

A NEW LOOK ON ALD VANADIUM OXIDES FOR 3D THIN-FILM LITHIUM-ION BATTERIES

CONTEXT

ALD for 3D thin-film electrodes

Lithium-ion batteries require both high power and high energy density. The high power aspect can be achieved by scaling down the thickness of thin-film batteries, as lithium-ion diffusion pathways shorten along with the thickness of the films. The decrease in capacity accompanied by this down-sizing can be compensated by placing the thin-films on 3D templates, establishing a 3D thin-film lithium-ion battery that has both high capacity and high power density. Atomic layer deposition is excellently suited for the deposition of the films on challenging 3D current collectors.

Vanadium oxides as lithium-ion electrodes

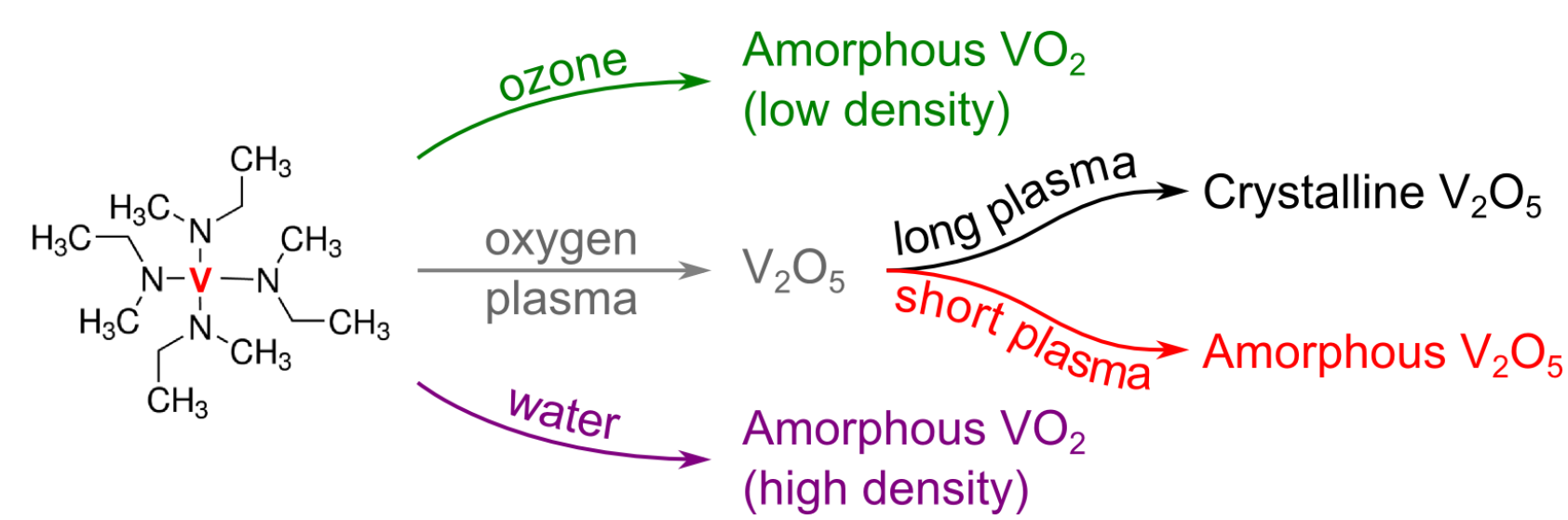
Vanadium oxides have been studied since the early days of lithium-ion batteries, with crystalline V_2O_5 at the heart of the interest. However, despite the high theoretical capacity of $Li_3V_2O_5$, its true potential has never been fully achieved due to the low reversibility of this insertion. Vanadium oxide has many other crystalline forms and oxidation states besides V_2O_5 . In this work, we aim to demonstrate the deposition of all layered vanadium oxides as thin-film electrodes, and identify the top candidates as 3D thin-film electrodes on challenging current collectors.

