

## **Supporting Information**

# Enhanced Lithiation Cycle Stability of ALD-Coated Confined a-Si Microstructures Determined Using In Situ AFM

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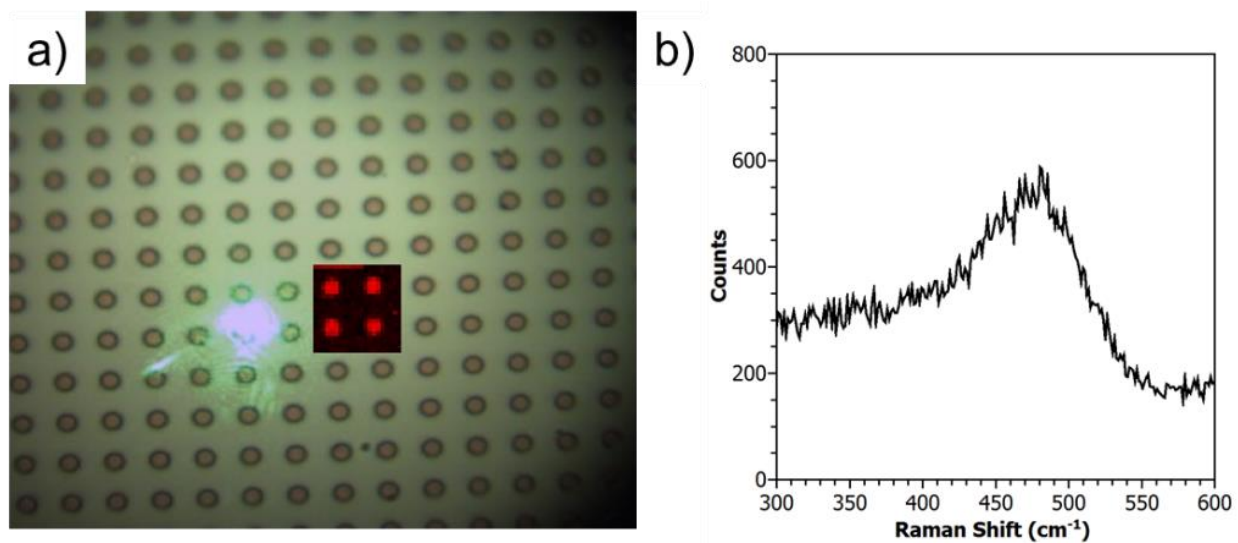


Figure S 1: Raman mapping of an as-fabricated sample a) with red indicating the peak displayed in b)

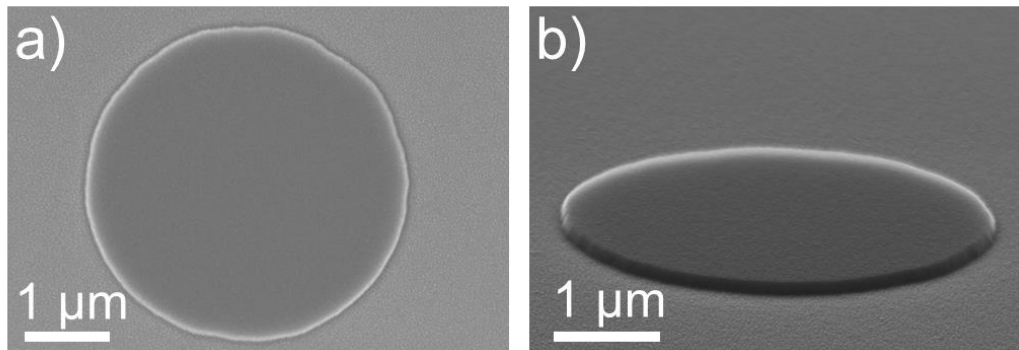


Figure S 2: SEM images of the as-fabricated a-Si pillars a) top view and b) oblique view

