Supporting Information

3D Activated Microporous Protective Layer for High-Energy Lithium Metal Batteries

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Methodology for Conversion Rate Calculation

The conversion rate of PCH was determined using ^{1}H NMR spectroscopy (Fig. S1) and validated through elemental analysis (EA, Table S1). For the NMR analysis, the aromatic protons in the polymer backbone (C3 and C4, 7–6 ppm) were selected as an internal standard due to their well-defined peaks and stable chemical environment. The integral values of these peaks were normalized to 1.0, as they correspond to two protons per PCH unit. Based on this normalization, the integral of the carboxylic acid (-COOH) proton (C5 peak) was measured and compared to its theoretical value of 1.0, assuming full retention of -COOH groups. The conversion rate was calculated using the following equation:

$$Conversion\ rate\ (\%) = \left(\frac{Measrued\ Value}{Theoretical\ Value}\right) \times 100$$

This calculation assumes that the ratio of aromatic protons to carboxylic acid protons remains constant and accurately reflects the chemical structure of PCH.

To validate the NMR results, EA data (Table S1) was employed to quantify the chemical transformation from PIM-1 to PCH. The nitrogen (N) and carbon (C) contents were measured and converted to molar ratios by dividing by their respective atomic weights. The nitrogen content was further normalized relative to the carbon content to account for the polymer structure. The theoretical nitrogen content for PIM-1 was assumed to be 2.0 mol-equiv per polymer unit, which was compared to the measured nitrogen content after conversion to PCH. The conversion rate was calculated as follows:

$$Conversion\ rate\ (\%) = \left(\frac{Initial\ N\ Count - Measured\ N\ Count}{Initial\ N\ Count}\right) \times 100$$

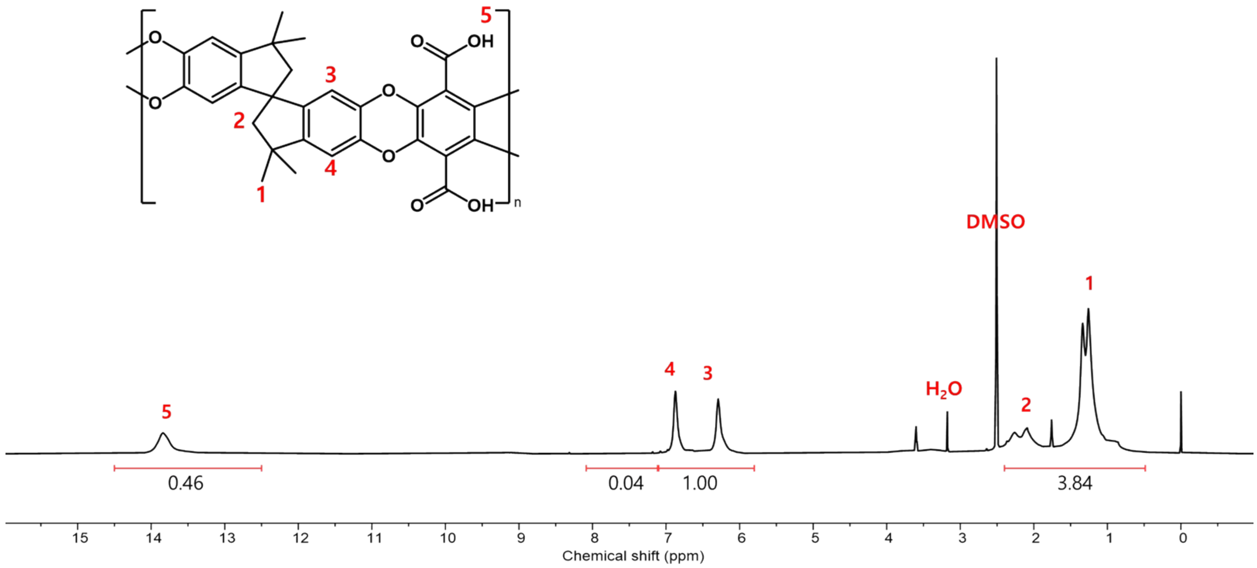

Fig. S1 ^{1}H NMR Analysis Results of PCH.

