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To cite this article: Dan Schneier et al 2020 J. Electrochem. Soc. 167 050511

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Analysis of Scale-up Parameters in 3D Silicon-Nanowire Lithium-Battery Anodes

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New, higher-capacity materials are required in order to address the growing need for batteries with greater energy density and longer cycle life for modern applications. We present here a study of silicon-nanowire (SiNW) anodes synthesized via a novel, catalyst-free and scalable chemical vapor deposition (CVD) on stainless-steel mesh. This is a continuation to our previous paper (Harpak et al., Nano Lett. (2019) http://pubs.acs.org/doi/10.1021/acs.nanolett.8b05127) that describes the progress we recently made. The study is focused on the adaptation of the SiNW anode in various large-scale configurations. Our research efforts have resulted in the successful scale-up of the silicon anode from Si/Li half-cells with high areal capacity of 14 mAh cm−2, to coin cells with commercial cathodes, industrial 1/3AAA cells and proof-of-concept multilayered pouch cells. Testing of our anodes in cylindrical cells demonstrated the applicability of these anodes in commercial lithium-ion batteries that can run for hundreds of cycles, withstanding fast charge and subzero temperatures. An all-solid Si/polymer electrolyte/NCA cell is also demonstrated as a proof of concept (POC). We assign the major degradation mechanism of the SiNW anodes to the growth of the SEI thickness and impedance during cycling. We found that the depth of lithiation/delithiation and the voltage profile of the cell significantly affect cell’s stability.

In order to address the rapidly growing need in portable energy, high-capacity lithium-ion anode materials are essential. Most commercially available lithium-ion batteries have, as the anode, graphite with a theoretical capacity of 372 mAh g−1. In order to increase the energy density of the lithium battery, better anodes and cathodes are still required. Silicon has attracted much attention due to its theoretical capacity of 4200 mAh g−1, an order of magnitude greater than that of graphite. Silicon exhibits a low lithiation potential against Li/Li+, thus high battery voltages can be reached. Furthermore, silicon is a low-cost and environmentally friendly material, and is the second most abundant element in the Earth’s crust. Because of the high melting points of lithium-rich silicon compounds, and higher working potentials (vs Li), these batteries are safer than both lithium-ion and lithium-metal cells.

Nevertheless, the main challenge with high-capacity lithium-alloy-forming anode materials, such as Si, Sn and Al, is their volume expansion of up to 300% during Li insertion, followed by cracking and pulverization of the anode material and the solid electrolyte interphase (SEI), which cause degradation of capacity and rate capability. Ideally, this SEI is permeable to lithium ions, but is intrinsically an electronic insulator, and its formation prevents (or slows) further electrolyte decomposition during the following cycles.

The most common approaches to addressing these challenges are reduction of the size of the anode materials down to the nanoscale, using protective coatings or formation of an artificial SEI. Silicon nanostructures provide the advantage of a higher surface-to-volume ratio, as well as a shorter diffusion distance for lithium ions, which may improve the power capabilities of the battery.

The existence of a strong particle-size-dependent fracture behavior of silicon nanoparticles during the first lithiation cycle has been shown experimentally. That is, there exists a critical particle size of ~150 nm and wire size of ~300 nm, below which cracking should not occur. One-dimensional silicon nanowires and nanotubes have certain advantages over other silicon-anode configurations, such as a continuous 1D electronic pathway to facilitate efficient charge transport and the advantage of allowing the radial expansion of silicon to minimize cracking. Ogata et al. presented an in situ NMR study of the lithiation processes on similar SiNW anodes directly grown on a carbon support, and the multiple silicon anode phase transitions were distinguished and correlated to silicon anode typical charge and discharge stages.

For the past decade, numerous studies of anodes based on silicon nanostructures, including various coating and alloying methods, have been conducted. Most of the studies demonstrated several desired properties, namely low initial irreversible capacity (Qir), high surface capacity or high cycle number. However, the development of a silicon-based electrode possessing all these attributes still presents a significant challenge. In many studies, the proposed technology may also be attractive from a scientific standpoint, although its industrial scalability is questionable.

Leveau et al. introduced interconnected SiNWs synthesized on a stainless-steel current collector by a two-step CVD process. The highly loaded silicon electrodes (2.47 mg cm−2) led to very high specific capacities of up to 7.1 mAh cm−2 at C/50. However, the need for a precious-metal catalyst and the use of a rigid substrate might make this anode commercially challenging.

