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Electrochemical Synthesis of the Allotrope *allo*-Ge and Investigations on the Use as an Anode Material

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PXRD pattern of LiGe

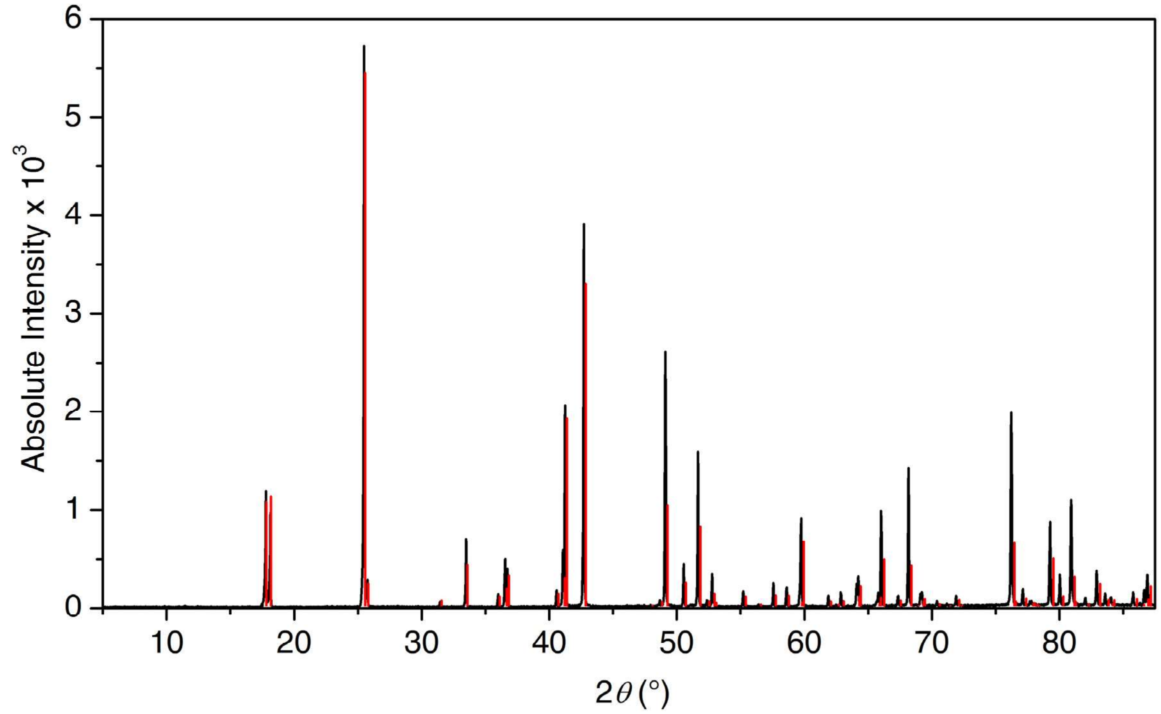

Fig. S1: Experimental (black) and calculated (red) PXRD patterns of LiGe. PSD steps 1.5 °, time/step 15 s.