Controlling the oxidation state and crystalline nature of vanadium oxide films during ALD and post-ALD annealing

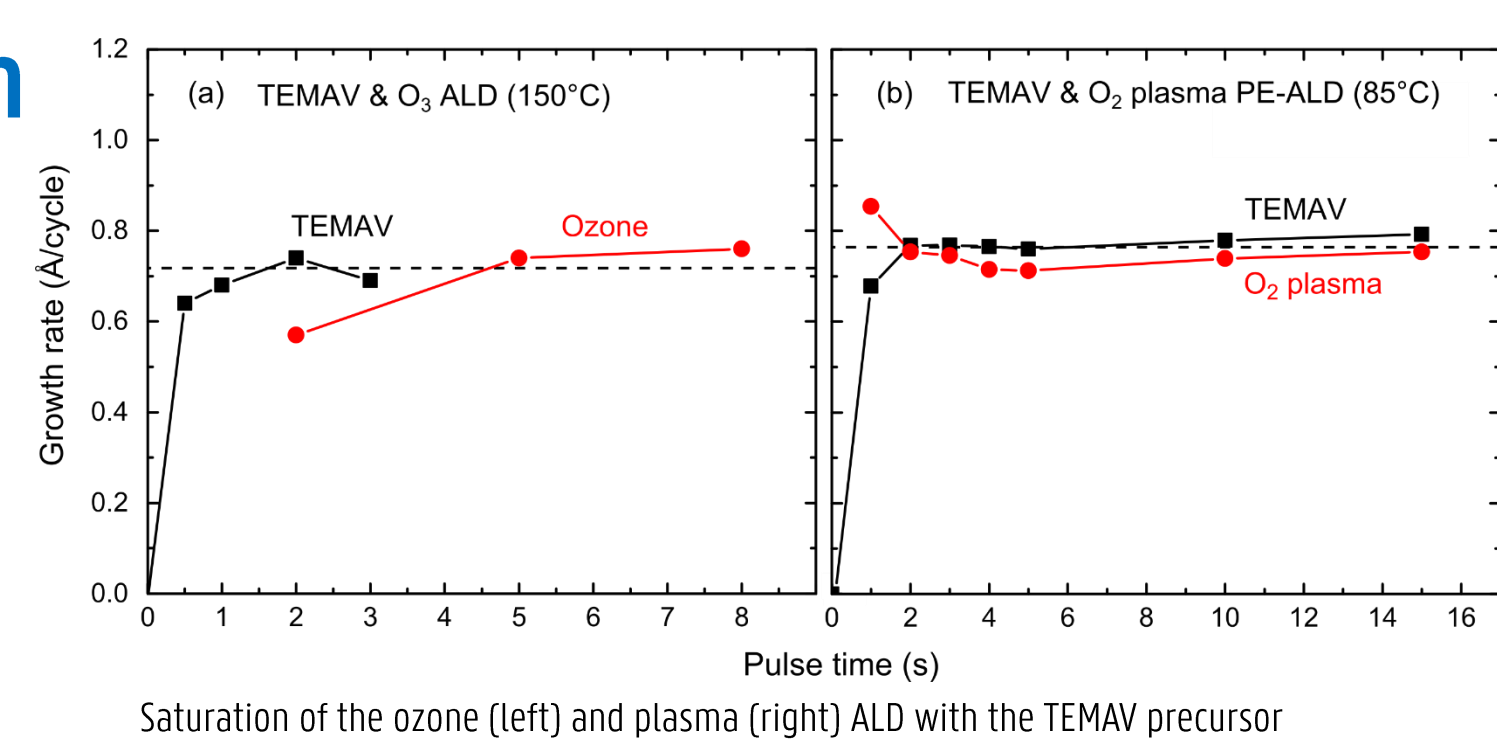
During atomic layer deposition

3 ALD processes using the TEMAV precursor were tuned: water, ozone and oxygen plasma ALD

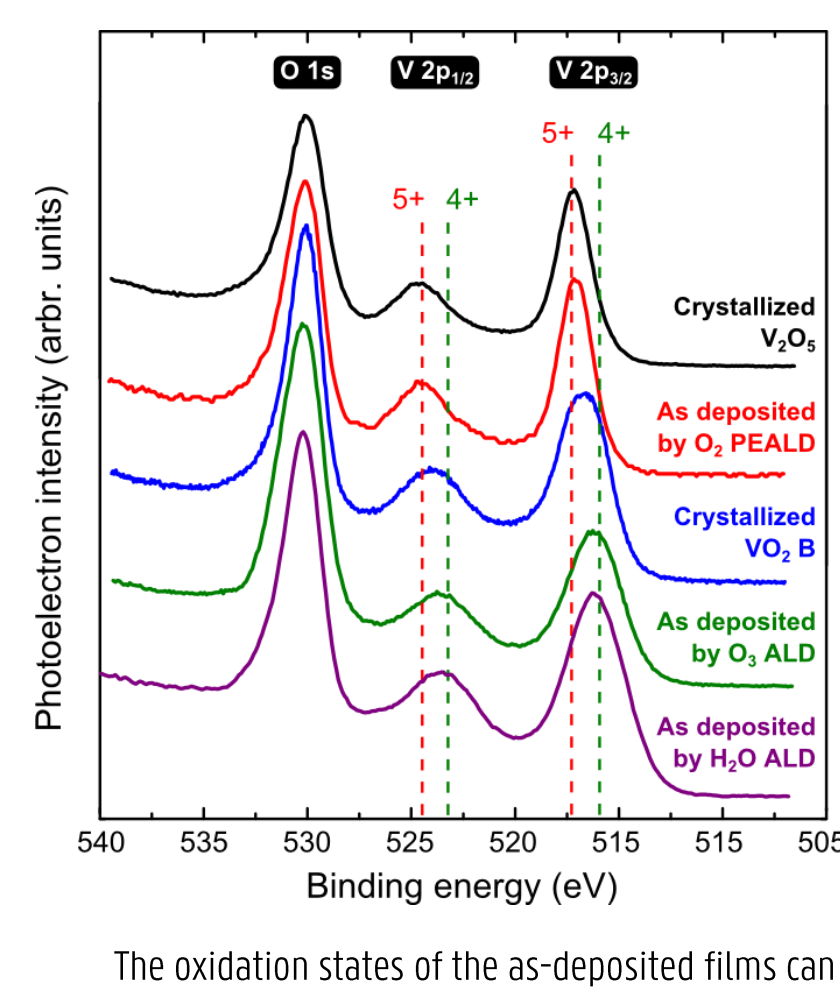
- Thermal processes (ozone, water) yield +4 valent amorphous vanadium oxide (VO_2), but with a density dependent on the process gas
- Oxygen plasma process yields +5 valent vanadium oxide (V_2O_5), but crystallinity can be controlled based on plasma pulse duration and temperature



A summary of the influences of the ALD process conditions using the TEMAV precursor



