

SUPPORTING INFORMATION

Uniform GeO₂ dispersed in nitrogen-doped porous carbon core-shell architecture: Anode material for Lithium Ion Batteries

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Table S1. Chemical composition of GeO₂/N-C.

Sample	Weight Content (wt%)				
	N	C	H	Sulfur	GeO ₂
GeO ₂ /N-C	1.22	15.86	0.22	0	82.7

*The weight contents of nitrogen, carbon, hydrogen, and oxygen were determined by elemental analysis (CHNS). The remaining content was GeO₂. This value is in good agreement with the TG data.

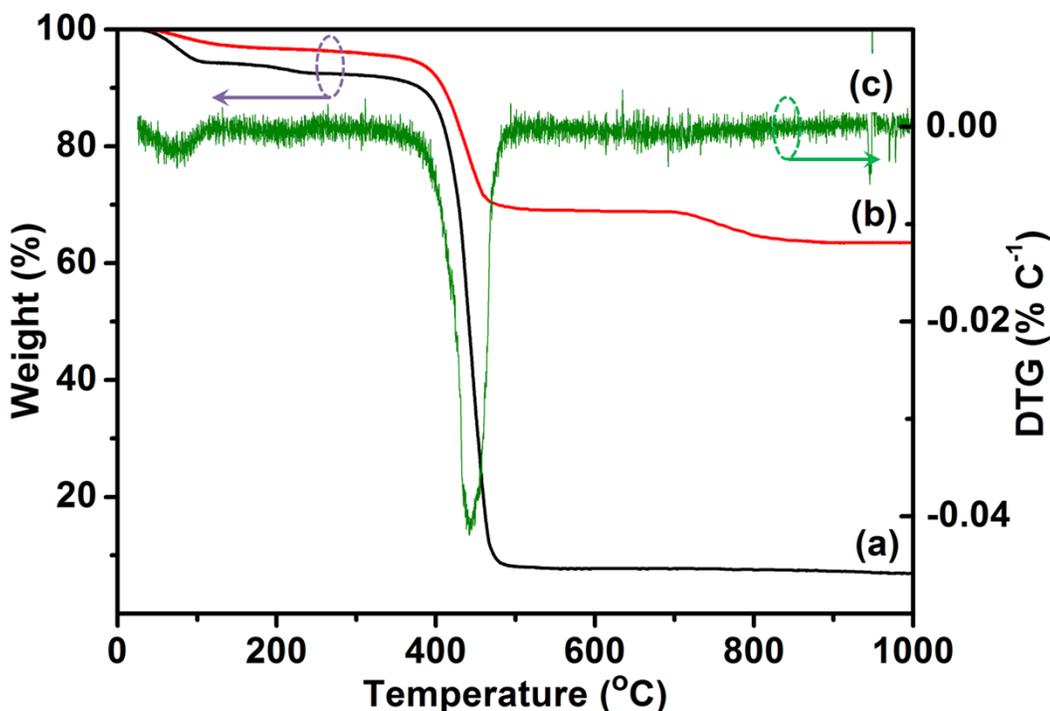


Fig. S1 Thermo-gravimetric (TG) analysis of (a) PVP and (b) mixture of GeO₂-PVP with a weight ratio of 2:1. (c) Derivative Thermogravimetric (DTG) analysis of PVP.

Thermo-gravimetric (TG) analysis of the samples was performed to study the thermal decomposition behavior of PVP and GeO₂/PVP. **Fig. S1** shows the TG curves of PVP and GeO₂/PVP obtained at a heating rate of 10 °C min⁻¹ under argon flux of 50 ml min⁻¹. For the PVP (**Fig. S1a**), the weight loss observed below 100 °C was attributed to the moisture removal. The subsequent weight loss corresponded to the decomposition of PVP. The weight loss started at around 298 °C and continued up to 482 °C with 91.9% weight loss, leaving only residual carbon. The dramatic weight loss observed in the TG curve is attributed to the result of the break-down of the side groups of PVP.¹ According to Imre et al.,² the main gases evolved during the decomposition of PVP were CO₂, H₂O, NO, and NO₂. This phenomenon was also confirmed by a very sharp endothermic peak observed at 442 °C in the DTG curve (**Fig. S1c**). Herein, the

TG behavior of GeO₂/PVP (**Fig. S1b**) was similar to that of PVP. According to the observed thermal behavior of GeO₂/PVP, the annealing temperature for the decomposition of GeO₂ in the PVP matrix to prepare GeO₂/N-C was fixed to 500 °C. At a higher temperature, the particle size of GeO₂ could become larger due to the agglomeration of GeO₂ at an elevated temperature.

