Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

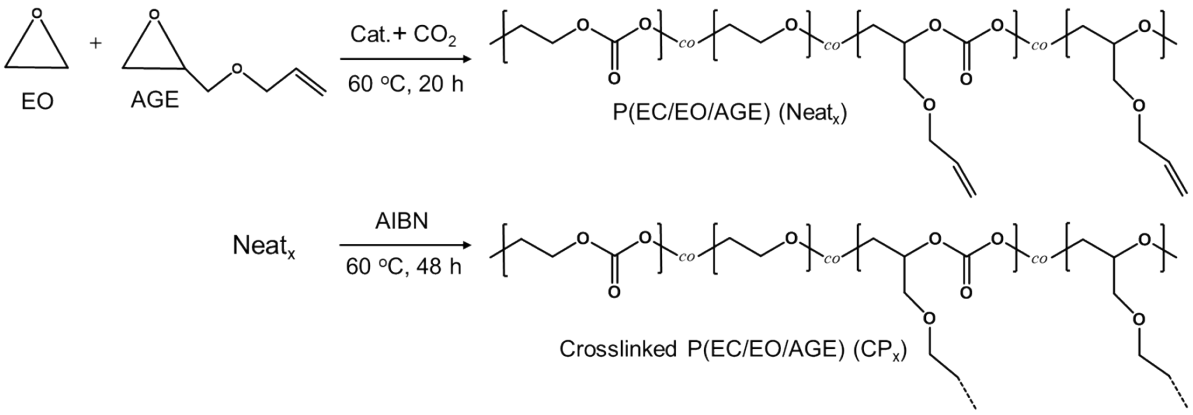
Highly salt concentrated ethylene carbonate-based self-standing copolymer electrolyte for solid-state lithium metal battery

*Nantapat Soontornnon [a], Kento Kimura [b], and Yoichi Tominaga [a]**

[a] Graduate School of Bio-Applications and Systems Engineering (BASE), Tokyo University of Agriculture and Technology, 2-21-16 Nakacho, Koganei, Tokyo 184-8588, Japan

[b] Department of Applied Chemistry, Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2-21-16 Nakacho, Koganei, Tokyo 184-8588, Japan

* Corresponding author: ytominag@cc.tuat.ac.jp



Scheme S1 Synthesis of random copolymer P(EC/EO/AGE) ($Neat_x$) and crosslinked copolymer (CP_x) (where x represents the AGE ratio).

