Obviating the need for nanocrystallites in the extended lithiation/de-lithiation of germanium

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Supplementary Calculations

Calculation S1. Calculations for determining the percent composition of the Ge(82.35%)-GeTe(17.65%) composite.

$$GeTe = 15 \text{ since we begin with 15\% Te}$$

$$Ge = 85 - 15 = 70$$

$$\% \ of \ GeTe = \frac{15}{70 + 15} * 100\% = 17.65$$

$$\% \, of \, Ge = \frac{70}{70 + 15} * 100\% = 82.35\%$$

Calculation S2. Example calculation for determining the theoretical capacity of $Ge_{0.85}Te_{0.15}$. The theoretical capacities of $Ge_{0.85}Te_{0.15}$ and $Ge_{0.88}Te_{0.12}$ are 1056 mA h g^{-1} and 1116 mA h g^{-1}, respectively.

Li reacts with Ge to form a final alloy composition of $Li_{3.75}Ge$. This is the only compound that contributes to the capacity as we are not cycling in a voltage range in which Li_2Te is reversibly lithiated and delithiated.

The equation for calculating specific capacity is:

$$specific \, capacity$$
$$= \frac{(Faraday's \, constant, 96485 \, C \, mol^{-1})/(3600\frac{seconds}{hour}) * (\# \, electro}{molar \, mass \, of \, compound}$$

The molar mass was calculated as follows:
$$\frac{Ge_{0.85}}{0.85}\frac{Te_{0.15}}{0.85} = Ge_1Te_{0.176}$$
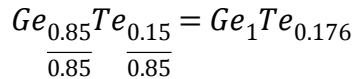
$$molar \, mass$$
$$= (molar \, mass \, Ge, 72.63 \, g \, mol^{-1}) + (0.176) * (molar \, mass \, Te, 127.$$
$$)$$

$$molar \, mass = 95.15 \, g \, mol^{-1}$$
$$specific \, capacity = \frac{(26.8 \, Ah) * (3.75 \, mol)}{95.15 \, g \, mol^{-1}} * \frac{1000 \, mA}{A} = 1056 \, mA \, h \, g^{-1}$$

The Coulombic efficiency (CE) for the first cycle of Ge and $Ge_{0.85}Te_{0.15}$, respectively, is 77.2%

and 71.1%. The CE for the second cycle of Ge and $Ge_{0.85}Te_{0.15}$, respectively, is 96.2% and

94.7%. The average CE for cycles 3-500 of Ge and $Ge_{0.85}Te_{0.15}$, respectively, are 99.5% and

98.2%. The capacity increases over the first few cycles, ; we hypothesize that during lithiation

the micrometer-sized particles break up slightly and expose new germanium surface area. The

increased surface area and reduced particle size allows each particle to be more completely

lithiated, which accounts for the increased capacity. The lower CE for $Ge_{0.85}Te_{0.15}$ corresponds

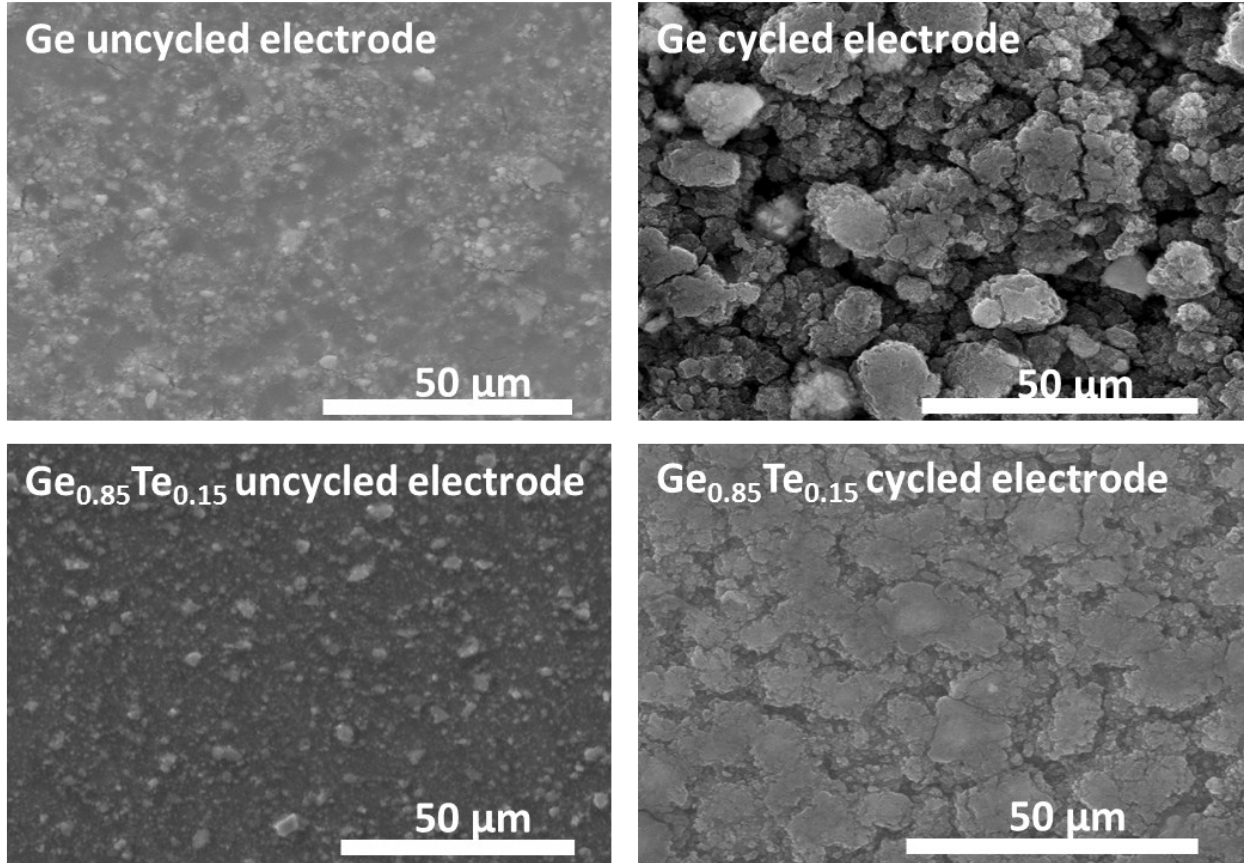to the loss of Li^+ to the lithiated interphase layer formed on newly exposed germanium surfaces.

