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► **To cite this version:**

Aurélien Etienne, Alix Tranchot, Thierry Douillard, Hassane Idrissi, Éric Maire, et al.. Evolution of the 3D Microstructure of a Si-Based Electrode for Li-Ion Batteries Investigated by FIB/SEM Tomography. *Journal of The Electrochemical Society*, 2016, 163 (8), pp.A1550-A1559. 10.1149/2.0421608jes . hal-03538469

HAL Id: hal-03538469

<https://hal.science/hal-03538469>

Submitted on 21 Jan 2022

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Evolution of the 3D Microstructure of a Si-Based Electrode for Li-Ion Batteries

Investigated by FIB/SEM Tomography

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Abstract

22
23
24 The evolution with cycling of the three-dimensional (3D) microstructure of a
25 silicon/carbon/carboxymethylcellulose (Si/C/CMC) electrode for Li-ion batteries is
26 investigated by combined focused ion beam (FIB) / scanning electron microscopy (SEM)
27 tomography. Using appropriate image processing methods, a volume of $20 \times 8 \times 11 \mu\text{m}^3$ is
28 reconstructed in which the Si and pore phases are clearly identified. Their respective
29 morphological characteristics (volume fraction, spatial distribution, size, connectivity, and
30 tortuosity) are determined before and after 1, 10 and 100 cycles. The Si particles (37 vol.%,
31 median size = $0.37 \mu\text{m}$) and pores (57 vol.%, median size = $0.40 \mu\text{m}$) are homogeneously
32 distributed and fully connected in the pristine electrode. Major changes in the electrode
33 morphology occur upon cycling due to electrode cracking and the growth of the solid
34 electrolyte interface (SEI) layer. It also appears that the size and shape of the Si particles
35 change upon cycling. They display a non-spherical, stringy morphology after 100 cycles
36 with a median size of $0.14 \mu\text{m}$.

37
38

Introduction

39 Silicon is an attractive candidate to replace graphite as the active material in Li-ion
40 battery anodes due to its ten times higher theoretical specific capacity (3578 mAh g^{-1} for
41 $\text{Li}_{15}\text{Si}_4$ compared to 372 mAh g^{-1} for LiC_6). However, the huge volume variation of the Si
42 material (up to $\sim 300\%$) with cycling induces a loss of electronic connectivity within the
43 composite electrode in addition to being unfavorable to the formation of a stable solid
44 electrolyte interface (SEI). Much research effort has been spent during the last decade to
45 improve the cycle life of Si-based electrodes through various strategies as reviewed in
46 references **1-4**. However, there are still several hurdles that must be overcome to obtain Si-
47 based anodes with acceptable coulombic efficiency and relevant areal, gravimetric and
48 volumetric capacities for use in commercial Li-ion batteries. In this context, it is essential
49 to better characterize the morphological evolution of the Si-based electrodes depending on
50 their formulation, fabrication method, electrolyte composition and cycling conditions. This
51 is challenging considering the complex three-dimensional structure of such composite
52 electrodes.

53 Recently, three-dimensional (3D) morphologies of various anodes and cathodes for
54 Li-ion batteries have been successfully characterized by focused ion beam/scanning
55 electron microscopy (FIB/SEM)⁵⁻¹² and X-ray computed tomography (XRCT)¹³⁻³⁰. 3D
56 imaging software allows automatic processing and quantitative measurements of various
57 morphological parameters (connectivity, tortuosity ...) by finite element calculations or
58 other numerical models. XRCT is non-destructive but conventional lab systems are limited
59 to micrometer spatial resolution. Top end synchrotrons can provide tens of nm resolution
60 with the correct setups. It is however non-trivial to design these setups for electrochemistry

61 experiments. On the other hand, FIB/SEM tomography is destructive but has the ability to
62 perform 3D imaging at high spatial resolution (typically, a few tens of nm), inaccessible
63 with laboratory X-ray tomography.²⁹ To date, FIB/SEM tomography of battery materials
64 has mostly been restricted to the characterization of pristine electrodes.⁵⁻¹¹ Recently,
65 nanostructural changes in Li-ion battery cathodes during cycling have been revealed by *ex-*
66 *situ* FIB-SEM tomography.¹² Particle cracking and delamination of Si-based anodes during
67 their first lithiation have been recently investigated by X-ray tomography^{21,30} but the
68 degradation after prolonged cycling of a realistic Si-based electrode has not been evaluated
69 at the composite electrode microstructure scale.

70 In the present study, for the first time, a 3D morphological analysis of a Si-based
71 electrode is performed by means of FIB/SEM tomography with a resolution of 25 nm. The
72 evolution of the electrode morphology is investigated by *ex-situ* analyses after increasing
73 numbers of charge/discharge cycles (0, 1, 10 and 100 cycles).

74

75 **Experimental**

76 *Electrode preparation.*— Pure Si (99.999%, 20 mesh) ball-milled for 20 h with a
77 ball-to-powder mass ratio of 5:1 using a SPEX 8000 mixer was used as active material.
78 Details on the morphological, structural and chemical characteristics of the ball-milled Si
79 powder are presented elsewhere.³¹ Super P carbon black (CB) was used as the conductive
80 agent and carboxymethyl cellulose (CMC) as the binder. 200 mg of (Si + CB + CMC) in a
81 weight ratio of 80:12:8 was mixed in 0.5 mL of a pH 3 buffer solution (0.173 M citric acid
82 + 0.074 M KOH) for 1 h at 500 rpm using a Fritsch Pulverisette 7 mixer. The pH 3 buffering
83 of the slurry was used for promoting covalent bonding (esterification) between -OH groups

84 present on the surface of the Si particles and -COOH groups of CMC, resulting in an
85 improvement of the electrode cycle life.³² The slurry was tape cast using a doctor blade
86 without calender pressure onto a 25 μm thick copper foil and dried for 12 h in air at room
87 temperature and then 2 h at 100°C under vacuum. Citric acid (16.62 mg) and KOH (2.08
88 mg) salts from the buffer solution contribute to the mass of the electrode, leading to a
89 Si/C/CMC/(citric acid + KOH) wt% composition of 73.1/11.0/7.3/(7.6+1.0). The electrode
90 loading was typically around 0.8-1 mg Si cm^{-2} .

91 Electrochemical cycling was performed at room temperature using two-electrode
92 Swagelok®-type cells. Cells were assembled in an argon-filled glove box and comprise:
93 (i) a 1 cm diam. disc of the composite working electrode; (ii) a Whatman GF/D borosilicate
94 glass-fibre separator soaked with electrolyte made of 1 M LiPF_6 in 1:1 ethylene
95 carbonate/dimethyl carbonate (LP30 electrolyte), and (iii) a 1 cm diam. Li metal disc as
96 the counter and reference electrode. Electrodes were cycled using an Arbin BT2000 cycler
97 at full capacity between 1 and 0.005 V vs. Li/Li^+ at a current density of 475 mA g^{-1} of Si
98 for the electrodes cycled for 1 and 10 cycles and of 600 mA g^{-1} of Si for the electrode
99 cycled for 100 cycles. After cycling, the Si-based electrodes in full charged (delithiated)
100 state were extracted from the cell and gently rinsed with dimethyl carbonate (DMC) solvent
101 in an Ar glove box to remove residual electrolyte. The samples were stored in ambient air
102 during one week prior to the FIB-SEM measurements. During this storage period, the SEI
103 products accumulated in the cycled electrodes react with air. This is highlighted in the
104 Supplementary **Figure S1**, which displays the evolution of the electrode mass gain as a
105 function of the storage time in ambient air for an electrode cycled 50 times. The initial
106 mass gain of 130% related to the accumulation of SEI products upon cycling increases to

107 190% after 5 h in contact with ambient air. No significant mass increase is observed over
108 this storage period.

109

110 *FIB-SEM* –Serial FIB/SEM imaging was performed using an FIB/SEM workstation
111 (NVision 40; Carl Zeiss Microscopy GmbH, Oberkochen, Germany) combining a SIINT
112 zeta FIB column (Seiko Instruments Inc. NanoTechnology, Japan) with a Gemini I SEM
113 column. The NVision 40 platform is also equipped with a multi-nozzle SIINT gas injection
114 system (GIS). The angle between the FIB and SEM columns was 54°. A carbon layer
115 (25x25x1 μm^3) was deposited on the top of the sample by *in-situ* ion beam induced
116 deposition (IBID) to protect the surface during slicing in order to achieve sharp upper edges
117 and minimize curtaining artefacts. Three reference lines were imprinted into the carbon
118 layer using the ion beam for post-stack alignment purposes. SEM imaging was done in
119 both secondary electron (SE) and backscattered electron (BSE) modes with an accelerating
120 voltage of 1.5 keV. Prior to serial sectioning, a trench was milled to a depth of ~20 μm .
121 This step was performed with a coarse ion beam current of 27 nA with an accelerating
122 voltage of 30 keV. Then, serial FIB sectioning was performed with a current of 3 nA at 30
123 keV and an incremental step of 25 nm (z-spacing). 3D reconstruction of the four composite
124 electrodes (before cycling and after 1, 10 and 100 cycles) was performed with a voxel size
125 of 25 nm³ from stacks of 440 images, corresponding to a volume of 20 x 8 x 11 $\mu\text{m}^3 = 1760$
126 μm^3 for all electrodes. SEM image of a FIB-sectioned electrode (uncycled) is shown in the
127 Supplementary **Figure S2**. The duration for sample preparation and image acquisition was
128 about 20 h per sample. The four electrodes were analyzed during successive days.
129 FIB/SEM study of several volume would have been preferable to analyze the representative

130 volume sizes. The limited accessibility to the equipment however does not allow repeating
131 the measurement necessary for this analysis.

