# Electronic Supporting Information

# Significant Suppression of Exothermic Heat Flow in Silicon Anodes via In-Situ Polymerization of Phosphonium Ionic Liquids

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**Table S1.** The corresponding $R_s$, $R_{SEI}$, and $R_{ct}$ values (ohm) were extracted from the equivalent circuit in the EIS data in Si||Li half-cell configuration.

| Cell state | LE | | | LE-A | | | LE-P | | |
|---|---|---|---|---|---|---|---|---|---|
| | $R_s$ | $R_{SEI}$ | $R_{ct}$ | $R_s$ | $R_{SEI}$ | $R_{ct}$ | $R_s$ | $R_{SEI}$ | $R_{ct}$ |
| **Before formation** | 2.547 | - | 223.6 | 2.582 | - | 150.9 | 2.588 | - | 204.9 |
| **After Formation** | 1.289 | 8.197 | 37.97 | 1.625 | 5.161 | 34.14 | 1.698 | 6.138 | 36.4 |

**Table S2.** DSC measurement results with different electrolytes. All the electrolytes are mixed with a fully lithiated Si anode.

| Electrolyte | Specific Heat Flow [W/g] | Exothermic Temperature [℃] | |
|---|---|---|---|
| **LE-VA** | 3.82 | 302 | With VC |
| **LE-V** | 48.95 | 335.6 | |
| **LE-VP** | 51.7 | 299 | |
| **LE-A** | 9.56 | 251.1 | Without VC |
| **LE** | 37.34 | 282.3 | |
| **LE-P** | 40.04 | 252.7 | |
| **LE-VA@Si + LE-V** | 3.28 | 291 | With VC |
| **LE-V@Si + LE-VA** | 38.79 | 283 | |