PXRD pattern of Li_7Ge_{12}

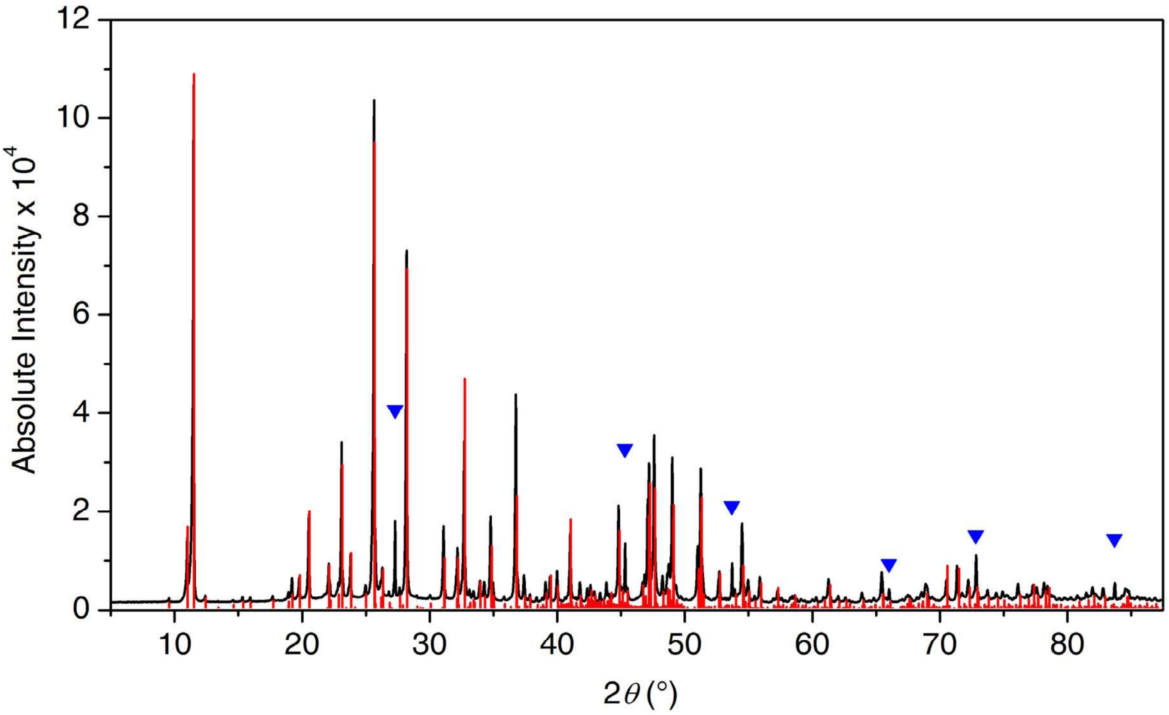

Fig. S2: Experimental (black) and calculated (red) PXRD patterns of Li_7Ge_{12}. Blue triangles denote traces of α-Ge. PSD steps 0.07 °, time/step 45 s.

PXRD patterns of extracted Li_7Ge_{12} electrode materials

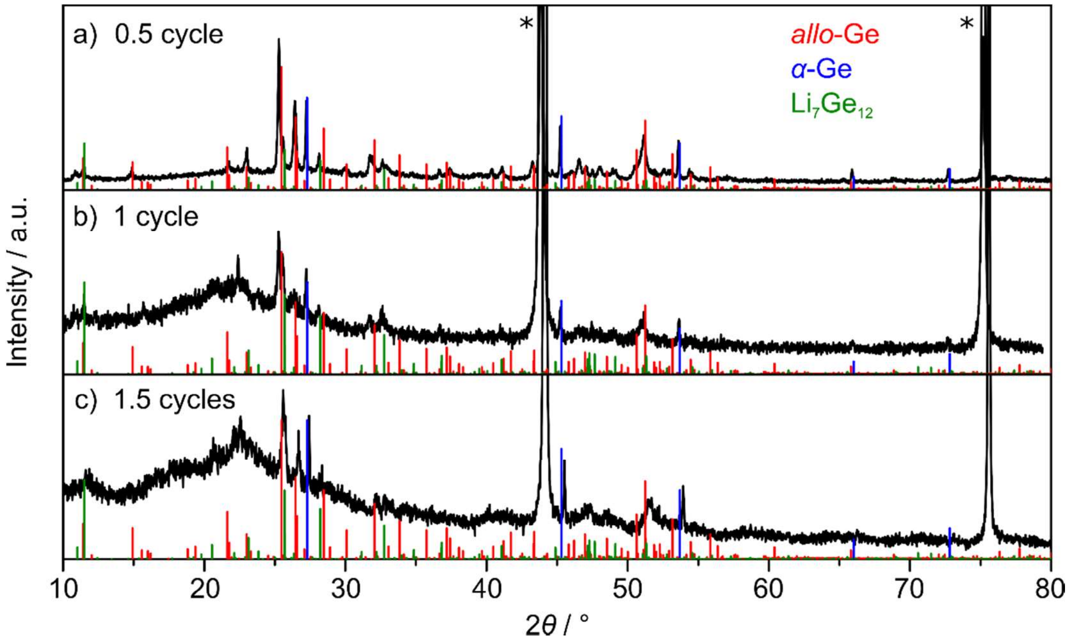

Fig. S3. Powder diffraction patterns of electrode material extracted from coin cells; a) after one delithiation step *allo*-Ge has clearly been formed, b) after one full delithiation/lithiation cycle less allo-Ge is present and a broad signal appears around 22°, c) after 1.5 cycles the ratio of crystalline phases does not change anymore but the broad signal grows; theoretical powder patterns of *allo*-Ge,[1] α-Ge,[2] and Li_7Ge_{12}[3] are given in red, blue, and green, respectively; diamond powder was added to all electrode materials post-cycling for easier handling of the material, corresponding reflexes are marked by an asterisk. The 1 and 1.5 cycle samples are mainly amorphous and are scaled differently than the 0.5 cycle samples to elucidate the remaining crystalline phases.