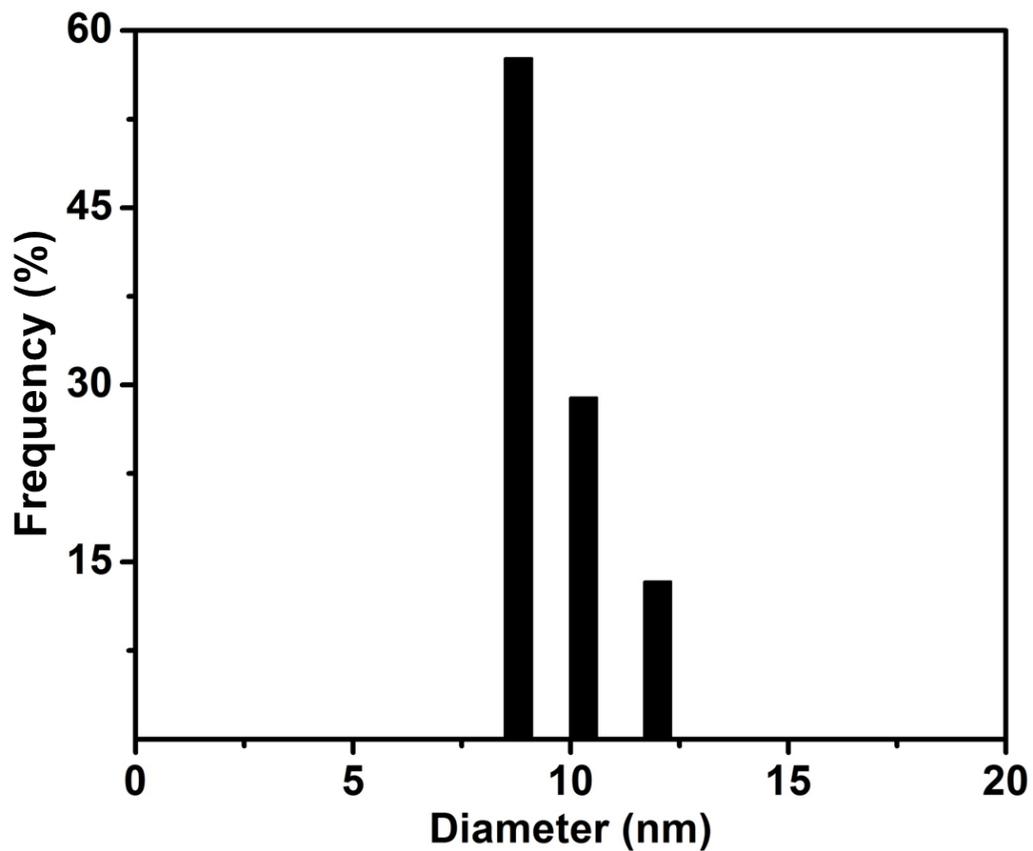


Fig. S2 Particle size distribution of GeO₂, prepared by sol-gel method, obtained from the DLS measurement.

The dynamic light scattering (DLS) measurement of the transparent colloidal dispersion exhibited a narrow size distribution of GeO₂ synthesized using the sol-gel method. As observed in **Fig. S2**, the particle size of GeO₂ was uniform with a diameter ranging from 8 to 12 nm, and the average diameter obtained from the DLS method was 10 ± 2 nm.

