

Nanowire Lithium-Ion Batteries as Electrochemical Energy Storage for Electric Vehicles

Investigators

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Abstract

The goal of this project is to explore nanowires (NWs) of Li-ion battery electrode materials for improving the battery energy and power density for electric vehicles. NWs offer advantages of a large surface to volume ratio, efficient electron conducting pathways and facile strain relaxation. With Yi Cui's Stanford startup fund support to initiate the project and the GCEP support since 2007, we demonstrated that Si and Ge NWs can be used as high-energy Li ion batteries anodes. Si NW anodes were shown to have a charge storage capacity 10 times the existing carbon anodes.

Introduction

The project objective is to explore NWs of high-energy electrode materials for Li ion batteries in electric vehicles. These high-energy materials can store a lot of Li ions but have large structure change and volume expansion, which can cause mechanical failure. We try to exploit NW morphology to solve these issues.

Background

The rechargeable battery is a promising technology for reversible electricity storage in electric vehicles. Current electric vehicles are powered by lead-acid, NiCd or nickel-metal hydride batteries, which are limited by their energy density and calendar lifetime. The existing Li-ion battery technology, which uses LiCoO_2 as cathode, lithiated graphite (LiC_6) as anode, and LiPF_6 -organic solvent as electrolyte, has been the most important power source for portable electronics. However, the high cost and low production volume due to the scarcity of Co are the major hurdles to their wide applications in light duty vehicles. The solution is to decrease the cost and maximize the performance. The electrolyte in general does not limit the Li-battery technology. We identify the following as the most important areas to improve: 1) Use alternative cheaper and higher energy density cathode materials to replace scarce Co oxides; 2) Replace the anode with higher energy density and cheaper materials; 3) Maximize the performance by optimizing battery device architecture. To realize electrochemical energy storage for electric vehicles, we are working on a nanowire battery architecture combined with selection of appropriate materials. We will explore the following advantages of using NWs: 1) NWs have a very large surface to volume ratio to contact with electrolyte. 2) NWs form continuous conducting pathways for electrons through the electrodes. 3) The NW geometry can promote facile strain relaxation during battery operation.

Results

With Yi Cui's Stanford Startup Funding and the GCEP support since March 2007, we have been making progress on new generation of anodes with Si and Ge NWs.

Silicon is an attractive anode material for lithium batteries since it has a low discharge potential and the highest known theoretical capacity (4200 mAh/g)². While this is more than ten times higher than existing graphite anodes and much larger than various nitride and oxide materials^{3,4}, silicon anodes have limited applications⁵ because the 400% volume change upon insertion and extraction of lithium² results in pulverization and capacity fading. Germanium has a theoretical capacity of 1600 mAh/g . Similar as Si, Ge also has the issue of large volume expansion. Here, we show that Si and Ge NW battery electrodes circumvent these issues as they can accommodate large strain without pulverization and provide good electronic contact and conduction, and short lithium insertion distances. We achieved the theoretical capacity and could maintain a discharge capacity close to 75% of the maximum with little fading during cycling. We will focus on SiNWs for this report.

A schematic of our Si nanowire (NW) anode configuration is shown in Fig. 1b. NWs are grown directly on the metallic current collector substrate. This geometry has several advantages and has led to improvements in rate capabilities in metal oxide cathode materials¹⁵. First, the small NW diameter allows for better accommodation of the large volume changes without the initiation of fracture that can occur in bulk or micron-sized materials (Fig. 1a). Second, each SiNW is electrically connected to the metallic current collector so that they all contribute to the capacity. Third, the SiNWs have direct 1D electronic pathways allowing for efficient charge transport. In electrode microstructures based on particles, electronic charge carriers must go through small interparticle contact areas. In addition, since every NW is connected to the current-carrying electrode, the need for binders or conducting additives, which add extra weight, is eliminated. We realized our SiNW battery electrode using the vapor-liquid-solid (VLS) growth directly on stainless steel current collectors.

