PCCP



PAPER



Cite this: Phys. Chem. Chem. Phys., 2015, 17, 11301

Pore collapse and regrowth in silicon electrodes for rechargeable batteries[†]

S. C. DeCaluwe, \ddagger^{abc} B. M. Dhar, \ddagger^{de} L. Huang,^d Y. He,^{df} K. Yang,^d J. P. Owejan,^g Y. Zhao,^f A. A. Talin,^{hi} J. A. Dura*^b and H. Wang*^{cde}

Structure and composition of an 11 nm thick amorphous silicon (a-Si) thin film anode, capped with 4 nm of alumina are measured, *in operando*, by neutron reflectivity (NR) and electrochemical impedance spectroscopy in a lithium half-cell. NR data are analyzed to quantify the a-Si thickness and composition at various states of charge over six cycles. The a-Si anode expands and contracts upon lithiation and delithiation, respectively, while maintaining its integrity and low interfacial roughness (\leq 1.6 nm) throughout the cycling. The apparently non-linear expansion of the a-Si layer volume *versus* lithium content agrees with previous thin-film a-Si anode studies. However, a proposed pore collapse and regrowth (PCRG) mechanism establishes that the solid domains in the porous Li_xSi film expand linearly with Li content at 8.48 cm³ mol⁻¹ Li, similar to crystalline Si. In the PCRG model, porosity is first consumed by expansion of solid domains upon lithiation, after which the film as a whole expands. Porosity is reestablished at 5–28% upon delithiation. Data show that the alumina protective layer on the a-Si film functions as an effective artificial solid electrolyte interphase (SEI), maintaining its structural integrity, low interfacial roughness, and relatively small transport resistance. No additional spontaneously-formed SEI is observed in this study.

Received 22nd December 2014, Accepted 17th March 2015

DOI: 10.1039/c4cp06017b

www.rsc.org/pccp

1. Introduction

Rechargeable lithium ion batteries (LIBs) have become widely used as indispensable mobile energy sources in modern society.^{1–5} However, for extended applications it is desirable that both the energy and power densities of LIBs be greatly increased.

^a Department of Mechanical Engineering, Colorado School of Mines, Golden, CO, USA

^b Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD, USA. E-mail: jdura@nist.gov

^c Department of Materials Science and Engineering, University of Maryland, College Park, MD, USA. E-mail: wangh@umd.edu

^d Institute for Materials Research and Dept. of Mechanical Engineering, State University of New York, Binghamton, NY, USA

^e Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA

^fDepartment of Physics and Astronomy, University of Georgia, Athens, GA, USA

^g Department of Mechanical and Electrical Engineering Technology, State University of New York, Alfred, NY, USA

^h Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, MD, USA

ⁱ Sandia National Laboratories, Livermore, CA, USA

 \dagger Electronic supplementary information (ESI) available: EIS fitting parameters, impedance relaxation data for the delithiated states, analysis of irreversible electrochemical degradation with half-cell cycling, correction factors for substrate warping, interfacial roughness/width variations with SOC, and a-Si solid portion density calculations. See DOI: 10.1039/c4cp06017b

‡ These authors contributed equally to this work.

While graphite has traditionally been used as an anode material in commercial LIBs, silicon has recently emerged as a promising alternative $^{6-8}$ because of its high theoretical capacity $(\sim 4200 \text{ mA h g}^{-1})$, with 4.4 mol of lithium alloying per mole of silicon (Li₂₂Si₅ phase). At room temperature, the Li₂₂Si₅ phase is not realizable due to kinetic limitations and the Si lithiation proceeds through the formation of the Li₁₅Si₄ phase,⁹ resulting in a practically achievable capacity of 3579 mA h g^{-1} .¹⁰ Accompanying this high lithiation capacity is a large volume expansion ($\sim 370\%$ volume change at the maximum capacity), leading to cracking and fracturing of Si and irreversible and quick loss in the energy storage capacity. The inability of Si electrodes to withstand the volume change accompanying full lithiation-delithiation cycling is a major impediment to their use in commercial LIBs. Various morphological and materials approaches, such as Si-carbon nanocomposites,¹¹⁻¹³ nanowires,14,15 nanotubes,16,17 novel binders,18,19 very thin amorphous silicon (a-Si) films,^{6,20,21} and protective coatings^{22,23} have been demonstrated in the past to improve Si cyclability. In this study, we have investigated the nano-structure evolution of an a-Si thin-film anode with a protective alumina coating. We offer an explanation for apparently non-linear expansion of the a-Si film with lithiation, and suggest a mechanism to retain structural integrity upon higher degrees of lithiation.

To better understand the mechanisms coupling the structural variation and electrochemical operation, *in operando*

Paper

characterization of Si anodes in working LIBs is necessary. Various in operando techniques have been used to characterize lithium insertion and de-insertion in silicon anodes.9,24-34 Many are reviewed by Aurbach et al.,²⁴ and we summarize here a few notable examples. Dahn and coworkers²⁵ have reported in operando atomic force microscopy (AFM) studies on patterned silicon anodes in LIBs and have observed electrolyte decomposition as well as morphological changes in the anodes as a result of cyclic charge and discharge. Huang and coworkers have successfully performed in operando transmission electron microscopy (TEM) studies on nanostructured anodes in LIBs²⁷ showing reversible structural changes and dynamic defect formation as a result of lithiation. They have also observed anisotropic expansion of Si(110) nanowires during lithiation, accompanied by large strains at the lithiation front. The relationship between electrochemical lithiation and stressstrain evolution in Si thin films has also been studied by Sethuraman and coworkers using a reflected array of parallel laser beams to correlate the changes in wafer curvature to the lithium insertion and deinsertion during cycling.^{33,34} They have observed a rapid increase in the compressive and tensile stress during lithiation and delithiation, respectively, accompanied by a transition from elastic to plastic deformation at a capacity of roughly 355 mA h g^{-1.34} They have also observed stresspotential coupling as a result of cycling, which has been correlated to the relaxation in the open circuit voltage (OCV) observed for Si anodes. Key et al., 30,31 have used ex situ and in situ nuclear magnetic resonance (NMR) imaging to characterize the changes in short-range order that occur during cycling of Si anodes, elucidating atomistic mechanisms of lithiation and delithiation. They have demonstrated that the initial lithiation involves both Si-Si clusters and isolated Si atoms, while the isolated Si atoms dominate the NMR signal completely as lithiation proceeds. It has also been observed that the amorphous silicides are reactive with the electrolyte, which may also contribute to the relaxation in OCV, which has been attributed to stress-potential coupling by Sethuraman et al.³⁴

Although these findings offer meaningful insights into the operation of Si electrodes, many important aspects of their behavior remain unknown or ambiguous. For example, the role of electrode surface structure in SEI formation remains poorly understood. In addition, while the development of porosity in Si nanowire electrodes has been illustrated using *ex situ* TEM,²⁶ the evolution of porosity in thin films and nanostructured electrodes has not been characterized *in operando*. Furthermore, little is known about the electrode structure evolution during non-equilibrium lithiation and delithiation at high rates.

Herein we report *in operando* neutron reflectivity (NR) measurements on a working a-Si thin-film anode with a protective aluminum suboxide (AlO_x) thin-film coating. AlO_x is an electrical insulator and impedes liquid electrolyte degradation and SEI formation by preventing electronic charge injection from the anode to the adsorbed electrolyte molecules. The alumina does not block Li ion transport to the underlying Si and therefore acts as an electrolyte. Previous studies have shown that thin conformal layers of alumina deposited *via* atomic layer

deposition (ALD) onto electrodes such as $LiCoO_2$ films,²⁸ natural graphite,²⁹ or MoO_3 ,³⁵ have greatly improved the capacity retention, cycling stability, and rate performance. He *et al.*²³ have demonstrated increased Coulombic efficiencies and cycling stability as well as suppressed SEI formation and electrode fracturing during extended cycling of patterned silicon anodes with conformal ALD alumina coatings.

