Supporting Information

Reactivity-Guided Formulation of Composite Solid Polymer Electrolytes for Superior Sodium Metal Batteries

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$$\sigma = \frac{T}{AR_t}$$

Equation S1. Ionic conductivity (σ) of an electrolyte based on the EIS result of SS/SS cells, where A is the electrolyte cross-sectional area, T is the electrolyte thickness, and R_t is the electrolyte resistance.

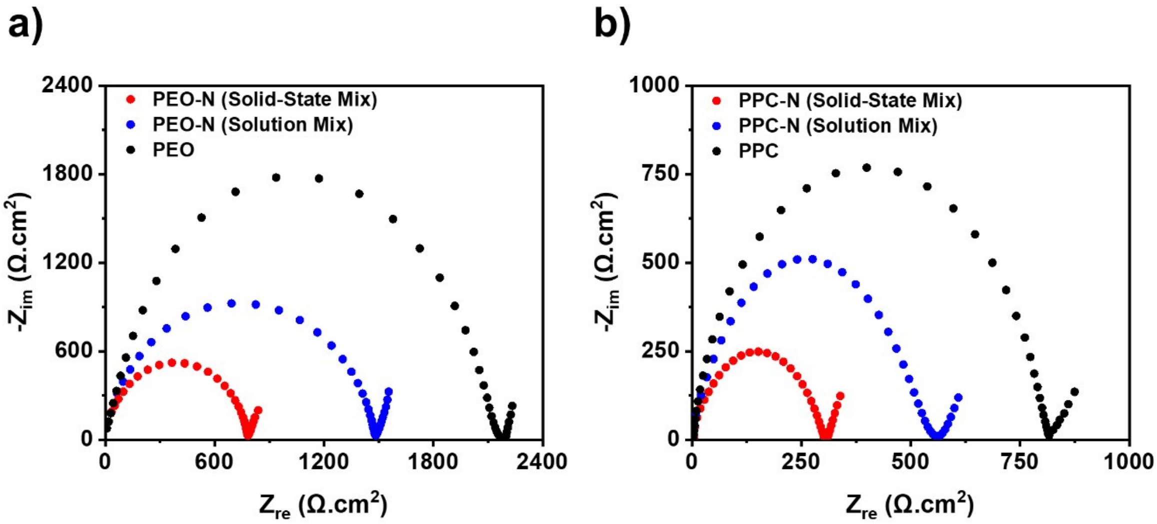

Figure S1. EIS measurements for ionic conductivity: SS/SS cells with a) pristine PEO, PEO-N prepared by conventional solution mixing as well as by solid-state reaction; and b) pristine PPC, PPC-N prepared by conventional solution mixing as well as by solid-state reaction.

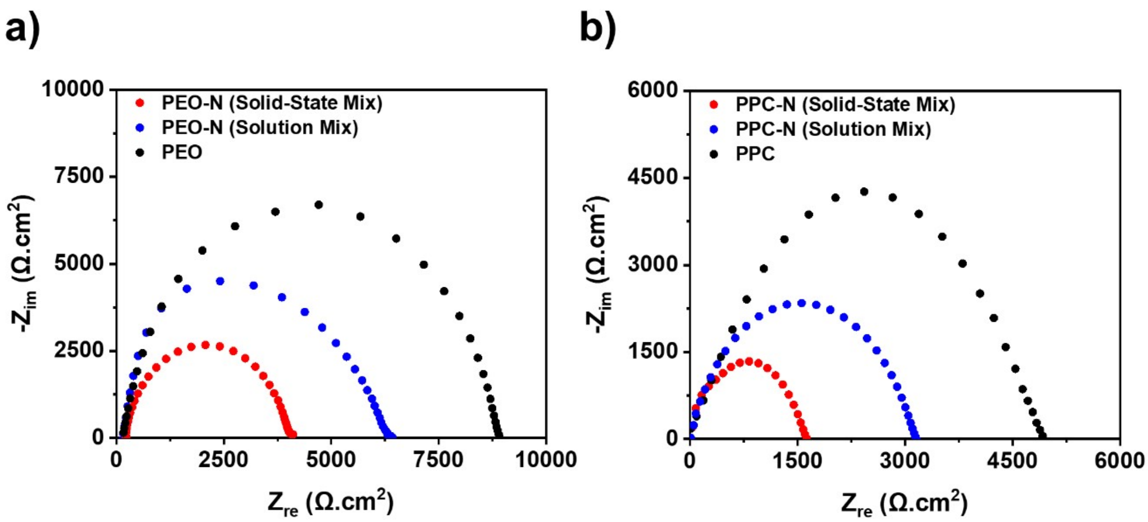

Figure S2. EIS measurements for interfacial impedance: Na/Na cells with a) pristine PEO, PEO-N prepared by conventional solution mixing as well as by solid-state reaction; and b) pristine PPC, PPC-N prepared by conventional solution mixing as well as by solid-state reaction.