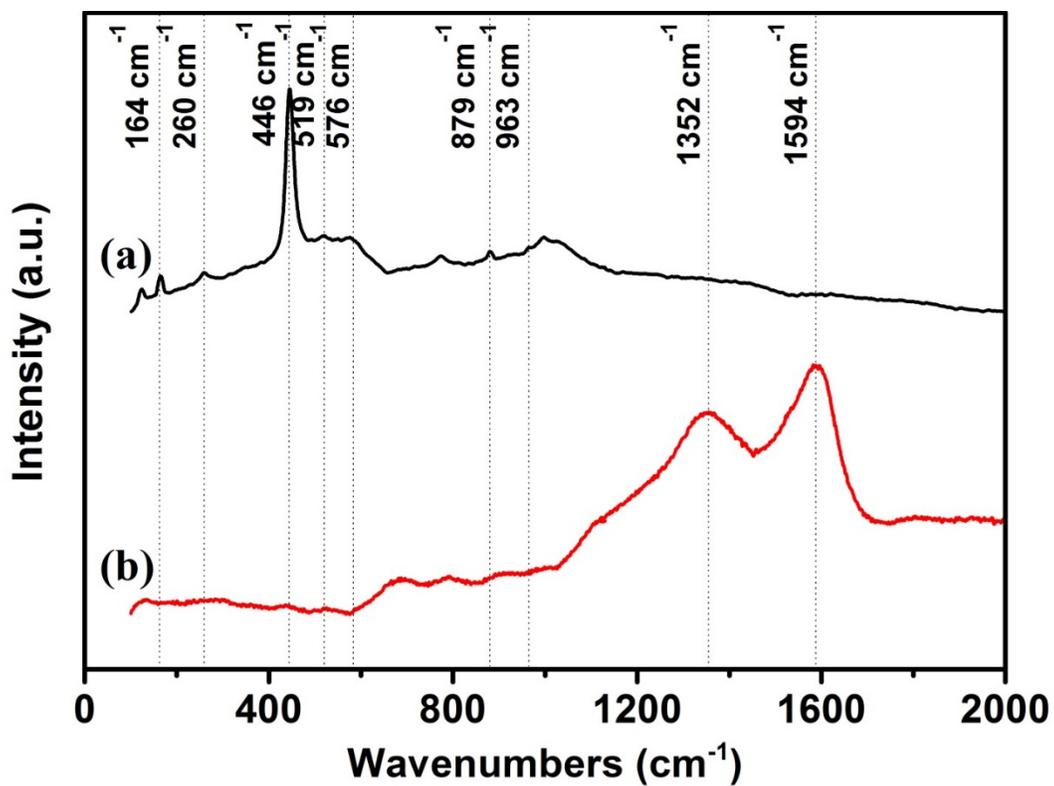


Fig. S3 Raman spectra of (a) GeO₂ and (b) GeO₂/N-C.

As shown in **Fig. S3a** (Raman shift of GeO₂), all peaks matched well with the vibration of GeO₂. The bands observed at 879 and 963 cm⁻¹ corresponded to the Ge-O stretching, while the peaks observed at 519 and 576 cm⁻¹ were attributed to the stretching of Ge-Ge. The band observed at 446 cm⁻¹ corresponded to the symmetric Ge-O-Ge stretching, and the two bands observed at 164 and 260 cm⁻¹ were related to the rotation of the GeO₄ tetrahedra.³

