

Supplementary Information:

Puckered-layer-structured germanium monosulfide for superior rechargeable Li-ion battery anodes

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Experimental

Material Synthesis. The solid-state synthesis of GeS was performed as follows. Stoichiometric amounts of Ge (Kojundo, 99.9%, average particle size: $\sim 20\ \mu\text{m}$) and S (Aldrich, 99.98%, average particle size: $\sim 50\ \mu\text{m}$) powders were thoroughly mixed by high-power ball milling (HPBM, Spex-8000) for 6 h. The GeS-C composite was produced by further HPBM as follows. In an Ar-filled glovebox, the as-prepared GeS, carbon (Super P), and stainless steel balls (diameters of 3/8 and 3/16 in.; ball-to-powder mass ratio of 20:1) were placed into an 80-mL hardened steel vial, and HPBM was conducted for 6 h. Preliminary electrochemical tests revealed that optimal performance was achieved for 60 wt.% GeS and 40 wt.% C.

Material Characterization. GeS and GeS-C samples were characterized using X-ray diffraction (XRD, DMAX2500-PC, Rigaku), high-resolution transmission electron microscopy (HRTEM, FEI F20, 200 kV), and HRTEM-coupled energy-dispersive X-ray spectroscopy (EDS), whereas the structural changes of these materials during Li insertion/extraction were investigated by *ex situ* XRD and Ge K-edge extended X-ray absorption fine structure (EXAFS). For *ex situ* analyses, the electrodes at selected potentials were detached from cells in an Ar-filled glove box and coated with polyimide tape (Kapton) serving as a protective film. Ge K-edge EXAFS spectra of GeS and GeS-C electrodes were recorded at the 8C (Nano XAFS) beamline in a 3.0-GeV storage ring at the Pohang Light Source (PLS), South Korea.

Electrochemical Measurements. The electrodes used to evaluate GeS and GeS-C composite samples were prepared by coating Cu foil with a slurry comprising the active powder material (70 wt.%), carbon black (Denka black, 10 wt.%, conducting agent), and an aqueous solution of Li polyacrylate (Li-PAA,

20 wt.%, binder). The coated foil was vacuum-dried at 120 °C for 3 h and pressed to obtain electrodes with a thickness of ~0.045 mm, an area of 0.79 cm², and an average active material weight of ~2.5 mg. Coin-type electrochemical cells were assembled in an Ar-filled glovebox using Celgard 2400 as a separator, Li foil as counter and reference electrodes, and 1 M LiPF₆ in ethylene carbonate/diethyl carbonate (1:1, v/v, Panax STARLYTE) as an electrolyte. With the exception of rate capability tests, all cells were tested galvanostatically between 0.0 and 3.0 V (vs. Li⁺/Li) at a current density of 100 mA g⁻¹ using an automated Maccor tester. In these tests, Li was inserted into the electrode on discharging and extracted on charging, and the gravimetric capacity was calculated from the weight of the active materials. Electrochemical impedance spectroscopy (EIS) measurements were conducted using an impedance analyzer (ZIVE MP2A, WonATech), and potentiostatic impedance patterns were recorded in a frequency range of 10⁵ to 10⁻² Hz at an amplitude of 5 mV. Cyclic voltammetry (CV) was measured in the range of 0.0–3.0 V at a scanning rate of 0.05 mV s⁻¹ using a SP-240 potentiostat (Bio-Logic).