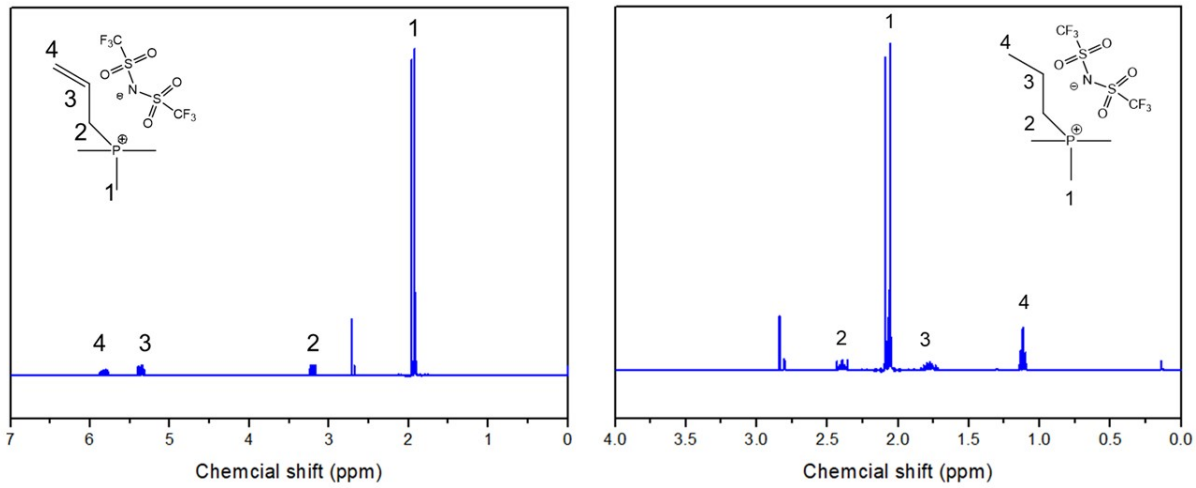


**Figure S1.** $^{1}$H NMR data of $AP_{111}T$ and $PP_{111}T$ monomer.

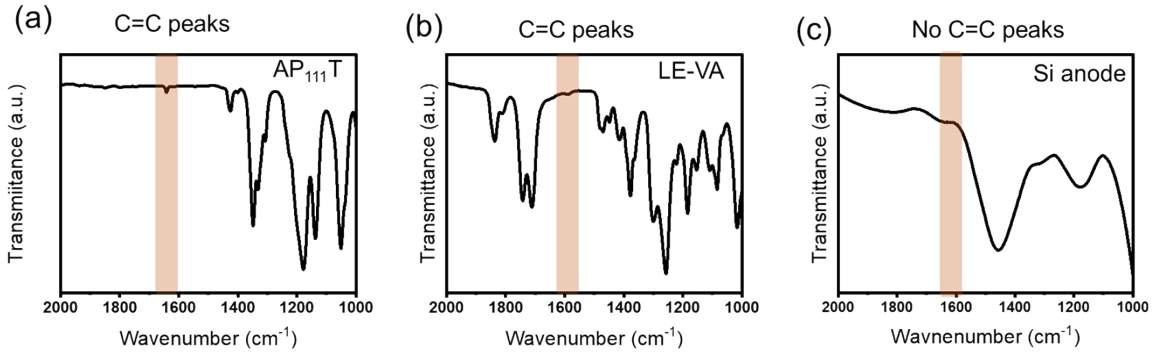


**Figure S2.** FT-IR spectra of (a) $AP_{111}T$, (b) LE-VA, and (c) the silicon anode surface after cycling in LE-VA. The absence of the C=C peak on the silicon anode surface indicates successful polymerization of the 5 wt.% $AP_{111}T$ monomer.

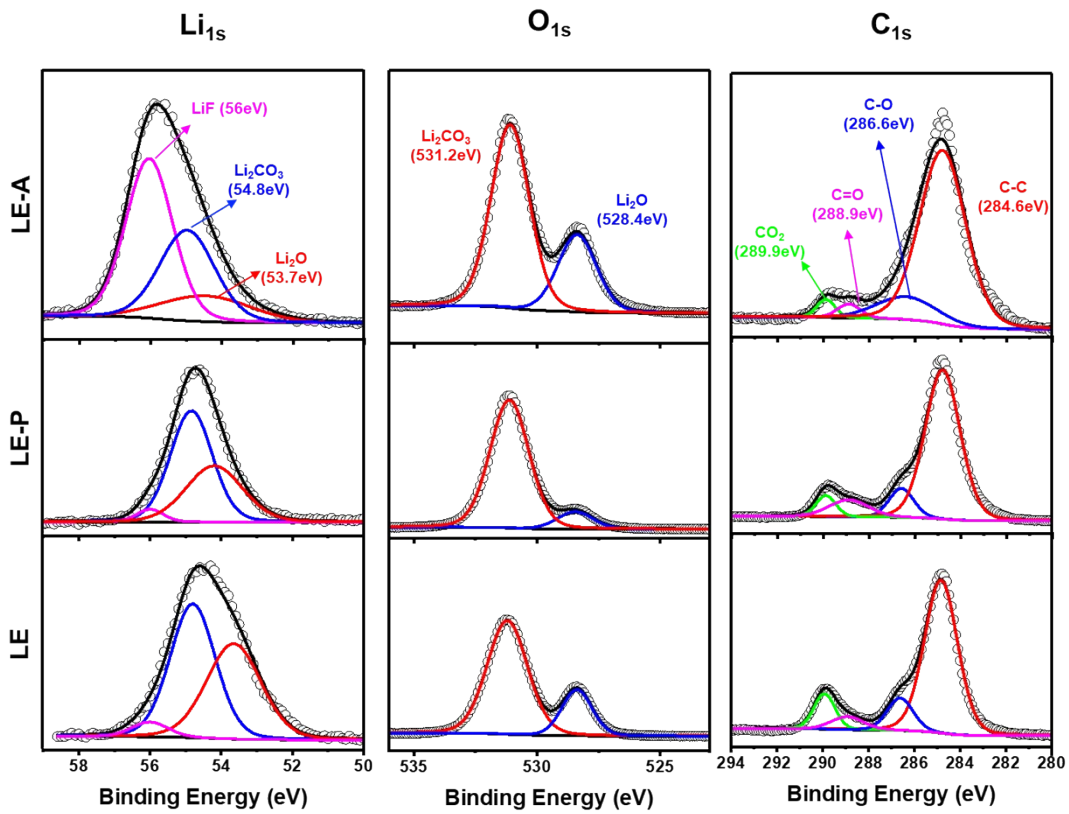


**Figure S3.** XPS spectra for one lithiated Si anode with different electrolytes. In the $Li_{1s}$ the LiF (56 eV), $Li_2CO_3$ (54.8 eV), $Li_2O$ (53.7 eV) peaks were observed.

