Fabrication and Characterization of Lithium-Silicon Thick-Film Electrodes for High-Energy-Density Batteries

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We have developed a method to operate lithium-silicon (Li-Si) thick-film electrodes in a manner consistent with traction applications. Key to the operating strategy is the voltage control of the electrode. It is expected that strong reducing environments, created by operating the electrode at low potentials (near that of Li), reduce battery life. We show that operating Li-Si at higher potentials is also damaging, and this is counterintuitive in that common negative electrodes (e.g., graphites and titanates) do not suffer from this limitation. Arguments based on measured Coulombic efficiencies, cycle life tests, in-situ stress measurements, and high-resolution microscopy resolve the otherwise anomalous findings. We show that promising half-cell (cells constructed with a lithium counter electrode) cycling data are reflected in full cells that employ a 622-NMC positive electrode (Ni0.5Mn0.4Co0.1O2). Last, a modified hysteresis model, based in part on our earlier approach to treat NiMH (nickel metal hydride) cells, is shown to represent well the constant-current cycling data, and open questions associated with needed improvements in modeling Li-Si hysterisis and related low-current phenomena are highlighted.

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Silicon film electrodes have been shown to be useful for characterization purposes insofar as one need not treat binders, various particle geometries, conductive diluents, and other complications inherent in the construction of porous electrodes.1–17 In this work, we focus on the potential utility of Si thick-film electrodes formed on roughened copper current collectors. If sufficient capacity can be obtained, such a geometry might simplify electrode fabrication, as the electrode host material would consist of nothing more than Si deposited on a current collector, and high specific energies (Wh/L) and energy densities (Wh/kg) could result.

Four topics are examined in this endeavor. First, by controlling the potential limits over which we operate a Li-Si electrode, can we obtain sufficient stability for relatively thick-film electrodes (i.e., yielding more than 2 mAh/cm²)? Second, how does the electrochemical performance correlate with stress in the electrode over the potential window of operation? Third, because the electrode consists of only Li and Si, we can isolate equilibrium hysteresis behavior associated with this alloy, and we derive and implement a simple model to represent the voltage-composition data that may be useful in subsequent engineering analyses of electrodes with a significant Li-Si contribution. Last, we examine full cells (Li-Si vs. an NMC622 positive electrode, corresponding to Ni0.5Mn0.4Co0.1O2) in the context of capacity, cycle life, cycle efficiency, microstructure, and elemental analysis. A cell modeling tool15 is used to examine the efficacy of the Si film electrodes for actual battery electric vehicle applications based on specific energy and energy density calculations.

Experimental

A Si target of 3-inch diameter was sputtered (Åmod deposition system manufactured by Angstrom Engineering Inc.) in Ar gas with a flow rate of 2 sccm (standard cubic centimeters per minute). The thickness of the Si film was controlled by the deposition time with a constant deposited rate of 0.4 nm per second by means of a calibrated quartz microbalance. For all electrochemical tests with the exception of the MOSS (Multi-beam Optical Stress Sensor) experiments described below, the electrode diameters were 12 mm, yielding a plan-view (geometric) area of 1.13 cm². The Si mass was calculated based on the deposition rate and time, the Si density (2.32 g/cm³), and the real surface area, which ranged between 1.3 to 1.4 times that of the projected surface area due to the roughness, as measured by an optical interferometer (Wyko NT 3300, made by Veeco). We note that the roughness factor can change with electrode thickness and fabrication conditions. For samples A through E associated with Figure 2 through Figure 10, the 2-micron-thick Si film (assumed to be conformal to the roughened Cu current collector, shown in Figure 1, for the purposes of estimating the Si loading) leads to a Si loading of 0.63 mg/cm² (geometric area) and a measured capacity of 2.28 mAh/cm², as shown in the uppermost plot in Figure 2 (1.2 to 0.05 V vs Li). This measured value is quite close to what we would expect for the Li-Si system. From References 16 and 17, we find that for the potential range of 1.2 to 0.05 V vs Li, the capacity corresponds to about Li1.77Si; that is, each Si can accommodate about 3.73 Li. Using this information, we estimate the capacity between 1.2 and 0.05 V vs Li to be

\[ (2 \mu\text{m Si)} (1.35 \text{ roughness factor}) \left( \frac{1}{10,000 \mu\text{m}} \right) \left( \frac{2.32 \text{ g Si}}{1 \text{ cm}^2 \text{ Si}} \right) \]

\[ \times \left( \frac{1}{28.01 \text{ mol Si}} \right) \left( \frac{3.73 \text{ mol Li}}{\text{mol Si}} \right) \left( \frac{96,487 \text{ C}}{\text{mol Li}} \right) \]

\[ \times \left( \frac{1,000 \text{ mAh}}{3,600 \text{ C}} \right) = 2.23 \text{ mAh/cm}^2 \]}

Thus, the measured value of 2.28 mAh/cm², about a 2 percent difference from 2.23 mAh/cm², is well within our experimental resolution. Last, we chose to subdivide the 2.28 mAh/cm² capacity into approximately five equal-capacity increments of about 1 mAh/cm² each (i.e., about 40% of the 2.28 mAh/cm² full capacity), by controlling the voltage limits associated with samples A through E.