132 After acquisition, the image processing and analysis were performed with Fiji
133 software.³³ In a first step, the images were aligned based on the reference lines to correct
134 small x - y drifts. The image contrast was then adjusted to correct its evolution upon ablation
135 (z direction) and the shade effect (y direction) associated with the acquisition geometry.
136 Finally, vertical stripes (curtaining effect) on the SEM images, associated with the FIB
137 ablation, were removed using a variational algorithm Fiji plug-in.³⁴

138

139 *Image segmentation.*— A key step in any sequence of image processing is the
140 segmentation step which aims at differentiating each constitutive element of the composite
141 electrode. SEM images obtained by FIB/SEM tomography are not straightforward to
142 segment due to the presence of the pores. This is due to the so-called “shine through
143 artefacts” induced by the fact that in SEM the solid phase located below the observed plane
144 is visible through the porosity. This prevents efficient image segmentation based on a
145 classical grey value threshold. Thus, a Fiji software macro has been developed based on
146 the segmentation method described in ref. **35**, and implemented in order to precisely
147 identify the pores and the solid phase. The segmentation method consists in several steps.
148 Several features, which indicate the presence of solid phase, artefacts or void phase are
149 firstly identified. The solid phase and the void are approximately extracted by thresholding
150 the SE images and the “shine through artefacts” are identified as a rise in the grey value
151 profile along the electron beam direction. Using the extracted features, preliminary
152 segmentation is achieved and is refined with a constrained watershed transformation.³⁵

153 Supplementary **Figure S3** shows the resulting segmentation outline, drawn in red on a
154 SEM image (SE mode) of a slice of the pristine anode. The quality of the segmentation is
155 demonstrated by this figure. Some accuracy of material segmentation may however remain
156 and the error rate were estimated around 12%, which is well below standard methods, in
157 Ref. [35].

158 In a second step, for the cycled electrodes, the Si particles can be distinguished from
159 the other solid phase components (CB, CMC, buffer salts and SEI products) by
160 thresholding of the BSE images, as shown in Supplementary **Figure S4**. Unfortunately,
161 CB, CMC, buffer salts and SEI products cannot be differentiated because they exhibit
162 similar grey values due to insufficient differences in their atomic *Z*-contrast. This
163 composite phase is labelled ‘Si-free solid phase’ in the present text. Finally, in order to
164 identify precisely the silicon phase for the pristine electrode, a complementary method was
165 used. It consists in filling the electrode pores with epoxy resin. As a result, due to the
166 absence of void phase, Si particles can be directly distinguished by thresholding of the BSE
167 grey level images (see Supplementary **Figure S5**).

168

169 *3D quantitative analysis.*— The spatial distribution, volume fraction, size, shape,
170 specific surface area, connectivity, and tortuosity of the pores and solid phase components
171 are key morphological parameters, affecting the electrode performance. Various methods,
172 previously described in ref. **36-38**, have been used in this paper to quantify these different
173 characteristics for the Si particles and pores.

174 The volumetric distribution of the pores and Si particles in the electrode have been
175 calculated in slices perpendicular to the *x*,*y* and *z* directions and then plotted as volume

176 fraction profiles along these axes, as shown in **Figure S6** for the pristine electrode. The
177 voxel number of the identified phases is counted in each slice and divided by the slice voxel
178 number. Their average volume fractions and relative standard deviations (RSD) are then
179 calculated.

180 The Si and pore sizes (diameter) have to be measured using a dedicated
181 mathematical morphology operation. This process consists in a combination, with
182 successive structural elements of size n , of image erosion followed by dilation. The
183 difference between the dilated and the initial image allows retrieving the fraction of
184 elements of thickness $2n$ in the image.^{36,37} In the present study, the structural element used
185 for the Si and pore phases is a sphere.

186 The connectivity of an identified phase can be determined by a counting procedure
187 detecting the 3D independent objects.^{36,37} Each object, defined as a cluster of connected
188 voxels, can then be labelled by a different grey level on resulting tomographic slices. The
189 connectivity of the Si and pore phases is calculated in this work as the ratio of the volume
190 of the largest cluster divided by the volume of all the clusters in the electrode.

191 The geometrical tortuosity of an identified phase is determined from labelled
192 trajectories followed through the network, starting from an initial seed plane, as described
193 elsewhere.³⁸ In the present case, the initial seed plane was placed near the current collector
194 and the tortuosity is calculated through the electrode thickness. First, the voxels in the
195 initial seed plane are labelled with distance of unity. By a recurrent process, the
196 neighbouring voxels are then progressively labelled with their effective distance. The
197 resulting voxel value is finally divided by the straight distance (*i.e.*, y-position). The
198 geometrical tortuosity has been calculated as the average of the tortuosity value along the

199 electrode thickness (y-direction). The efficiency of this method and the influence of the
200 calculation parameters have been recently investigated for evaluating the pore tortuosity of
201 a LiCoO₂ cathode.³⁹ It has been shown that this geometrical method produces results
202 similar to the diffusion method when the total tortuosity is defined as the average of the
203 tortuosities of each plane. In addition, the definition of the neighbouring voxel distance
204 strongly affects the tortuosity calculation. For our analysis, the results from quasi-
205 Euclidean and city-block as the neighbouring definition have been averaged for each voxel
206 to estimate the tortuosity of the Si and pore phases. Note that comparison of the tortuosity
207 values in literature shows a large dispersion, even for a same electrode material. It appears
208 that the method used to quantify the tortuosity has a major influence on the results. Higher
209 tortuosity values, typically between 2 and 8, are usually obtained by direct measurements
210 such as computational fluid dynamics simulation, porosimetry measurements or
211 electrochemical analysis (polarization-interrupt curve). Lower values, generally between 1
212 and 2, are determined by direct geometrical calculations (used in this paper) or finite
213 element modelling.

214

215

Results and discussion

216 *Electrochemical performance.*— The cycling performance of the Si-based
217 electrode is shown in **Figure 1**. The initial discharge capacity is 3306 mAh g⁻¹ Si, which is
218 close to the theoretical value (3578 mAh g⁻¹ for Li₁₅Si₄) suggesting that nearly all the Si
219 particles are electrochemically accessible in the composite electrode. A large capacity
220 decay is observed during the first cycle with a 1st charge capacity of 2645 mAh g⁻¹, leading
221 to a coulombic efficiency (CE) of 80%. During the subsequent cycles, the capacity decay

222 rate is lower and the CE tends to stabilize around 98% from the 5th cycle. The results
223 suggest that electrical disconnection of the Si particles related to the electrode volume
224 change and resulting cracking is more intensive during the first charge than for the
225 subsequent cycles. The accumulation of SEI products (*e.g.* Li₂CO₃) at the surface of the Si
226 particles also participates in the capacity decay by obstructing the Li ions in accessing to
227 the Si particles.^{40,41}

228

229 *SEM-EDX analyses.*— **Figure 2** shows surface SEM micrographs of Si-based
230 electrodes before cycling and after 1, 10 and 100 cycles. The pristine electrode does not
231 display any cracks. After one cycle, many large cracks (up to ~7 μm in width) are observed,
232 resulting in the formation of separated islands of irregular shapes (~20-50 μm in size). This
233 is in accordance with our previous studies on micrometric Si/CMC/C electrodes showing
234 that film cracking occurs during the first discharge due to its volume expansion and the
235 cracks enlarge during the first charge due to its volume contraction.^{42,43} After 10 cycles, the
236 surface electrode morphology has not significantly changed, confirming that its cracking
237 mainly occurs during the first cycle. After 100 cycles, cracks are less discernible ~~but a thick~~
238 ~~film~~, which could be associated with the accumulation of SEI products in the porosity of
239 the electrode and partially filling the cracks.⁴⁰ This is confirmed by EDX mapping analyses
240 performed on FIB ablated cross-sections of the pristine, 1st cycle and 100th cycle electrodes
241 (see **Figure 3**). The Si particles become less discernible as the cycle number increases and
242 are embedded in a growing film where carbon, oxygen and fluorine are detected. These
243 elements are in agreement with the possible electrolyte degradation products such as
244 Li₂CO₃, (CH₂OCO₂Li)₂, and LiF.⁴⁴ Note that the composition and thickness of this film are

245 affected by the storage period of the electrodes in ambient air (see Experimental section
246 and Figure S1).

247

248 *FIB/SEM analyses.*— In order to characterize the microstructural evolution in the
249 bulk of the electrodes, FIB/SEM tomography analyses have been performed on a volume
250 of $20 \times 8 \times 11 \mu\text{m}^3$ for the pristine and cycled electrodes. For the cycled electrodes, these
251 analyses have been focused in separated islands resulting from the film cracking and thus,
252 the large cracks observed in **Figure 2** are not quantified in the present study. The acquired
253 volume represents a tiny part of the whole electrode volume ($\sim 1\text{mm}^3$). The volume
254 fractions of the different phases nevertheless appear homogenous in the electrode along the
255 three Cartesian directions and thus, the data presented hereafter are not affected by the
256 volume size. Considering their typical sizes and the studied volume size, the Si and pores
257 morphological parameters can be considered as statistically relevant. The pore parameters
258 after 100 cycles however have to be considered with caution due to large typical
259 dimensions, compared to the acquired volume.

260 3D views of the Si-based electrodes before cycling and after 1, 10 and 100 cycles
261 are shown in **Figure 4**, where the white, grey, and transparent phases correspond to the Si
262 particles, Si-free solid phases (*i.e.*, CB, CMC, buffer salts and SEI products) and pores,
263 respectively. Important changes in the electrode morphology can be observed upon cycling.
264 A major increase of the volume fraction of the grey phase is observed. Major changes in
265 the volume fraction, particle size and shape of the Si phase are also observed. In order to
266 confirm these qualitative visualizations, quantitative analyses of the main morphological
267 characteristics of these electrodes have been performed as described below.

268 *Si phase distribution.*—The mean volume fraction of Si particles for the pristine anode is
269 37% (**Table 1**). It does not vary much along the three spatial directions (~~not shown~~ see
270 Supplementary **Figure S6C**), with relative standard deviations $RSD_x=8\%$, $RSD_y=RSD_z=$
271 5%. The Si particles are thus homogeneously distributed in the composite electrode. This
272 can be attributed to the extended conformation of the CMC chains in the slurry that favors
273 a homogeneous dispersion of the Si particles.³² The Si volume fraction strongly decreases
274 upon cycling to reach only 3% after 100 cycles (**Table 1**). This can be mainly explained
275 by the continuous growth of the SEI layer upon cycling, inducing an important irreversible
276 volume expansion of the electrode.⁴⁰ The SEI growth will be discussed in more detail
277 below. However, due to the reaction of the SEI layer with ambient air as previously
278 highlighted (see Figure S1), the volume fraction of Si in cycled electrodes is probably
279 underestimated. The presence of large cracks in the analysed volume of the 100th cycle
280 electrode (see below) can also explain the low Si volume fraction measured for this
281 electrode. Lastly, it is possible that some pulverized Si particles might be smaller than the
282 FIM/SEM resolution limit (25 nm), resulting in an underestimation of the Si content at 100
283 cycles. We believe however that this effect is small and that we capture most of the Si
284 particles.