Supplementary Figures
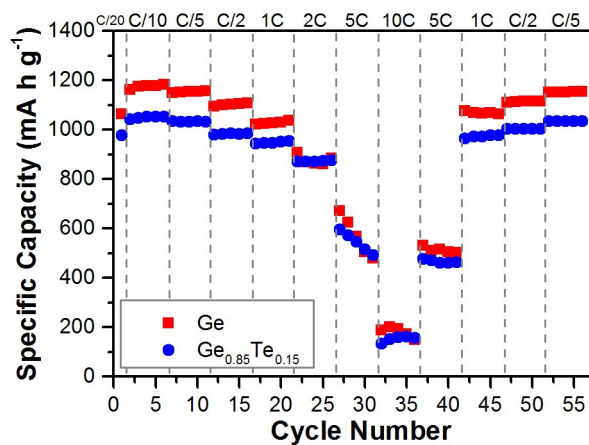
Figure S3. A plot of the capacity values at varying current densities for $Ge_{0.85}Te_{0.15}$ and Ge.
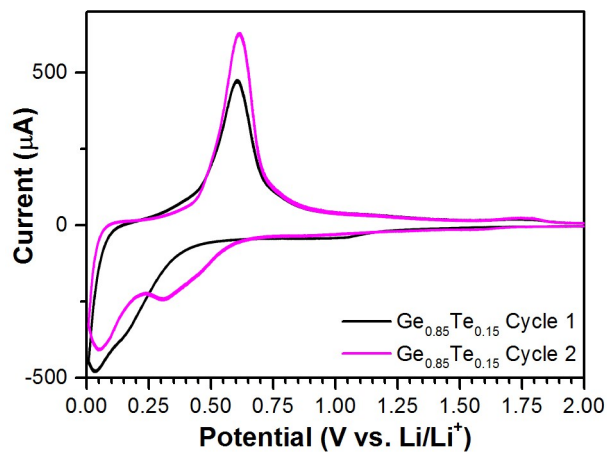

Figure S4. First and second cycle CVs of $Ge_{0.85}Te_{0.15}$.

**Figure S5.** SEM comparison of uncycled and cycled Ge and $Ge_{0.85}Te_{0.15}$ electrodes.

Material	Initial Charge Capacity (mA h g^{-1})	Capacity Retention (%)	Cycles	Cycling Voltage Window (V vs. Li/Li$^+$)	Charging rate	Coulombic Efficiency (CE) (%)	Synthesis	Particle size	Citation
Ge$_{0.85}$Te$_{0.15}$	1043	96	500	0.005-1.25	1C (1.6 A g^{-1})	98	facile melt-quench technique	3-5 μm	Current work
CuGeO3@RGO	1157	780 mA h g^{-1} after 130 cycles (67%)	130	0.02-3	100 mA g^{-1}	~100	hydrothermal	nanowires	19
		550 mA h g^{-1} after 300 cycles (48%)	300		2 A g^{-1}				
0-D Ge nanoparticles	1428 (initial discharge capacity)	1162 mA h g^{-1} after 100 cycles at 1C (85%)	100	0-1.2	1C (1.6 A g^{-1})	95	thermal annealing followed by HF etching	nanoparticles	22
3-D Ge nano particles	1380 (initial discharge capacity)	1415 mA h g^{-1} after 100 cyles at 1C (95%)	100	0-1.2	1C (1.6 A g^{-1})	99	thermal annealing followed by HF etching	nanoparticles	22
Ge nanoparticles/ N-doped RGO composite	1475 (initial discharge capacity)	700 mA h g^{-1} after 200 cycles	200	0-1.5	0.5 A g^{-1}	99	PVP-assisted thermal reduction	~5 nm	24
Ge nanotubes	1022	1002 mA h g^{-1} after 400 cycles (98%)	400	0-1.5	0.2C (200 mA h g^{-1})	>99	Kirkendall effect at 700°C	nanotubes	21
Ge nanowire sheathed with C	963	72% after 100 cycles	100	0-1.5	0.5C (400 mA g^{-1})	91	solid-liquid solution method	~80 nm	20
Ge@C core-shell nanoparticles	938	~950 mA h g^{-1} after 50 cycles	50	0-1	50 mA g^{-1}	>90% for 50 cycles	solution-based method	nanoparticles	25
Calcium germanate	420	~600 mA h g^{-1}	100	0.02-3	100 mA h g^{-1}	not reported for these results	hydrothermal	nanowires	20
Barium germanate	568	~400 mA h g^{-1}	100	0.02-3	100 mA h g^{-1}	not reported for these results	hydrothermal	nanowires	20