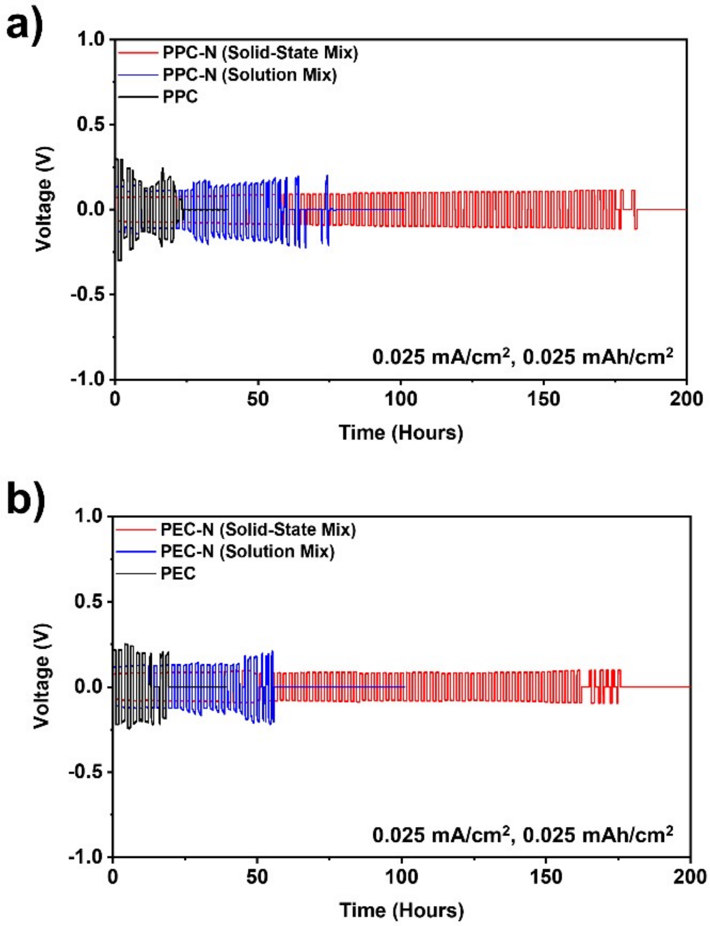

Figure S3. Electrochemical cycling performances of symmetric Na/Na cells at 0.025 mA/cm^2 current density and 0.025 mAh/cm^2 capacity with a) pristine PPC, PPC-N prepared by conventional solution mixing as well as by solid-state reaction; and b) pristine PEC, PEC-N prepared by conventional solution mixing as well as by solid-state reaction.

