Electronic Supplementary Information

Mesoporous germanium nanoparticles synthesized in molten zinc chloride at low temperature as high-performance anode for lithium ion batteries

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Experimental Section

Materials: Mg (99%, 100-200 mesh powder), ethanol (99.5%), HCl (37%), $ZnCl_2$ powder and Ge powder were purchased from Sinopharm Chemical Reagent Co. Ltd. (China). Commercial $LiCoO_2$ (LCO) materials were purchased from Ningbo Veken Battery Company (China). All the reagents used in the paper are of analytical grade without any further purification.

Synthesis of Materials

Synthesis of Mg_2Ge: Typically, 4.5 g Mg and 3.0 g bulk Ge were mixed and added into a 20 mL stainless autoclave. Subsequently, the autoclave was sealed and maintained at 500 ℃ for 10 h. Then, the autoclave cooled to room temperature naturally to obtain the precursor of Mg_2Ge.

Synthesis of mesoporous Ge nanoparticles: In a typical process, 5.0 g $ZnCl_2$ powder and 1.2g the above obtained Mg_2Ge powder were simply mixed by milling and loaded in a stainless steel autoclave with a volume of 20 mL. And then, the autoclave was sealed immediately and heated in a muffle furnace at 300 ℃ for 10 h with a heating rate of 5 ℃ min^{-1}. After the autoclave cooling down to room temperature naturally, we used 2 mol L^{-1} HCl, deionized water, and anhydrous ethanol to wash the products for several times, respectively. Finally, the products were dried in vacuum oven at 60 ℃ for 12h. As the reaction condition is relatively mild, and the yield of the products is over 85%.

Material characterization

The synthesized samples were investigated via X-ray diffraction (XRD) (Rigaku

D/MAX-2550-PC) with Cu Kα radiation with λ=1.54059 Å and Raman spectrometer (Lab-RAM HR UV/VIS/NIR). The morphology was characterized at 5 kV by field emission scanning electron microscopy (FESEM, Zeiss Ultra55) and transmission electron microscopy (TEM, Hitachi H7650), high resolution transmission electron microscopy (HRTEM, JEM-ARM 200F). The surface composition of the sample was examined by X-ray photoelectron spectroscopy (XPS; ESCA-Lab MKII X-ray photoelectron spectrometer), using Mg Kα X-ray as the excitation source. The nitrogen adsorption and desorption isotherms were measured with a VELSORP-mini II (BEL Japan, Inc.) at 473 K in the relative pressure range of P/P_0 from 0 to 1 to determine the Brunauer-Emmett-Teller (BET) surface areas and pore size distribution.

Electrochemical Measurements

Electrochemical Measurement of mp-Ge NPs: For electrochemical characterization, the active materials, sodium alginate (SA) and acetylene black were mixed with water by a weight ratio of 60: 20: 20. The slurry was pasted onto a copper foil and dried at 80 ℃ for 10 h in a vacuum oven. The mass of the active materials was measured to be 0.8~1.2 mg cm^{-2}. To assemble the half cells, lithium foil was used as the counter electrode and the electrolyte was a solution of 1 M $LiPF_6$ in a mixture of ethylene carbonate/ diethyl carbonate (EC/DEC; 1:1 by Volume). The separator in the coin cell was Celgard 2400. Electrochemical workstation (CHI660D) was applied to test cyclic voltammogram (CV) in a voltage window of 0.005-1.5 V at the scanning rate of 0.1 mV s^{-1}. Galvanostatic charge/discharge measurement was carried out on a battery tester (LANDCT2001A) at various current densities.

Electrochemical Measurement for a Ge-LCO Full Cell: The electrochemical analysis was carried out with a CR2016 coin-type full cell and the potential ranges from 2.50 to 4.20 V. The commercial LCO material, poly(vinyl difluoride) (PVDF) binder, acetylene black in a weight ratio of 8:1:1 were mixed to make the cathode electrode. The N-Methyl-2-pyrrolidone (NMP) was used as the solvent. The obtained slurry was pasted onto the Al foil and dried at 110 ℃ for 10 h. The mass of the active materials was calculated to be 7-8 mg cm^{-2}. The mp-Ge NPs electrodes were prelithiation in half-cell for three cycle before their assembly in full cells. The full cell was assembled in a glovebox filled with argon gas. The separators and electrolytes are the same as that of in half-cell.