285 The silicon-silicon connectivity (i.e. direct contact between Si particles) ~~of the Si~~
286 ~~particles~~ (**Table 2**) is 100% for the pristine electrode and is still high after the first cycle
287 (~97%) despite the huge volume variation of the Si particles occurring during the
288 lithiation/delithiation process. However, the present 3D analyses on cycled electrodes have
289 been focused on separated islands resulting from the film cracking and thus, the Si-Si
290 disconnections related to the formation of these macrocracks during the 1st cycle (**Figure**

291 **2b**) are not quantified. The Si particles in the islands become almost completely separated
292 after the 10th and 100th cycles with a Si-Si connectivity as low as 1% and 7%, respectively-
293 Note that a major decrease in the Si-Si connectivity does not mean a major loss in electrical
294 connectivity with the carbon additive and current collector since the electrode capacity is
295 still high at the 10th cycle (~2300 mAh g⁻¹, **Figure 1**).

296 The average Si phase geometrical tortuosity is estimated to be ~1.2 for the pristine
297 anode and increases to ~1.4 after the first cycle (**Table 2**). 3D views of the Si phase
298 tortuosity show a higher heterogeneity in the geometrical tortuosity after the first cycle
299 (**Figure 5b**) compared to the pristine anode (**Figure 5a**), highlighting the rupture of the
300 boundaries of some Si particles. The Si phase tortuosity was not determined for the
301 electrodes cycled 10 and 100 times since almost all Si particles are not directly connected
302 in these electrodes.

303

304

305

306 *Si particle size (diameter)*

307 **Figure 6** shows the Si particle size distribution (PSD) curves (**a**) and 3D views (**b**)
308 before cycling and after the 1st, 10th and 100th cycle. The Si particle size in the pristine
309 electrode typically varies from a few tens of nm to about 1.5 μm with a median size of 0.34
310 μm (**Table 2**). This result significantly differs from the PSD of the as-milled Si powder
311 determined by a laser scattering method, which shows a particle size range between 0.1
312 and 100 μm with a median size of 5.6 μm (see Supplementary **Figure S7**). This suggests
313 that the as-milled Si powder made of cold-welded submicrometric particles³¹ are fractured

314 during the slurry preparation. This assumption is confirmed by the laser scattering PSD
315 analysis of the milled Si powder submitted to a subsequent milling for 1 h at 500 rpm using
316 a Fritsch mixer as done for the slurry mixing (see Experimental section). It results in a
317 median particle size of 0.2 μm (see Supplementary **Figure S7**), which is not very far from
318 the PSD data obtained from the present 3D reconstruction analysis of the pristine electrode.
319 The specific surface area (SSA) of the Si phase (**Table 2**) is estimated to be 13.8 μm^{-1} (Si)
320 which corresponds to 5.9 $\text{m}^2 \text{g}^{-1}$ (Si).

321 As shown in **Figure 6** and **Table 2**, a progressive decrease of the Si particle size
322 occurs upon cycling to reach a median size of 0.14 μm after 100 cycles. This value is in
323 agreement with the critical particle size below which cracking does not occur.⁴⁵ The
324 progressive decrease of the Si particle size upon cycling is, however, in contradiction with
325 acoustic emission measurements, which suggest that the Si particle cracking occurs mostly
326 during the first cycle.^{42,46} It must however be noted that it is difficile to discriminate
327 between intra and inter particle cracking by acoustic emission. The fact that the initial
328 particle cracking is not discernible from the present FIB/SEM tomography analyses may
329 also be due to the small size of the intra particle cracks. The progressive decrease of the Si
330 particle size observed in **Figure 6** may thus reflect the progressive enlargement of the
331 particle cracks due to the growth of the SEI layer inside these cracks upon cycling. It must
332 also be noted that the shape of the Si particles also changes with prolonged cycling. They
333 display a nonspherical "stringy" morphology after 100 cycles, characterized for the 100
334 biggest particles by an axial ratio of 4.6 compared to 2.5 after 10 cycles. The particle
335 cracking and change in shape induce a progressive increase of the SSA of the silicon phase

336 that reaches $24.4 \mu\text{m}^{-1}$ (Si) after 100 cycles (**Table 2**). This increase should have a
337 deleterious effect on the electrode cycle life by exacerbating SEI reactions.

338 *SEI growth.*— As previously shown from cross-section SEM images and corresponding
339 EDX mappings (**Figure 3**) the cycled electrodes, the electrode is progressively filled with
340 SEI products upon cycling. This process was also confirmed from ex-situ measurements
341 of the weight and thickness of cycled Si-based electrodes.⁴⁰ Indeed, a significant increase
342 of the electrode weight was observed with cycling (up to 300% after 200 cycles), which is
343 attributed to the continuous accumulation of insoluble electrolyte degradation products in
344 the Si electrode. It is accentuated in the absence of additives in the electrolyte such as FEC
345 or VC, which are well known to favor the formation of a more stable SEI.^{40,44,47}

346 As previously explained, the image segmentation procedure does not permit to
347 differentiate the SEI products from the CB, CMC and salt buffer components. However,
348 considering that the amount of CB, CMC and salt buffer is low in the pristine electrode (6
349 vol%) and should not vary with cycling, the major increase of the Si-free solid phase
350 observed with cycling can be attributed to the SEI growth. This growth is however
351 overestimated due to the contact of the samples with ambient air as previously shown (see
352 **Figure S1**). As summarized in **Table 1**, the Si-free solid phase occupies 5460% of the
353 electrode volume after the 1st cycle by filling the electrode pore network. Indeed, this latter
354 decreases to 5 vol.% compared to 57 vol.% in the pristine electrode, while the Si volume
355 fraction is almost unchanged. The SEI-volume fraction of the Si-free solid phase increases
356 to 769% after 10 cycles, inducing an irreversible increase of the electrode volume since the
357 Si volume fraction decreases to 17%. After 100 cycles, its volume fraction is 61%. This

358 decrease can be explained by the accentuation of the electrode cracking, as confirmed by
359 the increase of the pore volume fraction (36% at the 100th cycle vs. 4% at the 10th cycle).

360 **Figure 7** shows the evolution upon cycling of the thickness of the Si-free solid phase
361 around the Si particles. Assuming that the Si-free solid phase is mainly constituted of SEI
362 products (90, 96 and 99 vol.% after 1, 10 and 100 cycles, respectively as calculated from
363 data in **Table 1**), **Figure 7** can be considered in first approximation as the evolution of the
364 SEI layer thickness around the Si particles. Its thickness after the 1st cycle varies from about
365 50 to 800 nm with a mean value of ~250 nm. As expected, the SEI layer becomes thicker
366 as the cycle number increases to reach a mean thickness of 450 and 850 nm after 10 and
367 100 cycles, respectively. For comparison, a 250 nm thick SEI layer was observed from ex-
368 situ SEM measurements of Si microwires cycled in LP30 electrolyte, but no SEI thickening
369 was highlighted after the first 3 cycles.⁴⁸ A 200 nm thick surface film was also observed
370 on Si nanowires after 30 cycles in LP30 electrolyte.⁴⁹ The larger thickness of the SEI layer
371 observed here may originate from the reaction of the SEI products with ambient air prior
372 to the FIB-SEM measurements. However, our results confirm that a major increase of the
373 SEI layer occurs upon cycling.

374 *Pore phase.*— An accurate characterization of the pore phase is highly relevant for
375 optimizing electrode performance. Indeed, the morphological characteristics of the pore
376 phase affects lithium ion transport in the electrodes, which can have a significant impact
377 on its power capability. It was also demonstrated that progressive clogging of the pores by
378 the SEI layer growth upon cycling inhibits lithium diffusion through the Si composite
379 electrode, which is the main cause of the capacity fade.⁴¹ The electrode porosity is also

380 likely to limit the electrode expansion by partially buffering the Si swelling associated with
381 its lithiation.^{43,50}

382 **Figure 8** shows the distribution curves (a) and color-scale 3D views (b) of the pore
383 size for the electrodes before cycling and after the 1st, 10th and 100th cycles. The pore
384 volume fraction in the electrodes is presented in **Table 1** and the main morphological
385 characteristics of the pore phase are summarized in **Table 3**. The pore volume fraction of
386 the pristine anode is estimated at 57% and is similar along the three spatial directions (~~not~~
387 ~~shown~~ see Supplementary **Figure S6D**), with relative standard deviations $RSD_x = RSD_y =$
388 $RSD_z = 4\%$. For comparison, graphite anodes in commercial Li-ion batteries have typically
389 a porosity of 20-30%. However, they are calendered, in contrast to the present Si-based
390 electrode. The pore size in the pristine electrode ranges from *ca.* 0.1 to 1.5 μm with a
391 median size of 0.4 μm (**Figure 8a**). The pore size appears homogeneously distributed in
392 the composite electrode (**Figure 8b**). In addition, all the pores are connected (**Table 3**).
393 From the 1st cycle, drastic decreases in the pore volume fraction, size and connectivity are
394 observed, reflecting the nearly complete filling of the electrode pore network by the SEI
395 products. However, it must be exaggerated in the present case due to the reaction of the
396 SEI products with air before the FIB-SEM analyses as previously discussed. Additionally,
397 it must be reminded that the FIB/SEM analyses have been performed on separated islands
398 resulting from the film cracking. As observed on the SEM images (**Figure 2**), these large
399 cracks appear empty and can insure an important part of the ion transport in the electrode.
400 At the 100th cycle, large pores are observed (**Figure 8**) with a median size of 1.75 μm , a
401 connectivity of 65% (**Table 3**) and a pore volume fraction of 36% (**Table 1**). This can be
402 explained by the cracking of the film islands resulting from their repeated volume

403 expansion/contraction upon prolonged cycling likely to induce major stress in the electrode
404 film.

405 **Figure 9** shows, for the electrodes before cycling and after 100 cycles, colour-scale
406 3D and 2D views of the geometrical tortuosity through the electrode thickness, starting
407 near the current collector towards the electrode surface. For the pristine electrode, the
408 average tortuosity is estimated at ~ 1.1 and is similar in the three spatial directions (*not*
409 *shown*). However, as highlighted in 2D view (**Figure 9b**), higher tortuosity values (see red-
410 to-green zones) are observed behind the larger Si particles (see black zones) since they act
411 as an obstacle, increasing the distance through the porous network. After 100 cycles, the
412 average pore tortuosity is still low (~ 1.0) despite the significant decrease in the pore volume
413 fraction and connectivity (**Tables 1 and 3**), resulting in a connected pore volume fraction
414 of 23% compared to 57% for the pristine electrode. This can be explained by the formation
415 of very large cracks in the film islands after 100 cycles as previously discussed. However,
416 as shown in **Figures 9c-d**, local heterogeneities of the pore tortuosity are observed in pore
417 regions (see white-to-green zones) surrounded by a large amount of SEI products (see black
418 zones).