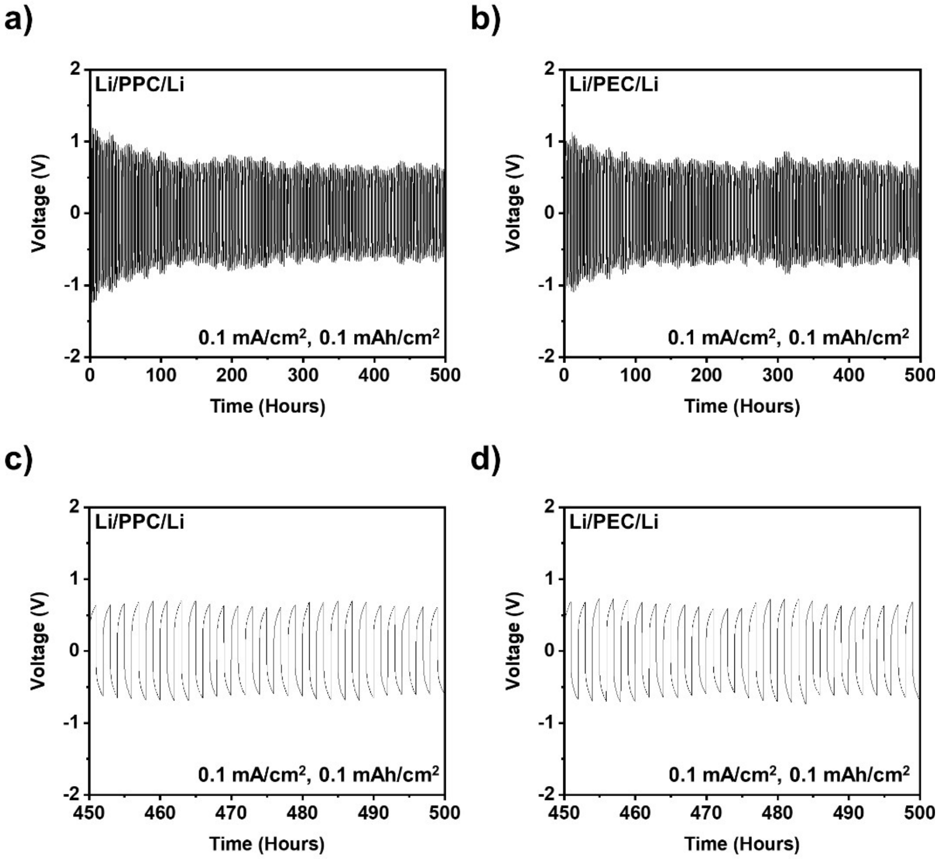

Figure S4. Electrochemical cycling performances of symmetric Li/Li cells at 0.1 mA/cm^2 current density and 0.1 mAh/cm^2 capacity with a) pristine PPC, b) pristine PEC, c) last 50 hours of Li/PPC/Li cycling, d) last 50 hours of Li/PEC/Li cycling.

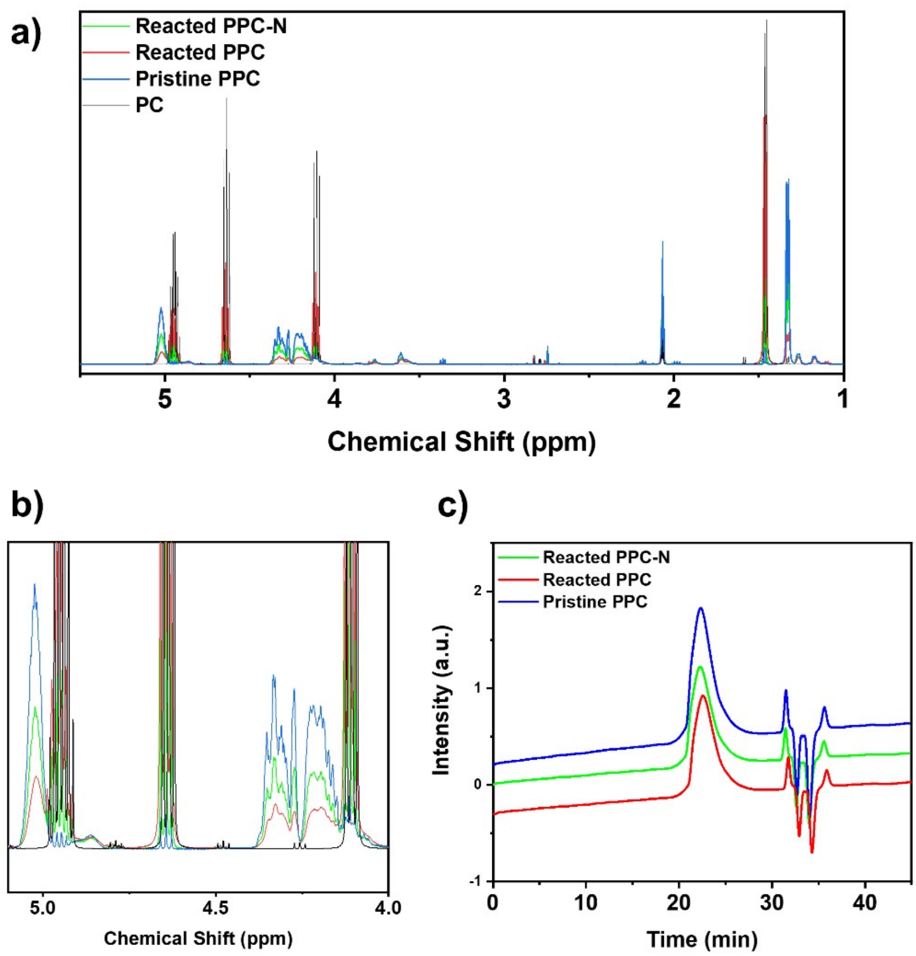

Figure S5. Quantification on the molar quantity of PPC before and after reacting with Na metal. a) H-NMR signals of pristine PPC, reacted PPC, reacted PPC-N and PC. b) Close-up H-NMR data for a better contrast in the differences between integral areas. c) GPC signals of pristine PPC, reacted PPC, reacted PPC-N.