For the electrochemical tests depicted in Figure 2 through Figure 10, the Si film electrodes were used as working electrodes, and pure lithium metal foil (purchased from MTI) as counter-reference electrode in CR2032 coin cells (i.e., a half cell configuration). A 21 μm thick separator (Celgard, USA) was placed between working electrode and lithium foil. The electrolyte was a mixture of 1 M LiPF6 in ethylene carbonate and diethyl carbonate (EC:DEC 1:1 volume ratio, BASF). The Arbin battery test system (BT-2000) was used for the electrochemical experiments. For the results depicted in Figure 2 through Figure 7, all samples were subjected to two formation cycles at a constant current of 0.25 mA, corresponding to a current density of 0.22 mA/cm² (about a C/10 rate based on the 2.28 mAh/cm² loading described above), from their initial open-circuit voltage (about 1.2 V vs Li) to 0.05 V, and then back to 1.2 V. A plot of the first two formation cycles (for case C) is provided in Figure 2 through Figure 7, all samples were subjected to
in Figure 5. Because less surface area per unit volume prevails for a thick film as compared to a porous electrode consisting of small particles, the current efficiencies shown in Figure 5 are relatively high (94.4% for the first cycle and 99.6% for the second cycle). After the formation cycles, the same current density (0.22 mA/cm²) was applied to each sample to reduce the potential from 1.2 V to the lower limit and then back to upper limit. This procedure generated the voltage profile of the designed potential window (cf. Figure 2 and Figure 3). The cycling tests depicted in Figure 9 and Figure 10 were conducted with the same potential windows for A through E as described in Figure 2 and Figure 3 and the same current density (0.22 mA/cm²). No potential hold was employed: when the potential reached its limiting value, the current was immediately reversed in sign.

For full cell tests results shown in Figure 11, a 6 μm thick Si film was deposited onto the Cu substrate as determined by the quartz microbalance. In an attempt to quantify the amount of Si deposited, three freshly coated electrodes (12 mm diameter) were weighed and subsequently dissolved in an acid solution, and inductively coupled plasma optical emission spectrometry was used to deduce the Si to Cu ratio, after which the mass of Si could be determined from the sample weight. Results for the three sample yielded 1.6, 1.6, and 1.5 mg Si/cm². We thus approximate our Si loading to be 1.6 mg Si/cm². By means of a calculation similar to that of Eq. 1, if we use a Si thickness of 6.5 μm and a Si density of 2.32 g/cm³, we can calculate a roughness factor of 1.05, which is reasonable for the thick Si film and consistent with the micrographs shown in Figures 13c, 13d, and 13e. We estimate the area-specific capacity to be 5.7 mAh/cm²:

\[
\frac{(1.6 \text{ mg cm}^2)}{28.01 \text{ mol Si g}^{-1}} \times \frac{3.73 \text{ mol Li mol}^{-1}}{96487 \text{ C mol}^{-1}} \times \frac{1 \text{ Ah}}{3600 \text{ C}} = 5.7 \text{ mAh cm}^2
\]

We note that Markevich et al. examined Si films of a similar thickness in the context of low-temperature performance. The 1.6 mg/cm² Si film electrodes were paired with NMC622 counter electrodes and cycled in CR2032 coin cells. The electrolyte was a mixture of 1 M LiPF₆ in a 45:45:10 EC:DEC:FEC volume-ratio solvent (EC, DEC, and FEC refer to ethylene carbonate, diethyl carbonate, and fluoroethylene carbonate, respectively). The formation cycles were performed in the voltage window from 4.23 volts down to 3.67 volts for three times at constant current (0.14 mA or 0.12 mA/cm²). Then the coin cells were...
cycled from 4.23 volts to 3.2 volts at constant current (0.93 mA or 0.82 mA/cm²) for the long-term cycle stability test. In the full cell cycling tests, the 3.2 to 4.23 V potential limits yield a (negative limited) capacity of about 2.3 mA/cm² initially, and this may be viewed as the cell’s nominal capacity. Thus, the 0.82 mA/cm² formation current density corresponds to about C/7 based on the total capacity of the Si electrode, and the about C/3 based on the specific capacity of each potential window.