NR is a useful technique for studying structures of surfaces. interfaces, and thin films, and provides a depth profile of the neutron scattering length density (SLD, which can be determined from the composition) with sub-Ångström precision for features over ≈ 1.5 nm thick.³⁶⁻³⁹ Because NR averages structural features in the plane of a thin-film, it complements localized characterization techniques such as TEM and AFM. Several features of NR make it advantageous for probing LIBs in operando. Neutrons are sensitive to light elements since neutrons scatter by nuclear interactions, in contrast to X-rays or electrons that probe structure through the electron density. Neutrons are non-destructive, do not alter sensitive specimens, and easily penetrate properly designed robust sample environments, making in situ measurements feasible. NR has been previously used to observe SEIs on a non-intercalating Cu anode.40 More recently, NR has been used to explore the structure and chemical interactions of a-Si anodes. Veith et al. report a 3.5 nm non-electrochemical reaction layer (likely an SEI precursor) that forms spontaneously upon exposure to electrolyte.⁴¹ Jerliu, Hüger, and coworkers have carried out in operando NR on a-Si anodes, reporting a 7.0 nm thick SEI and the change in SLD and thickness of an a-Si layer.^{42,43} Their initial study shows that the LixSi layer's fitted SLD values do not match those predicted by the cumulative charge, which was attributed to SEI formation and trace amounts of Cl and O from the electrolyte in the a-Si.⁴² Their second study compared a-Si layer thickness variations to the degree of lithiation based on the electrochemical data and assuming complete lithiation to Li4.2Si (SLD values were not reported), and found that the expansion matched expected trends for moderate degrees of lithiation.43 However, there are interesting unresolved observations in that report, e.g., results indicating zero expansion during the initial 1.5 hours of charging at 7.8 μ A cm⁻² (which represents 33% of the total charge delivered), and a film thickness that is 50% greater than the initial thickness after complete delithiation. The latter observation was attributed to residual lithium in the anode, while the former was left un-explained.

Herein, we utilize *in operando* NR to study the structural evolution of a working a-Si/AlO_x thin film electrode and correlate structural changes with simultaneous electrochemical characterization (electrochemical cycling and impedance spectroscopy, EIS) during shallow lithiation–delithiation cycles. Data show the structural integrity of both the a-Si film anode and the AlO_x capping layer after undergoing multiple charge–discharge cycles. This study extends those of Jerliu *et al.* and quantitatively demonstrates that the differences between predicted and measured anode characteristics, such as the thickness and SLD, are due to the evolution of porosity, which explains the lack of film expansion during the initial charging in previous studies, and residual lithium in the anode after delithiation.

2. Methods

2.1. Thin film preparation

A crucial requirement for NR is a film with minimal roughness, since roughness both degrades the signal and broadens interfaces (distributing interfacial structures over a larger depth range) decreasing both sensitivity to the structure and accuracy of thickness measurements. The multi-layered thin film anode was prepared by consecutive electron-beam evaporation onto polished silicon wafers, 76.2 mm in diameter and 3 mm in thickness. The sample consisted of a 5 nm thick Cu film as the current collector, followed by *ca.* 11 nm of a-Si and capped by an Al layer, which was exposed to air to form a *ca.* 4 nm AlO_x film (Fig. 1(a)). A second sample without the AlO_x layer was similarly prepared for direct measurement of the a-Si density and porosity.

2.2. Battery assembly

The anode wafer was annealed in a vacuum oven at 90 $^\circ\mathrm{C}$ overnight and assembled in an Argon-filled glove box as the active electrode of a Li half-cell. Fig. 1(b) shows a schematic of the complete battery stack, retained between Al compression plates. A 19 mm thick Si wafer was placed behind the anode wafer to provide a continuous Si transmission medium for the incident and reflected neutrons and help prevent warping of the anode substrate. For the counter electrode, which also served as the reference electrode, a 50 nm thick Cu film was deposited on a 1 mm thick silicon wafer as the current collector, onto which Li metal was coated by rubbing Li foil. A 700 µm thick Viton gasket was sandwiched between the two electrodes to define the electrolyte volume, which was filled with 1 M LiPF6 solution in a mixture of dimethyl carbonate and ethylene carbonate (1:1 volume ratio). Another 19 mm thick silicon wafer was placed over the counter electrode wafer to



Fig. 1 Illustration of lithium half-cell. (a) Cross-section of the anode thin film stack. (b) Schematic of the battery assembly for *in operando* NR experiment.

support the thin wafer, and the entire assembly was clamped between Al compression plates. The Al plates had a 25.4 mm deep \times 50.8 mm wide groove in the middle to remove Al from the transmitted beam path to reduce background scattering. The 3 mm anode substrate wafer used in this study, compared to the 5 mm wafers typically used for NR, led to increased warping and a small perturbation due to the reflection from the back of the anode wafer. Techniques applied to correct for these artifacts are discussed in the ESL;†

2.3. Neutron reflectivity measurements

NR measurements on the a-Si half-cell were performed at NIST Center for Neutron Research (NCNR) using the Advanced Neutron Diffractometer/Reflectometer (AND/R).⁴⁴ NR measures the intensity of neutrons undergoing specular reflection as a function of the scattering vector $Q_z = 4\pi \sin \theta / \lambda$, where θ is the angle of incidence and λ is the wavelength of the neutrons. The reflectivity is a function of the SLD depth profile, which for a given layer is:

$$SLD = \sum_{i} b_{i} n_{i} \tag{1}$$

where b_i is the scattering length and n_i the number density per unit volume of isotope *i*, summed over all isotopes in the layer.

In this study, NR was measured over the range $0^{\circ} < \theta < 4^{\circ}$. For $\theta > 0.5^{\circ}$, two slits on the incident beam side and two on the reflected beam side were opened linearly as a function of θ , with the former to maintain a fixed 43 mm-wide beam projection onto the sample plane, and the latter to minimize the background scattering into the detector. For $\theta \leq 0.5^{\circ}$, the resolution of the slit motors requires fixed slit widths. The background was measured using two off-specular scans, with the detector angle set to $1.5 \times \theta$ and $2.5 \times \theta$, respectively, which were then averaged to obtain an estimate of the background signal at the specular (detector = 2θ) condition. To obtain the reflectivity, R, as a function of Q_z , the background was subtracted from the specular reflection intensity, which was then normalized by the incident intensity, measured by an independent slit scan in the direct beam transmitted through the incident Si medium. Error bars on NR data were obtained by propagating the counting statistics from the specular, background, and slit scans, and indicate plus or minus one standard error.

NR data can be fitted to a model layered structure by adjusting the parameters of layer thickness, scattering length density, and layer interfacial width to arrive at a best fit determined by minimizing the χ^2 goodness-of-fit statistic. Data reduction was performed using Reflpak software⁴⁵ and the fitting utilized Refl1d.⁴⁶ Refl1d uses the matrix formalism given by Parrat,⁴⁷ and the DREAM algorithm⁴⁸ was employed to effectively sample the model parameter space. More detailed descriptions of Refl1d, including the calculation of confidence intervals for parameter values and SLD profiles, can be found elsewhere.^{39,40,46} In order to construct the initial layer model, which served as a guide for fitting the NR data, the anode wafer was characterized by X-ray reflectivity prior to battery assembly.