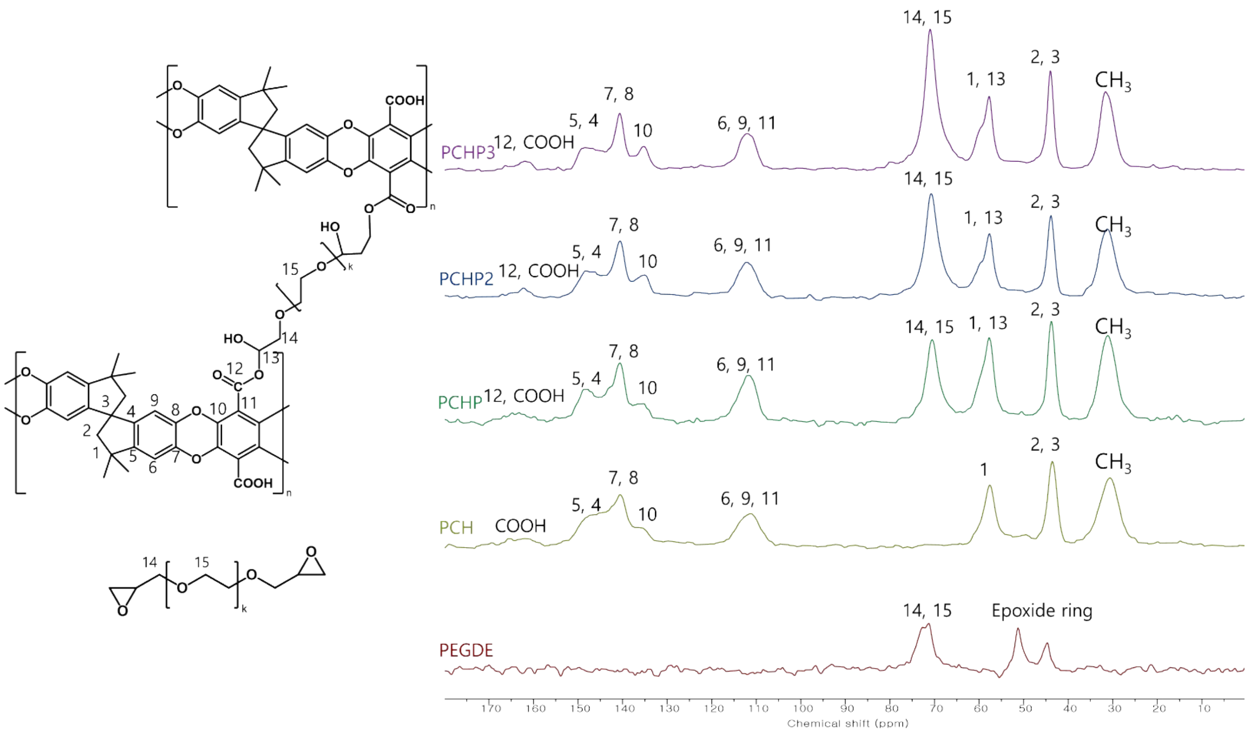

Fig. S2 Solid state C^{13} NMR results of PEGDE, PCH, Crosslinked PCH (PCHPs).