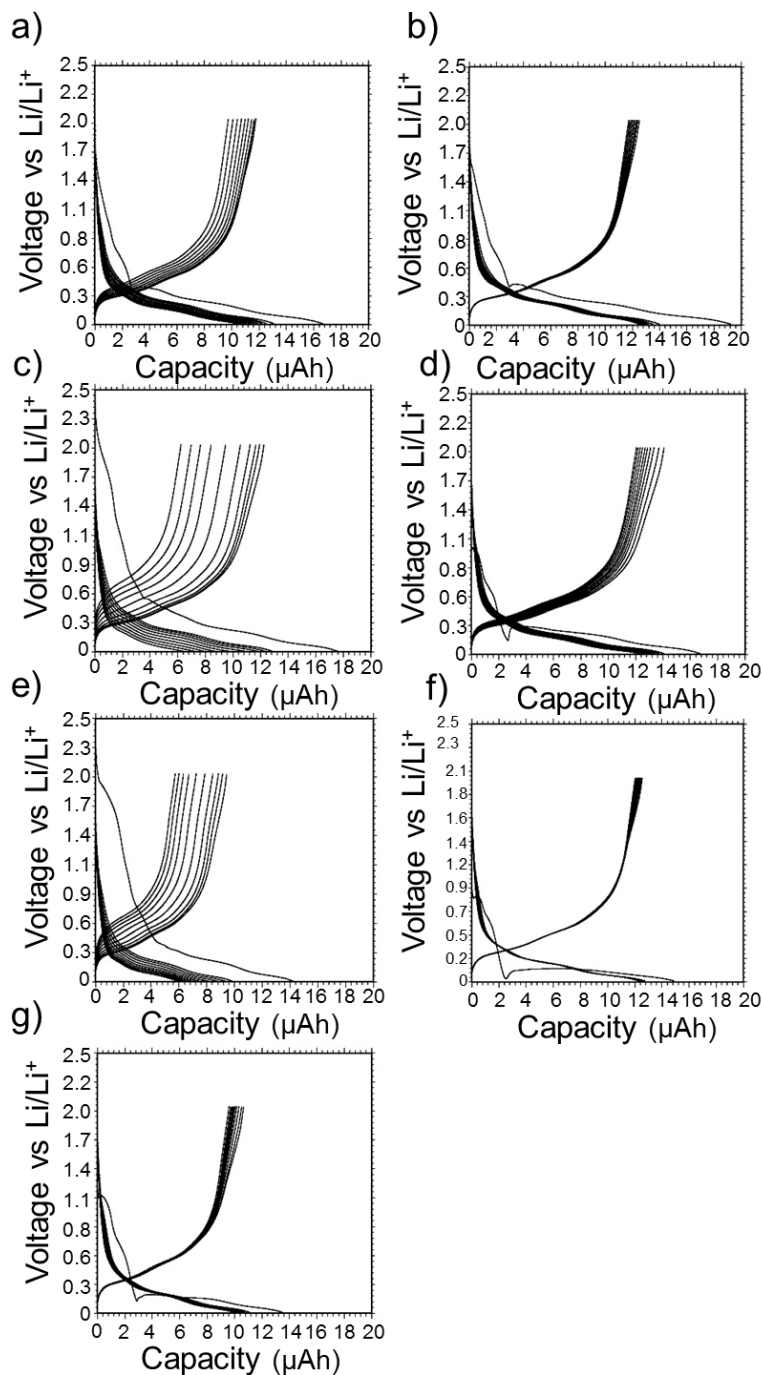


Figure S 3: Electrochemical capacity plots of a-Si pits with 1.5 nm ALD in G2 a) and pure FEC, b). Electrochemical capacity plots of a-Si pillars in G2 without ALD c) and with 3 nm of ALD, d). Electrochemical capacity plots of a-Si pits in G2 without ALD e) with 3 nm of ALD f) and with 3 nm ALD in 2% FEC g).

