There is great interest in developing rechargeable lithium batteries with higher energy capacity and longer cycle life for applications in portable electronic devices, electric vehicles and implantable medical devices. Silicon is an attractive anode material for lithium batteries because it has a low discharge potential and the highest known theoretical charge capacity (4,200 mAh g\(^{-1}\); ref. 2). Although 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 silicon's volume changes by 400% upon insertion and extraction of lithium, which results in pulverization and capacity fading. Here, we show that silicon nanowire battery electrodes circumvent these issues as they can accommodate large strain without pulverization, provide good electronic contact and conduction, and display short lithium insertion distances. We achieved the theoretical charge capacity for silicon anodes and maintained a discharge capacity close to 75% of this maximum, with little fading during cycling.

Previous studies in which Si bulk films and micrometre-sized particles were used as electrodes in lithium batteries have shown capacity fading and short battery lifetime due to pulverization and loss of electrical contact between the active material and the current collector (Fig. 1a). The use of sub-micrometre pillars and micro- and nanocomposite anodes led to only limited improvement. Electrodes made of amorphous Si thin films have a stable capacity over many cycles, but have insufficient material for a viable battery. The concept of using one-dimensional (1D) nanomaterials has been demonstrated with carbon, Co foil, CuO, (refs 11, 12), SnO\(_2\) (ref. 13) and TiO\(_2\) (ref. 14) anodes, and has shown improvements compared to bulk materials. A schematic of our Si nanowire (NW) anode configuration is shown in Fig. 1b. Nanowires 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 materials. 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). This is consistent with previous studies that have suggested a materials-dependent terminal particle size below which particles do not fracture further. Second, each Si NW is electrically connected to the metallic current collector so that all the nanowires contribute to the capacity. Third, the Si NWs have direct 1D electronic pathways allowing for efficient charge transport. In electrode microstructures based on particles, electronic charge carriers must move through small interparticle contact areas. In addition, as every NW is connected to the current-carrying electrode, the need for binders or conducting additives, which add extra weight, is eliminated. Furthermore,
our Si NW battery electrode can be easily realized using the vapour–liquid–solid (VLS) or vapour–solid (VS) template-free growth methods18–23 to produce NWs directly onto stainless steel current collectors (see Methods).

A cyclic voltammogram of the Si NW electrode is shown in Fig. 2a. The charge current associated with the formation of the Li–Si alloy began at a potential of ~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 anodes6. The magnitude of the current peaks increased with cycling due to activation of more material to react with Li in each scan6. The small peak at 150–180 mV may have been due to reaction of the Li with the gold catalyst, which makes a negligible contribution to the charge capacity (see Supplementary Information, Figs S1 and S2).

Si NWs were found to exhibit a higher capacity than other forms of Si (ref. 5). Figure 2b shows the first and second cycles at the C/20 rate (20 h per half cycle). The voltage profile observed was consistent with previous Si studies, with a long flat plateau (0.5–0.7 V) during the first charge (Fig. 2b)8. Although solid electrolyte interphase (SEI) formation has been observed in Si (ref. 28), we do not believe this is the cause of our observed irreversible capacity loss, because there is no appreciable capacity in the voltage range of the SEI layer formation (0.5–0.7 V) during the first charge (Fig. 2b)8. Although SEI formation may occur during cycling in Si NWs, the capacity involved in SEI formation would be very small compared to the high charge capacity we observed. The mechanism of the initial irreversible capacity loss in Si NW anodes is not yet understood and requires further investigation.

The structural morphology changes during Li insertion were studied to understand the high capacity and good cyclability of our Si NW electrodes. Pristine, unreacted Si NWs were crystalline.
with smooth sidewalls (Fig. 3a) and had an average diameter of ~89 nm (s.d., 45 nm) (Fig. 3e). Cross-sectional scanning electron microscopy (SEM) showed that the Si NWs grew off the substrate and had good contact with the stainless steel current collector (Fig. 3a, inset). After charging with Li, the Si NWs had roughly textured sidewalls (Fig. 3b), and the average diameter increased to ~141 nm (s.d., 64 nm). Despite the large volume change, the Si NWs 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.

The Si NWs may also change their length during the change in volume. To evaluate this, 25-nm Ni was evaporated onto as-grown Si NWs using electron beam evaporation. Because of the shadow effect of the Si NWs, the Ni only covered part of the NW surface (Fig. 3c), as confirmed by energy dispersed X-ray spectroscopy (EDS) mapping (see Supplementary Information, Fig. S4). The Ni is inert to Li and acts as a rigid backbone on the Si NWs. After lithiation (Fig. 3d), the Si NWs changed shape and wrapped around the Ni backbone in a three-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 a pathway for electrons all the way from the collector to the NW tips. With both a diameter and length increase, the Si NW volume change after Li insertion appears to be about 400%, consistent with the literature.