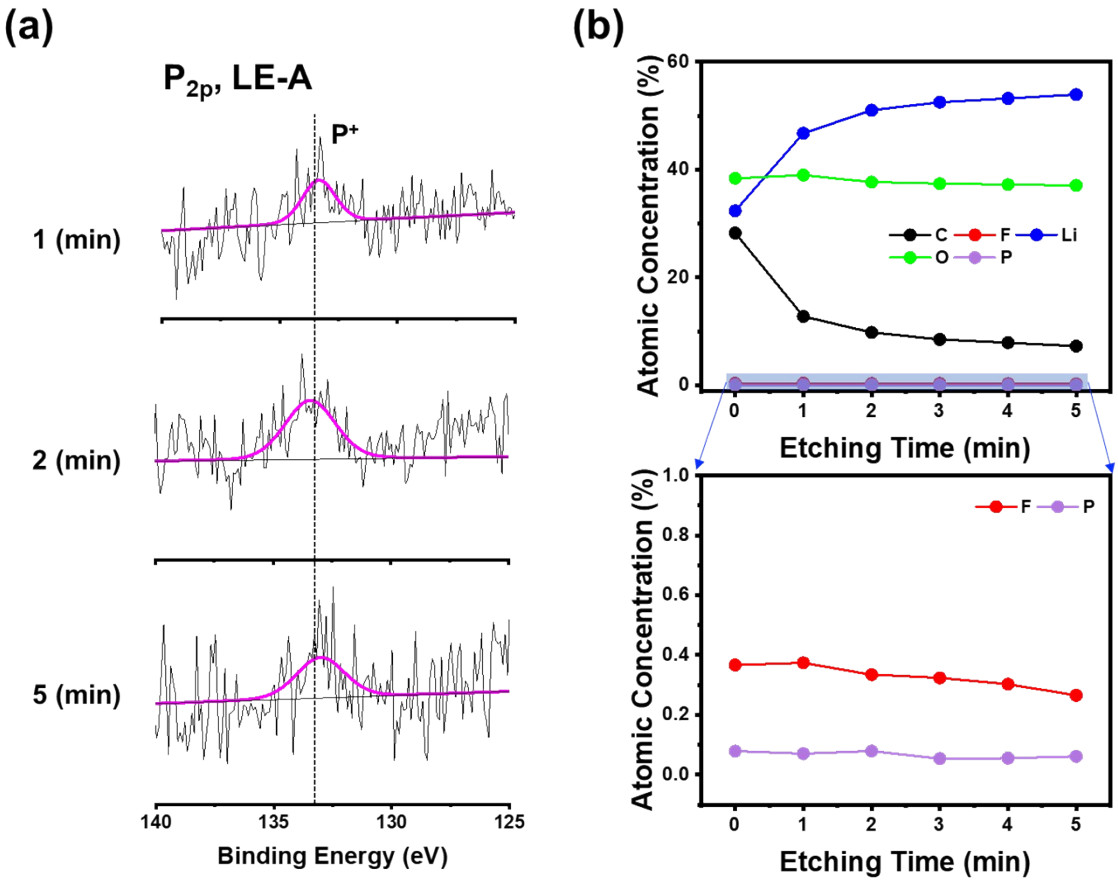


**Figure S4.** Depth profile along the Ar etching time. All the elements represented lithiated LE-A Si anode. (a) $P_{2p}$ spectra and (b) atomic ratio in the SEI layer.

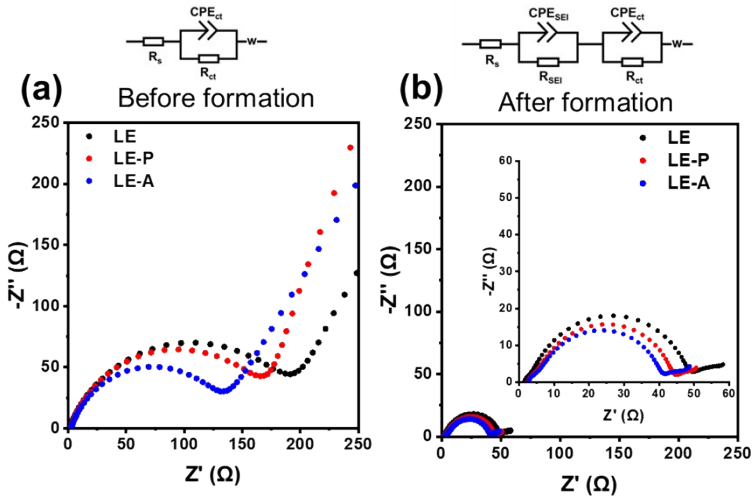


**Figure S5.** Electrochemical impedance spectroscopy (EIS) data and their equivalent circuits for Si half-cells were shown for (a) before and (b) after formation with different electrolytes. The inset profile in the (b) was presented in an enlarged view.