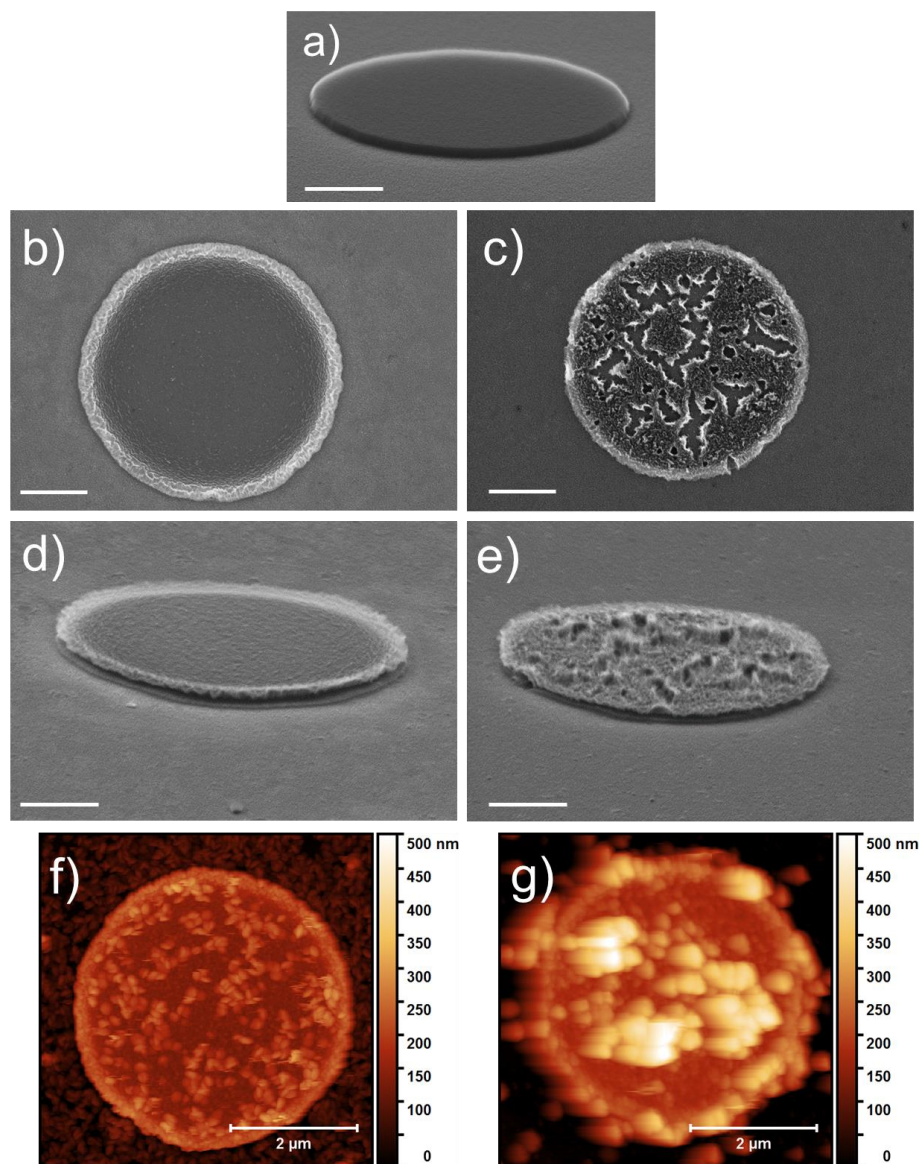


Figure S 4: a) SEM image of the as-fabricated a-Si pillar. SEM images of a-Si pillars post-cycling in G2 electrolyte with 3 nm ALD b) and d) and without ALD c) and e). AFM images of a-Si pillars post-cycling in G2 electrolyte with 3 nm of ALD f) and without ALD g). The scale bars in a)-e) are 1  $\mu\text{m}$  and in f)-g) are 2  $\mu\text{m}$ .

