Highly Interconnected Si Nanowires for Improved Stability
Li-Ion Battery Anodes

Hung T. Nguyen, Fei Yao, Mihai R. Zamfir, Chandan Biswas, Kang Pyo So, Young Hee Lee, Seong Min Kim, Seung Nam Cha, Jong Min Kim, and Didier Pribat*

1. Introduction

Rechargeable lithium-ion batteries are ubiquitous in our daily environment, since they power our mobile phones, lap-top computers and other personal mobile electronic devices such as cameras, organizers etc. Li-ion batteries are also seriously considered for applications in electric vehicles as well as for high capacity energy storage from intermittent green energy resources originating from the sun, including wind. Li-ion batteries contain no Li in metallic form, because of the formation of dendrites upon recharging, which can result in cell short-circuiting. Instead, Li ions are intercalated in host materials at both the cathode and the anode\(^1\) and in most commercial products, Li ions are shuttled back and forth between a graphite anode and a layered oxide cathode (the so-called “rocking chair” operation) as the battery is charged and discharged. Li-ion batteries can store up to \(\sim 180 \text{ Wh kg}^{-1}\) at an average voltage of 3.8 V. However, in order to respond to the increasing demand for portable systems as well as electric vehicles, battery scientists are actively searching for higher capacity electrode materials. On the anode side, silicon is recognised to exhibit the highest known Li insertion capacity,\(^2\) with a maximum theoretical value of 4200 mAh g\(^{-1}\), corresponding to the Li\(_{15}\)Si\(_4\) compound (which is a metastable phase, not appearing in the Li-Si phase diagram), to a maximum capacity of 3579 mAh g\(^{-1}\).\(^{4-7}\) Moreover, still at \(RT\), Li alloying with Si does not follow the equilibrium phase diagram in terms of phase formation. Because of the strain generated by the large volume expansion as well as the phase changes eventually occurring upon Li alloying at \(RT\), Si becomes powder-like after a few charge-discharge cycles and the electrode of the battery loses its integrity (a phenomenon known as decrepitation), which induces a poor capacity retention during charge-discharge cycling. In order to circumvent this problem and improve the cycling lifetime of Si-based anodes, many studies have dealt with structured Si electrodes, involving thin films, micro- and nano-particles as well as alloys and composites.\(^{[2]}\) Nanostructured materials\(^{[8-10]}\) are particularly attractive since they provide more resistance to strain-induced fracture and cracking,\(^{[11,12]}\) with the add-on advantage of shorter diffusion distances for Li species, thus offering the possibility to increase charging and discharging rates. Among the various Si nanostructures, silicon nanowires (Si NWs) represent a further progress, since while offering the general advantages of nanomaterials (in particular resistance to strain), they are directly connected to the current collector, being grown on it, thus eliminating the need for extra binder and conductive...
carbon-based materials.\textsuperscript{[11,14]} Even though Si NWs resist cracking very well, a decrease in the anode capacity can still be observed as the number of charge-discharge cycles increases. Although there are probably several degradation mechanisms operating in parallel, one of the reasons for this is the detachment of some wires from the substrate (which is also the current collector), due to the stress developed at their roots upon volume change, when Li is inserted. In other words, while the wires can expand longitudinally and laterally upon Li insertion, they are constrained at their roots by the stainless steel substrate/current collector whose volume does not change. As the wires detach from their substrate, the circulation of electrons is stopped and Li remains trapped in the now inactive Si material. The electrode capacity therefore quickly fades away as more NWs detach during sustained cycling. Indeed, we have found Si NWs in the electrolyte, when carefully filtering it after cycling. Indeed, we have found Si NWs in the electrolyte, when carefully filtering it after cycling experiments. \textbf{Figure 1} shows several scanning electron microscope (SEM) views of filtering residues after cycling an anode composed of Si NWs that were not interconnected (Figure 1d). After 40 cycles at C/10 rate the half cell was disconnected and opened. The tested electrolyte was carefully collected and diluted with acetone. The solution was filtered on a 175 μm thick polytetrafluoroethylene (PTFE) membrane with a pore size 0.2 μm (Millipore, Ireland) using a Venturi-type filtering system. The membrane was dried and analyzed by SEM after Pt metallization. Clearly some NWs are visible on these SEM pictures, embedded in other electrolyte residues. Some of these wires were probably broken when the cell was mounted (Figure 1b) as they do not look degraded and they are not covered by the so-called solid electrolyte interphase film that forms on the NW during the first lithiation (see below). This being said, we find wires that have been lithiated in every location on the filter (Figure 1c is a picture taken in a different place), which shows that they tend to detach from the substrate upon cycling.

