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In-Situ Lithiation/Delithiation Observation of Individual Amorphous Si Nanorods

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Lithium ion batteries are considered as the future power source for the electric vehicles and other portable electronic devices. The anode material properties, such as energy storage and its cycle life, basically limit the high efficiency of a lithium ion battery [1]. Silicon is the most attractive material due to its low discharge potential and the highest theoretical charge capacity, 4200 mAh/g. However, insertion/extraction of Li into the Si structure expands/shrinks its volume by 400%, which reduces the capacity as a result of pulverization, over time. Recently, it was shown that Si nanorods can prevent pulverization by lateral expansion [2]. No real-time study, yet, shows how the nanorods accommodate the strain upon lithiation/delithiation. Here, for the first time, we investigate the lithiation of individual amorphous Si nanorods using a unique in-situ transmission electron microscopy (TEM) technique. Two different diffusion paths, longitudinal and radial, were examined and the formation of Li_xSi phase was confirmed by diffraction pattern studies that are in good agreement with our ex-situ lithiation results. The induced-strain as a result of lithiation was measured around 270% and no pulverization in individual NRs was observed. Our results prove the fact that NR can accommodate the large strain by lateral expansion.

Individual Si NRs were attached on an Au wire by light mechanical scratching on the as grown samples. Figure 1a depicts the in-situ lithiation set-up where a drop of ionic liquid (IL) is placed on the STM tip and individual Si NRs are placed on the gold wire. The applied bias voltage flows the IL on the NR from STM side to the gold wire, as shown and indicated in Figure 1b. High-resolution TEM imaging and electron diffraction pattern were collected to characterize the formation of different phases during the lithiation of different individual Si NRs.

Figure 2 compares lithiation process of different individual Si NRs with two different lithium concentrations in the IL. Series I shows the insertion of Li into the Si NR from low concentration of IL. The experiment was carried out for 30 min. We, then, examined the effect of Li concentration in the IL as shown in Figure2 series II. At higher concentration of Li, our observations show that the formation

1 Uday Kasavajjula *et al.* Journal of Power Sources 163, (2007), 1003–1039
2 Candacek Chan *et al.* Nature Nanotechnology 3, (2008) 31-35

and growth of Li_xSi phase was expedited. As shown in Figure 2g, formation of Li_xSi particles starts just after 3 min of lithiation as a result of higher Li ion concentration. Following the lithiation process, after 10 min as shown in figure 2h, particles grow to ~6nm which is larger than the 4nm particles formed in the low concentration case as shown in Figure 2d, for 30 min of lithiation.

Figure 3a shows an individual Si NR placed on the high-concentration IL to make the is-situ experiment as similar as possible to the real-time ex-situ charging experiment. After lithiation the lateral expansion of NR was measured to be 70nm which is 270% expansion compared to the initial. This result is in strong agreement with real-time battery working condition where the NRs are actually dipped into the electrolyte and diffusion path is radial. As expected and shown by the ex-situ studies, no pulverization was captured.

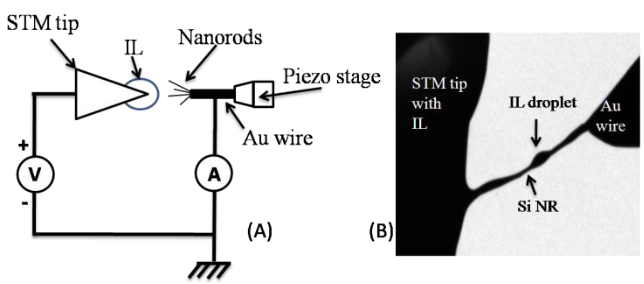

Figure 1 (a) schematic of the STM holder experimental setup. As the STM tip is positively biased, IL flows toward the nanorods and Li ions diffuse into nanorods. (b) low-magnification image during the lithiation experiment. The arrow indicates a droplet as the IL flows on the Si NR (the other arrow) from the STM side to the Au wire.

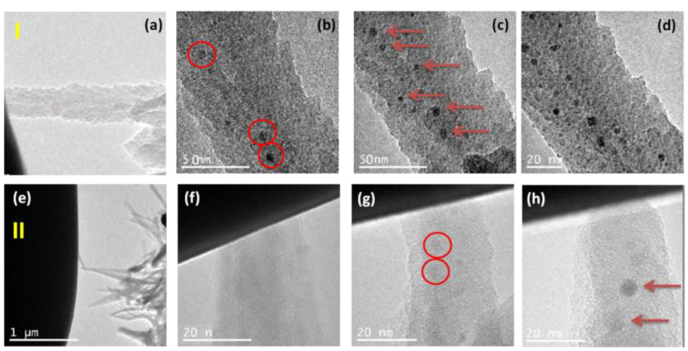

Figure 2.Series (I a-d) represent sequence of insertion of Li from low concentration IL into the Si NR during 30 min. (a) shows low magnification of individual Si NR connected to IL (dark triangle on left). (b) Red circles indicate the formation of Li_XSi phase after 10min. (c) and (d) show the growth and formation of new particles as the lithiation process continues, 20 min and 30min, respectively. Series (II e-f) show sequence of lithiation at higher Li concentration during 10 min. (e) and (f) show low- and high-magnification images of individual Si NR attached to IL. After 3 min, as shown in (g), the formation of new phase was detected. And (h), growth and formation of Li_xSi particles are indicated with arrows, after 10 min.

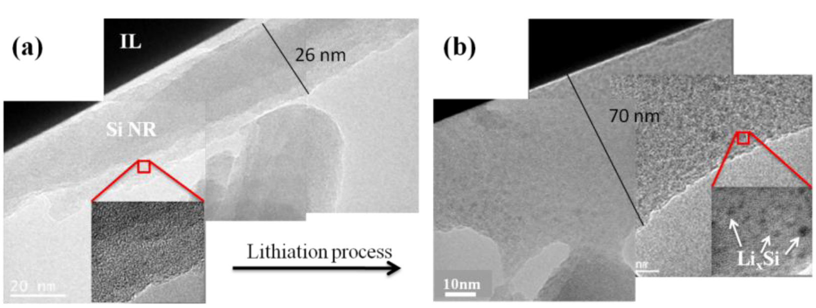

Figure 3 (a) individual Si NR in contact with IL from the side. The thickness of the NR was measured to be 26nm before the lithiation and high-resolution image (inset) shows amorphous structure. (b) After lithiation process the diameter of NR expands to 70nm and is dipped into the IL, inset show high-resolution image of Li_xSi particles formed as a result of lithiation.

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