Supporting information

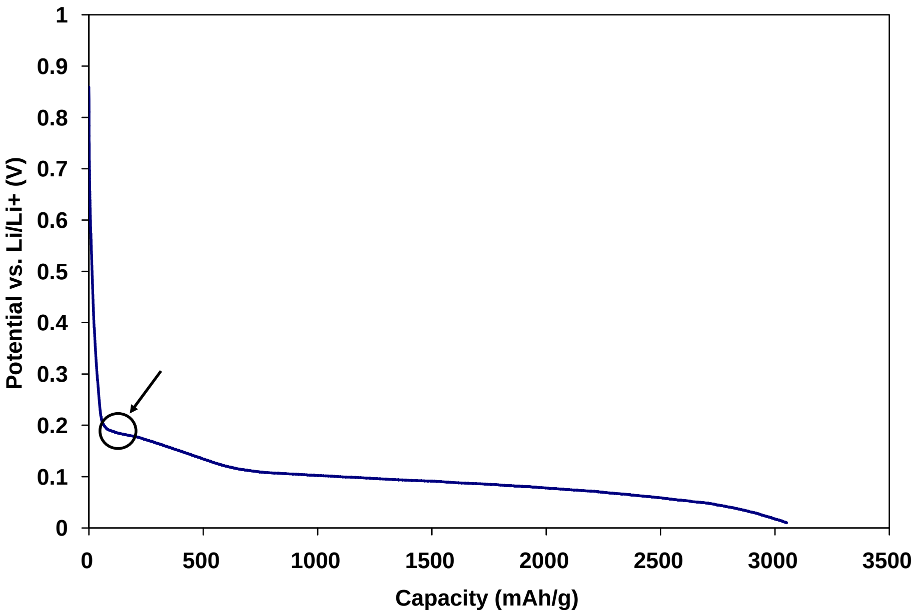

Figure S1: First lithiation response of SiNWs/SS highlighting the contribution of amorphous Si.

The SiNWs on SS were grown at a slightly lower temperature in order to achieve comparable mass loading of Si on the substrate. However, lower temperatures favor the formation of amorphous Si which does not lithiate showing the long flat plateau at 0.1V but a more sloping feature between 0.2 and 0.1 V (highlighted by the arrow) as can be seen in Figure S2. Absence of a sharp plateau is also seen from the second cycle onwards for (Al-coated) SiNWs on TiN in Figure 8, which shows that the SiNWs become amorphous in their delithiated state during cycling.

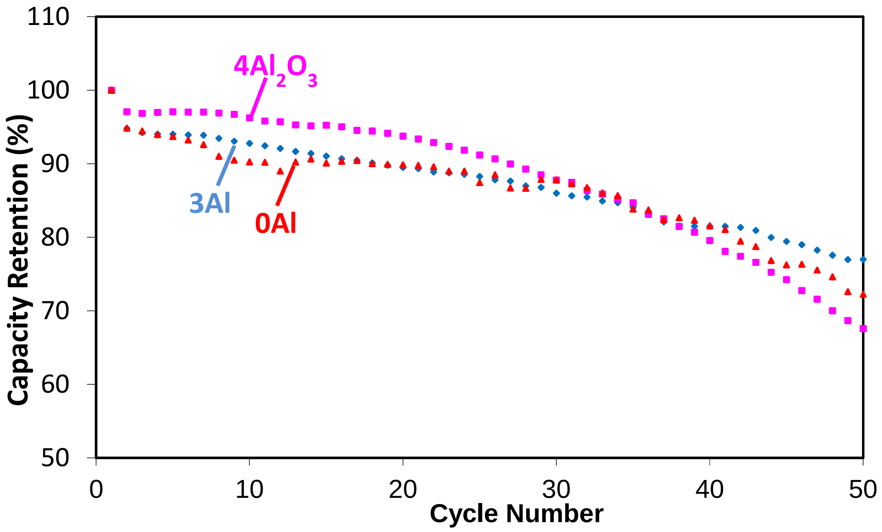

Figure S2: Cycling stability of bare SiNWs, 3Al/SiNWs and SiNWs coated with 4 wt.% Al_2O_3 deposited by ALD