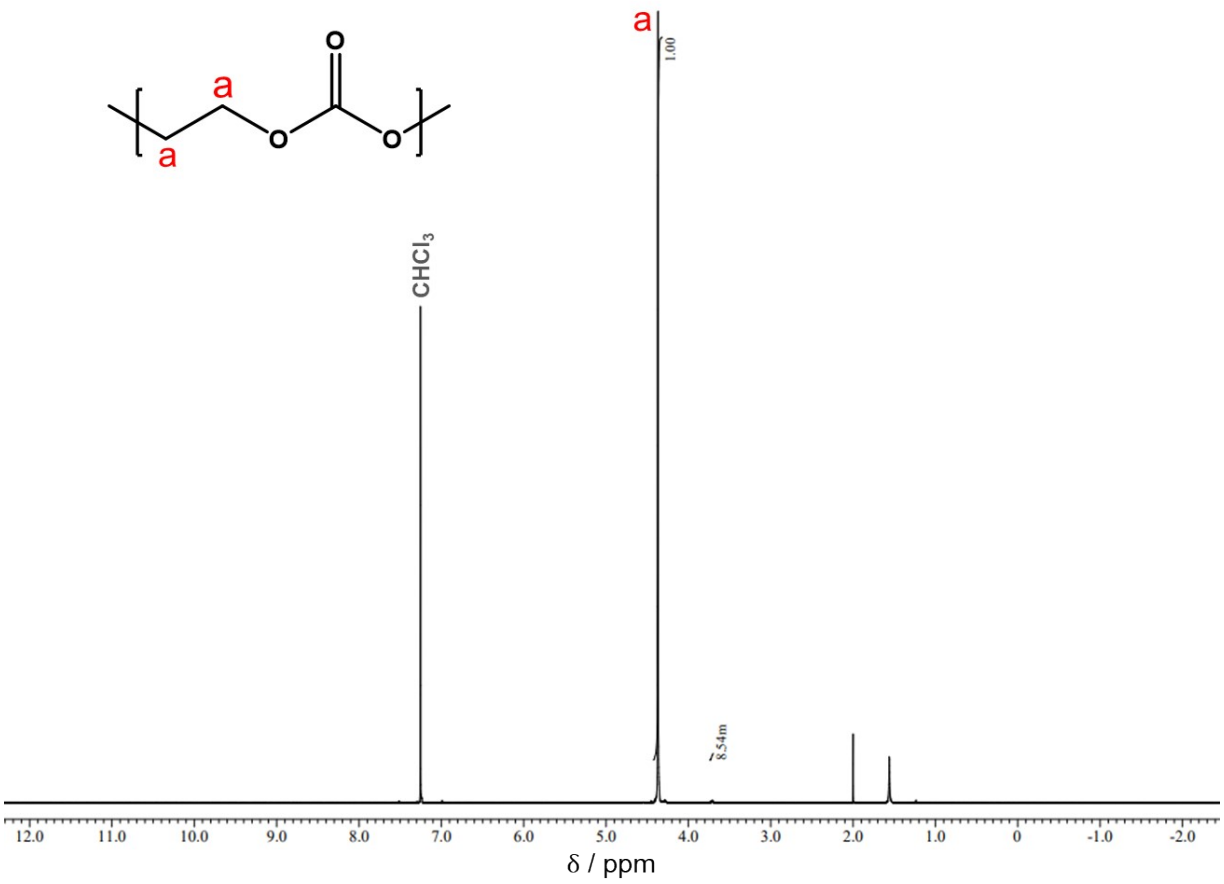


Figure S1 ^{1}H NMR spectrum of poly(ethylene carbonate) (PEC).