2.4. Experimental sequence

After X-ray characterization and battery assembly, the cell was installed on the AND/R sample stage. Electrochemical cycling and EIS of the battery was performed in situ using a Solartron Modulab potentiostat/frequency response analyser.§ EIS of the as-assembled cell was collected at the open circuit potential (OCP) followed by NR (test point OC). Subsequently, the thin film silicon anode underwent six alternating galvanostatic lithiation steps (i.e. discharge, D1 to D6) and delithiation steps (charge, C1 to C6) at a range of DC currents. The first cycle (D1 and C1) occurred at a constant current of 100 µA, which is a C-rate of about 0.5, and the anode voltage was kept between 0.03 V and 3.3 V vs. Li/Li⁺ for all measurements. Subsequent cycles limited the anode potential to a maximum of 3.0 V ν s. Li/Li⁺. After the first full cycle, the battery was cycled at 1 mA for 4 cycles. The current was then set to 200 μ A for the sixth (D6 and C6) cycle. NR measurements were taken after the 1st and 6th discharge/lithiation (test points D1 and D6, respectively) and after the 1st and 6th charge/delithiation (test points C1 and C6, respectively). All NR measurements were taken at OCP, after the corresponding lithiation/delithiation step and lasted between 1.5 and 5.25 hours. In addition to NR and galvanostatic cycling, EIS spectra were collected several times at each state of charge (SOC) in order to characterize the electrochemical state of the battery and ascertain any variations during the reflectivity measurements. EIS spectra from 100 mHz to 500 kHz were analyzed using E-Chem Analyst software (Gamry Instruments, Inc.). In this study, the SOC was restricted to a shallow degree of lithiation in order to explore the relationship between physical structure and electrochemical characteristics in a-Si anodes without adverse effects of excessive electrode degradation.

To relate the measured a-Si layer SLDs to the composition *via* eqn (1), the porosity of an a-Si film and the density of its solid domains in the as-deposited state were measured using NR on a similarly-prepared, uncapped a-Si specimen with a Cu substrate layer. NR data was measured on the specimen in air and in a cell filled with D_2O similar to that shown in Fig. 1(a) but without a counter/reference electrode, using the Horizontal Sample Neutron Reflectometer on beam line NG7 at the NCNR. The SLD difference of the anode layer for the two measurements normalized by the SLD of D_2O is the porosity of the sample, which, along with the measurement of the SLD of the sample in air, can be used to determine the density of the solid domains of the a-Si. Details of this measurement are given in the ESI.[†]

3. Results and discussion

3.1. Electrochemical lithiation and delithiation properties

Table 1 and Fig. 2 summarize the electrochemical chargedischarge data collected during measurements. Throughout this manuscript, numbers in brackets and error bars represent 68% confidence intervals, the calculation of which is described previously.^{40,46} Table 1 shows the electrochemical properties at all test points, including the charge–discharge capacities, lithium content and the expected thicknesses, t_c , derived from the previously established relationship between the thickness and the SOC:⁴⁹

$$t_{\rm c} = t_{\rm o} \left(1 + \frac{2.7}{4.4} x \right) \tag{2}$$

where t_o is the thickness of the as-deposited film, as derived from NR fits to test point OC and *x* is the Li content in the formula Li_xSi, where the total moles of Li are derived from the total charge delivered during the galvanostatic charging and total moles of Si are derived from the thickness, an active anode area of 34.4 cm², and a measured density of 2.26 g cm⁻³ for a-Si (as discussed below). Because the specific capacity and degree of lithiation depend on the total Si mass and therefore on the Si thickness and porosity at OC, the uncertainty in these measured values are propagated through all of the electrochemical measurements in Table 1. For clarity of presentation, the associated error bars are omitted from Fig. 2.

Fig. 2 shows the galvanostatic charge (delithiation) and discharge (lithiation) data for the first and sixth cycles. To prevent Li plating on the anode, lithiation was stopped at 0.03 V. The first discharge curve in Fig. 2 starts at 0.4 V, with the lower-than-expected open circuit potential likely due to trace amounts of lithium deposited during EIS measurements collected before the first cell discharge. The lithiation steps D1 and D6 achieved capacities of 811 [753, 1047] mA h g^{-1} and 719 [667, 928] mA h g^{-1} , respectively, corresponding to 22.7 [21.0, 29.3]% and 20.1 [18.6, 25.9]% of the achievable capacity of 3579 mA h g⁻¹, as measured for bulk materials.⁵⁰ To achieve the desired capacities, the current was paused periodically during lithiation and de-lithiation and the voltage allowed to equilibrate, before resuming. Owing to non-equilibrium lithium insertion and removal, the lithiation and delithiation processes showed a larger voltage drop or gain, respectively, as a function of specific capacity than previous reports, with the voltage relaxing to equilibrium values upon cessation of the current, a phenomena previously observed by Sethuraman et al.33,34 As repeated NR scans at each test point did not show significant structural changes in the anode to accompany the observed voltage relaxation, possible causes of the voltage relaxation include the kinetic limitation of the charge transfer, surface chemical reconstruction, and the coupling with the mechanical stress relaxation.³⁴ As seen in Fig. 2, the delithiation capacities of 1150 [1068, 1485] mA h g^{-1} and 778 [722, 1005] mA h g^{-1} for steps C1 and C6, respectively, were higher than those during the preceding lithiation steps (D1 and D6, respectively). This slight degree of over-charging could be attributed to higher leakage currents at higher voltage or may imply that parasitic reactions are more significant during delithiation than during lithiation. The effect of the higher current density during the sixth cycle is also apparent in Fig. 2, with lower capacity and higher

[§] Certain commercial equipment, instruments, materials, suppliers, or software are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Table 1 Summary of the electrochemical cycling results. Calculations assume density of 2.26 g cm⁻³ for a-Si, an active anode area of 34.4 cm², and an initial porosity of 10.0 [5.4–28.0]%. The lithium content assumes 1 atom per electron delivered to the anode

	OC	D1	C1	D6	C6
	open circuit	1st lithiation	1st delithiation	6th lithiation	6th delithiation
Capacity (mA h g^{-1}) x in Li _x Si Predicted a-Si thickness (nm)	$ \\0 \\11.1^{a} [10.8, 11.3]$	$814 [755, 1051] \\ 0.85 [0.79, 1.10] \\ 16.9 [16.0, 18.9]$	1154 [1071, 1490] 0.00 [0.00, 0.00] 11.1 [10.8, 11.3]	718 [666, 927] 0.75 [0.70, 0.97] 16.2 [15.6, 18.0]	779 [723, 1005] 0.00 [0.00, 0.21] 11.1 [10.8, 12.8]

^{*a*} The thickness at test point OC, 11.1 [10.8–11.3] nm, is taken from fits to NR measurements at that test point. Other than test point OC, the predicted thickness is calculated using eqn (2).



Fig. 2 The galvanostatic charge-discharge curves for 1st lithiation (D1) and 1st delithiation (C1) occurred at 100 μ A; the 6th lithiation (D6) and 6th delithiation (C6) occurred at 200 μ A.

under/overpotentials observable for the sixth discharge-charge relative to the first cycle.

3.2. SLD profiles determined via NR

Fig. 3 presents the NR data and fitting results. Fig. 3(a) shows the measured reflectivity (symbols) of the anode at various SOCs, along with the confidence intervals of the calculated reflectivity for the best fits (shaded bands). The data in the plot are offset vertically for clarity. Results show an oscillation period that decreases with lithiation, indicating swelling of the anode film, and generally returns toward the open circuit periodicity upon delithiation. To quantify these effects by model fitting, test points OC and D1 were first fitted simultaneously to accurately determine fitting parameters for the substrate and electrolyte layers - specifically the thickness of the Cu layer, roughness and thickness for the Si substrate and SiO_2 layers, and SLD for the electrolyte – which were fit to common values in the simultaneous fit, then held fixed for all subsequent fits. SLDs for the Si substrate, native SiO₂, and Cu current collector were held fixed at bulk values for all fits. While assuming bulk values for the first two layers has been found to be valid in many studies, we also have confidence in using the bulk Cu SLD, given the high quality of the fits obtained (the χ^2 value is less than 1.25 for all fits reported here). In all subsequent fits, the SLD, thickness, and surrounding interfacial widths of the a-Si and AlO_r layers were allowed to vary to achieve the best fits. In order to carefully investigate for the presence of



Fig. 3 In operando NR from a-Si anode. (a) NR data and best fits for various SOCs of the battery. Shaded regions represent 68% confidence intervals for the best fits to the data. Individual reflectivity curves are *y*-offset for ease of visualization. (b) Profiles of SLD *vs.* depth (*z*) for the Si anode at various SOCs. Shaded curves represent 68% confidence intervals. Inset shows a detailed view of the AlO_x layer with profiles co-aligned at the AlO_x/electrolyte interface.

an SEI layer at the AlO_x-electrolyte interface, an additional series of fits to models that included an SEI layer were performed. These fits did not improve χ^2 for any of the tests points. Fig. 3(b) shows the 68% confidence intervals for the SLD depth profile corresponding to the fits shown in Fig. 3(a), plotted as a function of the depth *z* (as measured from the surface of alumina layer for OC).