The stress measurement (cf. Figure 7) was conducted in a customized in-situ electrochemical MOSS. An approximately 100 nm Si thin film was deposited on a quartz wafer with a 20 nm Ti interlayer as the current collector. The electrochemical test protocols were the same as for coin cell tests described previously. The curvature of the film and substrate assembly was recorded along with the current-potential data. The experimental and analytical details of the stress measurements are similar to those described in Ref. 5.

The effect of full cell cycling on the electrode structure in the 6 μm thick Si film electrodes was evaluated using a light microscope and an SEM (scanning electron microscope). Cycled electrodes in the delithiated state were rinsed with DMC (dimethyl carbonate) to remove the residual electrolyte and subsequently examined. A light microscope (Hirox) was used to examine the plan view of the delithiated Si electrodes and the back side of the Cu current collectors. The electrode cross-sections and the electrode current collector interfaces were assessed using an SEM. Electrodes were cross-sectioned using a broad Ar⁺ ion beam mill (Hitachi, IM4000) operating at 6 keV. SEM secondary-electron images, backscatter-electron images, and elemental maps were collected at an acceleration voltage of 5 keV. The secondary-electron micrographs provided images dominated by topographical contrast, while the backscattered-electron images provided images dominated by atomic number contrast. Elemental maps were collected with an EDS (energy dispersive X-ray spectroscopy) system equipped with a silicon drift detector (EDAX).

**Hysteresis Model**

The hysteresis voltage $U_H$ is the difference between the measured voltage of the Li-Si electrode (vs. a Li reference) minus the midpoint voltage $U_{avg}(Q)$, where $Q$ denotes Coulombic capacity or charge (i.e., $Q$ is the Ah employed in the axes of Figure 2 and Figure 3),
and $U_{\text{avg}}(Q)$ is the average of the maximum potential (oxidation or delithiation, uppermost solid black curve of Figure 8) and minimum potential (reduction or lithiation, lowermost solid black curve of Figure 8). We refer to the difference between the maximum potential and the midpoint potential as $U_H(\text{max})$. That is, for the low currents employed in this work, we assume equilibrium prevails, and the voltage (vs. a Li reference) is bounded between $U_{\text{avg}} + U_H(\text{max})$ (corresponding to the charge-increasing branch of the open-circuit potential) and $U_{\text{avg}} - U_H(\text{max})$ (corresponding to the charge-decreasing branch of the open-circuit potential).

We shall use the following differential equation to represent the hysteresis potential $U_H$:

$$\frac{\partial U_H}{\partial t} = -k I(t) \left[ U_{\text{max}}(t) + U_H(t) \text{sign}(I(t)) \right]$$

which is similar to that employed in Ref. 19 for NiMH batteries. The cell current is given by $I(t)$. For NiMH batteries, $U_{\text{max}}$ can be assumed constant, independent of $Q$, which simplifies the analysis relative to the Li-Si system. Because $I(t) = \frac{dQ}{dt}$, we can rewrite Eq. 3 as

$$\frac{\partial U_H}{\partial Q} = -k \left[ U_{\text{max}}(Q) + U_H(Q) \text{sign} \left( \frac{dQ}{dt} \right) \right]$$

The voltage of the Li-Si electrode is given by

$$U(Q) = U_{\text{avg}}(Q) + U_H(Q)$$

We shall treat $k$ as the lone adjustable constant, independent of time $t$ and charge $Q$ for the range over which we apply the model (isothermal conditions prevail). Equations 3 and 4 can be recast as integrals over

Figure 6. Coulombic efficiencies for A through E (cf., Figure 2 and Figure 3). The dashed lines reflect the potential ranges.

Figure 7. Upper plot: stress measured over the full potential range and for A through E. Lower plot: corresponding potential measurements.
time or charge, respectively:
\[
\int_{U_H(0)}^{U_H(t)} dU_H = -k \int_0^t I(\bar{t}) \left[ U_{H,\text{max}}(\bar{t}) + U_H \text{sign}(I(\bar{t})) \right] d\bar{t}
\]
\[
\int_{U_H(0)}^{U_H(Q)} dU_H = U_H(Q) - U_H(0) = -k \int_{Q(0)}^Q \left[ U_{H,\text{max}}(q) + U_H \text{sign} \left( \frac{dQ}{dt} \right) \right] dq \tag{6}
\]

where \(\bar{t}\) and \(q\) are dummy variables of integration for time and charge, respectively. The second line of Eq. 6 indicates that one can treat the Coulombic capacity \(Q\) as the independent variable, instead of time, which is consistent with true hysteresis not having a time dependence.\(^a\) Time only shows in line two of Eq. 6 to indicate which equilibrium potential branch (oxidation or reduction) is of interest (i.e., the sign term).

