

# High Storage Capacity Sodium-Ion Battery Electrodes of Solution-Grown Germanium Nanowires

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## Introduction:

Sodium-ion batteries (NIBs) have attracted attention as an alternative to lithium-ion batteries (LIBs) because sodium (Na) is so much more abundant and inexpensive than lithium (Li). NIBs, however, require much higher performance in order to displace the use of LIBs. One problem is that graphite—the negative electrode material used in LIBs—has no considerable reversible capacity for NIBs [1]. Therefore, NIBs require the development of new electrode materials. Germanium (Ge) is one promising candidate for the negative electrode, with reversible sodiation at room temperature with a relatively high theoretical capacity (NaGe, 369 mAh/g) [2], comparable to graphite for LIBs. In nanowire form, Ge can also tolerate the volume changes that occur during cycling without degradation, and a high surface area-to-volume ratio yields suitable charge/discharge kinetics in the battery.

Ge nanowires (GeNWs) were synthesized by a supercritical-fluid-liquid-solid (SFLS) growth process [3] and three procedures were applied to improve NIB performance. First, GeNWs were activated for sodiation by an initial lithiation cycle that amorphized the nanowires. Kohandehghan, et al., showed that crystalline GeNWs do not sodiate until being activated with Li [4]. Second, the surface of Na foil counter electrodes were polished to remove surface oxide, which greatly enhanced the performance of GeNW half-cells. Third, the role of the thickness of GeNW electrode layer was studied to understand kinetic limitations of the battery.

## Experimental Procedure:

GeNWs were produced by the SFLS growth process. A reactant solution containing 25  $\mu\text{L}$  of Au nanocrystal stock solution, 190  $\mu\text{L}$  of DPG, and 85  $\mu\text{L}$  of monophenylsilane (MPS) in toluene was injected into a reactor heated to 380°C and pressurized to 6.2 MPa at a rate of 0.5 mL/min for 40 minutes.

For testing in coin cells, GeNWs were combined with poly(acrylic acid) (PAA) binder and conductive carbon at a weight ratio of 70:20:10 [5]. To obtain a viscous slurry,

the mixture was dispersed in 1-methyl 2-pyrrolidinone (NMP). Then, the slurry was doctor-bladed (50-200  $\mu\text{m}$  gap) onto copper (Cu) foil and vacuum dried at 150°C. Individual 11 mm diameter circular electrodes were hole-punched from the coated Cu foil.

The GeNWs were activated for sodiation by an initial lithiation step. An LIB half-cell was assembled from stainless steel coin cells, GeNW anode, Li foil counter

