Supporting Information

Three-dimensional porous structured germanium anode materials for High-Performance Lithium-Ion Full-cell

Yan Zhang[1], Naigen Zhou[2], Xiang Liu[2], Xinhua Gao[3], Shan Fang[2]*

[1]Engineering Research Center of Nuclear Technology Application, Ministry of Education, East China University of Technology, Nanchang, 330013, China

[2]School of Physics and Materials, Nanchang University, Nanchang, 330031, China

[3]State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering, Yinchuan, 750014, China

Corresponding Author: fangshan@ncu.edu.cn

Experimental section

Material synthesis

Synthesis of 3D Ge/C: Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), PEO-PPO-PEO (F127) was introduced as a structure direct agent, resol (phenol formaldehyde resin) as a carbon precursor which was synthesized according to a literature,[1] and germanium dioxide (GeO_2) as a germanium source. 3.0 g resol was dissolved in 15.0 g anhydrous ethanol, then add 1.0 g Pluronic F127 into this solution and stirred until it completes dissolved. 1.0 g GeO_2 dissolved in ethylenediamine (EDA) aqueous (5.2 g H2O+5.0 g EDA), after that add this Ge precursor solution into above solution and stirring at

50 °C for 48 h to evaporate the solution and form a homogeneous gel. After that, the sticky gel was transferred to an oven to further thermal polymerization phenolic resin at 100 °C for 24 h. The final products were obtained by carbonization the precursor at 750 °C for 5 h with a heating rate of 2 °C min^{-1} in an inert atmosphere. As a comparison, the Ge/C composite was synthesised under the same condition without adding F127.

Material characterization

The crystal structure of the Ge/C and 3D Ge/C nanocomposite was characterized by X-ray diffraction (XRD) (Bruker D8 advance) with Cu Kα radiation. Raman spectrum was performed with 514.5 nm wavelength to check the compositions and the carbon of the product by EA (Vario EL-III). The morphology of the samples was studied by SEM (HITACHI S-4800) and TEM (JEOL JEM-2010). Thermogravimetric analysis was conducted on a TGA instrument (NETZSCH STA 409 PC) under ambient flow, the heating rate is 10 °C min−1. The X-ray photoelectron spectroscopy (XPS) measured by a Perkin–Elmer PHI 550 spectrometer with the X-ray source of Al Ka (1486.6 eV). The surface area of the materials was characterised by an ASAP-2010 surface area analyser.

Electrochemical Test

Electrochemical characterizations were studied by galvanostatic discharge/charge in a 2016 coin-type cell for half-cell. The active materials, carboxymethyl cellulose, polyacrylic acid binder and carbon black were mixed with a mass ratio of 70: 7.5:7.5:15, deionized water was used as a solvent to form homogeneous slurry, and then uniformly coated it on a copper foil. According to the TGA result, the content of Ge in the 3D Ge/C composite is 69%. The active material percentage is 70% during slurry making. Thus, the actual weight percentage of Ge in

electrode is 48.3%. The area mass loading of active material was ~0.7 mg cm^{-2}, ~1.5 mg cm^{-2}, ~2.5 mg cm^{-2} and ~3 mg cm^{-2}. The cells were assembled with 3D Ge/C or Ge/C as working electrode, lithium metal was used as a counter and reference electrode in an Ar-filled glove box. The electrolyte was consist of 1 M $LiPF_6$ solution in a mixture of 1:1 v/v ethylene carbonate (EC) and dimethyl carbonate (DMC) and contained 2% (V) fluoroethylene carbonate (FEC). The electrolyte used in both half-cell is 60 μL. Galvanostatically discharge/charge cycles were measured between 0.01 and 1.5 V by a cell test device of CT2001A (LAND Electronic Co.). The volume capacity of the half-cell is calculated based on the thickness and surface area of the electrode. EIS measurements were performed at a frequency range of 0.01-100 kHz. As NCM cathode electrode, the slurry was consisting of NCM (811), carbon black and PVDF with a mass ration of 92:4:4, NMP was used as solvent. The active material mass loading is ~4 mg cm^{-2}. The prelithiation of the 3D Ge/C anode for the full-cell tests was performed by dis-/charging the half-cell at 0.1A g^{-1} for 10 cycles. Subsequently, the cell was disassembled under argon atmosphere to recover the electrode for the full-cell assembly, combining the prelithiated anode with the NMC811 cathode. The 3D Ge/C||NCM88 full cells were cycled between 2.0 - 4.1 V, after the first two cycle at 0.1 C (1 C = 200 mA g^{-1}), then cycled at 1 C. Galvanostatically discharge/charge cycles of the full cell were measured in a swagelok T-cell between 2.0 and 4.1 V, Li metal was used as reference electrode.