To understand the behavior of the model, it is helpful to look at a case wherein \(U_{H,\text{max}}\) is treated as a constant and the current is constant (the current is constant for the tests leading to the plots of Figure 2 and Figure 3). \(U_{H,\text{max}}\) does have a mild dependence on potential (or capacity): for test C, it varies from 126 mV at the lowermost potential, 0.1331 V vs. Li, to 93 mV at the uppermost potential, 0.5526 V vs. Li. For a constant value of \(U_{H,\text{max}}\), which we term \(\bar{U}_{H,\text{max}}\),

\[
U_H(Q) + \bar{U}_{H,\text{max}} = e^{-Q/k} \quad \text{for} \quad I \quad \text{and} \quad (dQ/dt) \quad > \quad 0
\]
\[
U_H(Q) - \bar{U}_{H,\text{max}} = e^{Q/k} \quad \text{for} \quad I \quad \text{and} \quad (dQ/dt) \quad < \quad 0
\]

Because we employ constant current for the experiments of Figure 2 and Figure 3, and because \(U_{H,\text{max}}\) is nearly constant, the model calculations of Figure 8 exhibit exponential-like behavior, consistent with Eq. 7, when the potential traverses between the equilibrium branches (thick, black lines of Figure 8).

For the calculations corresponding to the symbols in Figure 8, we employed the second line of Eq. 6 to calculate \(U_H(Q)\) and Eq. 5 to calculate \(U(0)\). The same value of \(k = 17,000\) Ah\(^{-1}\) was used for both oxidation and reduction. To start the calculation for delithiation (oxidation), \(Q(0) = 0\) when the voltage (solid blue curve in Figure 8) reaches 0.1331 V vs. Li. Upon reversing the current so as to scan back to 0.5526 V vs. Li, the flow of charge \(dQ/dt\) corresponding to the oxidation process is taken to be negative (Ah capacity of reversible Li in the electrode is being reduced) as is the current \(I\) in the context of Eq. 6. As Li is extracted from the electrode (solid red curve in Figure 8), the potential increases as \(U_H(Q)\) increases, and \(U_H(Q)\) eventually approaches \(U_{H,\text{max}}(Q)\) (solid red curve approaches the uppermost solid black curve in Figure 8). The process is reversed when the voltage reaches 0.5526 V vs. Li, yielding the solid blue curve in Figure 8 for the reduction (lithiation) process (\(I\) and \(dQ/dt\) > 0).
Figure 10. Left plot: voltage histories for the indicated cycles associated with Figure 9. Right plot: voltage versus state of lithiation for the indicated cycles.

Discussion of Results

An enabler for good adhesion between the expanding and contracting Li-Si\textsuperscript{32–36} active material (and alloys of Li-Si-Sn\textsuperscript{29}) and the copper current collector is the roughened surface of the copper. In a related vein, Kim et al.\textsuperscript{30} found that the cycle performance of the silicon-graphite composite electrodes that were slurry-coated onto Cu foils was enhanced when a nodule-type copper foil was employed, similar to the morphology depicted in Figure 1. As noted in the Experimental section, our roughness factor of 1.3 to 1.4 allows for a thinner film for the same loading (mAh per plan-view surface area). Early work regarding the fracture and capacity fade of thin-film electrode structures can be found in the paper by Huggins and Nix.\textsuperscript{30} Xiao et al.\textsuperscript{5} employed an equilibrium force balance that agreed well with experimental data and concluded that the driving force for cracking of Li-Si electrode films is proportional to the film thickness. A more detailed analysis was later provided by Halbaradaran et al.\textsuperscript{10} Li et al. examined the nature of cracks in film electrodes as a function of electrode thickness.\textsuperscript{31} In all of these analyses, thinner films are shown to be more robust and less subject to cracking and capacity fade.

Based on the total capacity of the electrodes associated with the results presented in Figure 2 and Figure 3, 2.3 mAh/cm\textsuperscript{2}, the time to remove all lithium from a fully lithiated electrode (i.e., to go from the equilibrated state at 0.05 to 1.2 V vs. Li) at the imposed current density of 0.22 mA/cm\textsuperscript{2} is about 10 hours, corresponding to the C/10 rate of current passage. At these low rates, we would expect the 2 \textmu m thick Li-Si electrode to be in a near equilibrium state. In support of this perspective, using a diffusion coefficient of Li in Si of $D = 5 \times 10^{-12}$ cm\textsuperscript{2}/s (cf., Figure 5 and related discussion in Ref. 16), we find $L^2/D = (2 \times 10^{-4} \text{ cm})^2/(5 \times 10^{-12} \text{ cm}^2/\text{s}) = 8000 \text{ s} = 2.2$ hours, about 1/5 of the 10 hours associated with the C/10 rate of current passage. These cycling results were for 2 \mu m thick Li-Si films, whereas the cycling results were for 2 \mu m thick films, and the electrode thickness will influence the stress distribution; hence, the explanations provided are consistent, but should be viewed as qualitative.