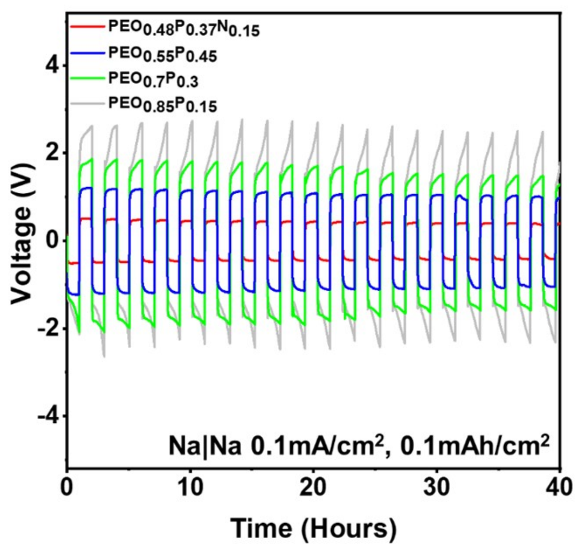

Figure S6. The first 40 hours of Na/Na cells cycling data from Figure 4a.

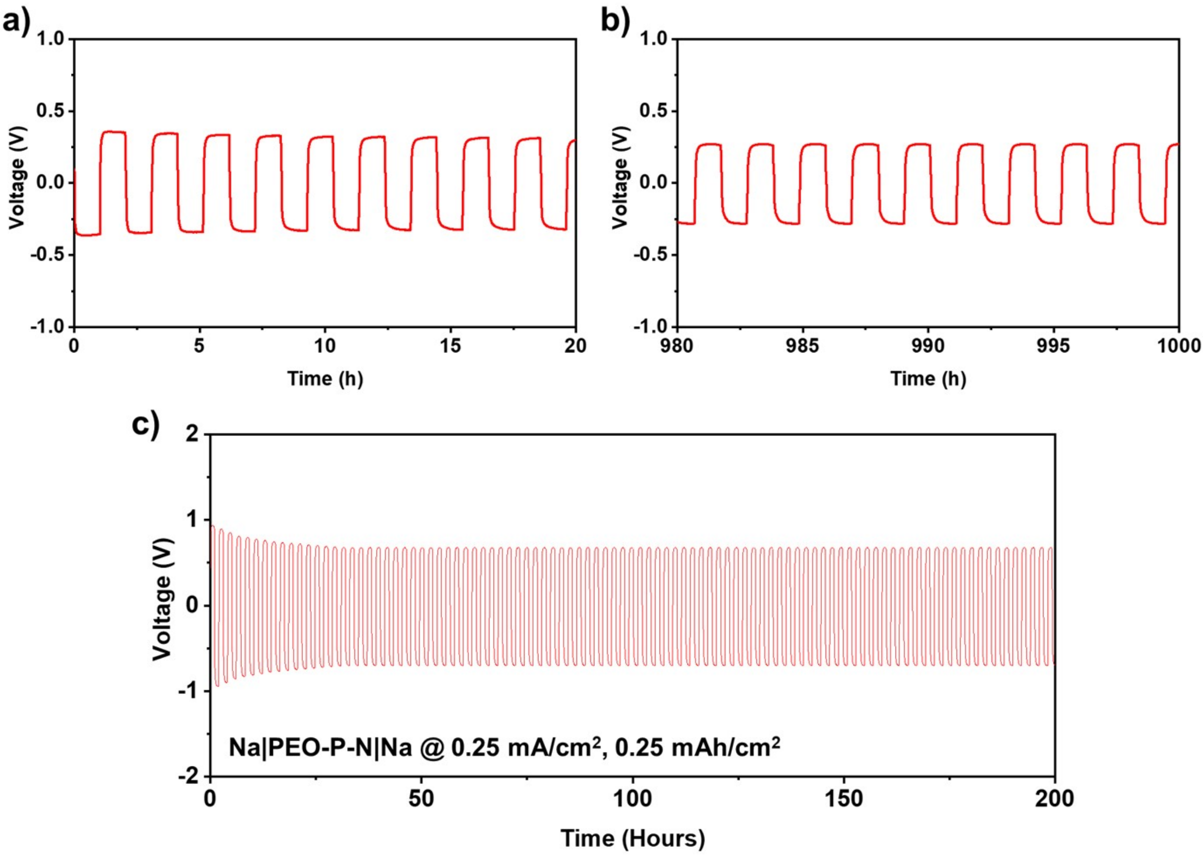

Figure S7. Na/Na cells cycling at 0.1 mA/cm^2 and 0.1 mAh/cm^2 with PEO-P-N for 1000 hours: a) first 20 hours, b) last 20 hours. c) 0.25 mA/cm^2 and 0.25 mAh/cm^2 for 100 cycles.

