Intramolecular Deformation of Zeotype-borogermanate toward Three-dimensional Porous Germanium Anode for High-rate Lithium Storage

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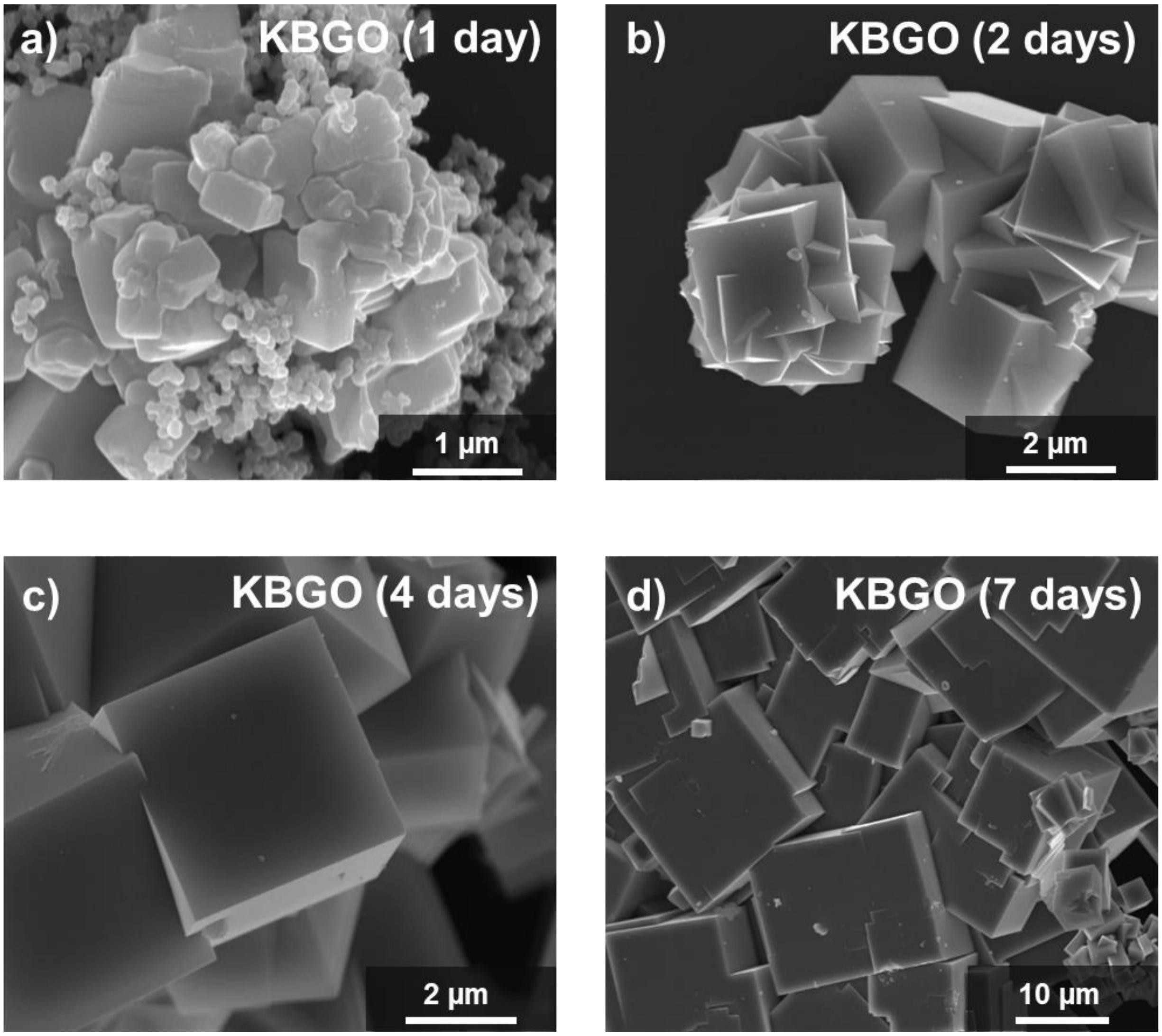

Figure S1. SEM images for variable KBGO morphology by tuning the reaction time to (a) 1 day, (b) 2 days, (c) 4 days, and (d) 7 days. To study the optimized particles of KBGO as starting material, we synthesized the variable KBGO particles by adjusting the reaction time. The KBGO (1day) observed the unreacted GeO_2 precursor showing nanometer-sized GeO_2 and the KBGO (2day) showed non-uniform particles due to insufficient reaction time. The KBGO (7day) also showed non-uniform and huge particles. Thus, the KBGO (4 day) sample was chosen as a starting material because of uniform size and morphology.

