Supporting Information

Directly Grown Germanium Nanowires from Stainless Steel: High-performing Anodes for Li-Ion Batteries

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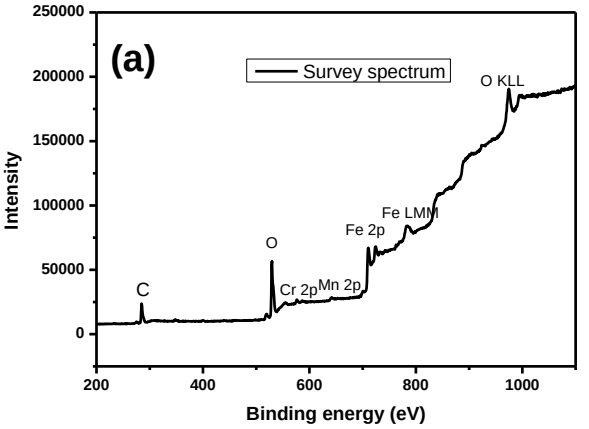
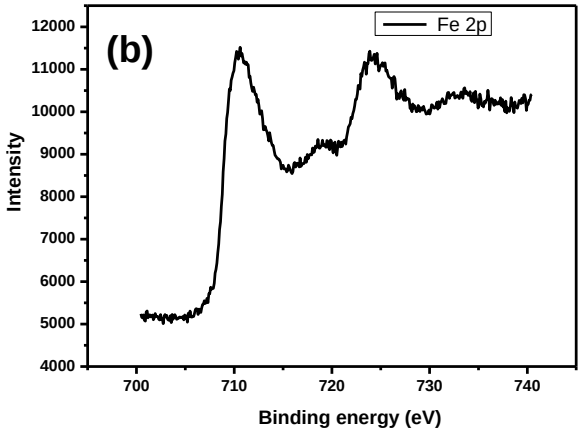
Experimental

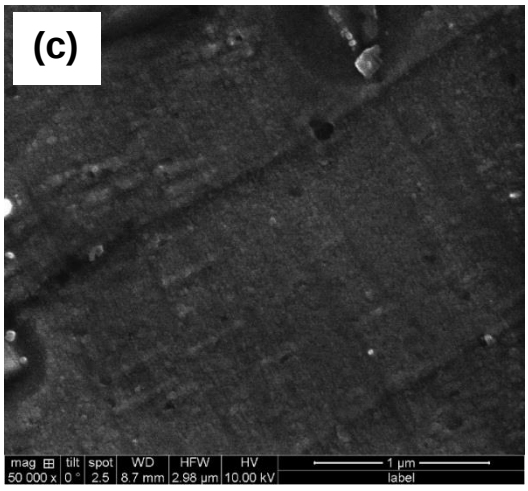
Ge nanowires were grown on stainless-steel current collectors via a continuous flow liquid-injection chemical vapor deposition (LICVD) technique using toluene as the solvent. Initially, grade 316 stainless steel (oxidised and unoxidised) substrates were loaded into a stainless-steel micro reactor cell and dried for 24 hr at 180 °C under vacuum. Oxidised stainless-steel foils were obtained by heating the as received foil in an ambient atmosphere at 450 °C for 2 hr. Solutions of diphenylgermane (DPG), the Ge precursor, in anhydrous toluene were prepared in an N_2 glove box with a typical concentration of 10 μmole ml^{-1}. The DPG solution was loaded into a Hamilton sample-lock syringe inside a nitrogen-filled glovebox. The precursor solution was then injected into the metal reaction cell using a syringe pump at a rate of 0.025 ml min^{-1}. A H_2/Ar flow rate of 0.5 sccm was maintained during the entire growth period, typically 2 hr. The reaction cell cooled to room temperature and disassembled to access the growth substrate. Nanowires were washed with dry toluene and subsequently dried under N_2 flow for further structural and electrochemical characterisation.