419

420

Conclusions

421 This study demonstrates that the 3D morphology of a composite Si-based anode can be
422 described in detail by means of FIB/SEM tomography using appropriate image processing
423 and analysing methods. As a result, key morphological parameters (volume fraction, spatial
424 distribution, size, specific surface area, connectivity, and tortuosity) of the Si particles and
425 pores can be determined in the three spatial directions of the electrode and their evolution

426 with cycling can be evaluated. For the pristine electrode, it is shown that the Si and pore
427 phases are homogeneously distributed, well connected and present a low tortuosity. The
428 cracking of the composite film and Si particles upon cycling is highlighted. This study also
429 confirms that it is essential to develop a more efficient electrolyte formulation than the
430 conventional LP30 electrolyte to prevent excessive SEI formation and thus to obtain viable
431 Si-based electrodes.

432

433

Acknowledgements

434 The authors thank the Natural Sciences and Engineering Research Council of Canada
435 (NSERC) for financial support of this work. We also thank the CLYM (Centre Lyonnais
436 de Microscopie: www.clym.fr) supported by the CNRS, the “GrandLyon” and the Rhône-
437 Alpes Region for use of the Zeiss NVision40 FIB/SEM.

438

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- 537

538 **Table captions**

539 **Table 1.** Volume fractions of the different phases in the Si-based electrodes determined
540 from 3D reconstruction of the pristine and cycled Si-based electrodes

541 **Table 2.** Main morphological characteristics of the Si phase determined from 3D
542 reconstruction of the pristine and cycled Si-based electrodes

543 **Table 3.** Main morphological characteristics of the pore phase determined from 3D
544 reconstruction of the pristine and cycled Si-based electrodes

545

546 **Figure captions**

547 **Figure 1.** Discharge-charge capacities and coulombic efficiency versus cycle number of
548 the Si-based electrode. The electrode mass loading is $0.8 \text{ mg Si cm}^{-2}$. Cycling was
549 performed at a current density of 600 mA g^{-1} of Si. Capacities are given per gram of Si.

550 **Figure 2.** Surface SEM images of the Si-based electrodes (a) before cycling, (b) after 1
551 cycle, (c) after 10 cycles and (d) after 100 cycles.

552 **Figure 3.** EDX maps of Si, C, O and F elements on FIB ablated cross-sections of the
553 pristine, 1st cycle and 100th cycle electrodes.

554 **Figure 4.** 3D views (volume of $20 \times 8 \times 11 \text{ } \mu\text{m}^3$) of the Si-based electrodes (a) before cycling,
555 (b) after 1 cycle, (c) after 10 cycles and (d) after 100 cycles.

556 **Figure 5.** 3D views of the Si phase tortuosity for the Si-based electrode (a) before cycling
557 and (b) after 1 cycle.

558 **Figure 6.** (a) Distribution curves and (b) 3D views of the Si particle size for the electrodes
559 before cycling and after the 1st, 10th and 100th cycle.

560 **Figure 7.** Distribution curves of the SEI layer thickness on the Si particles after 1, 10 and
561 100 cycles.

562 **Figure 8.** (a) Pore size distribution curves and (b) pore size 3D views of the electrodes
563 before cycling and after the 1st, 10th and 100th cycle.

564 **Figure 9.** Color-scale 3D and 2D views of the pore tortuosity for the pristine electrode (a,
565 b) and after 100 cycles (c, d).

566

567 **Table 1**

	pristine	1 st cycle	10 th cycle	100 th cycle
Si phase	37%	35%	17%	3%
Si-free solid phase	6%	60%	79%	61%
Pore phase	57%	5%	4%	36%

568

569

570 **Table 2**

	pristine	1 st cycle	10 th cycle	100 th cycle
Si phase connectivity	100%	97%	1%	7%
Si phase tortuosity	1.2	1.4	-	-
Specific surface area	13.8 $\mu\text{m}^{-1}_{\text{Si}}$	14.6 $\mu\text{m}^{-1}_{\text{Si}}$	17.4 $\mu\text{m}^{-1}_{\text{Si}}$	24.4 $\mu\text{m}^{-1}_{\text{Si}}$
Median Si particle size	0.34 μm	0.29 μm	0.25 μm	0.14 μm

571

572

573 **Table 3**

	pristine	1 st cycle	10 th cycle	100 th cycle
Pore connectivity	100%	4%	3%	65%
Pore tortuosity	1.1	-	-	1.0
Median pore size	0.40 μm	0.15 μm	0.15 μm	1.75 μm

574

575

Figure 1

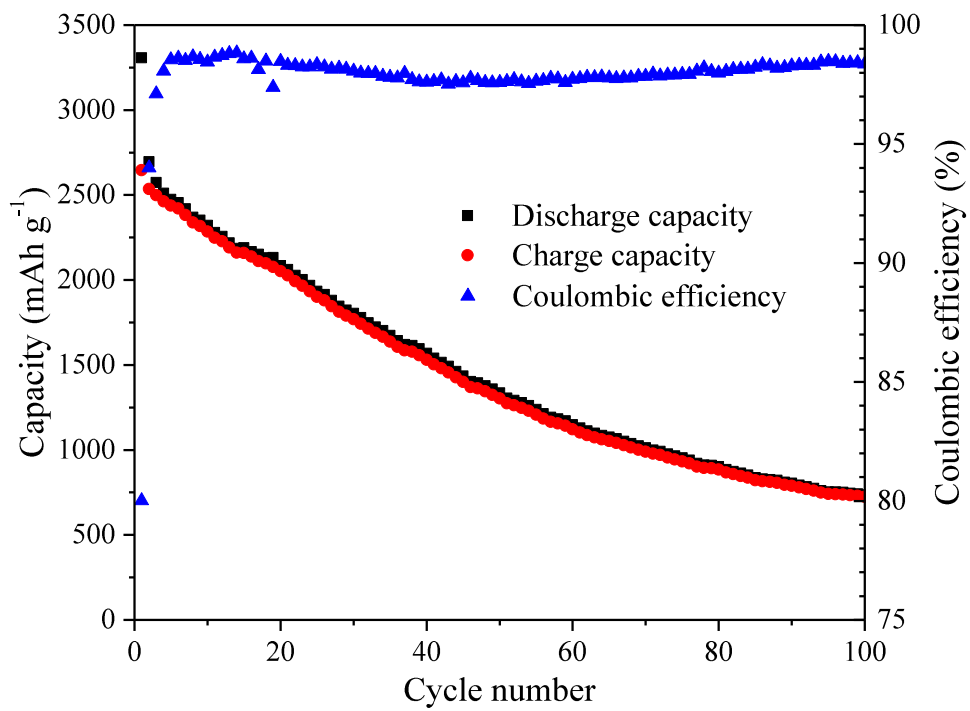
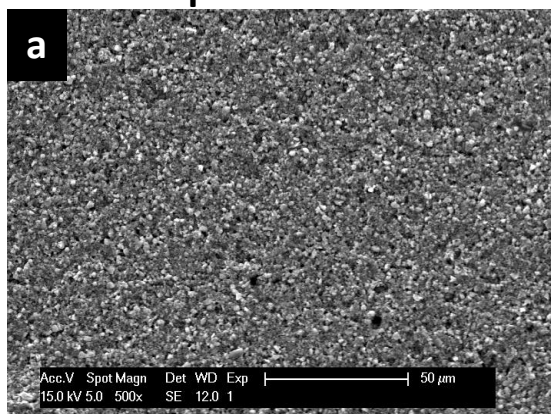
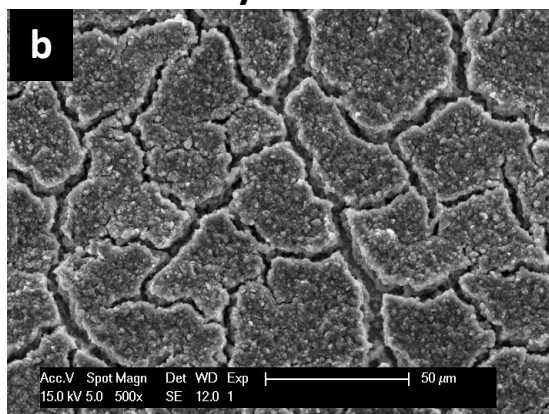