Reference

[1] A. Tejado, C. Pena, J. Labidi, J.M. Echeverria and I. Mondragon, Bioresource Technol, 2007, 98, 1655-1663.

[2] S. Choi, J. Kim, N.-S. Choi, M. G. Kim, S. Park, ACS Nano 2015, 9, 2203.

[3] D. T. Ngo, H. T. T. Le, C. Kim, J. Y. Lee, J. G. Fisher, I. D. Kim, C. J. Park, Energy Environ. Sci. 2015, 8, 3577.

[4] F. W. Yuan, H. Y. Tuan, Chem. Mater. 2014, 26, 2172.

[5] D. T. Ngo, H. T. T. Le, R. S. Kalubarme, J.-Y. Lee, C.-N. Park, C.-J. Park, J. Mater. Chem. A 2015, 3, 21722.

[6] C. Kim, G. Hwang, J. W. Jung, S. H. Cho, J. Y. Cheong, S. Shin, S. Park, I. D. Kim, Adv. Funct. Mater. 2017, 27, 1605975.

[7] Bangrun Wang, Jun Jin, Zhaoyin Wen, Chem Eng J, 2019, 360, 1301-1309.

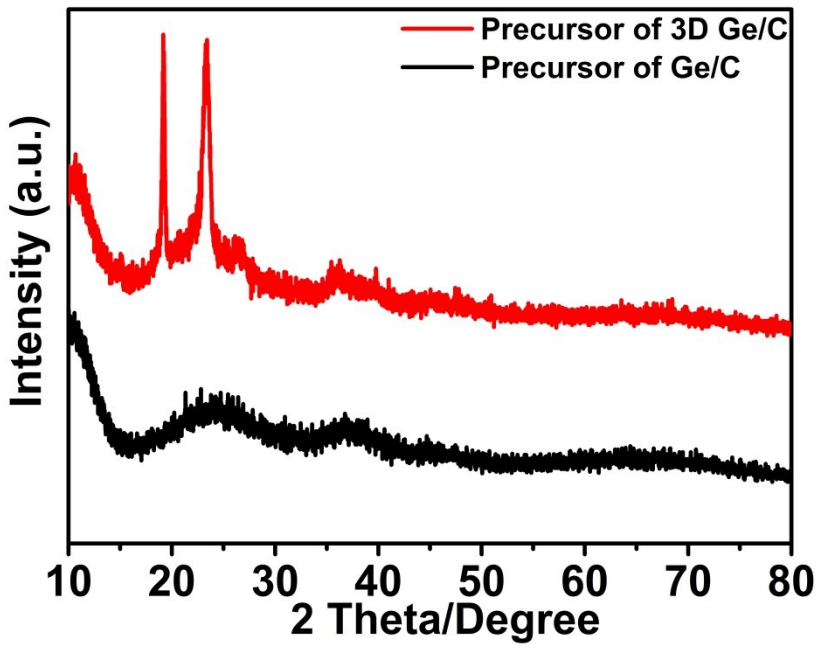

Figure S1. The XRD patterns of the precursor of 3D Ge/C and Ge/C.