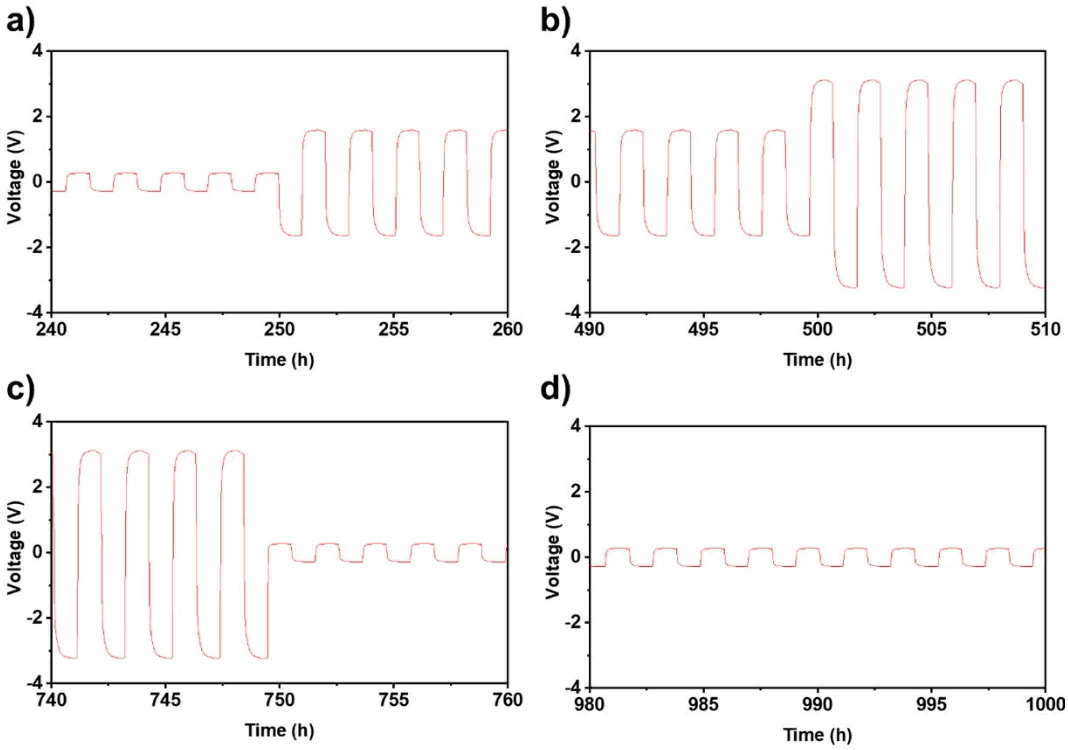

Figure S8. Na/Na cells cycling at 0.1 mA/cm^2, 0.5 mA/cm^2 and 1 mA/cm^2 with PEO-P-N: a) 0.1 to 0.5 mA/cm^2, b) 0.5 to 1 mA/cm^2, c) 1 to 0.5 mA/cm^2 and d) final 10 cycles.

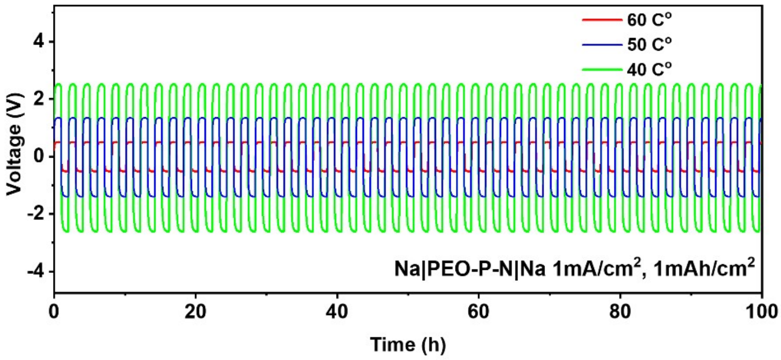

Figure S9. Electrochemical cycling performances at 40 °C, 50 °C, and 60 °C for Na/Na cells with PEO-P-N cycling at 1 mA/cm^2 rate and 1 mAh/cm^2 capacity.