The second challenge facing silicon anodes—the stability of the SEI layer—has also been the subject of extensive research. It is rooted in the major volume changes between the lithiated and delithiated states of silicon that cause cracks in the SEI and expose the bare silicon surface to the electrolyte. This is followed by the creation of fresh SEI, thus consuming more electrolyte,
increasing the impedance of the battery and lowering capacity.\textsuperscript{4,21} Although multiple studies of the silicon anode were conducted in the last two decades, a thorough understanding of the complex phase transitions in silicon anode during cycling is essential for its successful application as a functional anode material.

In our previous works we have shown a three-dimensional (3D) growth of highly dense, mostly amorphous SiNWs on carbon-fiber-based open-structure conductive networks.\textsuperscript{22} It was concluded that the major degradation mechanism in the tested cells is an increase in cell impedance, and not loss of contact between the wires and the current collector, disintegration or pulverization of the SiNWs. After 200 cycles, 80\% of the SiNWs were found to maintain their low-rate capacity.

That work was followed by a novel anode structure that replaced the carbon-fiber substrates with a stainless-steel (SS) mesh.\textsuperscript{23} The Au-catalyzed vapor-liquid-solid (VLS) mechanism used previously to grow the wires was replaced with a self-catalyzed vapor-solid-solid (VSS) mechanism, in which a single-step chemical pretreatment of the stainless-steel mesh enables the growth of nanostructures directly out of the substrate without gold catalysts. This process should increase the affordability of growing these anodes on an industrial scale. Growing arrays of silicon nanowires on stainless-steel 3D mesh provides a highly porous medium, which allows easy expansion of silicon during lithium insertion, as well as sufficient free space between the nanostructures for stable SEI formation.

In this work, we explore the degradation mechanisms of the SiNW anode, not just on its own but in tandem with the cathodes used today in common commercial batteries, for example LiNi\textsubscript{0.5}Co\textsubscript{0.2}Mn\textsubscript{0.3}O\textsubscript{2} (NCA) and LiFePO\textsubscript{4} (LFP). It has long been known that the behavior of the two electrodes is strongly correlated in a way that affects each electrode and may differ when the anode and the cathode are co-dependent. As studied by Beattie et al.,\textsuperscript{24} the gradual capacity loss by both electrodes leads to higher charge voltages, essentially shifting the silicon away from its active voltage region and degrading the cathode.

Here, we investigate the behavior of our SiNW anodes with either NCA or LFP cathodes in a three-electrode cell configuration for the purpose of elucidating the effect these cathodes have on the degradation of the anode.

Furthermore, we demonstrate the scalability of our anodes by incorporating them in cylindrical cells, which were cycled for hundreds of cycles, at fast charge/discharge rates and in subzero temperatures, demonstrating that these anodes are compatible with the industrial equipment and materials used today in the battery industry.

Finally, we present proof-of-concept cells for further scaling up of the anodes by incorporating them in a multi-layer pouch cells, and by coating the SiNW anode with a solid polymer electrolyte and testing it in an all-solid-state coin cell vs a NCA cathode.

**Experimental**

The SiNW anodes were synthesized in a catalyst-free CVD process detailed in our previous work.\textsuperscript{23} Stainless-steel mesh with 25 um thick fibers, 316 L grade, was immersed in 25\% to 40\% HF solution (Merck, Sigma-Aldrich). The mesh was then rinsed with DI water, dried and put inside the CVD setup. Once inside the quartz tube, the chamber was evacuated to base pressure (5 mTorr), followed by the introduction of 5 sccm SiF\textsubscript{4}, 20 sccm Argon, at 460 °C, for growth times ranging from 30 min to 8 h.

