Supporting Information for

Mass-scalable Synthesis of 3D Porous Germanium-Carbon Composite Particles as an Ultra-high Rate Anode for Lithium Ion Batteries

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Sample	Weight Content (wt%)						
-	N	С	Н	0	Sulfur	Germanium	
3D-Ge/C	1.090	14.264	0.264	1.672	0	82.71	

Table S1. Chemical composition of 3D-Ge/C.

*The weight contents of nitrogen, carbon, hydrogen and oxygen were determined by the elemental analysis (CHNS-O). The remaining content was germanium.

Table S2. Lithium diffusion coefficient (D_{Li}) in the 3D-Ge/C and the pure Ge obtained from GITT.

Lithiation	Diffusion coefficient (cm ⁻² s ⁻¹)						
state (%)	3D-Ge/C	3D-Ge/C	Pure Ge	Pure Ge			
	Discharge	Charge	Discharge	Charge			
10	6.45 ×10 ⁻¹¹	7.62 ×10 ⁻¹¹	7.14 ×10 ⁻¹²	1.11 ×10 ⁻¹¹			
20	3.06 ×10 ⁻¹¹	6.05 ×10 ⁻¹¹	2.83 ×10 ⁻¹²	4.59 ×10 ⁻¹²			
30	2.78 ×10 ⁻¹¹	5.08 ×10 ⁻¹¹	2.26 ×10 ⁻¹²	3.72 ×10 ⁻¹²			
40	2.37 ×10 ⁻¹¹	3.59 ×10 ⁻¹¹	1.67 ×10 ⁻¹²	7.37 ×10 ⁻¹³			
50	3.25 ×10 ⁻¹¹	2.29 ×10 ⁻¹²	3.61 ×10 ⁻¹²	1.46 ×10 ⁻¹³			
60	1.84 ×10 ⁻¹¹	3.42 ×10 ⁻¹²	1.15 ×10 ⁻¹²	4.44 ×10 ⁻¹⁴			
70	4.04 ×10 ⁻¹²	1.12 ×10 ⁻¹¹	8.80 ×10 ⁻¹²	1.04 ×10 ⁻¹⁴			
80	7.88 ×10 ⁻¹²	3.24 ×10 ⁻¹¹	1.33 ×10 ⁻¹³	5.81 ×10 ⁻¹⁴			
90	4.65 ×10 ⁻¹¹	6.74 ×10 ⁻¹¹	2.43 ×10 ⁻¹²	9.96 ×10 ⁻¹³			



Fig. S1. (a) X-ray diffraction pattern, (b) particle size distribution, and (c, d) low and high magnification SEM images of GeO_2 .

Fig. S1a shows the X-ray diffraction pattern (XRD) of GeO₂. All the observed peaks of GeO₂ were matched to the hexagonal phase of GeO₂ (ICCD no. 36-1463). It is noticeable that the XRD peaks corresponding to GeO₂ were quite broad, indicating that nano-sized GeO₂ was obtained by the sol-gel method. From the XRD pattern of GeO, the crystallite size of GeO₂ was calculated to be ~11 nm using the Scherrer equation, which is also in good agreement with the size calculated from dynamic light scattering (DLS) shown in **Fig. S1**b (9.7±1.4 nm). The morphology of GeO₂ synthesized by the sol-gel method is shown in **Figure S1**c-d. The GeO₂ consisted of nanoparticles, but the nanoparticles agglomerated into coarser particles having a size exceeding 100 nm.



Fig. S2. Thermo-gravimetric analysis (TGA) of (a) PVP and (b) GeO_2/PVP measured at heating rate of 10 °C min⁻¹ under argon flux of 50 ml min⁻¹.

Thermo-gravimetric analysis (TGA) of the PVP and GeO₂/PVP was performed to find the optimum temperature for synthesis of 3D-Ge/C. For the PVP, initial weight loss observed below 100 °C was attributed to the moisture removal (**Fig. S2**a). The subsequent weight loss corresponded to the decomposition of PVP. The weight loss started at around 300 °C and continued up to 480 °C with the weight loss of 91.9 %, leaving only residual carbon. The dramatic weight loss observed in the TGA curve resulted from the break-down of the side groups of PVP.¹ The TGA of GeO₂/PVP exhibited two major stages of weight loss (**Fig. S2**b). In the first stage, the weight loss started above 700 °C and finished at ~840 °C. This is ascribed to the reaction of residual carbon, which formed by the decomposition of PVP in Ar atmosphere, with nano GeO₂ particles.