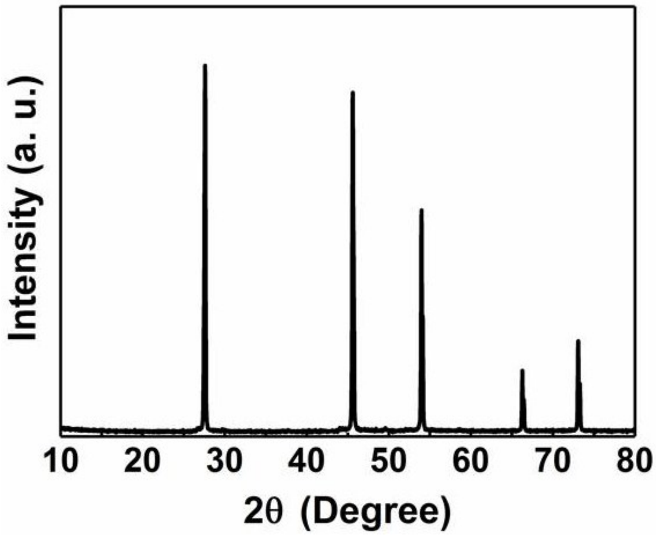

Figure S1 shows the XRD patterns of the precursor commercial Ge, all peaks could be indexed to be the cubic phase Ge (JCPDS No. 03-0486).

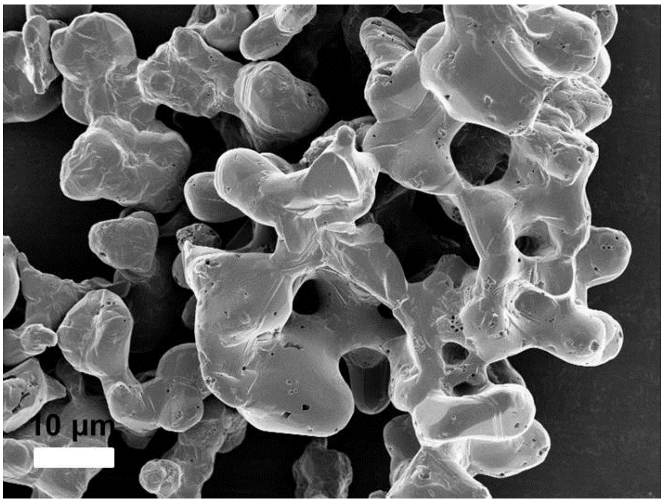

Figure S2. SEM of the commercial Ge.

The origin Ge is commercial available, and the particles size is about few micrometers (shown in Figure S2).

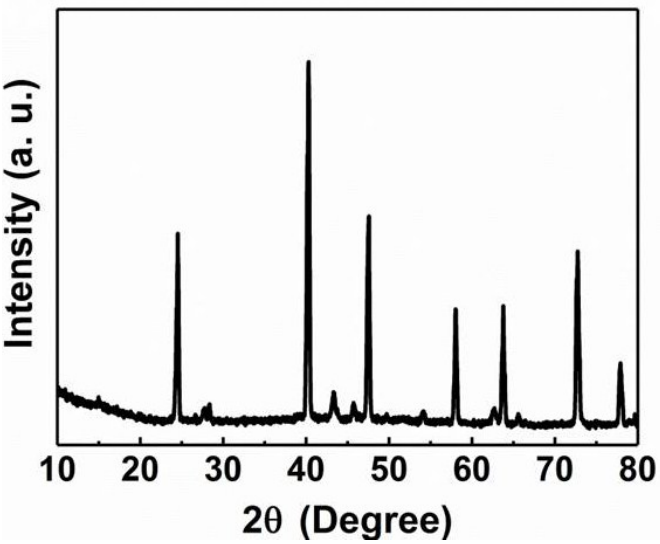

Figure S3 shows the XRD patterns of the pre-synthesized Mg_2Ge, all peaks could be indexed to be the cubic phase Mg_2Ge (JCPDS No. 86-1028).