The anodes for all coin cells were cut into 10 mm (only for half cells) or 12 mm (half and full cells) disks, and the back of each anode was coated with a thin layer of SWCNTs suspension (OCSIAI) for better electrical contact with the SS current collector of the coin cell. The anodes were dried under vacuum for 12 h at 50 °C and 2 h at 100 °C. The mass loading of the anodes was 0.7–4.6 mgSi cm\textsuperscript{-2}. CR2032 coin cells were assembled inside a glove-box filled with ultra-high-pure argon (content of O\textsubscript{2} and H\textsubscript{2}O < 0.1 ppm). The coin cell comprised a silicon composite anode, a 2400 Celgard separator and either a lithium-foil (15 mm in diameter, Rockwood Lithium Inc.) or commercially available cathode—NCA (Tadiran Batteries Ltd.) or LFP (LITHOPS) commercial cathode, 12 mm in diameter. The reversible capacities of the cathodes used for the coin cells were 1.7 mAh cm\textsuperscript{-2} for the LFP, and 2 mAh cm\textsuperscript{-2} for the NCA. In cells that were designated to function as three-electrode cells, two separators were used, and a 20 μm-thick copper strip partially covered with metallic lithium was inserted between them. The strip was insulated from the cell’s components by covering the middle part of it with another piece of Celgard. In all coin cell tests, the electrolyte was 1 M LiPF\textsubscript{6} in EC:DEC (1:1) with 2\% (v/v) VC to which was added 15\% (v/v) fluoroethylen carbonate (FEC) (Solvay-Flour). The battery-grade electrolyte was purchased from Solvionic. The cells were tested in a Biologic BCS-805 cyclic or VMP3 potentiostat. Electrochemical impedance spectroscopy (EIS) was performed with a Biologic potentiostat from 1 MHz to 0.01 Hz. The results were analyzed with the Zview software. The cylindrical cells (1/3AAA), with an active surface area of 17.1 cm\textsuperscript{2} were assembled by Tadiran Batteries Ltd. with a designated Tadiran Commercial NCA cathode and electrolyte. The capacities of the NCA of the cylindrical cells were 1.8–2.1 mAh cm\textsuperscript{-2}. The pouch cells were assembled by ETValue Ltd. using a designated NMC (622) cathode with a capacity of 3.5 mAh cm\textsuperscript{-2} and an electrode area of 23.4 cm\textsuperscript{2}.

For the all-solid cell, a mixture of polyethylene oxide (PEO, Mw = 5,000,000) and polyethylene glycol (PEG, Mw = 2000) was dissolved in acetonitrile for 12 h in the glovebox. A ceramic nanosize filler (Al\textsubscript{2}O\textsubscript{3} powder, 3\%v/v) and the salt- Lithium bis(trifluoromethane)sulfonimide (LiTFSI, molar ratio of 1:20 with PEO) were then added and the mixture was mixed for another 12 h.

Part of the prepared solution was cast in a Teflon template and vacuum dried at 60 °C to be used as a solid electrolyte. A SiNW anode with a loading of 0.7 mg cm\textsuperscript{-2} was coated with a mixture of PEO (16): PEG(6): LiTFSI(1) + 15\%v/v FEC. The cell consisted of the coated anode, the dried disc-shape solid electrolyte and an NCA cathode (1.9 mAh cm\textsuperscript{-2}), without any added liquid electrolytes.

The morphology of the samples was examined by several techniques: scanning electron microscopy (Quanta 200FEG ESEM equipped with an energy-dispersive X-ray spectrometer), TEM (FEG-HRTEM Fei Tecnai F20) and X-ray photoelectron spectroscopy (Physical Electronics Inc., USA). Depth profiles were obtained by argon ion sputtering, at a sputtering rate of 3.85 nm min\textsuperscript{-1}, on the basis of a SiO\textsubscript{2}/Si reference.