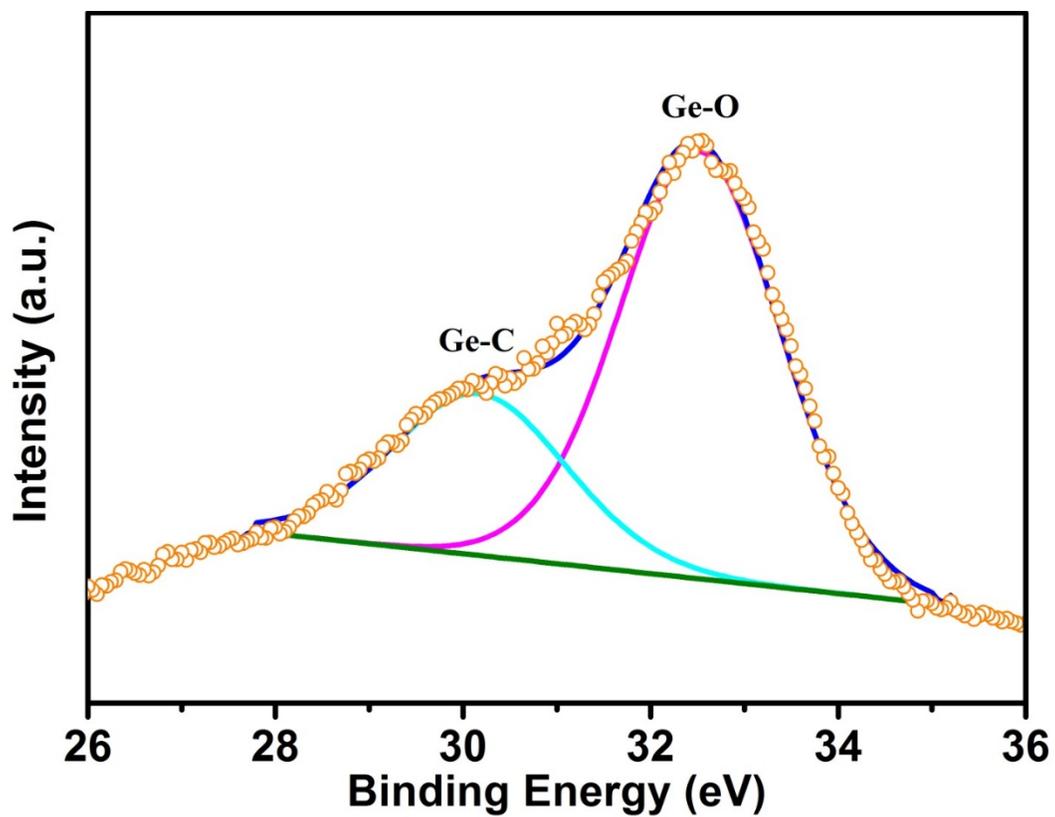


Fig. S4 High-resolution XPS core spectrum of Ge for the 3d level of GeO₂/N-C.

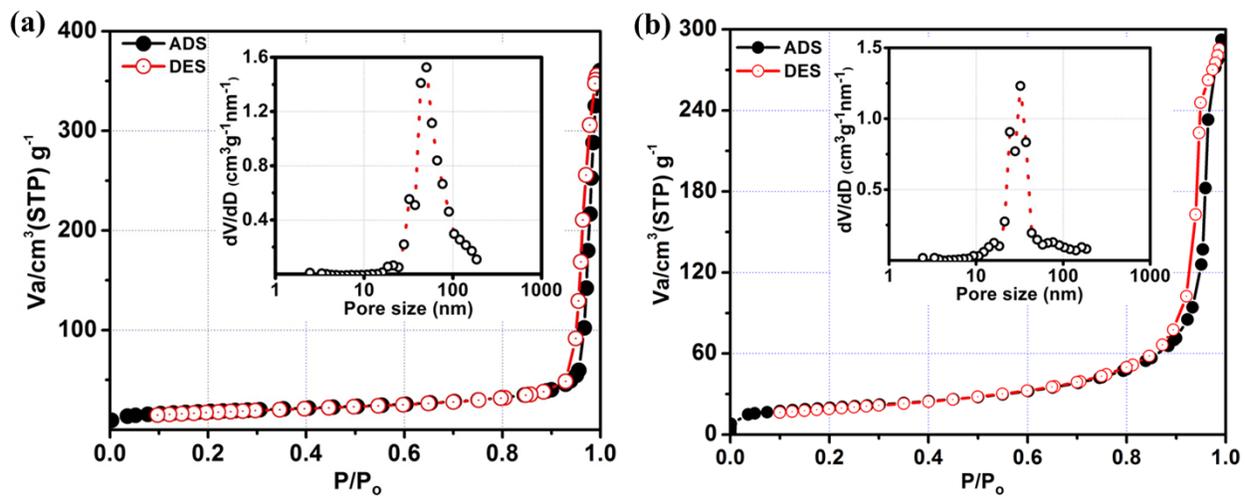


Fig. S5 N_2 adsorption/desorption isotherms of the samples (a) GeO_2 and (b) $GeO_2/N-C$. The inset figures show pore size distribution calculated using the Barrett-Joyner-Halenda (BJH) formula.

