Multiple-Stripe Lithiation Mechanism of Individual SnO_{2} Nanowires in a Flooding Geometry

Li Zhong, Xiao Hua Liu, Guo Feng Wang, Scott X. Mao, and Jian Yu Huang

Multiple-stripe lithiation mechanism of individual SnO_2 nanowires in a flooding geometry

Li Zhong,[2] Xiao Hua Liu,[1] Guo Feng Wang,[2] Scott X. Mao,[2] Jian Yu Huang[1*]

[1]Center for Integrated Nanotechnologies, Sandia National Laboratories,
Albuquerque, New Mexico 87185, USA
[2]Department of Mechanical Engineering and Materials Science, University of
Pittsburgh, Pittsburgh, Pennsylvania 15261, USA

Abstract: The atomic scale lithiation mechanism of individual SnO_2 nanowires in a flooding geometry with the entire wires being immersed in the electrolyte was revealed by in-situ transmission electron microscopy. The lithiation was initiated by formation of multiple stripes with width of a few nanometers parallel to the (020) plane traversing the entire wires, serving as multiple reaction fronts for later stages of lithiation. Inside the stripes, we identified high density of dislocations and enlarged inter-planar spacing, which provided effective path for lithium ion transport. The density of the stripes increased with further lithiation, and eventually they merged with one another, causing a large elongation, volume expansion, and the crystalline to amorphous phase transformation. This lithiation mechanism characterized by multiple stripes and multiple reaction fronts was unexpected and differed completely from the expected core-shell lithiation mechanism.

---

[*] Corresponding author: jhuang@sandia.gov

Charging a lithium ion battery (LIB) leads to lithiation of the anode. Understanding the atomic scale lithiation process is the key to unfold the operation mechanism of LIBs, thus providing the critical science for designing better LIBs [1, 2]. Although lithiation has been investigated extensively by theoretical simulation over a wide range of electrode materials [3–14], there is lack of direct experimental evidence and fundamental understanding on the initiation and evolution of the atomic scale lithiation mechanisms [15, 16]. We have demonstrated very recently that it is possible to study the lithiation process at an atomic scale and in real time by transmission electron microscopy (TEM) [17]. Direct visualization of the lithiation process can provide important insight on how LIBs work and guide the development of advanced LIBs for powering future electrical vehicles and electrical devices.

In the recent publication, we created a nanoscale battery [Fig. S1] consisting of a single nanowire anode, an ionic liquid based electrolyte (ILE), and a $LiCoO_2$ cathode, and conducted in-situ charging/discharging experiments on an individual SnO_2 nanowire anode inside a TEM. However, in that experiment, one end of the nanowire is in contact with the electrolyte as illustrated in Fig. S2(a) (hereafter referred to as "end-contact"). Therefore, the lithiation is featured by a single reaction front advancing in the axial direction [Fig. S2(b)]. However, in a real battery, the nanowires were immersed entirely in the electrolyte in a flooding geometry (hereafter interchangeably referred to as "flooding" or "side-contact", Fig. S2(c)). One fundamental question that needs to be addressed is: does the same lithiation mechanism operating in the end-contact also operate in a flooding geometry? It is speculated that the previously observed large elongation during charging of SnO_2 nanowires might be related to the end-contact geometry, as it is expected that in an end-contact geometry, the reaction interface is perpendicular to the nanowire axis, and the elongation should occur in a direction that is perpendicular to the reaction interface, thus the observed superelongation [Fig. S2(b)]. In a similar vein, when the nanowire is flooded in the electrolyte, it is

expected to swell rather than elongate [Fig. S2(d)] [18, 19]. To clarify the above argument, we conducted further experiments under both the end-contact and the side-contact (flooding) geometries. Although superelongation and a high density of dislocations occurred also in a flooding geometry, we found lithiation occurred preferentially along the (020) plane, producing multiple stripes parallel to the (020) plane and causing its expansion. Lithiation in the crystal lattice generated a high density of dislocations in the stripes. With further lithiation, the density of the stripes increased and finally amorphization occurred inside the stripes.