**Results and Discussion**

As described in the experimental section, the SiNW anodes were fabricated on a self-catalyzed stainless-steel mesh by a single-step CVD process. We found that the surface of the SS fibers was covered with a thin silicide layer (mostly iron, nickel and copper) that is the connecting phase between the mesh and the nanostructures.\textsuperscript{23} Figure 1a presents a SEM image of the pristine SS mesh before pretreatment with HF. Each fiber of the mesh is approximately 25 microns thick, and the free space between the fibers is roughly 25 microns, as well. The mesh used here is woven, giving it a total thickness of approximately 50 microns. The 25 microns free space is crucial for the unrestricted expansion of SiNWs and the penetration of the electrolyte between the SiNWs. Figure 1b shows the anode after the CVD growth of the SiNWs. As can be seen, the active material in the anodes consists solely of long, thin nanowires with short, bulky nanoparticles between them. A TEM image of a single wire, showing the crystalline core-amorphous shell structure of the silicon, is presented in Fig. 1a in the supporting information section (available online at stacks.iop.org/JES/167/050511/mmedia). A native oxide layer can be seen around the SiNWs, and XPS measurements have confirmed its thickness to be about 1.4 nm (supporting info Fig. 1b). Figure 1c displays a broken stainless-steel fiber covered with silicon nanowires (SiNWs) with interconnected silicide phase on the top of the SS fiber.
Characterization of Si/Li half cells.—Anodes with silicon loading of 0.9 mg cm$^{-2}$ were tested in half-cells, and their cycle life can be seen in Fig. 2a. The cells were cycled at approximately 0.1 mA cm$^{-2}$ for three cycles for the purpose of SEI formation. After three cycles, the current density (CD) was raised to approximately 1 mA cm$^{-2}$ for both charge and discharge, and was held constant until the 100th cycle, after which the CD was lowered for three cycles. The voltage range in all half-cells was 0.05–1 V. The capacity fade at higher CD stems mainly from the overpotential buildup on the electrode that may result from the rise of the resistivity of the SEI, and so it is highly informative to lower the CD to reveal the real capacity degradation that stems from the loss of active material. The areal capacity delivered by the cells is about 2.4 mAh cm$^{-2}$, and the gravimetric capacity is about 2600 mAh g$^{-1}$. As can be seen in Fig. 2a, the capacity retention is 100% at 0.1 mA cm$^{-2}$ from cycles 1–3 to cycles 101–103 (the values were taken from the average of each set of three cycles). The cells were cycled further for over 400 cycles, and while the capacity loss at 1 mA cm$^{-2}$ after 400 cycles stands at 64%, at 0.1 mA cm$^{-2}$ it is only 23%. This supports our previous findings$^{22}$ of the reason for the main degradation of SiNWs being the secondary SEI buildup and increased diffusion limitation of lithium ions, and not pulverization of the active material, or loss of contact with the SS mesh. As is clear from the graph, most of the capacity fade occurs before the 20th cycle. This is due to the formation and stabilization process of the SEI layer that requires more than a single cycle to reach a steady state. The cells containing an anode with 1.6 mgSi cm$^{-2}$ were cycled under the same conditions and the cycle life is presented in Fig. 2b. The cells provided 4.5 mAh cm$^{-2}$ and 2900 mAh g$^{-1}$ but, predictably, the capacity retention is lower than that of the cells with smaller loading. After 100 cycles, the cells lost 14% of their capacity at 0.1 mA cm$^{-2}$ and 38% at 1 mA cm$^{-2}$, and after 200 cycles the capacity loss was 39% at 0.1 mA cm$^{-2}$ and 68% at 1 mA cm$^{-2}$. dQ dV$^{-1}$ plots of these cells are presented in Supporting information (Figs. 2a–2b, 2d–2e), and show the two distinctive peaks of lithiation and delithiation of silicon at low current densities. At high current densities they show an overlap of the lithiation/delithiation peaks and also a gradual increase of charge/discharge overpotential. This leads to the conclusion that the dominant transition that takes place at high current densities is from silicon to lithium-poor silicides and back- the peak at low CD of the 1st transformation shifts down at high CD due to overpotential (0.25 v to 0.22 V at discharge, 0.45 V to 0.5 V at charge) while the 2nd transformation mostly shrinks. The voltage profiles of the 1st cycles of these cells are presented in Supporting information Fig. 3. The anode with high loading of 4.6 mgSi cm$^{-2}$ (Fig. 2c) was cycled first at 0.2 mA cm$^{-2}$ and then at 2 mA cm$^{-2}$, and its initial reversible capacity was 14 mAh cm$^{-2}$ and 3000 mAh g$^{-1}$. The Qir is also impressively low, only 4.8%, exemplifying the high efficiency of the nanowire lithiation. However, the degradation of this cell is very rapid, and at 2 mA cm$^{-2}$ it did not retain its capacity for more than 40 cycles. Lowering the current to 0.2 mA cm$^{-2}$ returned the capacity to 5.4 mAh cm$^{-2}$, 40% of its capacity at the initial cycles. The dQ dV$^{-1}$ plots of this cell (Supporting info. Figs. 2c, 2f) show peaks that are less well-defined, mainly at lower voltages. This is possibly due to the different transformations occurring in parallel in the dense electrode, which are more affected by a thicker SEI (in other words the Si close to the surface lithiates/delithiates faster than the Si deeper in the anode so the phase transformations aren’t uniform across the anode). The buildup of overpotential is most evident at 2 mA cm$^{-2}$ (Supporting info. Fig. 2f), where the lithiation peak shifts to lower voltages every 10 cycles. The delithiation peaks mostly diminish in size. Considering the nanometric size of the SiNWs and their direct chemical connection to the substrate, it is unlikely that mechanical fractures or loss of electrical conductivity are the main causes of this trend. Metal silicides, which form an intermediate phase at the grain-boundary of the SiNWs and SS mesh, are the main causes of this trend. Metal silicides, which form as an intermediate phase at the grain-boundary of the SiNWs and SS mesh, are more affected by a thicker SEI (in other words the Si close to the surface lithiates/delithiates faster than the Si deeper in the anode so the phase transformations aren’t uniform across the anode). The build-up of overpotential is most evident at 2 mA cm$^{-2}$ (Supporting info. Fig. 2f).
contribution to the capacity loss at high loading levels, after full lithiation/delithiation or after long cycling. This issue could be addressed in the future either by optimizing the morphology of the wires or using meshes of different size or geometry as substrate. The most effective approach for the current anodes, however, would be simply to limit their lithiation during cycling. Delivery of even partial anode capacity would still offer a significant improvement over graphite at a much lower anode thickness. For this reason, the full cells presented in the next section have been limited by their cathodic capacity.

