Electronic Supplementary Material (ESI) for Materials Advances.

Supplementary Information

Single-Ion Polymer/LLZO Hybrid Electrolytes with High Lithium Conductivity

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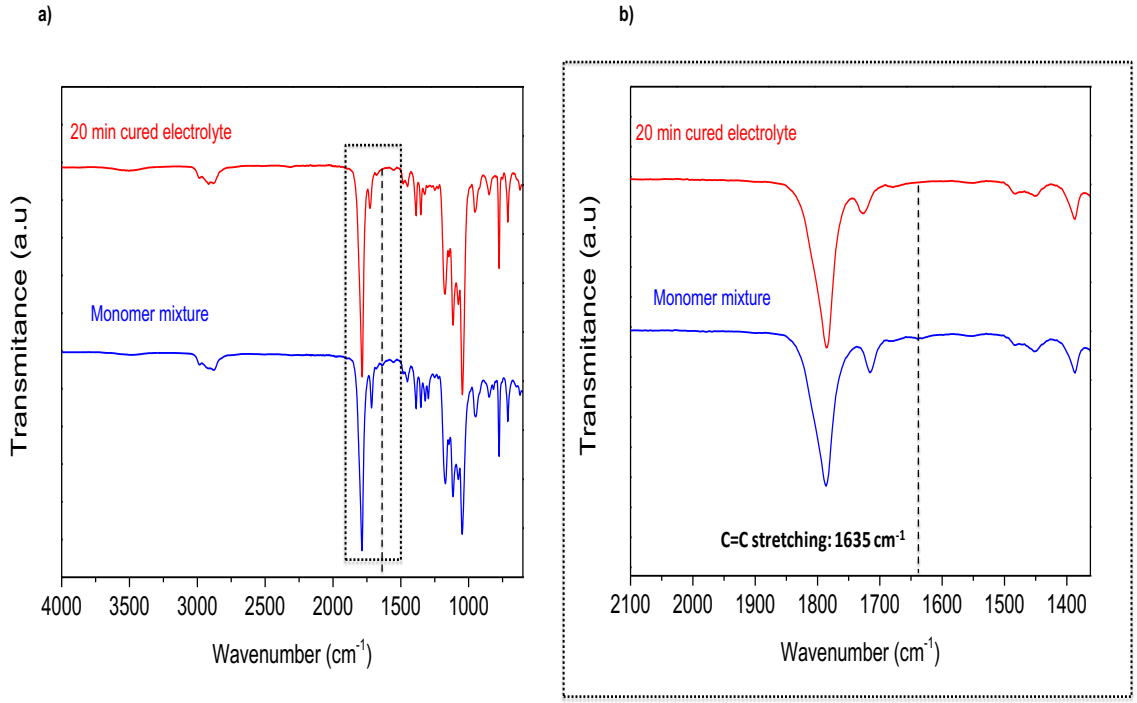

Fig.S1. (a) FTIR spectra of monomers mixture and 20 min cured SIPE
(b) Zoom to show the disappearance of C=C stretching band after curing

