Supporting Information

Activation with Li Enables Facile Sodium Storage in Germanium

Alireza Kohandehghan,^{a,b} Kai Cui,^b Martin Kupsta,^b Jia Ding,^{a,b} Elmira Memarzadeh Lotfabad,^{a,b} W. Peter Kalisvaart,^{a,b} David Mitlin^{a,b,c**}*

^a University of Alberta Department of Chemical and Materials Engineering, 9107 116th Street, T6G 2V4, Edmonton, AB, Canada

^b National Institute for Nanotechnology (NINT), NRC, 11421 Saskatchewan Dr., Edmonton, AB, T6G 2M9, Canada

^c Clarkson University Chemical & Biomolecular Engineering and Mechanical Engineering
8 Clarkson Avenue, Potsdam NY 13699, USA

*kohandeh@ualberta.ca

**david.mitlin2@gmail.com

Experimental section

GeNWs arrays were synthesized in a low-pressure CVD tube furnace (Tystar, Inc.). The arrays were grown directly onto mirrored-finished (polished down to 1 μm) 316L stainless steel spacers (MTI Corporation) with diameter of 15.4 mm covered with 50 nm Ti adhesion and 100 nm TiN diffusion barrier layers. Prior to nanowire growth, in order to de-wet the 10 nm Au catalyst film the samples were annealed at 320 $^{\circ}\text{C}$ under vacuum for one hour. A 1:4 mixture of GeH_4 : H_2 was utilized as the working gas with the total pressure of 100 Torr, with growth being done at 320 $^{\circ}\text{C}$ for 2 minutes. The average GeNWs mass loading was 0.2212 mg, measured with a Mettler Toledo MX5 microbalance (0.1 μg resolution). A series of 100 nm thick Ge films (0.0865 mg average mass loading) were deposited at nominally ambient temperature onto polished (P-4000 SiC) stainless steel spacers using RF-magnetron sputtering (max. base pressure of 5×10^{-8} Torr).

We employed 2032 button half-cells versus Li or Na metal (MTI). Li activation was done with 1 M LiPF_6 in EC:DEC:DMC 1:1:1 by volume (MTI and Alfa Aesar). Li activated electrodes were disassembled, rinsed in acetonitrile (Fisher Scientific) and dried in a glovebox (< 0.2 ppm H_2O and O_2 content) overnight. They were then reassembled in the same glovebox for NIB testing, employing 1 M NaClO_4 (Alfa Aesar, 98-102% purity) EC:DEC 1:1 by volume. Polyethylene separators (MTI Corporation) with 36 – 44% porosity and 0.03 μm pore size ($\varnothing$ 19 mm) were used for both LIB and NIB assemblies. Electrochemical impedance spectroscopy (EIS) measurements were performed on Versa STAT3 potentiostat (Princeton Applied Research) in a frequency range of 1000 kHz – 1 mHz with an AC amplitude of 10 mV. All the electrochemical experiments were performed at room temperature.

Electron energy loss spectroscopy (EELS) and energy-dispersive X-ray (EDX) spectroscopy were performed using a JEOL 2200FS (200 kV) with an in-column Ω filter in scanning mode (STEM) with a nominal analytical beam size of 0.5 nm. The standard procedure of pre-edge background subtraction and integration on the edge was used for the data extraction from the recorded EELS spectra.¹ For each elemental map, a thickness profile was calculated from low-loss EELS spectrum to check for possible artifacts due to large variation in thickness. Ge-*M*, Li-*K*, C-*K*, and Na-*L* edges were used for elemental mapping in cycled materials. We used multiple linear least squares (MLLS) fitting of EELS spectra for separating Ge-*M* and Na-*L* edges.

Figure S1. (a) Top-view SEM micrograph and (b) cross sectional SEM image of as-grown GeNWs array at 320 °C for 2 minutes. (c,d) Histogram diagram of projected diameter and length of the nanowires, respectively.

Figure S2. TEM micrographs of as-grown GeNWs: (a) bright-field, (b) corresponding indexed selected area diffraction (SAD) pattern of the nanowire oriented near the $[01\bar{1}]$ zone axis, (c) dark-field micrograph obtained using $g = 022_{\text{Ge}}$ reflection, and (d) HRTEM micrograph with the corresponding Fast Fourier Transform (FFT) pattern insert.

Figure S3. XPS spectra of as-grown GeNWs and GeNWs after first delithiation (2 V vs. Li/Li^+) at 0.1C and 5C. Panels present C 1s, O 1s, Ge 3d, Li 1s, F 1s, and P 2p.