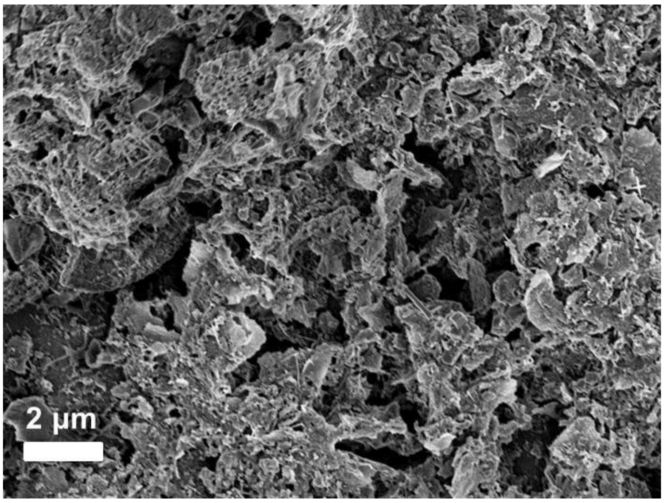

Figure S4. SEM of the intermediate Mg_2Ge.

As shown in Figure S4, the particles size of Mg_2Ge becomes smaller than that of the commercial Ge.

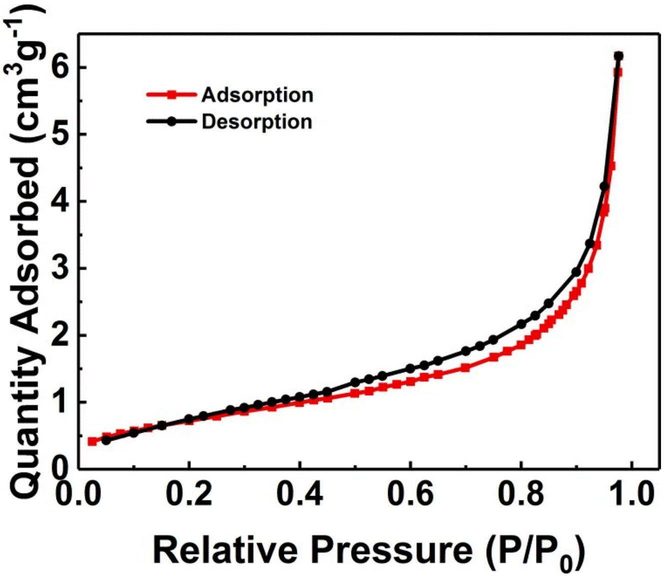

Figure S5. N_2 adsorption-desorption isotherms of commercial Ge.

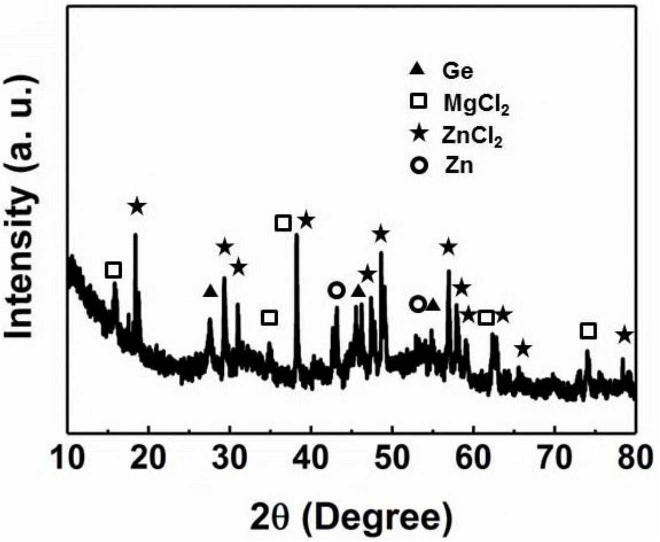

Figure S6. XRD pattern of the sample without any treatment.

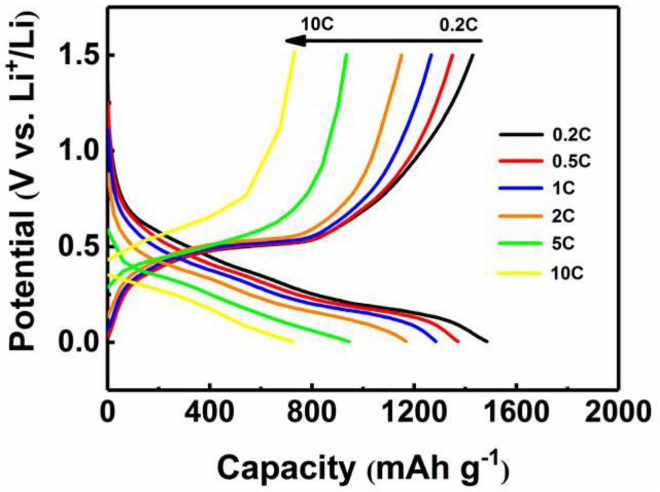

Figure S7. The typical galvanostatic discharge-charge curves of mp-Ge NPs anode at different current densities from 0.2 to 10 C