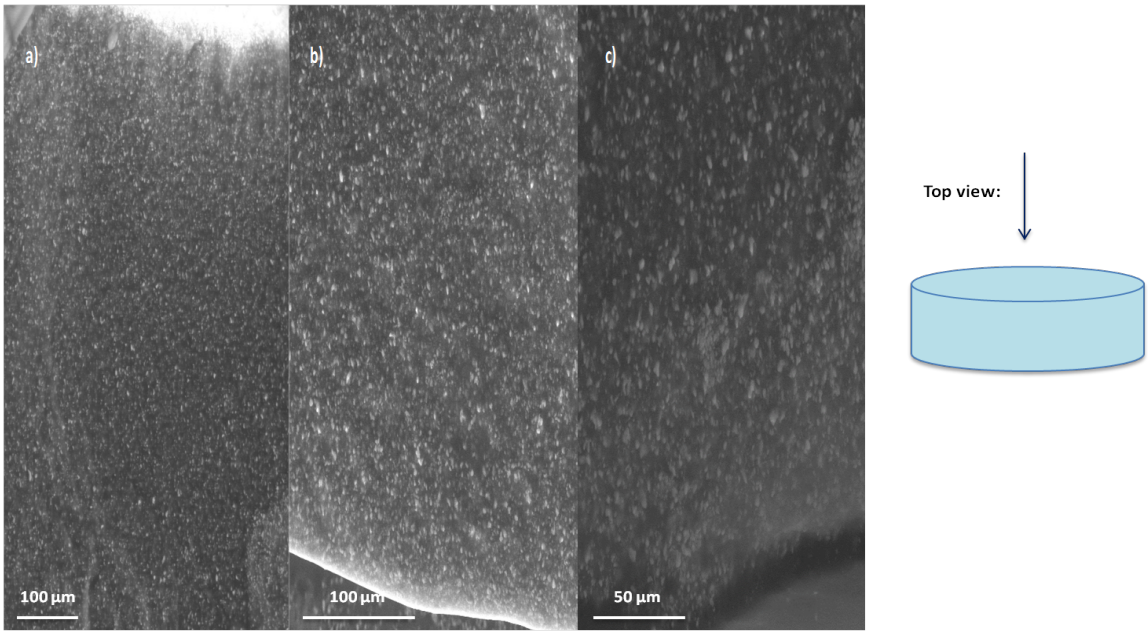

Fig.S2. ESEM pictures on top view of single ion hybrid crosslinked polymers: (a) HSIPE-26, (b) HSIPE-40, (c) HSIPE-50

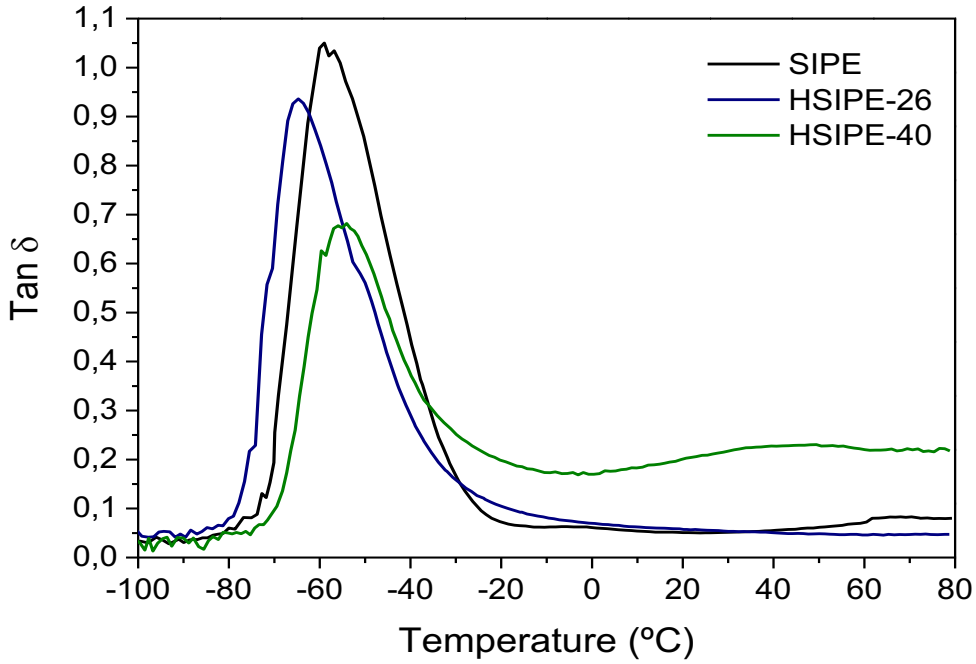

Fig.S3. Tan (δ) in function of temperature for pristine and hybrid single ion crosslinked polymer electrolytes

Table S4: Comparison of different LLZO hybrid polymers in terms of ionic conductivity and galvanostatic cycling