Efficient electron transport from the current collector to the Si NWs is necessary for good battery cycling. To evaluate this, we conducted electron transport measurements on single Si NWs before and after lithiation (see Methods). The current versus voltage curve on a pristine Si NW was linear, with a 25 kV resistance (resistivity of 0.02 V·cm) (Fig. 3f). After one cycle, the NWs became amorphous, but still exhibited a current that was linear with voltage with an 8 MΩ resistance (resistivity of 3 V·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 Si NWs 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. The X-ray diffraction (XRD) patterns were taken for initial pristine Si NWs, Si NWs charged to 150 mV, 100 mV, 50 mV and 10 mV, as well as after 5 cycles (Fig. 4a). XRD patterns of the as-grown Si NWs...
showed diffraction peaks associated with Si, α-FeSi₂, Au (the Si NW catalyst) and stainless steel (SS). The α-FeSi₂ forms at the interface between the SS and the Si wires during the high temperature (530 °C) NW growth process. The α-FeSi₂ was not found to appreciably react with Li during electrochemical cycling, although a small amount of reaction has been reported. After Si NWs were charged to 150 mV, the higher angle Si peaks disappeared. Only the Si(111) peak was still visible, but its intensity was greatly decreased. This is consistent with the disappearance of the initial crystalline Si and the start of the formation of amorphous LiₓSi. The four broad peaks that appeared in the lower angles are due to the formation of Li₁₅Au₄ (see Supplementary Information, Fig. S5). At 100 mV, the pure Au peaks disappeared, indicating that the Au had completely reacted with Li. The Si(111) peak was very weak at 100 mV, and disappeared completely at 50 mV. It appears that Si NWs remain amorphous after the first charge, consistent with the non-flat voltage charging/discharging curve in Fig. 2b. This contrasts, however, with other studies on Si electrodes, which have reported the formation of crystalline, Liₓ₁₂₃₂Si at potentials less than 30–60 mV. In situ XRD studies have determined that this crystalline phase forms at <50 mV for films thicker than ~2 μm (ref. 27). We did not observe this to be the case in our Si NWs, most likely because of their shape and small dimensions.

The local structural features of Si NWs during the first Li insertion were studied with transmission electron microscopy (TEM) and selected area electron diffraction (SAED). The as-grown Si NWs were found to be single-crystalline. Figure 4b shows an example of a typical Si NW with a ⟨112⟩ growth direction. Figure 4c shows a Si NW with a ⟨112⟩ growth direction that was charged to 100 mV. In this case there were two phases present, as expected from the voltage profile. Both crystalline and amorphous phases were clearly seen. The distribution of the two phases was observed both across the diameter (a crystalline core and an amorphous shell) and along the length. The SAED showed the spot pattern for the crystalline phase (Si), but weak diffuse rings from the amorphous phase (LiₓSi alloy) were also observed. Li ions must diffuse radially into the NW from the electrolyte, resulting in the core–shell phase distribution. The reason for phase distribution along the length is not yet understood. At 50 mV, the Si NW became mostly amorphous with some crystalline Si regions embedded inside the core, as seen from the dark-field image and HRTEM (Fig. 4d). The SAED showed spotty rings representative of a polycrystalline sample and diffuse rings for the amorphous phase. At 10 mV (Fig. 4e), all of the Si had changed to amorphous Li₁₂₃₂Si, as indicated by the amorphous rings in the SAED. These TEM observations were consistent with the XRD results (Fig. 4a) and voltage charging curves (Fig. 2b).

METHODS

Si NWs were synthesized using the VLS process on stainless steel substrates using Au catalyst. The electrochemical properties were evaluated under an argon atmosphere by both cyclic voltammetry and galvanostatic cycling in a three-electrode configuration, with the Si NWs on the stainless steel substrate as the working electrode and Li foil as both reference and counter-electrodes. No binders or conducting carbon were used. The charge capacity referred to here is the total charge inserted into the Si NW, per mass unit, during Li insertion, whereas the discharge capacity is the total charge removed during Li extraction. For electrical characterization, single Si NW devices were contacted with metal electrodes by electron-beam lithography or focused-ion beam deposition. For more detailed descriptions of NW synthesis, TEM and XRD characterization, electrochemical testing, and device fabrication, see the Supplementary Information.

Received 23 July 2007; accepted 14 November 2007; published 16 December 2007.

References
et al

13. Park, M.-S.


**Acknowledgements**

We thank Dr Marshall for help with TEM interpretation and Professors Brongersma and Clemens for technical help. Y.C. acknowledges support from the Stanford New Faculty Startup Fund and Global Climate and Energy Projects. C.K.C. acknowledges support from a National Science Foundation Graduate Fellowship and Stanford Graduate Fellowship. Correspondence and requests for materials should be addressed to Y.C. Supplementary information accompanies this paper on www.nature.com/naturenanotechnology.

**Author contributions**

C.K.C. conceived and carried out the experiment and data analysis. H.P., G.L., K.M. and X.F.Z. assisted in technical help. Y.C. acknowledges support from the Stanford New Faculty Startup Fund and Global Climate and Energy Projects. C.K.C. acknowledges support from a National Science Foundation Graduate Fellowship and Stanford Graduate Fellowship. Correspondence and requests for materials should be addressed to Y.C. Supplementary information accompanies this paper on www.nature.com/naturenanotechnology.

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/