Figure 1 shows morphology and structure evolution of a SnO_2 nanowire anode during lithiation process in a partially flooded geometry. The initial single crystalline nanowire was 45 μm long and 220 nm thick [Figs. 1(a) and 1(o)]. About one third of the nanowire was immersed into the ILE, and the rest of the nanowire was out of the ILE [Fig. 1(b)]. A −3.5 V bias was then applied to the anode with respect to the $LiCoO_2$ cathode, which initiated an electrochemical charging in the nanowire. The reaction front (marked by red arrowheads) moved along the nanowire from the ILE side (right) to the substrate (left) [Figs. 1(c)–1(k)]. As the reaction front passed by, the nanowire became bent and twisted. Surprisingly, the flooded segment showed similar morphology to the non-flooded segment with elongation, spiral, buckling and twist after the ILE was retracted [Fig. 1(l)]. Electron diffraction patters (EDPs) corresponding to the non-flooded [Fig. 1(m)] and flooded [Fig. 1(n)] segments indicated both reaction products comprised of small Sn and Li_xSn particles dispersed in amorphous Li_2O matrix. Similar results were obtained in many other flooding tests (e.g., Fig. S3). Again, we saw similar morphology changes in the flooded and non-flooded segments after lithiation, both undergoing similar elongation and swelling, and exhibiting a typical amorphous gray contrast [Figs. S3(l) and S3(m)]. Elongation of the flooded segment was also measured in Fig. S3. With two reference marks visible before and after charging in the flooded segment [Figs. S3(j) and S3(k)], the elongation of the flooded segment after charging was estimated to be 65%,

comparing to a 60% total elongation of the whole nanowire, indicating a 55% elongation of the non-flooded segment, which is consistent with that measured from the in-situ experiments [17].

To understand further the lithiation mechanism in a flooding geometry, we stopped lithiation at various intermediate stages and retracted ILE to inspect the structure evolution of the flooded segment. Figure 2 is morphology and structure changes at different lithiation stages of several SnO_2 nanowires in a flooding geometry. A pristine SnO_2 nanowire was smooth and straight, with a single crystalline rutile structure before lithiation [Figs. 2(a) and 2(g)]. After a −3.5 V bias was applied to the SnO_2 nanowires against $LiCoO_2$ cathode, there was no detectable changes until after approximately 90 s, when a set of dark-contrasted stripes inclined 61° with respect to the side surface of the nanowire emerged [Fig. 2(b)]. After a few more seconds, the spacing between the stripes became smaller and there was dislocation contrast all over the nanowire [Fig. 2(c)]. These stripes were induced by lithiation. The EDP of the striped nanowire [Fig. 2(h)] showed single-crystal diffraction spots superimposed on a diffuse scattering background caused by inelastic scattering originating from lithiation induced defects. These strips were likely nucleated from local surface regions with atomic scale defects [Fig. S4] and each traversed the entire nanowire [Fig. S5]. Upon further lithiation, the contrast of these stripes became blurred (red rectangle in Fig. 2(d)). In the mean time, some weak arcs around the single-crystal diffraction spots emerged [Fig. 2(i)] due to lithiation induced polycrystallization of the nanowire. With further lithiation [Figs. 2(e) and 2(f)], the arcs around SnO_2 diffraction spots became much weaker [Fig. 2(j)] and finally barely discernible [Fig. 2(k)], and the whole nanowire was converted to Sn, Li_xSn and Li_2O amorphous matrix [Fig.2 (k)].

It took about 2–5 minutes to fully lithiate a nanowire of 15 μm long in a flooding geometry. In comparison, fully lithiation of the same length of a nanowire in an

end-contact configuration took ~ 30 minutes. Obviously, the multiple stripes acted as multiple reaction fronts in the side-contact geometry, in contrast to the single reaction front in the end-contact geometry.