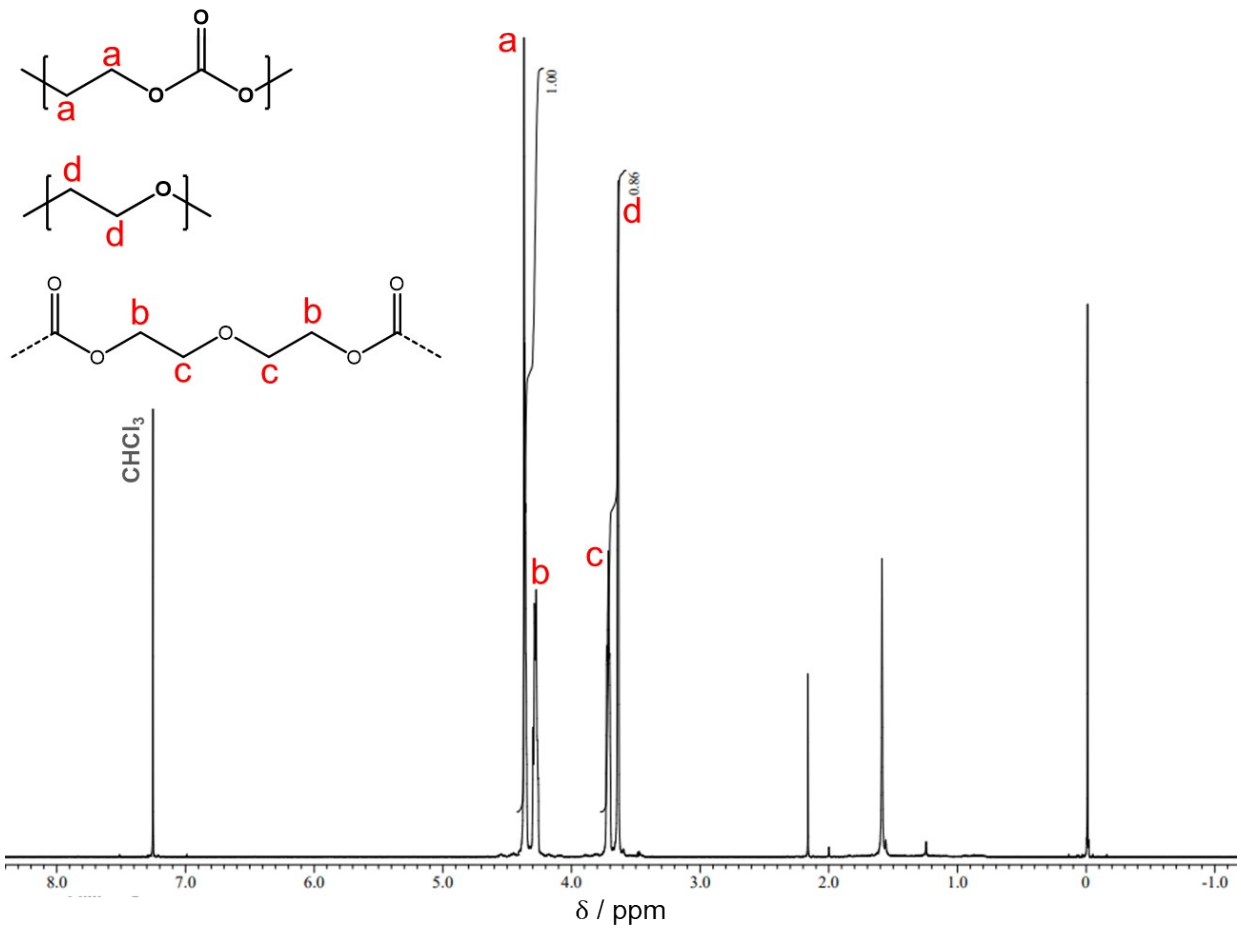


Figure S2 ^{1}H NMR spectrum of poly(ethylene carbonate-*co*-ethylene oxide) (P(EC/EO)).