We are now positioned to provide an explanation as to why test C provides the best performance of tests A – E. First, we consider the formation and stability of the “SEI” (solid-electrolyte interphase) over a Li-Si electrode.\textsuperscript{32–36} In Ref. 37, it was shown that for Li-Si film electrodes, more negative potentials promoted a thinner and stiffer SEI that yielded a higher current efficiency. (For example, 0.2 vs. 0.4 V, with respect to a Li reference.) References to past works with similar findings can be found in Ref. 37. A consistent theme is that organic breakdown products resulting from Li reactions with solvent molecules are formed at higher potentials, and inorganic breakdown products form at lower potentials, with the latter yielding a more compact and protective composite layer of constituents in terms of reducing unwanted side reactions. These considerations would point to continued improvement in current efficiencies in going from A to E. However, when the surface is highly reducing (potentials approaching that of Li), the surface layer is no longer protective, unwanted
Electrolyte-reduction reactions commence, and the current efficiency declines (cf. Case E, Figure 6). In this context, C may represent the right balance, yielding the higher current efficiency and most robust SEI.

A second consideration that helps to explain why test C may yield the highest current efficiency stems from the MOSS results. Given that C experienced the lowest stress magnitude (i.e., the absolute value of the measured stress at the highest voltage minus that of the lowest voltage), there is less of a mechanical driving force to disrupt the surface layer (“SEI”) over the Li-Si electrode for test C relative to all other test samples. More generally, fatigue, failure, crack growth, and mechanical decohesion are exacerbated by larger stress magnitudes, which is consistent with C showing the best life performance. Last, we note also that for much of the potential window associated with test C, the stress is compressive, indicating a stress condition that would suppress the nucleation and propagation of cracks in the SEI layer as well as Si film; hence, test C experiences the lowest stress magnitude, and the stress is mostly compressive, and both observations are consistent with a more robust SEI being maintained for test C.

For modeling Li-Si electrodes38–40 and for constructing state estimators to integrate batteries employing Li-Si negative electrodes41,42 into various applications (e.g., from various small hand-held devices to electrified vehicles), a mathematical representation of the hysteresis behavior is key. The simple model implemented here, Eqs. 3 to 6, represents the data well insofar as the differences between the calculations and the data are similar to the differences associated with experimental reproducibility. As constructed, however, the model cannot account for the influence of side reactions; cf. Figure 6 of Sehuraman et al.22 In Ref. 15, the electrode behavior was modeled by means of double-layer capacitance and kinetics expressions for the main and side reactions, whereas a true hysteresis approach is employed in this work (i.e., the observed hysteresis is a function of the charge Q only and is independent of time or rate20). The influence of side reactions complicates the transient behavior and makes it difficult to determine where the potential might tend to between the oxidation and reduction branches of the open-circuit potential. It should also be noted that the hysteresis represents an energy loss, especially for cell operation corresponding to full charges and full discharges, as more energy is put into charging the cell than is delivered by the cell on the subsequent discharge, even at very low rates that we identify with equilibrium behavior. More experimental and theoretical work is needed in this topic area.

Consistent with the data and analysis of Figure 2 through Figure 7, we find that in half cells (Li-Si working electrode opposed by a Li metal counter electrode), C yields the best cycle life, as shown in the upper plot of Figure 9. We take the nominal capacity to be 1 mAh/cm², as noted for the A – E tests depicted in Figure 2 and Figure 3; 550 full charge-discharge cycles are obtained before the capacity falls below the nominal value for C, clearly outperforming A, B, D, and E. Current efficiency measurements for C correspond to about 0.998 for the first 500 cycles (lower plot of Figure 9). Voltage profiles taken at cycles 10, 100, 200, 300, 400, 500, and 600 for C are presented in Figure 10. The left plot (voltage vs. time into cycle) shows the capacity fade, while the right plot shows increased voltage losses upon cycling. Thus, as the cell is cycled at constant current, a higher oxidation (lithiation) voltage is required with each passing cycle, and the reduction (delithiation) potential declines with cycles in a continuous manner. While there is capacity fade and increased voltage loss upon cycling, the results are quite promising relative to previous cycling studies of higher capacity Li-Si films.

