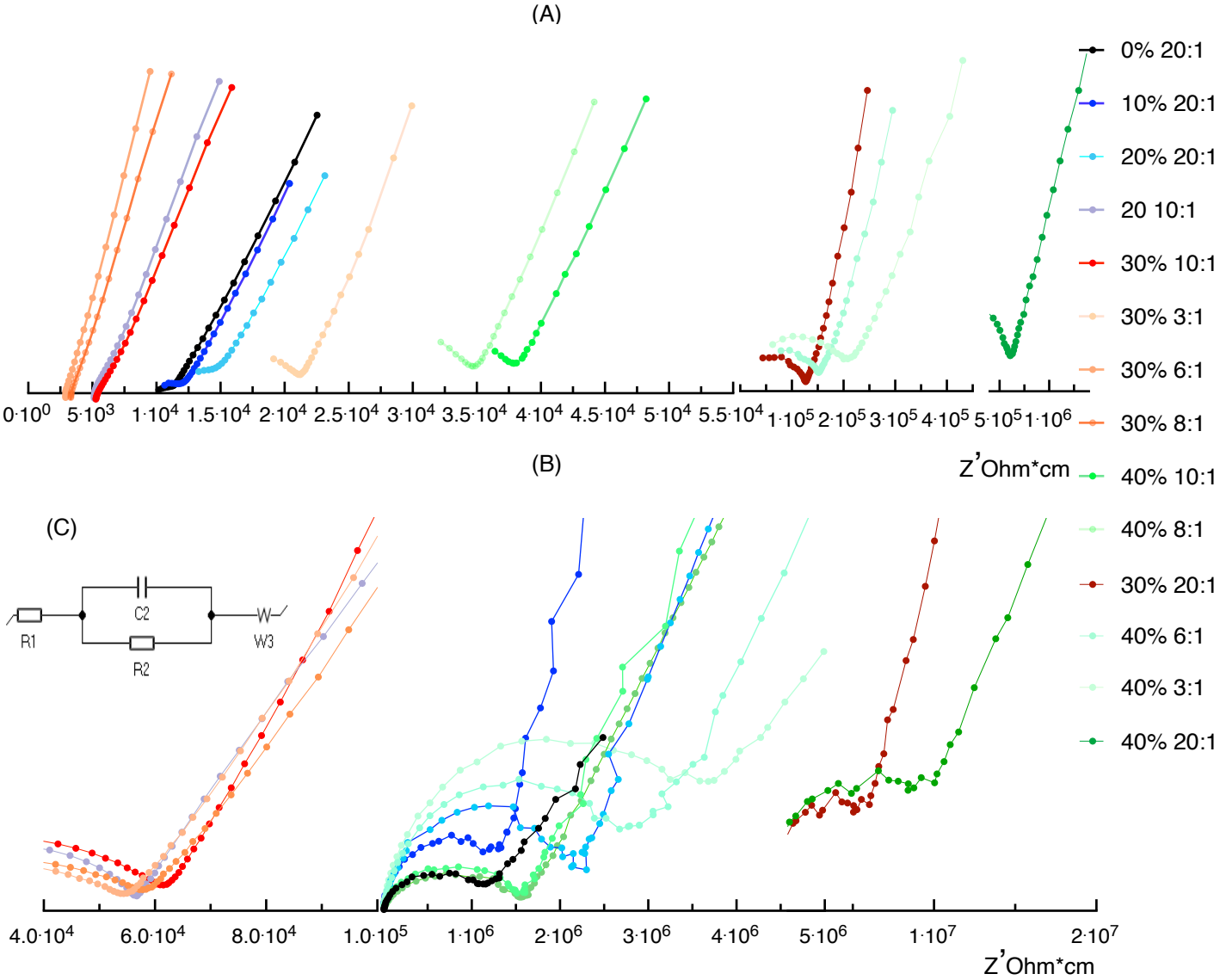


Figure S1. Nyquist plots of electrochemical impedance spectroscopy (EIS) for determining ionic conductivity of PEO-PVDF based polymer films at **(A)** 60 and **(B)** 25°C. The measurements were performed in two-electrode symmetric cell with stainless steel electrodes ($S_{electrode}$ = 1.77 cm^2). **(C)** The equivalent circuit for calculating film resistance. R1, R2 are the contact and bulk film resistance, respectively, C2 is a film capacity, W3 is a Warbourg element.

Table S1. Calculated ionic conductivity (σ, S/cm) and specific resistance (1/σ, Ohm*cm) of PEO-PVDF based polymer films at **(A)** 60 and **(B)** 25°C.

(A)

	Conductivity, S/cm				
60C	40%	30%	20%	10%	0%
20	1.66E-06	7.98E-06	6.93E-05	8.09E-05	8.78E-05
10	2.64E-05	1.84E-04	1.94E-04		
8	2.88E-05	2.98E-04			
6	6.66E-06	3.45E-04			
3	4.93E-06	4.77E-05			
60C	Spesific resistance (1/conductivity) Ohm*cm				
20	6.01E+05	1.25E+05	1.44E+04	1.24E+04	1.14E+04
10	3.79E+04	5.45E+03	5.16E+03		
8	3.48E+04	3.36E+03			
6	1.50E+05	2.90E+03			
3	2.03E+05	2.10E+04			

(B)

	Conductivity, S/cm				
25C	40%	30%	20%	10%	0%
20	1.14E-07	1.91E-07	4.60E-07	8.24E-07	8.65E-07
10	6.44E-07	1.65E-05	1.77E-05		
8	6.60E-07	1.76E-05			
6	3.83E-07	1.86E-05			
3	2.85E-07	1.84E-06			
25C	Spesific resistance (1/conductivity) Ohm*cm				
	8.74E+06	5.24E+06	2.17E+06	1.21E+06	1.16E+06
	1.55E+06	60761.09	56619.82		
	1.52E+06	56976.81			
	2.61E+06	53636.27			
	3.50E+06	544614.8			