**Characterization of SiNW anode vs commercial cathodes.**—To showcase the applicability of SiNW anodes in commercial cells, the anodes were tested vs commonly used cathodes. NCA and LFP were selected for this purpose as two common cathodes with different electrochemical charge/discharge characteristics. SiNW/NCA and SiNW/LFP cells were assembled and tested. Both cells were cycled over a 1.0 V voltage window, namely 3–4 V for cells with NCA and 2.6–3.6 V for the cells with LFP cathodes. In both cases anodic excess was used (anode-to-cathode ratio of approximately 1.5). For better understanding of the lithiation processes, a small sliver of metallic Li was used as a reference electrode, as detailed in the experimental section. A photo of the three-electrode coin cell can be seen in Supporting information Fig. 4. Figure 3 shows the cycle life of cells with anodes of about 3 mAh cm\(^{-2}\) capacity vs NCA (Fig. 3a) or LFP (Fig. 3b). The cells show high cycling stability with a capacity fade rate of only 0.06% per cycle at 0.1 mA cm\(^{-2}\) and 0.08% per cycle at 1 mA cm\(^{-2}\) with NCA and 0.32% per cycle at 0.1 mA cm\(^{-2}\) and 0.25% per cycle at 1 mA cm\(^{-2}\) with LFP.

Figures 4a and 4b shows voltage profiles of these cells, with the voltages of the anode and cathodes presented vs lithium reference electrode. The typical sloping character of anode and cathode charge/discharge curves in SiNW/NCA cells points to partial lithiation/delithiation in both electrodes (Fig. 4a). That does not seem to be the case for the LFP cathode. It can be seen in Fig. 4b that upon charging of the cell with LFP, the cathode is delithiated beyond its active region, which creates an overpotential that can accelerate its degradation. The over-delithiation of the LFP can also be seen to have an effect on the anode—the small rise in voltage at the end of lithiation indicates that once the LFP exits its active region (full depletion of lithium) lithiation into the anode stops and some de-intercalation of lithium from the anode takes place leading to the increase of its voltage (Fig. 4b). The voltage profiles of the full cell (anode vs cathode) are presented in Supporting information Fig. 5.

Considering the above, it is interesting to note that the voltage rise on the silicon shown in Fig. 4b is noticeable in cycles 25 and 50 as well, but not in cycle 102, which presumably can be the result of the poorer lithiation state of the silicon. The less lithiated the silicon is to begin with, the less likely it will self-discharge at the end of the charge.

Figure 4c shows the plots of the end-of-charge and end-of-discharge voltages on the anodes as a function of cycle number. For both cells with different cathodes, the anode voltage at the end of discharge shows little increase during cycling —0.3 mV per cycle vs NCA and 0.8 mV per cycle vs LFP. However, it is higher for the LFP cell, indicating more pronounced lithium depletion in the anode. The anode voltage at the end of charge also increases slightly with cycle number —0.4 mV per cycle vs NCA and 1.7 mV per cycle vs LFP—indicating a loss of lithium (and capacity) from the anode. However, the voltage at the end of charge is higher for the LFP cell, thus suggesting a lithium-poor (or smaller capacity) anode. The anode that was cycled vs NCA experienced a voltage window of approximately 0.45 V, vs a 0.55 V window for the anode coupled with LFP. In addition to having a narrower window, the anode coupled with NCA was also cycled at an electrochemical window (EW) that was on average about 0.1 V below the EW of the anode coupled with LFP. This means that SiNWs coupled with NCA were delithiated to a lesser extent and therefore less cracking occurred in the SEI layer as a result of the contraction of silicon. As suggested by Beattie et al.,24 the inevitable capacity loss at each cycle forces
more lithium out of the cathode, which raises the cutoff voltages on
the cathode and hence on the anode as well. This, in turn, lowers the
efficiency of the anode. What is noticeable here is the difference in
correlation between the silicon anode and the two vastly different
cathodes. However, the data analysis does not include the contribu-
tion of the increasing resistivity of the SEI to the capacity
degradation.