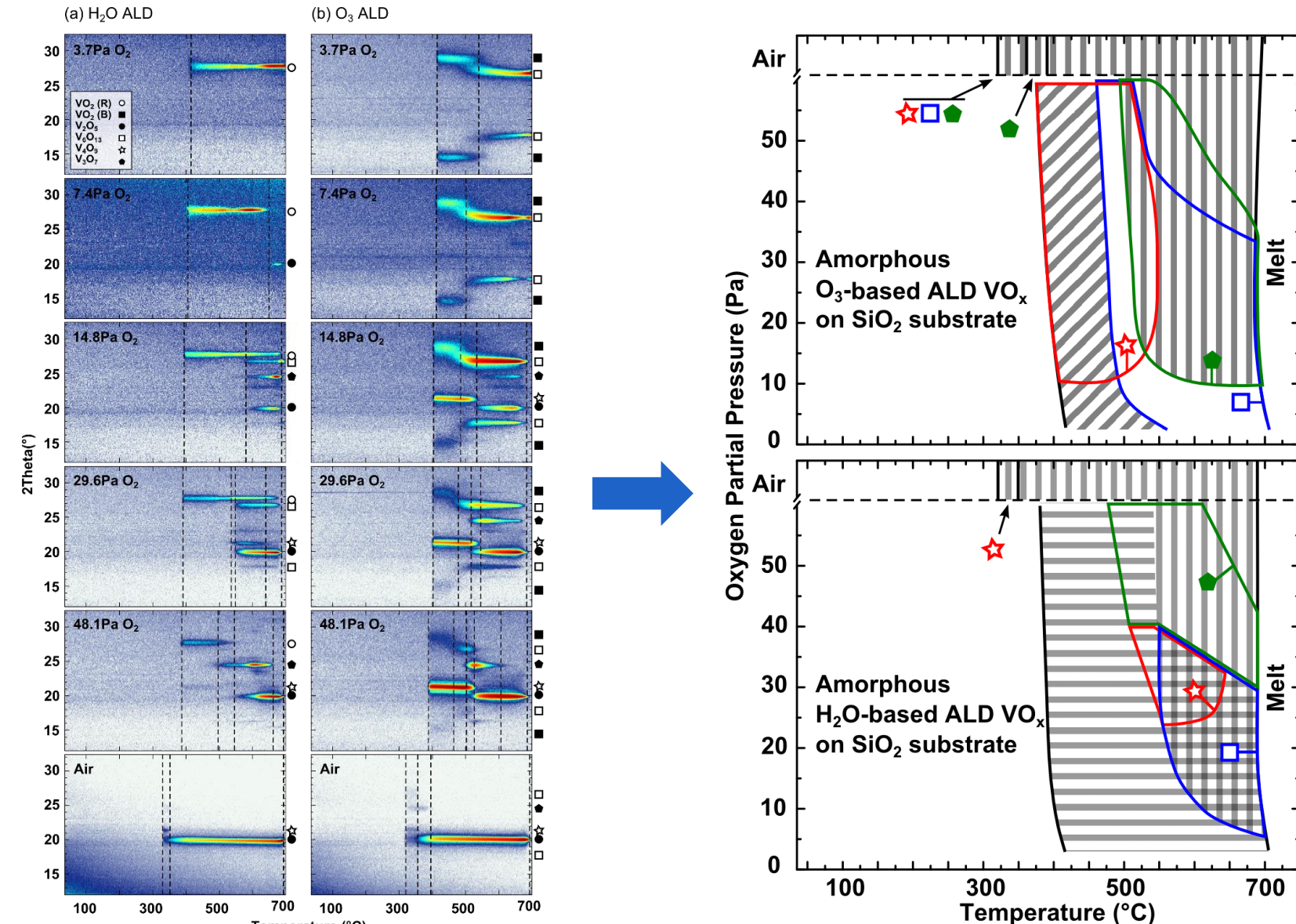
Saturation of the ozone (left) and plasma (right) ALD with the TEMAV precursor



The oxidation states of the as-deposited films can be determined from XPS

Post ALD annealing to obtain V_2O_5 , V_3O_7 , V_4O_9 , V_6O_{13} and VO_2 (B)

The influence of atmosphere, temperature, substrate and as deposited film were studied using *in-situ* X-ray diffraction during ramp anneals. We devised a 'recipe' to obtain every vanadium oxide phase in the Wadsley series (V_2O_x with $4 \leq x \leq 5$).