It is interesting to note that during the whole lithiation process in a flooding geometry, even though lithium ions diffuse from the surface towards the interior of the nanowire, the assumed core-shell structure [Fig. S2(d)] was never observed. Instead, the unexpected multiple stripes and multiple reaction fronts appeared throughout the nanowire, leading to large elongation. Therefore, it is important to understand the nature of the multiple stripes.

Figure 3(a) is the morphology of a SnO_2 nanowire with [011] growth direction [Fig. S6] at the initiation stage of lithiation, showing again multiple stripes inclined to the nanowire axis, and Fig. 3(b) is a high-resolution transmission electron microscopy (HRTEM) image and an EDP of the same nanowire before lithiation. The stripes were parallel to the (020) plane, which was apparently the preferred lithium insertion plane. HRTEM images [Figs. 3(c) and 3(d)] of the same nanowire showed lithiation induced dislocations along the stripe. Possible Burgers vector of the dislocations was determined to be [001] or [100] [20, 21]. The lithiation induced dislocation cores may act as fast lithium diffusion channels and may increase the lithiation kinetics [22]. Based on previous studies [4–6, 23], [001] is the diffusion channel in a rutile structural crystal such as SnO_2. Therefore, the initial lithiation process can be interpreted as follows: lithiation initiated at some surface defects, continued along [001] direction in the (020) plane. The lithiation induced stress led to formation of dislocations along the stripes, which further facilitated lithium diffusion into the interior of the nanowire. The multiple-stripe formation process was rather quick and the density of stripes increased with progression of lithiation [Figs. 3(e) and 3(f)]. HRTEM images [Figs. 3(g) and 3(h)] from another striped nanowire identified a high density of dislocations with Burgers vectors of [100] and [001]. The crystal lattice became

5

indiscernible at some areas inside the stripes, indicating the beginning of the reaction to form Sn and amorphous Li_2O. Therefore, lithiation-driven dislocation plasticity in the stripes occurred and was a precursor of the crystalline to amorphous phase transition. The dislocation density was estimated to be $\sim$ $5 \times 10^{16}/m^2$ based on Fig. 3(h), similar to that in the Medusa zone observed in a non-flooded nanowire [17]. Such a high dislocation density can provide the necessary energy and kinetic pathway towards complete amorphization.

Figure 4 shows the evolution of the lattice spacing changes with lithiation obtained from EDPs. When the stripes formed, the (020) diffraction spots were split into two [Figs. 4(c) and 4(d), and the corresponding insets]. The brighter spot corresponded to a d-spacing of 2.36 Å, which matched well with the SnO_2 (020) plane, while the darker spot had a d-spacing of 2.43 Å, which was caused by lithiation induced lattice expansion [Fig. 4(c) inset]. With further lithiation, the spot from the pristine lattice became much weaker, and the brighter spot corresponded to a d-spacing of 2.49 Å, $\sim$ 5.5% increase with respect to the pristine structure [Fig. 4(d) inset]. It confirmed that the transverse (020) plane was the preferred lithiation plane, which may be ascribed to the side-contact geometry as shown in Fig. 4(e). Since (020) plane traverses the nanowire, lithium ions diffuse into the [001] channels in the (020) plane inside the nanowire through surface defects. The special one-dimensional geometry of nanowires plays an important role in this multi-stripe lithiation mechanism. The flexibility in the longitudinal direction and the small diameter facilitate lithium insertion [24–30], leading to easier lithium intercalation along (020) plane which traverses the nanowire.

In summary, we have conducted in-situ TEM observation on the lithiation process of SnO_2 nanowires in a flooding geometry. We found a multiple-stripe multiple-reaction-front lithiation mechanism, in which multiple stripes along the (020) plane traversing the nanowire were formed. Lattice expansion and dislocations were observed inside the stripes. The nanowires were elongated after

lithiation. The new lithiation process that we discovered here has important implications to real lithium ion batteries in which the electrodes are immersed in the electrolyte.