*Post mortem analysis of the SiNW anodes.*—After cycling, the
anodes in half cells were fully delithiated up to 2 V, and full cells
were discharged down to 2 V. The cells were then disassembled in
the glovebox. The electrodes were divided into two parts: part A was
washed with dimethyl carbonate (DMC) in the glovebox and part B
was washed with DMC, then with ethanol and water outside the
glovebox. This procedure enabled the removal of the excess salts,
electrolyte and semi-soluble secondary porous SEI components from
the anode first, and the removal of most inorganic and organic SEI
components by ethanol and water in order to expose the SiNWs
skeleton. SEM images of the anodes washed by DMC after cycling
vs LFP (Fig. 5a) show that SiNWs are covered with a thick layer of
granular electrolyte-reduction products that cover the full length of
the SiNWs. XPS analysis (supporting info. Figs. 6 and 7, Table 1)
shows peaks related to the presence of Li2O, Li2CO3, LiF and
residual LiPF6, as well as oligomers such as polyolefins and PEO25
EDS also confirmed the presence of carbon, oxygen, fluorine and
phosphorus, as well as elements from the substrate such as iron and
chromium.

Further washing of the electrodes with ethanol and DI water
(Fig. 5b) revealed SiNWs covered by a thinner and porous film of
reduction products. The morphology of the SiNWs, which are
contorted and deformed, also resembles the cycled SiNWs presented
in our previous work.22 The skeletal appearance of the wires is likely
a result of the rippling effect suggested by Ryu et al.,26 where layers
of Si and Li3Si apply different stresses on one another, bending the
wires back and forth. As more lithium is trapped inside the silicon,27
the deformation of the wires becomes more apparent. The same
morphologies can be seen in anodes that were cycled vs lithium for
100 cycles (Figs. 5c and 5d), proving that the degradation of the
silicon and the accumulation of electrolyte-reduction products is not
related to the counter electrode.

*Characterization of industrial-size cells.*—After demonstrating
the capability of our anode to be paired with commercial cathodes,
the next step in our development process was to test them in
commercial cylindrical-cell configuration (1/3AAA size). This step
bears with it both challenges and advantages compared to coin cells.
Since these anodes are grown as dual-sided, they can be interposed
between two cathodes, a step which would shorten diffusion lengths
between the cathode and the backside of the anode. In addition, as
mentioned above, the use of a bare SS tab for electrical conductivity
instead of applying the current directly to the SiNWs should
significantly lower the overpotential in the cell. Our binder-free
anodes are flexible enough to be rolled with a cathode and separator.
However, in addition to high flexibility, high tensile strength of the

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*Figure 5.* SEM images of SiNW anodes with 2 mg cm\(^{-2}\) loading, after cycling—(a) cycled vs LFP for 300 cycles, washed with DMC, (b) cycled vs LFP for 300 cycles, washed with DMC, ethanol and water, (c) cycled vs Li for 100 cycles, washed with DMC, (d) cycled vs Li for 100 cycles, washed with DMC, ethanol and water.
nanowires and good adhesion to the stainless steel mesh are essential. This is important in order to eliminate SiNW fracture and disconnection from the substrate on rolling. For this task, anodes were synthesized with a loading of 1.8–3.9 mgSi cm$^{-2}$, and at the edge of each anode the deposition of silicon was suppressed by submerging the edge of the SS mesh in dilute nitric acid following the HF etching.23 This treatment led to passivation of the mesh, which inhibited the growth of SiNWs, thus creating a current collector to be welded into the cell (supporting info. Fig. 8). No CNT coating was required for these anodes. The first batch of these cells was assembled with an anode-to-cathode capacity ratio of approximately 1.1. The cycle life of these batteries is presented in Fig. 6a. The very first prototype of this kind of cell (cell #1, red and black curves) was cycled at 3–4 V, C/6 after 3 cycles of C/20. It provided an initial capacity at C/6 of 2.8 mAh cm$^{-2}$ and 1400 mAh g$_{Si}^{-1}$, and 68% capacity retention after 300 cycles.23 The
results for a cell of a different batch are presented in the blue and green curves of Fig. 7a (cell #2). In order to test the anodes under more moderate conditions, the anode-to-cathode capacity ratio was increased to approximately 1.9, and the voltage range was reduced to 3.1–3.9 V. The cycling profile for this cell was C/6 at charge with constant voltage to C/12 (CCCV) and C/3 at discharge. The cell was also cycled for 20 cycles (#23–#43) at −12 °C to test the ability of our anodes to perform under real-world conditions. The initial capacity of the cell at C/6 was 3 mAh cm−2. Its capacity under subzero conditions was 1.6 mAh cm−2, and it rose back to 3 mAh cm−2 when the temperature was returned to 30 °C. After 300 cycles, it retained 77% of its initial capacity. Overall this cell has, on the one hand, gravimetric capacity that is significantly lower than is achievable with our anodes, yet the increase of active materials still allows for the same areal capacity as that of the first cell, while cycling over a narrower range. Fig. 6b shows the performance of a different cell (cell #3) at various C-rates. At first the charge rate was tested between C/6 and 2 C, while the discharge rate was kept at C/6; following that, various discharge rates were tested while the charge rate remained at C/6. At an anode-to-cathode ratio of approximately 1.0, the initial capacities of this cell at C/6 were about 3.5 mAh cm−2 and 1930 mAh g−1. At charge and discharge rates of up to 2 C, the cells exhibit more than 30% of their maximum capacity (at C/20). In addition to this, the capacity of the cells remained almost the same whether the fast step was lithiation or delithiation. Considering the fact that delithiation is much faster kinetically than lithiation, this result suggests that the limiting factor at high rates in our anodes is diffusion-related and not due to lithiation kinetics. More than 40 cells were successfully assembled and tested by our group for hundreds of cycles for each cell, and while the road to optimal cell design may still be long, these cells are already showing potential in a variety of crucial parameters for industrial LIBs.