Fig. 4 Thickness and SLD of a-Si and AlO_x layers for test points, according to NR fits. Lines connecting a-Si quantities in the upper panel are guides to the eyes, while the lines through AlO_x quantities represent the best fitted average values.

The remaining profiles are shifted to co-align at the interface between the native oxide and the Cu layer in the main figure and at the AlO_x /electrolyte interface in the inset. The narrow confidence intervals in Fig. 3 demonstrate that the fitting procedure determines the layered structure with high precision. The SLD profiles also demonstrate how the AlO_x layer enhances the SLD contrast of the a-Si layer for these NR measurements.

Fig. 4 shows the thicknesses and SLD values from the NR fits for both the a-Si layer and the AlO_x artificial SEI at each SOC. Both the SLD and the thickness of the a-Si layer change with SOC, as suggested by the NR data in Fig. 3(a) and seen in the fits in Fig. 3(b). The as-deposited a-Si anode is 11.10 [10.79, 11.32] nm thick with a layer SLD of 1.96 $[1.90, 2.02] \times$ 10^{-4} nm⁻². The incorporation of Li (which has a negative scattering length) into the a-Si increases the thickness and decreases the SLD of the alloy film in the discharged state. The thickness increases to 14.46 [14.33, 14.65] nm and 13.48 [13.34, 13.53] nm, and the layer SLD decreases to 0.98 $[0.89,\,1.06]\times10^{-4}~\mathrm{nm}^{-2}$ and 1.11 $[1.11,\,1.17]\times10^{-4}~\mathrm{nm}^{-2}$ for test points D1 and D6, respectively. Upon delithiation, the a-Si layer thickness and SLD return back toward the initial values; the thickness decreases to 11.43 [11.47, 11.84] nm and 12.42 [12.59, 12.88] nm, and the layer SLD increases to 1.88 $[1.66, 1.91] \times 10^{-4} \text{ nm}^{-2}$ and 1.75 $[1.62, 1.74] \times 10^{-4} \text{ nm}^{-2}$ for test points C1 and C6, respectively. Despite roughly equivalent capacities, the thickness and layer SLD values during the 6th cycle do not completely return to the values seen after the first cycle. This is shown clearly by both the SLD profile plots in Fig. 3(b) and the SLD and thickness plots in Fig. 4. The physical interpretation is discussed below. The SLD and thickness of the AlO_x layer can be considered constant with charge-discharge, within the margins of error, as shown in Fig. 4 and the Fig. 3(b) inset, indicating the integrity of the AlO_r capping layer throughout the battery operation.

3.3. Modelling porosity via a reduced average density

NR fits show that incorporation of Li into the Si anode affects both the anode thickness and SLD. To correlate the a-Si layer SLD with the Li content, we employ the concept of "integrated" SLD of the a-Si layer (SLD_I) to simplify the conservation of Si mass across all of the measured SOCs,

$$SLD_{I} = SLD \times t = \sum_{i} b_{i}n_{i}t = \sum_{i} b_{i}n_{i,I}, \qquad (3)$$

which relates the SLD to the total amount of both Si and Li per unit area of the layer. Here, *t* is the thickness of the layer and b_i and n_i are defined in eqn (1). The parameter, $n_{i,1}$, is the area density, or number of isotope *i* per unit area of the anode film. Multiple previous studies of a-Si do not directly incorporate porosity effects into their analysis.^{25,42,43} If one assumes that vacancies and pores are inaccessible, and do not evolve with time or processing, their effects can be modeled as a reduction of the average density of the macroscopic a-Si layer (*i.e.* the density averaged over both the pores and the solid Si domains within the layer). To explore this common usage in the literature, we assume that the a-Si anode consists entirely of Si and Li, and eqn (3) therefore becomes:

$$SLD_{I} = b_{Si}n_{Si,I} + b_{Li}n_{Li,I}$$
(4)

where $b_{\rm Li}$ and $b_{\rm Si}$ are physical constants known from the literature.⁵¹ By limiting the number of terms in eqn (4) using this approximation, it is possible to determine the Si moles per unit area, $n_{\rm Si,I}$, from the SLD at OC, assuming that the asdeposited state is free of Li, $n_{\rm Li,I} = 0$, and therefore $n_{\rm Si,I} = \text{SLD}_{\rm OC} \times t_{\rm OC}/b_{\rm Si}$. By employing conservation of Si ($n_{\rm Si,I}$ is constant), the Li content per unit area can then be calculated at each SOC:

$$n_{\mathrm{Li},\mathrm{I}} = \frac{\mathrm{SLD} \times t - b_{\mathrm{Si}} n_{\mathrm{Si},\mathrm{I}}}{b_{\mathrm{Li}}} \tag{5}$$

The Li composition, x in Li_xSi, calculated by dividing $n_{\text{Li},\text{I}}$ from eqn (5) by $n_{\text{Si},\text{I}}$, is shown in Fig. 5, lower panel, and the a-Si layer



Fig. 5 Thickness (upper) and composition (lower) of the Li_xSi at various SOCs. Filled symbols are values from NR fits assuming no open porosity, open symbols are from electrochemical data and the predicted linear relationship expansion, and dots represent composition calculations according to the PCRG model, as discussed below.

PCCP

thickness from Fig. 4, upper panel, is reproduced as closed squares in the upper panel. As a comparison, the open symbols in Fig. 5 are the corresponding *t* and *x* values calculated based on electrochemical data and eqn (2), assuming that the total Li ionic current transported into and out of the a-Si layer equals the cumulative electric charge measured by the potentiostat. While x from NR and electrochemical measurements are comparable, there are large discrepancies between the corresponding thickness values. The differences are more prevalent for lithiated states, and increase with the cycle number. To understand these thickness discrepancies in terms of fundamental physical properties of the Li_xSi, the data in Fig. 5 are converted to volume per mole of the lithiated a-Si, $\overline{V}_{\text{Li Si}}$, and plotted as a function of x in Fig. 6(a). Because the film can only expand and contract in the direction normal to the substrate surface, t is proportional to its volume, and discrepancies in tindicate a difference between $\overline{V}_{\text{Li},\text{Si}}$ values determined by NR and those expected from linear volume expansion. Fig. 6(a) shows the calculated $\overline{V}_{\text{Li.Si}}$ as a function of x for each test point (symbols), compared to predictions for c-Si (blue line) a in situ AFM measurements of a-Si micro-pillars reported by Dahn and coworkers (green curve).49,52 Because none of the cases explicitly accounts for the layer porosity, there is no distinction between the molar volume of the macroscopic layer itself and the molar volume of solid domains of Si within the layer in Fig. 6(a). Note that the AFM data was reported as a "fractional volume change" by Chevrier and Dahn.⁴⁹ Therefore to calculate the absolute molar volume, an initial volume of 12.31 cm³ mol⁻¹ is assumed, which is an average of previous literature values for bulk a-Si.53-55 It is also noteworthy that Chevrier and Dahn reported a fractional volume change of 15% for fully delithiated a-Si, relative to the initial state. While this effect is not remarked upon explicitly in their report, such macroscopic volumetric irreversibility is consistent with the volume expansion between points OC and C6 in this study. While the molar volumes for the fully delithiated tests points in Fig. 6(a) therefore agree well with previous measurements, this does not explain the physical origin of the irreversibility. Furthermore, the obvious under-estimation of $\overline{V}_{\text{Li}_x\text{Si}}$ for D1 and D6 indicates the need to re-examine the method for evaluating $\overline{V}_{\text{Li}_x\text{Si}}$.