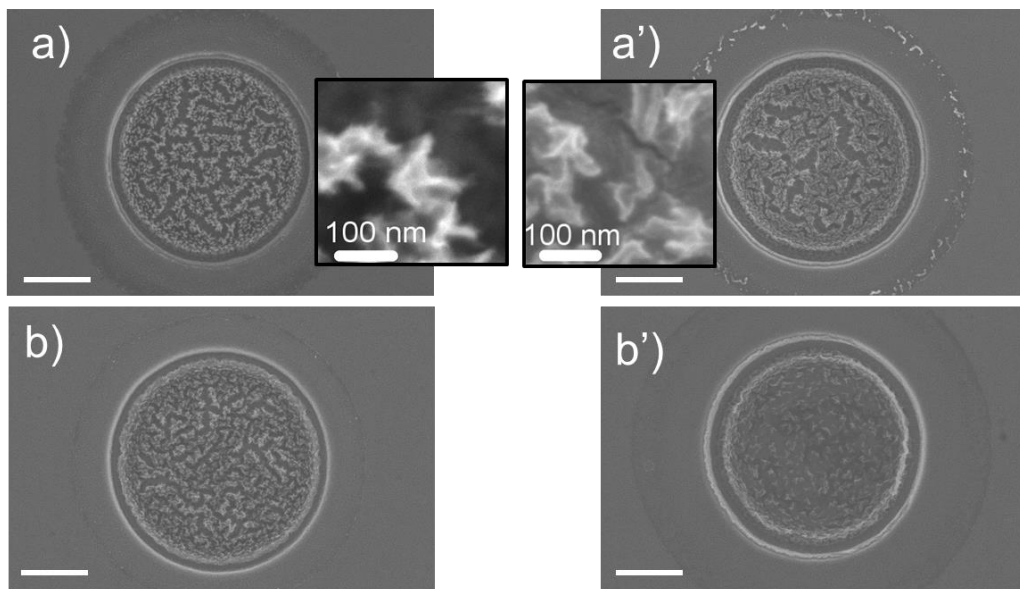


Figure S 5: Post-cycling SEM images of a-Si pits cycled in pure FEC a-a') and in G2 with 2% FEC b-b'). The samples without ALD are a-b) and with 3 nm of ALD are a'-b'). Even with pure FEC, at low magnification the surface appears similar to the sample with 3 nm ALD. The inset images show high magnification images of the surface structure of the pure FEC sample. Without ALD there is more bulk removal of material and higher surface roughness. With ALD, there is still scalloping of the surface, and while there are small cracks, the surface is smoother.

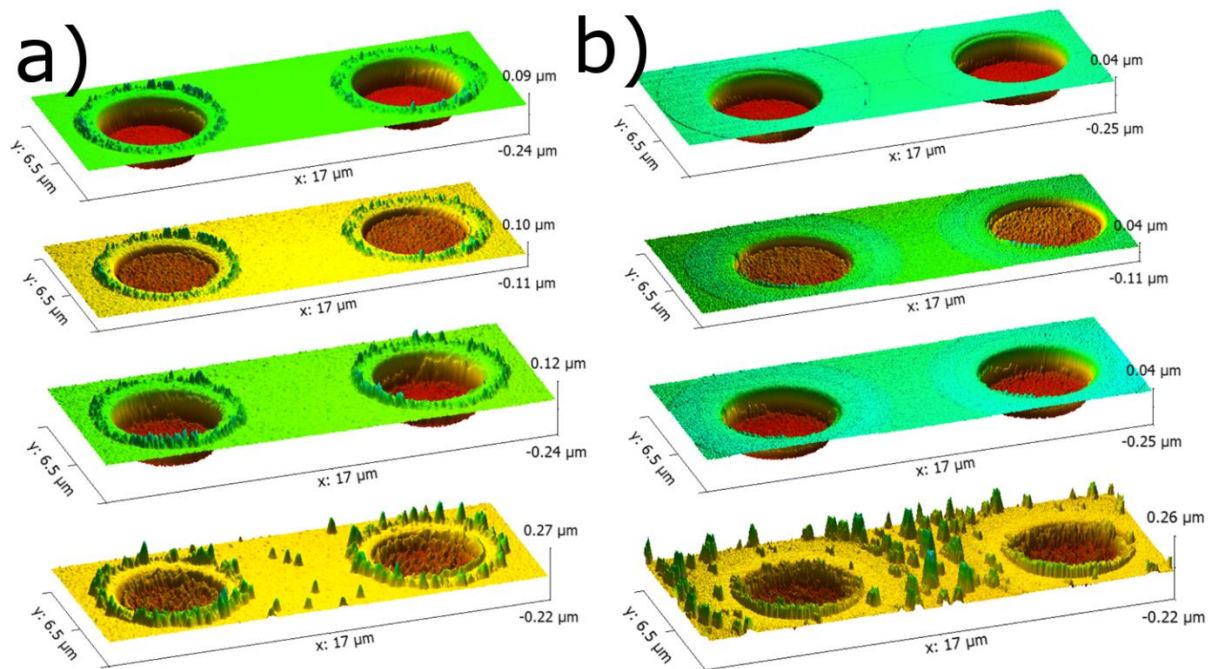


Figure S 6: In situ atomic force microscopy images of 1.5 nm ALD a-Si pits cycled in G2 a) and pure FEC b). The top row is the sample at OCP, the second row is the first lithiation, the third row is the first delithiation, and the final row is after a full 10 cycles.



