

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. Detailed characterization has been carried out to understand the important information about the structure change, solid electrolyte interphase (SEI) and the impedance at each components/interfaces. A crystalline-amorphous core-shell Si NW electrode concept has also been developed. Spinel LiMn_2O_4 nanorods have been developed as a low-cost, environmentally friendly, and highly abundant material for Li ion battery cathodes.

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

Anodes

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). While this is more than ten times higher than existing graphite anodes and much larger than various nitride and oxide materials, silicon anodes have limited applications because the 400% volume change upon insertion and extraction of lithium 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. We have shown 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 (Fig. 1). We achieved the theoretical capacity and could maintain a discharge capacity close to 75% of the maximum with little fading during cycling.

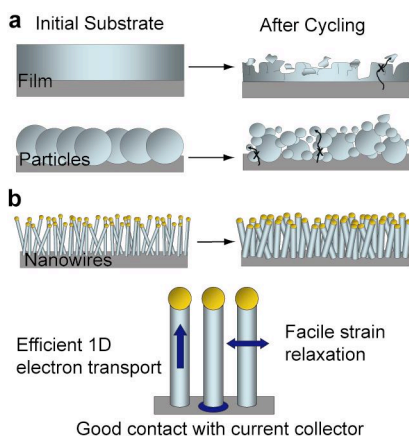


Figure 1 Cartoon depiction of morphological changes that occur in Si during electrochemical cycling. **(a)** The volume of silicon anodes changes by about 400% during cycling. As a result, Si films and particles tend to pulverize during cycling. **(b)** NWs grown directly on the current collector do not pulverize or break into smaller particles after cycling.

In past one year, we have performed detailed characterization of Si NW and try to understand the important information about the structure change, solid electrolyte interphase (SEI) and the impedance at each components/interfaces. We have also developed a crystalline-amorphous core-shell Si NW electrode concepts, which show further improvement.

