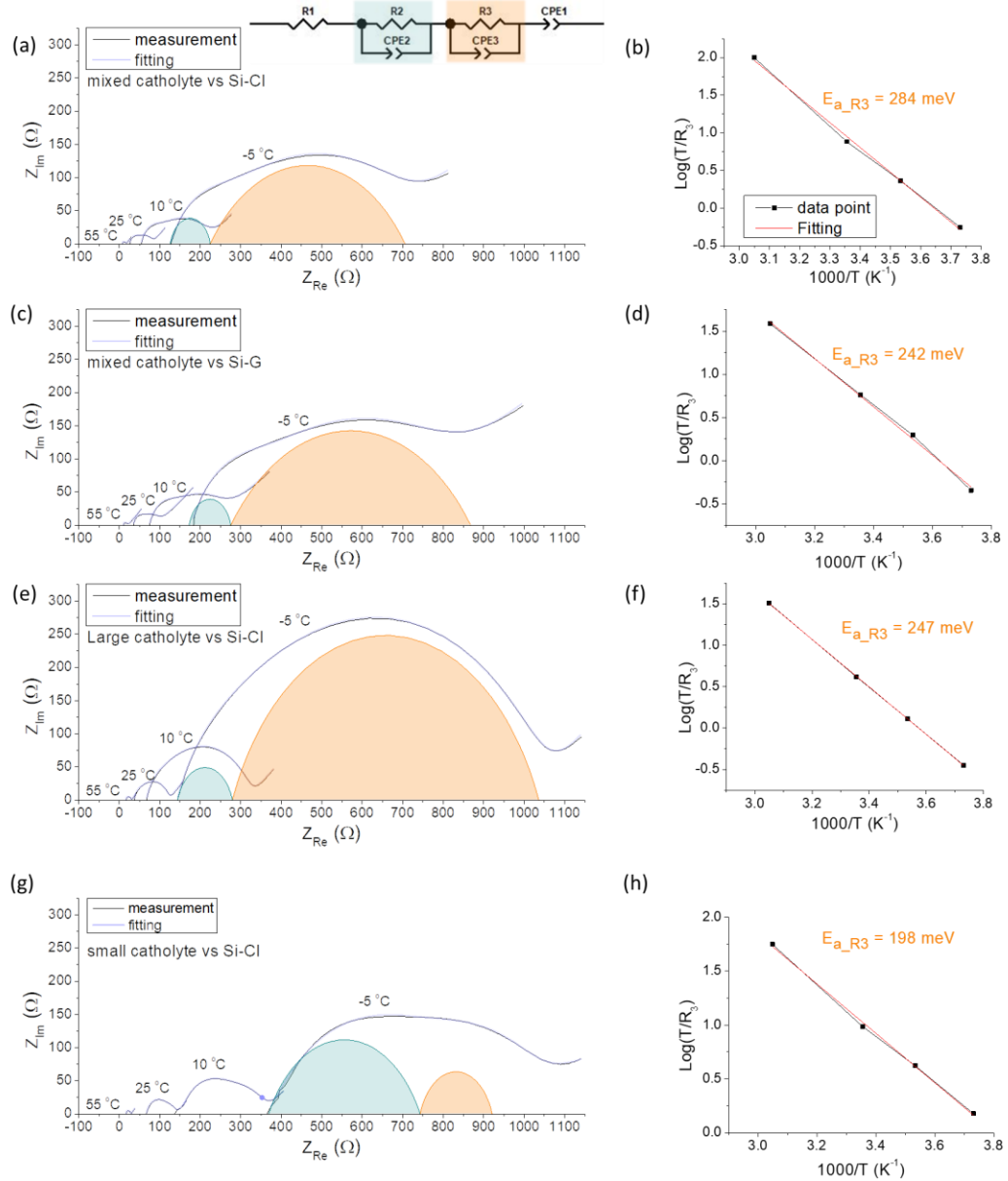


## Supplementary Materials

### Fast Kinetics Design for Solid State Battery Device



**Figure S1.** (a, c, e, g) Impedance measurement and circuit model fitting for different cathode and anode combinations of SSB at -5 °C, 10 °C, 25 °C, and 55 °C. (b, d, f, g) Activation energy of R3 of different SSBs, where R3 represents the interface resistance between active material and solid electrolyte. (a, b) Mixed catholyte vs. Si-Cl; (c, d) Mixed catholyte vs. Si-G; (e, f) Large catholyte only vs. Si-Cl; (g, h) Small catholyte only vs. Si-Cl.

