

Electronic supplementary information

Cycle-dependent morphology and surface potential of germanium nanowire anode electrodes

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Experimental details

Fabrication of Germanium nanowires (GeNWs)

Substrate preparation and post synthetic treatment

Circular stainless-steel (SS316, Pi-Kem Ltd.) discs (0.64 cm²) of known mass and thickness (0.1 mm) were used as conductive substrates for direct growth of Ge NWs. Sn was chosen as a suitable catalyst due to its ease of eutectic formation with Ge at high temperatures (> 231 °C). Prior to Sn deposition, the stainless-steel substrates were sanded with P600 grit sandpaper to improve film adhesion. Residual particles were washed away with acetone. To prepare Sn-coated stainless-steel substrates, a 20 nm Sn film (99.99% Sn, Kurt J Lesker Company) was thermally deposited onto stainless-steel using an ultra-high vacuum thermal evaporation unit. The substrates were stored in an Ar-filled glovebox and contact with O₂ was minimized. After synthesis, the substrates were rinsed with toluene, to remove excess solvent, and dried using nitrogen. No additional cleaning steps were required.

Reaction setup

Reactions were carried out in custom made Pyrex, 100 mL round bottomed flasks (RBFs). The growth substrates were positioned vertically within the neck of the RBF using custom-made stainless-steel holders, and the flask was attached to a Schlenk line setup via a water condenser. The condenser was sealed at the top with a septum cap. Squalane (7 mL, 96 % Sigma Aldrich) was used as a suitable high boiling point solvent. The system was placed under vacuum (40 mTorr) at room temperature for 30 min before being slowly ramped to 125 °C using a three-zone furnace. The RBF was held under vacuum at 125 °C for 1 hr to remove all moisture. The system was then flushed with Ar gas before being ramped to the desired reaction temperature of 430 °C. Water flow through the condenser cooled the boiling squalane mixture, establishing reflux conditions. Diphenylgermane (0.1 mL, 97 % Gelest Inc.) was injected through a septum cap into the system. The reaction proceeded for 15 min, after which the reaction was cooled to room temperature under constant Ar flow.

Electrochemical Testing and Post-Mortem Treatment

GeNW anodes were tested in half cells (HCs) vs Li metal using a BioLogic MPG-2 multichannel potentiostat. Electrodes were cycled in a two-electrode Swagelok configuration, over a potential range of 0.01-1.50 V vs Li/Li⁺, using a porous polypropylene Celgard 2325 separator and a battery-grade 1 M LiPF₆ in EC-DEC (1:1 v/v, Sigma Aldrich) electrolyte + 3 wt.% vinylene carbonate. Cells were charged/discharged symmetrically at a 1C rate (i.e., 1 hour to fully discharge the anode). For GeNW anodes with surface area of 0.64 cm² and areal loadings of 0.3 mg cm⁻², the applied current needed to achieve a 1C rate was calculated to be 266 μA (taking the gravimetric capacity of Ge to be 1384 mAh g⁻¹). To ensure fair comparison, GeNW anodes of comparable areal loading (Δ Loading = +/- 0.01 mg cm⁻²) were used throughout electrochemical testing.

In this work, the effects of SEI and state-of-charge (SOC) on the morphology of cycled GeNW anodes were investigated. Cycled electrodes were prepared with and without the SEI layer intact for both charged and discharged states after 50 and 1500 cycles. To achieve stable SOC extremes (i.e., fully charged or fully discharged), cells were fully charged/discharged slowly under low current density (10C = 138.4 mA g⁻¹) and then held at open-circuit voltage overnight before disassembling the cell. To remove the SEI, electrodes were soaked in acetonitrile overnight first washing away residual electrolyte, before being sequentially washed in acetic acid (0.1 mM), water, and ethanol and left to dry in inert conditions.

Analysis

AFM measurements

A commercial AFM system (MFP-3D, Asylum Research, USA) was used in this study. Pt/Ir-coated conductive probes (PPP-EFM Nanosensors, with nominal tip radius <15 nm, resonant frequency of 75 Hz, and a spring constant of 2 N/m) were used for both topography and KPFM measurements. KPFM scanning was operated in dual pass mode in air, in which the topography of the surface is obtained in the first pass in amplitude modulation mode, while in the second pass the tip is lifted to a defined height (50 nm) and an AC voltage $V_{ac} \sim 3$ V is applied to the tip at the cantilever's resonance frequency, generating an electrostatic force between the tip and the sample. CPD of the surface is obtained by monitoring the DC offset (V_{dc}) applied to nullify the first harmonic in phase electrostatic force between the tip and the sample. A scan of freshly cleaved HOPG surface is performed to calibrate the AFM probe work function before all sample measurements. The process is repeated after scanning the sample under investigation to observe any change in the CPD of HOPG before and after the sample scan, ensuring the work function of the probe does not change significantly over time due to, e.g., contamination or wear. The typical work function of the probes used was 4.9 eV and the work function of HOPG was 4.6 eV. AFM probes were cleaned using a UV ozone chamber and cleaned for 1 hour.

Each scan area was adjusted according to the features that needed to be measured. Each topography and KPFM map consisted of 256 pixels × 256 pixels. The mean value and the standard deviation of the Gaussian distribution of entire images or of selected 2 μm × 2 μm areas within images were taken as the measured CPD and uncertainty, respectively. For a given sample, 3 different areas were scanned and the measured CPD values agreed within 4%, indicating the consistency and robustness of the measurements.

Work function calculations

Work function values for the materials tested are calculated using the measured CPD value and the tip work function (obtained from scanning the reference sample immediately beforehand) and shown in Table 1. The work function of the pristine GeNWs is close to the literature value for standard Ge, which is 5.0 eV.¹ As the sample is cycled, the work function of the material decreases, due to the SEI layer formation and other organic impurities. The work function of the charged samples with SEI layer present is stable over longer cycle times. The work function of discharged samples also reduces gradually with the number of cycles. The work function drops by almost 0.5 eV from the pristine state to 1500 cycles in the discharged state. The gradual transformation of GeNWs to agglomerates coincides with a decrease in the work function.

It is worth noting that the SEI layer serves as a passivation layer formed on the electrode during cycling and can potentially play a critical role in the prolonged cycling of the battery electrodes. The initial formation of the SEI layer in the first few cycles reduces the charging and discharge capacity as Li is consumed, but over cycling time the SEI layer helps retain the charge and discharge capacity of the battery. The relative change in work function from 50 to 1500 cycles for charged electrodes with SEI present is less ($\sim +0.06$ eV) than the change in work function for discharged electrodes with SEI layer removed (~ -0.2 eV). Thus, the work function of the electrode with SEI present changed by just 0.06 eV from 50 to 1500 cycles, illustrating the stability of the electrode. Changes in the SEI work function may be due to changes in the SEI layer composition, which is a combination of organic impurities lithium ion and mechanically disintegrated GeNWs. Overall, GeNWs are more efficient than standard electrodes in volumetric expansion and charge capacity.² SEI layer is an important component in longer cycle life of the battery electrodes.³

Table 1. Work function values calculated from CPD and work function of tip.

Sample	CPD (mV)	Work function (eV)
Pristine GeNWs	627 \pm 32	5.527 \pm 0.032
Charged 50 cycles SEI present	507 \pm 15	5.407 \pm 0.015
Charged 1500 cycle with SEI	568 \pm 24	5.468 \pm 0.024
Discharged 50 cycles without SEI	265 \pm 9	5.165 \pm 0.009
Discharged 1500 cycles without SEI	46 \pm 9	4.947 \pm 0.009

References

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