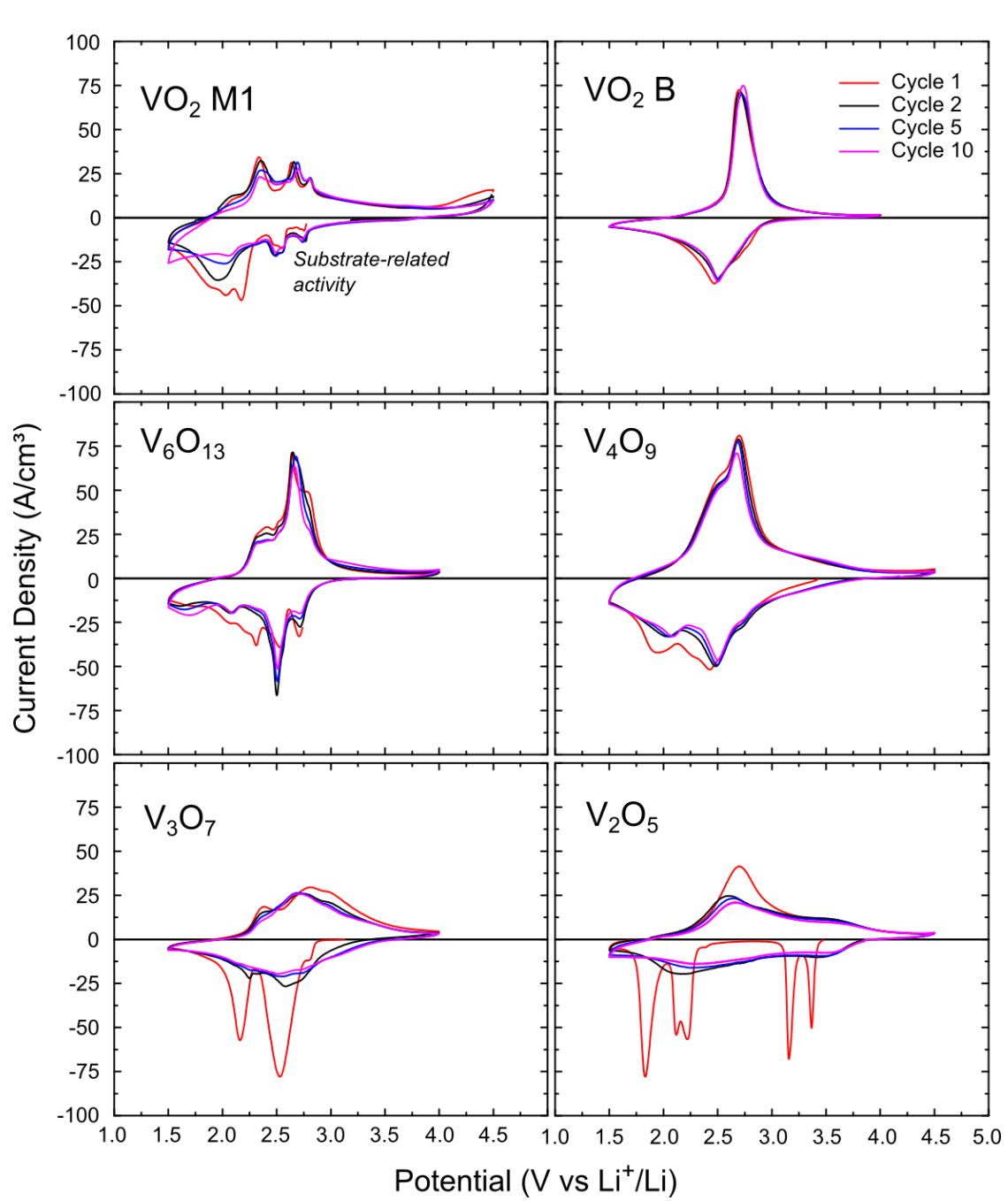
In-situ XRD measurements during annealing in various oxygen ambients of the water- and O_3 -grown VO_2 films on SiO_2 substrates

Resulting phase formation diagrams on the SiO_2 substrates, extracted from the in-situ XRD data on the left

Summary of the influences

- Temperature induces crystallisation and raises oxidation state where possible
- Higher oxygen partial pressure causes higher valent vanadium oxides
- The density of the initial films (water- or ozone-grown VO_2) results in crystallisation into different VO_2 phases (VO_2 M1 and VO_2 B, respectively)
- The substrate can act as an oxygen scavenger and delay further oxidation (not shown here)