3.4. Pore collapse and regrowth (PCRG) mechanism

A possible cause for both the thickness irreversibility and the molar volume discrepancies for lithiated states is the presence of nanopores in the a-Si and their evolution during electrochemical cycling. Dealloying of metal alloys has been used in the past to create nanoporous morphologies,⁵⁶ and Hu et al. have used electrochemical lithiation and delithiation of metal oxides as a strategy to synthesize nanoporous materials.⁵⁷ Recently, Choi et al. have demonstrated that when silicon nanowires are subjected to electrochemical lithium insertion and deinsertion, the nanowires become porous and the pore size increases with cycling, analogous to Ostwald ripening in nanoparticles.²⁶ Similarly, Chen and Sieradzki have explored kinetic and transport effects for the control of nanoporosity formed during electrochemical delithiation of Li-Sn.58 Such effects have also been observed in germanium nanowires using in situ TEM.⁵⁹ Similar to the Li_xSi compounds formed in this study, Dura et al. have found that volume expansion from hydrogenation of Mg thin films to form a MgH₂ compound thin film is irreversible upon dehydrogenation, due to pores that are formed when the sample is de-hydrogenated.⁶⁰

While the interpretation presented in Fig. 6(a) allows for closed pores in the as-deposited a-Si film *via* a nominal SLD,



Fig. 6 Volume per mole of the solid domains of L_{ix} Si as a function of the lithium content. As a comparison the values for crystalline silicon (blue dashed line) and amorphous silicon (green dashed curve) have been plotted. (a) Volume expansion calculated assuming a static porosity that is inaccessible to the electrolyte. (b) Volume expansion of the solid domains according to the PCRG mechanism. Black dashed line represents a linear fit to test points OC, D1, and D6. The inset to (b) illustrates the PCRG mechanism whereby, while the solid portions of the Si expand linearly, the macroscopic film thickness expansion is flat at low Li content (as shown in the green curve) until the porosity is collapsed. Error bars represent 68% confidence intervals. a-Si values adopted from Chevrier and Dahn.⁴⁹

Paper

it does not account for either pore evolution during cycling or for filling of the pores by electrolyte. It is plausible in the case of thin a-Si films that the evolution of electrolyte-filled pores contributes to the thickness irreversibility and the lower than expected volume changes during cycling. We propose here a "pore collapse and regrowth" (PCRG) mechanism: (i) during lithiation, Si solid domains in the anode film initially expand isotropically, collapsing pores that exist in the as-deposited anode. (ii) After the porosity is eliminated, subsequent volume expansion is anisotropic, along the surface normal direction (due to substrate clamping), increasing the film thickness. (iii) During delithiation, volume contraction occurs first anisotropically, via decreased film thickness, then isotropically, via the re-growth of collapsed pores. Thus, with each cycle the porosity of the a-Si film evolves; the volume expansion is absorbed by the pores during lithiation, and pores form during delithiation, resulting in the observed thickness discrepancies. Calculating volume expansion based solely on thickness variations would thus underestimate the full degree of volume expansion of the solid Si domains within a porous film. Such a mechanism is consistent with the porosity evolution observed by Choi et al.,26 and could explain the absence of any thickness change at low degrees of lithiation, as observed by Jerliu et al.,43 and by Chevrier and Dahn, as seen by the significantly smaller slope of the green dashed line in Fig. 6 for x < 0.249.²⁵

Here, *in operando* NR goes beyond previous observations to quantify this phenomenon by determining the porosity and composition in the delithiated states. The calculation of *x* and $\overline{V}_{\text{Li}_x\text{Si}}$ in Fig. 6(a) does not explicitly account for open porosity in the a-Si layer, but rather assumes a constant unfilled porosity resulting in a reduced macroscopic density of the a-Si film. The PCRG mechanism, however, takes into account pores that are open and entirely filled with electrolyte in the as-deposited and delithiated films, and are completely collapsed upon lithiation. Because the as-deposited film (OC) is assumed to be free of lithium and decomposition products, the porosity ϕ_{OC} can be determined:

$$\phi_{\rm OC} = \frac{\rm SLD_{aSi-s} - \rm SLD_{OC}}{\rm SLD_{aSi-s} - \rm SLD_{elec}} \tag{6}$$

where SLD_{aSi-s}, SLD_{elec}, and SLD_{OC} refer to the SLDs of the solid a-Si domains, the electrolyte in the pores, and the volumeweighted average SLD of the layer (solid a-Si plus electrolytefilled pores), respectively. SLD_{OC} is obtained from fitting the NR at OC, and SLD_{elec} (1.57 \times 10^{-4} $nm^{-2})$ is taken from the simultaneous fit to NR at OC and D1. Calculating SLD_{aSi-s} requires an accurate estimate of the density of the solid domains in a-Si. Literature values for a-Si density range from 2.21 to 2.40 g cm $^{-3}$, $^{53-55}$ a wide range which would result in a $\phi_{\rm OC}$ between 0.0% and 41.4%. An additional set of NR measurements was therefore performed on a similarly prepared, uncapped a-Si thin film in air and in D₂O to directly determine the SLD (and therefore the density) of the solid Si domains, as described in the ESI.[†] The best fit to this data yielded SLD_{aSi-s} = 2.01 [2.00, 2.02] \times 10⁻⁴ nm⁻², corresponding to a density for the solid a-Si domains of 2.26 [2.25, 2.27] g cm⁻³, which is 97.0 [96.6, 97.4]% that of c-Si and well within the range of previously reported values. Using eqn (6), $\phi_{\rm OC}$ was found to be 10.0 [5.4, 28.0]%.

Incorporating the PCRG mechanism requires re-calculation of the composition at each test point, *via* eqn (4) and (5). Allowing for a volume fraction of electrolyte-filled pores at OC changes the calculated amount of Si $(n_{Si,I})$ and the initial volume that it occupies, which therefore impacts the amount of lithium $n_{Li,I}$ calculated at all other test points *via* eqn (5). Furthermore, the integrated SLD at each test point *j* now consists of silicon, lithium, and electrolyte-filled pores, adding an additional term to eqn (4):

$$SLD_{I,j} = b_{Si}n_{Si,I} + b_{Li}n_{Li,I,j} + b_{elec}n_{elec,I,j}$$
(7)

Note that the area number density of silicon $n_{\text{Si},\text{I}}$ is assumed not to vary with SOC, and thus does not have a subscript *j*. Furthermore, $n_{\text{elec},\text{I}}$ is related to the porosity:

$$\phi_j = \frac{\overline{V}_{\text{elec}} n_{\text{elec},\text{I},j}}{t_j} \tag{8}$$

where $\overline{V}_{\text{elec},j}$ is the volume per mole of electrolyte. The molar volume of the solid portion of the Li_xSi can be calculated by dividing the solid volume of the anode by n_{si} :

$$\overline{V}_{\text{Li}_{x}\text{Si}, j} = \frac{\left(1 - \phi_{j}\right)A_{\text{anode}}t_{j}}{n_{\text{Si}}} = \frac{\left(1 - \phi_{j}\right)t_{j}}{n_{\text{Si},\text{I}}}$$
(9)

and the degree of lithiation *x* is found by dividing the number density of lithium by that of silicon:

$$x_j = \frac{n_{\text{Li},\text{I},j}}{n_{\text{Si},\text{I}}} \tag{10}$$

Using eqn (7) through (10), $\overline{V}_{\text{Li},\text{Si}}$ and x are calculated for OC by assuming $n_{\text{Li,I,OC}} = 0$, and for D1 and D6 by assuming zero porosity ($n_{\text{elec},I,j} = 0$). For C1 and C6, both $n_{\text{Li},I}$ and $n_{\text{elec},I}$ are unknown, requiring an additional assumption. Fig. 6(b) shows the molar volume, $\overline{V}_{\text{Li},\text{Si}}$ of the solid portion of the anode vs. the degree of lithiation x, after incorporating porosity. As seen by the black dashed line, a linear fit through OC and the lithiated states D1 and D6, $\overline{V}_{\text{Li},\text{Si}}$ follows the linear relationship similar to that seen for c-Si with remarkable accuracy. The slope indicates a volume expansion coefficient of 8.48 cm³ per mole of Li inserted, 10% lower than the coefficient in eqn (2), but generally in good agreement with previous measurements and calculations.43,49,52,61 Given the linear volume expansion from x = 0 for OC through x > 0.5 for the lithiated states, the departure from linearity at small x is likely minimal. For delithiated states C1 and C6, we therefore assume that the volume expansion of the solid portion of the Li_xSi layer also follows this linear trend:

$$\overline{V}_{\text{Li}_x\text{Si}, j} = 8.48x_j + 12.42 \text{ cm}^3 \text{ mol}^{-1}.$$
 (11)