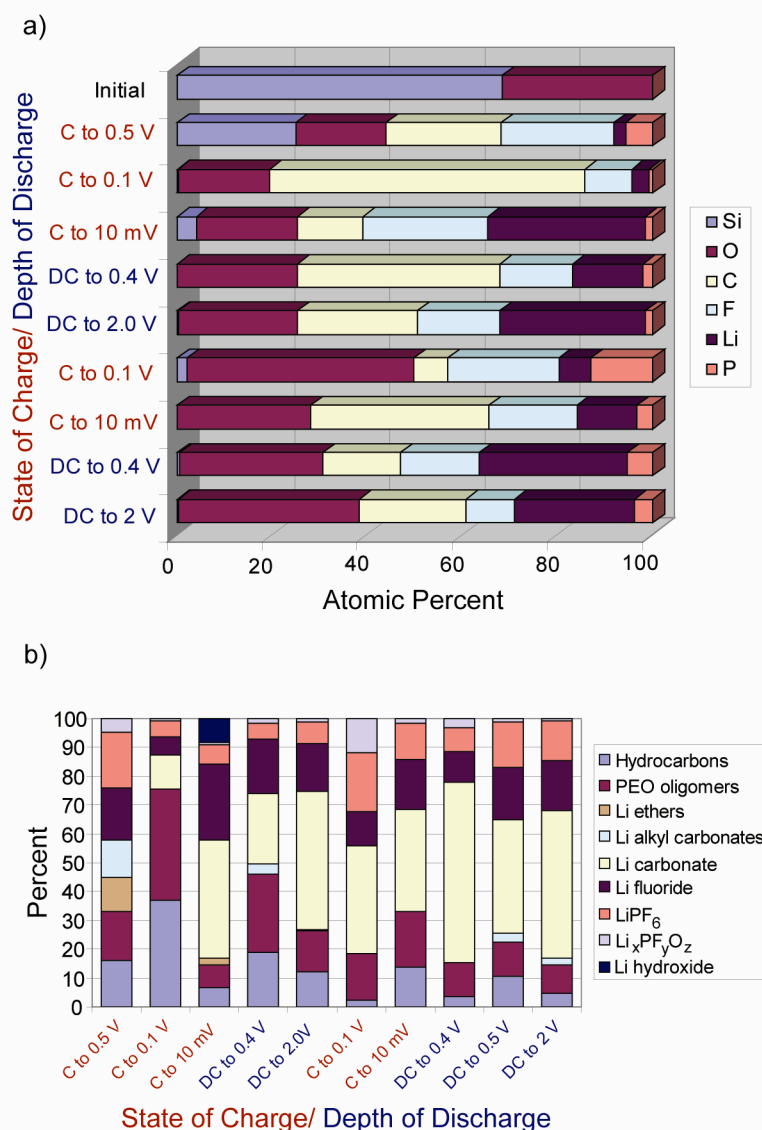


Figure 2. (a) Surface composition of the SiNW samples as derived from the XPS survey scan. The atomic percentages are shown for different potentials during the charge and discharge. (b) Molecular species found on the surface of the SiNW samples at different potentials as determined from the XPS high resolution scans.

The formation of SEI layers is critical for the battery operation and safety. We have characterized the nature of the SEI layer formed on Si NW anodes. We found that a great deal of the SEI formation occurs at potentials where Li insertion into the Si is also taking place. The SEI is composed of reduction products similar to that found on graphite electrodes, with Li_2CO_3 as an important component. The SEI consists of two main layers: inorganic lithium compounds as inner layers and organic lithium compounds as an outer layer (Fig. 2). The fact that the Si expands in volume at the same time also contributes to the dynamic nature of the SEI film. The morphology of the SEI was found to be voltage-dependent, with a thick layer consisting of large particles forming at low potentials, which partially dissolves and forms cracks as the potential is increased in the discharge.

Improved cycling performance was observed when tuning the voltage cutoffs to avoid large changes in SEI morphology, suggesting that the cycle life in SiNWs may rely a great deal on the SEI layer. This may be due to the enhanced reactivity of SiNWs due to the large surface area, as well as the composition of SEI products formed on the surface of the NW. Thus, it will be beneficial to explore different electrolytes and additives to determine the optimal SEI layer for long-term cycling.

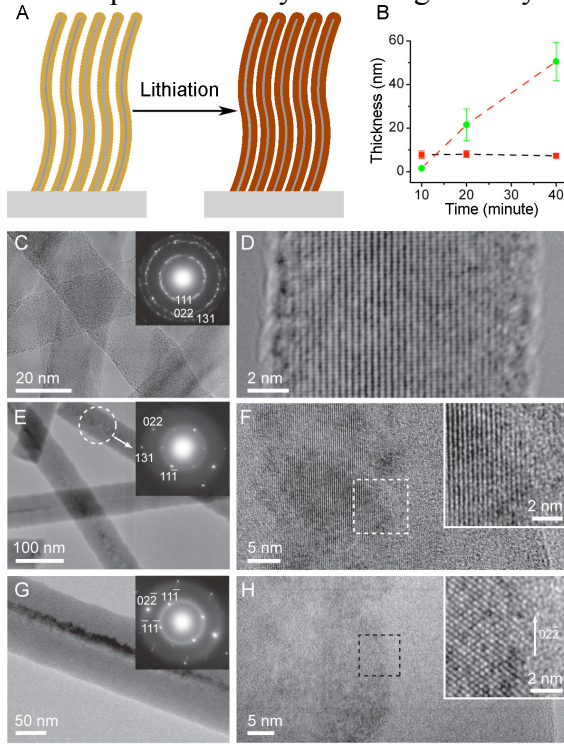


Figure 3. (A) Schematic illustration of the lithiation of the Si c-a core-shell NWs grown on a SS substrate. (B) Statistics of the core radius (red) and shell thickness (green) versus growth time. The growth temperature was 485 °C. (C) TEM and SAED images of NWs grown for 10 minutes. (D) HRTEM image of a NW grown for 10 minutes. (E) TEM and SAED images of NWs grown for 20 minutes. (F) HRTEM images of a NW grown for 20 minutes. (G) TEM and SAED images a NW grown for 40 minutes. (H) HRTEM images of a NW grown for 40 minutes.