Authors	Matrix	Li salt	Composition	Ionic conductivity ($S.cm^{-1}$)	Li/Li galvanostatic cycling
Our study	Single ion crosslinked polymer	Salt free	26 wt.%	$1,17.10^{-4}$ (25 °C)	At 60°C: Without short circuit -0.1 $mA.cm^{-2}$ for 6h, -0.25 $mA.cm^{-2}$ for 6h, -0.5 $mA.cm^{-2}$ for 6h, -1 $mA.cm^{-2}$ for 6h With short circuit -2 $mA.cm^{-2}$ for 6h, -4 $mA.cm^{-2}$ for 6h
Huo & al [1]	PEO	Salt free	15 vol.%	$2,2.10^{-4}$ (25 °C)	At 30°C: - 0.5 $mA.cm^{-2}$ for 7500 min - 1 $mA.cm^{-2}$ for 500 min before short circuit
Choi & al [2]	PEO	$LiClO_4$	52.5 wt.%	$4,42.10^{-4}$ (55 °C)	-
Zhang & al [3]	PEO	Salt free	12.7 vol.%	$2,1.10^{-4}$ (30 °C)	At 60°C: - 3 $mA.cm^{-2}$ over 750h without short circuit. When LiTFSI is added, short circuit over 25h cycling
Chen & al [4]	PEO	LiTFSI	7.5 wt.%	$5,5.10^{-4}$ (25 °C)	At 60°C: - 0.2 $mA.h.cm^{-2}$ over 15h
Zheng & al [5]	PEO/ TEGDME	$LiClO_4$	40 wt.%	4.10^{-5} (25 °C)	-
Keller & al [6]	PEO	LiTFSI	70 wt.%	$\approx 10^{-5}$ (25 °C)	At 60°C: - 5 $\mu A.cm^{-2}$ for 20h - 10 $\mu A.cm^{-2}$ for 10h - 20 $\mu A.cm^{-2}$ for 5h - 50 $\mu A.cm^{-2}$ for 2h - 100 $\mu A.cm^{-2}$ for 1h
Langer & al [7]	PEO	$LiClO_4$	40 wt.%	5.10^{-5} (80 °C)	-

Cheng & al [8]	PEO	$LiClO_4$	30 wt.%	$3,1.10^{-6}$ (25ºC)	-
Zagórski & al [9]	PEO	LiTFSI	10 vol.% (31 wt.%)	$4,5.10^{-4}$ (70ºC)	At 70ºC - 0.1 $mA.cm^{-2}$ for 2h For PEO-LITFSI, short circuit over 88h cycling For PEO-LiTFSI-LLZO, cycling over 750h but voltage instabilities (first 70h)

References:

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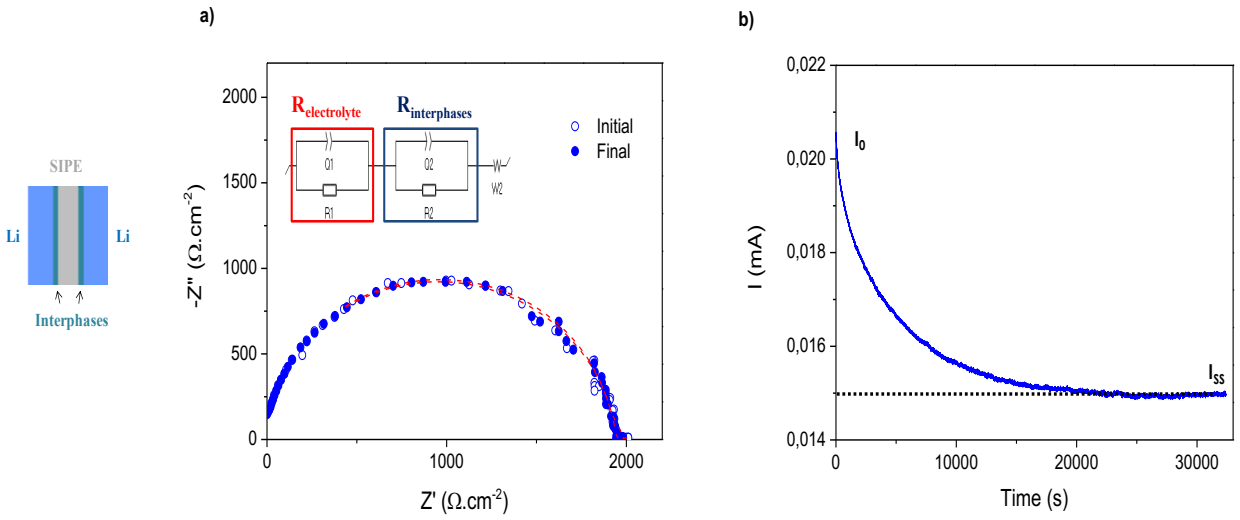