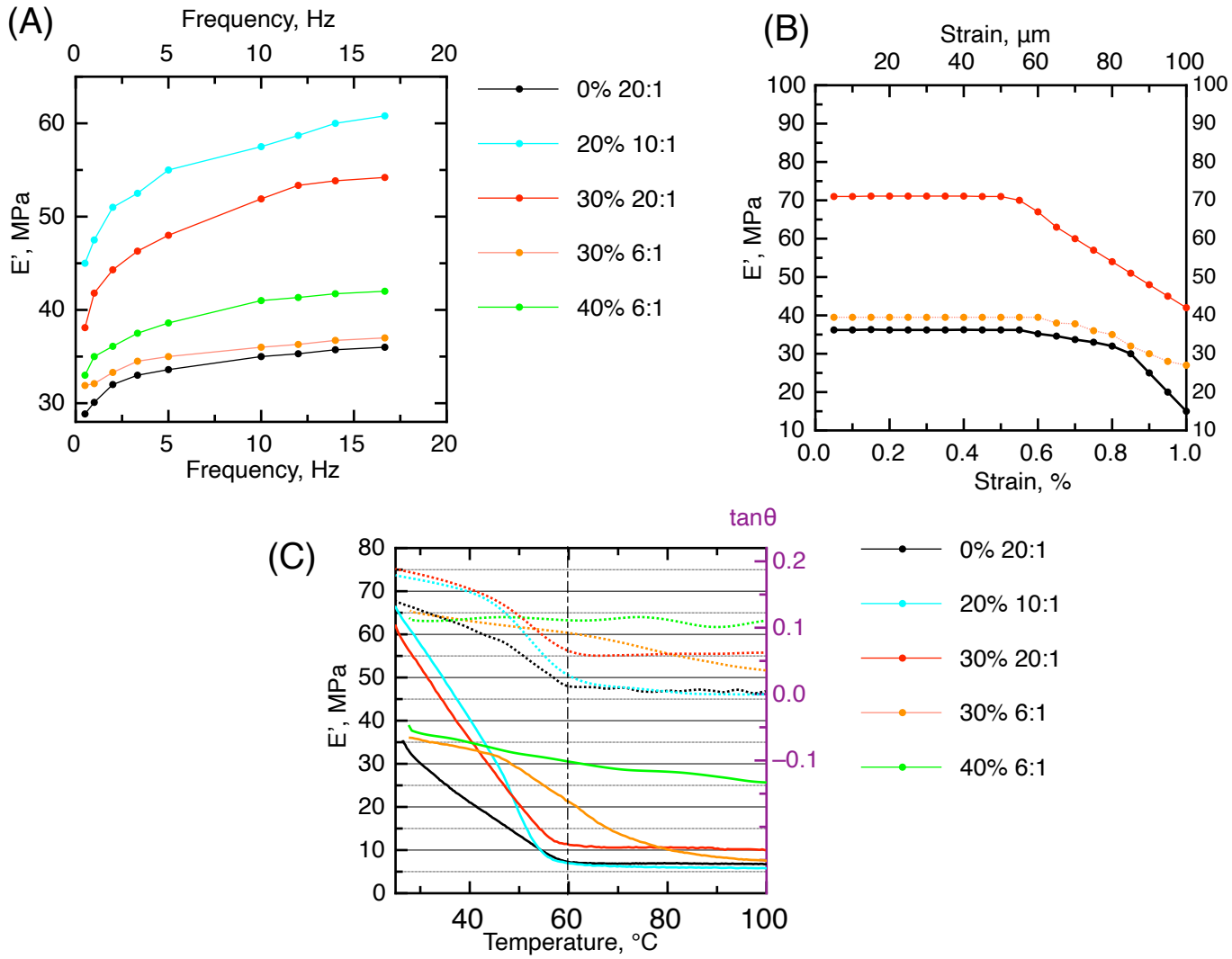


Figure S2. Dynamic mechanical analysis and the photographs of the films. **(A)** Dependence of the storage modulus E' on frequency for PEOxLiTFSI*m%PVDF SPEs. Testing parameters: Streching amplitude A=0.3% (30 μm), frequency range - from 0.05 to 16Hz, T=25°C. **(B)** Strain-stress diagram recorded with a step dynamic load for defining range of E' linear responce. The amplitude was increased by 5 μm at each step. Loading frequency f = 10 Hz, temperature 25^{0}C. Sample size: 10.5mm x 4mm x 0.1mm. **(C)** The temperature dependence of the storage modulus E' (solid line) and tanθ (dotted line) for PEOxLiTFSI*m%PVDF SPEs. Testing parameters: amplitude A = 0.3%, frequency f = 10 Hz, Temperature range from 25 to 10025°C. **(D)** Pictures of the free standing PEO_6LiTFSI*30% PVDF film: pristine film (left) and stretched (right). **(E)** PEO_{10}LiTFSI film (PVDF-free) on laminated aluminum foil.

