

## Chemical Switch Enabled Autonomous Two Stage Crosslinking Polymeric Binder for High Performance Silicon Anodes

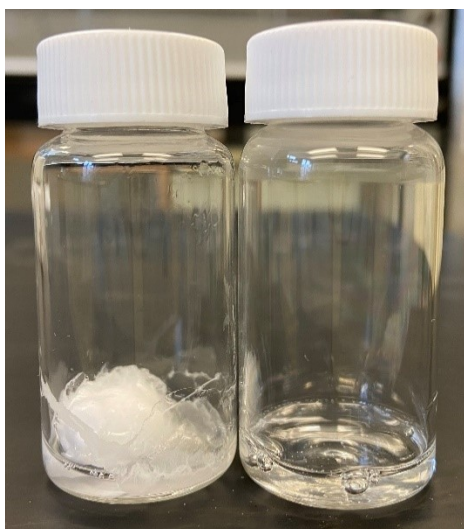
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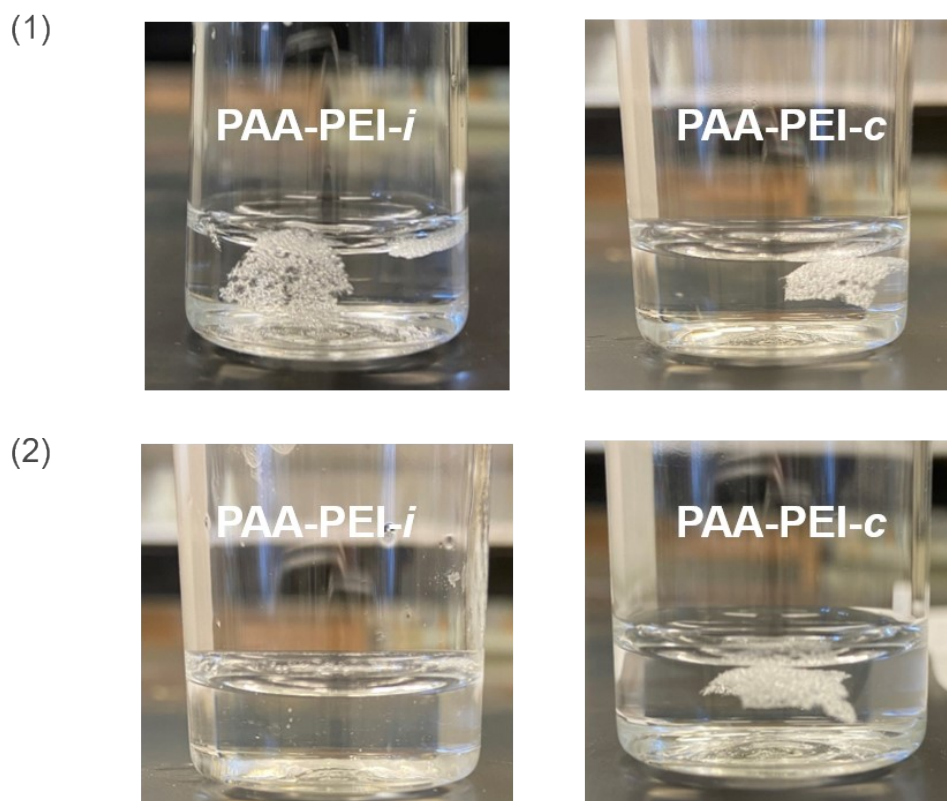
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**Figure S1.** PAA and PEI form precipitates upon being mixed in water (left), clear solution is observed when PAA is neutralized by  $\text{NH}_4\text{OH}$  before PEI is added (PAA- $\text{NH}_3$ -PEI). (right).



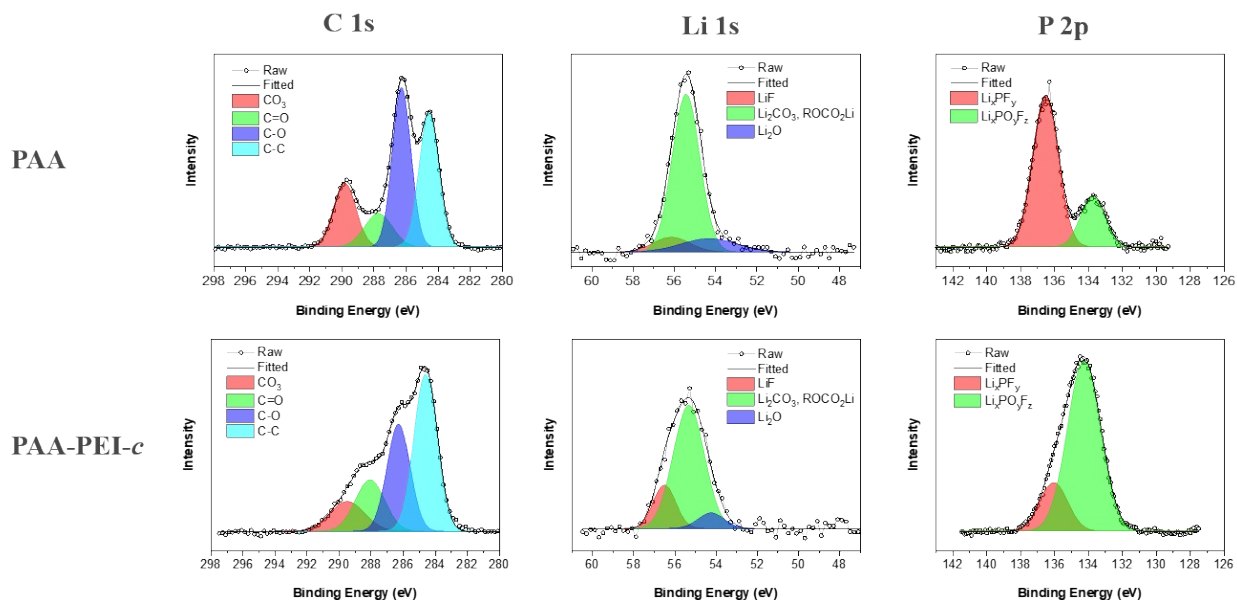
**Figure S2.** (1) PAA-PEI-*i* and PAA-PEI-*c* immersed in 1 M LiOH solution at the beginning of solubility test. (2) PAA-PEI-*i* after 10 min and PAA-PEI-*c* after one week.