To investigate the effect of oxidation of the Al on the capacity retention of SiNWs we deposited the equivalent of 4 wt.% Al_2O_3 onto SiNWs on TiN by atomic layer deposition. Figure S3 shows the comparison between bare SiNWs, 3Al/SiNWs and $4Al_2O_3$/SiNWs. Clearly the Al_2O_3 coating performs worse than even bare SiNWs, which shows the Al should be mostly metallic in our Al-coated materials, in agreement with our electron diffraction patterns.

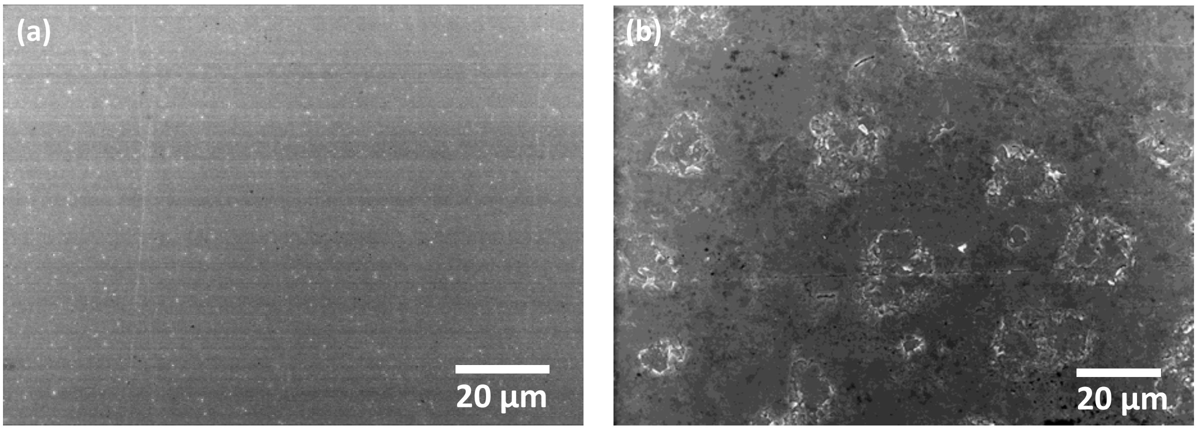

Figure S3: Surface of the stainless steel substrate after polishing steps (a) and after lithiation/delithiation cycle and removal of the Si nanowires (b).

In figure 4, the electrochemical response of the bare SS spacer was shown. The above figure shows that also with SiNWs grown on the surface, corrosion reactions clearly occur. However, it is not possible to determine whether the most severely corroded regions are also the ones where the SiNWs were attached, and the influence of the Cr_2O_3 reaction with Li on the cycling stability therefore remains unclear. The damage to the surface can also be due to penetration of the liquid Au-Si eutectic during the growth of the nanowires. Penetration of Au-containing melts into stainless steel is a well-known, but poorly understood phenomenon (see D. Favez et al., *Acta Mater.*, 2011, 59, 6530-6537) and probably causes different research groups to use widely different methods for growing SiNWs. For instance, Chan et al. (*J. Power Sources*, 2009,189, 34-39 and *J. Power Sources*, 2009, 189, 1132-1140) used 50 nm Au and 485°C growth temperature and after much trial and error, we converged on the same conditions. On the other hand Chen et al. (*J. of Power Sources*, 2011, **196**, 6657–6662 and *J. Solid State Electrochem.*, 2010, **14**, 1829-1834) used 10 nm Au on SS, but much higher growth temperatures and the resulting nanowires were comparable in size to our SiNWs grown in TiN. This further emphasizes the benefits of using a TiN interlayer as it may allow for more uniformity in experimental conditions among different researchers.

