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

 Investigators
Yi Cui, Assistant Professor, Materials Science and Engineering and Geballe Laboratory for Advanced Materials; Friedrich B. Prinz, Professor, Materials Science and Engineering and Mechanical Engineering; Candace K. Chan, Yuan Yang, Seung Sae Hong and Li-Feng Cui Graduate and Postdoctoral Researchers.

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. Core shell NW concepts including crystalline-amorphous Si and carbon-Si core-shell have also been developed. Spinel LiMn2O4 nanorods have been developed as a low-cost, environmentally friendly, and highly abundant material for Li ion battery cathodes. Single nanowire battery diagnostics method has also been developed to correlate structure change with electrochemical property.

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 nickelmetal hydride batteries, which are limited by their energy density and calendar lifetime. The existing Li-ion battery technology, which uses LiCoO2 as cathode, lithiated graphite (LiC6) as anode, and LiPF6-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](image)

**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.

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. 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$_2$CO$_3$ 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 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 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 $2 \times 10^{-10}$ cm$^2$/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.

**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.
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 ~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).

In addition, we also designed carbon-Si core-shell structure, in which carbon core is electrically conducting and mechanical stable.

**Cathodes:**
Spinel LiMn$_2$O$_4$ 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 $\beta$-MnO$_2$ nanorods and their chemical conversion into free-standing single-crystalline LiMn$_2$O$_4$ nanorods using a simple solid-state reaction (Fig. 4). The LiMn$_2$O$_4$ nanorods have an average diameter of 130 nm and length of 1.2 μm. Galvanostatic battery testing showed that LiMn$_2$O$_4$ 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$_2$O$_4$ 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$_2$O$_4$ nanorods. Right, battery cycling of nanorods versus commercial powders.

We also developed single nanostructure devices as a powerful new diagnostic tool for batteries with LiMn$_2$O$_4$ nanorod materials as an example. LiMn$_2$O$_4$ and Al-doped LiMn$_2$O$_4$ nanorods were synthesized by a two-step method that combines hydrothermal synthesis of $\beta$-MnO$_2$ nanorods and a solid state reaction to convert them to LiMn$_2$O$_4$ nanorods. $\lambda$-MnO$_2$ nanorods were also prepared by acid treatment of LiMn$_2$O$_4$ nanorods. The effect of electrolyte etching on these LiMn$_2$O$_4$-related nanorods is investigated by both SEM and single-nanorod transport measurement, and this is the first time that the transport properties of this material have been studied at the level of an individual single-
crystalline particle. Experiments show that Al dopants reduce the dissolution of Mn\(^{3+}\) ions significantly and make the LiAl\(_{0.1}\)Mn\(_{1.9}\)O\(_4\) nanorods much more stable than LiMn\(_2\)O\(_4\) against electrolyte etching, which is reflected by the magnification of both size shrinkage and conductance decrease. These results correlate well with the better cycling performance of Al-doped LiMn\(_2\)O\(_4\) in our Li-ion battery tests: LiAl\(_{0.1}\)Mn\(_{1.9}\)O\(_4\) nanorods achieve 96% capacity retention after 100 cycles at 1C rate at room temperature, and 80% at 60°C, while LiMn\(_2\)O\(_4\) shows worse retention of 91% at room temperature, and 69% at 60°C. Moreover, temperature-dependent I-V measurements indicate that the sharp resistance increase due to charge ordering transition at 290 K does not appear in our LiMn\(_2\)O\(_4\) nanorod samples, suggesting good battery performance at low temperature.

**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\(_2\)O\(_4\) 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 would like to ask for no-cost extension until 2/28/201. We plan to carry out the following studies to realize our nanowire batteries with high energy and power density: a) The in-situ NW battery device inside TEM to correlate the structure and property. b) The in-situ NW battery device inside X-ray to correlate the structure, bonding and property. c) Further Si NW anode development particularly on SEI layer formation and control. d) Cathode NW materials development, particularly on LiNixMn\(_{1-x}\)O\(_2\) materials system.

**Presentation Resulted from This Project**

2. *(Talk)* “Metal Oxide Nanowires as Li Battery Electrodes” MRS Spring meeting, Symposium JJ, San Francisco, California, Apr.11 , 2007.
33. *(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.
42. *(Invited talk)* “Designing Nanomaterials for Energy Conversion and Storage” The American Vacuum Society Thin Film Users Group Meeting, San Jose, California, Feb 18, 2009.
47. (Invited talk) “Designing Nanostructured Materials for Photovoltaics and Energy Storage” Fudan University, Shanghai, China, Apr 7, 2009.


Publications


**Contacts**
Yi Cui: yicui@stanford.edu
Friedrich B. Prinz: fbp@cdr.stanford.edu