Potential plot of Li_7Ge_{12} half-cells

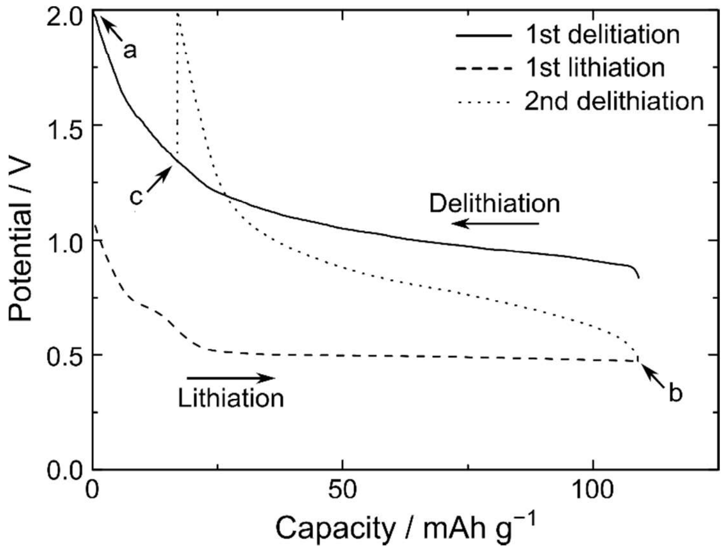

Fig. S4. Potential curves of the first 1.5 cycles of Li_7Ge_{12} half-cells beginning with the first delithiation cycle to 2 V. The powder diffraction state of powder diffraction patterns a–c in Fig. S3 are marked with the respective letters.

PXRD pattern of *m-allo*-Ge

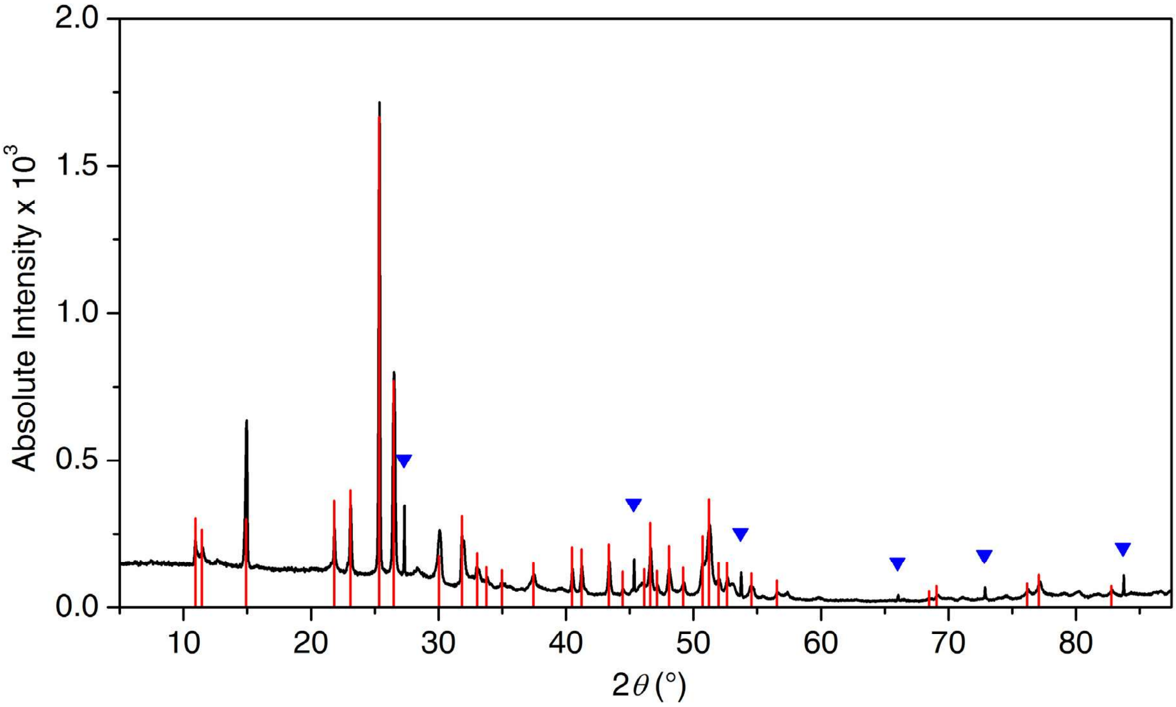

Fig. S5: Experimental (black) and calculated (red) PXRD patterns of *m-allo*-Ge. Blue triangles denote traces of α-Ge. PSD steps 0.07 °, time/step 30 s.