**Table S1** Fitted R2 and R3 values.

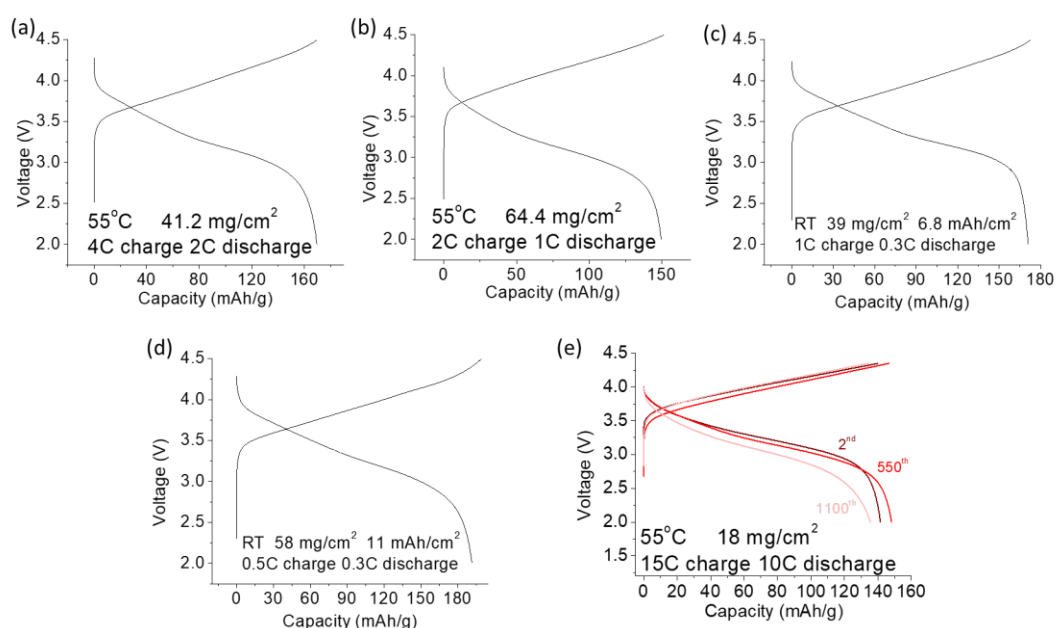
|                                  |                           |                          |                                |                                |
|----------------------------------|---------------------------|--------------------------|--------------------------------|--------------------------------|
| -5 °C                            | Mixed catholyte vs. Si-Cl | Mixed catholyte vs. Si-G | Large catholyte only vs. Si-Cl | Small catholyte only vs. Si-Cl |
| R2 (Ω)                           | 98.59                     | 102.8                    | 135.8                          | 374                            |
| R3 (Ω)                           | 480.9                     | 592.3                    | 756.5                          | 177.7                          |
| 10 °C                            | Mixed catholyte vs. Si-Cl | Mixed catholyte vs. Si-G | Large catholyte only vs. Si-Cl | Small catholyte only vs. Si-Cl |
| R2 (Ω)                           | 38.9                      | 39.87                    | 35.11                          | 129.4                          |
| R3 (Ω)                           | 122.2                     | 143.7                    | 217.9                          | 67.73                          |
| 25 °C                            | Mixed catholyte vs. Si-Cl | Mixed catholyte vs. Si-G | Large catholyte only vs. Si-Cl | Small catholyte only vs. Si-Cl |
| R2 (Ω)                           | 15.74                     | 17.61                    | 12.36                          | 41.84                          |
| R3 (Ω)                           | 38.96                     | 51.36                    | 71.97                          | 30.88                          |
| 55 °C                            | Mixed catholyte vs. Si-Cl | Mixed catholyte vs. Si-G | Large catholyte only vs. Si-Cl | Small catholyte only vs. Si-Cl |
| R2 (Ω)                           | 3.276                     | 0.914                    | 2.755                          | 6.047                          |
| R3 (Ω)                           | 5.59                      | 8.517                    | 10.18                          | 5.844                          |
| Activation energy E <sub>a</sub> | Mixed catholyte vs. Si-Cl | Mixed catholyte vs. Si-G | Large catholyte only vs. Si-Cl | Small catholyte only vs. Si-Cl |
| E <sub>a</sub> R2 (meV)          | 193                       | 270                      | 223                            | 239                            |
| E <sub>a</sub> R3 (meV)          | 284                       | 242                      | 247                            | 198                            |