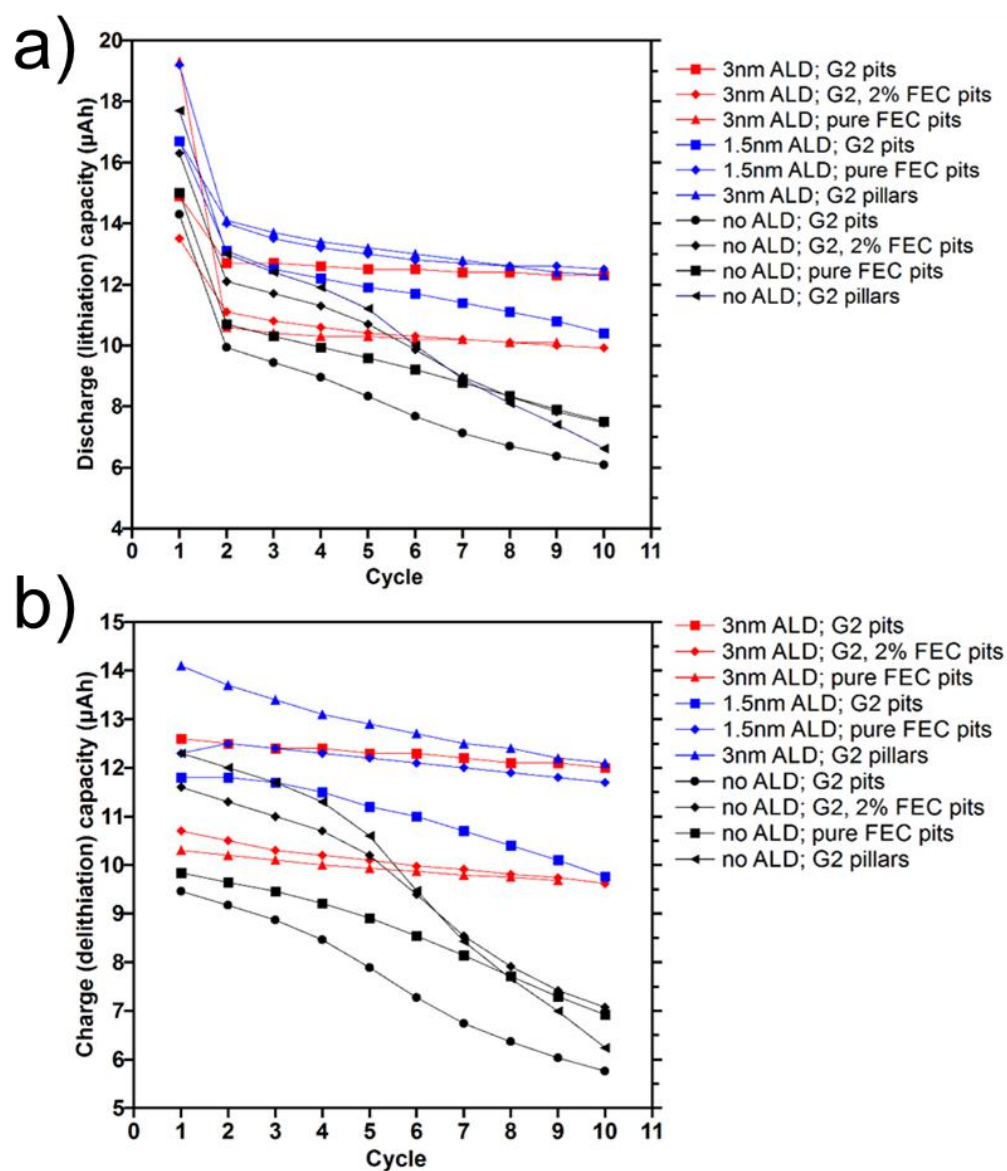


Figure S 7: Lithiation a) and delithiation b) capacity in  $\mu\text{Ah}$  for all samples in the study. ALD a-Si pit samples with 3 nm are in red, pits with 1.5 nm and pillars with 3 nm in blue, and samples without ALD in black.