Figure Captions

FIG. 1. Structure evolution of a SnO_2 nanowire anode in a flooding geometry during charging at -3.5 V with respect to the $LiCoO_2$ cathode. (a) A 45 μm long and 220 nm thick pristine SnO_2 nanowire with single crystalline structure (o). (b) Flooding geometry in which about one third of the nanowire was immersed in the ILE. (c)–(k) Sequential images showing the morphology change during charging. The reaction front (pointed by the red arrowheads) progressed continuously along the nanowire's axial direction. (l) Lithiated nanowire after the ILE was withdrawn. Similar morphology was observed for both the flooded and the non-flooded segments. The corresponding EDPs of non-flooded (m) and flooded (n) segments showed almost identical structure after lithiation.

FIG. 2. Multiple stripes formation in flooded SnO_2 nanowire anodes during charging at -3.5 V against the $LiCoO_2$ cathode. (a) Pristine single crystalline nanowire and its corresponding EDP (g) which can be indexed to the $[10\bar{1}]$ zone axis of the rutile SnO_2. (b)–(c) Multiple stripes formed after lithiation. A set of parallel stripes with dark contrast inclined 61° to the side surface of the nanowire. The corresponding EDP (h) showed single-crystal diffraction spots superimposed on a diffuse scattering background. Morphology [(d)–(f)] and the corresponding EDPs [(i)–(k)] after further lithiation. After further lithiation, the stripes disappeared completely and the nanowire underwent both elongation and swelling. The corresponding EDP [(j), (k)] showed that the SnO_2 nanowire has been reduced to $Sn + Li_2O + Li_xSn$. Note the images shown in (d)–(f) are from different nanowires immersed in the ILE for different time and all the viewing direction is $[10\bar{1}]$.

FIG. 3. Microstructure of the lithiation induced multiple stripes in SnO_2 nanowires. (a)–(b) Low and high magnification images of the charged (a) and

pristine (b) nanowire. The orientation of the nanowire is [$10\bar{1}$] zone axis. Stripes inclining 61° to the (111) planes of the nanowire (see also Figs. 2(b) and 2(c)) are parallel to the (020) plane. (c)–(d) A raw and a Fourier filtered HRTEM image of the multiple stripes. (d) High magnification image of the framed area in (c), showing dislocations with Burgers vector [001] or [100] in the stripes. (e)–(f) Images of the nanowire after further lithiation. (f) High magnification image of the framed area in (e), showing a high density of stripes formed after prolonged lithiation. (g)–(h) A raw and a Fourier filtered HRTEM image of another nanowire after lithiation, showing a high density of dislocations with Burgers vectors of [100] and [001], and even disordering. The nanowire is orientated at [$1\bar{1}0$] zone axis and the growth direction is [011].

FIG. 4. EDPs from the striped nanowire indicated lattice expansion caused by lithiation. (a)–(d) Structure evolution viewed from [$10\bar{1}$] zone axis. (a) Stripes parallel to the (020) plane formed after initial lithiation. (b)–(d) The (020) diffraction spot was split into two with different d-spacings (insets in (c) and (d)), with the brighter spot corresponding to a d-spacing of 2.36 Å, matching that of the (020) plane in the pristine structure, while the darker spot having a d-spacing of 2.49 Å, indicating a 5.5% lattice expansion induced by lithiation. (e) Schematic illustration of lithium intercalation along [001] in the (020) plane in a side-contact geometry. The nanowire's growth direction is [011].

References

[1] S. Choi and A. Manthiram, J. Electrochem. Soc. **149**, A1157 (2002).

[2] M. M. Thackeray, Y. Shao-Horn, A. J. Kahaian, K. D. Kepler, E. Skinner, J. T. Vaughey, and S. A. Hackney, Electrochem. Solid State Lett. **1**, 7 (1998).