PXRD pattern of α-Ge

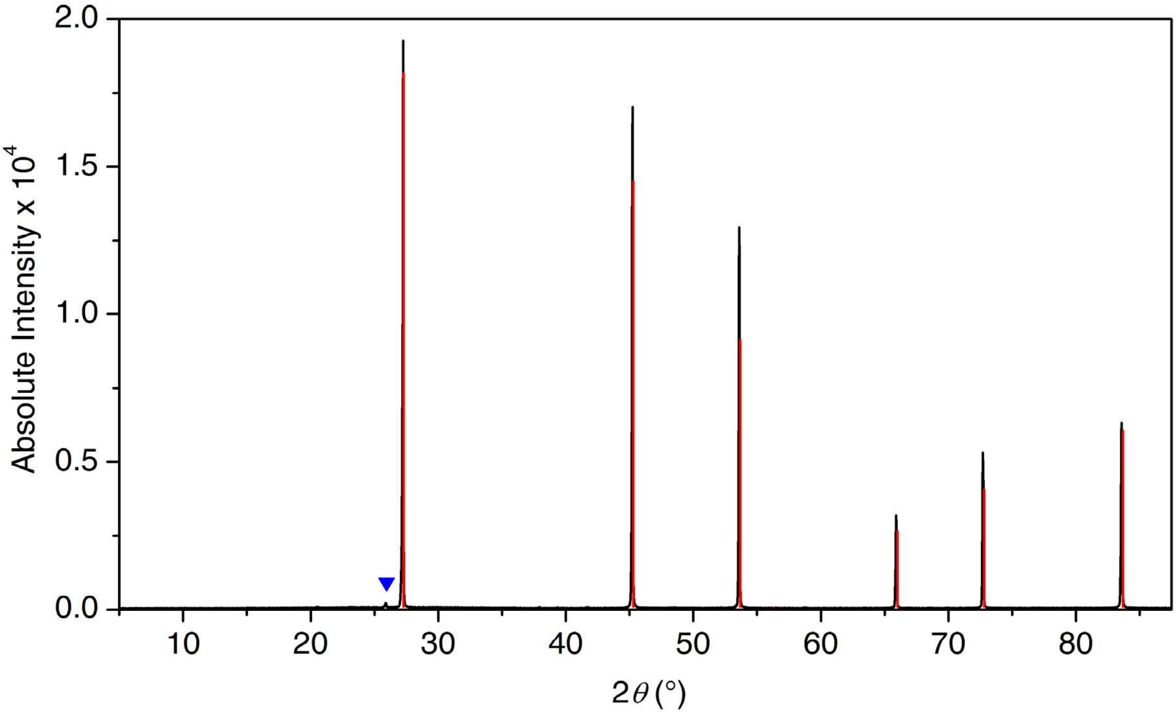

Fig. S6: Experimental (black) and calculated (red) PXRD patterns of α-Ge. The blue triangle marks traces of GeO_2. PSD steps 1.5 °, time/step 15 s.