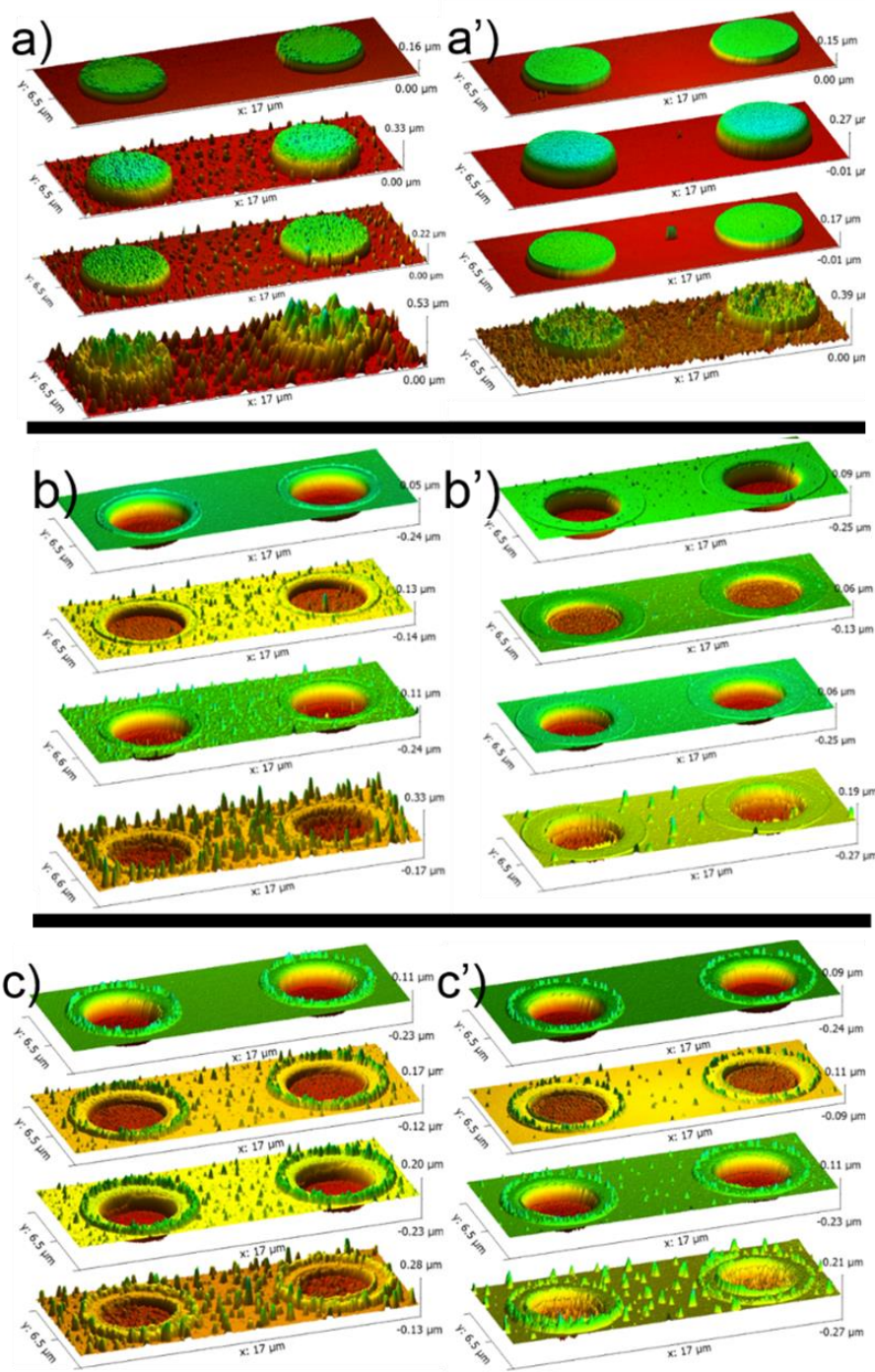


Figure S 8: AFM images of samples without ALD, a-c) and with 3 nm ALD a'-c'). In each figure the top row is the sample at OCP, the second row is the first lithiation, the third row is the first delithiation, and the final row is after a full 10 cycles. The samples in a-a') are pillars tested in G2, b-b') are pits in G2 with 2% FEC, and c-c') are pits in pure FEC.