**Table S2** Fitted CPE2 and CPE3 values.

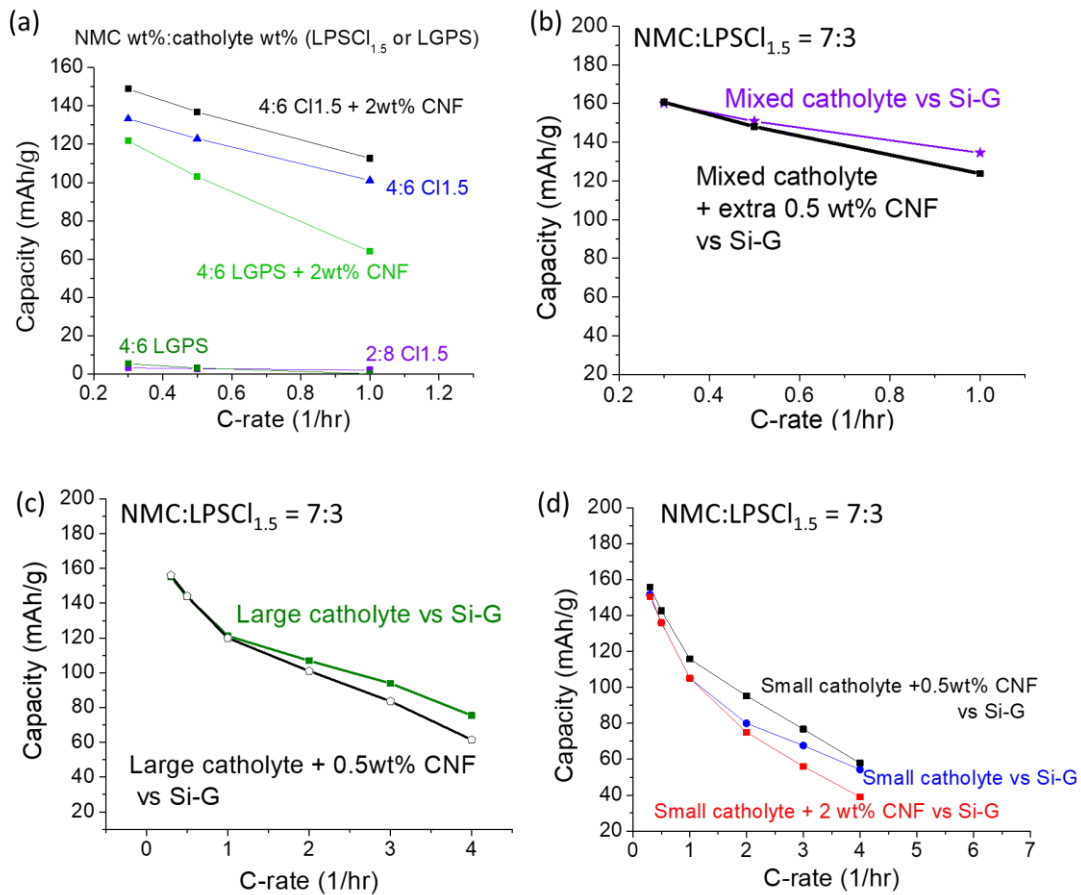
|                                      | -5 °C    | 10 °C    | 25 °C    | 55 °C    |                                      | -5 °C    | 10 °C    | 25 °C    | 55 °C    |
|--------------------------------------|----------|----------|----------|----------|--------------------------------------|----------|----------|----------|----------|
| large catholyte vs Si-Cl             |          |          |          |          | small catholyte vs Si-Cl             |          |          |          |          |
| R2 (Ω)                               | 135.8    | 35.11    | 12.36    | 2.755    | R2 (Ω)                               | 374      | 129.4    | 41.84    | 6.047    |
| CPE2-T                               | 1.75E-05 | 8.36E-06 | 3.31E-06 | 6.07E-07 | CPE2-T                               | 2.21E-05 | 1.66E-05 | 8.78E-06 | 1.09E-06 |
| CPE2-P                               | 0.7987   | 0.907    | 1.012    | 1.195    | CPE2-P                               | 0.686    | 0.7445   | 0.844    | 1.089    |
| ω <sub>max</sub> " <sub>2</sub> (Hz) | 1.93E+03 | 7.84E+03 | 2.17E+04 | 6.82E+04 | ω <sub>max</sub> " <sub>2</sub> (Hz) | 1.09E+03 | 3.84E+03 | 1.17E+04 | 5.74E+04 |
| C2 (F)                               | 3.81E-06 | 3.63E-06 | 3.73E-06 | 5.32E-06 | C2 (F)                               | 2.46E-06 | 2.01E-06 | 2.04E-06 | 2.88E-06 |
| R3 (Ω)                               | 756.5    | 217.9    | 71.97    | 10.18    | R3 (Ω)                               | 177.7    | 67.73    | 30.88    | 5.844    |
| CPE3-T                               | 2.55E-05 | 2.64E-05 | 2.60E-05 | 2.76E-05 | CPE3-T                               | 2.27E-04 | 2.44E-04 | 2.56E-04 | 9.87E-05 |
| CPE3-P                               | 0.74     | 0.76     | 0.7879   | 0.85     | CPE3-P                               | 0.79183  | 0.73795  | 0.68392  | 0.802    |
| ω <sub>max</sub> " <sub>3</sub> (Hz) | 33.11304 | 140.7688 | 461.3498 | 2398.122 | ω <sub>max</sub> " <sub>3</sub> (Hz) | 9.191509 | 41.24988 | 188.5386 | 1739.561 |
| C3 (F)                               | 6.35E-06 | 5.19E-06 | 4.79E-06 | 6.52E-06 | C3 (F)                               | 9.74E-05 | 5.70E-05 | 2.73E-05 | 1.57E-05 |