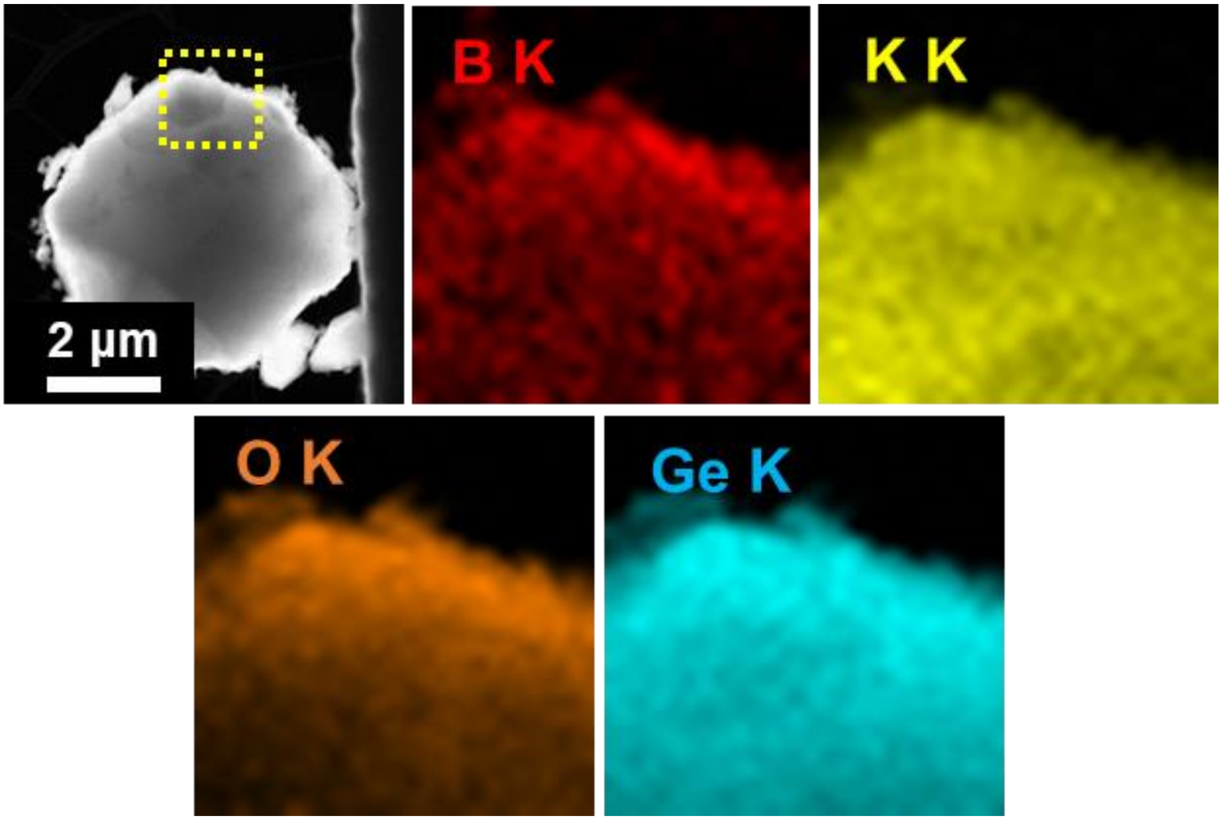

Figure S2. STEM-HAADF image of KBGO (4days) and its EDX mapping results.