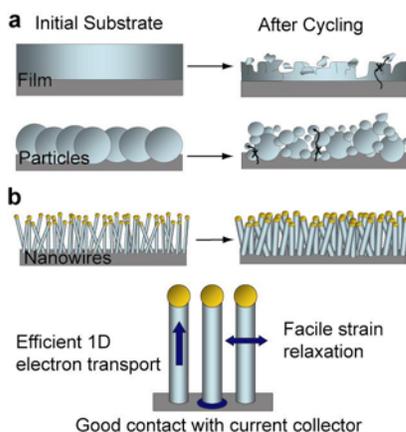


Figure 1 Cartoon depiction of morphological changes that occur in Si during electrochemical cycling. (a) The volume of silicon anodes changes by about 400% during cycling. As a result, Si films and particles tend to pulverize during cycling. (b) NWs

grown directly on the current collector do not pulverize or break into smaller particles after cycling.

SiNW battery electrodes have been tested with cyclic voltammetry and constant current charging and discharging (Fig. 2). The charge current associated with the formation of the Li-Si alloy began at ~ 330 mV and became quite large below 100 mV. Upon discharge, current peaks appeared at about 370 and 620 mV. The current-potential characteristics were consistent with previous experiments on microstructured Si anodes. Fig. 2b shows the first and second cycles at the C/20 rate (20 hr). The voltage profile observed was consistent with previous Si studies, with a long flat plateau during the first charge, during which crystalline Si reacted with Li to form amorphous Li_xSi . Subsequent discharge and charge cycles had different voltage profiles characteristic of amorphous Si. Significantly, the observed capacity during this first charging operation was 4277 mAh/g, which is essentially equivalent to the theoretical capacity within experimental error. The first discharge capacity was 3124 mAh/g, indicating a coulombic efficiency of 73%. The second charge capacity decreased by 17% to 3541 mAh/g although the second discharge capacity increased slightly to 3193 mAh/g, giving a coulombic efficiency of 90%. Both charge and discharge capacities remained nearly constant for subsequent cycles with little fading up to 10 cycles (Fig. 2d). As a comparison, our charge and discharge data are shown along with the theoretical capacity (372 mAh/g) for the graphite currently used in lithium battery anodes, and the charge data reported for thin films containing 12 nm Si nanocrystals (NCs) in Fig. 2d. This improved capacity and cycle life in the SiNWs indicates the advantages of our SiNW anode design. The SiNWs displayed high capacities at higher currents as well. Fig. 2c shows the charge and discharge curves observed at the C/10, C/5, C/2, and 1C rates. Even at the 1C rate, the capacities remained >2100 mAh/g, which is still five times larger than that of graphite.