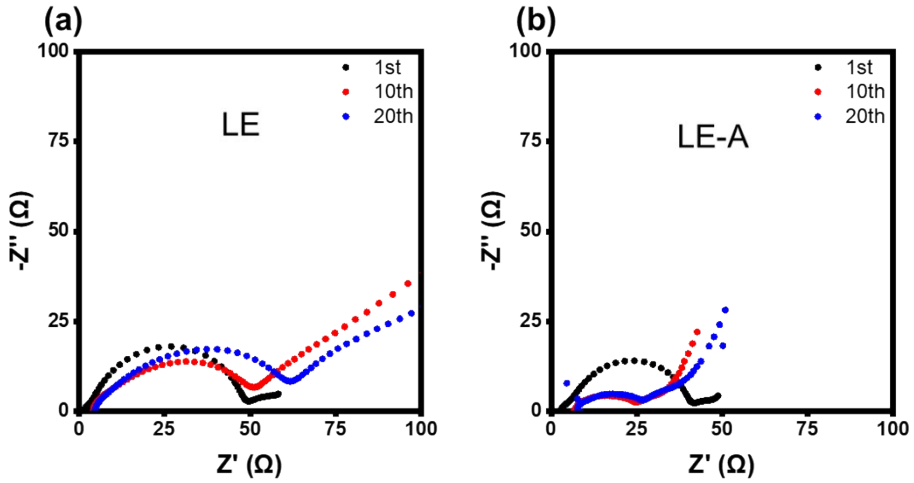


**Figure S6.** Electrochemical impedance spectroscopy (EIS) data for Si half-cells after the 1st, 10th, and 20th cycles are shown for (a) the LE and (b) the LE-A.