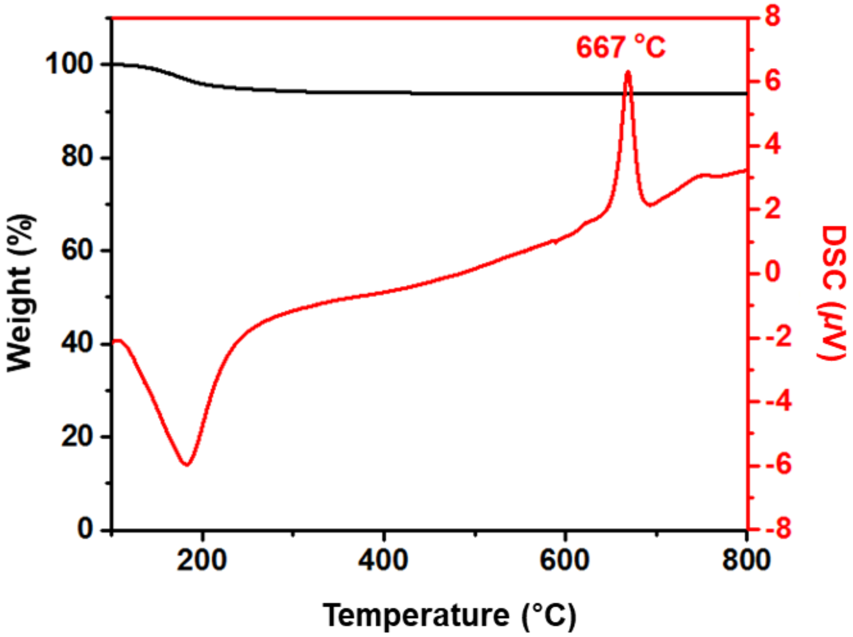

Figure S3. Thermogravimetric analysis-differential scanning calorimeter (TGA-DSC) curve for KBGO materials. The TG curve exhibited weigh loss at around 200 °C, which was resulted from the release of absorbed moisture. At temperature above 200 °C, the TG curve indicated no weight loss till 800 °C. However, the DSC diagram showed exothermic peak at 667 °C, which was resulted from the deformation of KBGO. The integration of this peak was 69.14 J g^{-1}.

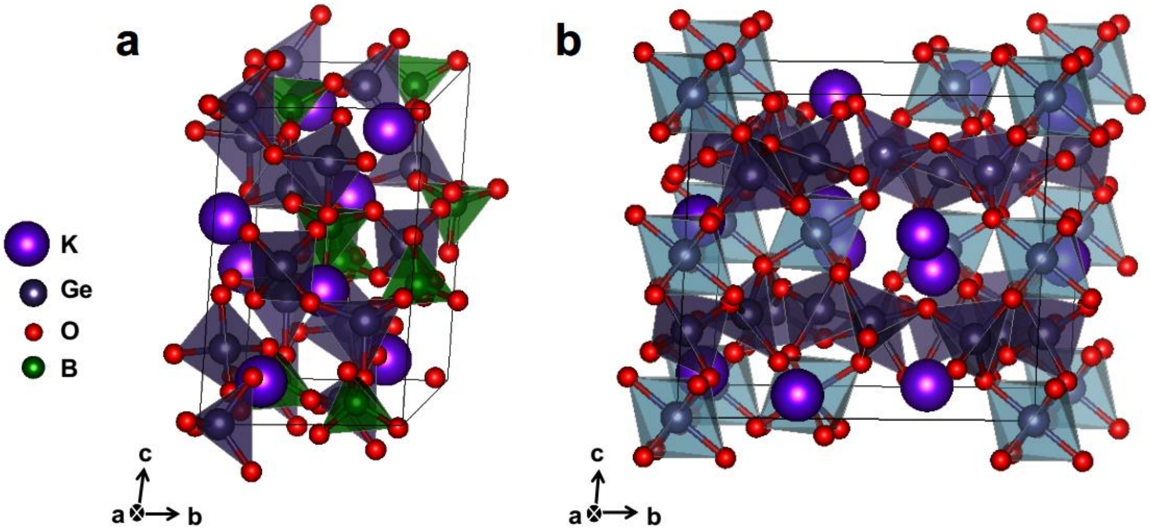

Figure S4. (a) The monoclinic unit cell of $K_2B_2Ge_3O_{10}$ (KBGO). GeO_4 tetrahedrons (grey) and BO_4 tetrahedrons (green) compose elliptical channels in the crystal. K^+ ions are coordinated by O atoms filling these channels. (b) The trigonal unit cell of $K_2Ge_4O_9$ (KGO). The octaheral-tetrahedral frameworks of crystal are composed of GeO_4 tetrahedrons (grey) and GeO_6 octahedrons (blue). The cavities in this framework are filled with K^+ ions.[1]

