Kinetics-driven high power Li-ion battery with $a$-Si/NiSi$_x$ core-shell nanowire anodes†

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We report amorphous-Si nanowire shell anodes, supported by NiSi$_x$ nanowire cores, by catalyst-free two-step SiH$_4$ chemical vapor deposition, where the metallic core acts as a mechanical supporter and a kinetically unlimited charge supplier. We have achieved highly reversible capacitance of over 3000 mAh g$^{-1}$ even at a 2C rate, with stable cyclic retention which stems from the altered electrochemical reactions with relatively small volume expansion routes by a kinetic effect.

Introduction

Anode architectures, particularly when they are three-dimensional at the nanometre scale, are closely related with cell performances in Li-ion batteries.$^{1-6}$ Therein, the achievable electrochemical capacity and the power characteristics are inherently determined by a series of phase transitions involved in the anode during lithiation/delithiation. The electrochemical Li–Si system forms various Li-rich Li$_x$Si intermetallics (0 ≤ $x$ ≤ 4.4), correspondingly symptomatic of the largest known gravimetric charge capacity of up to 4200 mAh g$^{-1}$ in the bulk limit, thus can represent an attractive anodic system for the high capacity Li-ion battery.$^{1,3-5}$

However, the system undergoes notoriously large volume-changes up to 400% during the cyclic lithiation and delithiation, resulting in poor cyclic retention in its cell capacity and output power.$^{1,3-5}$ It is suggested that this severe anode pulverization upon the cyclic volume changes can be alleviated by adopting one-dimensional Si nanocrystals, such as Si nanowires (NWs), based on the promises of their affordable accommodation of large volume-changes and the efficient charge collection capability.$^{4,5,7-11}$ Yet, monolithic single-crystalline Si NWs exhibit cyclic degradation in their cell capacity particularly at the high charging/discharging rate, thus limiting their integration into the high power cells.$^{3,12-18}$

Here, we report amorphous-Si ($a$-Si) shell anodes, supported by NiSi$_x$ NW cores, by a catalyst-free two-step SiH$_4$ chemical vapor deposition, where the metallic core acts as a mechanical supporter and a kinetically unlimited charge supplier. Spontaneous silicide NWs, such as NiSi$_x$, FeSi, CoSi, TaSi$_2$, have been recently investigated, and among others NiSi$_x$ NWs are of particular interest because their growth can be easily integrated with silicon processing technology. Besides, NiSi$_x$ exhibits the lowest resistivity and makes good contacts with Si.$^{25-27}$ In this regard, we designed the core-shell NW anode architecture in this work. We have achieved the highly reversible capacity over 3000 mAh g$^{-1}$ even at 2C rate, with stable cyclic retention which stems from the altered electrochemical reactions with relatively small volume expansion routes by a kinetic effect.

Results and discussion

$a$-Si NW shells, supported by metallic NiSi$_x$ NW cores ($a$-Si/NiSi$_x$ NW), were grown by a simple two-step SiH$_4$ CVD process: (i) the self-catalytic NiSi$_x$ NWs were grown on Ni thin films, (ii) followed by $a$-Si shells deposition on the NiSi$_x$ NWs, as illustrated in Fig. 1(a). We start off the NiSi$_x$ NW synthesis by thermal evaporation of Ni films on Ag-coated stainless steel (SUS) substrates of a circular shape disk in 15mm diameter. Ag acts as a diffusion barrier of Fe from SUS into the Ni films. The Ni/Ag/SUS substrates were annealed with oxygen at 400 °C, and then reacted with 50 Torr of SiH$_4$ (10% diluted in H$_2$) at 420 °C, as described in Ref. 26,27. The $a$-Si shell deposition was conducted by using thermal decomposition of SiH$_4$ (10% diluted in H$_2$) at 550 °C for 30 min. Here we note that $a$-Si shells are formed, when NiSi$_x$ NWs are oxygen-exposed prior to the SiH$_4$ flows, whereas the crystalline Si shell ($c$-Si) was formed otherwise, as shown in Fig. S1.† We also prepared $a$-Si shell NWs on the insulating $c$-Si core NWs, and describe a series of
substrate. (c) HRTEM image of an individual a-Si/NiSi2 NW shows a plan-view SEM image of a-Si/NiSi2 NW at the core region and the corresponding FFT-DP along the [1–10] zone axis (inset).