Characterization. The one-dimensional Ge nanostructures were imaged using a FEI quanta 650 scanning electron microscope (SEM). High resolution transmission electron microscope (TEM) and scanning transmission electron microscopy (STEM) and high resolution STEM was performed using JEOL 2100 operated at 200 kV, FEI Titan Themis double-corrected and monochromated TEM at 300kV and FEI Titan operating at 300 kV. Raman scattering spectroscopy was performed with a Renishaw InVia Raman spectrometer equipped with a 2400 lines/mm grating using a 514 nm laser. Spectra were collected using a RenCam CCD camera, with the beam focused onto the samples using either a 50 × objective lens. The crystal structure of the product was confirmed by X-ray diffraction (XRD) using a Philips X'pert Pro MPD equipped with a Panalytical Empyrean Cu X-ray tube and a Philips X'celerator detector.

The electrochemical properties of Ge nanowire anodes assembled as half-cells with a pure Li anode in a coin cell configuration and carried out using a BioLogic VSP Potentiostat/Galvanostat. The electrolyte was a 1 mol dm^{-3} solution of $LiPF_6$ in a 1:1 (v/v) mixture of ethylene carbonate in dimethyl carbonate with 3 wt% vinylene carbonate; 200 µL of electrolyte was used in each cell. The separator used was a glass fibre separator (El-Cell ECC1-01-0012-A/L, 18 mm diameter, 0.65 mm thickness). The mass loading for anode samples was ~ 0.3 mg and no additional conductive additives or binders were added. A Mettler Toledo XP2U ultra microbalance was used to determine the mass of Ge nanowires on the stainless-steel substrates. The size of the stainless steel substrates was 0.5 × 1.0 cm, therefore the areal mass loading of the Ge nanowires on the stainless steel current collectors was ~ 0.6 mg/cm^2. Cyclic voltammetry was performed at a scan rate of 0.1 mV/s in a potential window of 1.5 – 0.01 V (vs Li/Li^+). Galvanostatic cycling was performed at 0.2 C in a potential window of 1.5 – 0.01 V (vs Li/Li^+).


(a)
Survey spectrum
O KLL
Fe LMM
Fe 2p
O
C
Cr 2p
Mn 2p
Intensity
Binding energy (eV)


(b)
Fe 2p
Intensity
Binding energy (eV)


(c)
mag tilt spot WD HFW HV
50 000 x 0 ° 2.5 8.7 mm 2.98 µm 10.00 kV
1 µm
label

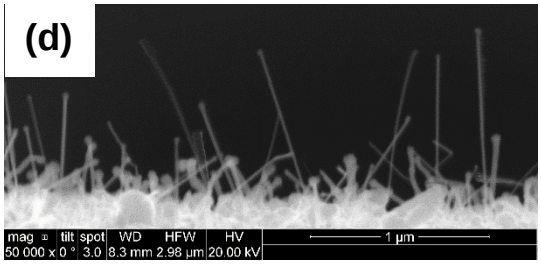

(d)
mag tilt spot WD HFW HV
50 000 x 0 ° 3.0 8.3 mm 2.98 µm 20.00 kV
1 µm

Figure S1. (a) XPS survey spectrum of oxidised stainless steel showing predominant iron oxide on the surface. (b) High resolution XPS spectrum of Fe 2p shows satellite peak at 720 eV which indicate Fe exist as Fe^{3+} . (c) SEM image of oxides stainless steel showing rough granular surface of the substrate. (d) Side-view SEM image of the Ge nanowires grown on stainless steel.