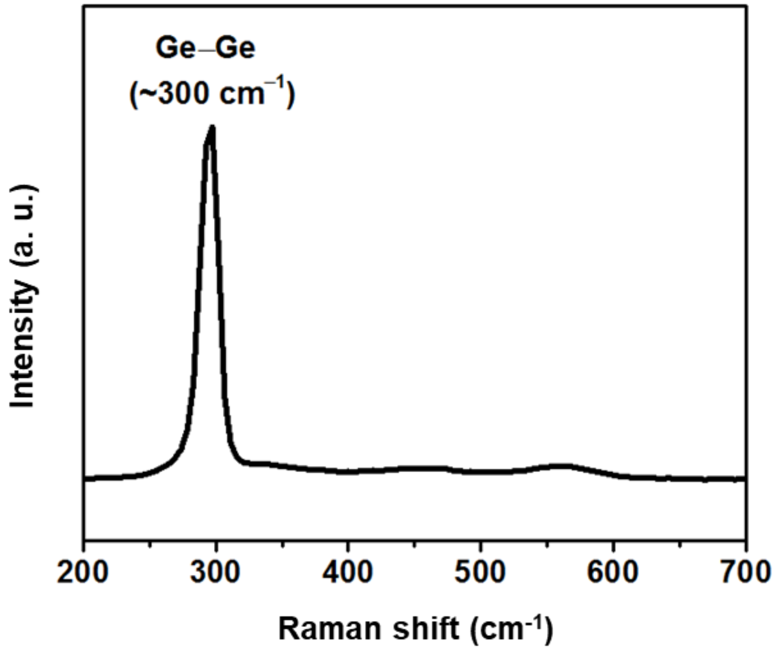

Figure S5. Raman spectra measured in 3D-pGe. The 3D-pGe showed a single sharp peak with a Raman frequency of ~300 cm^{-1}, which was consistent with Ge-Ge mode in metallic Ge. In addition, other Ge in an oxidation state (~440 cm^{-1}) was not observed.[2]