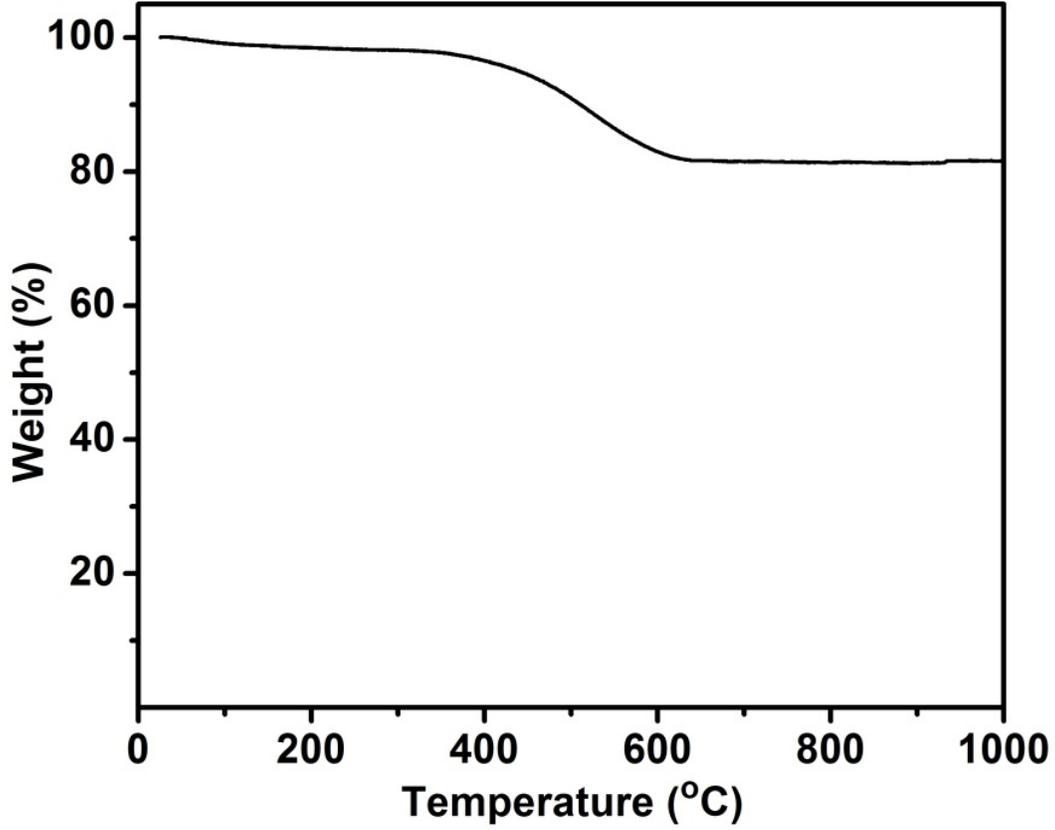


Fig. S6 Thermo-gravimetric analysis of GeO₂/N-C in air at a heating rate of 10 °C min⁻¹.