In order to circumvent this problem, we present here a nanowire growth strategy yielding highly interconnected Si NWs. In this manner, the detachment of individual nanowires is prevented and the capacity fading is limited. Our study shows that the cycling stability of anodes based on highly interconnected Si NWs is improved as, for instance, we get almost 100% charge retention (3100 mAh g\textsuperscript{-1}) after 40 cycles at a C/2 rate (corresponding to a charge-discharge current of 2.1 A g\textsuperscript{-1}), without limiting the Li alloying voltage. We also show that these anodes can be cycled at rates up to 8C (33.6 A g\textsuperscript{-1}) without destroying the Si NW structure and we manage to grow nanowires with a silicon density of 1.2 mg cm\textsuperscript{-2}, yielding an area charge capacity of ~4.2 mAh cm\textsuperscript{-2} for the corresponding anodes (at C/20 rate), a value which is already competitive with current commercial anodes. Finally, we find that Si from the NWs tends to dissolve in the LiPF\textsubscript{6}-based electrolyte that we use here, a problem which underlines the crucial need for future studies specifically oriented towards the understanding of Si interactions with various electrolytes.

\section{Results and Discussion}

Schematically, upon Li electrochemical alloying at RT, crystalline Si transforms to some amorphous a-Li\textsubscript{x}Si phase during the first Li insertion step (starting around 100 mV vs. Li/Li\textsuperscript{+}) down to ~60 mV. If the lithiation is carried-on to lower voltages (down to ~10 mV and below), then the a-Li\textsubscript{x}Si phase suddenly crystallises to Li\textsubscript{11}Si\textsubscript{4}. The first de-alloying step destroys this Li\textsubscript{11}Si\textsubscript{4} crystalline phase, leaving Si in the amorphous state at the end of the Li extraction process. During subsequent alloying cycles, there are no more crystalline phases involved, except upon deep lithiation (below 50 mV), where the Li\textsubscript{11}Si\textsubscript{4} compound crystallises again.\textsuperscript{[4–7]} Note that during Li alloying with Si at RT, the formation of the Li\textsubscript{11}Si\textsubscript{4} phase depends on the size/thickness of the Si particles/films.\textsuperscript{[15,16]} Recent measurements even seem to indicate the possible formation of the Li\textsubscript{12}Si\textsubscript{5} compound at RT, when doped Si nanowires (instead of Si nanoparticles) are used for alloying.\textsuperscript{[16]} Over the past 3 years, extensive characterizations of anodes based on Si NWs have been published,\textsuperscript{[17–20]} showing that good cycling stability could be obtained as long as the voltage window was reduced, in particular when the charging voltage was kept above ~100 mV (vs Li/Li\textsuperscript{+}). This voltage limitation prevents the above-mentioned crystallization.
of the amorphous lithium silicide phase into Li$_{15}$Si$_4$, which occurs at deep lithiation.\cite{4–7} Avoiding crystallization and maintaining Si and Si-Li alloys in the amorphous state yields homogeneous volume changes during alloying, thus enhancing the electrode stability and the capacity retention upon cycling.\cite{7}