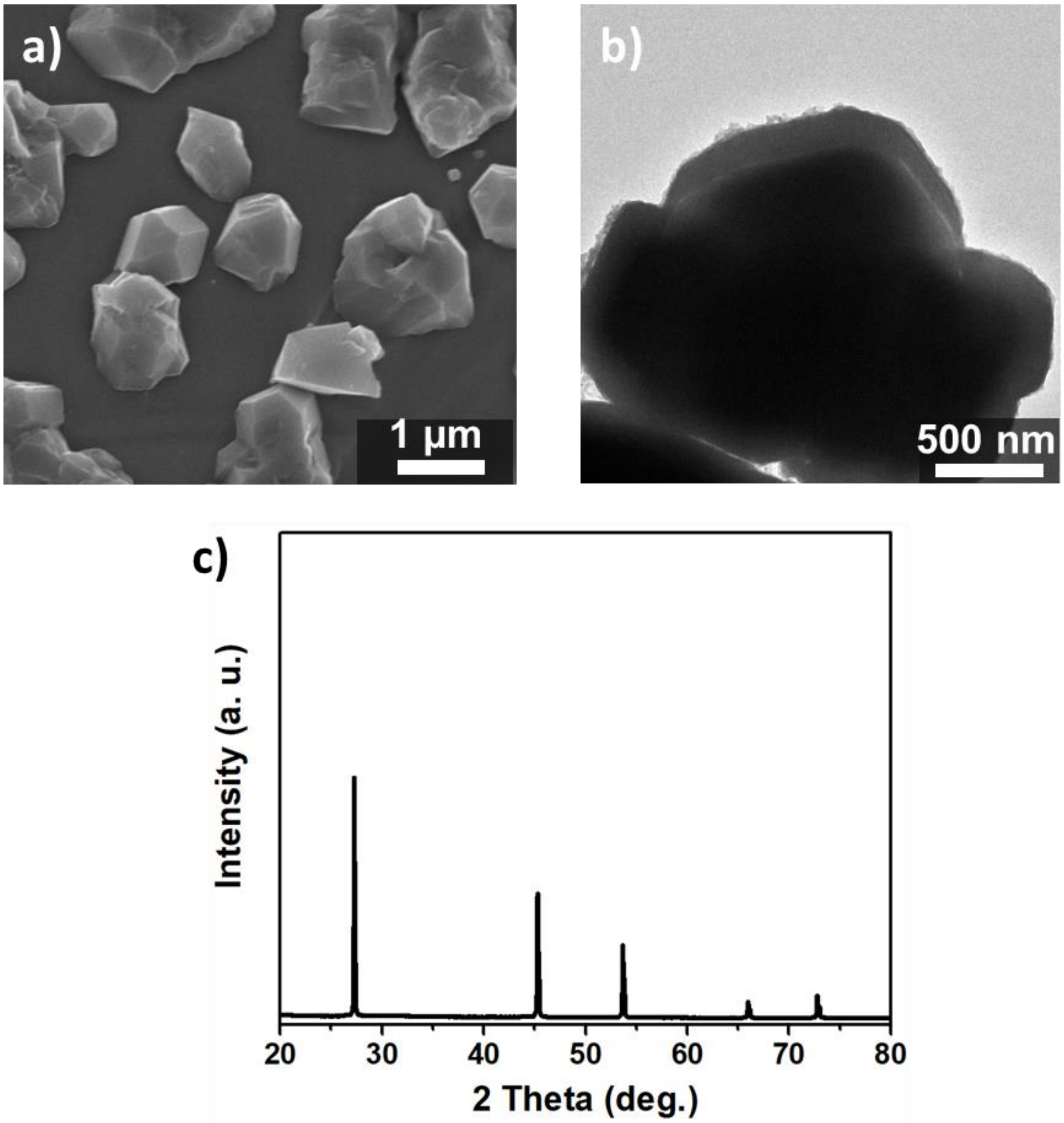

Figure S6. Characterizations of Bulk-Ge. (a) SEM image, (b) TEM image, and (c) XRD patterns.

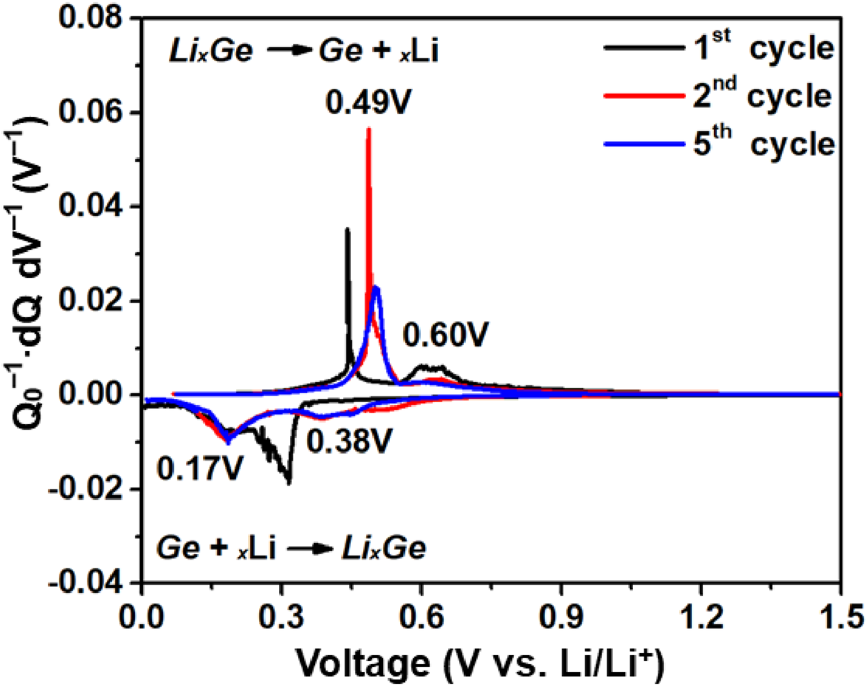

Figure S7. Differential charge/discharge capacity of 3D-pGe at featured cycles at C/20 (1st cycle) and C/5 (other cycles).