Figure S4. CC voltage profile for cycle 1 and corresponding dQ/dV plot insert for GeNWs at (a) 0.1C and (b) 5C with 0.01 – 2 V vs. Li/Li⁺ window.

Figure S5. TEM analysis of GeNWs after one lithiation – delithiation at 5C. (a) Bright-field micrograph with the corresponding indexed simulated and experimental SAD patterns, inserted. (b) HRTEM micrograph with the corresponding FFT pattern insert. (c) HAADF micrograph and EELS elemental maps of Ge, Li, C, and O. The Ge and Li maps are obtained from the solid rectangular, while the C and O maps are recorded from dashed rectangular.

Figure S6. (a) Cyclic voltammetry (CV) curves for cycles 1 – 10 at the rate of 0.1 mV/s and (b) galvanostatic voltage profiles of GeNWs-A-5C at cycle 1, 2, 10, 30, and 50 at charging rate of 0.15C. Both CV and CC measurements were conducted within 0.01 – 2 V vs. Na/Na⁺ window.

Figure S7. Coulombic efficiency (%) of GeNWs-A-0.1C and GeNWs-A-5C anodes at 0.15C.

Figure S8. Plan-view SEM micrographs of GeNWs-A-0.1C after (a) first and (b) 55 cycles in desodiation state cycled at 0.15C.

Figure S9. XPS spectra of GeNWs and GeNWs-A-0.1C after first sodiation (0.01 V vs. Na/Na⁺) and desodiation (2 V vs. Na/Na⁺). Panels present C 1s, O 1s, Na 1s, Cl 2p, Ge 3d, Li 1s, F 1s, and P 2p.

Figure S10. C 1s, O 1s, Na 1s, Cl 2p, Ge 3d, Li 1s, F 1s, and P 2p high resolution XPS spectra for GeNWs and GeNWs-A-0.1C anode materials cycled against Na after 55 cycles at 0.15C.

Figure S11. TOF-SIMS depth profiles of Na and Fe concentration for GeNWs-A-0.1C anode after 55 cycles in desodiation state.

Figure S12. (a) Electrochemical impedance spectroscopy (EIS) spectra for GeNWs after first delithiation (2 V vs. Li/Li^+) at 0.1C and 5C. EIS spectra for GeNWs-A-0.1C and GeNWs-A-5C anodes after (b) initial sodiation (0.01 V vs. Na/Na^+), (c) first desodiation (2 V vs. Na/Na^+), and (d) 55 cycles at 0.15C in desodiated state with the high frequency portion of the spectra inserts.

Figure S13. Equivalent circuit used for fitting electrochemical impedance spectra.

Figure S14. HAADF images and corresponding EELS elemental maps of C and O for (a) GeNWs-A-0.1C after first sodiation, (b) GeNWs-A-0.1C after initial desodiation, and (c) GeNWs after first sodiation.

Figure S15. Conventional TEM analysis of GeNWs-A-0.1C, after sodiating once at 0.1C. Bright-field micrograph and SAD insert.

Figure S16. TEM analysis of GeNWs-A-0.1C, after a single sodiation – desodiation cycle at 0.1C. (a) Bright-field micrograph and SAD insert. (b) HRTEM image highlighting the amorphous structure of desodiated Ge.

Figure S17. TEM analysis of GeNWs after first attempted sodiation (a-c) and after first sodiation – desodiation (d-g). (a) Bright-field micrograph, (b) corresponding SAD pattern, the nanowire is oriented near $[001]$ zone axis, (c) dark-field micrograph, taken using $g = 220_{\text{Ge}}$ reflection. (d) bright-field, (e) SAD pattern of the GeNW oriented near the $[1-10]$ zone axis, (f) dark-field image, obtained using $g = 111_{\text{Ge}}$, and (g) HRTEM micrograph with the partially indexed FFT pattern insert.

Figure S18. TEM micrographs of GeNWs-A-0.1C after 5 cycles at 0.1C in desodiation state: (a-c) bright-field micrographs. The inserts in panel (a) are the simulated and experimental SAD patterns.

Figure S19. CC voltage profiles of GeTF-A-5C at cycle 1, 2, 10, 30, and 60 at charging rate of 0.15C.

Figure S20. CV curves for cycles 1 – 10 of (a) GeTF, (b) GeTF-A-0.1C, and (c) GeTF-A-5C. CV measurements were conducted at 0.1 mV/s.

Figure S21. Coulombic efficiency (%) of GeTF, GeTF-A-0.1C, and GeTF-A-5C anodes at 0.15C.