SEM images of electrochemically synthesized *allo*-Ge

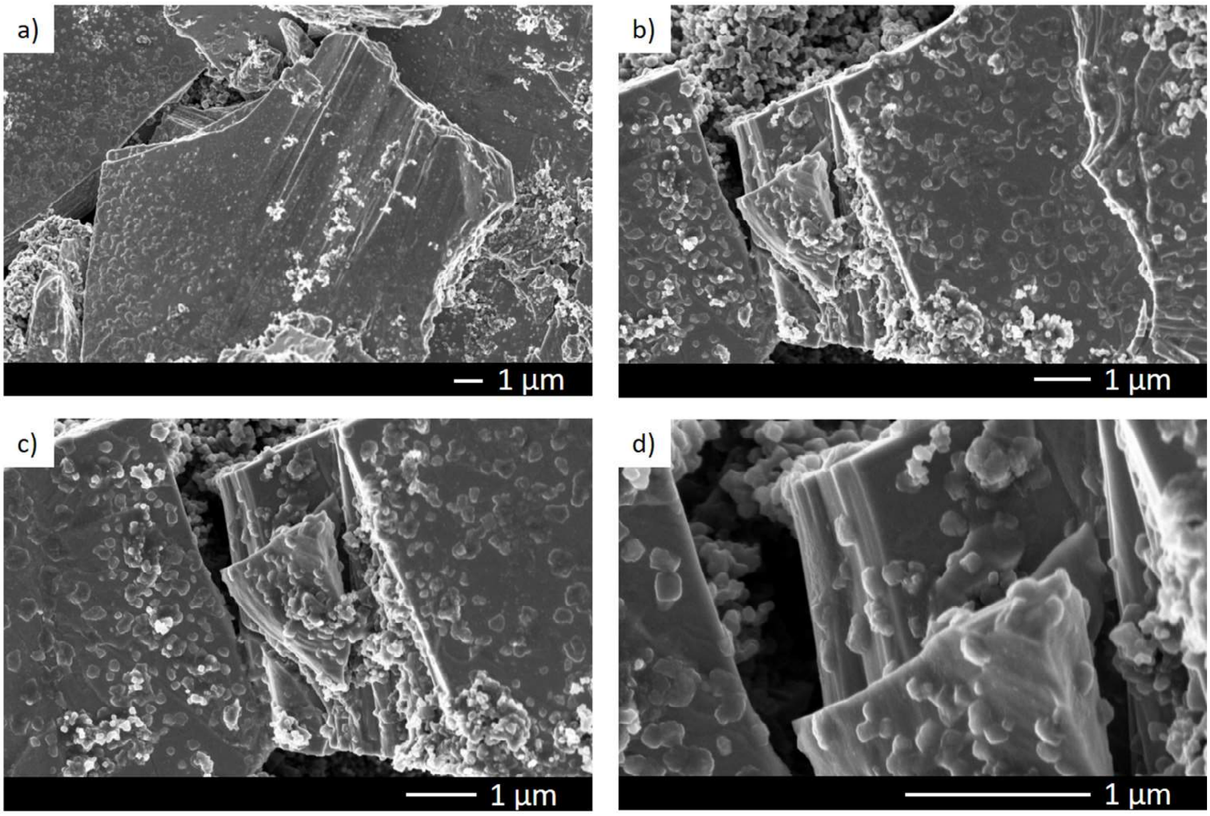

Fig. S7. SEM images of electrochemically synthesized *allo*-Ge.

Particle Size Analysis

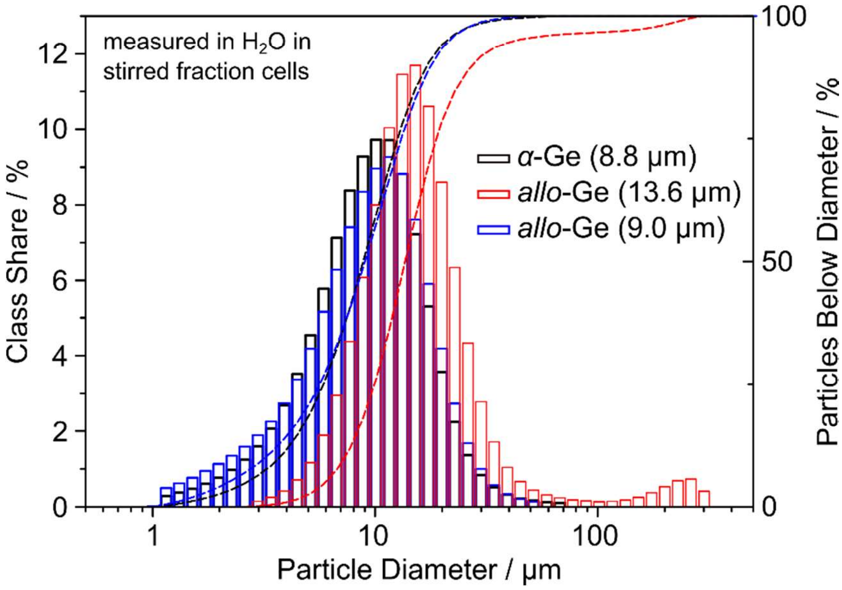

Fig. S8. Particle size analysis of Ge anode materials in H_2O in stirred fraction cell by laser scattering, volume-based distribution. The median of the respective samples is given.