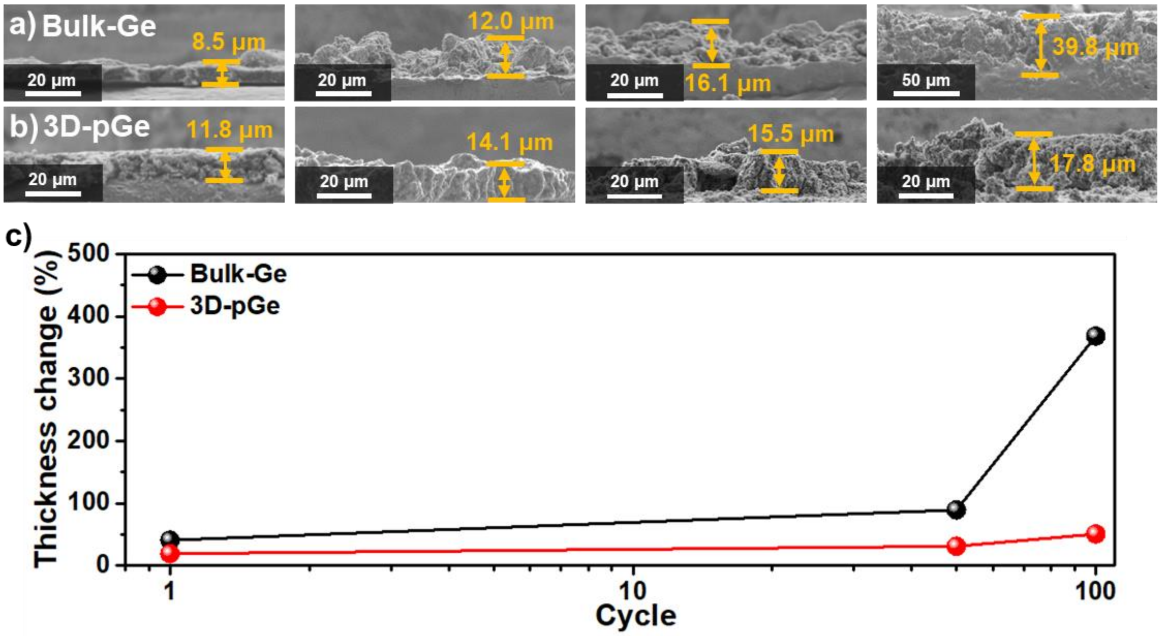

Figure S8. The cross-sectional SEM images to conform electrode swelling properties of (a) bulk-Ge and (b) 3D-pGe; pristine, after 1st cycle, 50th cycle, and 100th cycle from left. (c) The summarized graph of electrodes expansion based on (a) and (b).

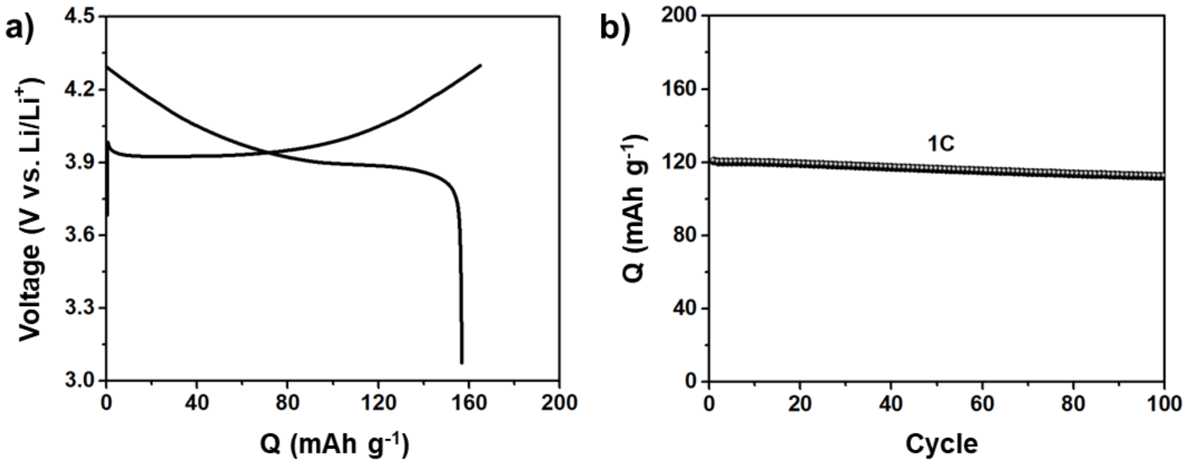

Figure S9. Formation cycle at C/10 and cyclic performance at 1C of LCO cathode.

