

Experimental Procedures

AAO Template preparation

99.99% pure Al foil was purchased from Alfa Aesar. It was degreased in acetone for 10 minutes. It was dried and placed in etching solvent composed of 800 mL of 200 proof ethanol and 160 mL of 70% perchloric acid at a temperature of 3°C. 15V was applied between the Al foil and stainless steel electrode for 5 minutes to electropolish the Al foil. The first anodization was performed in 0.3 M Oxalic acid at 8 °C under 40 V for 6 hours. The disordered AAO that formed from the first anodization step was removed by placing it in the mixture of 70 mL of 85% phosphoric acid, 180 mL of 10% chromic acid, and 750 mL of water at 60°C for 4 hours which left a patterned surface on the Al foil. This patterned aluminum was then used to grow ordered AAO films. By disrupting the anodization voltage from 40V to 20V and back to 40V with 2V step every 30 seconds, one interconnecting region can be added into the AAO film. By repeating this voltage disruption process, up to seven interconnecting regions are added in the AAO film. AAO film was left on the native Al foil for structural support. The pores were widened in 5% phosphoric acid at 38 °C at various times for different pore diameters. More detailed AAO preparation is described elsewhere.¹

Material deposition

Atomic layer deposition was used to conformally coat the walls of high aspect ratio pores. Vanadyl triisopropoxide was pulsed for 2.5 seconds and O₃ was pulsed for 5 seconds alternatively in Beneq TFS 500 ALD system at 170 °C for the deposition of V₂O₅.² For Ru metal, bis(ethylcyclopentadienyl) ruthenium was pulsed for 5 seconds and O₂ was pulsed for 6 seconds at 300 °C in home-built furnace reactor. Tescan FEG SEM and Hitachi Su-70 were used for morphological characterization.

Electrochemical cells

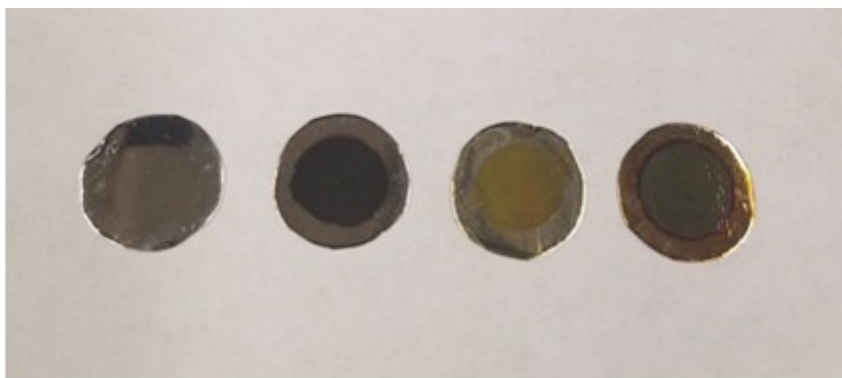
LiClO₄ ACS reagent grade, anhydrous 99.7%> purity propylene carbonate were purchased from Sigma Aldrich. LiClO₄ was dried at 180°C under vacuum for at least 24 hours before it was transferred to the glovebox where the electrolyte, 1 M LiClO₄ in PC, was prepared. T-cells were purchased from Swagelok and stainless steel rods were used for making contacts to the electrodes. The half cells were prepared in these T-cells as three-electrode systems with two separate Li metals

as the counter and reference electrodes. The active mass was calculated from the change in mass of the AAO template before and after the deposition steps. A Biologic MPG-12 was used for all electrochemical measurements.

Supplementary Figures

pore widening time (minutes)	# Int. Layer	Before ALD (nm)	After 200 cycles of Vanadium (nm)
11.5	0	75+/-2	48+/-3
11.5	7	70+/-3	51+/-4
15.5	0	83+/-2	61+/-3
15.5	7	80+/-4	63+/-4

Table S1 Average and standard deviation of pore sizes of various AAO templates before and after



200 cycles of Vanadium deposition measured by the ImageJ software.

Figure S1 Images of (from left to right) AAO before deposition, AAO with Ru integrated current collector, AAO with V₂O₅, AAO with V₂O₅ and Au planar current collector. The middle portion is the AAO while the rest is the Al support substrate.