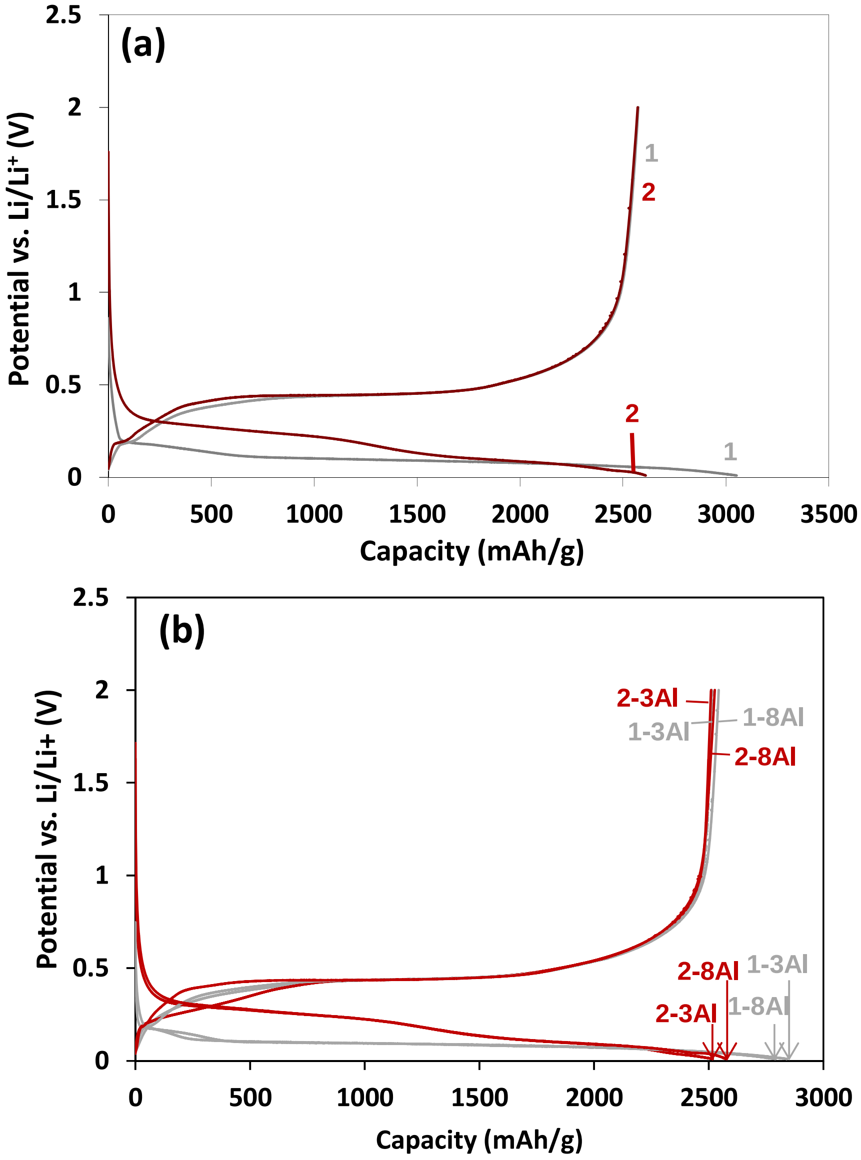

Figure S4: First and second cycles for SiNWs/SS (a) and 3Al/SiNWs/SS and 8Al/SiNWs/SS (b)

The effect of Al coating on the capacity and coulombic efficiency of SiNWs on SS is depicted in Figure S4. The first cycle discharge and charge capacities are 3050 mAh/g and 2571 mAh/g for SiNWs/SS and the coulombic efficiency is 84.3%. For 3Al/SiNWs/SS the capacities are 2830 and 2510 mAh/g giving a colombic efficiency of 88.7%. For 8Al/SiNWs/SS the capacities are 2790 and 2550 mAh/g and the coulombic efficiency is 91.5% which shows there is continuous improvement with increasing Al coating thickness in the coulombic efficiency. This shows that indeed large nanowires may be stabilized by Al coating, preventing them from pulverizing, although more detailed investigations with controlled nanowire diameters would be needed to ascertain this further.