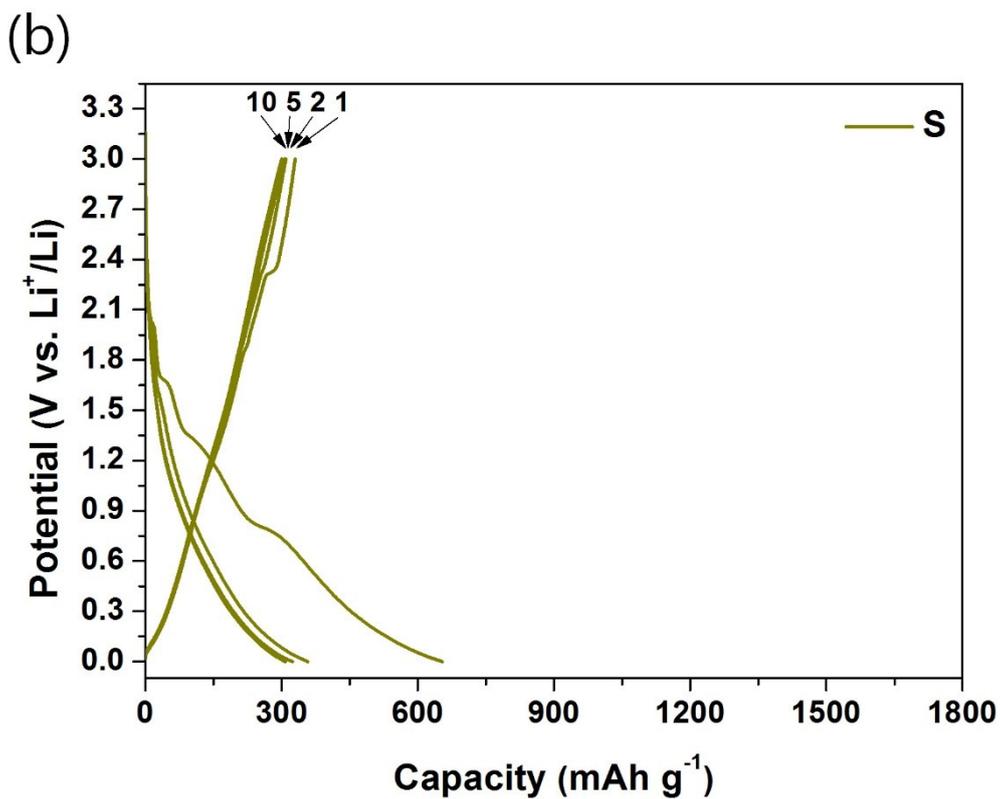
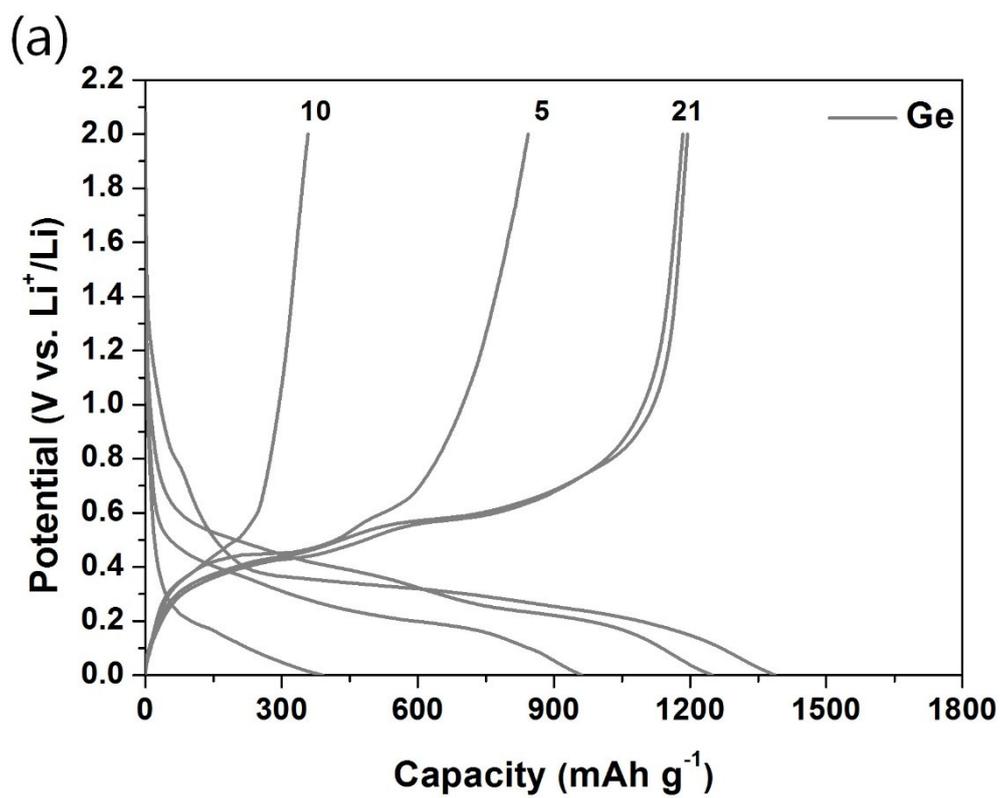


Figure S1. Electrochemical performances of the Ge and S electrodes: (a) Voltage profile of the Ge and (b) voltage profile of the S electrodes.