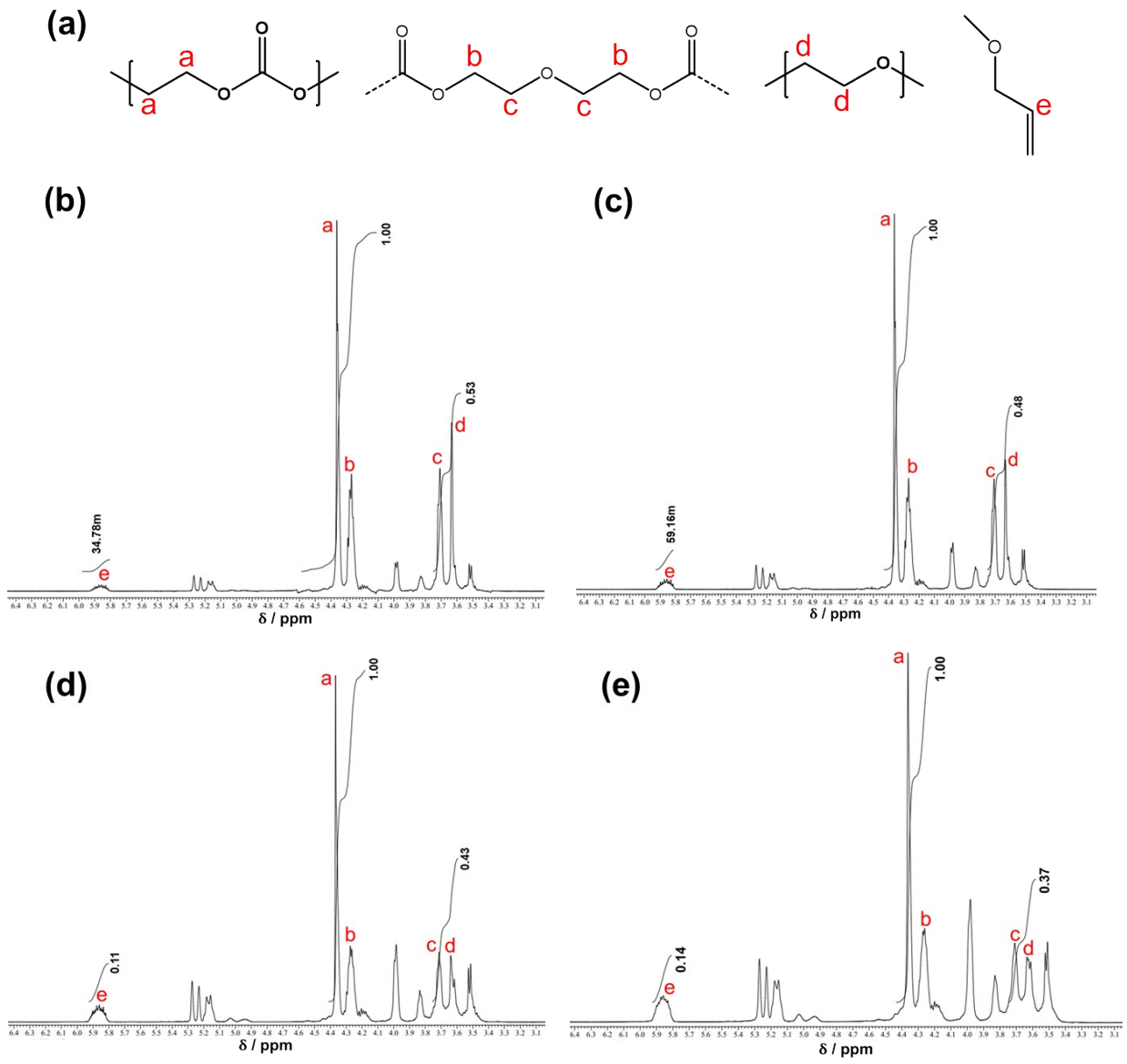


Figure S3 ^{1}H NMR spectrum of P(EC/EO/AGE) ($Neat_x$), which include the integral peak area of the EC/EO/AGE units. (a) Peak assignment (b) $Neat_8$, (c) $Neat_{14}$, (d) $Neat_{23}$, and (e) $Neat_{29}$.

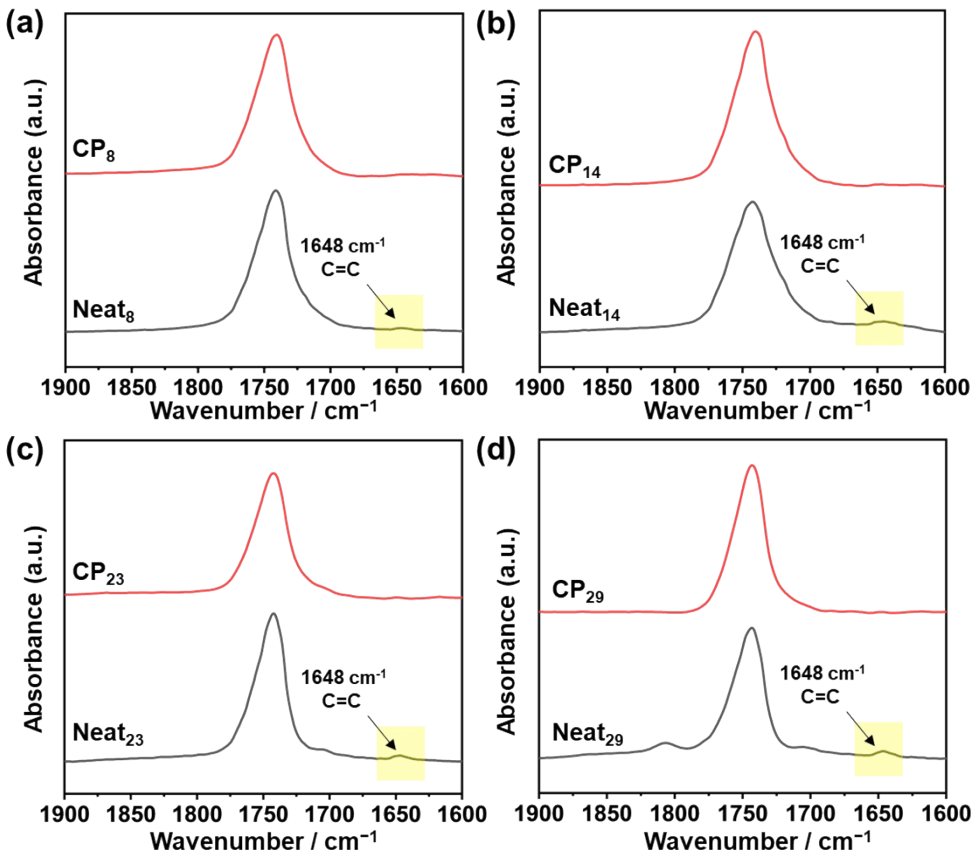


Figure S4 FT-IR spectra of 1900–1600 cm^{-1} for the uncrosslinked ($Neat_x$) and crosslinked copolymers (CP_x) with (a) 8 mol%, (b) 14 mol%, (c) 23 mol%, and (d) 29 mol% of AGE unit.

Table S1 Mechanical and thermal properties of CPs.