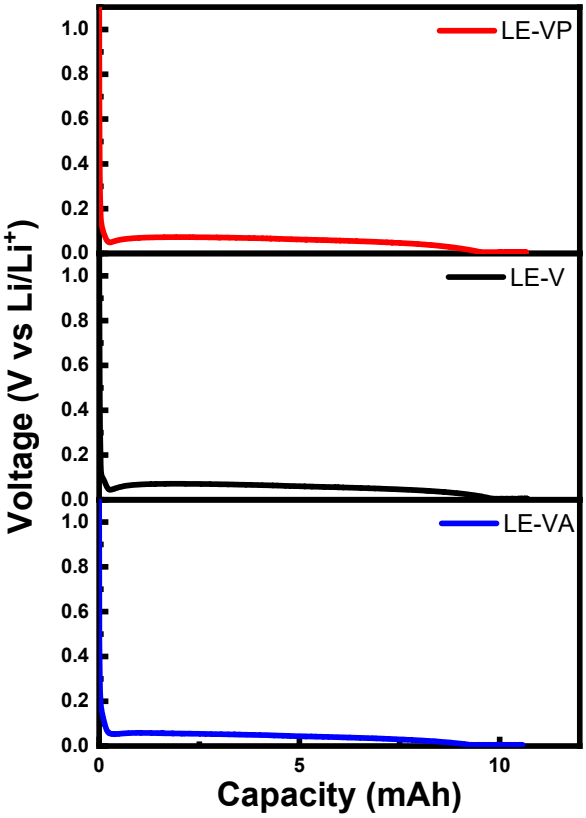


**Figure S7.** Discharge profiles for first lithiation of Silicon anode in this study with different electrolytes.

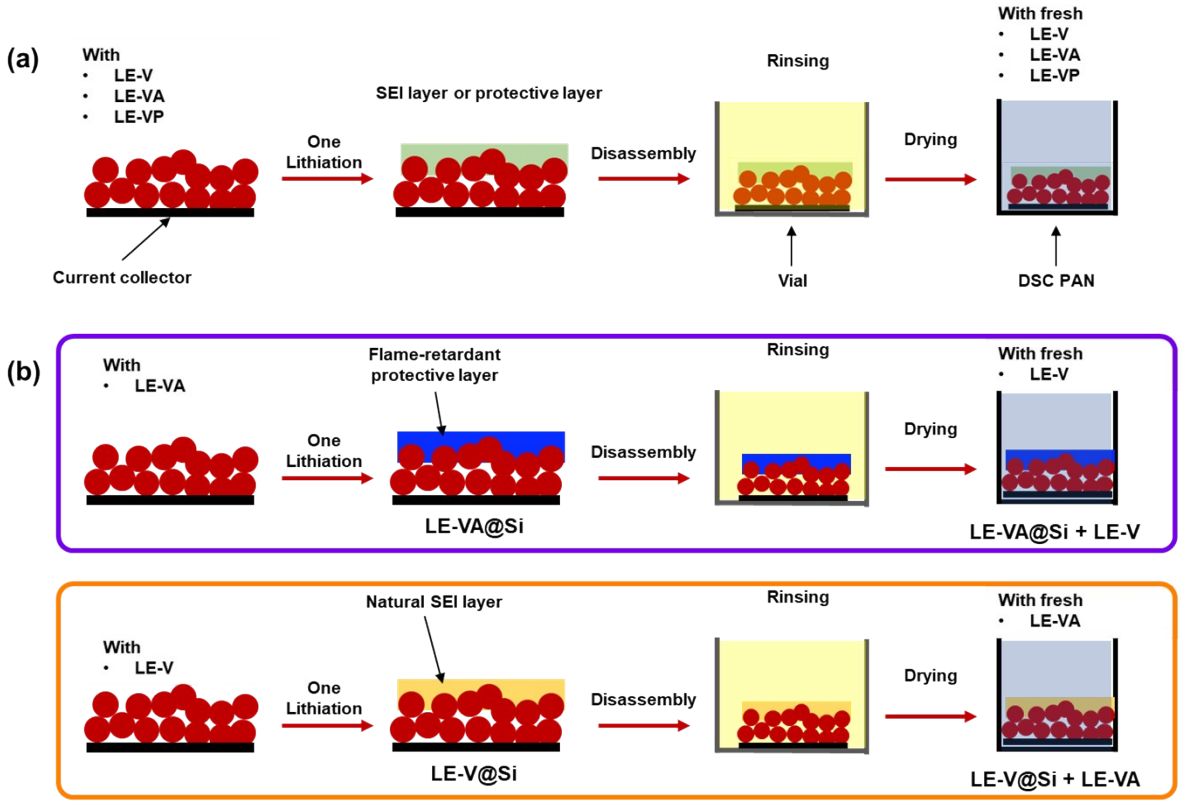


**Figure S8.** Preparation process for DSC sampling. (a) same electrolyte used for lithiation and DSC sampling. (b) Different electrolyte used for lithiation and DSC sampling.

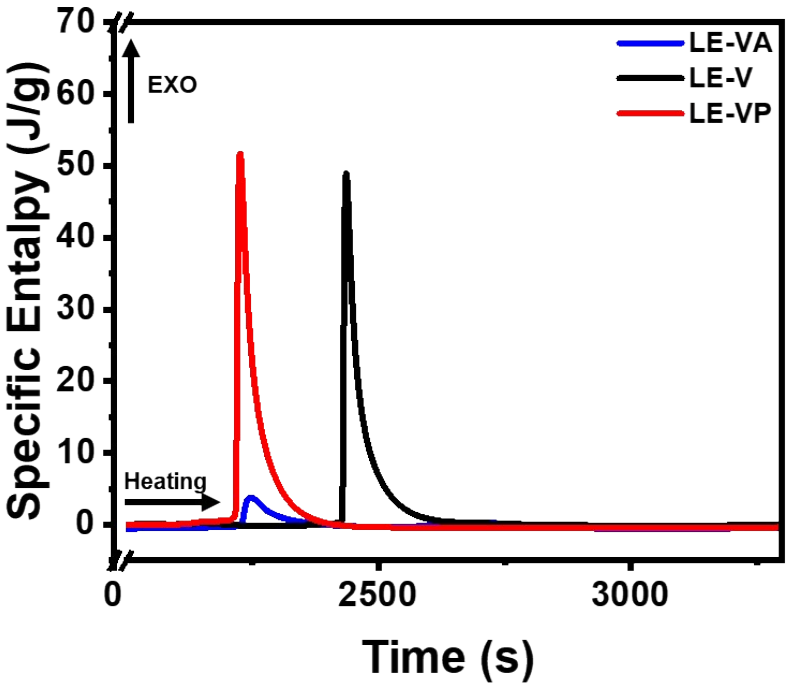


**Figure S9.** Specific enthalpy as a function of temperature for lithiated Si anodes in the presence of LE-V series electrolyte.