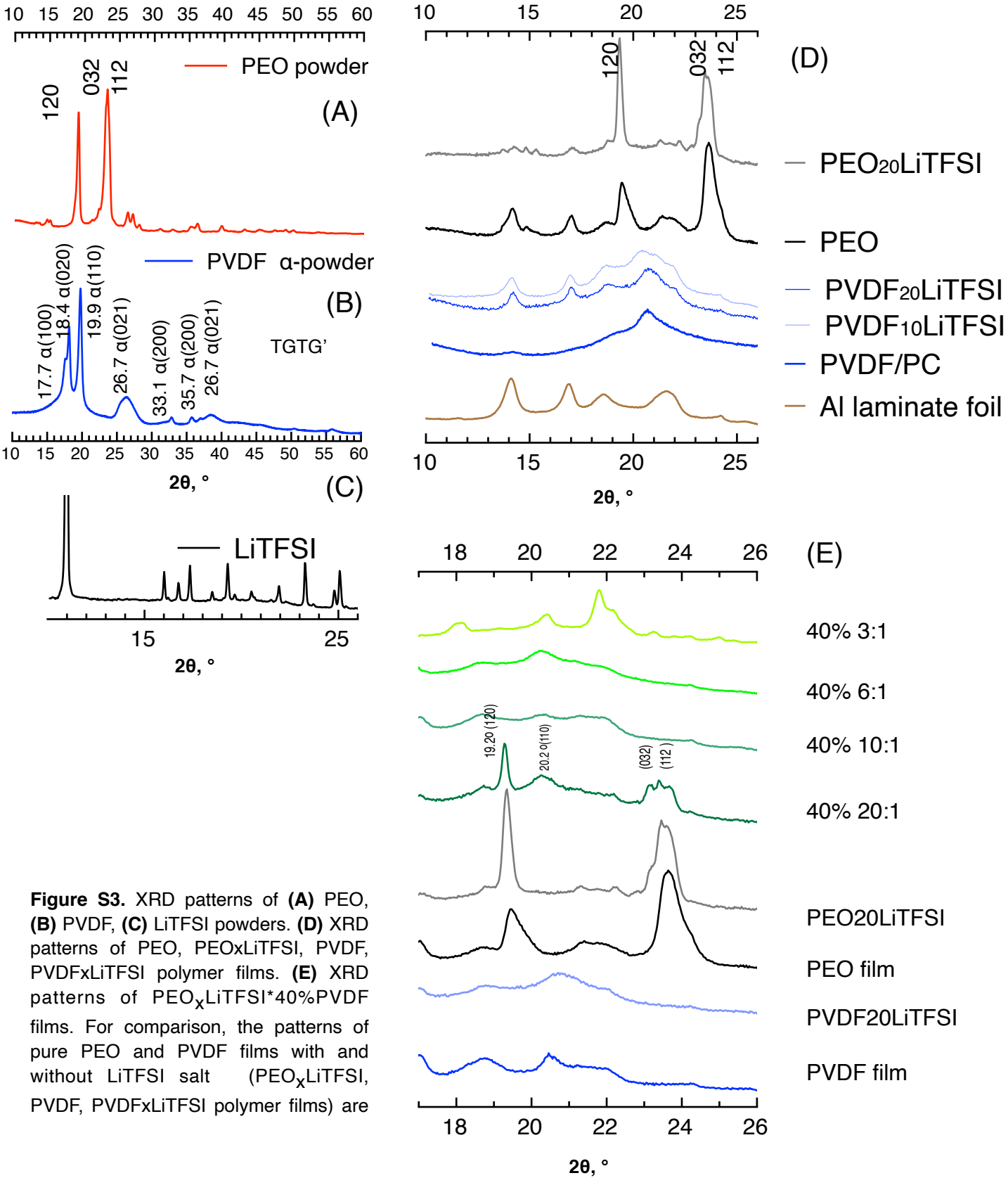


Figure S3. XRD patterns of **(A)** PEO, **(B)** PVDF, **(C)** LiTFSI powders. **(D)** XRD patterns of PEO, PEOxLiTFSI, PVDF, PVDFxLiTFSI polymer films. **(E)** XRD patterns of $PEO_xLiTFSI$*40%PVDF films. For comparison, the patterns of pure PEO and PVDF films with and without LiTFSI salt ($PEO_xLiTFSI$, PVDF, PVDFxLiTFSI polymer films) are