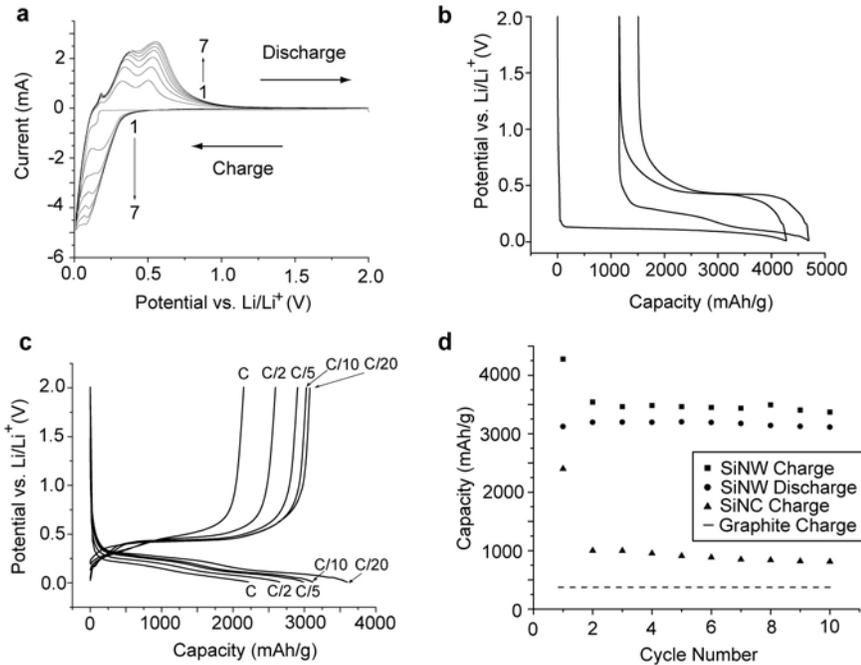


Figure 2 Electrochemical data for SiNW electrodes. (a) Cyclic voltammogram for SiNWs vs. Li/Li^+ . (b) The voltage profiles for the first and second galvanostatic cycles of the SiNWs at the C/20 rate. (c) The voltage profiles for the SiNWs cycled at different power rates. The C/20 profile is from the second cycle. (d) Capacity vs. cycle number for the SiNWs at the C/20 rate showing the charge (squares) and discharge capacity (circles). The charge data for Si nanocrystals (NCs) (triangles) and the theoretical capacity for lithiated graphite (dashed line) are shown as a comparison.

The structural morphology changes during Li insertion were studied to understand the high capacity and good cyclability of our SiNW electrodes. Pristine, unreacted SiNWs were crystalline with smooth sidewalls (Fig. 3a) and average diameter of ~ 89 nm (standard deviation 45 nm) (Fig. 3e). Cross-section SEM showed that the SiNWs grew off the substrate and had good contact with the stainless steel current collector (Fig. 3a, inset). After charging with Li, the SiNWs had roughly textured sidewalls (Fig. 3b) and the average diameter increased to ~ 141 nm (standard deviation 64 nm). Despite the large volume change, the SiNWs remained intact and did not break into smaller particles. They also appeared to remain in contact with the current collector, suggesting minimal capacity fade due to electrically disconnected material during cycling.

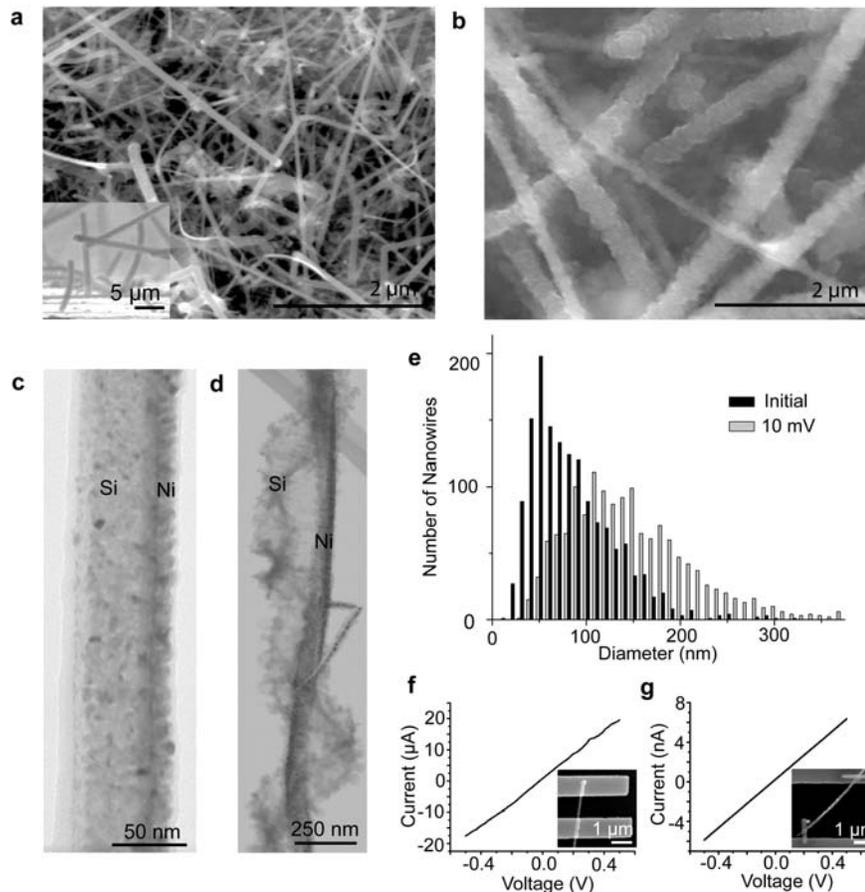


Figure 3 Morphology and electronic changes in SiNWs from reaction with Li. SEM image of pristine SiNWs before (a) and after (b) electrochemical cycling with the same