Figure S22. Indexed XRD patterns of as-deposited and delithiated (at 0.1C) Ge thin film.

Figure S23. EIS spectra for GeTF after first lithiation (0.01 V vs. Li/Li^+) and delithiation (2 V vs. Li/Li^+) at (a) 0.1C and (b) 5C. EIS spectra for GeTF, GeTF-A-0.1C, and GeTF-A-5C anodes after (c) initial sodiation (0.01 V vs. Na/Na^+), (d) first desodiation (2 V vs. Na/Na^+), and (e) 60 cycles at 0.15C in desodiated state with the high frequency portion of the spectra inserts.

Figure S24. C 1s, O 1s, Na 1s, Cl 2p, Ge 3d, Li 1s, F 1s, and P 2p high resolution XPS spectra for desodiated GeTF-A-0.1C after cycle 1 and cycle 60 at 0.15C.

Figure S25. TOF-SIMS depth profiles of Na and Fe concentration for (a) GeTF and (b) GeTF-A-0.1C anodes after 60 cycles in desodiation state.

Figure S26. (a,b) Plan-view and (c,d) cross sectional SEM micrographs of (a,c) GeTF and (b,d) GeTF-A-0.1C anodes after 60 cycles at 0.15C.

Figure S27. Galvanostatic voltage profiles of (a) SbTF and (b) SbTF-A-0.1C anodes at cycle 1, 2, 5, 10, and 20 at 0.1C within 0.01 – 2 V vs. Na/Na⁺ window. (c) Constant current cycling performance of SbTF and SbTF-A-0.1C anodes at 0.1C.

Table S1. Composition (in at.%) of delithiated GeNWs after first cycle at 0.1C and 5C, obtained from the XPS spectra shown in Figure S3.

	C	O	Ge	Li	F	P
0.1C	43.51	27.85	0.61	24.63	3.04	0.36
5C	41.11	32.90	3.02	20.14	2.28	0.55

Table S2. Composition (in at.%) of GeNWs-A-0.1C after first and 55 cycles in desodiated state, obtained from the XPS spectra shown in Figure S9 and Figure S10.

	C	O	Ge	Au	Na	Cl	Li	F	P
Cycle 1	43.44	28.21	1.58	0.02	3.61	0.49	21.61	0.80	0.24
Cycle 55	51.46	32.32	0.37	0.03	13.10	1.21	1.03	0.28	0.20

Table S3. Modeling results for EIS spectra of GeNWs anodes, shown in Figure S12.

Material	State	R_{es} (Ω)	R_{ct} + R_f (Ω)	C_{dl} (μF)
GeNWs	1 Delithiation @ 0.1C	3.8	286.2	137
	1 Delithiation @ 5C	2.7	244.9	84
GeNWs-A-0.1C	1 Sodiation	52.8	10832	-
	1 Desodiation	6.2	2854	45
	55 Desodiation	9.5	7469	61
GeNWs-A-5C	1 Sodiation	45.1	12887	-
	1 Desodiation	6.7	2381	39
	55 Desodiation	11.1	5293	67

Table S4. Modeling data for EIS spectra of GeTF anodes, shown in Figure S23.

Material	State	$R_{es} (\Omega)$	$R_{ct} + R_f (\Omega)$	$C_{dl} (\mu F)$
GeTF	1 Lithiation @ 0.1C	32.9	1827	2.6
	1 Delithiated @ 0.1C	5.4	238.4	107
	1 Lithiation @ 5C	15.9	1692	3.1
	1 Delithiation @ 5C	3.2	191.5	73
GeTF	1 Sodiation	25.9	3412	-
	1 Desodiation	6.9	456.2	5.9
	60 Desodiation	20.5	2965	8.1
	1 Sodiation	12.9	5704	-
GeTF-A-0.1C	1 Desodiation	3.2	528.3	31
	60 Desodiation	7.3	3543	54
	1 Sodiation	19.8	4391	-
GeTF-A-5C	1 Desodiation	3.7	499.6	27
	60 Desodiation	7.9	3389	56

Table S5. Composition (in at.%) of GeTF-A-0.1C after first and 60 cycles in desodiated state, obtained from the XPS spectra shown in Figure S24.

	C	O	Ge	Na	Cl	Li	F	P
Cycle 1	39.80	32.64	3.91	4.96	0.15	17.86	0.53	0.15
Cycle 60	44.78	38.72	2.14	11.84	0.16	2.01	0.20	0.15

References

- 1 R. F. Egerton, Electron energy-loss spectroscopy in the electron microscope, Springer, New York, 3rd edition, 2011.