Table S6. A comparison of the electrochemical cycling data of the current work with several other papers studying germanium materials.
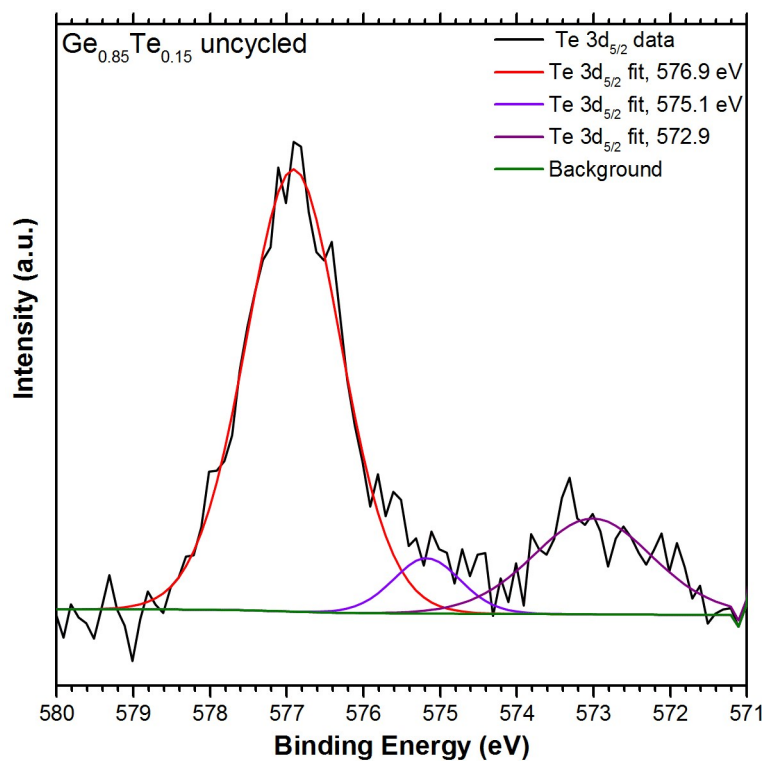
Figure S7. XPS of uncycled $Ge_{0.85}Te_{0.15}$ electrode after exposure to air.
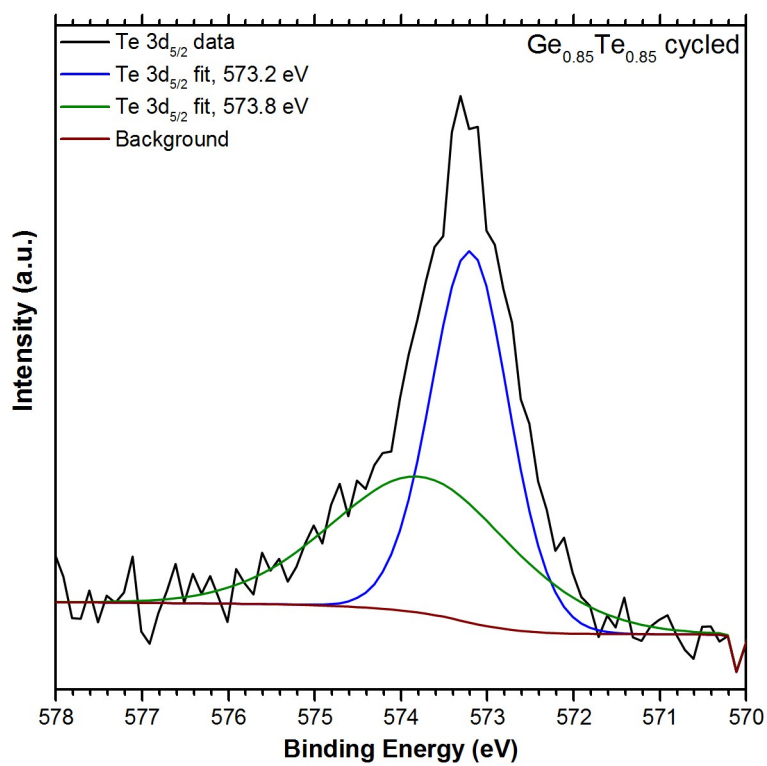
Figure S8. XPS of cycled $Ge_{0.85}Te_{0.15}$ electrode after at least 500 cycles.