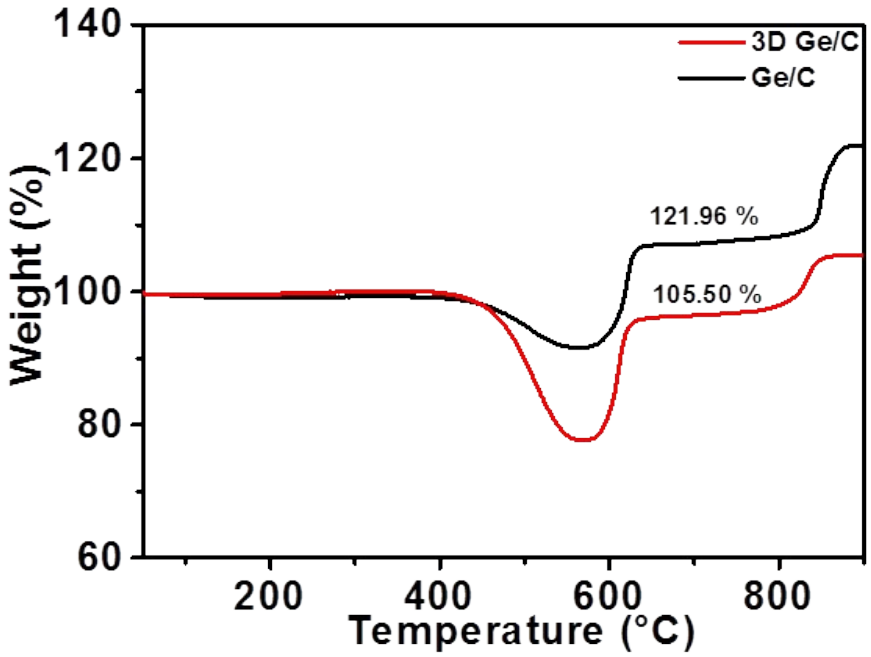

Figure S2. TGA curves of 3D Ge/C and Ge/C.

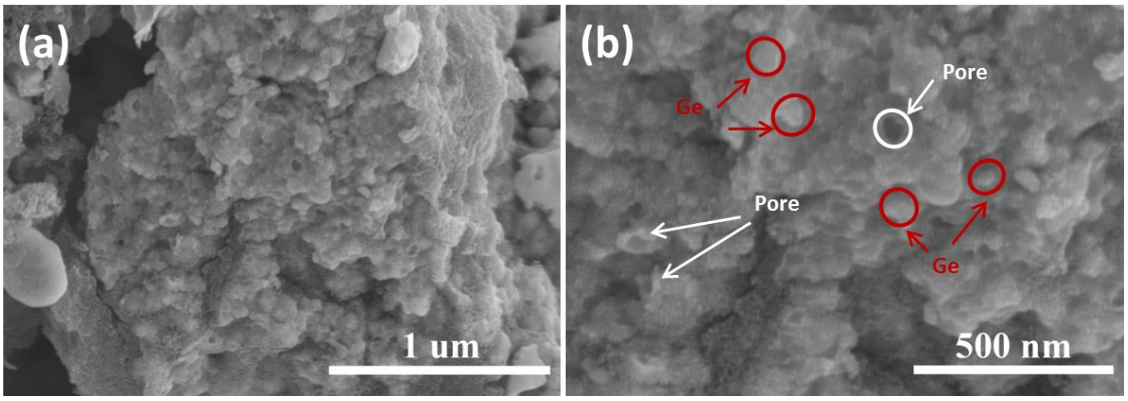

Figure S3 SEM images of Ge/C composite materials.

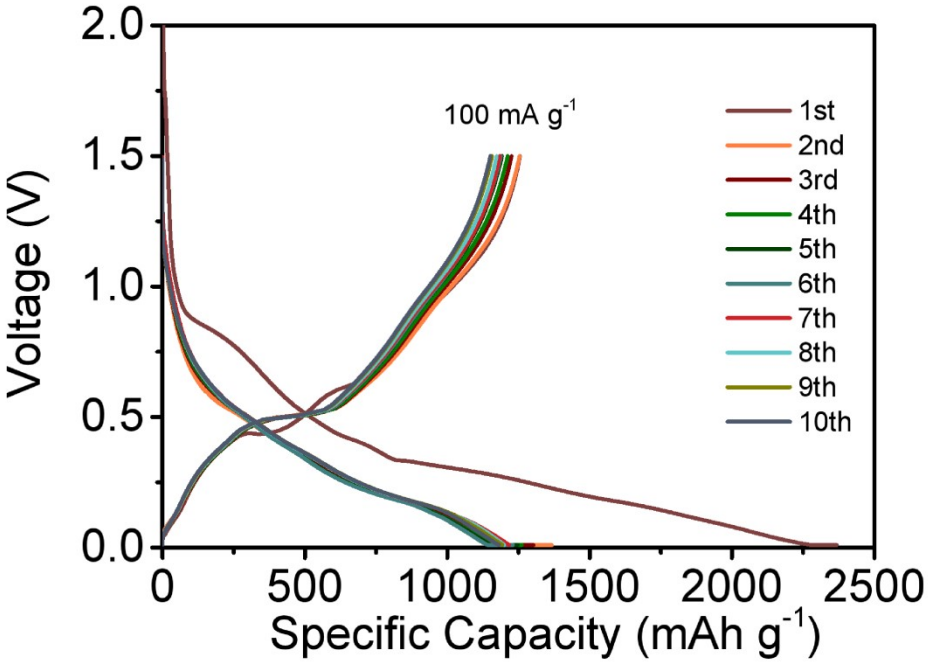

Figure S4. The first ten discharge/charge profiles of 3D Ge/C under the current density of 100 mA g^{-1}.