Fig.S5. Transference number determination for SIPE
(a) EIS spectra and simulated data from equivalent circuit modeling
(b) Intensity decay after polarization

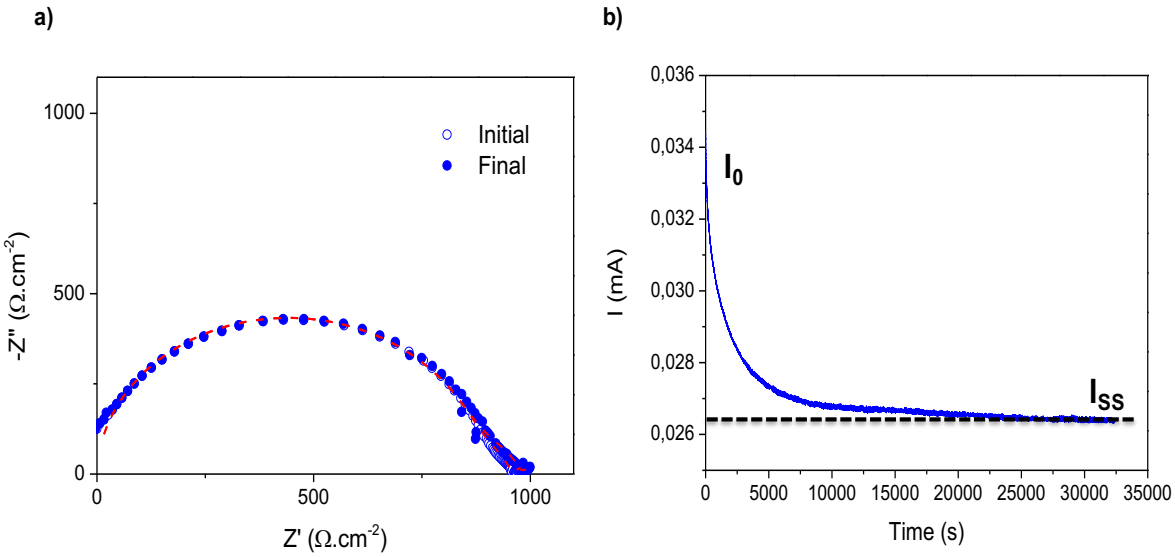

Fig.S6. Transference number determination for HSIPE-9
(a) EIS spectra and simulated data from equivalent circuit modeling
(b) Intensity decay after polarization