|                                      |          |          |          |          |                                      |          |          |          |          |
|                                      | -5 °C    | 10 °C    | 25 °C    | 55 °C    |                                      | -5 °C    | 10 °C    | 25 °C    | 55 °C    |
| mixed catholyte vs Si-Cl             |          |          |          |          | mixed catholyte vs Si-G              |          |          |          |          |
| R2 (Ω)                               | 98.59    | 38.9     | 15.74    | 3.276    | R2 (Ω)                               | 102.8    | 39.87    | 17.61    | 0.914    |
| CPE2-T                               | 1.12E-05 | 6.83E-06 | 3.67E-06 | 7.67E-07 | CPE2-T                               | 1.14E-05 | 7.79E-06 | 4.73E-06 | 6.84E-18 |
| CPE2-P                               | 0.846    | 0.89837  | 0.96574  | 1.134    | CPE2-P                               | 0.8318   | 0.8827   | 0.94267  | 4.916    |
| ω <sub>max</sub> " <sub>2</sub> (Hz) | 3.13E+03 | 9.56E+03 | 2.45E+04 | 8.67E+04 | ω <sub>max</sub> " <sub>2</sub> (Hz) | 3.34E+03 | 9.42E+03 | 2.13E+04 | 3.16E+04 |
| C2 (F)                               | 3.24E-06 | 2.69E-06 | 2.60E-06 | 3.52E-06 | C2 (F)                               | 2.91E-06 | 2.66E-06 | 2.67E-06 | 3.46E-06 |
| R3 (Ω)                               | 480.9    | 122.2    | 38.96    | 5.59     | R3 (Ω)                               | 592.3    | 143.7    | 51.36    | 8.517    |
| CPE3-T                               | 1.63E-04 | 2.01E-04 | 2.35E-04 | 2.04E-04 | CPE3-T                               | 1.59E-04 | 2.08E-04 | 3.30E-04 | 1.82E-05 |
| CPE3-P                               | 0.58194  | 0.63141  | 0.654    | 0.73542  | CPE3-P                               | 0.571    | 0.6158   | 0.604    | 0.83     |
| ω <sub>max</sub> " <sub>3</sub> (Hz) | 79.08812 | 355.3798 | 1308.238 | 10026.06 | ω <sub>max</sub> " <sub>3</sub> (Hz) | 62.65485 | 298.957  | 854.8485 | 3898.7   |
| C3 (F)                               | 2.63E-05 | 2.30E-05 | 1.96E-05 | 1.78E-05 | C3 (F)                               | 2.69E-05 | 2.33E-05 | 2.28E-05 | 3.02E-05 |