**EIS analysis of Si/NCA cells.**—In an attempt to better understand the mechanisms at play in our SiNW/NCA cells, EIS analysis was carried out both on the three-electrode coin cells (Figs. 7a and 7b) and on the second 1/3AAA cell in Fig. 6a (Figs. 7c and 7d). The EIS of the three-electrode cell at cycle 3 can be seen in Figs. 7a–7b, after charge and discharge, respectively. An equivalent circuit (as seen in Fig. 7a) was used to evaluate the resistance and pseudo-capacitance of each of the two semicircles noticeable in the figures. The fitting values of the resistors and the constant-phase-elements (CPEs) are shown in Tables I and II. On the basis of the frequencies and the pseudo-capacitance of the semicircles, it can be assumed that the first one may be assigned to the SEI on the electrodes. The second semicircle may be assigned to the charge transfer (CT) resistance of the resistance of the Faradaic reaction occurring at the electrode surface. As reported by Abraham et al., at a high state-of-charge (SOC), the NCA cathode shows its highest impedance as a result of the high activation-energy barrier for lithium mobility when the NCA is already lithium-rich. Sabet et al. also claimed for a graphite/NCA cell that it is reasonable to suggest that at high SOC of the full cell the impedance would be dominated by the anode, while in its discharged state, the cell would have an impedance that is dominated by the cathode charge transfer. In Fig. 7a the impedance of the charged state (black curve) is a combination of the cathode’s and the anode’s CT resistance. The full spectrum in the discharged state (Fig. 7b, black curve) appears to support the claim of cathode domination. The EIS spectra of the 1/3AAA cell can be seen in Figs. 7c–7d. As mentioned above, this cell was cycled at 30 °C except for cycles 13–33, which were tested at −12 °C. This cell was also tested over a more conservative range than the three-electrode cells, at 3.1 V–3.9 V, charged (CCCV) at C/6 with CV to C/12 and discharged at C/3. The spectra are composed of two semicircles, with the spectra taken at −12 °C (red curve) showing a small but reversible rise of the resistance of the electrolyte (R_{bulk}—the intersect with the X-axis), a reversible rise of the resistance of the SEI after charge compared to cycle 3 and a massive increase of resistance of the second semicircle. This rise of resistance may be ascribed to the charge transfer of lithium in the cell, hindered by the subzero temperature. The fitted values of the Nyquist plot can also be seen in Table II.

Several insights are obtained from the evolution of the spectra. First, from cycles 3 to 253 (Figs. 7c and 7d), the first semicircle grows while the second diminishes. This suggests that the growth of the SEI is the main cause of the increase in impedance. While both electrodes have passivation layers, it is logical that the SEI of the anode grows substantially faster than that on the cathode. The CV step at the end of each charge may also be a contributing factor to the growth of the SEI on the anode. In addition, the reduction of the second semicircle may be related to the depletion of lithium from the cathode. As more lithium is lost following irreversible reactions, the cathode remains on average closer to its mid-lithiated region where the CT resistance is lowest. As expected, the resistance values at all cycles at 30 °C were equal or larger in the cell’s discharged state than after charge, as a result of both lithiation of the cathode and crack formation on the anode’s SEI.
Table II. Fitting values for an equivalent circuit in EIS of 1/3AAA cell.