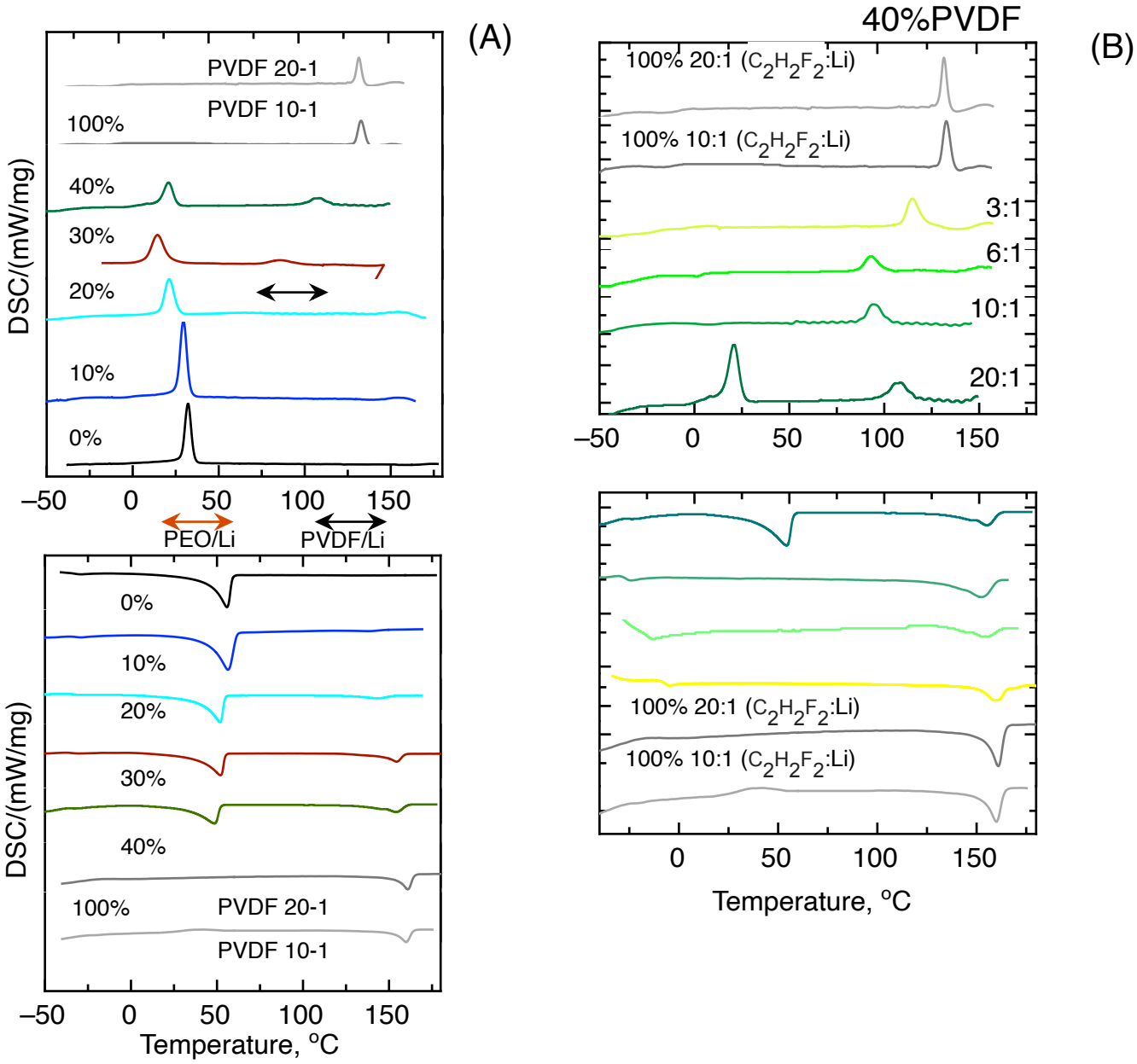


Figure S4. DSC thermograms for **(A)** PEOxLiTFSI*m%PVDF and

(B) PEOxLiTFSI*40%PVDF polymer films on heating and cooling (10^{o}C/min).

Table S2. DSC results for PEOxLiTFSI*m%PVDF films.

Mass% PVDF in PEOxLiTFSI*m%PVDF blend	Polymer type	PEO									PVDF					
	Procedure	Glass transition temperature			Heating			Cooling*			Heating			Cooling*		
	EO:Li ratio	T,C°					J/g	T,C°		J/g	T,C°		J/g	T,C°		J/g
		Tg0	Tg1	Tg	Tm10	Tm11	dH1	Tm10*	Tm11*	dH1*	Tm20	Tm21	dH2	Tm20*	Tm21*	dH2*
0	20:1	-29.5	-18.5	-23	45.55	58.95	56.1	35.73	28.6	54.94	------	------	------	------	------	------
10		-30.6	-28.73	-26.87	45.09	60.96	57.04	32.67	23.89	56.01	------	------	------	------	------	------
20		-34.5	-29	-30.81	40.66	54.62	44.57	25.58	16.36	44.52	128.26	153.73	8.331	------	------	------
30	20:1	-36	-30.5	-33.2	38.33	54.8	35.31	20.1	21.77	35.63	144.93	159.18	12.6	98.02	78.15	12.45
	10:1	-25.93	-18.51	-19.91	------	------	------	------	------	------	128.39	155.75	11.99	102.27	79.03	11.55
	8:1	-22.49	-17.19	-19.64	------	------	------	------	------	------	116.89	153.17	7.576	82.77	63.74	7.719
	6:1	-31.59	-26.02	-27.37	------	------	------	------	------	------	126.28	160.47	9.07	95.8	79.1	9.54
	3:1	-28.73	-23.4	-25.64	------	------	------	------	------	------	121.82	151.97	5.138	133.22	151.97	8.127
40	20:1	-37.65	-34.06	-34.38	29.85	52.05	31.287	25.91	15.52	31.04	144.95	160.87	16.42	119.86	99.9	16.67
	10:1	-38.87	-34.2	-36.48	------	------	------	------	------	------	135.72	159.73	14.41	102.05	88.82	13.3
	6:1	-22.83	-18.2	-18.88	------	------	------	------	------	------	139.56	161.5	8.001	100.97	86.75	10.47
	3:1	-18.8	-14.3	-16.5	------	------	------	------	------	------	163.8	149.4	21.243	140.9	109	13.434
100	20:1	-43.4	-19.9	-32.5	------	------	------	------	------	------	154	164.7	22.09	138.94	131.62	18.89
	10:1	-49.97	-27.02	-44.08	------	------	------	------	------	------	153.34	164.24	18.38	137.04	131.38	17.27