$Z_{CPE} = \frac{1}{T(i\omega)^P} (\Omega)$ .  $\omega_{max}'' = (RT)^{-1/P} = 1/RC$  is the frequency that maximizes the

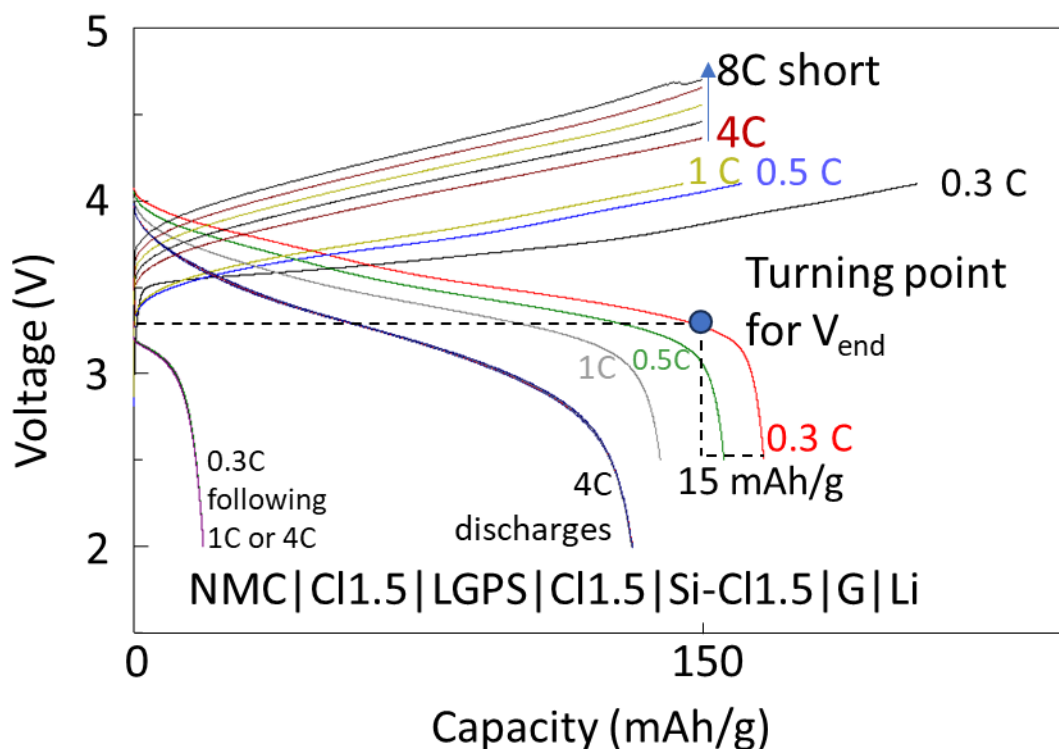
imaginary part of  $Z_{CPE}$ , and  $C$  is the equivalent capacitance.<sup>[1]</sup> The fitting at 55 °C could have certain error due to the small and overlapping semicircles. From large-only, to mixed, to small-only catholyte vs Si-Cl, the C2 values slightly decrease while C3 values more obviously increase for an order of magnitude. The C3 value increase suggests more charge accumulation at the small catholyte|NMC interface, which may point out a future direction to further optimize such interface. And there is no significant change between mixed catholyte vs Si-Cl and vs Si-G. Note that the capacitance of C2 in grain boundary of electrolyte particles here is much larger than the value measured from pure electrolyte pellet without cathode particles<sup>[2]</sup>, while it is just slightly higher than a similar full cell measurement previously<sup>[3]</sup>. The much higher capacitance is thus contributed from the chemical interphase<sup>[4-5]</sup> formed at the surface of electrolyte particles when pre-mixing them with the cathode particles before the assembly of full cells, as such reaction interphase is missing in the electrolyte-only pellet. The slightly higher capacitance is due to different interphase materials between the two full cell cases. In addition, our higher cathode loading here further increased the capacitance than the previous full cell due to larger area of the interphase<sup>[3]</sup>.