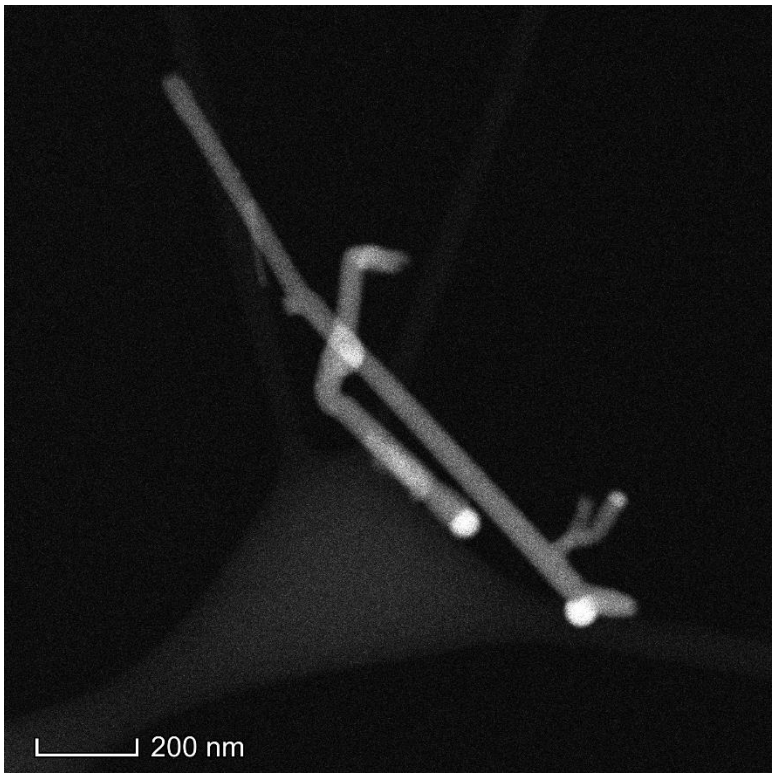
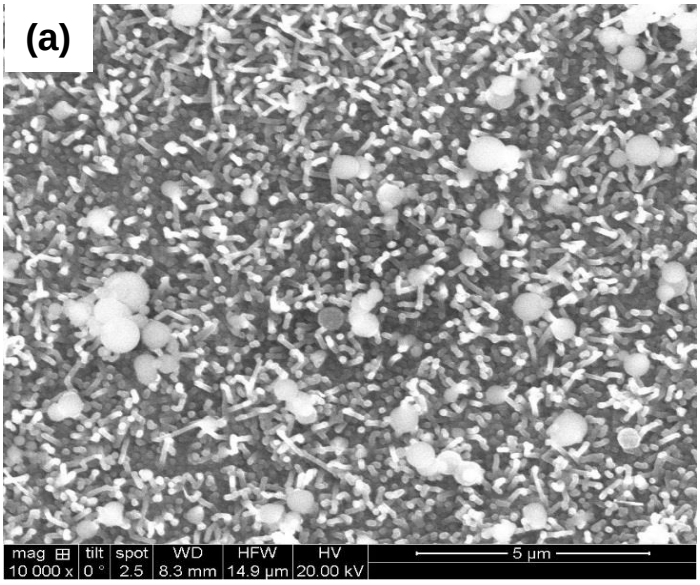
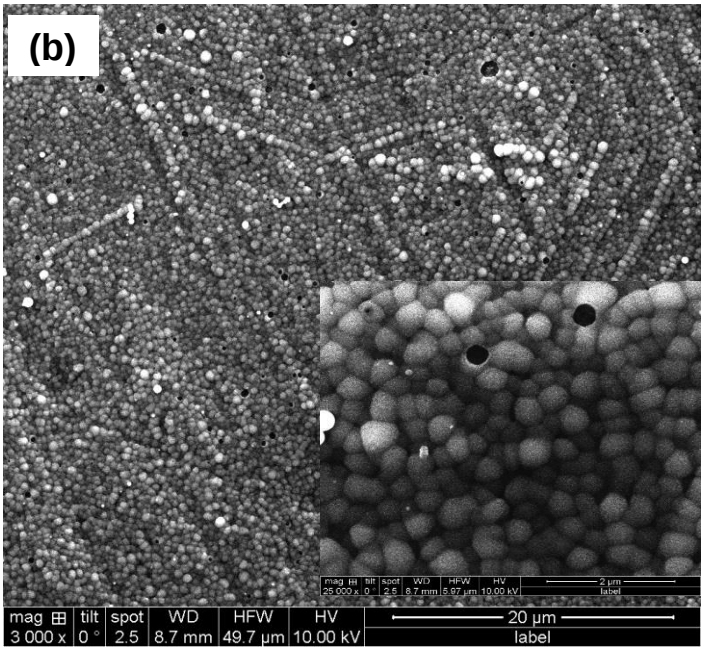


Figure S2. Dark field STEM image of nanowires with catalytic nanoparticles at the tip.