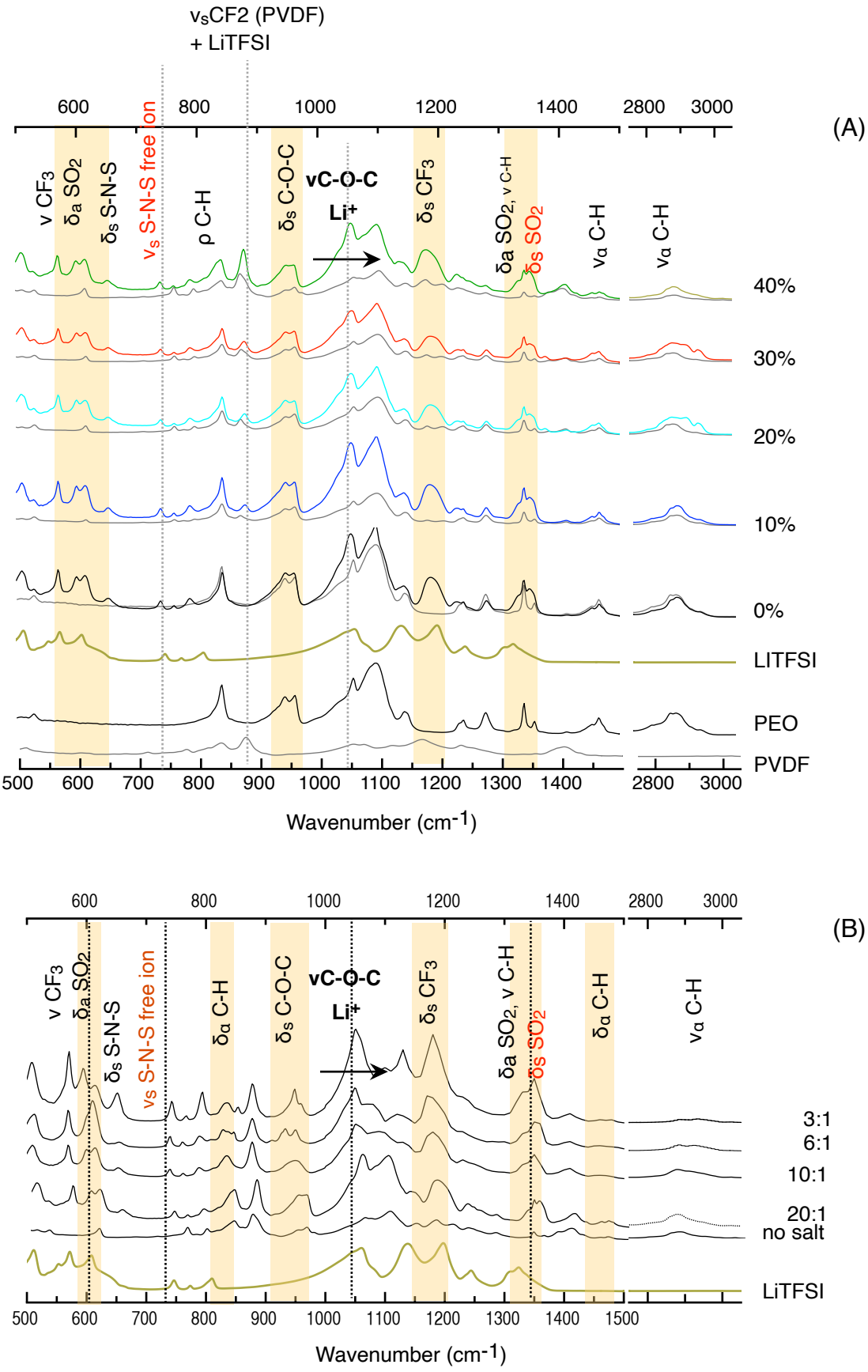


Figure S5. Fourier transform infrared spectroscopy (FTIR) spectra of **(A)** PEO_{20}LiTFSI*m%PVDF (grey lines denote the films of pure polymer PEO*m%PVDF blends of the corresponding composition, LiTFSI-free) and of **(B)** PEO_xLiTFSI*40%PVDF in the ranges 500-1500 and 2750-3050 cm^{-1}