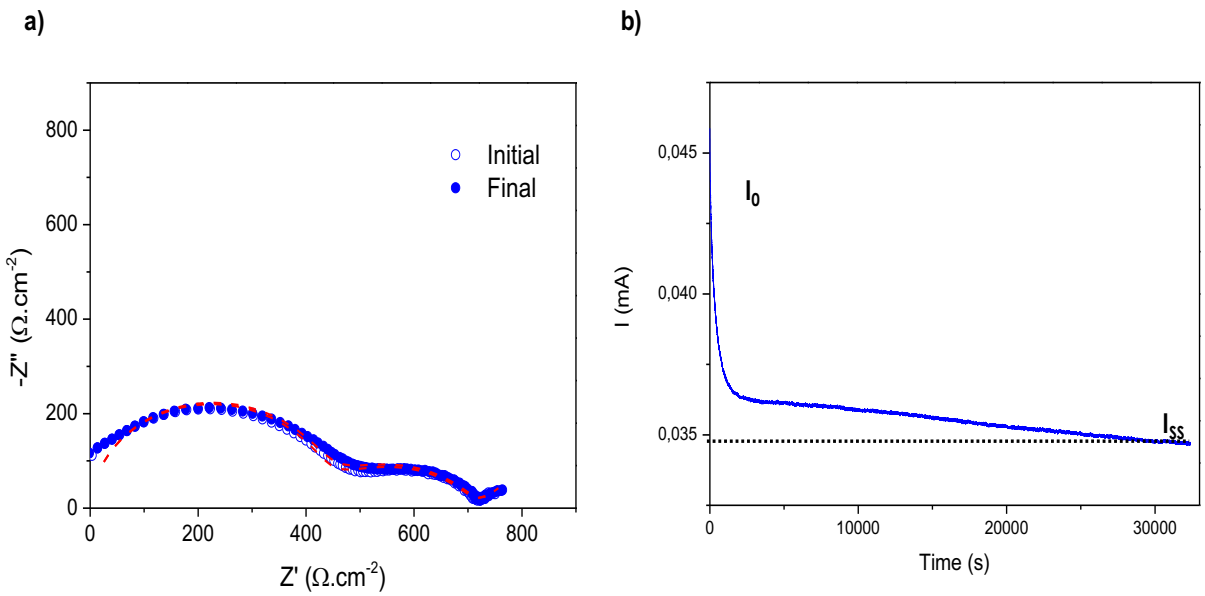

Fig.S7. Transference number determination for HSIPE-26
(a) EIS spectra and simulated data from equivalent circuit modeling
(b) Intensity decay after polarization

Table S8: Ionic conductivities for the different pristine and hybrid compositions

Compositions	$\sigma_{25°C}$ (10^{-4} S.cm^{-1})	$\sigma_{50°C}$ (10^{-4} S.cm^{-1})	$\sigma_{70°C}$ (10^{-4} S.cm^{-1})
SIPE	0.48	0.95	1.62
HPE-26	0.11	0.22	0.34
HSIPE-26	1.17	2.67	4.41
HSIPE-9	0.88	2.04	3.38
DIPE	21	42	106
HDIPE-26	14.2	28.9	48.4

Table S9: ^{7}Li T_1 relaxations times obtained by saturation recovery at 22°C

Samples	SIPE	HSIPE-26	HSIPE-9	DIPE	HDIPE-26
Narrow (s)	0.23	1.6	0.25	0.26	1.03
Broad (s)	-	15.8	6.9		15.0

Table S10: ^{7}Li diffusion coefficients at various temperatures

Composition	$D_{70°C}$ (10^{-12} m².s^{-1})	$D_{50°C}$ (10^{-12} m².s^{-1})	$D_{22°C}$ (10^{-12} m².s^{-1})
SIPE	13.1	6.77	2.05
HSIPE-26	17.1	7.03	2.94
HSIPE-9	15.3	8.68	2.78
DIPE	27.7	15.5	5.44
HDIPE-26	23.8	15.2	5.81

Table S11: ^{19}F diffusion coefficients at various temperatures

Composition	$D_{70°C}$ (10^{-11} m².s^{-1})	$D_{50°C}$ (10^{-11} m².s^{-1})	$D_{22°C}$ (10^{-11} m².s^{-1})
DIPE	16.4	10	3.91
HDIPE-26	10.3	5.65	1.98