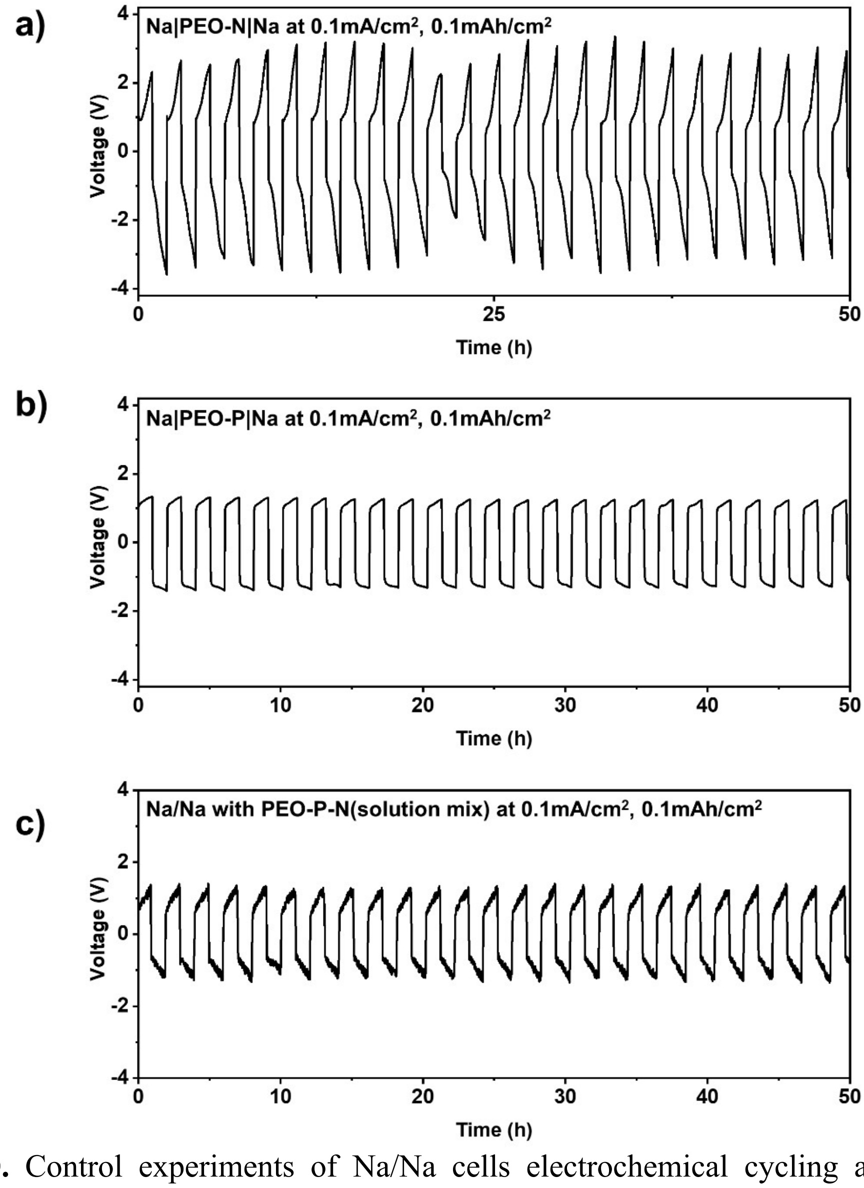

Figure S10. Control experiments of Na/Na cells electrochemical cycling at 0.1 mA/cm^2 current density and 0.1 mAh/cm^2 capacity with the less optimized SPEs, namely a) PEO-N, b) PEO-P and c) PEO-P-N prepared by conventional solution mixing method.