| Cycle | $R_{\text{bulk}}$ [ohm] | $R_{\text{SEI}}$ [ohm] | $C_{\text{SEI}}$ [F] | $R_{\text{CT}}$ [ohm] | $C_{\text{CT}}$ [F] |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 3     | 0.96            | 0.18            | 1.1E-05         | 0.32            | 9.6E-03         |
| 23    | 1.19            | 0.39            | 1.6E-03         | 5.87            | 8.2E-03         |
| 103   | 0.99            | 0.22            | 5.6E-06         | 0.22            | 1.1E-02         |
| 253   | 0.99            | 0.35            | 4.7E-06         | 0.43            | 3.5E-04         |
|       |                 |                 | 1.3E-05         | 1.02            | 1.3E-02         |
|       |                 |                 | 5.1E-06         | 12.95           | 6.2E-03         |
|       |                 |                 | 9.5E-06         | 0.28            | 1.4E-02         |
|       |                 |                 | 1.0E-05         | 0.57            | 4.6E-04         |

**Charge state**

**Discharged state**

**Figure 9.** Cycle life of an all-solid state SiNW/NCA coin cell at 0.1 mA cm$^{-2}$.

**POC pouch cell and all-solid-state coin cell.**—Many applications today, from mobile phones to EVs, have switched from cylindrical cells to pouch and prismatic cells. For that reason, and in an attempt to further increase the capacity of our SiNW containing cells, two POC pouch cells with silicon loading of approximately 5 mgSi cm$^{-2}$ were recently assembled and tested. Each cell contains six electrodes of approximately 24 cm$^2$ each. The cathodic loading of these cells is 3.5 mAh cm$^{-2}$, meaning an N/P ratio of approximately 1.1. The cycle life of the cells as of submission of this manuscript can be seen in Fig. 8. The cells provided initial reversible capacity of up to 720 mAh, or 5.2 mAh cm$^{-2}$ and around 1000 mAh gSi$^{-1}$, and are presently being tested further. Their cycling profile is 3–4 V at C/6 (at charge) and C/3 (at discharge).

Extensive research on solid electrolytes is also being conducted currently. Solid electrolytes are expected to drastically improve the safety of LIBs. In our work, an anode with 0.7 mgSi cm$^{-2}$ loading was coated with a mixture of PEO (16): PEG(6): LiTFSi(1) + 15%v/v FEC. An image of such a coated anode can be displayed in the inset of Fig. 9. The cell consisted of the coated anode, the cast free-standing film of solid electrolyte consisting of PEO (20): PEG(2): LiTFSi(1) + 3%v/v Al$_2$O$_3$ powder and an NCA cathode (1.9 mAh cm$^2$, N/P ratio of about 0.9). The cell was cycled at 60 °C and current density of 0.1 mA cm$^{-2}$, first at 3–4 V for 30 cycles and then at various other voltage ranges up to 2.8–4.2 V. The cycle life of the cell is shown in Fig. 9.

**Conclusions**

Our research efforts have culminated in the outstanding performance of the 3D SiNW anode: high areal capacity of up to 14 mAh cm$^{-2}$, gravimetric capacity of up to 3000 mAh gSi$^{-1}$ and a very low irreversible capacity of 4.8%, were demonstrated in Si/Li half-cells.

Pairing the 3D SiNW anode with a commercial cathode, resulted in a full lithium-ion battery with a cycle life of 500 cycles with less than 30% capacity fade at C/20. In order to achieve better understanding of the degradation mechanisms in both half cells and full cells, the morphology and the composition of the SEI were analyzed. It was concluded that the major cause of capacity loss in both full and half cells is the accumulation of excess secondary SEI as a result of the breakdown-and-repair mechanism of the SEI during repeated volume changes of silicon upon cycling. In that regard, both the depths of lithiation/delithiation and the voltage window applied on the anodes play a crucial role in the stabilization of the SEI on prolonged cycling.

The developed anodes have the potential to increase the energy density of lithium-ion batteries for electric vehicles, storage devices and portable applications, by a factor of 50%. Initial results with these anodes in cylindrical cells have already shown 300 stable cycles with under 25% capacity fade, charge rate of up to 2 C with over 30% capacity retention and 50% capacity retention at −12 °C, proving the scalable, industrial potential of these anodes. These anodes were scaled-up further and showed reversible capacities of up to 5.2 mAh cm$^{-2}$ in POC pouch cells.

An all-solid-state polymer-electrolyte battery ran more than 70 cycles at 60 °C.

**Acknowledgments**

The authors wish to thank, Dr Larisa Burstein for the XPS analysis, Tadiran Batteries Ltd. for their cooperation in assembly of the 1/3AAA cells and ETVenergy Ltd. for their cooperation in assembly of the pouch cells. This work was supported by the Momentum Fund, Ramot Ltd.

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