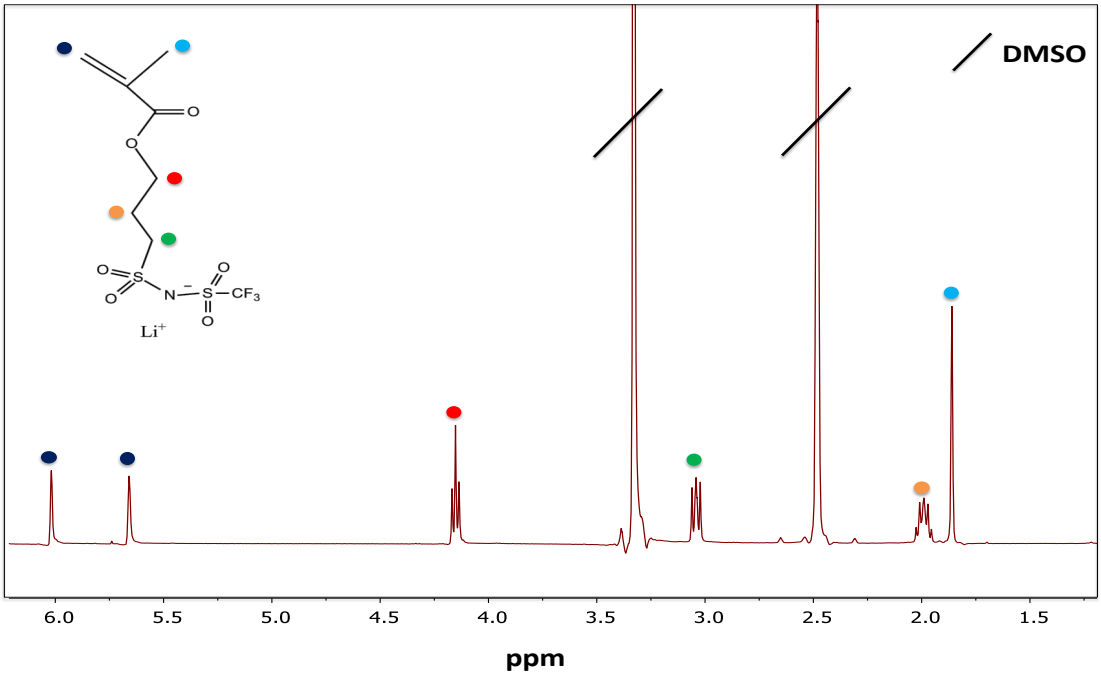

Fig.S12. ^{1}H NMR spectrum of single ion monomer LiMTFSI

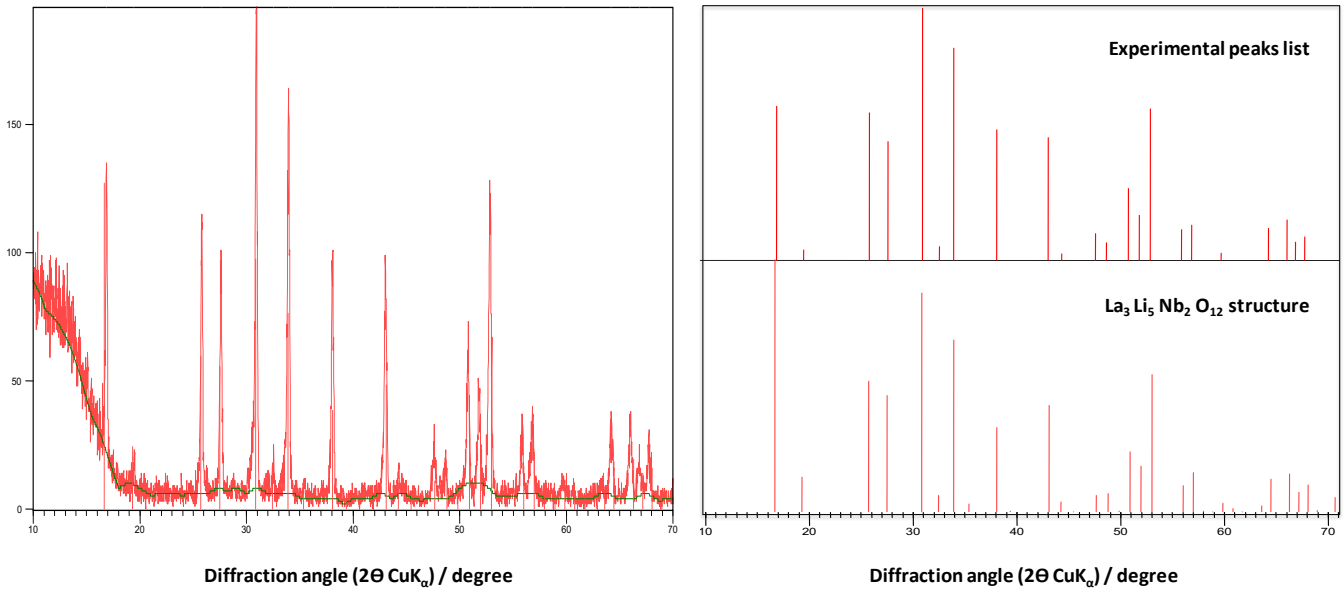

Fig.S13. XRD pattern of LLZO particles and their comparison with the crystalline $La_3Li_5Nb_2O_{12}$ structure (Ia3d)