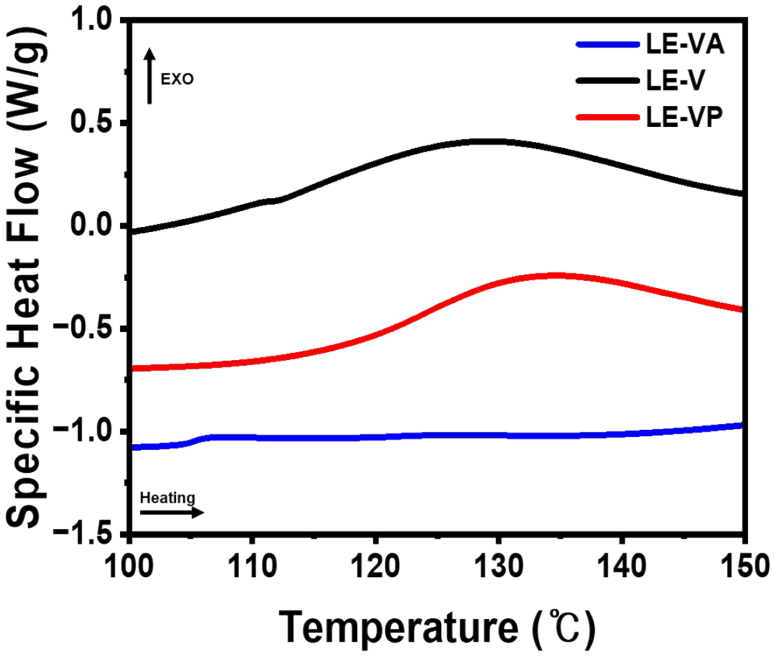


**Figure S10.** Specific heat flow in the low-temperature range (100-150 °C) for lithiated Si anodes in the presence of LE-V with or without additives.