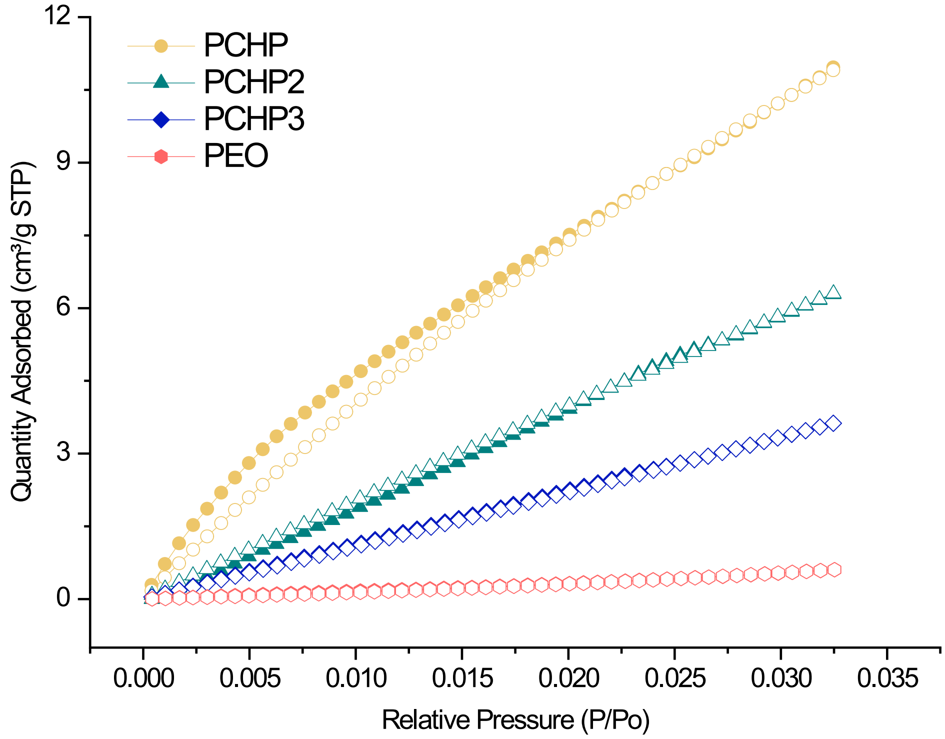

Fig. S3 Enlarged CO_2 sorption isotherm curve of PCHPs.