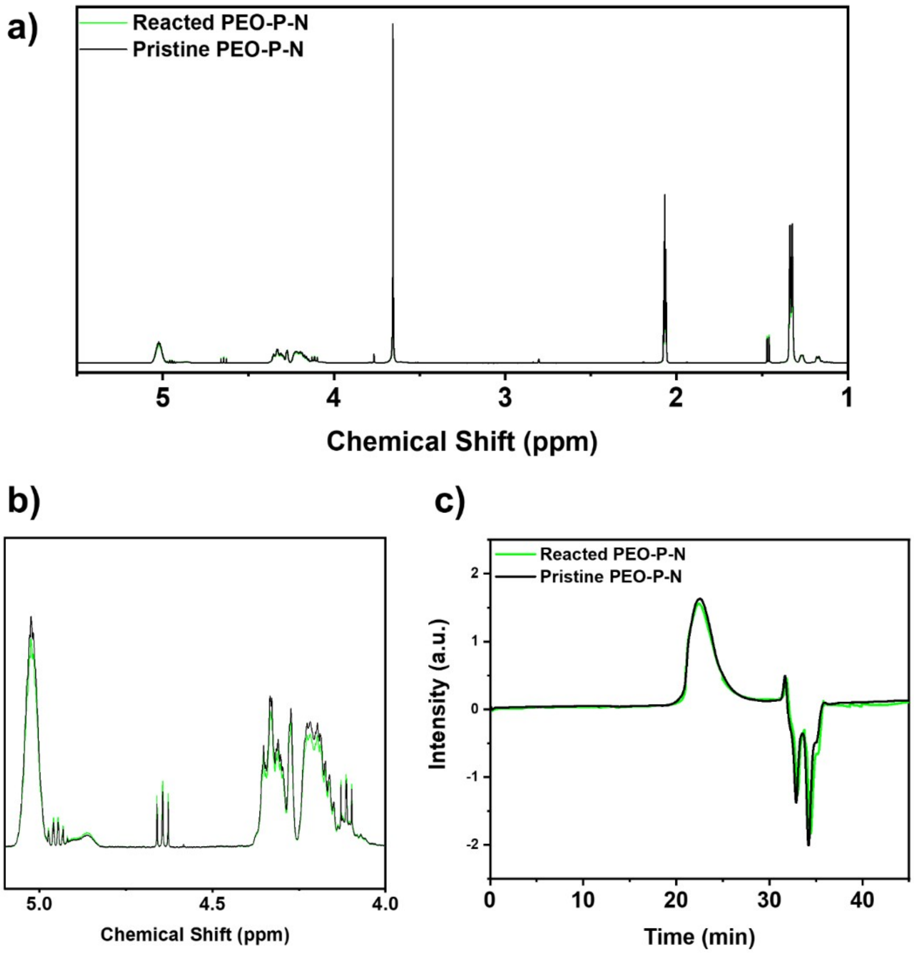

Figure S11. Quantification on the molar quantity of PEO-P-N before and after reacting with Na metal. a) H-NMR signals of pristine PEO-P-N and reacted PEO-P-N. b) Close-up H-NMR data for a better contrast in the differences between integral areas. c) GPC signals of pristine PEO-P-N and reacted PEO-P-N.

Table S1. H-MNR and GPC data for PEO-P-N reacted with Na for various time durations.

	1 Day	**1 Month**	**3 Months**	**6 Months**
H-NMR	99.6% ± 0.1%[a)]	99.4% ± 0.1%	99.4% ± 0.1%	99.4% ± 0.1%
GPC	99.7% ± 0.1%	99.5% ± 0.1%	99.5% ± 0.1%	99.5% ± 0.1%

[a)] Integral area under the curve from H-NMR and GPC quantification analysis.

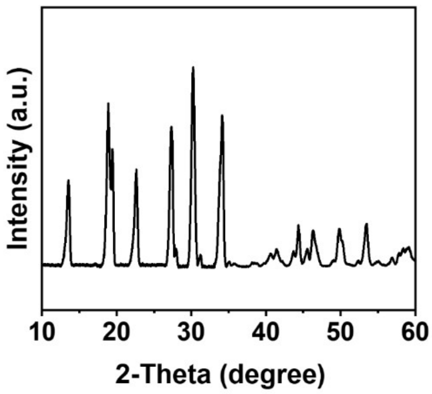

Figure S12. The XRD pattern of NASICON with typical crystalline peaks.

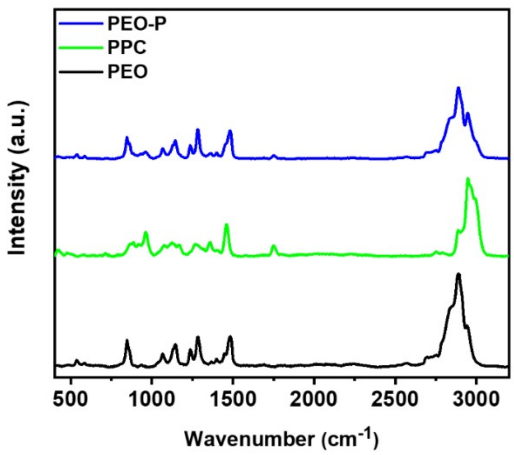

Figure S13. Raman spectroscopy for studying the chemical structures of various SPEs.