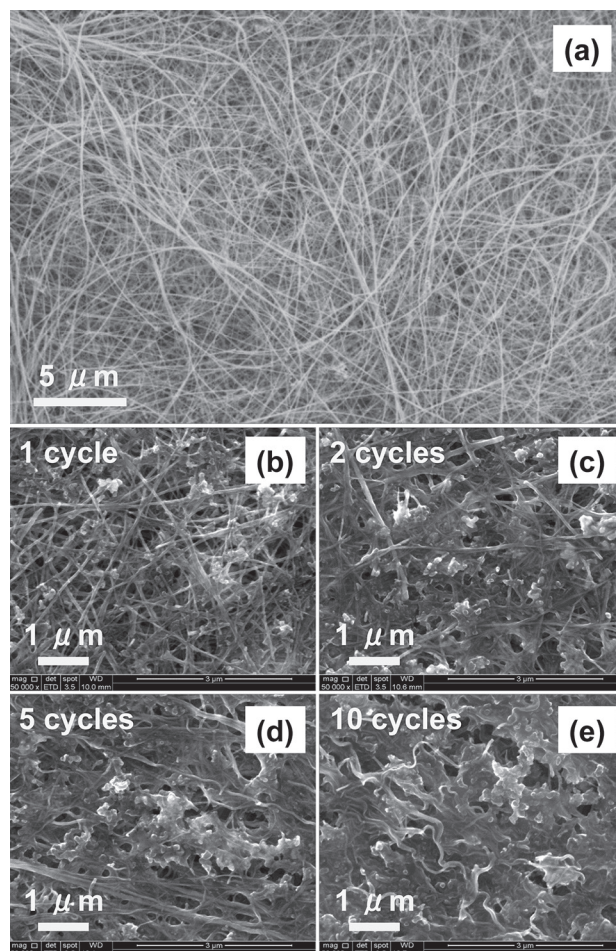
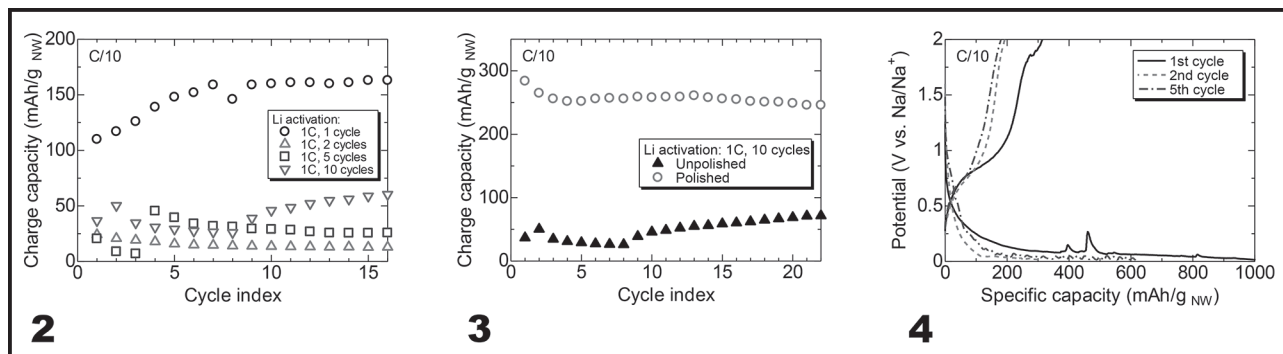


Figure 1: SEM images of (a) as-grown GeNWs and (b)-(e) Li-activated GeNWs with 1, 2, 5, and 10 cycles.



**Figure 2, left:** The charge capacity of NIBs with Li-activated GeNW anode with each cycle. **Figure 3, middle:** The charge capacity of NIBs with polished and unpolished Na foil counter electrode. **Figure 4, right:** The voltage profile of NIB with GeNW electrode film thickness of 1.0 μm.

electrode, a few drops of electrolyte, and separator. After charging and discharging with Li for one cycle at a rate of 1C, the LIB is disassembled. The GeNW anode is then reassembled into a half-cell with a Na foil counter electrode. The NIB was tested at a rate of C/10.

## Results and Conclusions:

Figures 1(a) and (b)-(e) show SEM images of the GeNWs before and after cycling against Li. In Figures 1(b)-(e), the SEM images show that the solid electrolyte interphase (SEI) layer increased in thickness with each lithiation cycle. Figure 2 shows the cycle performance of NIBs made with GeNWs activated with Li with a different number of cycles. The highest charge capacity in the NIB was obtained with a single lithiation/delithiation activation cycle. Based on the SEM data, it appears that thicker SEI layers formed during the Li activation step hampers NIB performance and should be limited as much as possible.

Figure 3 shows NIB data for GeNW coin cells made with polished and unpolished Na foils. The polished Na foil counter electrode led to charge capacities that were three times higher than the NIBs made with unpolished electrodes. To improve reversibility, the effect of GeNW electrode film thickness was studied. Figure 4 shows the voltage profile of the NIB with a GeNW layer thickness of 1.0 μm. A charge capacity of more than 300 mAh/g was obtained. Changes in the layer thickness from 0.7 μm to 1.3 μm did not affect the battery performance. This electrode layer thickness probably represents a rate-limiting thickness.

## Future Work:

Future work will involve the synthesis of tin (Sn)-coated GeNWs to enhance reversibility and rate capability in

the electrode. The influence of thinner electrode layers on the NIB rate capability and charge capacity will also be studied. Further optimization of the electrode layer density to improve the specific capacity and the Coulombic efficiency of NIBs is also desirable.

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