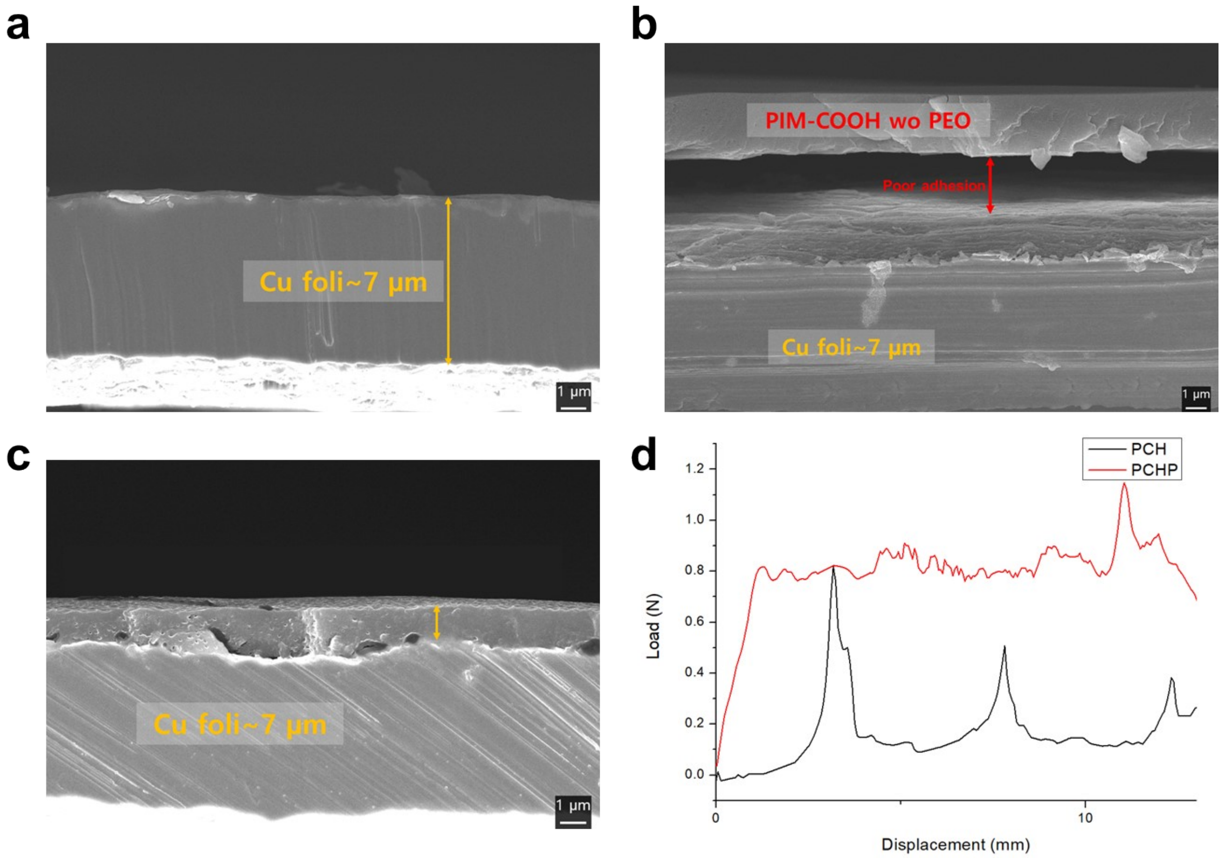

Fig. S4 SEM cross-section images of (a) copper foil, (b) PCH on copper foil and (c) Cross-linked PCH on copper foil, (d) peel test curve with UTM of PCH and PCHP.

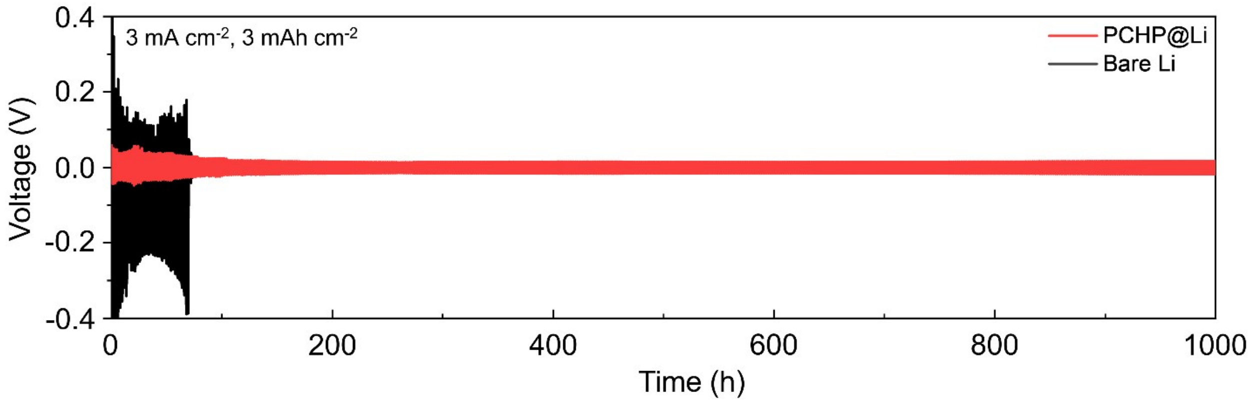

Fig. S5 Cycling stability of Li|Li symmetric cells at 3 mA cm^{-2} and 3 mAh cm^{-2}.

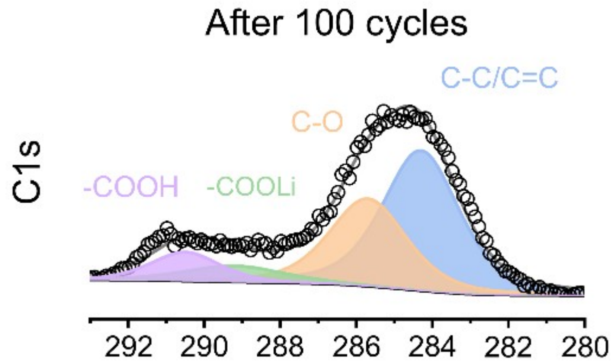

Fig S6. High-resolution C 1s XPS spectrum after 100 cycles in Li|Li symmetric cell configuration.