Coin Cell dQ/dV Curves

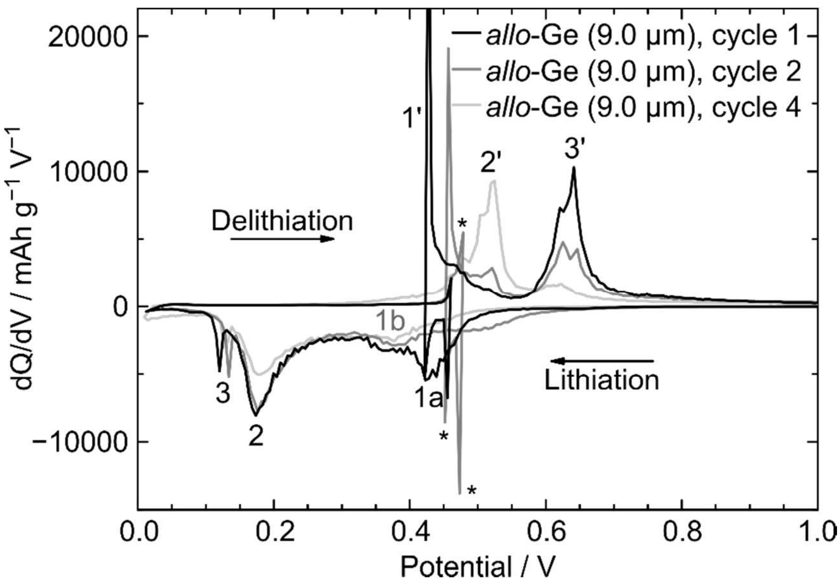

Fig. S9. dQ/dV curves from *allo*-Ge coin cells. Features marked with (*) are artifacts due to over-potentials. First, second and fourth cycles shown.

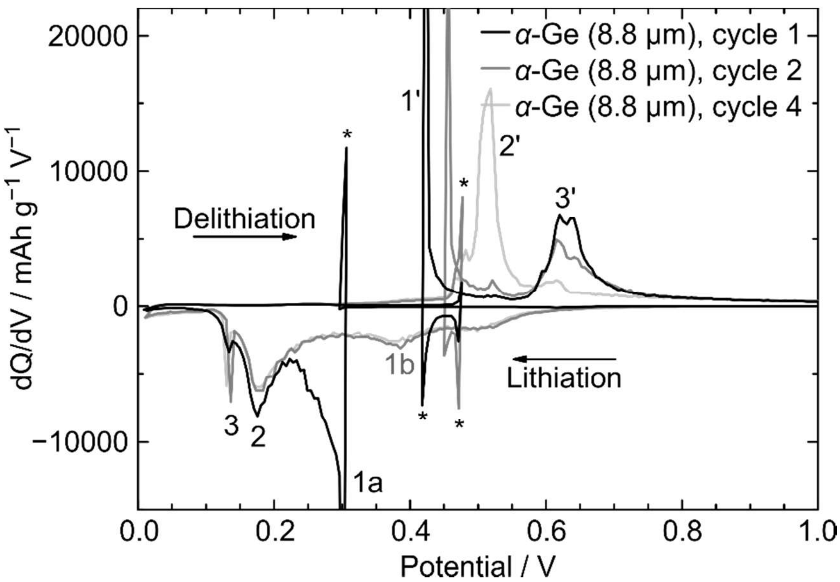

Fig. S10. dQ/dV curves for α-Ge coin cells. Features marked with (*) are artifacts due to overpotentials. First, second and fourth cycles shown.