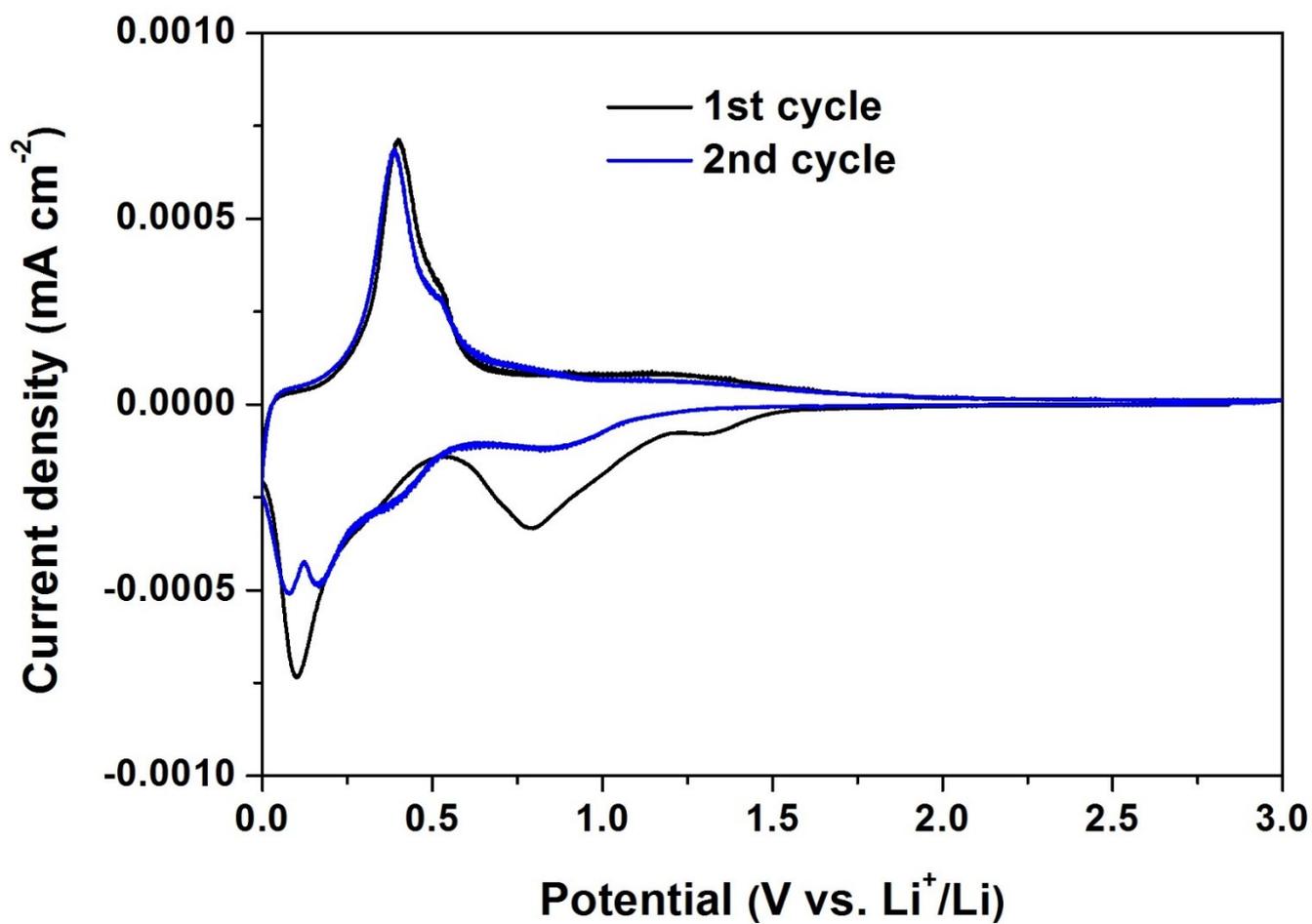


Figure S2. CV result of the first and second cycles for the GeS electrode (voltage range from 0 to 3 V under a scan rate of 0.05 mV s⁻¹).