As in our previous work,\cite{14} we have used the vapour-liquid-solid (VLS) method\cite{21} for the growth of Au-seeded Si NWs. Here also, we have used gold for the eutectic-forming metal. However, instead of thermally pyrolysing SiH$_4$ inside a tubular-type furnace, in a chemical vapor deposition (CVD) mode,\cite{16} we have used here plasma-enhanced (PE) CVD, with a planar type heating element in the reactor (see Figure 2a). The structure and morphology of the nanowires are totally different in the two situations. While long and straight nanowires with low defect densities are obtained by CVD in the tubular reactor (see e.g., Figure 2 of Reference 14), relatively short ones are obtained by PECVD and they are highly curved, with their tips going backward in the substrate direction after some initial growth period (see Figure 2b, where the curvature of the NWs is striking). This difference is due to the peculiarities of the VLS growth mechanism: the Au-Si liquid eutectic alloy at the tip of the wires will tend to move towards the higher temperature region,\cite{22} a phenomenon similar to the temperature-gradient zone melting (TGZM) studied by Pfann long ago.\cite{23} Hence, since in a cylindrical furnace/reactor the walls of the reaction tube tend to be at a slightly higher temperature than the substrate holder in the center of the tube (convective cooling is higher at the center, even if the gas flow is not turbulent), a radial growth of long NWs is observed. On the other hand, when a planar furnace is concerned, the wires will tend to kink and curve their growth direction after some time, since the temperature of the gas phase decreases rapidly as the distance from the sole of the furnace increases, thus inducing a thermal gradient in which the substrate is at the highest temperature. The phenomenon can be amplified by abruptly changing the substrate temperature during growth.\cite{22} Now, because of this change in growth direction, the NWs that we synthesize become highly entangled, so that when the PECVD conditions are changed in order to promote isotropic Si growth, they will start to interconnect, due to uniform Si deposition around them, resulting (at relatively low temperature) in a core-shell structure where the core is crystalline (c-Si) and the shell amorphous (a-Si) (see Supporting Information, Figures S1, S2, S3 and S4). Figure 2c shows such interconnected NWs after a first growth step of 60 minutes at 420°C, followed by a second one (50 minutes) where the SiH$_4$ partial pressure was increased in order to yield isotropic deposition conditions (see Experimental Section). As a consequence of the highly interconnected network, individual NWs cannot detach from the substrate, since they are held by the whole array, forming a kind of highly porous, rigid block. Even if one NW loses contact

![Figure 2](image-url)
with the substrate, electron circulation in it will still be provided by neighboring specimens that are physically in contact. Figure 2d summarizes the situation. Although Li is known as a shallow interstitial donor in Si,[24,25] we performed the first growth step mentioned above with PH3 in the gas phase (see Experimental Section), in order to yield NWs with their core n-doped, the idea being to improve electrical interconnection, particularly at the end of the de-lithiation process. Also, since the NW array is very dense, it favors physical contact between the eutectic drop at the wire’s tip with a neighboring wire (particularly when growth is heading down towards the substrate), leading to splitting of the drop and highly branched growth as seen on Figure 2c (dotted arrows). Transmission electron microscope (TEM), X-ray diffraction and Raman observations/analysis confirm that the wires are composed of an amorphous shell which covers a crystalline core (see Supporting Information, Figures S1, S2, S3 and S4). In a former study, the fabrication of c-Si/a-Si core-shell structures did not yield interconnected nanowires, since growth was performed in a tubular-type CVD reactor and no catalyst was used.[26]

One of the drawbacks of using nanomaterials in battery electrodes is the low volumetric energy density,[27] which translates to a low surface energy density for anodes based on Si NWs (small and insufficient active material load). Because we use a ~200 nm-thick Au film to form the catalyst particles (see Experimental Section), and because of the entanglement after the first phase of growth, the quantity of Si that can be grown is typically of the order of 1.2 mg per squared cm of current collector electrode, i.e. ~6 times more than a typical Si “load” (~200 μg cm¬2) obtained with thinner (or without) Au films.[17,26] Hence, assuming an average capacity of 3500 mAh g¬1 for the Si NWs that we use (see below), we can obtain an area capacity of more than 4 mAh cm¬2 for the anode, which is already competitive with commercial batteries.[28] Last but not least, since the Si NWs grown with a planar-type furnace are not straight and do not expand more than 20–30 μm above the substrate’s surface, there are no risks of electrical short circuits between the anode and the cathode, when thin commercial separators (~25 μm thick) are used in battery testing experiments. Again this is in contrast with wires grown in tubular CVD furnaces that can be 5 to 10 times longer.[14]