By solving eqn (7)–(11), ϕ_j and $n_{\text{Li},\text{I},j}$ are calculated for the delithiated states, C1 and C6. Results show that the a-Si porosity is roughly recoverable with cycling. The porosity is 9.69 [2.97, 13.77]% at C1 and 13.08 [10.02, 15.73]% at C6,



Fig. 7 EIS spectra collected during NR measurements. Nyquist plots of: (a) the delithiated anode, Open Circuit (OC), after first charge (C1), and after sixth charge (C6), with the inset comparing the data and fitting at low impedance; (b) the lithiated anode, after first discharge (D1) and sixth discharge (D6). Frequency for all measurements ranged from 0.1 to 5×10^5 Hz.

compared to 10.0 [5.4, 28.0]% at OC. The x values calculated using the PCRG mechanism are displayed in Fig. 6(b) and in Fig. 5 as the red dots. Results show a small but noticeable discrepancy between the fitted x and that predicted by the electrochemical data. This discrepancy increases with additional cycling.

3.5. Electrochemical impedance spectroscopy

Simultaneous electrochemical measurements collected during the NR are consistent with the proposed PCRG mechanism. The EIS spectra are shown in Fig. 7(a) for the delithiated test points (OC, C1, and C6) and 7(b) for the lithiated test points (D1 and D6). The symbols are the experimental data and solid curves are the best fits to data using the equivalent circuit model shown in Fig. 8(a). For delithiated test points, significant relaxation and reduction of the electrochemical impedance occurred over a period of several hours before reaching a steady state, whereas little variation is observed after lithiation (see ESI[†]). The data in Fig. 7 are for the anode in the relaxed state, taken more than 2 hours after the charge-discharge, except for C6, for which the only data available was taken 21 minutes after delithiation. It is apparent that the C6 spectrum differs significantly from those of OC and C1, particularly in the low frequency/high impedance regime. In general, the delithiated states in Fig. 7(a) are marked by much larger impedance values than the lithiated states in Fig. 7(b). For all relaxed test points, the impedance as a function of SOC increases with additional cycling - the impedance is greater at C1 than at OC, and greater at D6 than at D1 - but the Nyquist plots generally maintain the same shape and features, implying a consistent lithiation/delithiation mechanism.

Fig. 8(a) shows the equivalent circuit model used to fit the EIS data. Each solid layer in the cell is modelled as a resistor-constant phase element (CPE) pair. The model and interpretation is based



Fig. 8 EIS fitting results. (a) The equivalent circuit model. (b) Fitted resistance of a-Si, interfacial layers, and electrolyte at various SOCs. The lines connecting symbols are guides to the eye. C6 is partially relaxed, and the corresponding $R_{\rm Si}$ is connected with a dashed line. The inset is an expanded plot to compare $R_{\rm int}$ and $R_{\rm elec}$.

on previous work by Aurbach.⁶² The high frequency intercept $(\sim 10^6 \text{ Hz})$ corresponds to ion transport in the electrolyte. The medium frequency range (10^3-10^4 Hz) represents the ionic transport through interfacial layers, in our case the protective AlO_x layer and any additional SEI that may have formed during cycling. The low-frequency features $(0.1 - 10^2 \text{ Hz})$ correspond to the charge transfer and lithium insertion into the a-Si film. The model also covers very low frequency (10 to 100 mHz) regimes corresponding to the double layer response, which has been modelled as a CPE in series. While the impedance was not measured in this frequency range, this element determines the asymptotic behaviour of the fits in the lowest frequencies measured, and was necessary to obtain suitable fits to the EIS data taken in the relaxed state.

Fig. 8(b) shows the variation in resistance of the a-Si film, interfacial layers, and the electrolyte at each SOC. A complete listing of the EIS fitting parameters is given in Table S1 of the ESI.[†] The resistance of the electrolyte is relatively invariant, in the range of 20–30 Ω for all SOCs. The resistance related to interfacial layers increases monotonically but moderately with cycling, from 130 Ω at OC to 210 Ω at C6. The resistance of the a-Si layer, meanwhile, varies dramatically with the SOC. For the four data points obtained at equilibrium (test points OC through D6), R_{si} varies reversibly between the two states, from $R_{\rm Si}$ = 1145 and 1153 Ω for delithiated test points OC and C1 to 60.1 and 62.3 Ω for lithiated test points D1 and D6. Similarly, the characteristic frequency of a-Si was significantly higher in the lithiated states, $\omega > 395$ Hz, compared to $\omega < 20$ Hz in the delithiated states. For the partially relaxed C6, a much larger resistance value, ca. 5000 Ω , is observed. Suitable fits to EIS at C6 were obtained only after removing the serial CPE from the equivalent circuit. As fitting of the C6 spectrum implies somewhat mixed states, we restrict ourselves from drawing significant conclusions on the basis of the EIS at C6.

3.6. PCRG effect on electrochemical performance

Despite cumulative charge data in Table 1 and Fig. 2 that imply complete delithiation, the assumption of linear expansion for test points C1 and C6 in Fig. 6(b) shows residual lithium content that increases with cycle number. Several explanations exist for this phenomenon. The fact that the capacity at each charge is greater than that at the immediately-proceeding discharge (Table I) does not indicate the violation of charge conservation, but instead implies the existence of parasitic processes. Parasitic side-reactions could result in discrepancies between the potentiostat-measured current and the Faradaic current (*i.e.*, the rate of lithiation and delithiation at the anode). Incomplete delithiation could therefore imply that parasitic processes are more severe during delithiation than during lithiation. It is also likely that leakage current at higher voltages during delithiation leads to greater potentiostat-recorded electric charge transfer than the actual Faradaic current. Finally, if the a-Si pores are present at voltages below the electrolyte stability limit, it is also possible that Li-rich electrolyte decomposition products are produced and retained within the pores of the anode thin film. Modifying the PCRG mechanism and eqn (7) through (10) to accommodate such an effect is beyond

the scope of this study, but given the low SLD of Li-rich decomposition products,^{40,63} modelling them here as residual Li serves as a suitable first approximation.

The EIS data also imply a degree of irreversible electrochemical deactivation of the thin-film anode during the delithiation step that may explain a fraction of trapped lithium that no longer participates in anode charge-discharge. As shown in Fig. 8(b), R_{int} values do not vary upon lithiation, but increase slightly after each delithiation (charge) step. The values in Table S1 and Fig. S3 (ESI⁺) show that this trend is repeated for the relative admittance associated with equivalent circuit parameters Rint, Qsi, and Qdl. They all decrease by 20-30% after each delithiation whereas they either remain constant or increase upon lithiation. Even though the PCRG analysis suggests that the porosity in the delithiated states is roughly constant and the a-Si film appears to maintain its mechanical integrity (with no roughening or increased pore volume which would accompany significant cracking of the electrode), this does not preclude electrical isolation due to nano-scale mechanical degradation. The electrochemical results are consistent with the scenario that portions of the anode become electrochemically isolated and therefore irreversibly deactivated during each delithiation. The trapped Li after delithiation implied by the PCRG calculations in Fig. 6(b) is also consistent with this interpretation, because electrochemical isolation would prevent Li extraction from those regions.