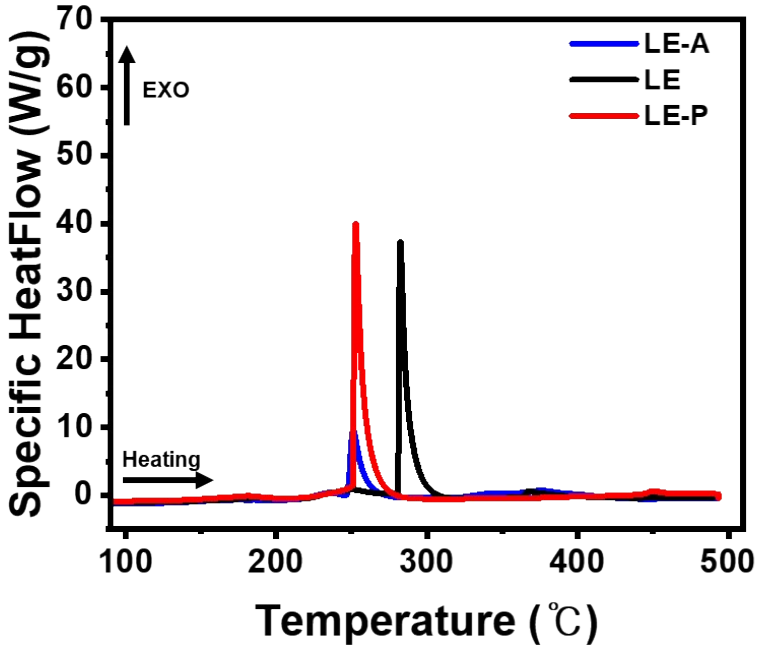


**Figure S11.** Specific heat flow for lithiated Si anodes with LE series. Which didn't include VC additive.

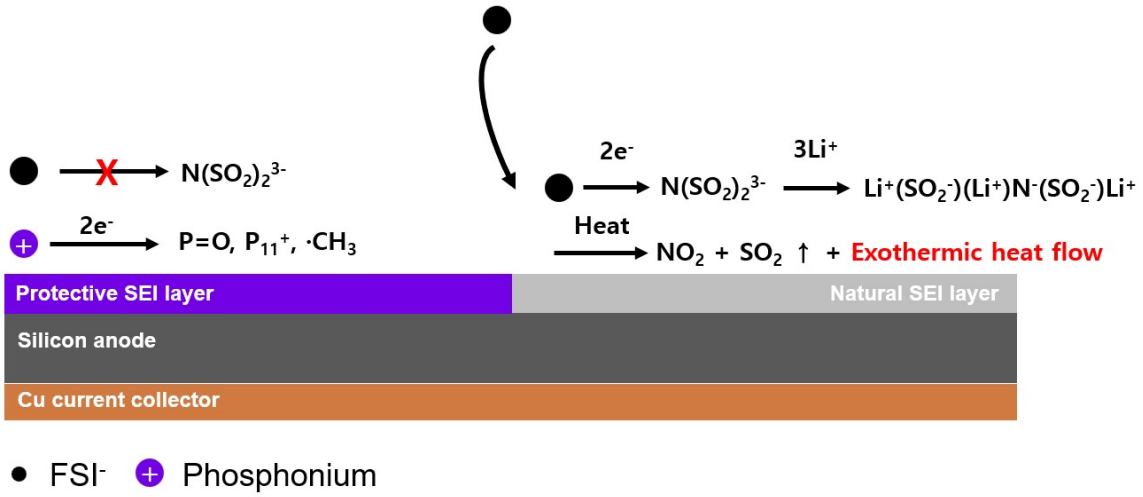


**Figure S12.** Possible mechanism for radical scavenging of $AP_{111}T$-derived protective layer.

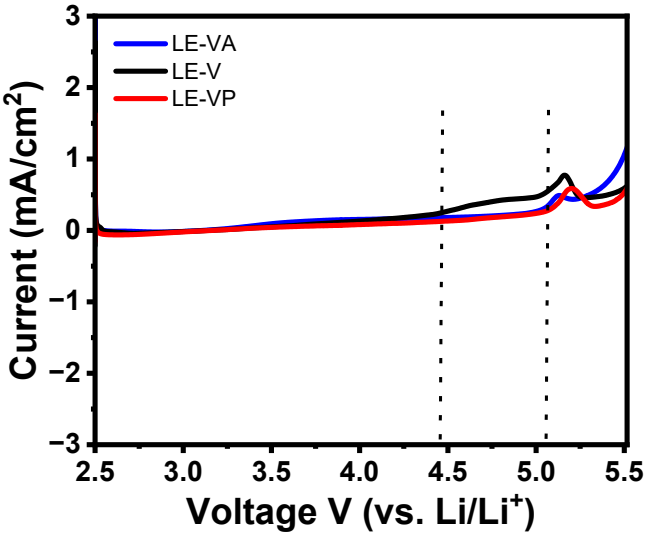


**Figure S13.** Linear sweep voltammogram (LSV) curves of Li||Pt cells with three different electrolytes as a scan rate of 0.1 mV/s.