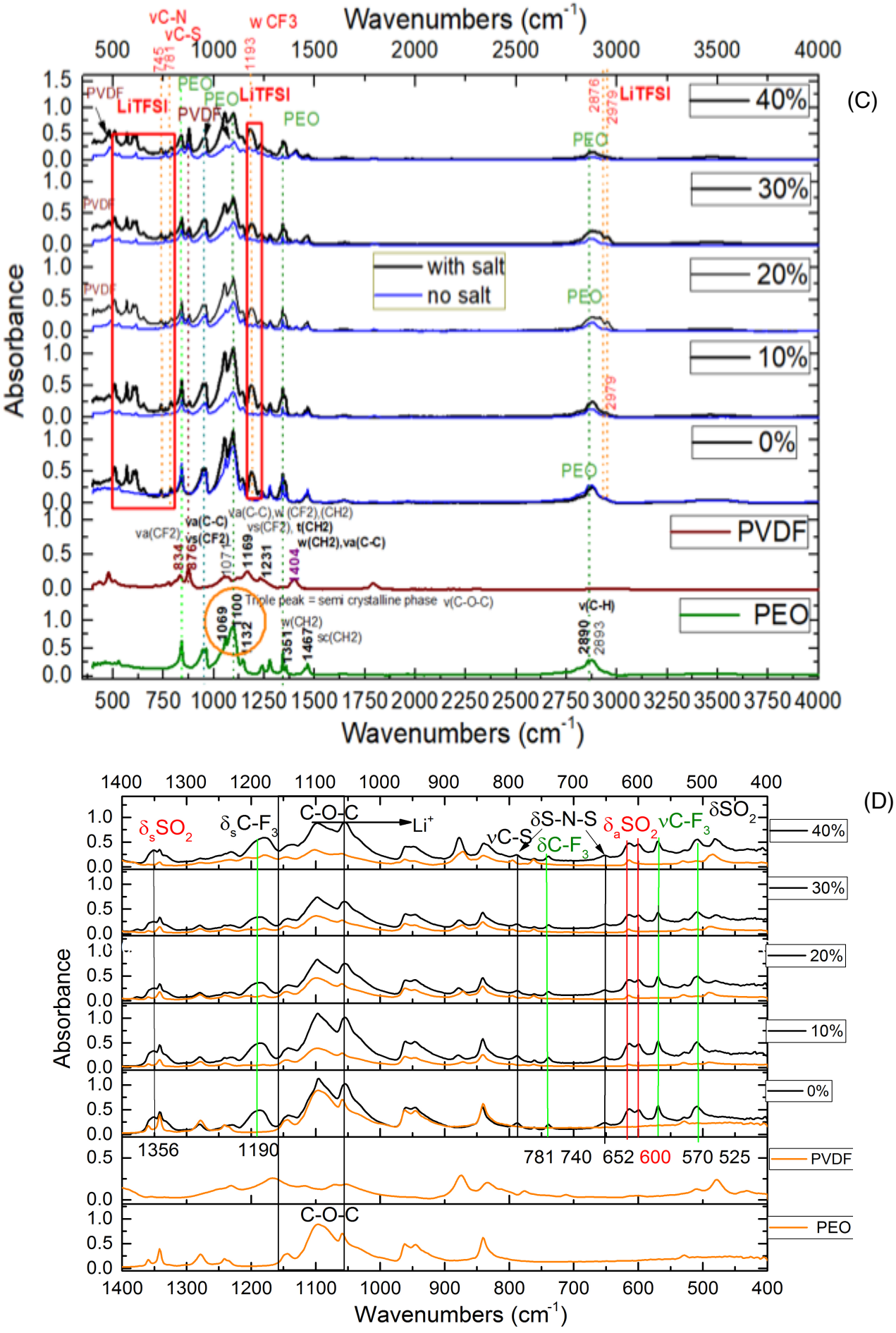
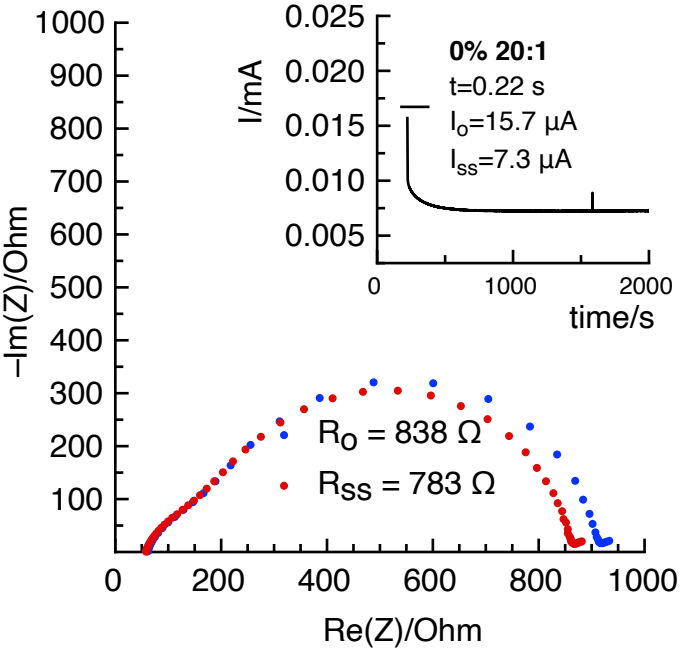
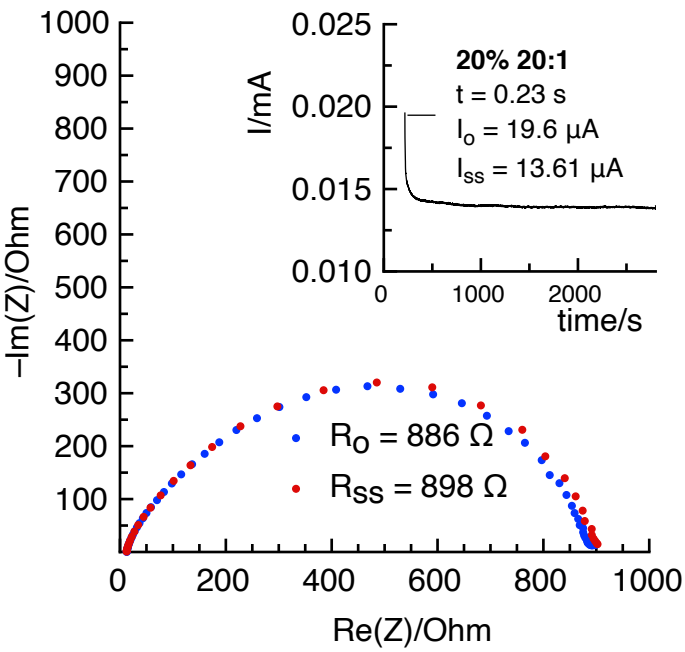
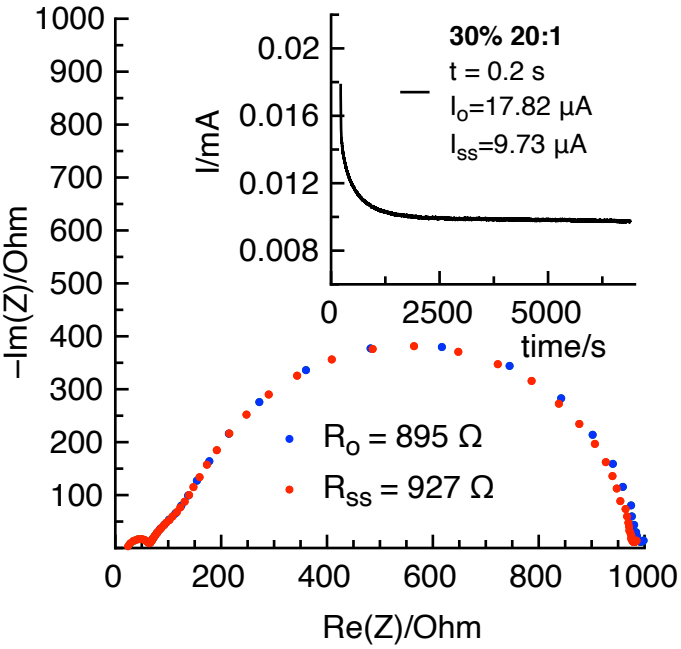
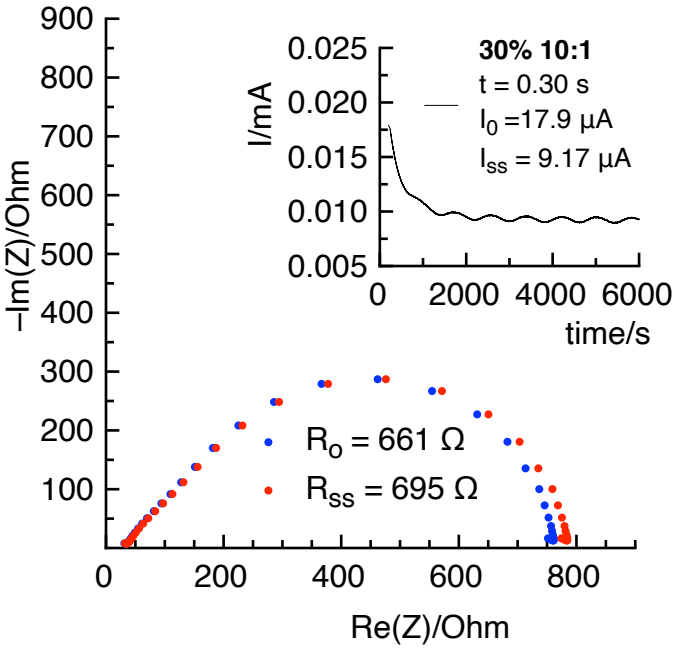