magnification. The inset is (a) is a cross-section image showing the NWs are directly contacting the stainless steel current collector. TEM image of a pristine SiNW with a partial Ni coating before (c) and after (d) after Li cycling. (e) Size distribution of NWs before and after charge to 10 mV (bin size 10 nm). The average diameter of the NWs increased from 89 to 141 nm after lithiation. (f) The I-V curve for a single NW device (SEM image, inset) constructed from a pristine SiNW. (g) The I-V curve for a single NW device (SEM image, inset), constructed from a NW that had been charged and discharged once at the C/20 rate.

The SiNWs also change their length during the change in volume. To evaluate this, 25 nm Ni was evaporated onto as-grown SiNWs using electron beam evaporation. Because of the shadow effect of the SiNWs, the Ni only covered part of the NW surface (Fig. 3c). Ni is inert to Li and acts as a rigid backbone on the SiNWs. After lithiation (Fig. 3d), the SiNW changed shape and wrapped around the Ni backbone in a 3-dimensionally helical manner. This appeared to be due to an expansion in the length of the NW, which caused strain because the NW was attached to the Ni and could not freely expand but rather buckled into a helical shape. Although the NW length increased after lithiation, the NWs remained continuous and without fractures, maintaining the continuous pathway for electrons all the way from the collector to the NW tips.

Efficient electron transport from the current collector to the SiNWs is necessary for good battery cycling. To evaluate this, we conducted electron transport measurements on single SiNWs before and after lithiation. The current vs. voltage curve on a pristine SiNW was linear, with a 25 k Ω resistance (resistivity of 0.02 Ω -cm) (Fig. 3f). After one cycle, the NWs became amorphous but still showed linear behavior with an 8 M Ω resistance (resistivity of 3 Ω -cm) (Fig. 3g). The good conductivity of pristine and cycled NWs ensures efficient electron transport for charge and discharge.

The large volume increase in the SiNWs is driven by the dramatic atomic structure change during lithiation. To understand the structural evolution of NWs, we characterized the NW electrodes at different charging potentials. We have used X-ray diffraction (XRD) and transmission electron microscopy to follow the structure transformation (Fig. 4). We found that single crystalline SiNWs become amorphous with Li insertion and stay at amorphous state after the first cycle.