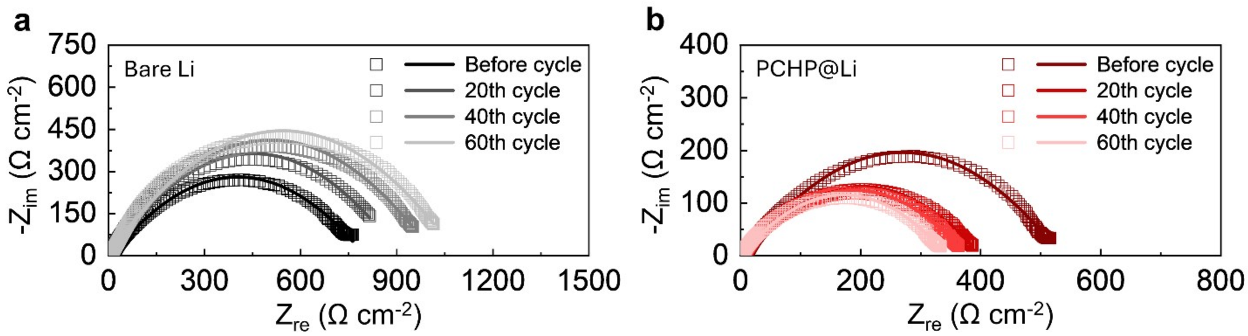

Fig. S7 Electrochemical impedance spectroscopy measurement of symmetric of (a) bare Li and (b) PCHP@Li at 1 mA cm^{-2} and 1 mAh cm^{-2}.

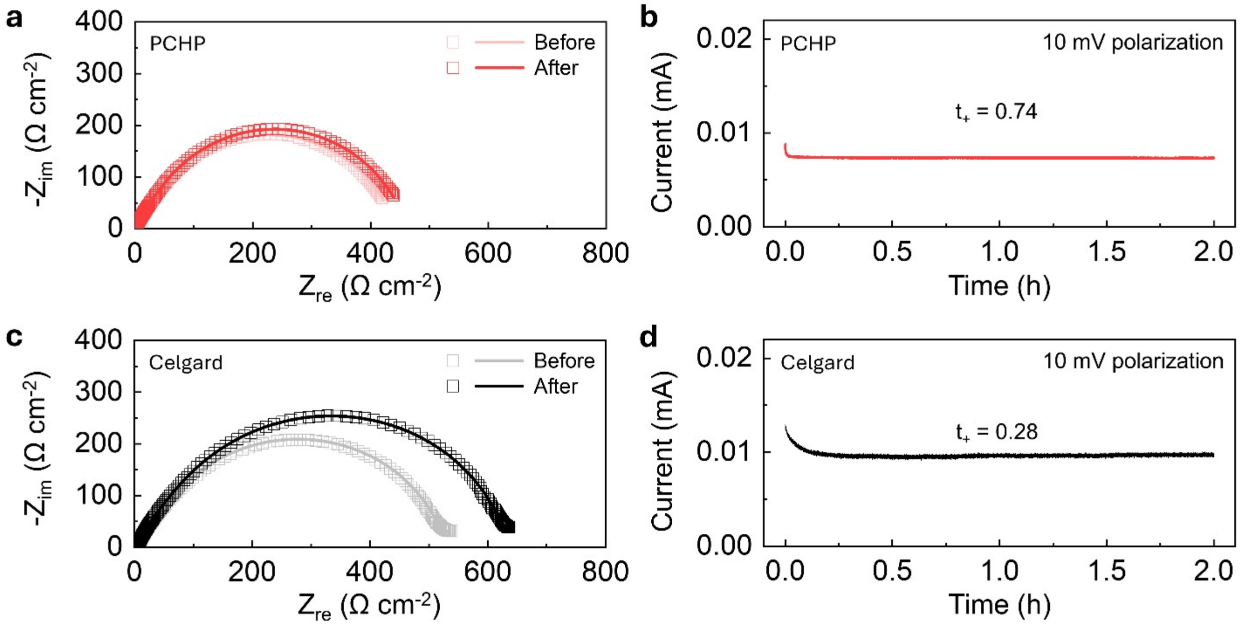

Fig. S8 Nyquist plot for (a) PCHP and (c) Celgard. Steady-state current over time under 10 mV polarization for (b) PCHP and (d) Celgard in Li symmetric cell configuration.