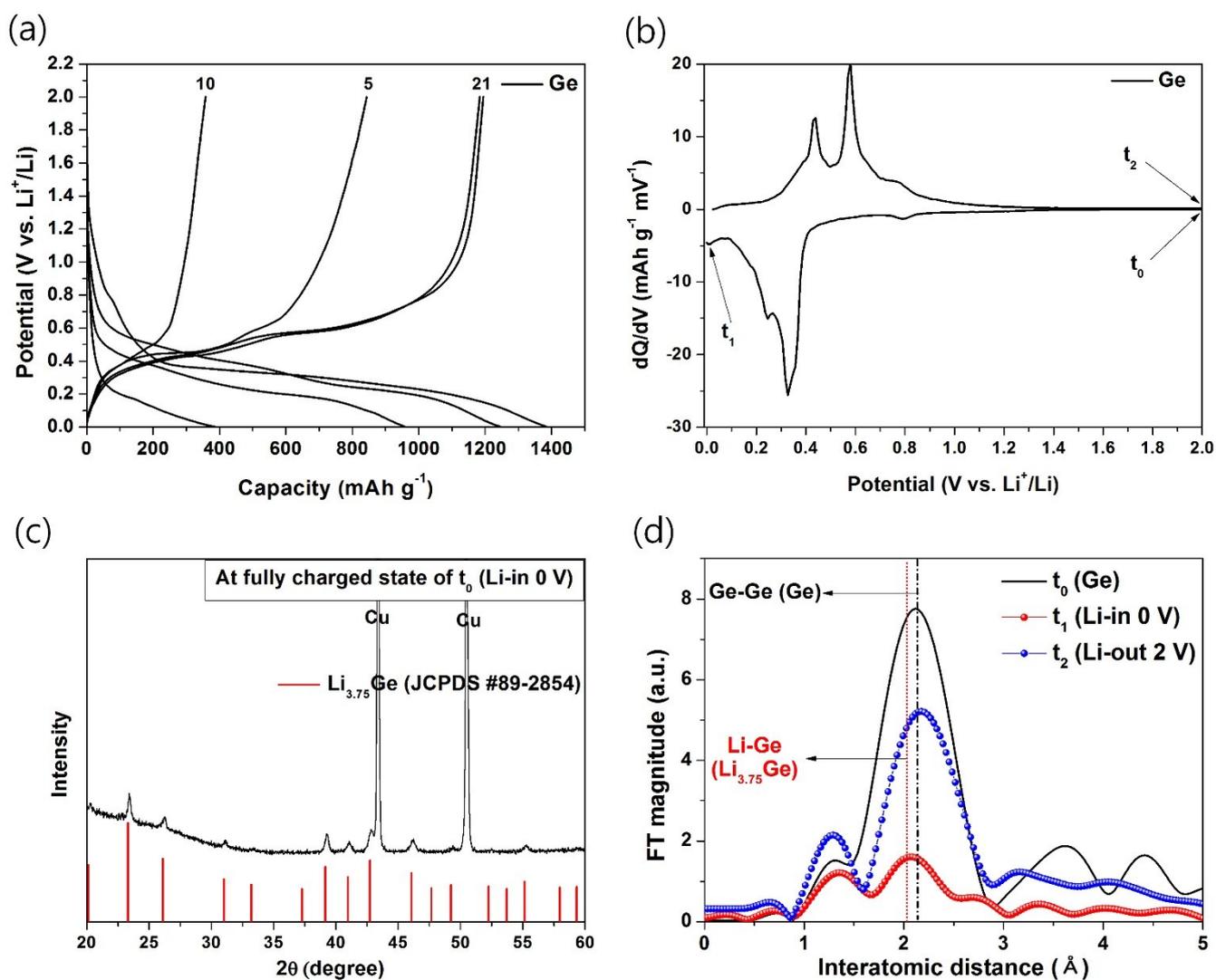


Figure S3. Demonstration of $\text{Li}_{3.75}\text{Ge}$ phase at the fully discharged state on the Ge electrode: (a) Voltage profile, (b) dQ/dV plot of the first cycle, (c) *ex situ* XRD result at the fully discharged state of 0 V, and (d) *ex situ* Ge K-edge EXAFS result at the fully discharged (0 V) and charged state (2.0 V) for the Ge electrode. The first discharge capacity (1390 mAh g^{-1}) of Ge electrode corresponded to $\text{Li}_{3.75}\text{Ge}$ phase, and *ex situ* XRD result at the fully discharged state of 0 V definitely demonstrates the formation of $\text{Li}_{3.75}\text{Ge}$ phase, which corresponded to the Ge K-edge EXAFS main bond (2.03 \AA) of $\text{Li}_{3.75}\text{Ge}$ phase.