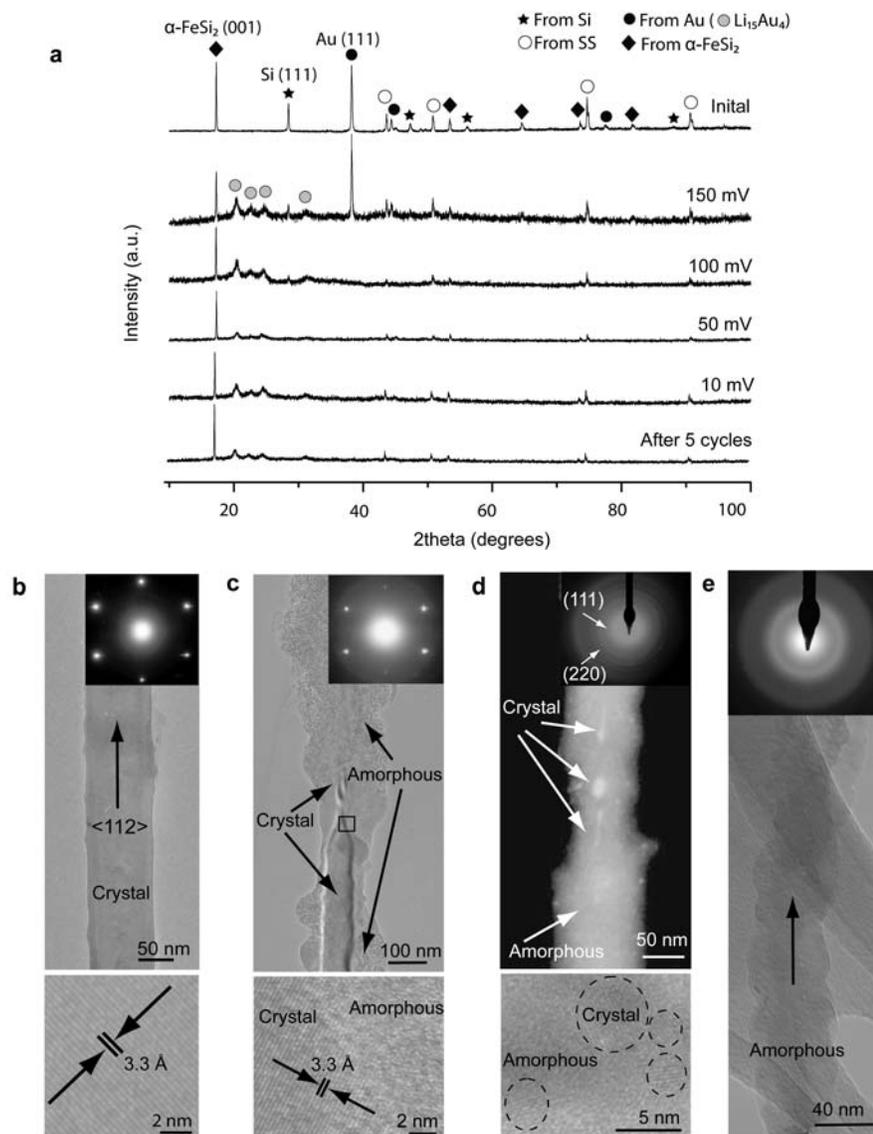


Figure 4 Structural evolution of SiNWs during lithiation. **(a)** XRD of SiNWs before electrochemical cycling (initial), at different potentials during the first charge, and after 5 cycles. **(b-e)** TEM data for SiNWs at different stages of the first charge. **(b)** A single crystalline, pristine SiNW before electrochemical cycling. **(c)** A NW charged to 100 mV showing a Si crystalline core and the beginning of a Li_xSi amorphous shell being formed. **(d)** Dark field image of a NW charged to 50 mV showing an amorphous Li_xSi wire with crystalline Si grains (bright regions) in the core. The spotty rings in the SAED are from crystalline Si. The HRTEM shows some Si crystal grains imbedded in the amorphous wire. **(e)** A NW charged to 10 mV is completely amorphous $\text{Li}_{4.4}\text{Si}$.

Progress

Transportation accounts for a quarter of global carbon dioxide emissions from energy use, which is expected to approach one-third over the coming decades as the mobility of the world's population increases. Our progress achieved in Si and Ge NWs will allow us to increase the anode charge storage capacity significantly (Si with 10 times, Ge with 4 times of the existing carbon anode). This is an important step towards the ultrahigh overall energy density of Li ion batteries. Our proposed nanowire Li battery devices inter-convert electrical and chemical energy with ~90% efficiency and can provide a carbon-free energy option for electrical vehicles. This can allow significant reductions of greenhouse gas emissions in the transportation sector, provided the electricity is produced with low net greenhouse gas emissions. We believe that if our research is successful, the global greenhouse gas emission can be substantially reduced over the long term.

Future Plans

We plan to carry out the following studies to realize our nanowire batteries with high energy and power density: 1) Anodes: we will continue developing Si and Ge NW anodes. We will study the chemical stability, mechanical stability, cycle life, calendar life and safety. 2) Cathodes: We will develop the synthesis for new high energy cathode nanowires and test their performance.