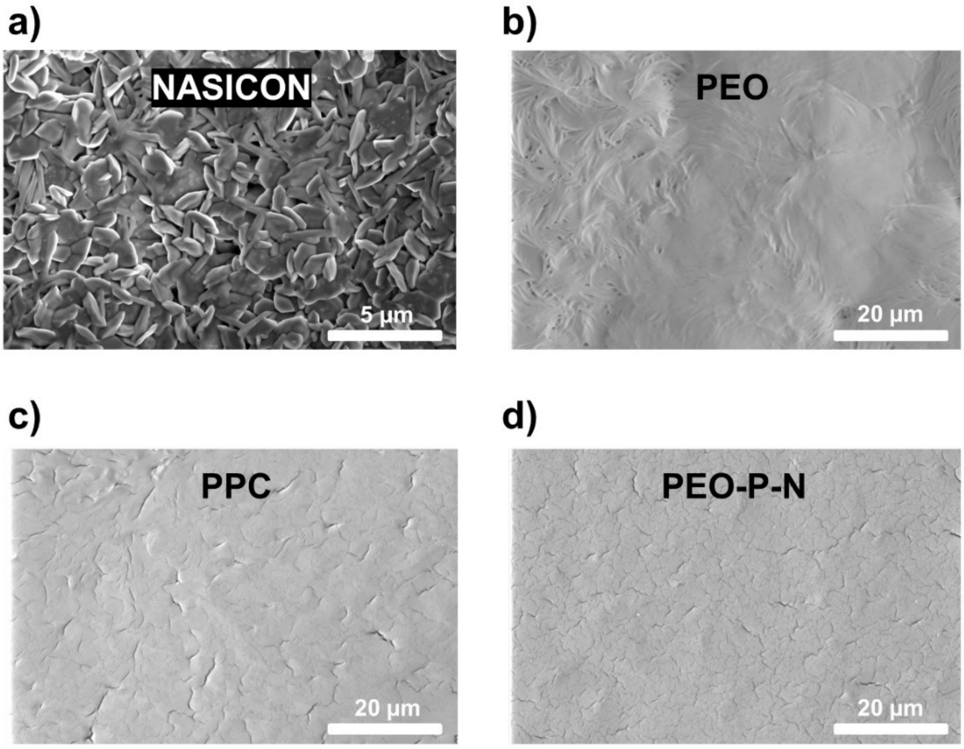

Figure S14. SEM imaging for a) NASICON, b) PEO, c) PPC and d) PEO-P-N.

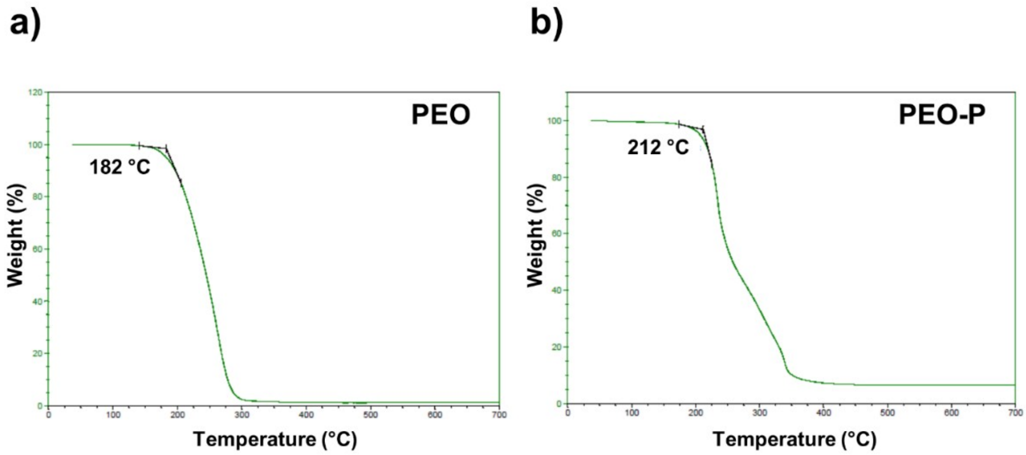

Figure S15. TGA analysis for the thermal stability study of a) PEO and b) PEO-P.

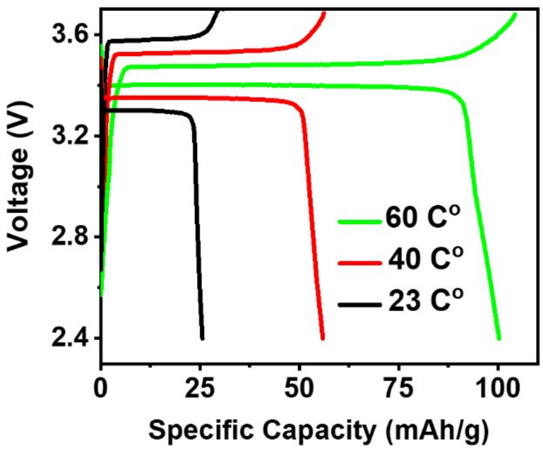

Figure S16. NVP/PEO-P-N/Na solid-state batteries discharge capacity at 1C rate at 23 °C (room temperature), 40 °C, and 60 °C.