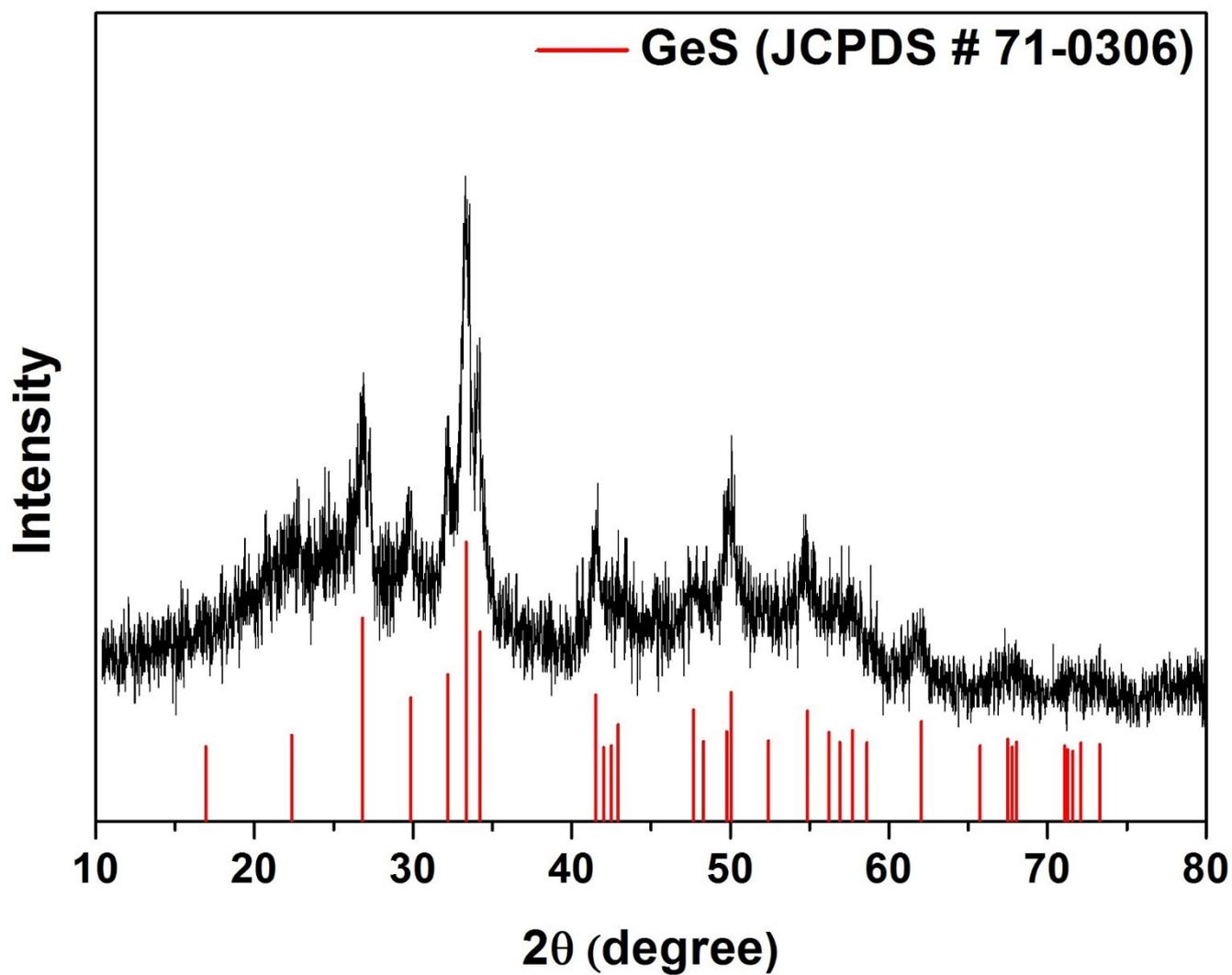


Figure S4. XRD pattern of the GeS/C nanocomposite synthesized by a HPBM process.