Presentation Resulted from This Project

1. (*Invited talk*) "Solar Cells and Batteries with Inorganic Nanowires" ACS spring meeting, One-dimensional Nanomaterials Symposium, Division of Inorganic Chemistry, Chicago, Illinois, Mar. 28, 2007.
2. (*Talk*) "Metal Oxide Nanowires as Li Battery Electrodes" MRS Spring meeting, Symposium JJ, San Francisco, California, Apr. 11, 2007.
3. (*Invited talk*) "Engineering Nanowires for Energy Sciences" SPIE Optics East Meeting, Boston, Massachusetts, Sep. 9-12, 2006.
4. (*Invited talk*) "Inorganic Nanowires for Energy Sciences and Nanoelectronics" UC Berkeley Nano Institute Seminar Series, Berkeley California Sep. 14, 2007.
5. (*Invited talk*) "Nanowires for Nanoscale Electronics, Biosensors and Energy Applications" The 2007 International Conference on Solid State Devices and Materials, Sep. 19-21, 2007, Tsukuba, Japan.
6. (*Invited talk*) "Inorganic Nanowires as Advanced Energy Conversion and Storage Materials" The Global Energy and Climate Projects Annual Symposium, Stanford, California, Oct. 1-3, 2007.
7. (*Invited talk*) "In-situ Electron Microscopy Studies of Transformation in Nanowires" Molecular Foundry User Workshop, Berkeley, California, Oct. 5, 2007.
8. (*Invited talk*) "Nanowire Lithium-Ion Batteries" Center for Probing the Nanoscale Introductory Seminar "The Tools of Nanotechnology", Stanford, California, Nov. 29, 2007.
9. (*Invited talk*) "Nanowires Enabled Energy- and Bio- Technologies", Seminar series, Center for Cancer Nanotechnology Excellence Focused on Therapy, Stanford, California, Dec. 18, 2007.
10. (*Invited talk*) "Synthesis of Nanowires in Vapor Phase and New Directions" Center for Integrated Nanotechnologies, the 6th User Workshop, Jan. 9-10, 2008, Albuquerque, New Mexico.
11. (*Invited talk*) "Nanowires as Energy Materials: Batteries and Solar Cells" Stanford Linear Accelerator Center Colloquium, Feb 25, 2008.

12. (Invited talk) “Next Generation of Battery Technology: When Nanotechnology Meets Energy Storage Applications” Chinese American Semiconductor Professional Association (CASPA) Symposium, San Jose, California, Mar 1, 2008.
13. (Invited talk) “Energy Nanowires” MRS Spring meeting, Symposium O, San Francisco, California, Mar 24-28, 2008.
14. (Invited talk) “Phase-Change Nanowires: Synthesis and Switching Properties” MRS Spring meeting, Symposium G, San Francisco, California, Mar 24-28, 2008.
15. (Invited talk) “Nanowire Materials for Energy and Nanoelectronics”, Stanford Physics/Applied Physics Colloquium, Apr 1, 2008.
16. (Invited talk) “Batteries, solar cells and transparent conducting electrodes with nanowires” ACS spring meeting, New Orleans, LA, Apr. 6-10, 2008.
17. (Invited talk) “Energy Nanowire Materials: Batteries and Solar Cells”, Electronic Materials Symposium, Santa Clara, California, Apr 11, 2008.
18. (Invited talk) “Nanowire Batteries” GCEP Student Forum, Stanford, California, Apr 14, 2008.
19. (Invited talk) “Nanotechnology-Enabled Memory and Energy Applications” Chinese American Information Storage Society dinner seminar, Sunnyvale, California, Apr 17, 2008.
20. (Invited talk) “Nanowire Li-ion Batteries” Electric Aircraft Symposium hosted by CAFE Foundation, Millbrae, California, Apr. 26, 2008.

Publications

1. C. K. Chan, H. Peng, G. Liu, K. McIlwrath, X. F. Zhang, R. A. Huggins, Y. Cui “High Performance Lithium Battery Anodes Using Silicon Nanowires” *Nature Nanotech.* 3, 31-35 (2008).
2. C. K. Chan, X. F. Zhang, Y. Cui “High Capacity Li-ion Battery Anodes Using Ge Nanowires” *Nano Lett.* 8, 307-309 (2008).

References

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