Crosslinked copolymer	Monomer unit (%)			EC/EO	Young's modulus (MPa)	Elongation at break (%)	T_g (°C)	T_{d5} (°C)
	EC	EO	AGE					
CP_8	60	32	8	1.9	2.5	23	−22	222
CP_{14}	58	28	14	2.1	6.6	17	−24	234
CP_{23}	54	23	23	2.3	16.8	16	−29	242
CP_{29}	52	19	29	2.7	23.5	15	−31	260

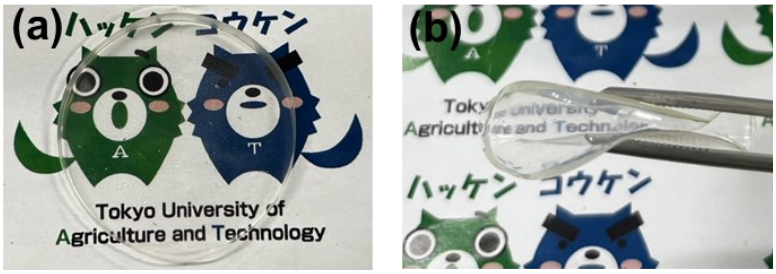


Figure S5 Photographs of CP_{29}. (a) CP_{29} ($\emptyset$ = 35 mm). (b) CP_{29} in a bending state.

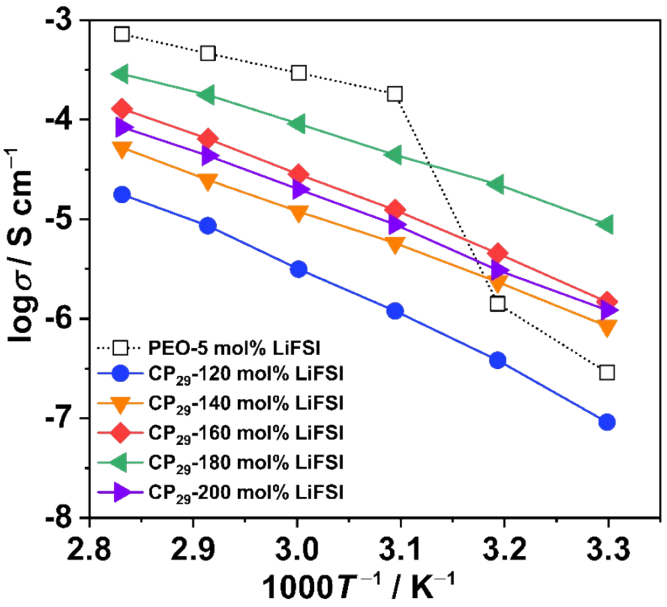


Figure S6 Temperature dependence of the ionic conductivity for PEO-5 mol% LiFSI and CP_{29}-SPEs at various salt concentration.

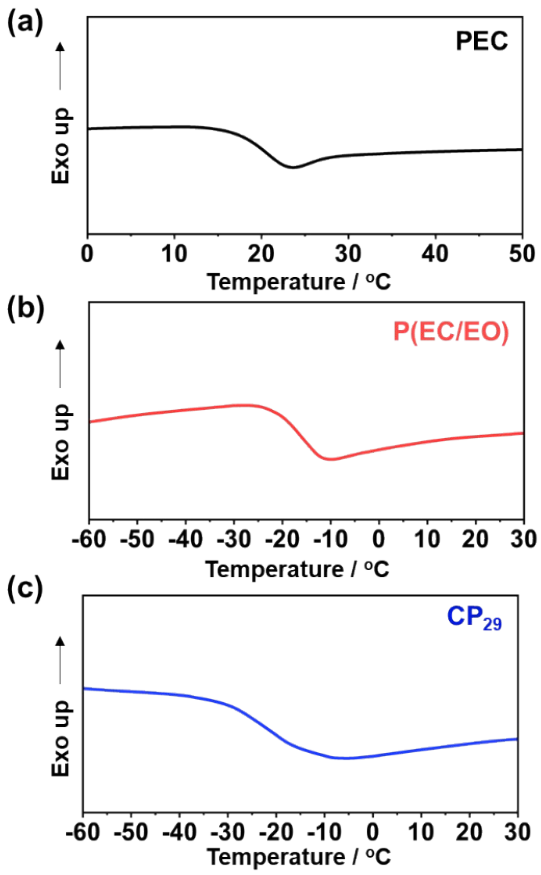


Figure S7 DSC curves of (a) PEC, (b) P(EC/EO), and (c) CP_{29}.