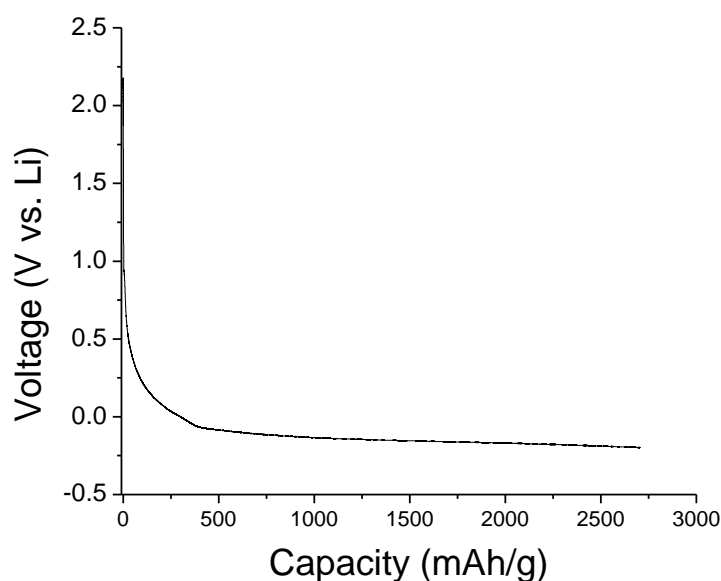
**Figure S2.** Voltage profile and cycling performance of batteries at different temperatures (55 °C or RT), cathode loading (18 ~ 58 mg/cm<sup>2</sup>), and C-rates (0.3 C ~ 15 C), as labeled in each panel.



**Figure S3.** The effect of carbon nano fiber (CNF) additive. (a) Adding CNF to cathode composite with low NMC ratio can increase capacity by connecting more NMC electronically. LPSCl makes the composite lose electronic percolation at a lower NMC ratio than in LGPS composite, i.e., NMC in LPSCl can better percolate than in LGPS. This is due to the different particle size distributions of the two catholytes. (b-d) Adding extra CNF to the cathode composite with NMC:catholyte weight ratio of 7:3 for (b) mix-sized catholyte, (c) large catholyte and (d) small catholyte.



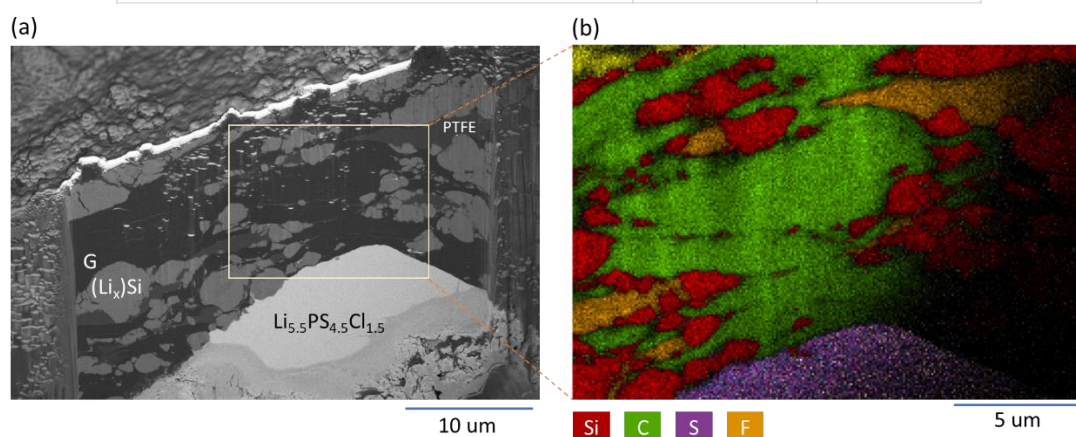
**Figure S4.** An example of critical C-rate and  $V_{\text{end}}$  measurement from a full cell with 18 mg/cm<sup>2</sup> cathode loading (2.7 mAh/cm<sup>2</sup> area capacity) and a battery configuration as labelled in the figure. The battery was first charged and discharged at 0.3 C to measure the  $V_{\text{end}}$  turning point defined at 15 mAh/g capacity to the full discharge. After cycling at 0.3 C, 0.5 C, and 1 C, the battery was then discharged to 2 V at 0.3 C. In subsequent cycles to test the critical C-rate, the battery was charged at increasing C-rates started from 4 C and increased by 1 C per cycle, where the charge cutoff is always at 150 mAh/g charge capacity and discharged first quickly at 4 C to 2 V and then followed by 0.3 C to 2V in each cycle.