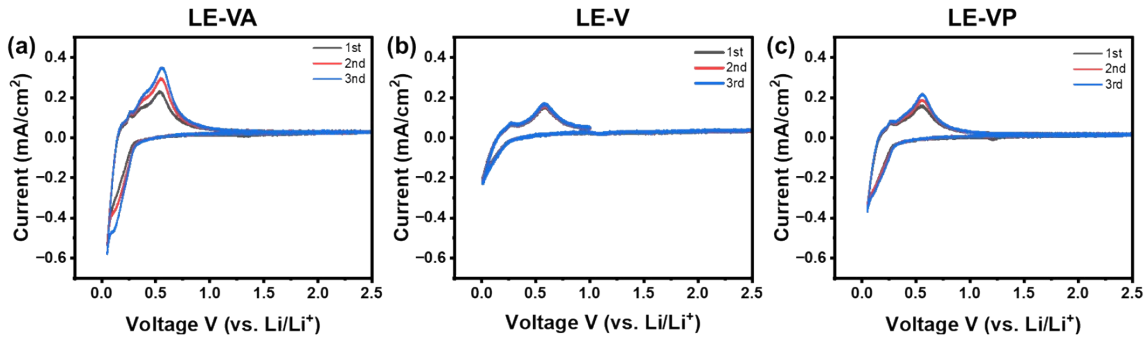


**Figure S14.** Cyclic voltammogram (CV) of different electrolytes for (a) LE-VA, (b) LE-V and (c) LE-VP.

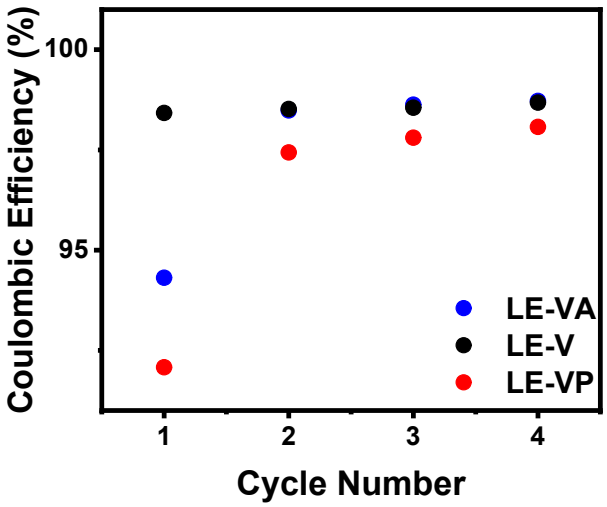


**Figure S15.** Initial coulombic efficiency of long-term cycling measurements.

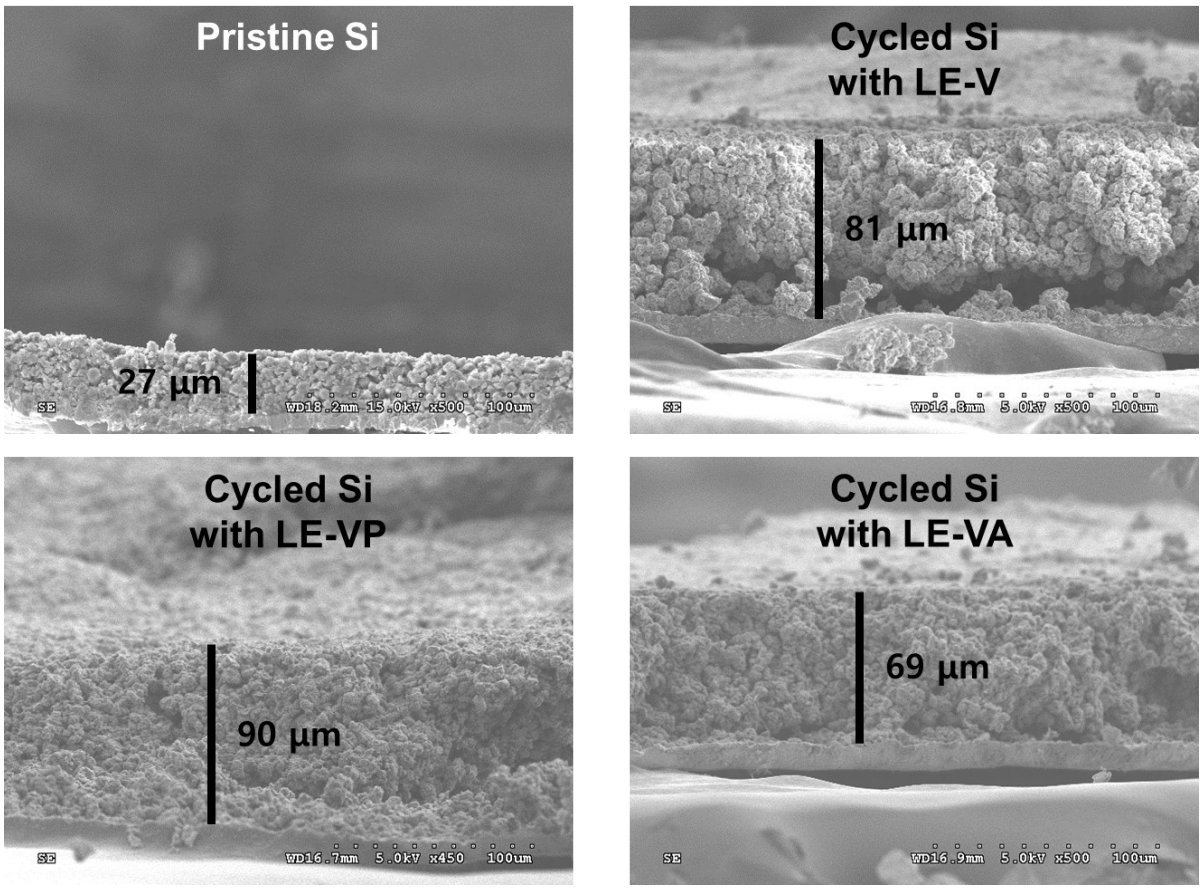


**Figure S16.** Cross-sectional SEM images of pristine state Si anode and cycled Si electrode with different electrolytes.