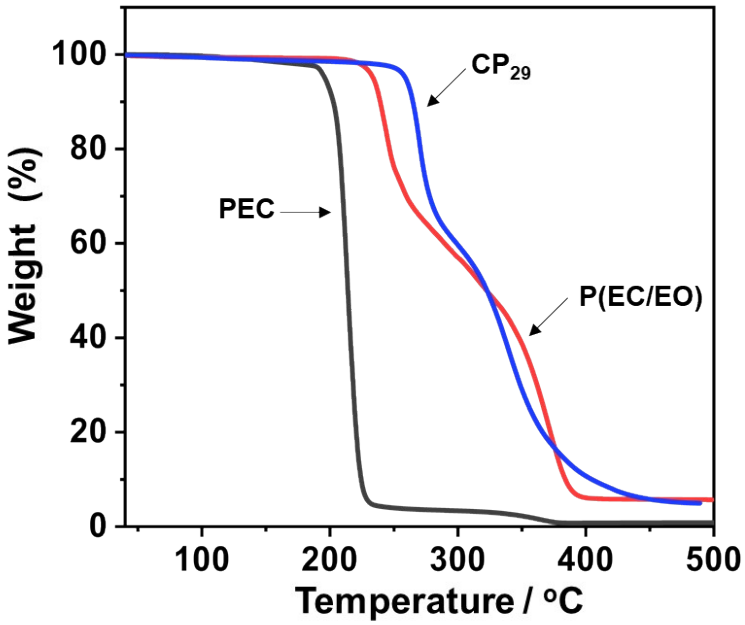


Figure S8 TGA thermograms of PEC, P(EC/EO), and CP_{29}.

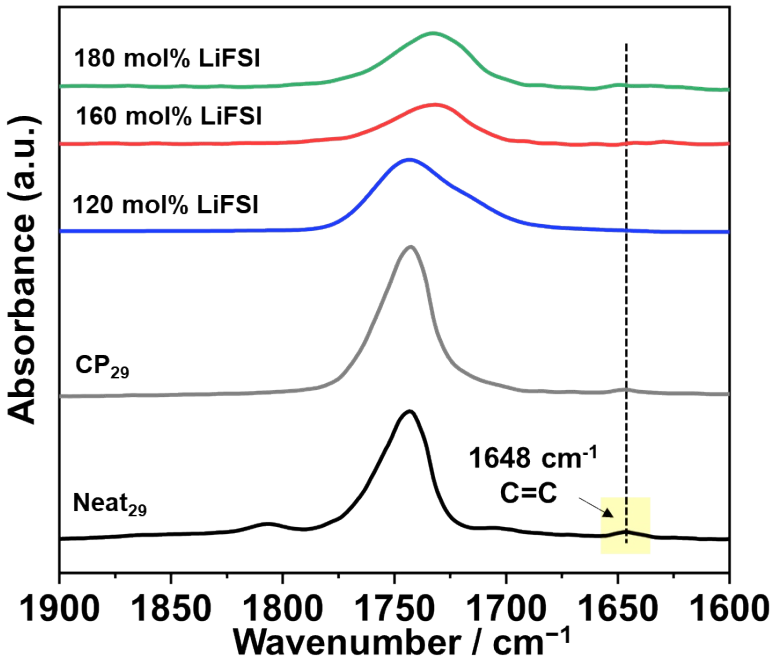


Figure S9 FT-IR spectra of (a) 1900–1600 cm^{-1} of the $Neat_{29}$ and CP_{29} and their electrolytes with LiFSI at various concentrations.