Two cells were constructed using an NMC622 positive electrode (Figure 11 and Figure 12). The cell was negative limited, and the cell potential limits were chosen so that the Li-Si negative electrode would cycle between potentials similar to those of test C (0.1331 to 0.5526 V vs. Li). Results for the full cell are similar to those for the half cells (Figure 9 and Figure 10), both in terms of capacity fade and current efficiency, which is encouraging in that the cells of Figure 9 had 2 μm thick Si films and were cycled at about a C/10 rate (based on the full capacity of the Li-Si electrode), whereas 6 μm thick Si films were employed for the full cell and were cycled at about a C/3 rate. Of the 5.7 mAh/cm² capacity of the 6 μm thick Si films (cf. Eq. 2), 2.3 mAh/cm² are employed (40%) due to the cell voltage limits. We believe this to be the best reported cycle-life data for full cells employing a Li-Si thick film; as with all of the half-cell work and the MOSS analysis, the superior performance is enabled by the rational selection of the voltage window applied to the Li-Si electrode; specifically operating the Li-Si electrode in accordance with test C test C (0.1331 to 0.5526 V vs. Li).

The impact of cycling on the change in the electrode structure is profound in the case of Li-Si, as compared to Li-graphite, for example. This initial cross-section is shown in Figure 13; these cross sections should be very flat surfaces, as would be expected from high-precision ion milling. The deposited Si has an average thickness of about 6.5 μm. Upon cycling, we obtain ion-milled cross sections such as those depicted in Figure 14 and Figure 15. By comparing Figure 13 with Figure 14, we see that the fresh 6.5 μm Si grows to about 27 μm upon cycling. Figure 14 and Figure 15 indicate that while the integrity of the Si-Cu interface is well maintained, fracture of

![Figure 11.](image)

Full-cell (Si-NMC) discharge capacity and Coulombic (or current) efficiency versus cycle number. Results for two cells are plotted (denoted by 1 and 2). The current density and voltage limits are indicated. Upon reaching a voltage limit, the polarity of the current was immediately changed (i.e., no voltage holds).

![Figure 12.](image)

Cell voltage histories for the indicated cycles associated with Figure 11.
the larger Si columns into smaller structures is evident near the Cu current collector. Overall the micrographs are consistent with (1) good adherence of the Si to the Cu throughout cycling and (2) increasing fracture of the Si upon cycling. More work needs to be done relative to film growth versus cycle number. From our viewing of various cross-sectional micrographs, it would appear that the Si host expands irreversibly upon lithiation; at this time, we are unsure of how the irreversible expansion progresses with cycling. That is, we do not know if the irreversible expansion is effectively complete within the first few cycles or if it occurs in smaller and continual increments upon cycling. For the substantially invariant (expanded) structure, conservation of mass would indicate that the electrode is less dense and perhaps more porous upon delithiation. For the 1.6 g Si/cm² (geometric area) density of dense Si (2.32 g/cm³ density) is about 0.25:

\[
\frac{1.6 \text{ g/cm}^2}{1000 \text{ g/cm}^2} \times \frac{1 \text{ cm}^3 \text{Si}}{2.32 \text{ gSi}} \times \frac{27 \text{ cm}^3}{10000 \text{ cm}^3} = 0.255 \text{ cm}^3 \text{Si/cm}^3
\]

[8]
corresponding to a total porosity (non-Si fraction) of 0.75.

From elemental mappings of cycled, DMC-washed electrodes (Figure 16), we find that the surfaces of the expanded (porous) Si are coated with species containing carbon, oxygen, and fluorine. The Si intensity is opposite to those of C, O, and F, consistent with lithium carbonates and organic adducts, and variants of lithium oxides and fluorides, covering the Si surface, as has been reported in prior surface-speciation work on Li-Si electrodes.43,44 In addition, upon cycling, in some portions of the electrode, small Cu particles are seen to have separated from the Cu current collector (cf. the Cu elemental mapping of Figure 16); this is consistent with the substantial mechanical deformation of the entire electrode and current collector system, as is made clear in Figure 17. Plan views of the Si electrode (i.e., the face of the Si electrode that had been in contact with the electrolyte during cell operation) and the Cu current collector back side both show significant cracking and large-scale deformation. This is likely due to two reasons. First, as shown in the lowermost micrographs of Figures 17e and 17f, the structure comprising the Li-Si electrode and the Cu current collector bends, as would be expected when the electrode expands upon operation. This can cause compression and buckling of the Cu. Second, locally (e.g., around Cu nodules on the surface of the current collector), Li-Si expansion and contraction can enhance stress nonuniformly, leading to localized cracking. Overall, however, the Cu current collector remains substantially functional, as

Figure 13. Secondary-electron micrographs of the Si electrode and Cu current collector (broad-beam ion-milled cross sections) associated with the cells used to acquire the data shown in Figure 11, prior to cycling. The width of the white-background rectangle corresponds to the length provided within the respective rectangle.