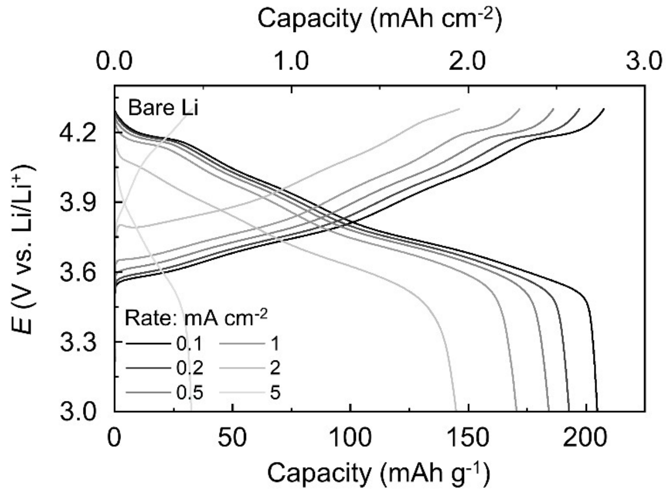

Fig. S9 Charge/discharge profiles of the full cell with bare Li anode and NCM83 cathode at different current densities.

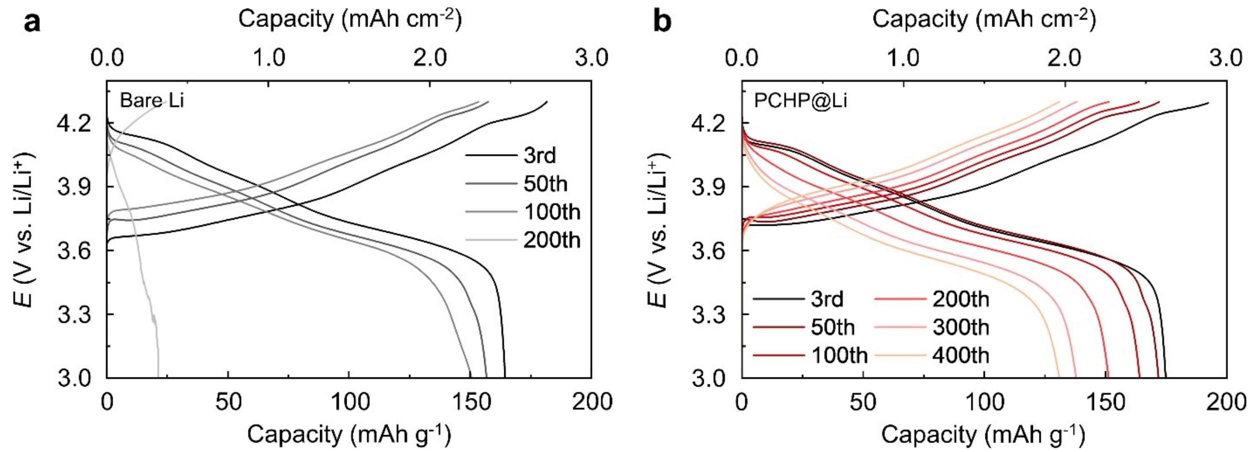

Fig. S10 Charge/discharge profiles for (a) bare Li and (b) PCHP@Li anode with NCM83 cathode.