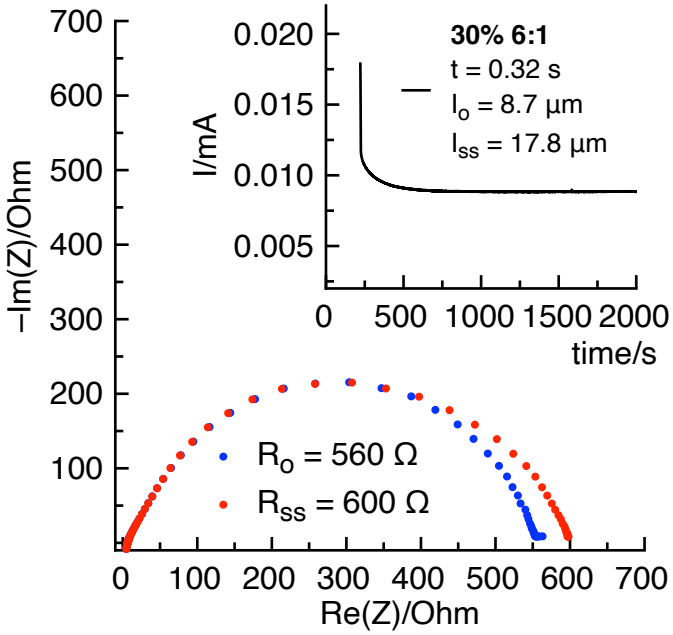
Figure S5 (continued). Vibrational fingerprints of PEO and PVDF **(C)** and LiTFSI **(D)** polymers shown on FTIR spectra of PEO_{20}*m%PVDF.

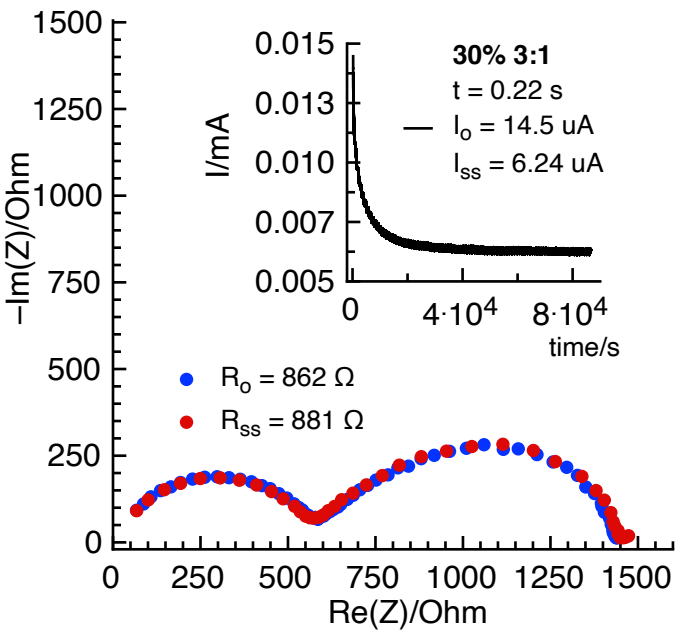

0% 20:1
t=0.22 s
I_o=15.7 µA
I_{ss}=7.3 µA
I/mA
time/s
R_O = 838 Ω
R_{SS} = 783 Ω
–Im(Z)/Ohm
Re(Z)/Ohm


20% 20:1
t = 0.23 s
I_o = 19.6 µA
I_{ss} = 13.61 µA
I/mA
time/s
R_O = 886 Ω
R_{SS} = 898 Ω
–Im(Z)/Ohm
Re(Z)/Ohm