Figure 14. Secondary-electron (a and c) and backscattered-electron (b and d) micrographs of the delithiated Si electrode and Cu current collector associated with the cells used to acquire the data shown in Figure 11 after 395 cycles. The upper micrographs each show a 15 μm scale bar (lower right corner), and lower micrographs each show a 6 μm scale bar.

Figure 15. Secondary-electron micrographs of the delithiated Si electrode and Cu current collector associated with the cells used to acquire the data shown in Figure 11 after 395 cycles (a and c) and 795 cycles (b and d). The upper micrographs each show a 6 μm scale bar (lower right corner), and lower micrographs each show a 3 μm scale bar.
Figure 16. Secondary-electron micrograph (upper left) and elemental maps of the electrode cross-section for Si, C, Cu, O, and F after 395 cycles (cf. Figure 11).

is evidenced by cross sections e and f, but the character of the current collector deformation in large-format cells must be considered for practical applications; e.g., the influence of the cracking of the Cu on the overall in-plane electronic resistance.

We now evaluate the Si film electrode in a full-cell configuration for application in a 200-mile Battery Electric Vehicle (BEV). We estimate the cell energy density (Wh/L) and the cell specific energy (Wh/kg) at the beginning of life (BOL). We have chosen a nickel-rich cathode (positive electrode) and paired that with the Si film anode. For comparison, we have also considered porous electrodes including a Si-enhanced anode material and a Si alloy-graphite mixture, containing 60% weight percent of the alloy in the active material. We assume that both the Si electrodes are pre-lithiated, to counter capacity loss otherwise seen over the first cycle. Although the Si film electrode expansion was measured only after 395 cycles, we assume that the expansion occurs within the first few cycles and hence the Si film porosity of 75% essentially represents BOL conditions (cf. Eq. 8). We further assume that this expansion is irreversible, consistent with experimental observations, and further particle expansion upon lithiation is small (nominally assigned to be 5%). Table 1 lists the cell design and configuration, and the positive and negative electrode properties used in our estimates.

We examined the effect of Si film thickness and the window of electrode utilization. We varied the expanded film thickness between 20 and 60 μm (initial coating thickness of 4.8 and 14.4 μm, respectively) and the utilization window between 0.4 and 0.5 (reflective of test C). Note that the effective electrode capacity corresponds to the full capacity of 3.6 Ah/g multiplied on to the utilization. The negative capacity is usually in excess over the positive (N/P > 1), but since we are utilizing only a part of the Si film capacity, there is excess capacity at the anode, and we set the N/P ratio, based on the effective Si film capacity, to 1. We also considered the thickness of the copper current collector at two values: 8 μm and 16 μm. The energy density estimates are shown as contour plots in Figure 18. The highest energy density we can achieve is about 850 Wh/L, at a fractional utilization of 0.5, expanded Si film thickness of 60 μm, and current collector thickness of 8 μm. All the three variables – film thickness, utilization, and current collector thickness – have a significant effect on the energy density.

For specific energy (Wh/kg) estimates, we need to account for the electrolyte in the pores of the electrode because the electrolyte contribution to the total cell mass is significant. The non-Si volume,
Table I. Inputs for battery sizing estimates.

| Cell Configuration                        | length (cm) | width (cm) |
|-------------------------------------------|-------------|------------|
| Positive coat                             | 25.8        | 8.91       |
| Negative coat                             | 26.05       | 9.11       |
| Cell packaging                            | 30.15       | 9.97       |
| No of cells in parallel                   | 3           |            |
| No of cells in series                     | 96          |            |

Cell Requirements

| Vehicle usable energy (kWh)              | 58.5        |
| Usable SOC Window                        | 90%         |
| Required Wh/cell total                   | 226         |

Cell Requirements

| Vehicle usable energy (kWh)              | 58.5        |
| Usable SOC Window                        | 90%         |
| Required Wh/cell total                   | 226         |