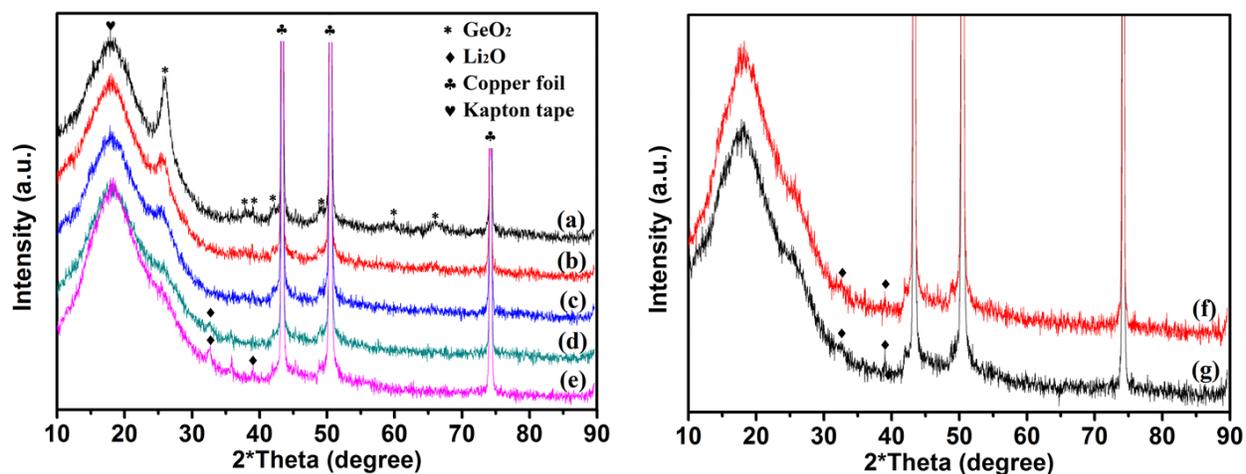


Fig. S7 XRD patterns of GeO₂ electrodes measured at the different states of discharge in the first cycle; (a) as-prepared, (b) discharged to 0.75 V, (c) discharged to 0.50 V, (c) discharged to 0.25 V, and (d) discharged to 0.01V. XRD patters of GeO₂/N-C electrodes tested after 50 cycles; (f) fully discharged and (g) fully charged.

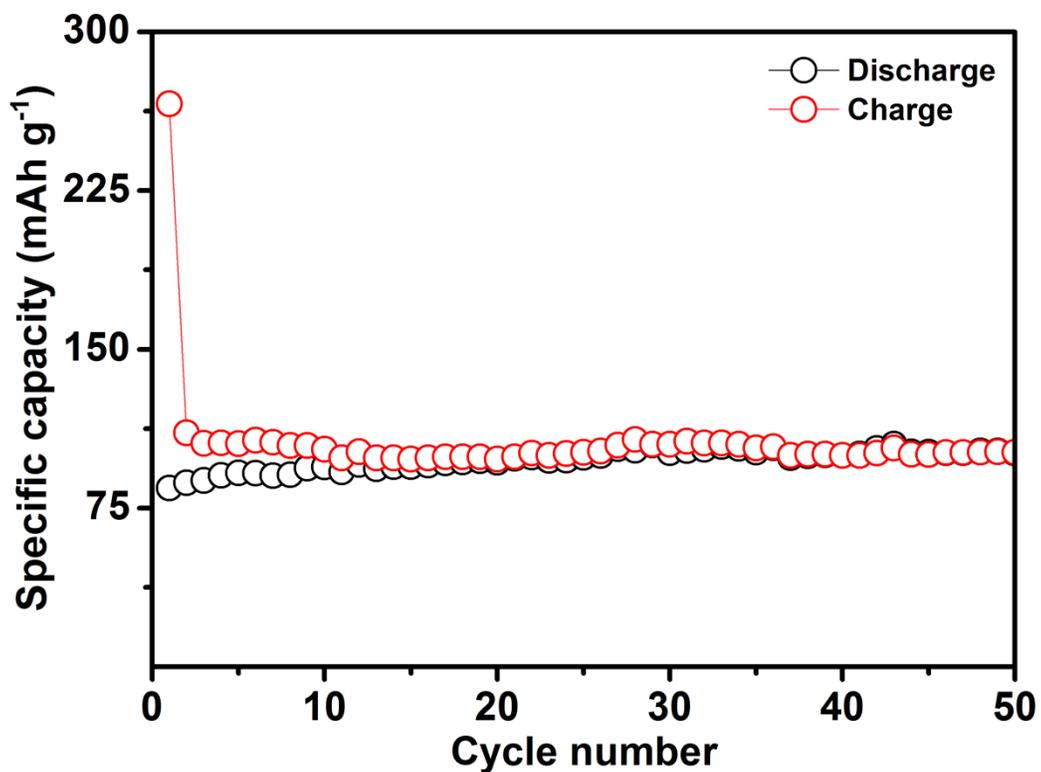


Fig. S8 Cyclability of pyrolysis carbon.