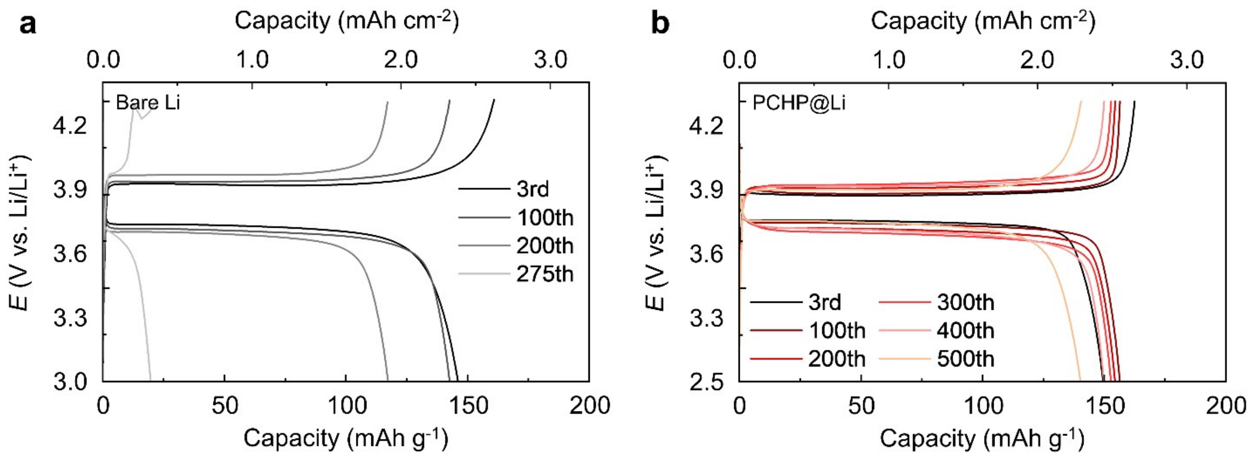

Fig. S11 Charge/discharge profiles for (a) bare Li and (b) PCHP@Li anode with LFP cathode.

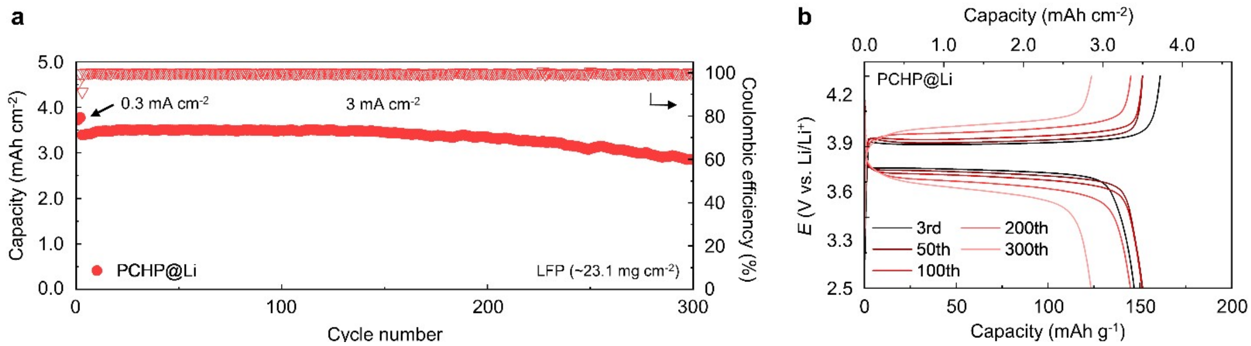

Fig. S12 (a) Cycling performance and (b) corresponding charge/discharge profiles of PCHP@Li anode with high loading LFP cathode.

Table S1 Elemental analysis results of PCH

	N	**C**	**H**	**O**	**Total**
1	0.371796	67.7137	4.873611	25.45865	98.42
2	0.366815	67.62182	4.946304	25.66906	98.60
3	0.365261	68.66715	5.088803	24.82762	98.95
Average	0.36796	68.0009	4.96957	25.3184	98.66

Table S2 Surface Area and Pore Volume of PCH and PCHP Series

	PCH	**PCHP**	**PCHP2**	**PCHP3**
Surface area (m^2/g)	512.1	183.6	130.9	75.4
Pore volume (cm^3/g)	0.205	020735	0.0525	0.0302

References

1. J. W. Jeon, D.-G. Kim, E.-h. Sohn, Y. Yoo, Y. S. Kim, B. G. Kim and J.-C. Lee, *Macromolecules*, **2017**, 50, 8019-8027.
2. J. Evans, C. A. Vincent and P. G. Bruce, *Polymer*, **1987**, 28, 2324-2328.