The impedance behavior of Si NW electrodes has been investigated to understand the electrochemical process kinetics that influences the performance when used as a high capacity anode in a lithium-ion battery. The ac response was measured using impedance spectroscopy in equilibrium conditions at different lithium compositions and during several cycles of charge and discharge in a half cell vs. metallic lithium. The impedance analysis shows the contribution of both surface resistance and solid state diffusion through the bulk of the NWs. The surface process is dominated by a solid electrolyte layer (SEI) consisting of an inner, inorganic insoluble part and several organic compounds at the outer interface, as seen by XPS analysis. The surface resistivity, which seems to be correlated with the coulombic efficiency of the electrode, grows at very high lithium contents due to an increase in the inorganic SEI thickness. We estimate the diffusion coefficient of about 2×10^{-10} cm²/s for lithium diffusion in silicon. A large

increase in the electrode impedance was observed at very low lithium compositions, probably due to a different mechanism for lithium diffusion inside the wires. Restricting the discharge voltage to 0.7 V prevents this large impedance and improves the electrode lifetime. Cells cycled between 0.07 and 0.70 V vs. metallic lithium at a current density of 0.84 A/g (C/5) showed good coulombic efficiency (about 99%) and maintained a capacity of about 2000 mAh/g after 80 cycles.

We also introduced a core-shell design of Si NWs (Fig. 3) for high power and long life lithium battery electrodes. Silicon crystalline-amorphous core-shell NWs were grown directly on stainless steel current collectors by a simple one-step synthesis. Amorphous Si shells instead of crystalline Si cores can be selected to be electrochemically active due to the difference of their lithiation potentials. Therefore, crystalline Si cores function as a stable mechanical support and an efficient electrical conducting pathway while amorphous shells store Li^+ ions. We demonstrate that these core-shell NWs have high charge storage capacity (~ 1000 mAh/g, 3 times of carbon) with $\sim 90\%$ capacity retention over 100 cycles. They also show excellent electrochemical performance at high rate charging and discharging (6.8 A/g, ~ 20 times of carbon at 1 hour rate).

Cathodes:

Spinel LiMn_2O_4 is a low-cost, environmentally friendly, and highly abundant material for Li ion battery cathodes. We have successfully carried out the hydrothermal synthesis of single-crystalline $\beta\text{-MnO}_2$ nanorods and their chemical conversion into free-standing single-crystalline LiMn_2O_4 nanorods using a simple solid-state reaction (Fig. 4). The LiMn_2O_4 nanorods have an average diameter of 130 nm and length of 1.2 μm . Galvanostatic battery testing showed that LiMn_2O_4 nanorods have a high charge storage capacity at high power rates compared with commercially available powders. More than 85% of the initial charge storage capacity was maintained for over 100 cycles. The structural transformation studies showed that the Li ions intercalated into the cubic phase of the LiMn_2O_4 with a small change of lattice parameter, followed by the co-existence of two nearly identical cubic phases in the potential range of 3.5 to 4.3V.

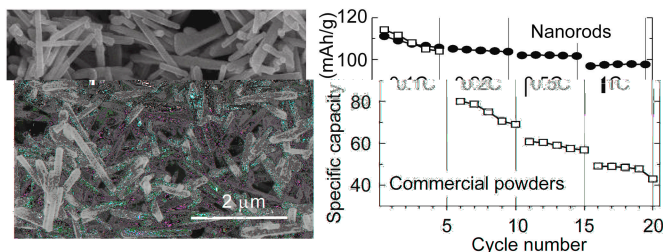


Figure 4. Left, SEM image of LiMn_2O_4 nanorods. Right, battery cycling of nanorods versus commercial powders.