The EIS fitting results, as detailed in the ESI,† also support the PCRG mechanism. While the large estimated errors for C_{Si} in the lithiated states (due to overlapping frequencies for the a-Si and double-layer circuit elements) make it difficult to draw conclusive evidence, the pseudo-capacitance $C_{\rm Si}$ of the a-Si layer in Fig. S2(b) (ESI⁺) appears to be higher in the delithiated states than in the lithiated states, which would correlate with higher surface area in the porous delithiated films. Additionally, the transient relaxation of Csi observed for Li-poor states OC and C1 may indicate that the surface area is initially larger (hence higher C_{si}) and decreases with time (lower C_{si}). The agglomeration of smaller pores to form larger ones while conserving the total pore volume, as in Ostwald ripening would explain these transient shifts in Csi and also correlate with the prominent decrease of transient R_{a-Si} at OC and C1, as shown in Fig. S2(a) (ESI⁺), via the formation of less tortuous transport path upon pore merging. Such a process is consistent with the diffusion of atomic Si and slow evolution of pores, as reported by Choi et al.²⁶ These observations provide additional evidence of pore regrowth and evolution upon delithiation, further supporting the PCRG mechanism.

4. Conclusions

In summary, we report the successful application of *in operando* neutron reflectivity measurements with simultaneous electrochemical characterization as a diagnostic tool to study amorphous thin film silicon anodes in operating LIBs. It is shown that the a-Si film expands and contracts as a result of lithiation

and delithiation, respectively. The cycling was accompanied by irreversible electrochemical degradation of the electrode, possibly associated with portions of active materials becoming electrically isolated during the delithiation step. However, both the a-Si anode and the AlO_x artificial SEI layer remained structurally stable during the six shallow lithiation–delithiation cycles. We did not observe SEI formation due to electrolyte decomposition or reaction with Si, indicating the efficacy of the deposited AlO_x artificial SEI.

While the macroscopic volume expansion based on thickness changes alone does not follow the empirical linear relationship reported for crystalline silicon, evidence suggests that pores in the film collapse to absorb the isotropic volume expansion during lithiation, and that pore volume is recovered during delithiation, as described by the proposed PCRG (pore collapse and regrowth) mechanism. The changes in porosity are associated with significant changes in the electrochemical characteristics of the a-Si thin film, *i.e.*, a significant increase in the electrical resistance of the a-Si layer in the delithiated, porous state. This study employs fundamental measurements to quantify the porosity evolution and demonstrates that linear expansion of the solid portion of the a-Si thin is achieved within the PCRG mechanism. In this and other studies, apparent departures from linear expansion of the overall film thickness are observed for low Li content due to the porosity evolution and accumulation of trapped lithium in the electrode. The reversible pore collapse and regrowth in a thin a-Si film, while demonstrated here for a shallow degree of lithiation and a few cycles, can help improve Si anode durability if it can be extended to more severe cycling conditions. The findings from this study therefore offer insights into the electrode design strategies to improve the cycling life of silicon anodes in LIBs, which include incorporating a sufficient volume fraction of nanopores in active materials to support subsequent volume expansion, and attaching active anode materials to a rigid support (similar to substrate clamping in thin films), if needed, to promote reversible recovery of the porosity. However, while catastrophic electrode failure due to pulverization is not observed here, lithiation steps are accompanied by an increase in resistance associated with interfacial processes, which would need to be mitigated for long-term durability. Further studies on the application of the PCRG mechanism to deeper lithiation-delithiation and larger cycle numbers are needed for better understanding the role of porosity in Si anodes.

Acknowledgements

HW acknowledges NIST and General Motors for their generous financial support. SCD thanks the National Research Council for funding *via* the Research Associates Program. YPH and YPZ were supported by US Army Research Laboratory with the contract number of W911NF-10-2-0107. Sandia is a multi-program laboratory operated by San Corporation, a Lockheed Martin Company, for the U.S. DOE National Nuclear Security Administration under Contract DE-AC04-94AL85000. AAT acknowledges partial support for data analysis and writing of the manuscript by Science of Precision Multifunctional Nanostructures for Electrical Energy Storage (NEES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, and Office of Basic Energy Sciences under DESC0001160.

Notes and references

- 1 A. S. Arico, P. Bruce, B. Scrosati, J. M. Tarascon and W. Van Schalkwijk, *Nat. Mater.*, 2005, **4**, 366–377.
- 2 J. B. Goodenough and Y. Kim, Chem. Mater., 2010, 22, 587-603.
- 3 J. M. Tarascon, Philos. Trans. R. Soc., A, 2010, 368, 3227-3241.
- 4 J. M. Tarascon and M. Armand, Nature, 2001, 414, 359-367.
- 5 M. S. Whittingham, Chem. Rev., 2004, 104, 4271-4301.
- 6 S. Bourderau, T. Brousse and D. M. Schleich, *J. Power Sources*, 1999, **81**, 233–236.
- 7 H. Li, X. J. Huang, L. Q. Chen, Z. G. Wu and Y. Liang, *Electrochem. Solid-State Lett.*, 1999, 2, 547–549.
- 8 J. Yang, Y. Takeda, N. Imanishi, C. Capiglia, J. Y. Xie and O. Yamamoto, *Solid State Ionics*, 2002, **152**, 125–129.
- 9 P. Limthongkul, Y. I. Jang, N. J. Dudney and Y. M. Chiang, *Acta Mater.*, 2003, **51**, 1103–1113.
- 10 M. N. Obrovac and L. Christensen, *Electrochem. Solid-State Lett.*, 2004, 7, A93–A96.
- 11 M. Holzapfel, H. Buqa, W. Scheifele, P. Novak and F. M. Petrat, *Chem. Commun.*, 2005, 1566–1568.
- 12 C. S. Wang, G. T. Wu, X. B. Zhang, Z. F. Qi and W. Z. Li, *J. Electrochem. Soc.*, 1998, 145, 2751–2758.
- 13 X. W. Zhang, P. K. Patil, C. S. Wang, A. J. Appleby, F. E. Little and D. L. Cocke, *J. Power Sources*, 2004, **125**, 206–213.
- 14 C. K. Chan, R. N. Patel, M. J. O'Connell, B. A. Korgel and Y. Cui, *ACS Nano*, 2010, 4, 1443–1450.
- 15 L. F. Cui, Y. Yang, C. M. Hsu and Y. Cui, *Nano Lett.*, 2009, 9, 3370–3374.
- 16 M. H. Park, M. G. Kim, J. Joo, K. Kim, J. Kim, S. Ahn, Y. Cui and J. Cho, *Nano Lett.*, 2009, **9**, 3844–3847.
- 17 T. Song, J. L. Xia, J. H. Lee, D. H. Lee, M. S. Kwon, J. M. Choi, J. Wu, S. K. Doo, H. Chang, W. Il Park, D. S. Zang, H. Kim, Y. G. Huang, K. C. Hwang, J. A. Rogers and U. Paik, *Nano Lett.*, 2010, **10**, 1710–1716.
- 18 I. Kovalenko, B. Zdyrko, A. Magasinski, B. Hertzberg, Z. Milicev, R. Burtovyy, I. Luzinov and G. Yushin, *Science*, 2011, 333, 75–79.
- 19 L. F. Cui, L. B. Hu, H. Wu, J. W. Choi and Y. Cui, *J. Electrochem. Soc.*, 2011, 158, A592–A596.
- 20 J. P. Maranchi, A. F. Hepp and P. N. Kumta, *Electrochem.* Solid-State Lett., 2003, 6, A198–A201.
- 21 J. T. Yin, M. Wada, K. Yamamoto, Y. Kitano, S. Tanase and T. Sakai, *J. Electrochem. Soc.*, 2006, **153**, A472–A477.
- 22 L. Baggetto, J. F. M. Oudenhoven, T. van Dongen, J. H. Klootwijk, M. Mulder, R. A. H. Niessen, M. de Croon and P. H. L. Notten, *J. Power Sources*, 2009, **189**, 402–410.
- 23 Y. He, X. Q. Yu, Y. H. Wang, H. Li and X. J. Huang, *Adv. Mater.*, 2011, 23, 4938-4941.