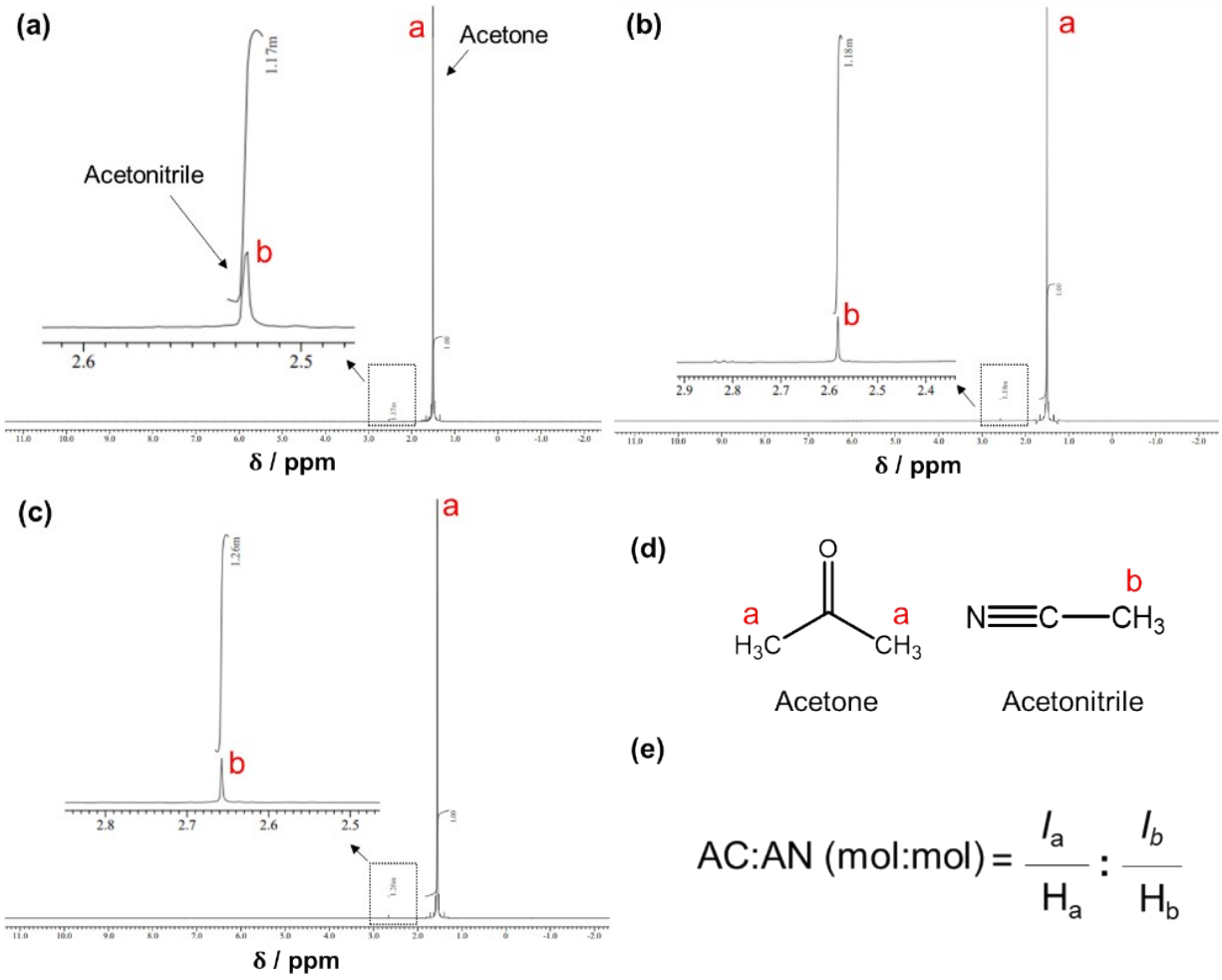


Figure S10 ^{1}H NMR spectrum of residual solvent (acetonitrile, AN) extracted from CP-SPEs and acetone (AC) of (a) CP_{29}-120 mol% LiFSI, (b) CP_{29}-160 mol% LiFSI, and (c) CP_{29}-180 mol% LiFSI. (d) Chemical structure for peak assignments. (e) An equation for the AC:AN (mol:mol) ratio calculation, where *I* and H are the integral area of each peak and the number of protons for each unit, respectively (H_a=6, H_b=3). The number of molecules of the residual AN was calculated combining the AC:AN ratio and the weight of added AC (0.1 g). Afterwards, the weight of the residual AN (wt%), which was present in the 0.01 g of CP-SPE was calculated. To better understand, we give an example calculation of CP_{29}-120mol% LiFSI as follows;

$$= \frac{1.00}{6} \quad \frac{1.17 \times 10^{-3}}{3}$$

Mass of AN (g) $=$

$$1.17 \times 10^{-3} \times 6 \times 0.1\ g \times 41.05\ g/mol$$

Mass of AN (g) $= 0.000165\ g$

Mass of AN (wt%) $= \dfrac{0.000165\ g\ \times 100}{0.0159\ g}$

Mass of AN (wt%) $= 1.04\ wt\%$

where 58.08 g/mol is molecular weight of acetone, 41.05 g/mol is molecular weight of acetonitrile, and 0.0159 g is a recorded mass of CP_{29}-120 mol% LiFSI.