Figure 2

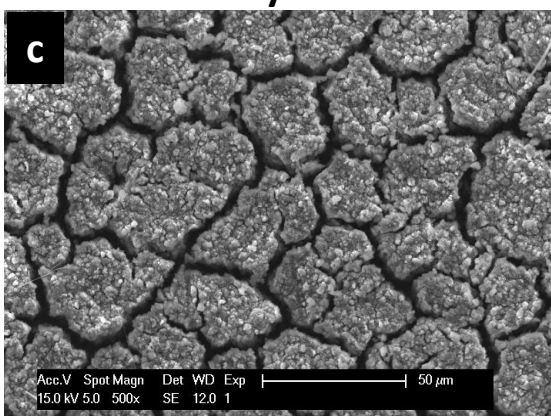
pristine



1 cycle



10 cycles



100 cycles

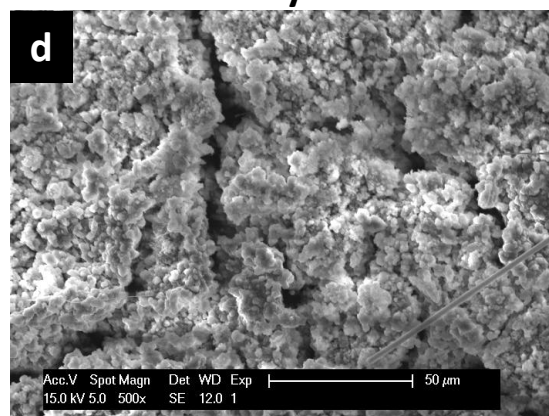


Figure 3

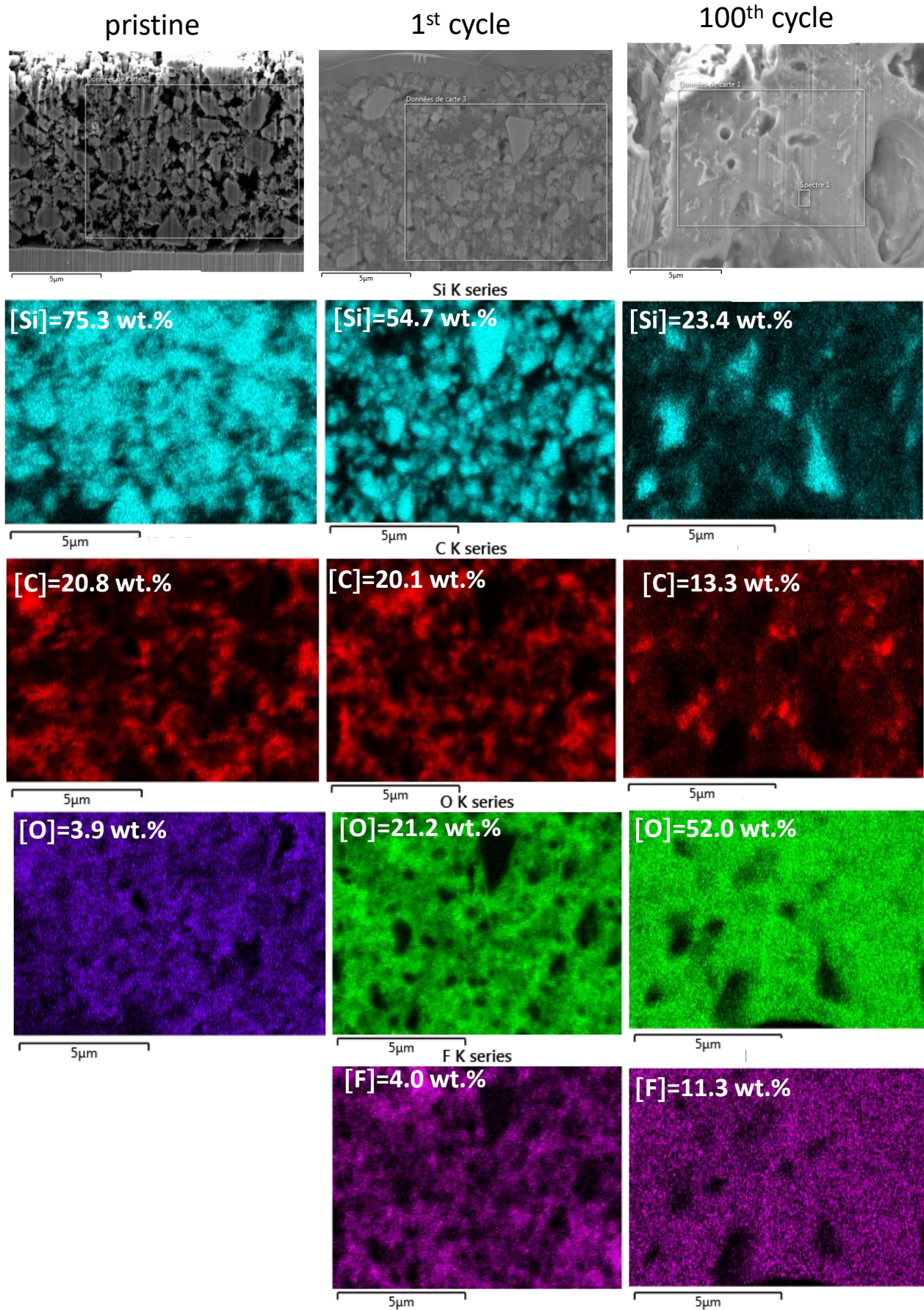


Figure 4

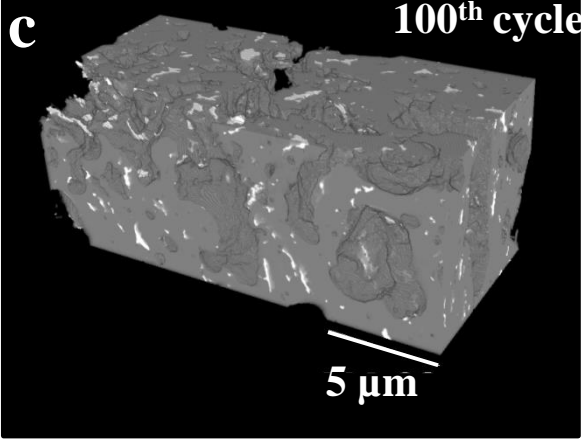
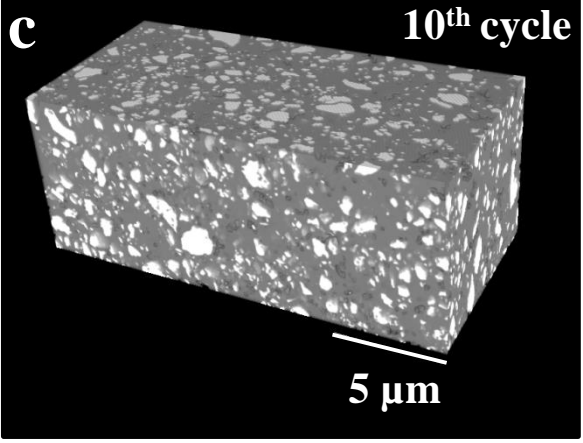
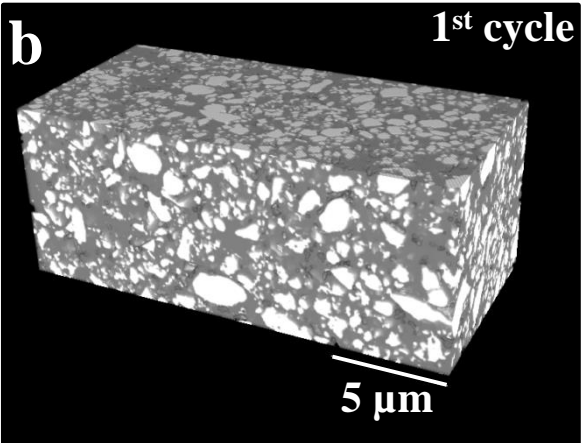
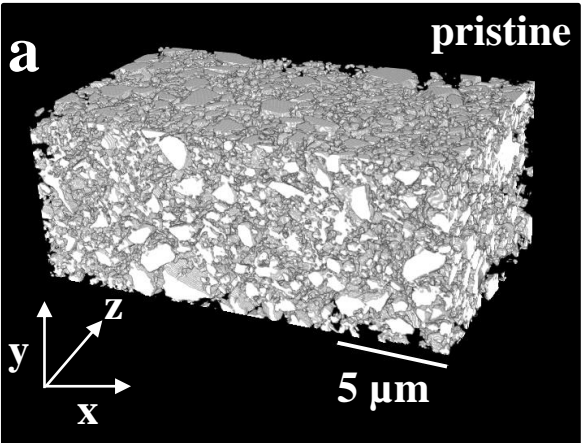
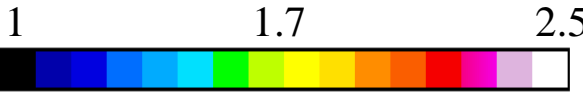
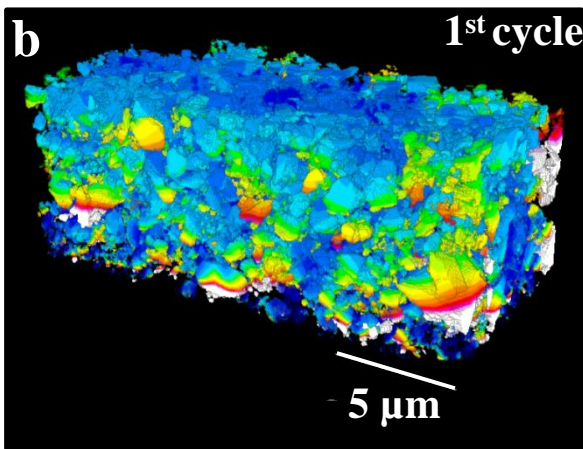
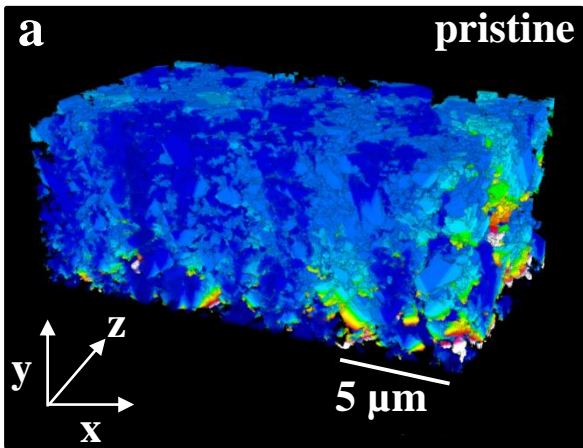
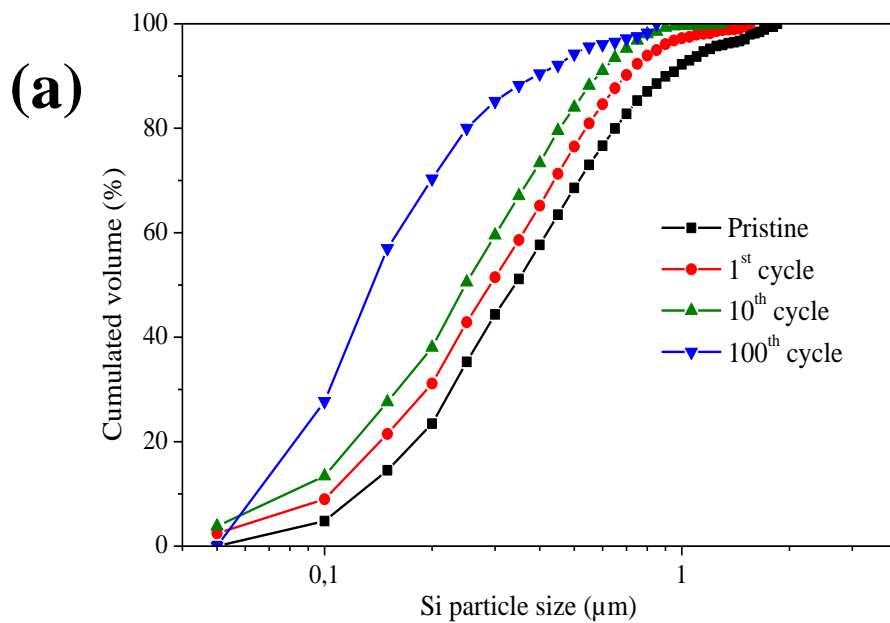