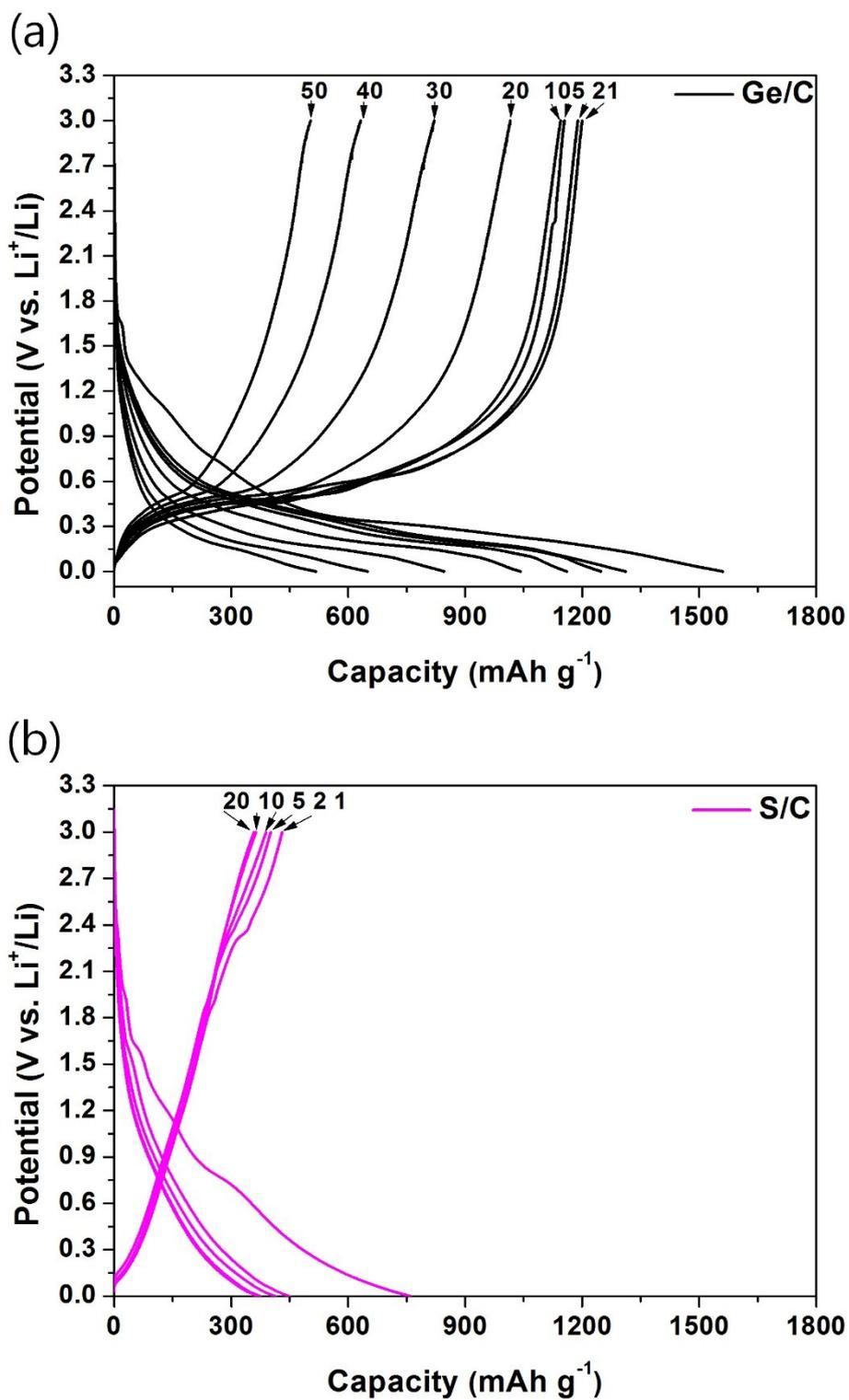


Figure S5. Electrochemical performances of the Ge/C and S/C nanocomposite electrodes: (a) Voltage profile of the Ge/C nanocomposite and (b) voltage profile of the S/C nanocomposite electrodes.

