Supplementary information

AFM studies of films deposited on silicon

To quantitatively study the surface morphology and roughness, AFM was performed. The AFM-images are shown for samples deposited on silicon wafers and steel discs with different thicknesses in Supplementary 1 and in Supplementary 2, respectively. In order to investigate if the surface area is related to the electrochemical properties, the surface area and surface roughness was extracted as shown in Supplementary 3, however there is no clear trend between the electrochemical properties and the roughness. Apart from the thinnest samples, it seems to be a clear trend between the rate performance and the inverse of the surface area. The plate dimensions display an anisotropic variation during growth as shown in Supplementary 4. As the crystallites grows fastest in along the a- and b-axes the first part consists of c-axis oriented grains which fills the surface with freestanding nano-crystals. After 500 cycles the surface is filled, and the crystals oriented along the a- or b-axes will dominate. This trend is also valid for samples deposited on steel substrates.



Supplementary 1. AFM images of samples with varying number of ALD cycles on silicon (A-E), showing the evolution of morphology. Plate like crystals starts to form already at 250 cycles, which grows and aggregate into large crystals



Supplementary 2. AFM images of samples with varying number of ALD cycles on steel discs (A-C + E), showing the evolution of morphology. The same morphology is present at the steel discs as on silicon and the pattern of evolution is similar.



Supplementary 3. Surface roughness and surface area per mass of electro active material deposited on silicon with different number of cycles as measured by AFM.



Supplementary 4. Average platelet dimension for samples deposited with different number of ALD-cycles on silicon as measured by AFM. Thickness is measured along the proposed *c*-direction and diameter is measured along the proposed *a*-direction.

Extended electrochemical characterizaiton

After the initial electrochemical characterization which was performed with CV, galvanostatic cycling was performed for 75 cycles in order to verify a minimum cycling stability. As shown in Supplementary 5, all samples endured at least 75 cycles, however the thinnest sample showed a sharp decrease in capacity. Among the other samples, ALD5000 shows the highest initial capacity of 105 mAh/g. However, ALD5000 has a relatively large capacity fading reaching 96 mAh/g after 75 cycles, corresponding to a decrease of 0.1 % per cycle. Whereas the two thickest films exhibit capacity fading during cycling, the two films deposited using 500 and 1000 ALD cycles show excellent cycleability, where the initial capacities increase during cycling with 7 and 17 %, respectively over 75 cycles. Increasing capacity during cycling has previously been observed in other V_2O_5 nano-structures.^{4, 32}



Supplementary 5. Cycling performance of coin cells with V₂O₅ deposited from 250–5000 ALD-cycles at 1 C rate in the voltage range 2.75–3.80 V.

Upon finer examination of the CV-curves shown in Figure 4 there is a subtle shift in the position of the redox peaks for the different samples as shown in Supplementary 6. The shift can be interpreted as the overpotential of the reaction and suggests that the activation energy of the intercalation is smaller for smaller particles.



Supplementary 6. The shift in the reduction and oxidation peaks from the cyclic voltammetry as a function of film thickness. The dotted lines indicates the thermodynamic values.

After the capacity had dropped below 80% of the initial capacity as was presented in Figure 9, the test was continued until 4000 cycles where the battery still showed some capacity, as shown in Supplementary 7. The capacity after 4000 cycles is about 20 mAh/g at 120 C, which is about 33% of the peak capacity.



Supplementary 7. High discharge rate cycling stability test performed at 120 C after the rate performance test in Figure 8andFigure 9. The battery still shows a capacity of ca 20 mAh/g after 4000 cycles at 120 C. The observed break at 2000 cycles is due to that the battery was left in a discharged state for 1 week before the measurement was continued.