Based on the TGA data, we carbonized GeO₂/PVP at various temperatures of 700, 750, 775, and 800 °C in a vertical furnace for 1h. Although the carbothermal reduction occurred above 700 °C according to TGA result, in the vertical furnace the GeO₂ was completely reduced to Ge at 775 °C. This can be attributed to slow kinetics for the reduction of GeO₂ at temperatures below 775 °C. In addition, we used larger amount of GeO₂/PVP for the reduction compared with the small amount of GeO₂/PVP used for TGA. Accordingly, the carbonization temperature of 775 °C was selected as an optimum temperature for preparation of 3D-Ge/C.



Fig. S3. Raman spectrum for the 3D-Ge/C.



Fig. S4. (a-d) SEM images of 3D-Ge/C from low to higher magnification, respectively.



Fig. S5. N₂ adsorption/desorption isotherms: (a) the as-prepared GeO₂; (b, c, e, f) the sample obtained after the carbonization of the GeO₂/PVP composite at 700 °C (GeO₂/C), 750 °C (GeO₂-Ge/C), 775 °C (3D-Ge/C), and 800 °C (3D-Ge/C) in argon atmosphere for 1 h, respectively; (d) SEM image of GeO₂-Ge/C synthesized at 750 °C. Inset in Fig. S4b-c shows the XRD patterns of GeO₂ and GeO₂-Ge/C, respectively. Inset in Fig. S4e shows the pore size distribution calculated from the Barrett-Joyner-Halenda (BJH) formula of 3D-Ge/C. Inset in **Fig. S5**f shows SEM images of the sample obtained after carbonization at 800 °C.

The specific area of as the prepared GeO₂ sample was $64.8 \text{ m}^2 \text{ g}^{-1}$. The specific area of the sample increased to 96.6 m² g⁻¹ after dispersion in PVP and carbonization at 700 °C (GeO₂/C), during which the reaction between GeO₂ and carbon did not occur (as shown in inset **Fig. S5**b; all peaks matched with the hexagonal phase of GeO₂). After carbonization at 750 °C, partial GeO₂ was carbothermal reduced into Ge as observed in the inset of **Fig. S5**c. Accordingly, the specific surface area of GeO₂-Ge/C sample increased up to 116.4 m² g⁻¹. At 775 °C, the GeO₂ reacted with carbon completely leading to reduction of GeO₂ into Ge, and the specific area of the sample increased further to 124.9 m² g⁻¹. When carbonized at 800 °C, the aggregation of particles at higher temperature, as shown in the inset **Fig. S5**f. These results demonstrate that the decomposition of PVP and the thermal reduction of GeO₂ by carbon increased the specific area of the sample. This can be attributed to the release of gases during carburization.



Fig. S6. (a) TEM-EDS spectra and (b) TEM elemental mapping of 3D-Ge/C corresponding to TEM and STEM images.



Fig. S7. (a) XPS general survey spectrum of 3D-Ge/C; high resolution XPS spectra of (b) Ge 3d, (c) C 1s, and (d) O 1s of 3D-Ge/C, respectively.

The XPS general survey spectrum of 3D-Ge/C confirmed the presence of Ge, C, N, and O (**Fig. S7**a). In the high-resolution XPS core spectrum of Ge for the 3d level (**Fig. S7**b), the spectrum of Ge 3d was separated into three peaks, corresponding to Ge-Ge (29.7 eV), Ge-C (30.3 eV), and Ge-O (32.7 eV) bonding.²⁻⁴ The Ge-C bonds can be easily formed due to the carbon atoms penetrating into the Ge network. These carbon atoms randomly bonded with Ge in sp3 hybridization to form the interfacial layer. The high-resolution XPS spectrum of C 1s could be de-convoluted into four peaks at 284, 284.6, 285.8, and 287.1 eV, corresponding to C-Ge, C-C, C-O, and C=O, respectively, as shown in **Fig. S7**c.³⁻⁵ In **Fig. S7**d showing the XPS spectrum of O 1s, the peaks observed at 530.6, 531.9, and 533.1 eV corresponded to the O-Ge bonding, the C=O bonding, and the C-O bonding, respectively.⁶ The presence of oxygen can be attributed to the surface oxidation of Ge and oxygen adsorption by carbon.