[3] C. Uthaisar and V. Barone, Nano Lett. **10**, 2838 (2010).

[4] M. V. Koudriachova, N. M. Harrison, and S. W. de Leeuw, Phys. Rev. B **65**, 235423 (2002).

[5] M. V. Koudriachova, N. M. Harrison, and S. W. de Leeuw, Solid State Ionics **157**, 35 (2003).

[6] F. Gligor and S.W. de Leeuw, Solid State Ionics **177**, 2741 (2006).

[7] M. V. Koudriachova, N. M. Harrison, and S. W. de Leeuw, Phys. Rev. Lett. **86**, 1275 (2001).

[8] A. Stashans, S. Lunell, and R. Bergström, Phys. Rev. B. **53**, 159 (1996).

[9] T. L. Chan and J. R. Chelikowsky, Nano Lett. **10**, 821 (2010).

[10] Q. F. Zhang, W. X. Zhang, W. H. Wan, Y. Cui, and E. Wang, Nano Lett. **10**, 3243 (2010).

[11] M. Anicete-Santos, L. Gracia, A. Beltrán, J. Andrés, J. A. Varela, and E. Longo, Phys. Rev. B **77**, 085112 (2008).

[12] S. Sharma, J. K. Dewhurst, and C. Ambrosch-Draxl, Phys. Rev. B **70**, 104110 (2004).

[13] J. S. Braithwaite, C. R. A. Catlow, J. D. Gale, and J. H. Harding, Chem. Mater. **11**, 1990 (1999).

[14] A. R. Armstrong, C. Lyness, P. M. Panchmatia, M. S. Islam, and P. G. Bruce, Nature Mater. **10**, 223 (2011).

[15] P. Gibot, M. Casas-Cabanas, L. Laffont, S. Levasseur, P. Carlach, S. Hamelet, J. M. Tarascon, and C. Masquelier, Nature Mater. **7**, 741 (2008).

[16] C. Delmas, M. Maccario, L. Croguennec, F. Le Cras, and F. Weill, Nature Mater. **7**, 665 (2008).

[17] J. Y. Huang *et al.*, Science **330**, 1515 (2010).

[18] Y. M. Chiang, Science **330**, 1485 (2010).

[19] T. Song *et al.*, Nano Lett. **10**, 1710 (2010).

[20] H. Iwanaga, M. Egashira, K. Suzuki, M. Ichihara, and S. Tacheuchi, Philos. Mag. A **58**, 683 (1988).

[21] K. Suzuki, M. Ichihara and S. Takeuchi, Philos. Mag. A **63**, 657 (1991).

[22] M. Legros, G. Dehm, E. Arzt, and T. J. Balk, Science **319**, 1646 (2008).

[23] O. W. Johnson, Phys. Rev. **136**, A284 (1964).

[24] M. A. Reddy, M. S. Kishore , V. Pralong, V. Caignaert, U. V. Varadaraju, and B. Raveau, Electrochem. Commun. **8**, 1299 (2006).

[25] D. Larcher, C. Masquelier, D. Bonnin, Y. Chabre, V. Masson, J. B. Leriche, and J. M. Tarascon, J. Electrochem. Soc. **150**, A133 (2003).

[26] Y. S. Hu, L. Kienle, Y. G. Guo, and J. Maier, Adv. Mater. **18**, 1421 (2006).

[27] E. Baudrin, S. Cassaignon, M. Koelsch, J. P. Jolivet, L. Dupont, and J. M. Tarascon, Electrochem. Commun. **9**, 337 (2007).

[28] S. Bach, J. P. Pereira-Ramos, and P. Willman, Electrochim. Acta **55**, 4952 (2010).

[29] G. Jain, M. Balasubramanian, and J. J. Xu, Chem. Mater. **18**, 423 (2006).

[30] N. A. Milne, M. Skyllas-Kazacos, and V. Luca, J. Phys. Chem. C **113**, 12983 (2009).