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Supporting Information

Conducting additive-free amorphous GeO₂/C composite as a high capacity and long-term stability anode for lithium ion batteries

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Fig. S1 Fourier transforms infrared (FTIR) spectrum of GeO₂/C.

It is easy to see appearance of a strong absorption peak at 876 cm⁻¹, which represents the v_3 vibration mode of GeO₄ tetrahedra. Besides, the triplet band in the region 516 - 586 cm⁻¹ is also observed corresponding to the v_4 vibration mode.¹ Specially, it should be noted that, the peak corresponding to v_3 vibration mode showed broadening around 876 cm⁻¹, indicating the distorted tetrahedral structure of GeO₂.



Fig. S2 Raman spectrums of as-prepared GeO_2/C .

The Raman spectra of as-prepared GeO₂/C is shown in **Fig. S2**. Two main peaks appeared at ~ 1348 and 1572 cm⁻¹ corresponding to the disorder-induced D band and graphitic G band of carbon, respectively. The intensity ratio of G band to D band (I_D/I_G) of GeO₂/C sample before and after graphitization was about 1.08 (Fig. S2) and 0.96 (Fig. 1c), respectively. According to Tuinstra and Koenig, the I_D/I_G is inversely proportional to the graphitization degree of carbon.^{2, 3} Therefore, obtained Raman spectroscopy results showed that after annealing at 700 °C the graphitization degree of carbon in GeO₂/C increased significantly.



Fig. S3 N_2 adsorption/desorption isotherms for (a) GeO_2/C and (b) mixture of GeO_2/C and carbon black with weight ratio of 8:1; the insets show the pore size distribution calculated using the Barrett-Joyner-Halenda (BJH) formula.

The GeO₂/C composite had a specific surface area of 15.4 m² g⁻¹ and average pore diameter of 56 nm. The mixture of GeO₂/C and carbon black had a specific area of 144.6 m² g⁻¹ and average pore diameter of 18 nm.



Fig. S4 Electrochemical impedance spectra for (a) CB-GeO₂/C and (b) GeO₂/C electrodes, measured under the potential of 0.75 V vs. Li/Li⁺ at the temperatures of 5~45 °C after 5 discharge-charge cycles.

The charge transfer resistances (R_c) were calculated based on EIS using a circular fitting mode. The R_c of all samples obtained at various temperatures are listed in Table S1.

Sample	Calculated		Temperature (K)			
	value	278 K	288 K	298 K	308 K	318 K
	$R_{c}(\Omega)$	77.9	37.1	18.5	10.1	6.2
CB-GeO ₂ /C	1/R _c	0.0128	0.0270	0.0541	0.0990	0.1613
	log(1/R _c)	-1.892	-1.569	-1.267	-1.004	-0.792
	$R_{c}(\Omega)$	205.5	90.1	43.7	21.1	10.49
GeO ₂ /C	1/R _c	0.0049	0.0111	0.0229	0.0474	0.0953
	log(1/R _c)	-2.313	-1.955	-1.640	-1.324	-1.021
1000/T		3.597	3.472	3.356	3.247	3.145

Table S1 Calculated R_c , $1/R_c$, and log $(1/R_c)$ of the electrodes and 1000/T at different temperatures.



Fig. S5 Arrhenius plot for the (a) CB-GeO₂/C and (b) GeO₂/C electrodes.

The Arrhenius plots derived from the values in **Table S1** showed straight lines. The slopes were calculated based on linear fitting and are enumerated in **Table S2**.

The activate energy was calculated based on the Arrhenius equation as follows:

$$log \frac{1}{R_c} = log A - \frac{E_a}{2300 K_b} * \frac{1000}{T}$$
$$log \frac{1}{R_c} = log A + slope * \frac{1000}{T}$$
$$(slop e = -\frac{E_a}{2300 Kb})$$

R_c: Charge transfer resistance (Ω)

- E_a: Activation energy (eV)
- K_b: Boltzmann constant (8.617*10⁻⁵ eVK⁻¹)
- T: Absolute temperature (K)

Slope: Calculated from Arrhenius plot.

$$E_a = -Slope * 0.023 * 8.617 (eV)$$

Table S2. Slope of Arrhenius	plot and activation	energy (E _a) for t	the electrodes.
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Sample	Slope	E _a (eV)
CB-GeO ₂ /C	-2.399	0.475
GeO ₂ /C	-2.785	0.552



Fig. S6 Reversible capacity of as-prepared GeO₂/C calculated based on total electrode weight.

Herein, for comparison, the as-prepared GeO₂/C electrode was prepared without carbon black by slurry casting process, similar to GeO₂/C electrode. **Fig. S6** shows the specific capacity (based on the total weight of electrode) of the as-prepared GeO₂/C. The specific capacity of GeO₂/C after graphitization was remarkably larger than that of as-prepared GeO₂/C. This is due to increase in the content of GeO₂ and increase the graphitization of carbon in obtained GeO₂/C after annealing.



Fig. S7 Photographs of the surface of (a) CB-GeO₂/C and (b) GeO_2/C electrodes after 400 cycles.



Fig. S8 SEM images of the as prepared (a) CB-GeO₂/C, (b) GeO_2/C electrodes, (c) CB-GeO₂/C, and (d) GeO_2/C electrodes cyclic tested for 400 cycles.



Fig. S9 Electrochemical impedance spectra for (a) CB-GeO₂/C and (b) GeO₂/C electrodes after 5 and 400 cycles.

Electrochemical impedance spectra for the electrodes measured at a charged state of 0.75 V after the first 5 and 400 charge-discharge cycles are shown in ESI,**† Fig. S9**. Resistance R_s includes the resistance of electrolyte and resistance of contact. After fitting the equivalent circuit according to the circular mode, the charge transfer resistance R_c was calculated and is enumerated in ESI,**†** Table 3. After the first 5 cycles, the solution resistance R_s of the electrode CB-GeO₂/C was smaller than that of the electrode GeO₂/C, illustrating that due to the presence of carbon black in the sample the conductivity of the electrode was improved. After 400 cycles, the solution resistance R_s of the samples was only slightly changed, but the charge transfer resistance R_c of the samples increased remarkably.

Table S3. Increase in solution resistance (ΔRs).

 $\Delta Rs = Rs$ (after 5 cycles) -Rs (after 400 cycles)

Sample		Rs(Ω)	ΔRs(Ω)
	After 5 cycles	4.53	0.44
CB-GeO ₂ /C	After 400	4.97	
	cycles		
	After 5 cycles	6.99	
GeO ₂ /C	After 400	7.89	0.90
	cycles		



Fig. S10 Coulombic efficiency of the CB-GeO₂/C and GeO₂/C electrodes with discharge-charge cycle.

Reference

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- 2. F. Tuinstra and J. L. Koenig, *The Journal of Chemical Physics*, 1970, **53**, 1126-1130.
- 3. F. Tuinstra and J. L. Koenig, *Journal of Composite Materials*, 1970, **4**, 492-499.