Electrode Properties

| Electrode Properties | POSITIVE | NEGATIVE |
|----------------------|----------|----------|
| Electrode material   | Nickel rich Si film (this work) | Si alloy (60%-graphite (40%) |
| Reversible specific capacity at C/5 (Ah/g) | 0.205 | 3.6 | 0.86 |
| Average voltage      | 3.80     | 0.41     | 0.40 |
| Electrode porosity   | 22%      | 75%      | 39%  |
| Active material mass fraction | 97% | 100% | 93% |
| N/P ratio (based on effective capacity) | NA | 1.0 | 1.15 |
| Particle volumetric expansion | 0.00 | 5% | 51% |
| Electrode utilization | 1      | 0.4 to 0.5 | 1    |
| Current collector thickness (μm) | 12 | 8 & 16 | 8    |

Other Cell Components

| Other Cell Components | Separator thickness (μm) | Separator porosity | Electrolyte density (g/cm³) | Excess electrolyte in cell | Pouch volume (thickness) | efficiency |
|-----------------------|--------------------------|--------------------|----------------------------|---------------------------|--------------------------|------------|
|                       | 15                       | 40%                | 1.16                       | 20%                       | 95%                      |

*at 100% utilization. Effective capacity = Reversible capacity x utilization.

nominally defined as porosity, for the initial (before cycling) Si film can be estimated to be 21% (see discussion immediately before Eq. 2) and for the expanded film about 75% (Equation 7). It is expected that the electrolyte will fill the initial porosity, but it is not clear at this time whether the electrolyte can penetrate into the columnar structures as they irreversibly expand (e.g., the porosity may correspond to nano-pores within low-density Si that has no significant electrolyte mass). Therefore, we estimate the cell specific energy at both limits; i.e., porosity filled by the electrolyte at 21% and 75%. The specific energy estimates for the Si-film/Ni-rich-NMC cell at these bounds are shown in Figure 19 as contour plots. The maximum achievable specific energy for these two cases are about 410 and 375 Wh/kg, respectively.

The most promising anode material is a mixture of a Si alloy and graphite, with the alloy content at 60%. For the same Ni-rich-NMC cathode, we compared the energy density and the specific energy of cells with this anode material versus our Si-film anode. We varied the positive coating thickness and at each thickness and estimated the anode coating thickness, the cell energy density, and the cell specific energy. For the Si film, we limited the Si (expanded) coat thickness to 60 μm. We considered Si film utilization of 0.44 (our experimental conditions for case C) and 0.5. In addition, for the cell specific energy comparison, we considered the two electrolyte filling scenarios as in Figure 19. The results are shown in Figure 20. The curves terminate in Figure 20a and Figure 20b at different cathode thicknesses because

Figure 18. Contour plots of cell energy density (Wh/L) estimates for the Si-film/Ni-rich-NMC cell for 200-mile BEV. Blue and red contour lines represent 8 and 16-μm thick copper current collector, respectively.

Figure 19. Contour plots of cell specific energy (Wh/kg) estimates for the Si-film/Ni-rich-NMC cell for 200-mile BEV. Plots a and b correspond to electrode-filled porosity of 21% and 75%, respectively.
Conclusions

We elucidate the effects of voltage limits on the operational performance of cells employing a Li-Si thick-film negative electrode, an electrolyte mixture of 1M LiPF$_6$ in a 45:45:10 EC:DEC:FEC volume-ratio solvent (EC, DEC, and FEC refer to ethylene carbonate, diethyl carbonate, and fluoroethylene carbonate, respectively), and a lithium or a Li$_{0.5}$Ni$_0.2$Mn$_{0.5}$O$_2$/Li$_2$O$_2$ counter electrode. When the Li-Si electrode is operated between 0.13 and 0.55 V vs. a Li reference, promising cycling operation is achieved (i.e., greater than 500 cycles with retention of 75% of the initial cell capacity). Cell modeling is used to examine the efficacy of the Si thin film for actual battery electric vehicle applications. Microscopy results show that the Si host formed by physical vapor deposition consists of columnar, relatively dense, microstructures that form a contiguous and uninterrupted interface with the roughened Cu current collector. The robust interface is largely maintained upon operation (cycling) of the electrode, but the Si host expands irreversibly (normal to the current collector) by about 31.5%, yielding a low-density Si structure upon delithiation. Cracking of the Si host and of the Cu current collector is also observed upon prolonged cycling. Elemental mapping is consistent with the Li-Si electrode being covered by lithium carbonates and organic adducts, and variants of lithium oxides and fluorides; these byproducts result from reactions between electrode and electrolyte species and yield a protective layer over the electrode, giving rise to what is often referred to as the solid electrolyte interphase. A simple hysteresis model is shown to work well for constant current operation. We are aware that it fails to capture operational characteristics under conditions beyond the scope of this work, and this matter must be addressed more fully for the successful implementation of Li-Si in traction applications.

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