Figure 5



Color scale bar of the Si phase tortuosity

Figure 6



(b)

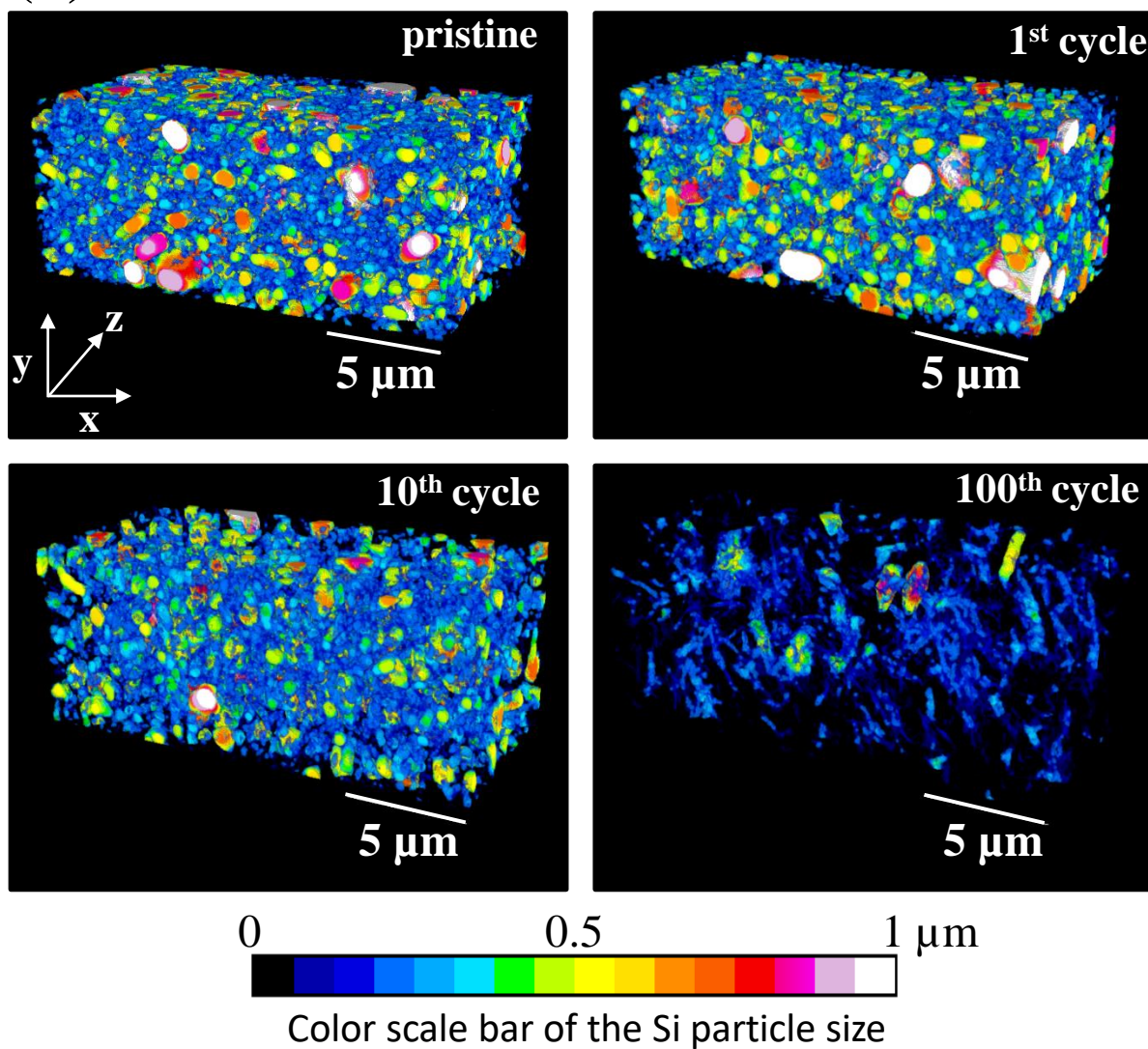


Figure 7

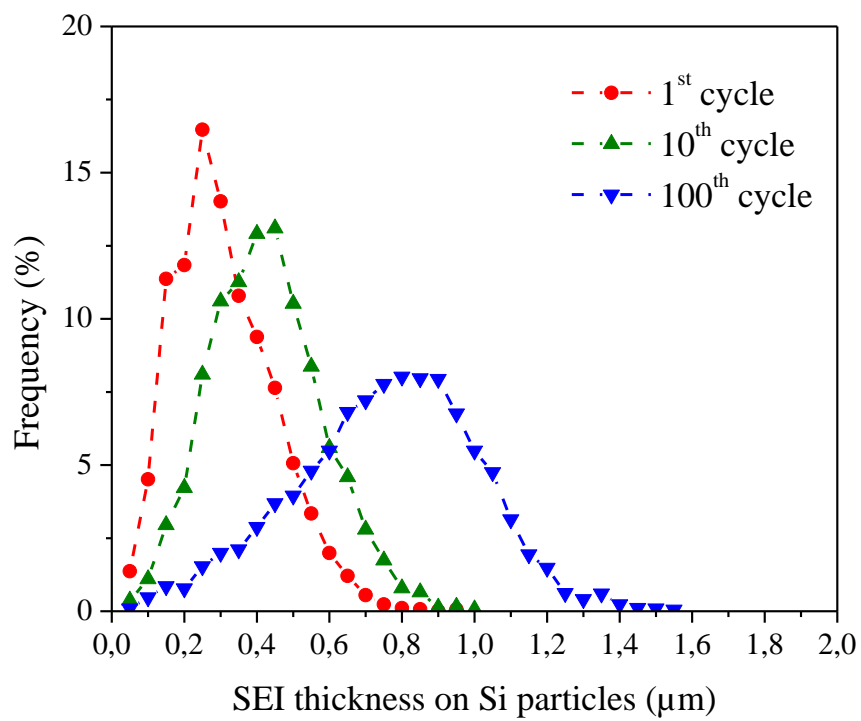
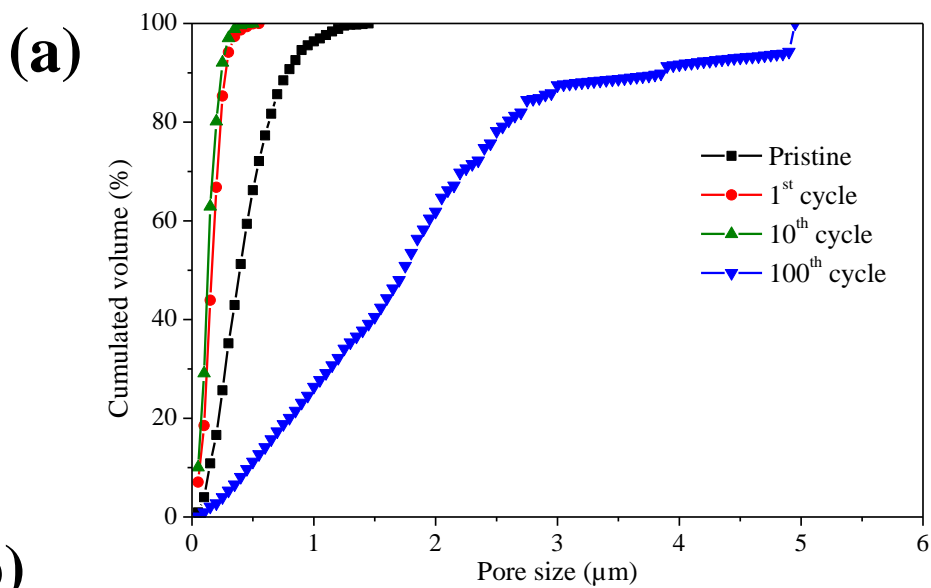


Figure 8



(b)