Fig. S8. Thermogravimetric analysis (TGA) of 3D-Ge/C in air at the heating rate of 10 °C min⁻¹.

$$Ge\% = GeO_2\% \times (Molecular weight of Ge/Molecular weight of GeO_2)$$
$$= 118.8\% \times 72.64/104.64 = 82.5\%$$

The germanium content in 3D-Ge/C sample calculated based on the TG method (82.5%) agrees well with the germanium content calculated from elemental analysis (**Table S1**, 82.71%).



Fig. S9. (a) Low and (b) high magnification SEM images of pyrolytic carbon; (c) cyclability and coulombic efficiency of residual carbon at a current density of 160 mA g^{-1} .

The pyrolytic carbon was prepared by carbonized PVP (without nano GeO₂) at 775 °C for 1 h in argon atmosphere to investigate the contribution of residual pyrolytic carbon to the reversible capacity of 3D-Ge/C sample. The morphology of pyrolytic carbon was investigated by scanning electron microscopy (SEM) as shown in **Fig. S9**a-b. The pyrolytic carbon showed the compact structure without any pore. The electrochemical of pyrolytic carbon is presented in **Fig. S9**c. The specific capacity of pyrolytic carbon was ~470 mAh g⁻¹, which was much lower than that of 3D-Ge/C. Over 100 cycles the specific capacity of pyrolytic carbon was quite stable with the specific capacity of 382 mAh g⁻¹.



Fig. S10. Cyclability of GeO₂-Ge/C synthesized at 750 °C and 3D-Ge/C synthesized at 800 °C under C/10 rate for 100 cycles.



Fig. S11. (a) Coulombic efficiency of 3D-Ge/C electrode under various charge rates while the discharge rate was kept at C/2 rate. Before the tests, all the samples were activated at a lower rate. Here, the coulombic efficiency during the activation process is not been shown. (b) Charge potential profile versus time for 3D-Ge/C at charge rate of 100 C and discharge rate of C/2.



Fig. S12. (a-b) Potential profile of 3D-Ge/C corresponding to Fig. 5a-b, respectively. The potential profile at 100 C charge/discharge rate was not shown since too short time of charge/discharge.

To elucidate the role of the carbon buffer layer in 3D-Ge/C electrode, especially in terms of lithium diffusivity, pure Ge electrode was also prepared for comparison. In detail, the nano GeO₂ with particle size of ~11 nm (prepared by sol-gel method as reported in experimental section) was reduced in vertical tube furnace at 650 °C for 1 h under Ar/H₂ atmosphere (Ar:H₂=95:5, by volume) at a heating rate of 10 °C min⁻¹. It should be noted that the vertical tube furnace had been evacuated to eliminate the air before Ar/H₂ was introduced. The lithium diffusion coefficient was measured by using Galvanostatic Intermittent Titration Technique (GITT) and calculated based on Equation (1) as follows.⁷⁻⁹

$$D = \frac{4L^2}{\pi\tau} (\frac{\Delta E_s}{\Delta E_t})^2 \tag{1}$$

Where *t* is the duration of the current pulse (s), τ is the relaxation time (s), and ΔE_s is the steady-state potential change (V) by the current pulse. ΔE_t is the potential change (V) during the constant current pulse after eliminating the *iR* drop (**Fig. S13**). *L* is lithium ion diffusion length (cm); for compact electrode, it is equal to thickness of electrode.



Fig. S13. E vs. t profile of the 3D-Ge/C electrode for a single GITT during discharge process, which is composed of 10 min galvanostatic charge (pulse) at C/10, and followed by 20 min relaxation time. The iR drop is shown along with the ΔE_t and ΔE_s .