Anodes consisting of interconnected Si NWs grown on stainless steel foils were tested in half cells where Li metal was used as a counter electrode (see Experimental Section). All measurements were performed in an Ar-filled glove box, with oxygen and moisture levels controlled below the ppm range. In order to understand the thickness/size dependent phase transformations[8,15] occurring in our NWs upon Li alloying, we first studied the charge-discharge behavior of the Si-based anodes during the first few cycles. Here, we use the terms “charge” and “discharge” relative to battery operation and not relative to the change of the oxidation state of Li (as electrochemists usually do, see e.g., Reference 2). Figure 3 shows galvanostatic cycling (GC) curves (C/20 rate), as well as cyclic voltammetry (CV) curves (0.05 mV s¬1 scan rate) taken from similar samples during the 2 first charge-discharge cycles (the contribution of the stainless steel substrate can be neglected, as shown in Figure S5, Supporting Information). For the 1st cycle, the GC curve shows that Li de-alloying starts around 200 mV and the occurrence of the plateau at 400 mV indicates the presence of two distinct phases, namely the Li11Si6 crystalline phase, which coexists with amorphous Si (a-Si) resulting from Li extraction. The second Li alloying (dash line) starts at ~500 mV and shows two sloping plateaus. At the end of the lithiation process, the amorphous Li-Si alloy crystals again to Li11Si6. The second de-alloying step is essentially similar to the first one, with Li11Si6 and a-Si coexisting as indicated by the plateau at 400 mV. The coulombic efficiency in the first cycle is ~96%, whereas it is almost 100% in the second cycle.

**Figure 3.** Galvanostatic (210 mA g¬1, C/20 rate) curves for the first and second charge-discharge cycles of the interconnected Si NWs at room temperature. Inset shows the corresponding cyclic voltammetry (CV) scans taken on similar samples (scan rate: 0.05 mV s¬1). The first lithiation (solid line) starts at ~200 mV, indicating that the NW shells are essentially amorphous. There is a broad gently sloping plateau masking the lithiation of the core crystalline Si (c-Si), occurring around 100 mV. However, the shoulder in the corresponding peak of the CV characteristic at ~100 mV (inset, solid line) indicates this lithiation of c-Si. The change of slope at the end of the lithiation process is characteristic of the transformation of the saturated amorphous Li-Si alloy into the crystalline Li15Si4 compound. The first discharge curve shows that Li de-alloying starts around 200 mV and the occurrence of the plateau at 400 mV indicates the presence of two distinct phases, namely the Li11Si6 crystalline phase, which coexists with amorphous Si (a-Si) resulting from Li extraction. The second Li alloying (dash line) starts at ~500 mV and shows two sloping plateaus. At the end of the lithiation process, the amorphous Li-Si alloy crystals again to Li11Si6. The second de-alloying step is essentially similar to the first one, with Li11Si6 and a-Si coexisting as indicated by the plateau at 400 mV. The coulombic efficiency in the first cycle is ~96%, whereas it is almost 100% in the second cycle.
changes, indicating the crystallization of the saturated a-Li$_2$Si phase into Li$_{15}$Si$_4$. A corresponding peak appears in the CV curve. The 1st discharge starts around 400 mV and the long plateau in the GC curve is typical of a 2-phase behavior (crystalline Li$_{15}$Si$_4$ + an amorphous Si-based phase), see References 5, 7 and 15. The 2 corresponding peaks in the CV curve at ~330 mV and ~490 mV mark the change of slope at the beginning and the end of the plateau in the GC curve. During the second charge, Li insertion occurs at an earlier stage, i.e., at a voltage of ~500 mV, a behavior already reported and assigned to surface changes, especially due to the formation of the solid electrolyte interphase (SEI) film occurring in parallel with alloy formation during the first charge. Then two slopping plateaus appear in the GC, in total agreement with earlier observations.[15-7] The presence of these 2 plateaus is not explained. The 2 peaks in the CV curve indicate the 2 first changes of slope in the GC curve. The crystallization of the Li$_{15}$Si$_4$ phase is again evidenced by the last (3rd) change of slope in the GC curve at the end of the lithiation process, corresponding to the shoulder at the end part of the second broad peak, below 60 mV in the CV curve. The second de-lithiation step is essentially identical to the first one, with a large plateau corresponding to a 2-phase region where Li$_{15}$Si$_4$ and a-Si coexist. When alloying is stopped before full lithiation, the discharge plateau at 400 mV in the GC curve is progressively replaced first by two slopping plateaus (also corresponding to the peaks in the CV curves at ~300 and 500 mV) and then by only one slopping plateau, for a cut-off voltage of 150 mV and above (see Supporting Information, Figures S6, S7 and S8). Although cutting the charging voltage around 150 mV is interesting for improving charge retention upon cycling,[10] it induces a considerable loss of capacity (see Supporting Information, Figures S6, S7 and S8). For instance, in Reference 26, the initial capacity (at C/5 rate) shifts from ~2400 mAh g$^{-1}$ to ~1050 mAh g$^{-1}$ (corresponding to a 56% capacity loss) when the cut-off charging voltage goes from 10 to 150 mV.