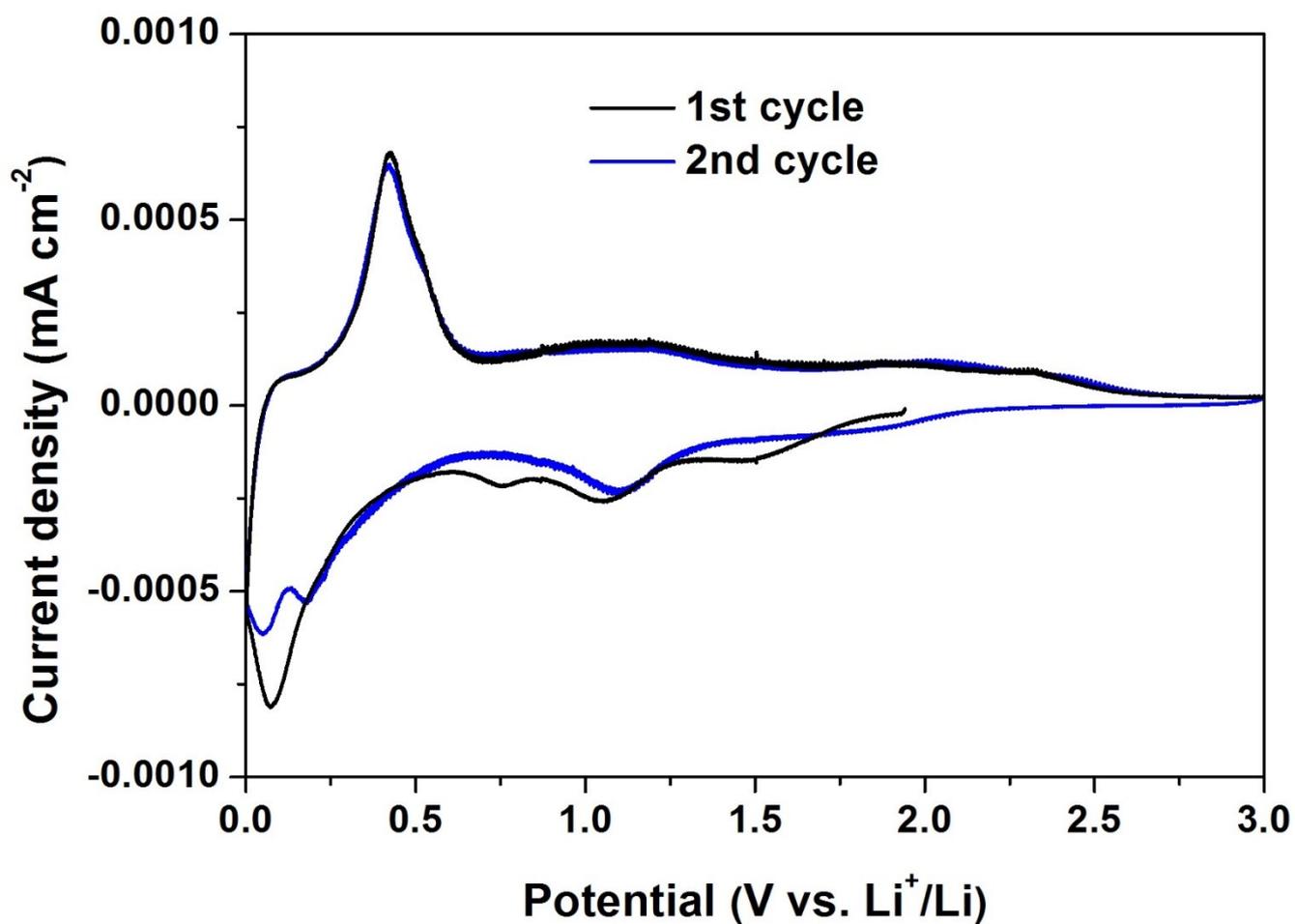


Figure S6. CV result of the first and second cycles for the GeS/C nanocomposite electrode (voltage range from 0 to 3 V under a scan rate of 0.05 mV s⁻¹).

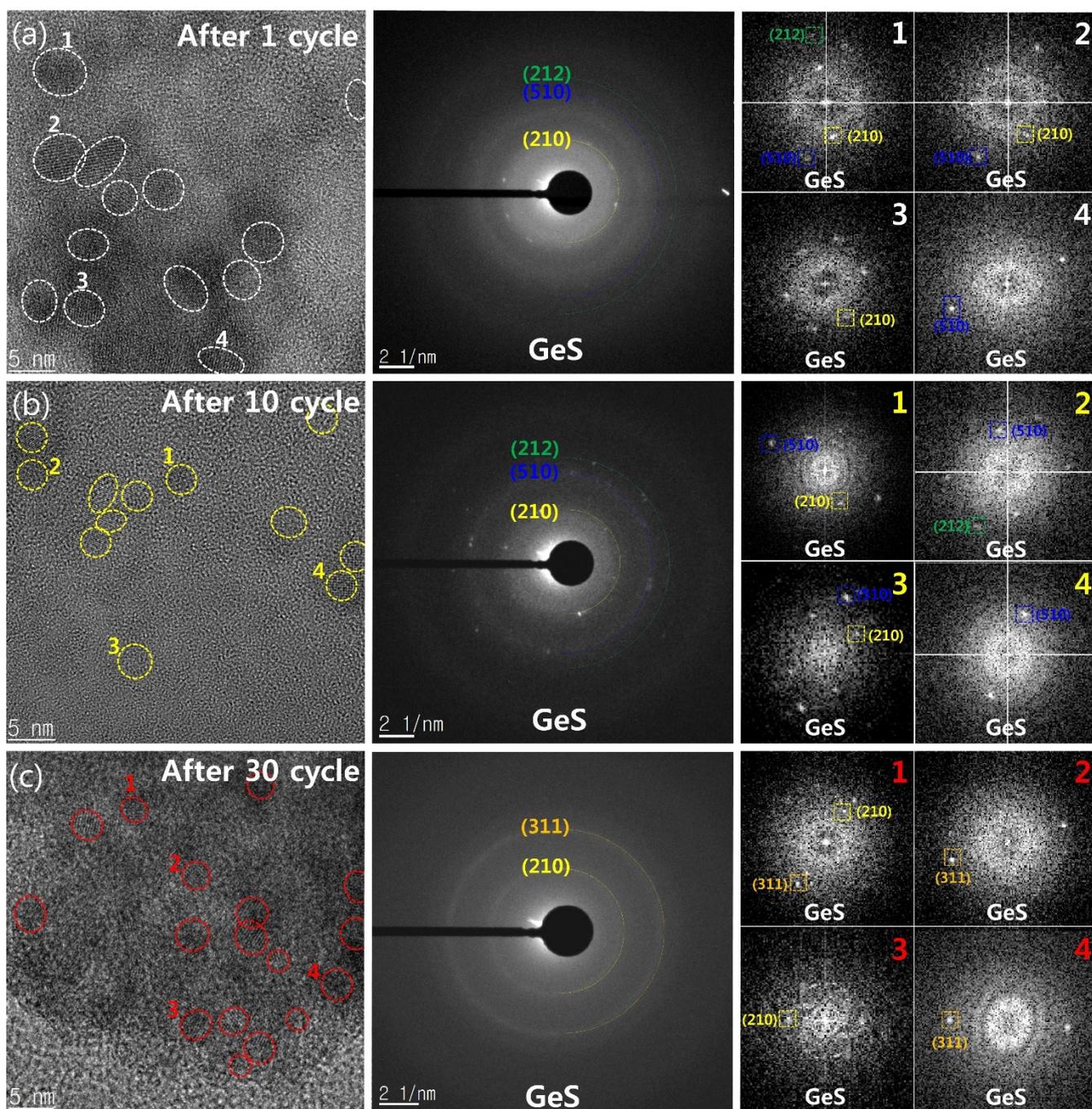


Figure S7. *Ex situ* HRTEM results of GeS/C nanocomposite electrode during cycling. (a) GeS/C nanocomposite electrode after 1 cycling, (b) after 10 cycling, and (b) after 30 cycling.