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 results in LiMn_2O_4 nanorods afford good cathode materials as cathodes. 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 with core-shell structures. 2) Cathodes: We will develop the synthesis for new high energy cathode nanostructures 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.
21. (*Invited guest lecturer*) “Nanomaterials for Energy Storage and Conversion”, ME 370C Course: Advanced Energy System Modeling, Stanford University, Apr. 29, 2008.
22. (*Invited guest lecturer*) “Nanowire Materials for Energy and Nanoelectronics” Symyx Technologies, Inc., Sunnyvale, California, Apr. 30, 2008.
23. (*Invited talk*) “Nanowires as New Generation of Materials for Battery and Solar cells” Round Table Day, Center for Integrated Systems, Stanford University, May 13, 2008.
24. (*Talk*) “Nanowire Electrodes for Next Generation of Li-Ion Battery” Electrochemical Society Annual Meeting, Phoenix, Arizona, May 18-23, 2008.
25. (*Invited talk*) “In-situ TEM Studies of Phase-Change Nanowires” *International Workshop on In Situ Electron Microscopy in Advanced Materials Research*, Beijing, China, June 1-2, 2008.
26. (*Invited talk*) “Energy Nanowire Materials” Chinese National Center for Nano science and Technology, Beijing, China, June 2, 2008.
27. (*Invited talk*) “Nanowire Energy Materials” Micronano08 conference, Hong Kong, June 3-4, 2008.
28. (*Invited talk*) “In-situ TEM Dynamics of Phase-Change Nanowires” Conference on Innovative Dynamic Studies of Materials at the Nanoscale, June 29-July 4, 2008 Gyeong-ju, Korea.
29. (*Invited talk*) “Nanoscale Transformation in Nanowires and Nanocrystals: Implication to Energy and Electronics Science” PULSE seminar, Stanford Linear Accelerator Center, Jul. 10, 2008.
30. (*Invited talk*) “Energy Storage Research at Stanford” The first annual meeting of the Affiliates Program for the Woods and Precourt Institutes, Stanford University, Sep 12, 2008.
31. (Poster) “Nanowire Electrodes as Li-Ion Battery Anodes and Cathodes” the 1st International Conference on Advanced Lithium Batteries for Automobile Applications, Argonne National Laboratory, Sep. 15-17, 2008.
32. (*Invited talk*) “Materials Science: Where Nanotechnology, Energy Technology and Biotechnology Meet”, Stanford Freshman Orientation, Sep. 18, 2008.
33. (*Invited talk*) “Next Generation of Battery Technology for Green Energy” Annual Conference of North America Chinese Semiconductor Association (NACSA), San Jose, CA, Oct. 4, 2008.
35. (*Invited talk*) “Nanowire Energy Sciences”, School of Engineering Seminar, University of California, Merced, Oct. 17, 2008.
36. (*Invited talk*) “Nanowire Energy Sciences”, the local San Francisco section of the Electrochemical Society, Palo Alto, California, Nov 6, 2008.
37. (*Invited talk*) “Energy Nanowires”, 4th Annual Minnesota Nanotechnology Conference, University of Minnesota, Nov. 12, 2008.

38. (Invited talk) “Designing Nanomaterials for Energy Storage: Batteries and Supercapacitors” Stanford Energy Seminar, Nov. 19, 2008.
39. (Invited talk) “Application and Commercialization Plan in Batteries and Fuel Cells” KAUST Workshop: Commercialization of Next Generation Energy Technologies, Stanford University, Nov. 24, 2008.
40. (Invited talk) “Nanowire Batteries for Next Generation of Electronics”, IEDM Meeting, San Francisco, California, Dec 15-18, 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).
3. L.-F. Cui, R. Ruffo, C. K. Chan, H. Peng, Y. Cui “Crystalline-Amorphous Core-Shell Silicon Nanowires for High Capacity and High Current Battery Electrodes” *Nano Lett.* 9, 491-495 (2009).
4. C. K. Chan, R. Ruffo, S. S. Hong, R. A. Huggins, Y. Cui “Structural and Electrochemical Study of the Reaction of Lithium with Silicon Nanowires” *J. Power Sources* 189, 34-39 (2009).
5. D. K. Kim, P. Muralidharan, H.-W. Lee, R. Ruffo, Y. Yang, C. K. Chan, H. Peng, R. A. Huggins, Y. Cui “Spinel LiMn_2O_4 Nanorods as Li-ion Battery Cathodes” *Nano Lett.* 8, 3948-3952 (2008).
6. C. K. Chan, S. T. Connor, C.-M. Hsu, R. A. Huggins and Y. Cui “Nanowire Batteries for Next Generation of Electronics” *IEDM* (Invited paper, submitted).
7. R. Ruffo, S. S. Hong, C. K. Chan, R. A. Huggins, Y. Cui “Impedance Analysis of Silicon Nanowire Lithium-ion Battery Anodes” *J. Phy. Chem. C* (submitted).

References

None.

Contacts

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