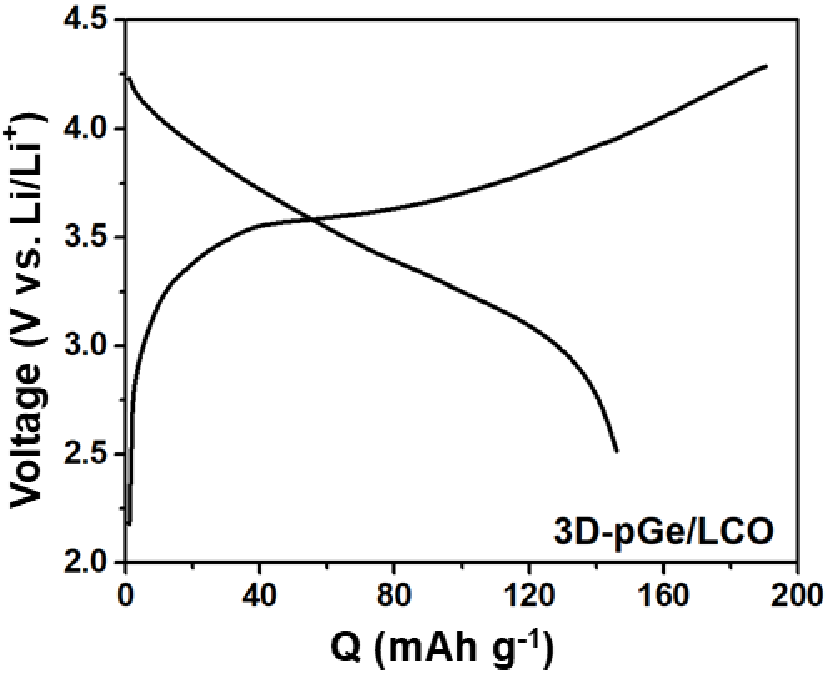

Figure S10. The formation cycle of 3D-pGe/LCO full cell at C/10.

Table S1. Comparison of capacitive current and faradaic current of Bulk-Ge at various scan rate.

Scan rate [mV s^{-1}]	**Capacitive current [%]**	**Faradaic current [%]**
0.2	19.0	81.0
0.4	23.4	76.6
0.6	34.2	65.8
0.8	40.4	59.6
1.0	45.0	55.0
2.0	61.2	38.8
3.0	75.4	24.6
4.0	73.3	26.7
5.0	78.8	21.2

Table S2. Comparison of capacitive current and faradaic current of 3D-pGe at various scan rate.

Scan rate [mV s^{-1}]	**Capacitive current [%]**	**Faradaic current [%]**
0.2	17.7	82.3
0.4	31.9	68.1
0.6	49.3	50.7
0.8	63.7	36.3
1.0	74.3	25.7
2.0	79.1	20.9
3.0	88.6	11.4
4.0	94.8	5.2
5.0	95.9	4.1

Table S3. Comparison of the energy/power density of Ge-based anodes.

Materials	Energy density (Max.) [Wh kg^{-1}]	Power density (Max.) [W kg^{-1}]	Reference
Mesoporous Ge microparticles	315.8	315.8	3
Hoenycomb-like Ge	470	199	4
3D-pGe	348	365	This work

The energy density of 3D-pGe/LCO full cell was calculated using the following equation,

$$\text{Energy density (Wh kg}^{-1}\text{)} = \text{Average voltage (V) x gravimetric capacity (mAh kg}^{-1}\text{)}$$

The weight corresponds to the sum of cathode and anode weights in a cell. Average voltage ($V_{avg.}$) can be calculated from the equation as follows,

$$V_{avg.} = \frac{\int_0^x v(x)\,dx}{\int_0^x dx}$$

where $v(x)$ is the curve of voltage profile (Capacity versus V).

Table S4. Comparison of the tap density of Ge-based anodes.

Materials	**Tap density (g cm^{-3})**	**Reference**
Ge@carbon cubes	1.13	5
Hollow Ge particles	1.16	6
Mirconized Ge_3N_4@carbon	1.10	7
3D-pGe	1.50	This work

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