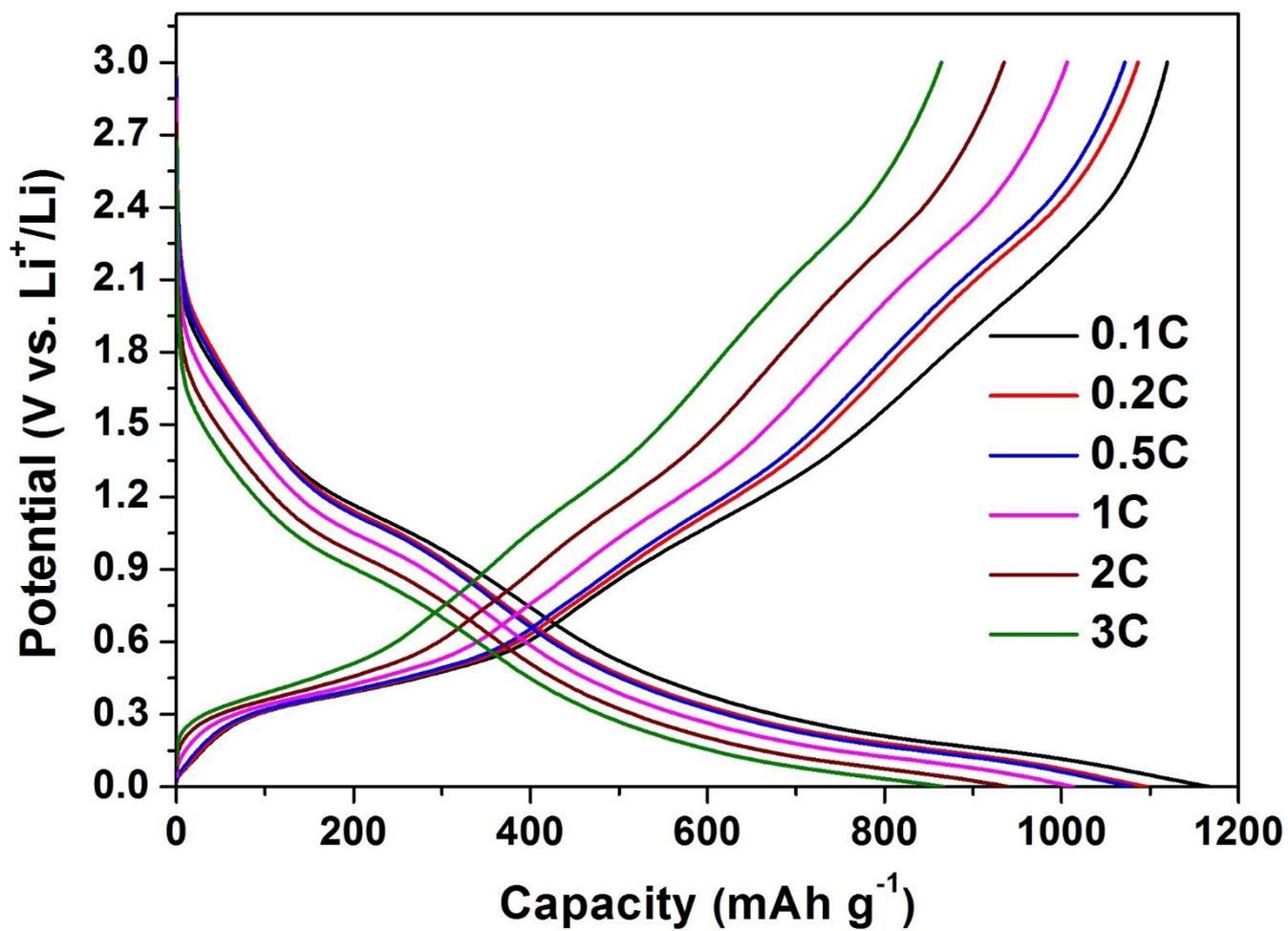


Figure S8. Voltage profiles at various C-rates (0.1, 0.2, 0.5, 1, 2, and 3 C) for the GeS/C nanocomposite electrode.