Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Germanium-Based High-Performance Dual-Ion Batteries

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Preparation of the Ge/CNFs

In a typical preparation procedure, 0.6 g of polyacrylonitrile (PAN, MW150000, Aldrich) and 1 mL of tetramethoxygermanium solution (Alfa Aesar, 98%) were added in 5 mL of N, N-dimethylformamide (DMF, Aladdin, 99.9%), and stirred at room temperature for 3 h. The mixed solution was then loaded into a plastic syringe, which the distance between the tip of the syringe and Al collector was 15 cm, and the flow rate was adjusted to 0.2 mL min^{-1}. A high voltage of 15 kV was applied during the electrospinning process. The as-spun nanofiber membranes were first dried at 100 °C in vacuum for 12 h, and then annealed using a tube furnace in an Ar and hydrogen gas mixture (95:5 by volume) at 700 °C for 8 h with a ramping rate of 10 °C min^{-1}. CNFs were prepared in the same procedure without adding tetramethoxygermanium solution. Bulk Ge was purchased from Aladdin reagent company (> 200 mesh).

Sample Characterization

The morphologies of the samples were characterized by the scanning electron microscope (SEM, JEOL JSM-7500F) and transmission electron microscopy (TEM, JEM-2200FS). X-ray diffraction (XRD, LabX XRD-6000) characterization was performed using Cu Kα radiation from 10° to 80° at a scan rate of 2° min^{-1}. The surface chemistry of the samples was examined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi). Raman spectrum was recorded by a LabRAM HR800 with a 532 nm laser excitation line. Thermogravimetric (TGA, METTLER TOLEDO) analysis was conducted from room temperature to 1000 °C at a heating rate of 10 °C min^{-1} in air atmosphere.

Electrochemical measurements

All the battery performance tests were performed in CR 2032 coin-type cells. For the half-cell tests, a lithium foil was employed as the counter electrode. The electrolyte was 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:2 v/v). Glass fabric (Whatman) was employed as the separator. The Ge/CNFs and CNFs films were cut into round shape and used as the working electrode without any binders or conductive additives; the graphite and bulk Ge electrodes were prepared by mixing active materials, carbon black and PVDF in a mass ratio of 8:1:1 and grinding with several drops of NMP solvent to form a slurry. The slurry was then coated onto Al foil and Cu foil, respectively, and dried at 60 °C for 12 h in vacuum. For full cells, the active mass of anode and cathode were around 0.6 g and 4.5 mg cm^{-2}, with the mass ratio set to be 1:12. The capacities of cells were calculated based on the mass of Ge in the anode. The cells were all assembled in an argon-filled glove box. Galvanostatic charge/discharge tests were performed using the Land CT 2001A system. Cyclic voltammograms (CV) measures and electrochemical impedance spectroscopy (EIS) were tested on the electrochemical workstation (Solartron 1470E). The EIS data were recorded in the frequency range of 100 kHz to 0.1 Hz, and fitted with ZView software.

Calculation of the lithium-ion diffusion coefficients within electrodes

The lithium-ion diffusion coefficients (D_{Li^+}) within electrodes can be calculated using the following eq 1: [1]

$$D = R^2T^2/(2A^2n^4F^4C^2\sigma^2) \qquad (1)$$

where R is the gas constant, T is the absolute temperature, A is the surface area of the electrodes (0.6 cm^2 for CNFs, 0.5 cm^2 for the Ge/CNFs and 1.54 cm^2 for bulk Ge), n is the number of electrons per reaction species (4.4 for the Ge/CNFs and bulk Ge, and 1 for CNFs), F is Faraday constant, C is the concentration of Li$^+$ ions in the electrode (1 M), and σ is Warburg factor obtained by linear fitting of the straight sloping lines at low frequencies using the eq 2 and the results were shown in Figure S6:[2]

$$Zreal = Re + Rct + \sigma\omega^{-1/2} \qquad (2)$$

the lithium-ion diffusion coefficients (D_{Li^+}) within the Ge/CNFs, CNFs and bulk Ge were calculated to be 5.1 × 10^{-12}, 2.7 × 10^{-10} and 2.4 × 10^{-14} cm^2 s^{-1}, as shown in Figure 2i.

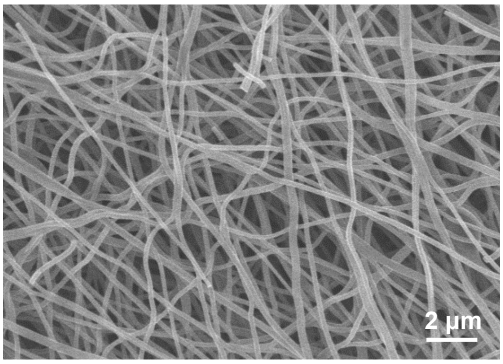

Fig. S1 SEM image of the CNFs.