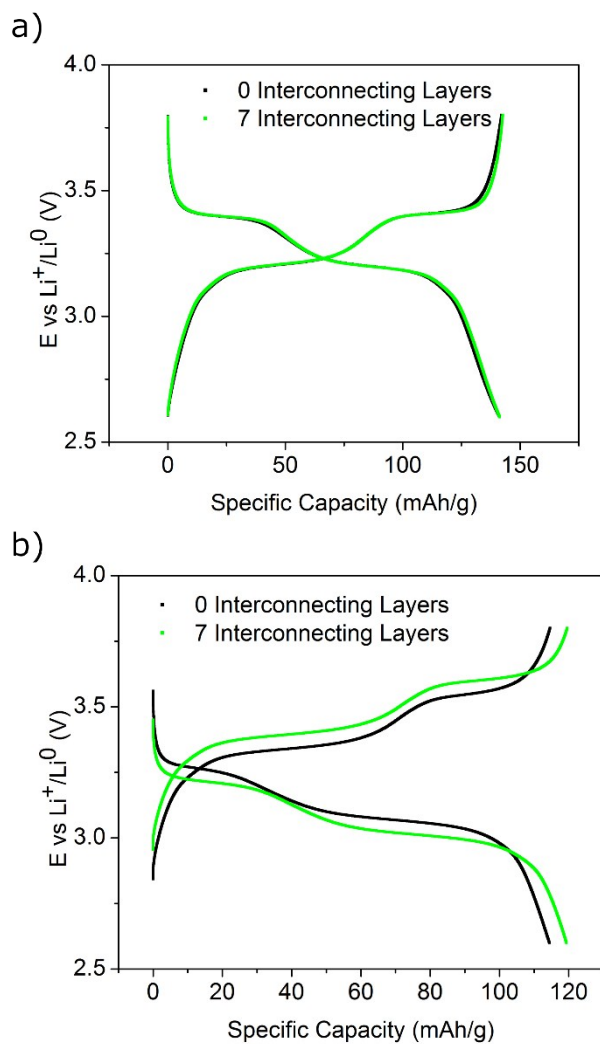


Figure S2 Voltage profiles of electrodes with zero and seven interconnecting layers when cycled within one-Li insertion regime at a) 0.5C and b) 25C.

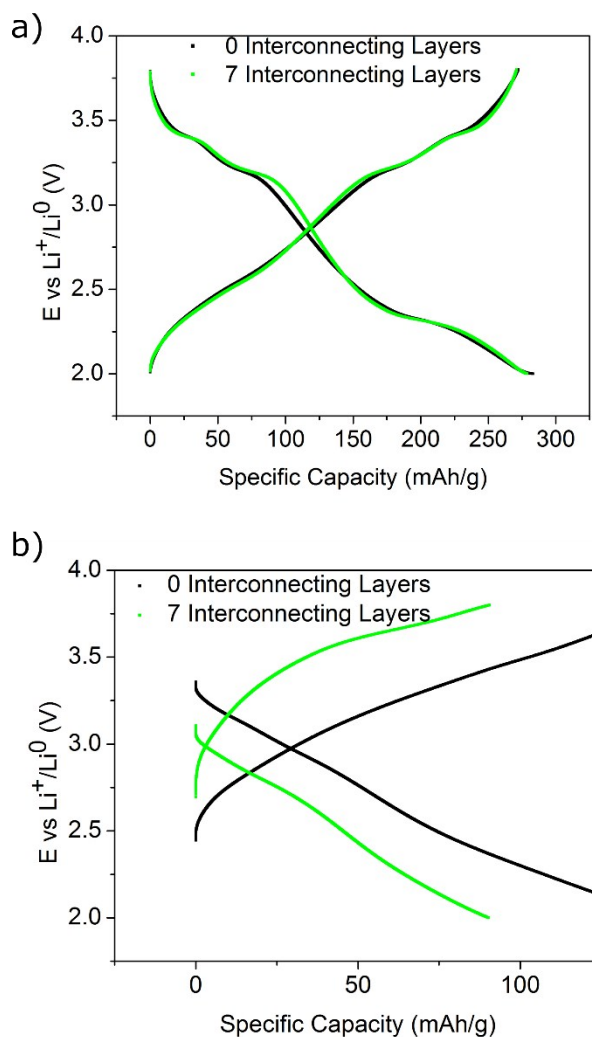


Figure S3 Voltage profiles of electrodes with zero and seven interconnecting layers within two-Li insertion regime at a) 0.5C and b) 25C.

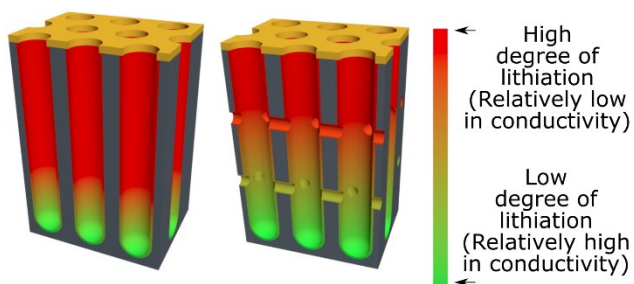


Figure S4 Proposed illustrations the differences in the degree of lithiation of electrodes with no interconnections (left) and with interconnections (right) under high current densities. These are purely illustration and not simulated data.

To further illustrate the impact of the electrode polarization on the degradation, Figure S4 can be used. Under high current densities, the electrode will be polarized leading to higher overpotentials compared to those expected at low current densities. With more poorly electronically conducting V_2O_5 material near the current collector, and the addition of longer electronic pathways from the interconnections, active material near the current collector sees higher overpotentials than those without any interconnections. There is also a smaller difference in the peak potentials between the first and second lithiation versus the second and third lithiation. The peak potential difference between the first and second lithium insertion is about 0.8V while between the second and third is only about 0.4V.³ With the smaller peak potential difference between the second and third lithiation, when the electrodes are cycled in the two lithiation regime under high current densities, the larger overpotentials seen in the active material with interconnecting layers could lead to irreversible, partial third lithium insertions. These third Li insertions are likely the cause of the faster capacity fade of electrodes with seven interconnecting layers as seen in Fig. 7B

Reference:

1. E. Gillette, S. Wittenberg, L. Graham, K. Lee, G. Rubloff, P. Banerjee and S. B. Lee, *Phys. Chem. Chem. Phys.*, 2015, **17**, 3873-3879.
2. X. Y. Chen, E. Pomerantseva, P. Banerjee, K. Gregorczyk, R. Ghodssi and G. Rubloff, *Chem. Mater.*, 2012, **24**, 1255-1261.
3. X. Y. Chen, E. Pomerantseva, K. Gregorczyk, R. Ghodssi and G. Rubloff, *RSC Adv.*, 2013, **3**, 4294-4302.