Ex-situ PXRD patterns of coin cell anode materials after cycling

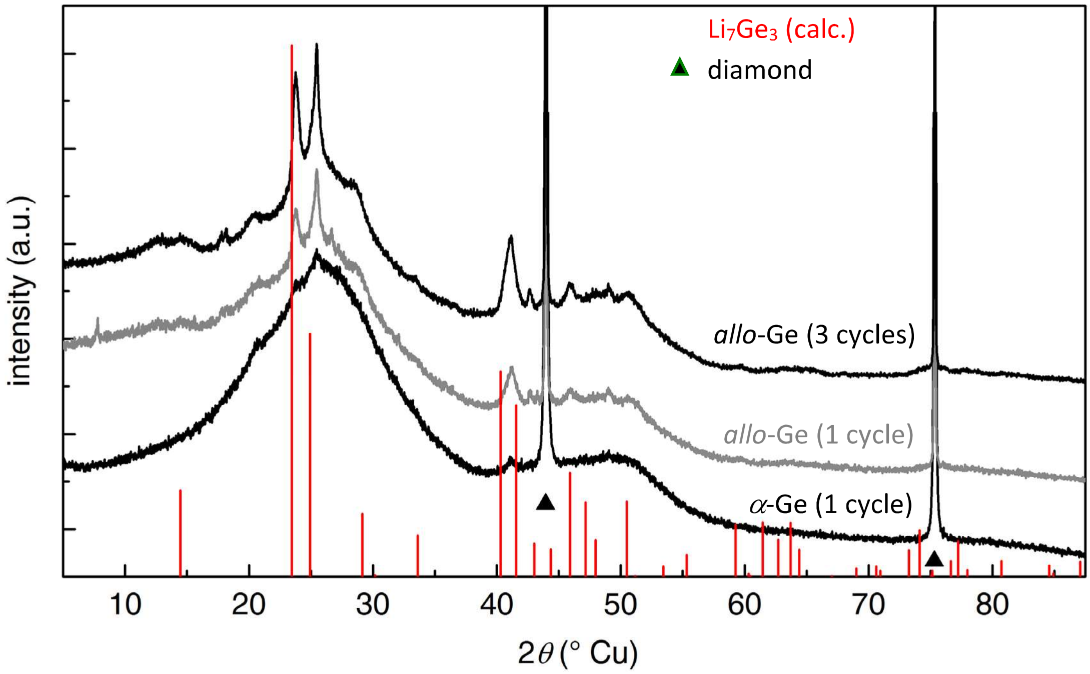

Fig. S11. *Ex-situ*-PXRD patterns of anode materials *α*–Ge after 1 discharge/charge cycle, *allo*-Ge after 1 discharge/charge cycle, and *allo*-Ge after 3 discharge/charge cycles. All materials contain varying amounts of a crystalline phase resembling Li_7Ge_3 (calculated diffraction pattern in red). Black triangles denote reflections of diamond which was mixed with the anode materials for easier handling.

Selected in-situ PXRD patterns

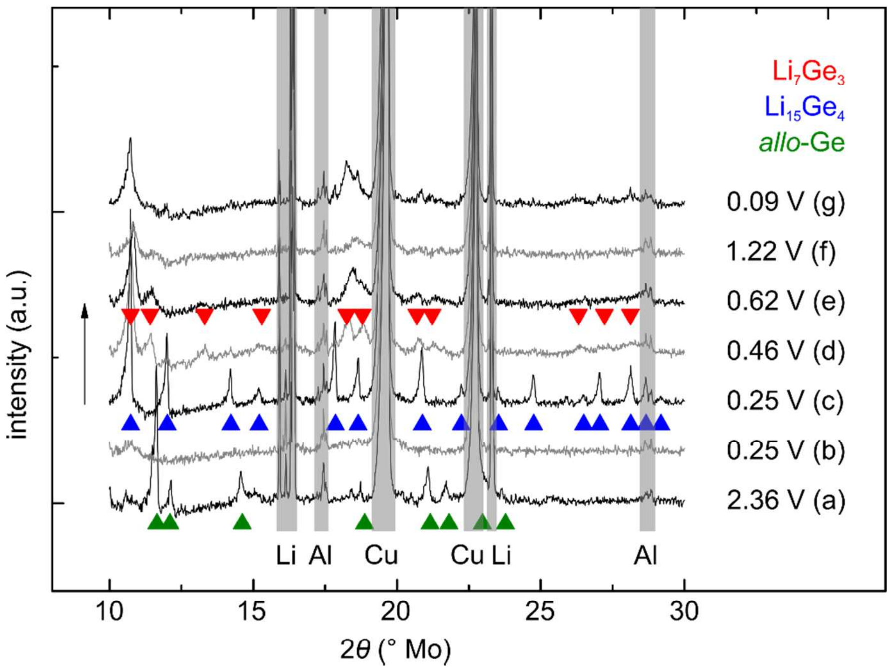

Fig. S12. Selected diffraction patterns from *allo*-Ge pouch cell. Data shown is averaged over 4 raw data files, i.e. one hour of measurement. The main reflections of all observed crystalline phases are marked. The average voltage and the position in Fig. 5 is indicated.