**Table S1.** Loading, initial capacity, initial Coulombic efficiency, average Coulombic efficiency, and capacity retention of cells assembled with lithium metal/Si electrodes using PAA, PAA-PEI-*i*, or PAA-PEI-*c* binder.

Electrode	Loading [mg/cm <sup>2</sup> ]	Initial capacity <sup>a</sup> [mAh/g]	Initial Coulombic efficiency [%]	Average Coulombic efficiency <sup>b</sup> [%]	Capacity retention [%]
PAA	0.73	2356	94.4	98.9	10
PAA-PEI- <i>i</i>	0.67	2224	95.1	98.0	25
PAA-PEI- <i>c</i>	0.67	2350	95.4	99.3	77

<sup>a</sup> Determined as the specific delithiation capacity at the first C/3 cycle

<sup>b</sup> Averaged value for the 150 cycles at C/3 rate



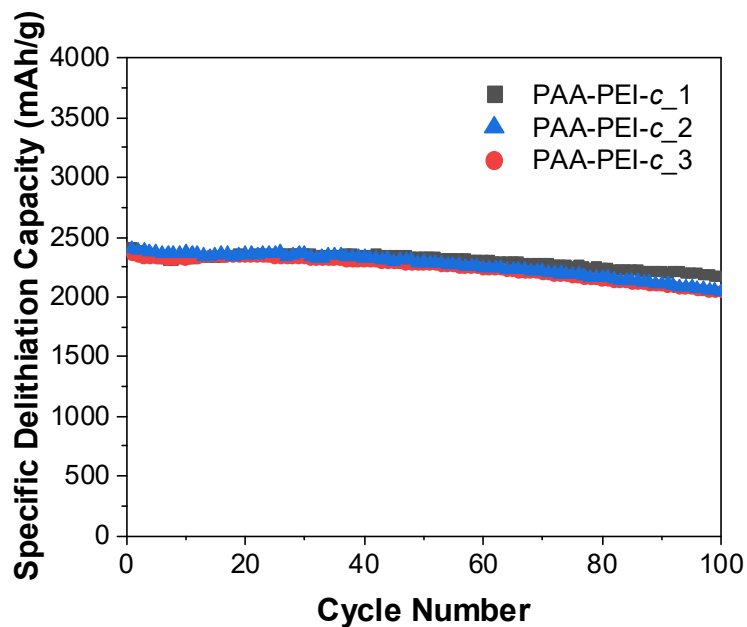
**Figure S3.** C 1s, Li 1s, and P 2p XPS spectra of PAA and PAA-PEI-*c* electrodes after 150 cycles.

**Table S2.** Loading of active materials, N/P ratio, initial capacity, initial Coulombic efficiency, and capacity retention results of cells assembled with NCM622/Si electrodes using PAA and PAA-PEI-*c* binder, respectively.

Cell	Loading (NCM622) [mg/cm <sup>2</sup> ]	Loading (Si) [mg/cm <sup>2</sup> ]	N/P ratio	Initial Capacity <sup>a</sup> [mAh/g]	Initial Coulombic Efficiency <sup>b</sup> [%]	Capacity Retention [%]
PAA	9.5	1.01	1.1	164	93.5	59
PAA-PEI- <i>c</i>	9.5	0.95	1.1	168	98.8	73

<sup>a</sup> Determined as the specific delithiation capacity at the 3<sup>rd</sup> cycle of formation

<sup>b</sup> Determined at the first C/3 cycle



**Figure S4.** Cycling profiles of Li half-cells containing three batches of Si electrodes fabricated using PAA-PEI-*c* binder. The cells were subjected to three formation cycles between 0.01 V and 1.50 V at C/20 rate followed by 100 cycles at C/3 rate.