30% 20:1
t = 0.2 s
I_o=17.82 µA
I_{ss}=9.73 µA
I/mA
time/s
R_o = 895 Ω
R_{ss} = 927 Ω
–Im(Z)/Ohm
Re(Z)/Ohm


30% 10:1
t = 0.30 s
I_0 =17.9 µA
I_{ss} = 9.17 µA
I/mA
time/s
R_o = 661 Ω
R_{ss} = 695 Ω
–Im(Z)/Ohm
Re(Z)/Ohm


30% 6:1
t = 0.32 s
I_o = 8.7 µm
I_{ss} = 17.8 µm
I/mA
time/s
R_o = 560 Ω
R_{ss} = 600 Ω
–Im(Z)/Ohm
Re(Z)/Ohm


30% 3:1
t = 0.22 s
I_o = 14.5 uA
I_{ss} = 6.24 uA
I/mA
time/s
R_o = 862 Ω
R_{ss} = 881 Ω
–Im(Z)/Ohm
Re(Z)/Ohm

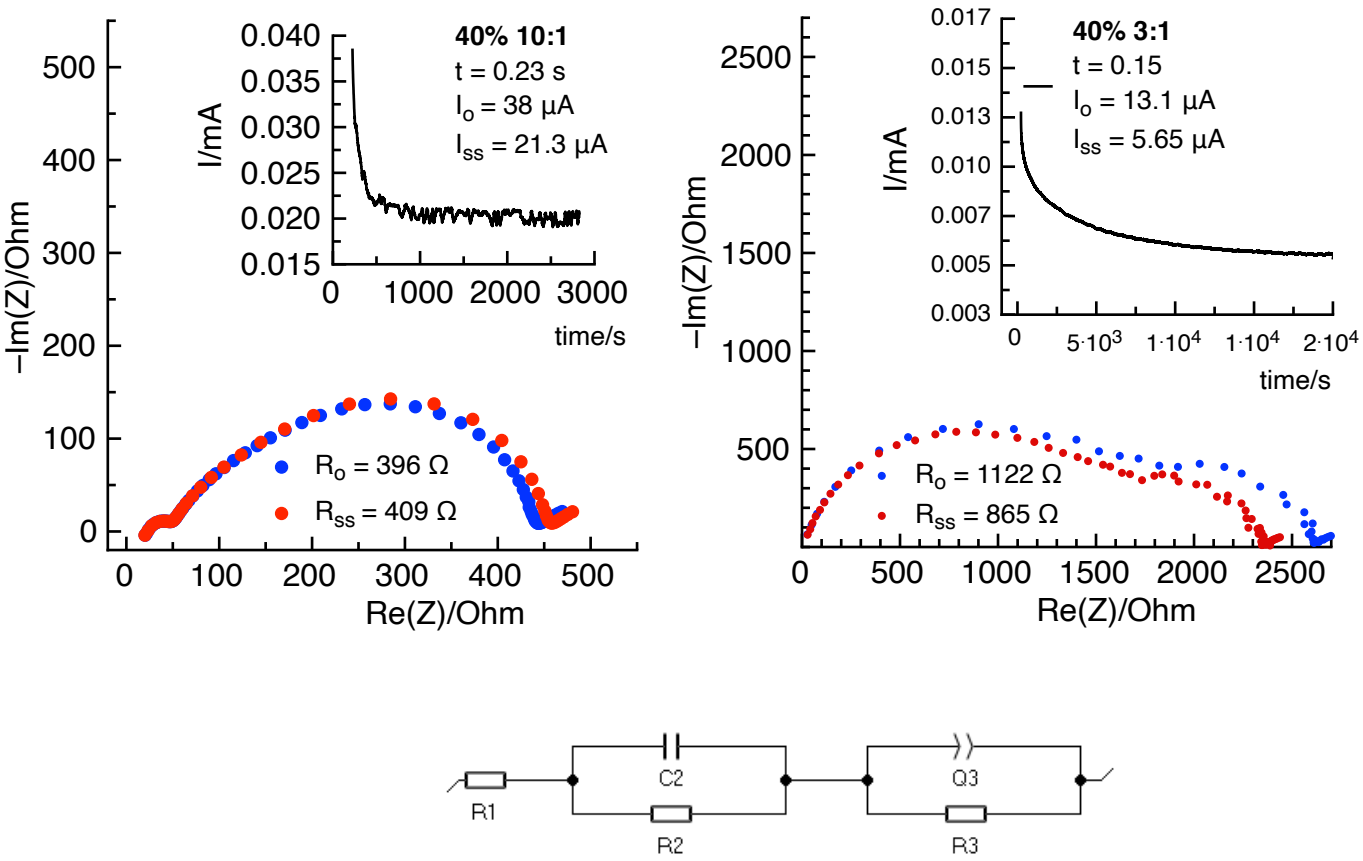


Figure S6. Li transference number determination for PEO_XLiTFSI*m%PVDF SPEs. Current transients at constant voltage polarization of 20 mV are shown in the insets, Nyquist plots before and after polarisation - in the main figures. The equivalent circuit for calculating the resistance in the experiment of determining Li^+ transfer numbers (t_{Li+}) is shown below the data. R1, R2 are the contact and bulk electrolyte resistance, respectively, R3 is the interphase resistance, C2 ia a film capacity, Q is a constant phase element.

Table S3. The calculated values of Li^+ transference numbers for PEO_XLiTFSI*30%PVDF and PEO_XLiTFSI*40%PVDF compositions

EO:Li ratio	30%	EO:Li ratio	40%
20	0.2	20	0.16
10	0.3	10	0.23
8	0.3	6	0.26
6	0.32	3	0.15
3	0.22		