From Equation 1 and obtained GITT for the 3D-Ge/C and the pure Ge (Fig. S14a-b), the lithium diffusion coefficient (D_{Li}) corresponding to various lithiation state was calculated and summarised in Table S2. The D_{Li} in the 3D-Ge/C exhibited the values ranging from 4.04×10^{-12} to 6.45×10^{-11} cm⁻²s⁻¹ during the discharge process and ranging from 2.29×10^{-12} to 7.62×10^{-11} cm⁻²s⁻¹ during the charge process. Obviously, the D_{Li} in pure Ge was found to be much lower than that in 3D-Ge/C, which exhibited D_{Li} values ranging from 8.80×10^{-14} to 3.61×10^{-12} cm⁻²s⁻¹ during the discharge process and ranging from 1.04×10^{-14} to 4.59×10^{-12} cm⁻²s⁻¹ during the discharge process and ranging from 1.04×10^{-14} to 4.59×10^{-12} cm⁻²s⁻¹ during the discharge process and ranging from 1.04×10^{-14} to 4.59×10^{-12} cm⁻²s⁻¹ during the discharge process and ranging from 1.04×10^{-14} to 4.59×10^{-12} cm⁻²s⁻¹ during the discharge process and ranging from 1.04×10^{-14} to 4.59×10^{-12} cm⁻²s⁻¹ during the discharge process and ranging from 1.04×10^{-14} to 4.59×10^{-12} cm⁻²s⁻¹ during the discharge process and ranging from 1.04×10^{-14} to 4.59×10^{-12} cm⁻²s⁻¹ during the charge process and ranging from 1.04×10^{-14} to 4.59×10^{-12} cm⁻²s⁻¹ during the charge process and ranging from 1.04×10^{-14} to 4.59×10^{-12} cm⁻²s⁻¹ during the charge process. This suggests that the 3D-Ge/C is much more favourable compared with pure Ge in an aspect of lithium diffusion in the bulk active electrode material. Accordingly, the 3D-Ge/C electrode could exhibit better electrochemical performance over the pure Ge electrode.



Fig. S14. Charge/discharge GITT curves for (a) the 3D-Ge/C and (b) the pure Ge with time in the potential range of 0.01-1.5V at charge/discharge rate of C/10 for each pulse for 10 min and following relaxation for 20 min. The lithium diffusion coefficient (D_{Li}) in the 3D-Ge/C and the pure Ge during (c) the discharge process and (d) the charge process as a function of lithiation state.



Fig. S15. Rate capability of 3D-Ge/C with different electrode loading mass.



Fig. S16. High-resolution XPS spectra of Ge 3d of 3D-Ge/C; (a) as-prepared and (b) after cycling.

After cycling, the 3D-Ge/C electrode was disassembled in a glove box, washed with EC-DMC solvent, and rinsed with Tetrahydrofuran (THF). Then, the 3D-Ge/C electrode was dried in a vacuum oven to prevent the re-oxidation of Ge. Immediately after taking out of the vacuum oven, the 3D-Ge/C sample was analysed using XPS. **Fig. S16**b shows the high-resolution XPS spectrum of Ge 3d of the 3D-Ge/C after cycling. The spectrum of Ge 3d was separated into two peaks corresponding to Ge-Ge bonding observed at 28.9 eV and Ge-C bonding at 29.9 eV, respectively. Compared with the as-prepared 3D-Ge/C (**Fig. S16**a), for the 3D-Ge/C after cycling, the Ge-O bonding completely disappeared due to the decomposition of GeO₂ into Ge and LiO₂ in the first discharge. In addition, the peaks corresponding to Ge-Ge and Ge-C bonding tend to shift to the lower binding energy due to the amorphisation of Ge.¹⁰ Interestingly, the presence of Ge-C bonding was still retained implying the stable chemical bonding between Ge and C in the 3D-Ge/C.



Fig. S17. (a) Cyclability and coulombic efficiency of LiCoO₂ electrode at the rate of C/10 for 60 cycles. (b) Coulombic efficiency and (c) potential profile of pre-lithiated 3D-Ge/C in half-cell.



Fig. S18. (a) Electrochemical impedance spectra for the $LiCoO_2/Li$ half-cell, the (3D-Ge/C)/Li half-cell, and the $LiCoO_2/(3D-Ge/C)$ full cell, respectively. (b) Enlarged image of Fig. S18a.

In order to investigate the contribution of anode and cathode to impedance of the $LiCoO_2/(3D-Ge/C)$ full cell, we measured the impedance of $LiCoO_2$ half-cell at the 100% state of charge, the impedance of 3D-Ge/C at 100% depth of discharge, and the impedance of the $LiCoO_2/(3D-Ge/C)$ full cell at 100% state of charge. Herein, it is worth to note that, the 100% state of charge of the full cell corresponded to 100% of depth discharge of anode part. As observed in **Fig. S18**, when coupling $LiCoO_2$ with 3D-Ge/C to assemble the full cell, the charge transfer resistance and electrolyte solution resistance of the full cell increased significantly. Due to the increase in the charge transfer resistance and electrolyte resistance, the performance of the full cell at the high charge-discharge rate was affected seriously.



Fig. S19. (a-d) Photographs of a lithium ion battery prototypes using 3D-Ge/C anode and $LiCoO_2$ cathode to light up 50 LED bulbs; after 1 min, 10 min, 20 min, and 30 min, respectively.

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