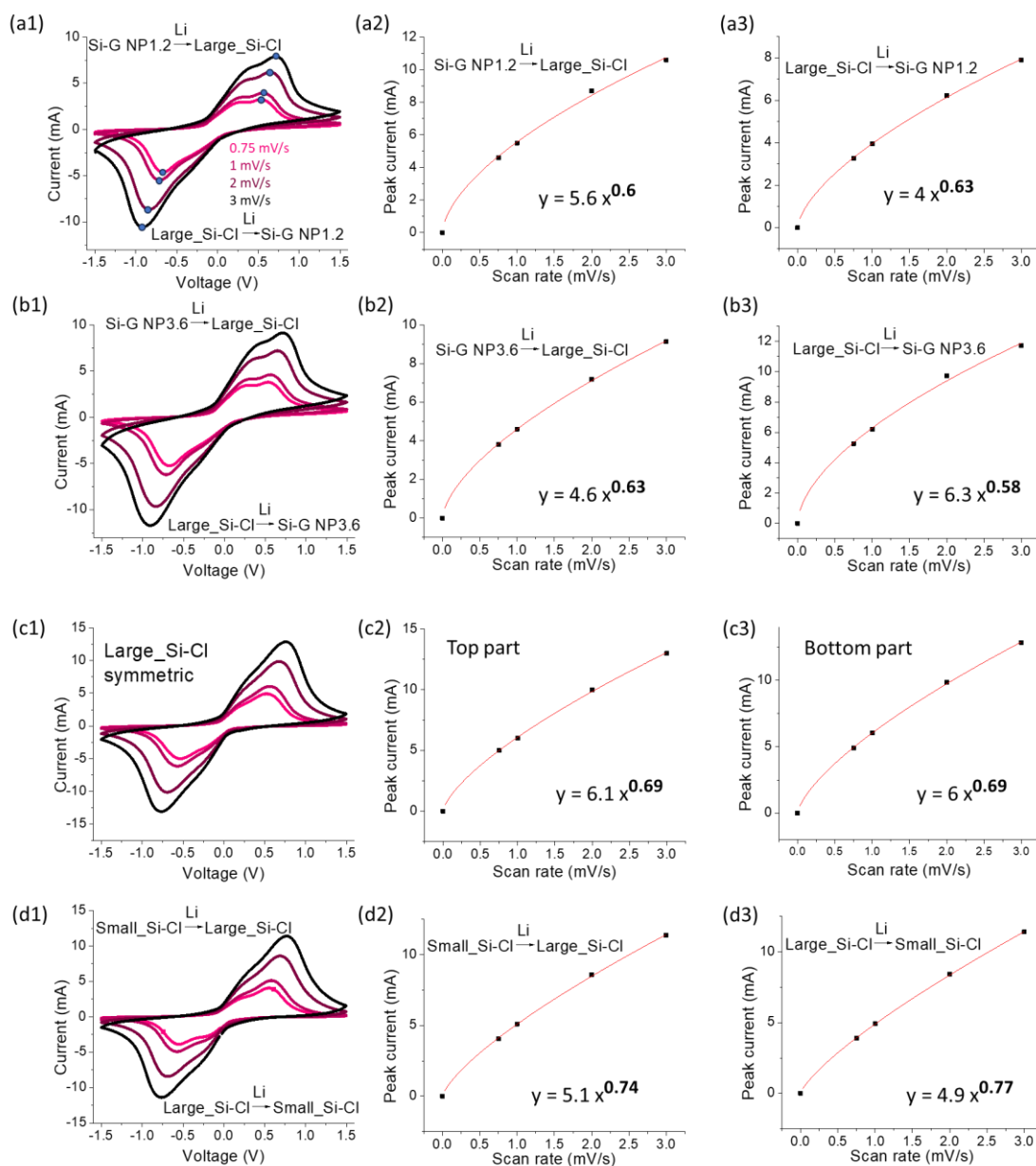
**Figure S5.** Si-G|Li anode discharge voltage profile in a SSB with the configuration of Li|G|Li<sub>5.5</sub>PS<sub>4.5</sub>Cl<sub>1.5</sub>|LPSCl-I|Li<sub>5.5</sub>PS<sub>4.5</sub>Cl<sub>1.5</sub>|Si-G at the current density of 0.2 mA/cm<sup>2</sup> at room temperature.