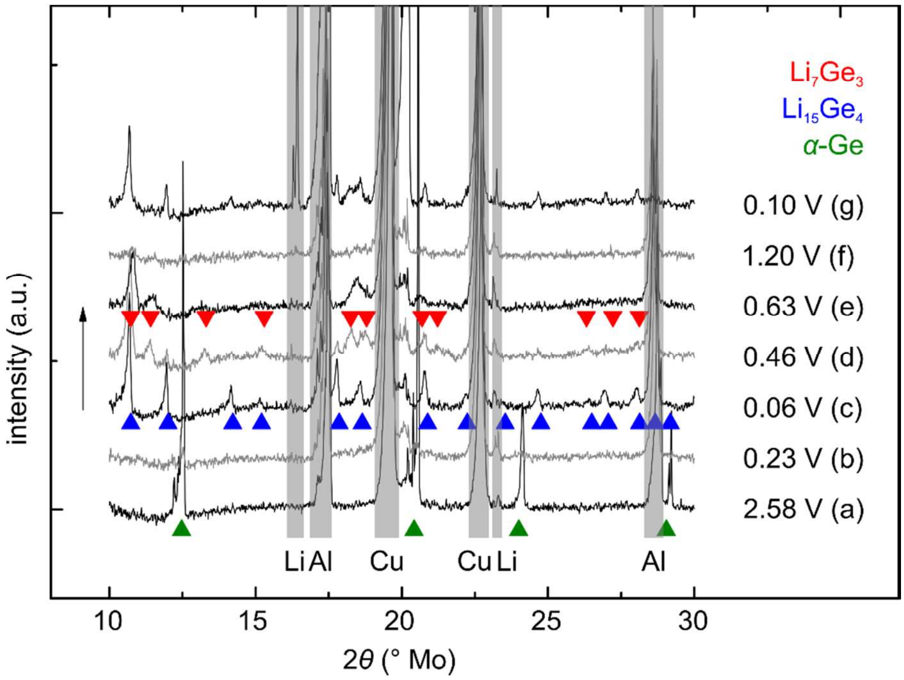

Fig. S13. Selected diffraction patterns from α-Ge pouch cell. Data shown is averaged over 4 raw data files, i.e. one hour of measurement. The main reflections of all observed crystalline phases are marked. The average voltage and the position in Fig. 6 is indicated.

dQ/dV Plot for α-Ge pouch cells

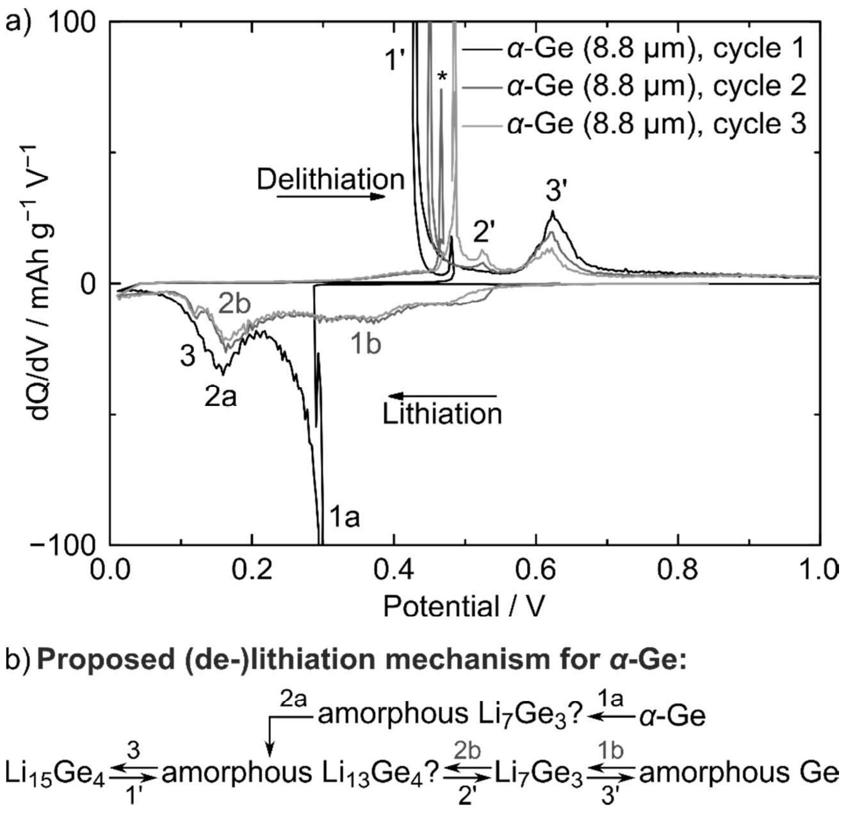

Fig. S14. a) dQ/dV plot of α-Ge in in-situ PCRD pouch cell. An overpotential leads to an artifact peak and is marked by (*), b) proposed (de-)lithiation mechanism for α-Ge, in agreement with Grey *et al.*[4]

References

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