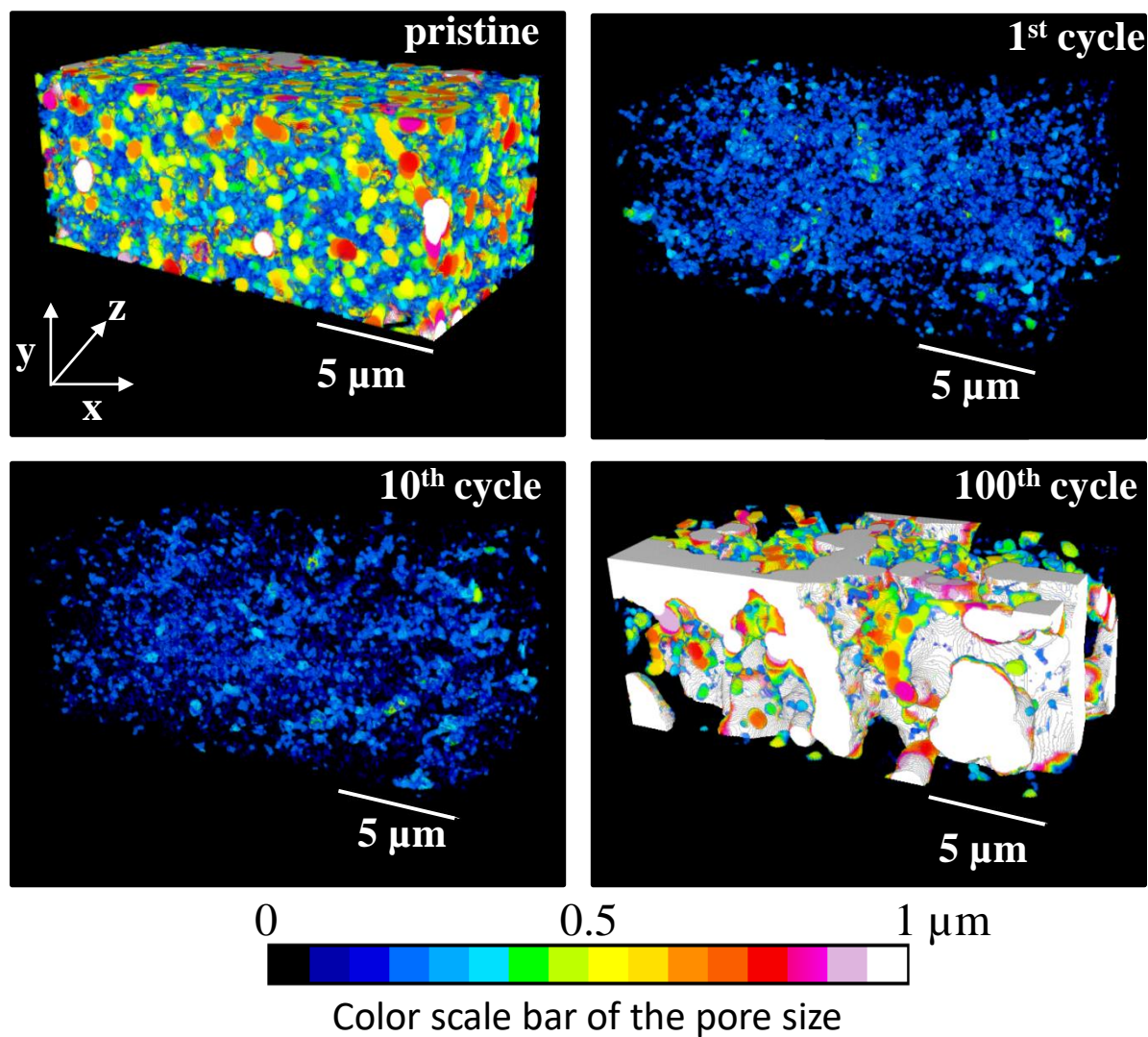
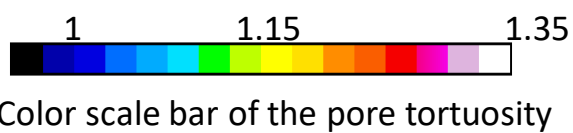
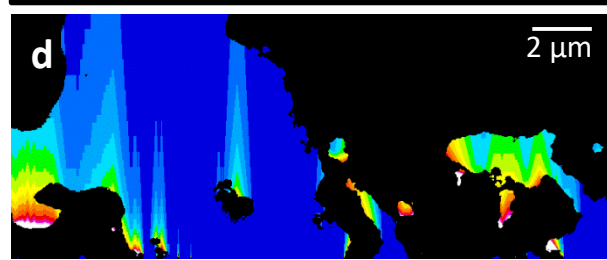
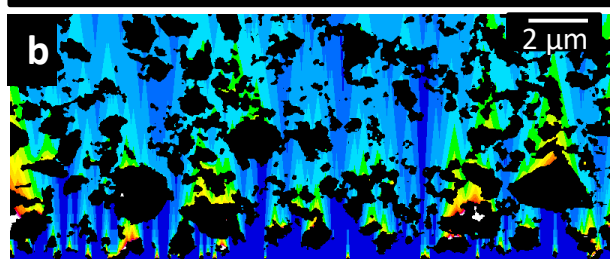
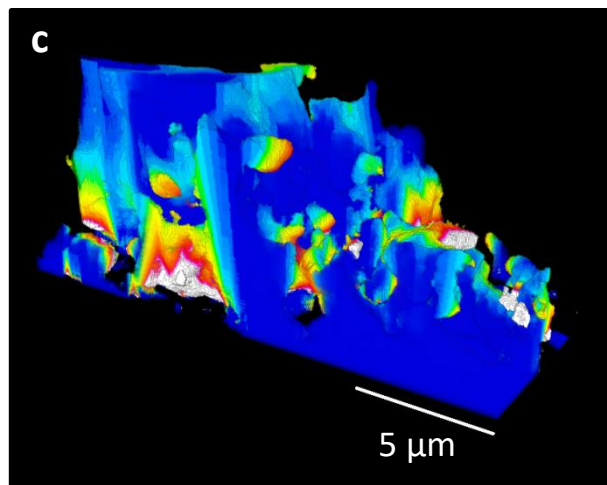
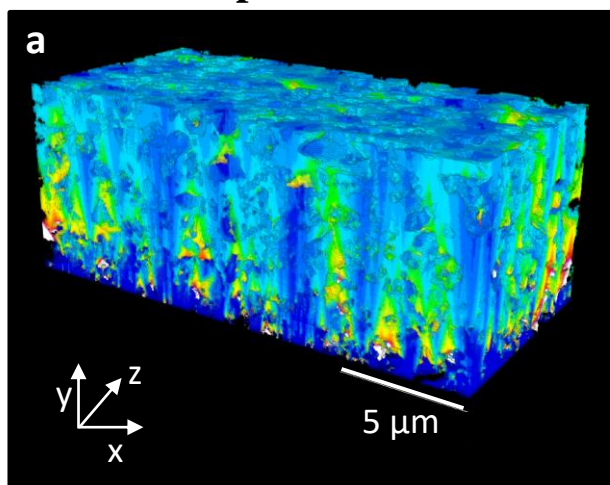


Figure 9

pristine

100th cycle



Supplementary Information

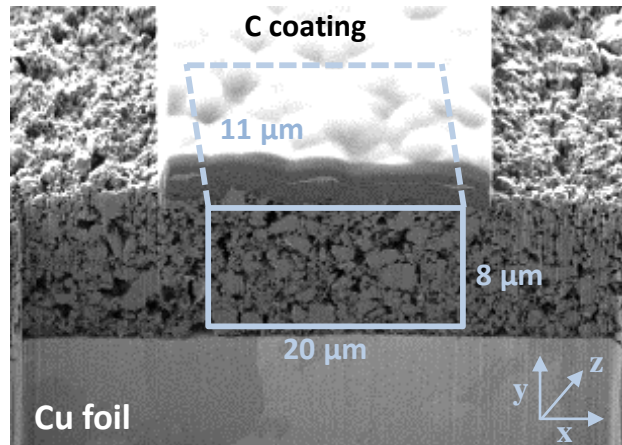


Fig. S1. SEM image of the FIB ablated region of the Si-based electrode. The size of the reconstructed volume (represented by the blue lines) is $20 \times 8 \times 11 \mu\text{m}^3$.

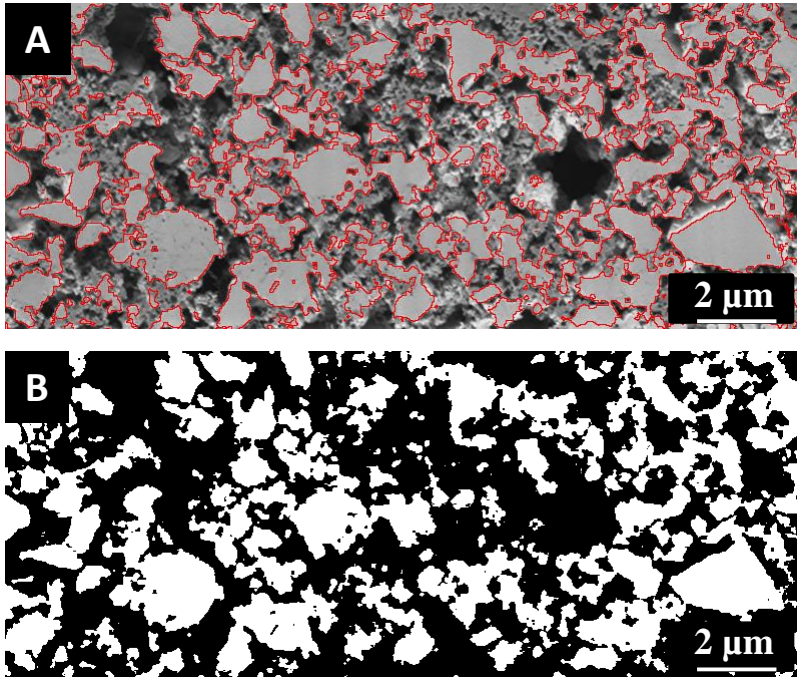
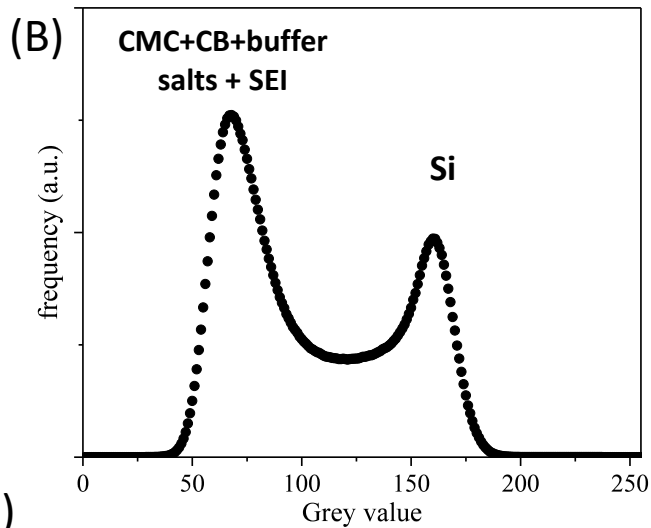
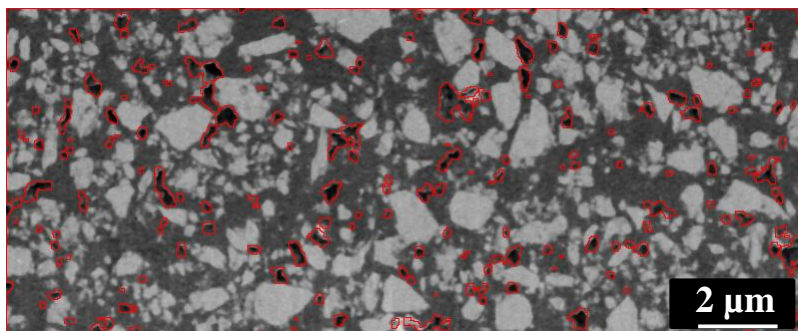


Fig. S2. (A) grey-scale SEM image (SE mode) of a slice of the Si-based electrode with segmentation outlines (red) using Fiji software macro [\[39\]](#); (B) same slice after binarization into solid phase (white) and pores (black).