**Table S3.** Data points in Figure 4d with  $V_{\text{end}}$  and critical C-rate being obtained following the procedure described in Figure S4.

|   | $V_{\text{end}}$ (V) | Critical C-rate |
|---|----------------------|-----------------|
| Si-G NP1.2                                    | 3.35                 | 4               |
| Si-G NP1.7                                    | 3.25                 | 4               |
| Si-G NP2.4                                    | 3.15                 | 8               |
| Si-G NP3.4                                    | 3.06                 | 9               |
| Si + 1wt% Ag _Hand mill                       | 3.1                  | 7               |
| Si + 2wt% Ag _Hand mill                       | 3.07                 | 7               |
| Si + 1wt% Ag _Ball mill                       | 3.18                 | 8               |
| Si + 2wt% Ag _Ball mill                       | 3.11                 | 7               |
| Si + 2wt% Mg2Si _Ball mill                    | 3.18                 | 6               |
| Si + 5wt% LiAl alloy _Hand mill               | 3.23                 | 4               |
| Si + 1wt% Sn _Ball mill                       | 3.22                 | 7               |
| Si + 2wt% Sn _Ball mill                       | 3.254                | 6               |
| Si + 2wt% Al _Ball mill                       | 3.24                 | 6               |
| Si + 5wt% Al _Ball mill                       | 3.22                 | 6               |
| Si + 2wt% Mg _Ball mill                       | 3.05                 | 8               |
| pre-heating Li Si-G at 200 oC                 | 3.23                 | 4               |
| Si + 1wt% Pb _Ball mill                       | 3.23                 | 6               |
| Si + 5wt% LPSCl1.5 NP 2.1                     | 3.2                  | 6               |
| Si + 2wt%total GeSnPb _Ball mill              | 3.215                | 6               |
| Si-Hard carbon (HC) 1:1 NP1.6                 | 3.215                | 6               |
| Si + 10wt% Ge _Ball mill                      | 3.215                | 6               |
| Si-HC(1:1) Si-HC(1:9) Li, total NP = 1        | 3.19                 | 7               |
| Si + 10wt% LPSCl1.5 NP2                       | 3.23                 | 7               |
| Si + 10wt% LPSCl1.5 G NP2                     | 3.27                 | 8               |
| 1uSi + 20wt% 3uLPSCl1.0 G (Small Si-Cl) NP1.9 | 3.16                 | 11              |
| Si + 20wt% Cl1.5 G (Large Si-Cl) NP1.9        | 3.27                 | 8               |



**Figure S6.** FIB-SEM-EDS of cycled Li|Si-G anode after critical C-rate test of a SSB with NP ratio of 2.4 and a battery configuration of mixed catholyte|LPSCl1.5|LPSCl-I|LPSCl1.5|Si-G|Li. The Li metal layer originally at the top surface of the SEM image here was stripped during cycling and merged into the Si-G layers. (a) FIB-SEM image. (b) EDS of the inset of (a).



**Figure S7.** The b value measurement from CV sweeping test of different anode configurations in the battery of anode<sub>1</sub>|electrolyte|anode<sub>2</sub> in Figure 4f. NP ratio is defined as if it is paired with 18 mg/cm<sup>2</sup> cathode to represent different thickness of the anode. Anode<sub>1</sub> is always the configuration of Si + 20wt% Cl<sub>1.5</sub>G|Li using large particles of Si and LPSCl<sub>1.5</sub> (Large Si-Cl). Anode<sub>2</sub> is (a) Si-G|Li NP1.2; (b) Si-G|Li NP3.6; (c) Large\_Si-Cl|G|Li using large particles of Si and LPSCl<sub>1.5</sub>; (d) Small\_Si-Cl|G|Li using small particles of Si and LPSCl<sub>1.0</sub>. Peak currents (y) at each CV scan rates (x) are used to fit  $y = ax^b$ . The average b value of top part (charge) and bottom part (discharge) of the CV scan is presented in Figure 4f. Multi-electrolyte-layer configuration of LPSCl<sub>1.5</sub>|LPSCl-I|LPSCl<sub>1.5</sub> is used as the separator.

## Reference

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