(a)
mag
10 000 x
tilt
0 °
spot
2.5
WD
8.3 mm
HFW
14.9 µm
HV
20.00 kV
5 µm


(b)
mag
3 000 x
tilt
0 °
spot
2.5
WD
8.7 mm
HFW
49.7 µm
HV
10.00 kV
20 µm
label

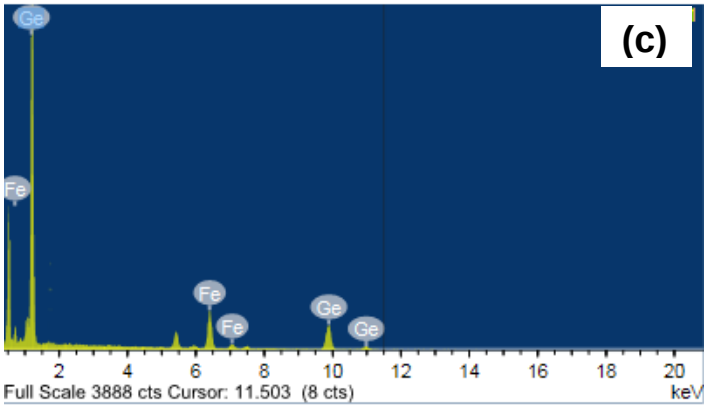

(c)
Ge
Fe
Fe
Fe
Ge
Ge
2
4
6
8
10
12
14
16
18
20
Full Scale 3888 cts Cursor: 11.503 (8 cts)
keV

Figure S3. SEM images of Ge nanowires grown after 20 min growth time shows (a) very short nanowire with catalytic tip and (b) rough growth surface underneath with particulate formation (shown in the inset). (c) EDX spectra from the substrate with particulate showing the presence of iron and germanium.

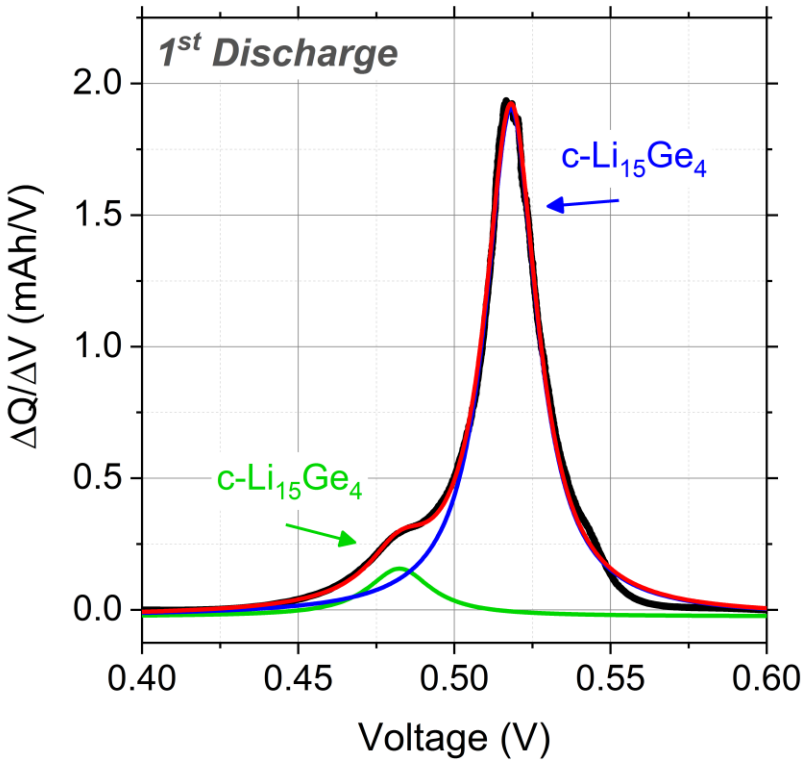


Figure S4. Deconvoluted delithiation peak in the differential capacity plot calculated from the 1st discharge curve for a Ge nanowire sample cycled in a potential window from 1.5 – 0.01 V (vs Li/Li^+) at 0.2 C.