Herein, to investigate the contribution of pure N-carbon derived from PVP (pyrolysis carbon), we prepared pyrolysis carbon through carbonization of PVP at 500 °C for 1 h in argon atmosphere. As shown in **Fig. S8**, the specific capacity of pyrolysis carbon ($\sim 90 \text{ mAh g}^{-1}$) was much smaller than that of GeO_2 based electrodes.

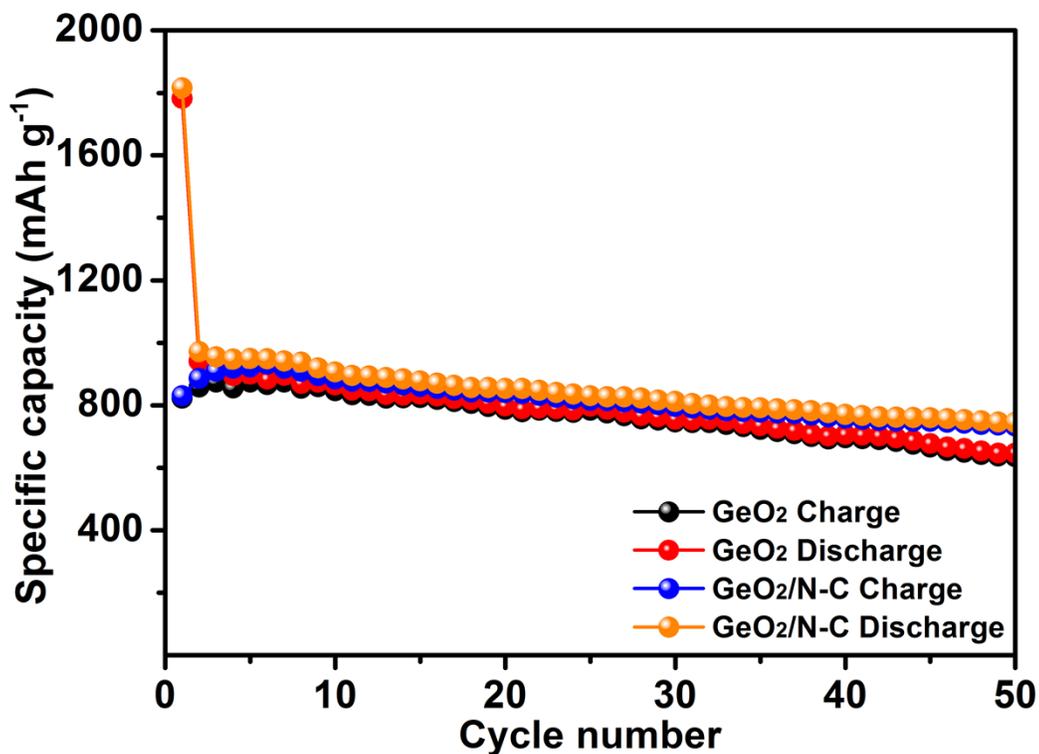


Fig. S9 Cyclability of GeO₂ and GeO₂/N-C electrodes with the high loading mass of 2 mg cm⁻², measured at the rate of C/2.

References

1. M. F. Silva, C. A. da Silva, F. C. Fogo, E. A. G. Pineda and A. A. W. Hechenleitner, *J. Therm. Anal. Calorim.*, 2005, **79**, 367-370.
2. I. Szilágyi, E. Santala, M. Heikkilä, M. Kemell, T. Nikitin, L. Khriachtchev, M. Räsänen, M. Ritala and M. Leskelä, *J. Therm. Anal. Calorim.*, 2011, **105**, 73-81.
3. V. V. Atuchin, T. A. Gavrilova, S. A. Gromilov, V. G. Kostrovsky, L. D. Pokrovsky, I. B. Troitskaia, R. S. Vemuri, G. Carbajal-Franco and C. V. Ramana, *Cryst. Growth Des.*, 2009, **9**, 1829-1832.