(d) HRTEM image of an individual a-Si/NiSi2 NW at the shell region and the corresponding FFT-DP (inset). (e) HAADF image of a-Si/NiSi2 NW. (f and g) EDX elemental mapping images of Si (f) and Ni (g) in (e).

Fig. 1 (In color) (a) The schematics of the NW heterostructure growth in this study. (b) TEM image of an individual a-Si/NiSi2 NW. The inset shows a plan-view SEM image of a-Si/NiSi2 NWs grown on SUS substrate. (c) HRTEM image of an individual a-Si/NiSi2 NW at the core region and the corresponding FFT-DP along the [1–10] zone axis (inset). (d) HRTEM image of an individual a-Si/NiSi2 NW at the shell region and the corresponding FFT-DP (inset). (e) HAADF image of a-Si/NiSi2 NW. (f and g) EDX elemental mapping images of Si (f) and Ni (g) in (e).

comparative cyclic cell performances in greater details,28 and discuss them around the roles of the metallic core for altered electrochemical reactions.29,30

Fig. 1(b) shows the representative microstructures of a-Si/NiSi2 NWs by transmission electron microscope (TEM), where the average diameter of a-Si/NiSi2 NW is 190 nm with the 20 nm thick NiSi2 core NWs. Scanning electron microscope (SEM) images in the inset illustrate that the shell NWs were conformally deposited onto the whole NWs in the substrate – see also Fig. S2 in Supporting Information.† High-resolution TEM (HRTEM) images and corresponding fast fourier transform diffraction patterns (FFT-DP) in Fig. 1(c) and 1(d) confirm that Si/NiSi2 NW features amorphous Si NW shells and single-crystalline NiSi2 NW cores.31 High-angle annular dark field (HAADF) images, where the intensity is roughly proportional to square of atomic number, and energy dispersive X-ray spectroscopy (EDX) mapping images in Fig. 1(e), (f) and (g) also demonstrate that core/shell NW structures are clearly discernable, and the elemental distribution of Ni is locally limited in the core region within the instrumental resolution.

The a-Si/NiSi2 NW anodes were incorporated into a coin-type half cell (CR2016 coin-type). The cell uses Li metal foils as the counter and the reference electrode, and 1M LiPF6 dissolved in a 1 : 1 (by volume, provided by Techoro. Semichem. Co.) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) as the electrolyte. The cell assembly was carried out in an Ar-filled glove box with less than 0.1 ppm each of oxygen and moisture. The charge capacity of the a-Si/NiSi2 NW cell was measured over the potential range of 0.01 to 2.00 V (vs. Li/Li+).

during the initial 50 cycles in the galvanostatic mode. The measured discharge capacity is carefully normalized into the gravimetric capacity, as described in Fig. S3.† Fig. 2 shows the cyclic retention of two types of NWs: a-Si/NiSi2 NW cells and a-Si/cSi NW cells. It is found that a-Si/NiSi2 NWs retain almost the 83% of the first discharge capacity after the 50th cycle with the high charge capacity above 3000 mAh g–1. For a check, we tested the bare NiSi2 NW anodes in the galvanostatic mode; however, we did not observe any apparent potential plateau over the potential range of 0.01 to 3.00 V – also see Fig. S4.† This suggests that the bare NiSi2 NWs alone are electrochemically inactive in our experimental conditions. We have also tested the rate dependent capacity by charging the cell at a constant rate of 0.1C and discharging it at the various rate from 0.1C to 2C (1C=1 h per half-cycle). Fig. 2(b) shows that the discharge capacity of a-Si/NiSi2 NWs is maintained over 94% of the first discharge capacity, and weakly depends on the C-rate up to 2C. The discharge capacity of a-Si/c-Si NWs, on the other hand, fades significantly and strongly depends on the C-rate. It is obvious that a combination of a-Si shells and metallic NiSi2 NW cores is responsible for the unprecedented reversible lithiation/delithiation in a-Si shells at the high charge/discharge rate.