Next, we have studied the charge-discharge behavior of the interconnected Si NW anodes upon repeated cycling, using galvanostatic operations. Cycling was performed between 0 and 1.5 V, i.e., without any cut-off voltage above 0 V that would prevent the crystallization of the Li$_{15}$Si$_4$ phase. At low rate (C/20, i.e., 210 mA g$^{-1}$), the initial capacity is 3500 mAh g$^{-1}$ as evidenced on Figure 3. As quoted above, since we grow typically 1.2 mg Si NWs per cm$^2$ of the surface of stainless steel substrates, this yields a capacity of 4.2 mAh cm$^{-2}$ for the anode, which is comparable with present commercial batteries.[28] In order to check that the Au catalyst does not significantly contribute to the electrode capacity,[14] we have grown some Si NW arrays with 3 nm-thick Au films (instead of 200 nm, see Experimental Section). The initial capacity for C/20 charge-discharge rates was also ~3500 mAh g$^{-1}$ (see Supporting Information, Figure S9), indicating that Au does not participate to the build-up of the capacity, probably because it is alloyed with Si.

Figure 4a shows cycling experiments performed at C/2 (2.1 A g$^{-1}$) and 2C (8.4 A g$^{-1}$) rates during respectively 50 and 70 cycles. In this figure, the Coulombic efficiency is also plotted for the C/2 cycles (it is always ~100% for the 2C cycles, as the gray dots indicating discharge screen the black squares indicating charge for all cycles, except the 1st one). At C/2 rate, the capacity retention is almost 100% over the first 40 cycles (~3100 mAh g$^{-1}$) and it falls to 94.5% after 50 cycles (2930 mAh g$^{-1}$). This compares favorably with the results of Reference 26, where the capacity retention was ~83% (2000 mAh g$^{-1}$) after 30 cycles at C/5 rate and with a 10 mV cut-off voltage. At 2C rate, the capacity slightly increases during the 40 first cycles and then it starts to slowly decrease, so that the retention after 70 cycles is ~90% (~1800 mAh g$^{-1}$). Figure 4b shows the behavior over 72 cycles, when the C rate is progressively increased from C/10 to 8C, the latter rate corresponding to a charge-discharge current of 33.6 A g$^{-1}$. Note that at 8C, the capacity is still ~430 mAh g$^{-1}$, i.e., larger than that of graphite at low C rate. After the 70 cycles with the increased C rates up to 8C, the capacity at a C/10 rate is still ~2600 mAh g$^{-1}$, see the 2 last cycles at the extreme right-hand side of Figure 4b. Note that for Si NW arrays grown with a 3 nm-thick Au catalyst film that yields a much less interconnected NW structure (compare Figure 2c and Figure S10), the capacity retention upon cycling is lower. Figure S9 (Supporting Information) shows a 7% loss of the anode capacity over 25 cycles at C/20 rate. When the charging voltage is limited to 60 mV, this loss is reduced to 3% over 35 cycles (C/10 rate, see Figure S9). These observations confirm that a high NW interconnection yield is necessary for improving anode stability.