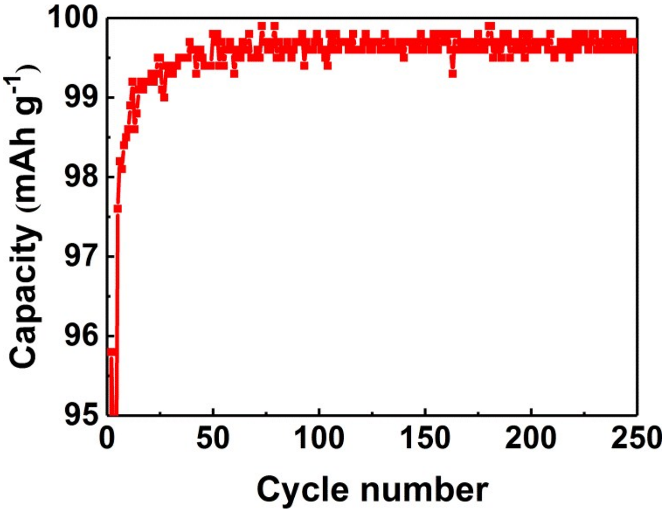

Figure S8. The coulombic efficiency of the mp-Ge NPs electrode at the current density of 0.5C.

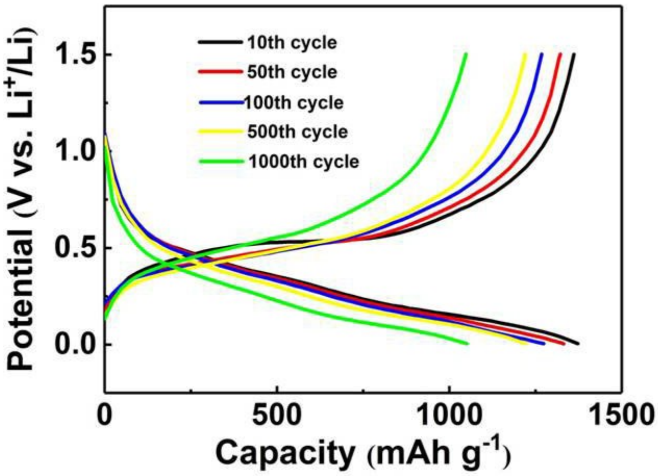

Figure S9. Voltage-Capacity profiles of mesoporous Ge nanoparticles at a current density of 1.0 C.

Table S1. The comparison of electrochemical performance between this work and previous Ge nanomaterials synthesized from other methods.

Sample	**Preparation method**	**Specific capacity after cycling (mA h g^{-1})**	**Current density (mA g^{-1})**	**Charge-discharge cycles demonstrated**	**References**
Ge NWs	Vapor-liquid-sold method	1141	50	20	Nano Lett., 2008, 8, 307-309
mp-Ge	Ball-milling method	789	150	20	Electrochem. Commun., 2010, 12, 418-421
Ge NCs	Gas-phase laser photolysis	800	160	50	J. Phys. Chem. C, 2012, 116, 26190-26196
mp-Ge NPs	Redox-transmetalation reaction	1400	800	300	ACS Nano, 2015, 9, 2203-2212
np-Ge	Chemical dealloying method	1191	160	160	Nano Energy, 2015, 13, 651-657
Ge NPs	Magnesium thermal method	909	3200	250	Dalton Trans.,2016, 45, 2814-2817
mp-Ge NPs	Molten salt method	1048	1600	1000	This work

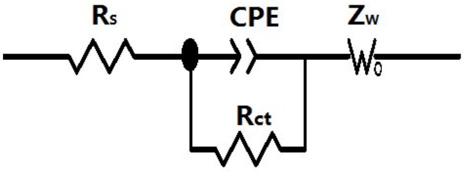

Figure S10. Equivalent circuit used to model the impedance spectra in the fresh state.

Table S2. Simulated kinetic parameter for the cell of the mp-Ge NPs and commercial Ge electrodes in the fresh state.

Electrode	**R_s (Ω)**	**R_{ct} (Ω)**	**CPE (F)[a]**
mp-Ge NPs	1.127	41.7	2.15×10^{-5}
Commercial Ge	2.981	108.9	1.03×10^{-5}

[a]CPE: represent the resistor with constant phase elements.