![Image](https://example.com/image1.png)

Fig. 1 (In color) (a) The schematics of the NW heterostructure growth in this study. (b) TEM image of an individual a-Si/NiSi2 NW. The inset shows a plan-view SEM image of a-Si/NiSi2 NWs grown on SUS substrate. (c) HRTEM image of an individual a-Si/NiSi2 NW at the core region and the corresponding FFT-DP along the [1–10] zone axis (inset). (d) HRTEM image of an individual a-Si/NiSi2 NW at the shell region and the corresponding FFT-DP (inset). (e) HAADF image of a-Si/NiSi2 NW. (f and g) EDX elemental mapping images of Si (f) and Ni (g) in (e).

![Image](https://example.com/image2.png)

Fig. 2 (In color) (a) The discharge capacity retention for the a-Si/NiSi2 NW (red circles) and the a-Si/c-Si NW (blue circles), respectively. The inset shows the specific capacity for the a-Si/NiSi2 NW (red close circles-charge and red open circles-discharge) and the a-Si/c-Si NW (blue close circles-charge and blue open circles-discharge), respectively. (b) The rate capability for the a-Si/NiSi2 NW (red circles) and the a-Si/c-Si NW (blue circles), respectively.
Identification of the fully lithiated phase whether it is $a$-$Li_x$Si to $c$-$Li_x$Si is critical, since the $a$-$Li_x$Si to $c$-$Li_x$Si or vice versa among the series of lithiation/delithiation reactions involves the largest volume changes, which is in turn the major source for the deterioration in the anodic reversibility.\textsuperscript{34–37} During the discharge process, $a$-$Si/c$-$Si$ NWs display the dominant oxidation peak at 450 mV, marked as $F$, assigned to the dissociation of $a$-$Li$-$x$Si to $a$-$Li_x$Si or $a$-$Si$, indicating that its reduction peak below 80 mV corresponds to the nucleation of a crystalline lithium silicide ($c$-$Li_x$Si).\textsuperscript{34–36} By contrast, $a$-$Si/ NiSi_x$ NWs exhibit two dissimilar oxidation peaks between 250 mV and 500 mV, marked as $D$ and $E$, which are assigned to the dissociation of $a$-$Li_{x+y}$Si to $a$-$Li_x$Si or $a$-$Si$.\textsuperscript{32,34–37} This finding can be back-traced to assign another phase transition, $C$ during the Li charging to the formation of $a$-$Li_{x+y}$Si. In other words, the full lithiation into $a$-$Li_{x+y}$Si in $a$-$Si/ NiSi_x$ instead of $c$-$Li_x$Si in $a$-$Si/c$-$Si$ NWs, alleviates severe physical pulverization and leads to the stable reversibility in the cyclic cell performance. We speculate that kinetically unlimited electron supply from NiSi\textsubscript{x} NW core coupled with the properly absorbed volume change by $a$-$Si$ shell provides alternative electrochemical reactions of $a$-$Si/ NiSi_x$ NWs to skip over the nucleation of $c$-$Li_x$Si by a kinetic effect. We measured average resistivity of NiSi\textsubscript{x} NWs and $c$-$Si$ NWs to be $10^{-3}$ $\Omega$-cm, and $10^4$ $\Omega$-cm. It is known that monolithic Si crystals usually undertake temporal local-concentration of Li ions in Si matrices, followed by the rapid and spatially inhomogeneous evolution of fully lithiated crystalline lithium silicides ($c$-$Li_x$Si), which in turn results in severe Si pulverizations. Instead, we argue that uniform distribution of the electrochemical potential in our $a$-$Si/ NiSi_x$ NWs, which is provided by the metallic NiSi\textsubscript{x} cores is responsible for the reversible reaction route mediated by fully lithiated amorphous lithium silicides.\textsuperscript{3,32,36}

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**Notes and references**

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31 Crystal structure of Si: diamond cubic, lattice constant: 5.431 Å, space group: Fm3m, JCPDS 43–0989; Crystal structure of NiSi2: diamond cubic, lattice constant: 5.416 Å space group: Fd-3m, JCPDS 27–1402.