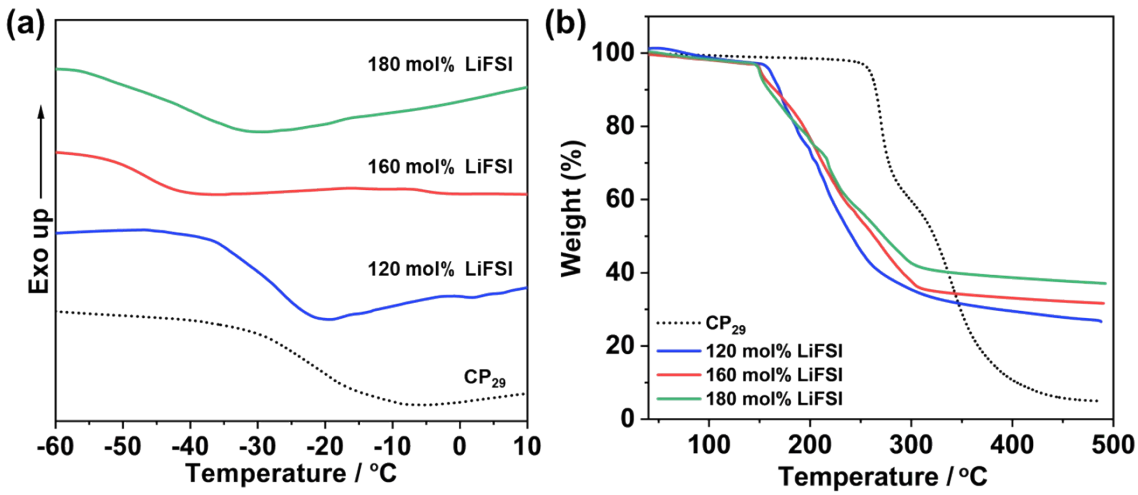


Figure S11 (a) DSC curves and (b) TGA thermograms of CP_{29}-based SPEs at various LiFSI concentrations.

Table S2 Thermal and mechanical properties of CP_{29} electrolytes at different salt concentrations.

Sample	T_g (°C)	T_{d5} (°C)	Young's modulus (MPa)	Elongation at break (%)
Original CP_{29}	−31	260	23.5	15
+ 120 mol% LiFSI	−36	160	0.80	163
+ 160 mol% LiFSI	−52	151	0.10	209
+ 180 mol% LiFSI	−55	149	0.09	190

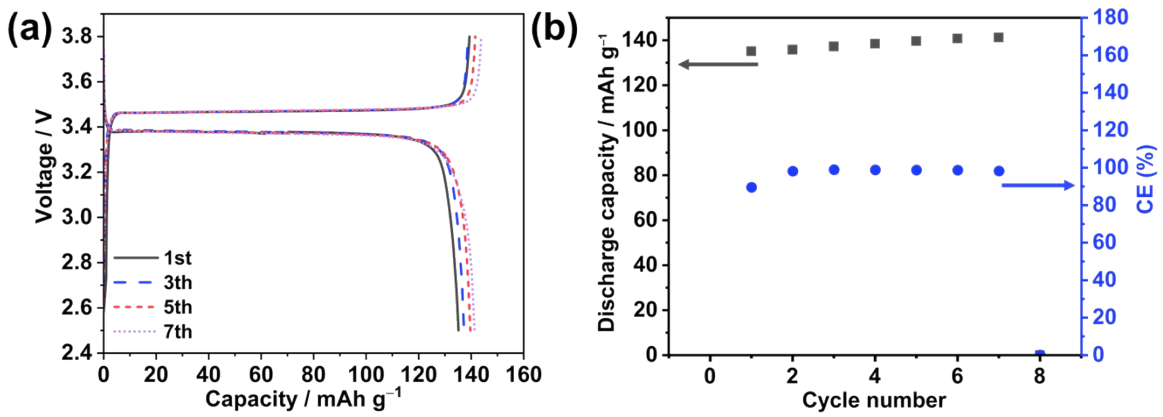


Figure S12 (a) Voltage profiles of charge/discharge at C/10 rate (1C =160 mA g^{-1}) and (b) cycling performance of Li//LFP cell (cathode mass loading: 2.3 mg cm^{-2} of active materials) using CP_{29}-180 mol% LiFSI as an electrolyte.

Table S3 Resistance values from fitting EIS curves of Li//LFP cell with CP_{29}-160 mol% LiFSI electrolyte at 40 ^{o}C using the equivalent circuit.

Cycle number	R_1 (kΩ)	R_2 (kΩ)	R_3 (kΩ)
Fresh	1.95	1.23	7.52
at 100th	2.62	0.64	12.54
at 200th	3.58	0.85	15.30
at 300th	4.13	1.36	23.04
at 400th	5.54	2.42	36.58