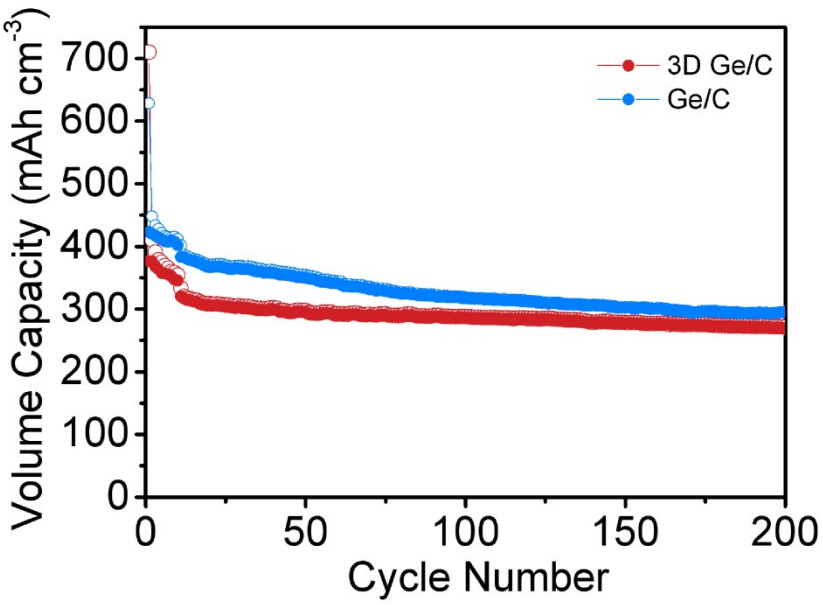

Figure S5. The volume capacity of 3D Ge/C and Ge/C half-cell calculated based on the thickness and surface area of the electrode.

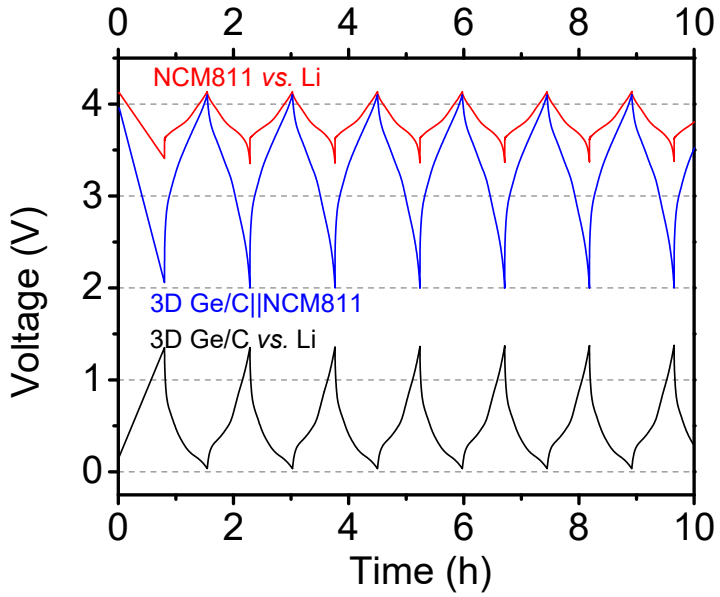

Figure S6. The voltage-time curves of the 3D Ge/C||NCM811 full cell (blue), NCM811 vs. Li (red) and 3D Ge/C vs. Li (black) for first few cycles.

Table S1. Full-cell electrochemical performance comparison with literature.

Anode material	Synthetic method	Initial CE of half-cell	Cathode material	Full-cell capacity retention	Energy density (Wh kg-1)	Ref.
Mesoporous Ge particles	Redox-Transmetalation reaction	89	$LiCoO_2$	80% retention after 100 cycles	N/A	2
3D porous Ge-C	Carbothermal reduction	70.16	$LiCoO_2$	94.7% retention after 50 cycles	N/A	3
GeNPs/graphene	Solution-based	43	$LiCoO_2$	90% retention after 50 cycles	N/A	4
GeO_2/N-C	Sol–gel and calcination	49.6	$LiCoO_2$	70% retention after 100 cycles	N/A	5
Micronized Ge_3N_4@C	Wet oxidation and nitridation	78	$LiCoO_2$	77% retention after 100 cycles	N/A	6
Ge@NC	spray pyrolysis technique	73	$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$	64% retention after 200 cyles	340	7
3D Ge/C	Solution-based	53	$LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$	84% retention after 100, 70% retention after 200 cycles	396	This work