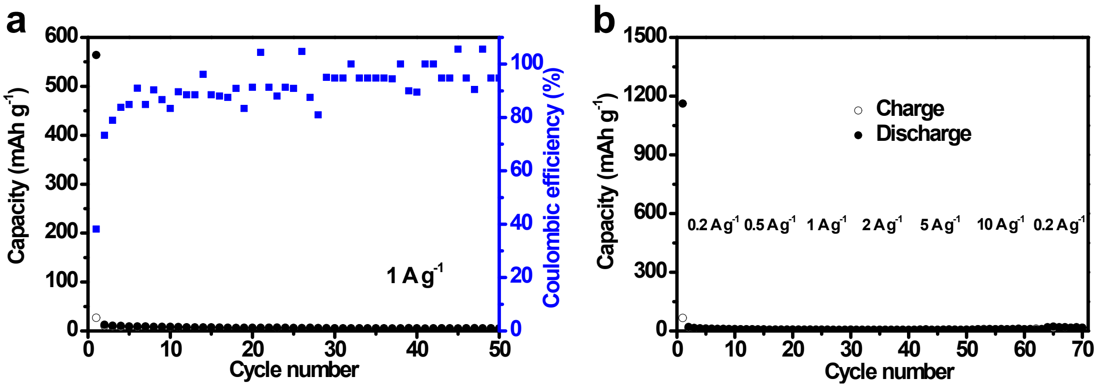

Fig. S2 (a) Cycling stability of the bare Ge at 1 A g^{-1}. (b) Rate capability of the bare Ge at various current densities.

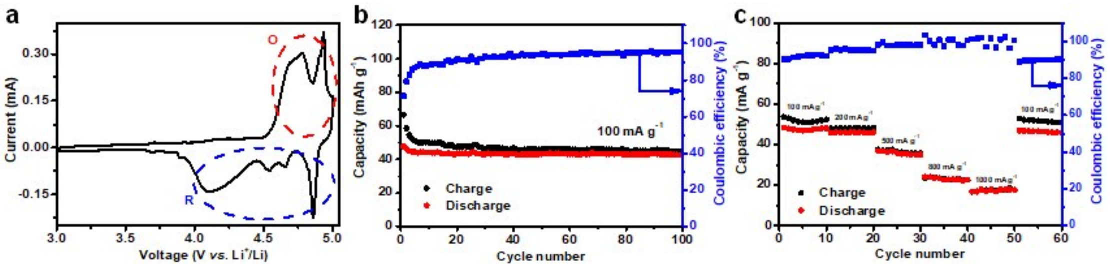

Fig. S3 (a) CV curve of the graphite cathode at a scan rate of 0.2 mV s^{-1} in the voltage window of 3-5 V. (b) Cycling stability at the current density of 100 mA g^{-1}. (c) Rate performance of the graphite cathode.

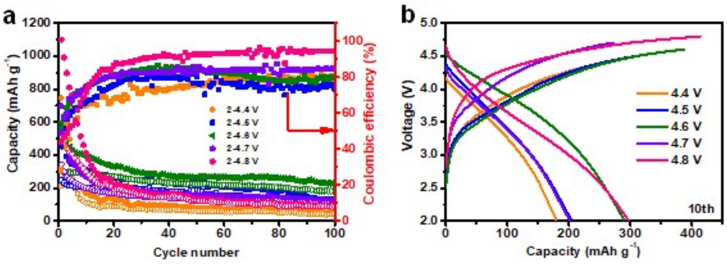

Fig. S4 (a) Cycling performance of the Ge/CNFs-G DIB with various upper cut-off voltages from 4.4 to 4.8 V at the discharge current density of 250 mA g^{-1}. (b) Corresponding charge/discharge profiles at various upper cut-off voltages.

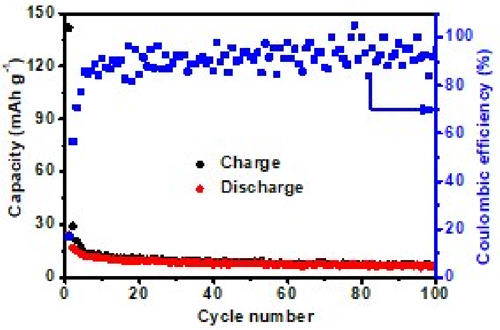

Fig. S5 Cycling stability of the CNFs-G DIB at the discharge current density of 250 mA g^{-1}.

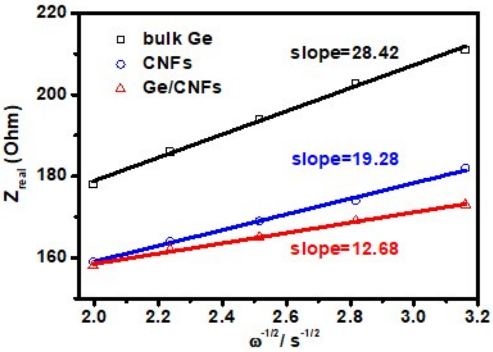

Fig. S6 Relationship between Z_{real} and $\omega^{-1/2}$ at low frequencies.

References

(1) Z. Li, Y. Wang, X. Bie, K. Zhu, C. Wang, G. Chen and Y. Wei, *J. Electrochem. Commun.,* 2011, **13**, 1016-1019.

(2) Y. Lin, Y. Yang, R. Yu, H. Lai and Z. Huang, *J. Power Sources*, 2014, **259**, 188-194.