Table S2 lists the simulated kinetic parameter, where R_s is the ohmic resistance for Li^+ transport in the electrolyte and R_{ct} is the interfacial charge transfer resistance. The resistor with constant phase elements (CPE) in parallel and the Warburg impedance (Z_W) describe the solid state diffusion of Li^+ in the mp-Ge NPs electrode.

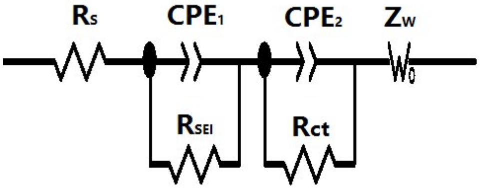

Figure S11. Equivalent circuit used to model the impedance spectra after 20th cycles.

Table S3. Simulated kinetic parameter for the cell of the mp-Ge NPs and commercial Ge electrodes after 20th cycles.

Electrode	**R_s (Ω)**	**R_{SEI} (Ω)**	**R_{ct} (Ω)**	**CPE_1 (F)[a]**	**CPE_2 (F)[a]**
mp-Ge NPs	2.32	57.3	35.36	2.5×10^{-4}	7.32×10^{-4}
Commercial Ge	7.29	72.5	96.1	2.1×10^{-5}	7.33×10^{-4}

[a] CPE_1 and CPE_2: represent the two resistors with constant phase elements.

Table S3 lists the simulated kinetic parameter, where R_s is the ohmic resistance for Li^+ transport in the electrolyte, R_{SEI} is the ohmic resistance in the interface of the SEI layer and R_{ct} is the interfacial charge transfer resistance. The two resistors with constant phase elements (CPE_1 and CPE_2) in parallel and the Warburg impedance (Z_W) describe the solid state diffusion of Li^+ in the mp-Ge NPs electrode.

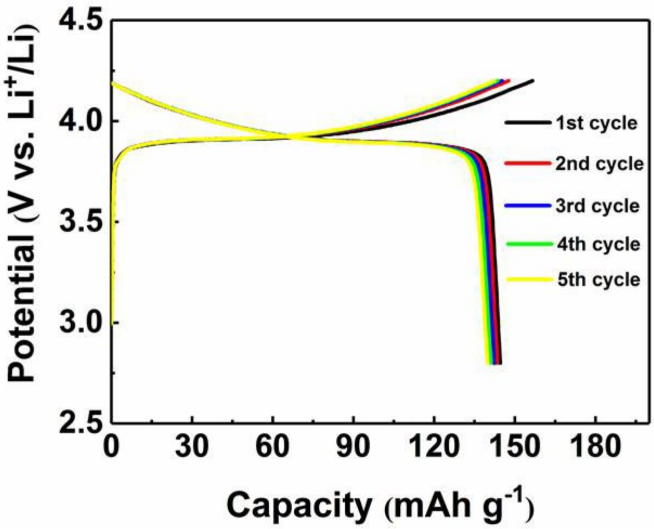

Figure S12. The typical galvanostatic discharge-charge curves of commercial $LiCoO_2$ electrode at current density of 0.2 C (1 C = 140 mA h $g^{-1}{}_{LCO}$).

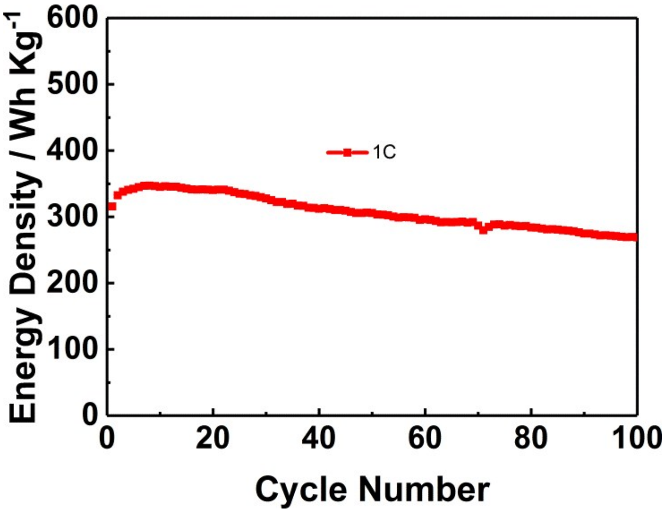

Figure S13. The discharge energy density of Ge-LCO full cell at the current density of 1 C (1 C = 140 mA h g^{-1}_{LCO}).