Finally, we have characterized the Si NWs after the 50 cycles at C/2 rate. Before observation, the tested anode samples were carefully cleaned using diethyl carbonate, followed by several rinses in acetone, in order to totally remove the electrolyte and those components of the SEI film that are soluble in a polar solvent. Figure 5 shows SEM pictures taken on the anode after cycling. The interconnected structure of the anode is preserved and the wires have kept their shape. However, their surface has considerably roughened and their diameter seems to have decreased (see the inset of Figure 5). X-ray diffraction analysis indicates that crystalline Si has completely disappeared from the core of the wires (see Supporting Information, Figure S11), as anticipated and also shown by others for deep lithiation conditions.[13,20] Because of the high surface roughness of the Si NWs after cycling, as well as their apparent decrease in diameter, we have analyzed the electrolyte after testing during 50 charge-discharge cycles, searching for some Si. Again here, the electrolyte was carefully filtered after cycling and before analysis. Table 1 shows the results of this analysis, performed using inductively coupled plasma (ICP) atomic emission spectroscopy (AES). An analysis on a reference sample of pristine, unused electrolyte is also shown for comparison. AES uses the wavelength and intensity of light emitted from excited atoms to characterize a sample, while a plasma (ICP) is one of several possible excitation sources for the sample.[31] A quick look at table 1 shows that Si is indeed found in the electrolyte after testing, and in relatively appreciable quantities. It is well known that LiF and PF$_5$, which in turn hydrolyses in the presence of traces of moisture to form HF and PF$_3$O$_5$. HF in water will etch and dissolve any oxidized Si.[31] However in alkyl carbonate solvents, the reaction will be different. Also, we note that porous Si can be produced by anodic oxidation in HF-based electrolytes.[34] It is not the scope of this paper to discuss the mechanism of Si etching during battery cycling, but rather to point out that ageing of Si-based anodes is certainly the result of several mechanisms operating in parallel. In particular, the formation of a chemically and mechanically stable passivating SEI film during the first Li
charging cycle is of paramount importance for further stability of the anode. We note that Pollak et al. have obtained a good cycling stability of anodes based on amorphous Si, using an electrolyte composed of lithium bis(oxalato)borate (LiBOB) salt (i.e., free of fluorine) in propylene carbonate. They advocate the formation of a stable SEI film to explain this stability. We are currently studying various electrolyte systems (in particular fluorine-free ones) in order to better understand the mechanism of SEI formation and further improve the cycling stability of our anodes based on interconnected Si NWs.

3. Conclusions

In conclusion, we have presented a novel type of Si anode, based on highly interconnected nanowires. The high interconnection yield prevents individual nanowires to detach from the substrate due to excessive strain at their root upon lithiation, which improves the cycling behavior. In particular, we report a ~100% charge retention after 40 cycles at a C/2 rate, and a ~90% charge retention after 70 cycles at a 2C rate. Our anodes withstand cycling at 8C without significant damage. We have also been able to grow NWs with a high surface density, corresponding to a Si load of ~1.2 mg cm\(^{-2}\) and yielding an area capacity of 4.2 mAh cm\(^{-2}\) for the Si-based anode, a value which is already competitive with those of anodes from commercial batteries. Last but not least, we find that Si from the anode tends to dissolve in the fluorine-containing electrolyte (LiPF\(_6\)) that we use. This finding clearly underlines the need to better understand Si interactions with electrolytes, in particular for the formation of a stable solid electrolyte interphase film that largely conditions ageing of the anode.

Figure 4. Galvanostatic cycling curves for the interconnected Si NW anodes. (a): 50 cycles at C/2 rate (2.1 A g\(^{-1}\)). The capacity retention is almost 100% after the 40 first cycles and starts to slightly decrease after, amounting to 94.5% after 50 cycles. At 2C rate (8.4 A g\(^{-1}\)) the capacity of the electrode slightly increases up to 40 cycles and then slowly decreases. After 70 cycles, the capacity is 90% of the initial one. The Coulombic efficiency is plotted for the C/2 rate. The gray dotted lines have been drawn to guide the eye. (b): Cycling with an increasing C rate, from C/10 up to 8C. Note that at 8C (33.6 A g\(^{-1}\)), the capacity is still ~430 mAh g\(^{-1}\). After cycling at 8C, the anode recovers a capacity of ~2600 mAh g\(^{-1}\) at C/10 rate (the 2 cycles at the extreme right-hand side of the figure).
Au thin film deposition: Au catalyst deposition was performed on stainless steel (SS) foils (~25 μm thick, 23 mg cm⁻²), which were cleaned by sonication in acetone first and then in ethanol, and dried with an air gun. Au thin films were deposited on top of stainless steel substrates by in situ sonication in acetone first and then in ethanol, and dried with an air flow of 15 l.min⁻¹.