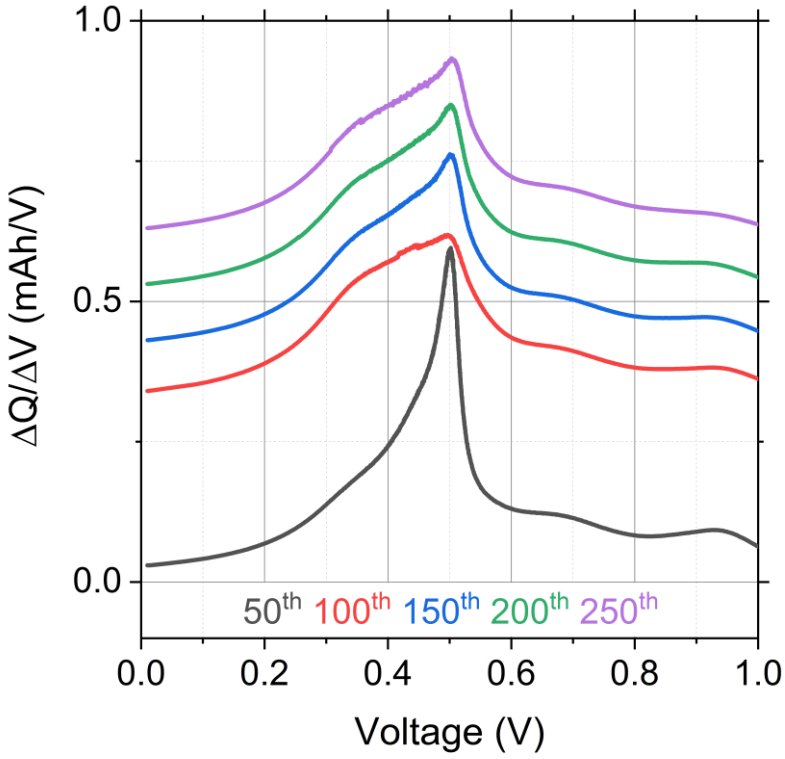


Figure S5. Differential capacity plots calculated from the 50th, 100th, 150th, 200th and 250th discharge curves for a Ge nanowire sample cycled in a potential window from 1.5 – 0.01 V (vs Li/Li^{+}) at 0.2 C.

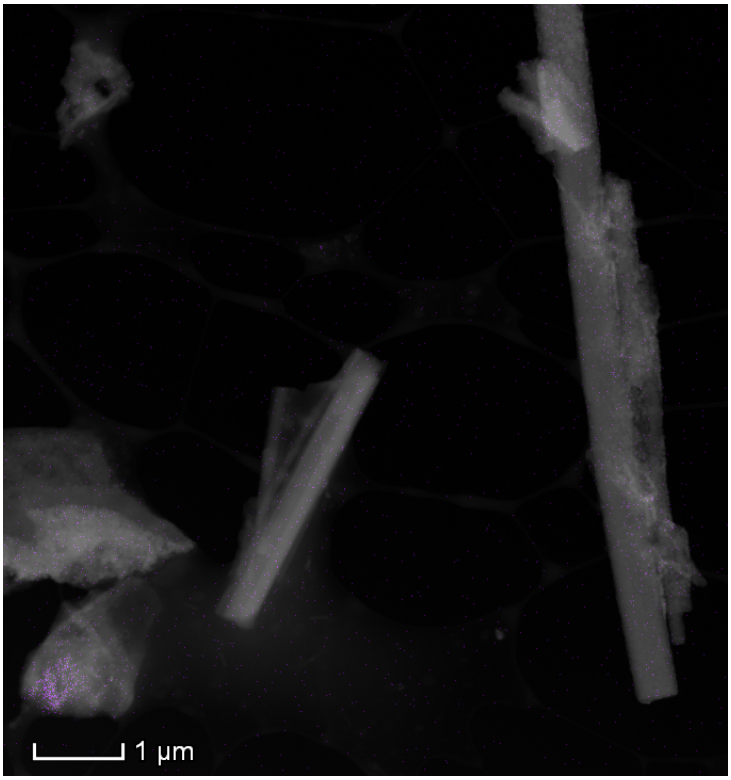


Figure S6. Dark-field STEM image of the Ge nanowires after 250 cycles. Sample was transferred to a TEM grid for the imaging.