- 24 S. F. Amalraj and D. Aurbach, *J. Solid State Electrochem.*, 2011, **15**, 877–890.
- 25 L. Y. Beaulieu, T. D. Hatchard, A. Bonakdarpour, M. D. Fleischauer and J. R. Dahn, J. Electrochem. Soc., 2003, 150, A1457–A1464.
- 26 J. W. Choi, J. McDonough, S. Jeong, J. S. Yoo, C. K. Chan and Y. Cui, *Nano Lett.*, 2010, **10**, 1409–1413.
- 27 J. Y. Huang, L. Zhong, C. M. Wang, J. P. Sullivan, W. Xu, L. Q. Zhang, S. X. Mao, N. S. Hudak, X. H. Liu, A. Subramanian, H. Y. Fan, L. A. Qi, A. Kushima and J. Li, *Science*, 2010, 330, 1515–1520.
- 28 Y. S. Jung, A. S. Cavanagh, A. C. Dillon, M. D. Groner, S. M. George and S. H. Lee, *J. Electrochem. Soc.*, 2010, 157, A75–A81.
- 29 Y. S. Jung, A. S. Cavanagh, L. A. Riley, S. H. Kang, A. C. Dillon, M. D. Groner, S. M. George and S. H. Lee, *Adv. Mater.*, 2010, 22, 2172–2176.
- 30 B. Key, R. Bhattacharyya, M. Morcrette, V. Seznec,
 J. M. Tarascon and C. P. Grey, *J. Am. Chem. Soc.*, 2009,
 131, 9239–9249.
- 31 B. Key, M. Morcrette, J. M. Tarascon and C. P. Grey, J. Am. Chem. Soc., 2011, 133, 503–512.
- 32 P. Limthongkul, Y. I. Jang, N. J. Dudney and Y. M. Chiang, J. Power Sources, 2003, 119, 604–609.
- 33 V. A. Sethuraman, M. J. Chon, M. Shimshak, N. Van Winkle and P. R. Guduru, *Electrochem. Commun.*, 2010, **12**, 1614–1617.
- 34 V. A. Sethuraman, V. Srinivasan, A. F. Bower and P. R. Guduru, *J. Electrochem. Soc.*, 2010, 157, A1253–A1261.
- 35 L. A. Riley, A. S. Cavanagh, S. M. George, Y. S. Jung,
 Y. F. Yan, S. H. Lee and A. C. Dillon, *ChemPhysChem*, 2010, 11, 2124–2130.
- 36 J. A. Dura, C. A. Richter, C. F. Majkrzak and N. V. Nguyen, *Appl. Phys. Lett.*, 1998, **73**, 2131–2133.
- 37 M. P. Seah, S. J. Spencer, F. Bensebaa, I. Vickridge, H. Danzebrink, M. Krumrey, T. Gross, W. Oesterle, E. Wendler, B. Rheinlander, Y. Azuma, I. Kojima, N. Suzuki, M. Suzuki, S. Tanuma, D. W. Moon, H. J. Lee, H. M. Cho, H. Y. Chen, A. T. S. Wee, T. Osipowicz, J. S. Pan, W. A. Jordaan, R. Hauert, U. Klotz, C. van der Marel, M. Verheijen, Y. Tarnminga, C. Jeynes, P. Bailey, S. Biswas, U. Falke, N. V. Nguyen, D. Chandler-Horowitz, J. R. Ehrstein, D. Muller and J. A. Dura, *Surf. Interface Anal.*, 2004, 36, 1269–1303.
- 38 M. P. Seah, W. E. S. Unger, H. Wang, W. Jordaan, T. Gross, J. A. Dura, D. W. Moon, P. Totarong, M. Krumrey, R. Hauert and Z. Q. Mo, *Surf. Interface Anal.*, 2009, 41, 430–439.
- 39 S. C. DeCaluwe, P. A. Kienzle, P. Bhargava, A. M. Baker and J. A. Dura, *Soft Matter*, 2014, **10**, 5763–5776.
- 40 J. E. Owejan, J. P. Owejan, S. C. DeCaluwe and J. A. Dura, *Chem. Mater.*, 2012, **24**, 2133–2140.

- 41 G. M. Veith, L. Baggetto, R. L. Sacci, R. R. Unocic, W. E. Tenhaeff and J. F. Browning, *Chem. Commun.*, 2014, 50, 3081–3084.
- 42 B. Jerliu, L. Doerrer, E. Hüger, G. Borchardt, R. Steitz, U. Geckle, V. Oberst, M. Bruns, O. Schneider and H. Schmidt, *Phys. Chem. Chem. Phys.*, 2013, 15, 7777-7784.
- 43 B. Jerliu, E. Hüger, L. Dorrer, B. K. Seidlhofer, R. Steitz,
 V. Oberst, U. Geckle, M. Bruns and H. Schmidt, *J. Phys. Chem. C*, 2014, 118, 9395–9399.
- J. A. Dura, D. J. Pierce, C. F. Majkrzak, N. C. Maliszewskyj,
 D. J. McGillivray, M. Losche, K. V. O'Donovan,
 M. Mihailescu, U. Perez-Salas, D. L. Worcester and
 S. H. White, *Rev. Sci. Instrum.*, 2006, 77, 074301.
- 45 P. A. Kienzle, K. V. O'Donovan, J. F. Ankner, N. F. Berk and C. F. Majkrzak, http://www.ncnr.nist.gov/reflpak.
- 46 P. A. Kienzle, J. A. Krycka and N. Patel, Refl1D: Interactive depth profile modeler, http://www.reflectometry.org/danse/ software.
- 47 L. G. Parratt, Phys. Rev., 1954, 95, 359-369.
- 48 J. A. Vrugt, C. J. F. ter Braak, C. G. H. Diks, B. A. Robinson, J. M. Hyman and D. Higdon, *Int. J. Nonlinear Sci. Numer. Simul.*, 2009, **10**, 273–290.
- 49 V. L. Chevrier and J. R. Dahn, *J. Electrochem. Soc.*, 2009, **156**, A454–A458.
- 50 T. D. Hatchard and J. R. Dahn, J. Electrochem. Soc., 2004, 151, A838–A842.
- 51 V. F. Sears, Neutron, 1992, 3, 26-37.
- 52 L. Y. Beaulieu, S. D. Beattie, T. D. Hatchard and J. R. Dahn, *J. Electrochem. Soc.*, 2003, **150**, A419–A424.
- 53 M. H. Brodsky, D. Kaplan and J. F. Ziegler, *Appl. Phys. Lett.*, 1972, **21**, 305–307.
- 54 J. S. Custer, M. O. Thompson, D. C. Jacobson, J. M. Poate, S. Roorda, W. C. Sinke and F. Spaepen, *Appl. Phys. Lett.*, 1994, 64, 437-439.
- 55 O. Renner and J. Zemek, *J. Phys. B: At. Mol. Phys.*, 1973, 23, 1273–1276.
- 56 J. Erlebacher, M. J. Aziz, A. Karma, N. Dimitrov and K. Sieradzki, *Nature*, 2001, **410**, 450–453.
- 57 Y. S. Hu, Y. G. Guo, W. Sigle, S. Hore, P. Balaya and J. Maier, *Nat. Mater.*, 2006, 5, 713–717.
- 58 Q. Chen and K. Sieradzki, Nat. Mater., 2013, 12, 1102-1106.
- 59 X. H. Liu, S. Huang, S. T. Picraux, J. Li, T. Zhu and J. Y. Huang, *Nano Lett.*, 2011, 11, 3991–3997.
- 60 J. A. Dura, S. T. Kelly, P. A. Kienzle, J. H. Her, T. J. Udovic, C. F. Majkrzak, C. J. Chung and B. M. Clemens, *J. Appl. Phys.*, 2011, **109**, 093501.
- 61 S. Huang and T. Zhu, J. Power Sources, 2011, 196, 3664–3668.
- 62 V. Etacheri, U. Geiger, Y. Gofer, G. A. Roberts, I. C. Stefan, R. Fasching and D. Aurbach, *Langmuir*, 2012, **28**, 6175–6184.
- 63 C. A. Bridges, X. G. Sun, J. K. Zhao, M. P. Paranthaman and S. Dai, *J. Phys. Chem. C*, 2012, **116**, 7701–7711.