4. Experimental Section

The growth of Si NWs was performed in a plasma-enhanced chemical vapor deposition (PECVD) reactor (A-Tech–South Korea). Figure 2a is a schematic representation of the reactor. The top RF (13.56 MHz) electrode of the chamber is fitted with a shower head through which the gases flow before reaching the substrate. The conditions for the whole process have been thoroughly calibrated and are summarized in Table 2 below. The SS foils with their Au thin films were loaded on the bottom electrode (substrate holder) of the PECVD reactor. The Au catalyst film was first in situ annealed at 420 °C, under an H₂ plasma (H₂ flow: 270 sccm; pressure 600 mTorr; 6.5 × 10⁻² W cm⁻² RF power) during 10 minutes, in order to break it into nanoparticles (dewetting). After annealing, silane (SiH₄) and phosphine (PH₃) diluted in H₂ (0.05 vol.%) were used with a volume ratio of 5:1 for the growth of n-doped core Si NWs. PH₃ was used only for the growth of the core Si NWs. The shell part was deposited in situ and in the same conditions as with the core part, except without PH₃, and less H₂ (higher SiH₄ partial pressure). After termination of deposition and temperature decrease below 50 °C, the samples were unloaded and immediately transferred into the Ar-filled glove box, situated beside the PECVD reactor (except for samples devoted to morphological analyses).

Table 1. Inductively coupled plasma atomic emission spectroscopy.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element</th>
<th>Unit</th>
<th>Value</th>
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<tbody>
<tr>
<td>ED/DEC [3/7 vol.] LiPF₆</td>
<td>Li</td>
<td>%</td>
<td>0.76</td>
</tr>
<tr>
<td>[1.15 M] (pristine)</td>
<td>p</td>
<td>%</td>
<td>3.46</td>
</tr>
<tr>
<td>Tested ED/DEC [3/7 vol.] LiPF₆</td>
<td>Li</td>
<td>%</td>
<td>0.71</td>
</tr>
<tr>
<td>[1.15 M], 50 cycles</td>
<td>p</td>
<td>%</td>
<td>3.31</td>
</tr>
<tr>
<td>Si</td>
<td>mg kg⁻¹</td>
<td>346.60</td>
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Table 2. PECVD conditions for Si NW growth with a 200 nm thick Au catalyst film.

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<tbody>
<tr>
<td>Core NWs</td>
<td>20</td>
<td>600</td>
<td>270</td>
<td>10</td>
</tr>
<tr>
<td>Shell a-Si</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>600</td>
<td>270/30/6</td>
<td>60</td>
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<tr>
<td></td>
<td>20</td>
<td>600</td>
<td>120/30/0</td>
<td>50</td>
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SELGARD 2500 microporous monolayer polypropylene membranes, with a thickness of 25 μm. Half cells were fabricated using PTFE swagelock components and two cylindrical stainless steel electrodes with a 12 mm diameter, which were cleaned by sonication several times in acetone and ethanol, respectively and dried carefully before cell installation. A 1.15 M LiPF₆ solution in a 3:7 (vol%) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC), respectively was used as the electrolyte. No electron-conducting fillers, or binders were used for the anodes. The electrochemical behavior of the electrodes was investigated by means of a battery tester system (BioLogic VSP) with various charge-discharge rates. Galvanostatic cycling was performed with a voltage window between 1.50 and 0 V vs. Li/Li⁺ and cyclic voltammetry (CV) was performed between 1.50 and 0 V vs. Li/Li⁺ and cyclic voltammetry (CV) was performed between 1.50 and 0 V vs. Li/Li⁺ at a rate of 0.05 mV s⁻¹. We have used 4200 mAh g⁻¹ as the maximum Si capacity for the determination of the C rates, which means that the actual C rates are higher than those indicated since the maximum Si capacity at room temperature is around 3500 mAh g⁻¹.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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