(A)



(C)

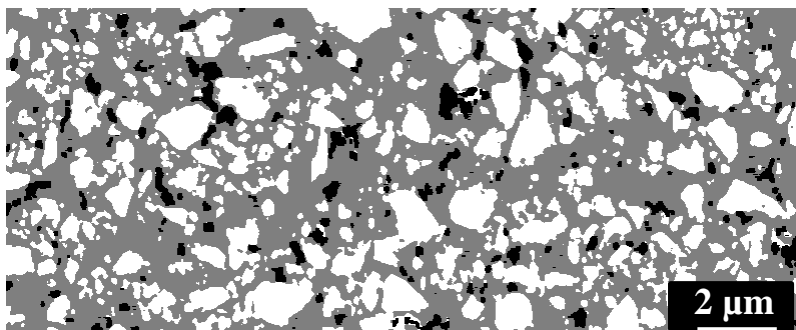


Fig. S3. (A) grey-scale SEM image (BSE mode) of a slice of the Si-based electrode (after 1 cycle) with pores segmentation outlines (red) using Fiji software macro [39]; (B) frequency grey-level histogram of the solid phase for the full image volume; (C) same slice after segmentation into pores (black), Si particles (white) and other solid phases (grey).

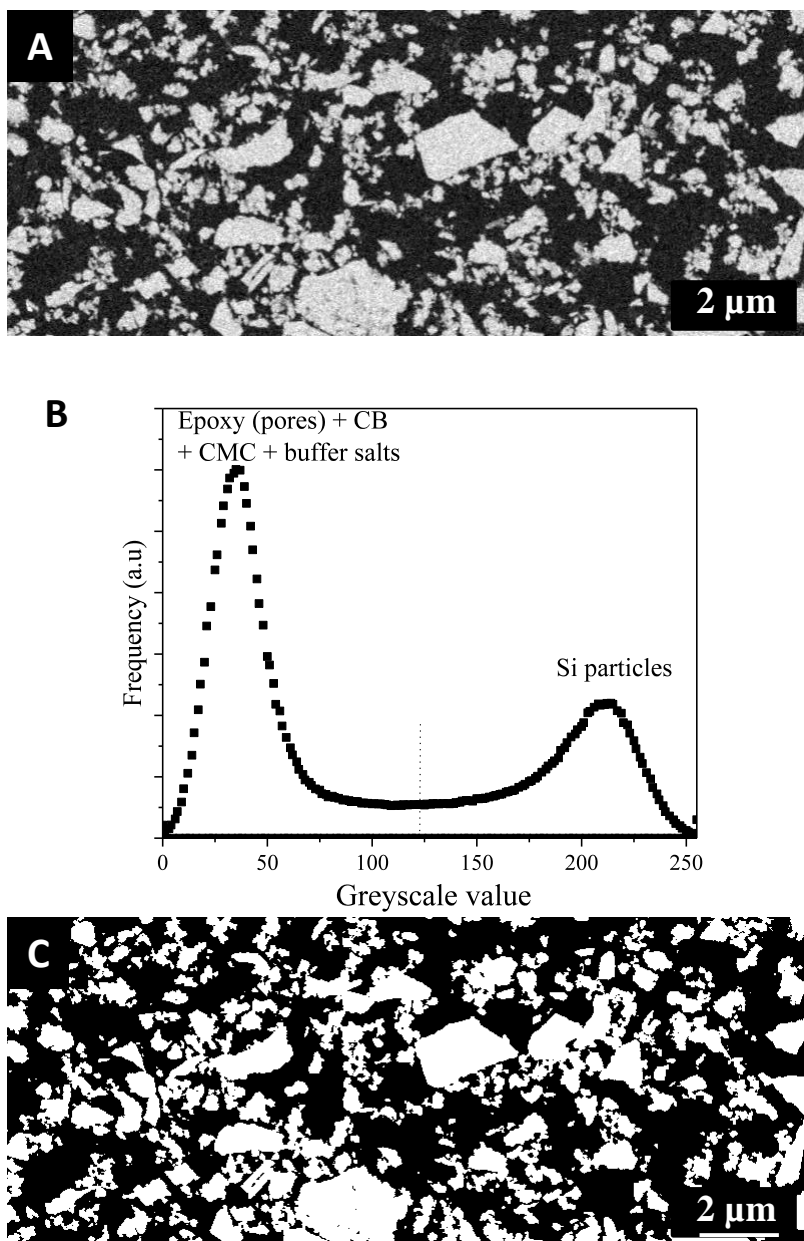


Fig. S4. Image segmentation process for the epoxy-infiltrated Si-based anode: (A) grey-scale SEM image (BSE mode) of a slice of the electrode; (B) frequency histogram of the grey-level for the full image volume; (C) same slice after binarization into Si particles (white) and carbon-based compounds (black).

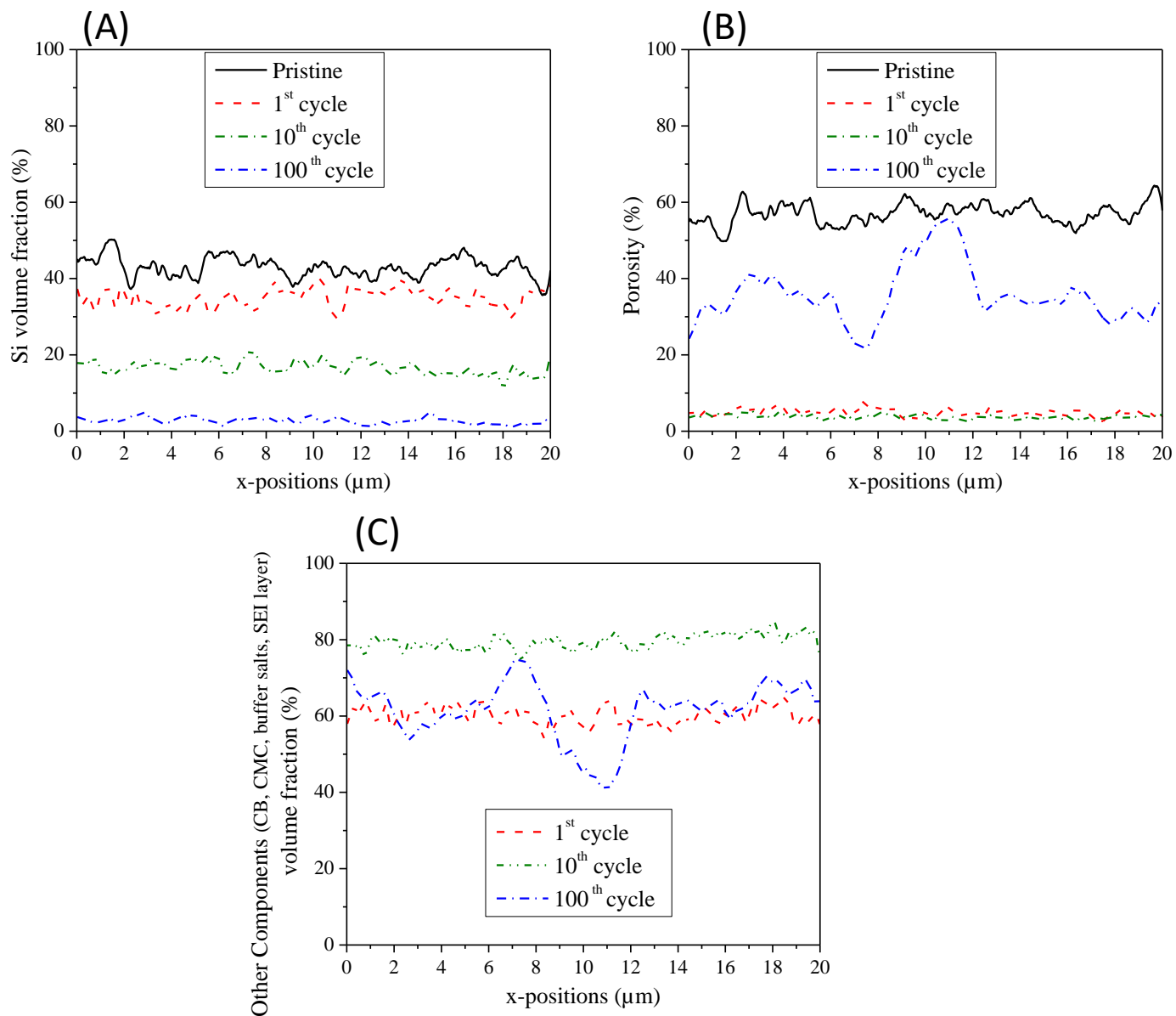


Fig. S5. Volume fraction profiles along x-direction of (A) silicon, (B) porosity and (C) the other components (CB, CMC, buffer salts and SEI layer) for Si-based anode before cycling, after 1, 10 and 100 cycles.

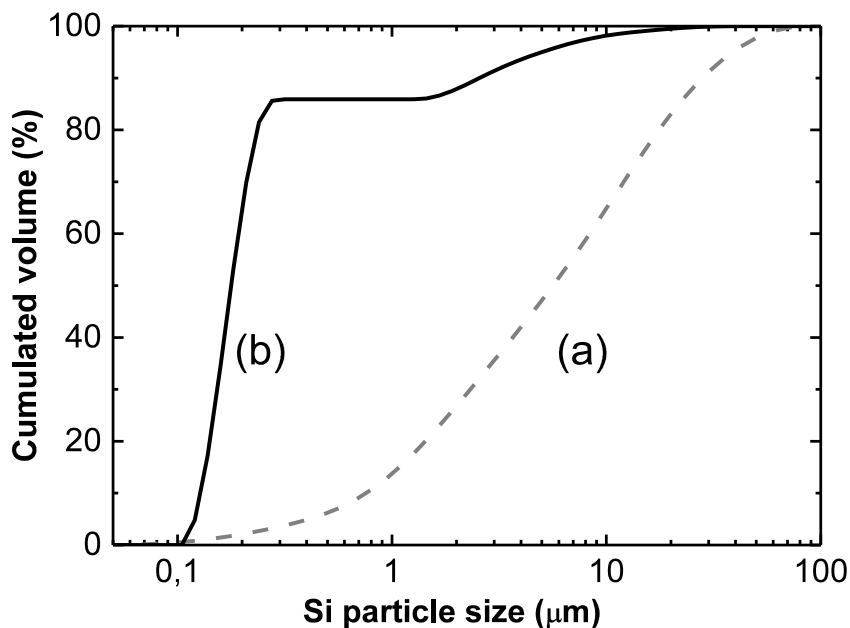


Fig. S6. Cumulated distribution curves of the Si particle size for (a) as-milled Si powder (*i.e.*, milled for 20 h using a Spex mixer) and (b) after a subsequent milling for 1 h using a Fritsch mixer as done for the electrode slurry preparation. The particle size distribution was determined in aqueous media by laser scattering method using a Mastersizer 2000 Malvern analyser.