Crystalline vanadium oxides as high capacity cathodes

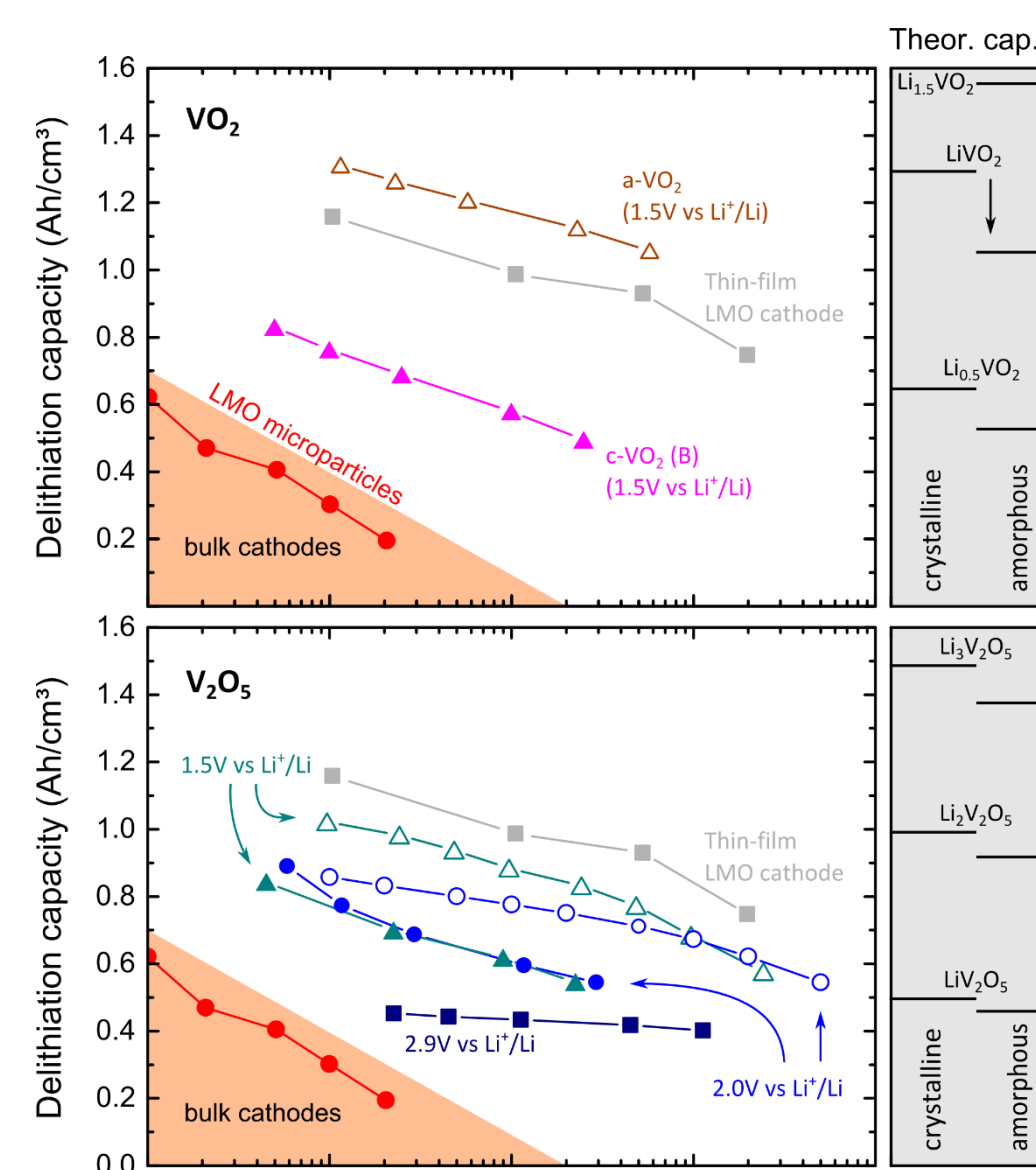


All obtained crystalline phases (except VO_2 M1) display excellent lithium storage behaviour, with exceptionally high capacities for V_4O_9 and V_3O_7 , which boast more than double that of $LiCoO_2$! However, further testing reveals the kinetics and cyclability are not perfect as is shown in the table below

Phase	Potential (V vs Li^+/Li)	Capacity ($mA h cm^{-2}$)	Kinetics	Cyclability
VO_2 (B)	1.5-4.0	805	75 %	+
V_6O_{13}	1.5-4.0	894	75 %	-
V_4O_9	1.5-4.0	1380	78 %	-
V_3O_7	1.5-4.0	1255	49 %	-
V_2O_5 (1 Li)	2.9-3.5	488	93 %	+
V_2O_5 (2 Li)	2.9-3.5	1010	86 %	-
V_2O_5 (3 Li)	1.5-4.0	810	78 %	--

(left) cyclic voltammograms demonstrate the lithiation and delithiation into the crystalline vanadium oxide thin films. Their properties, derived from a more in-depth electrochemical analysis, are summarized above.

Amorphous vanadium oxides as high power cathodes

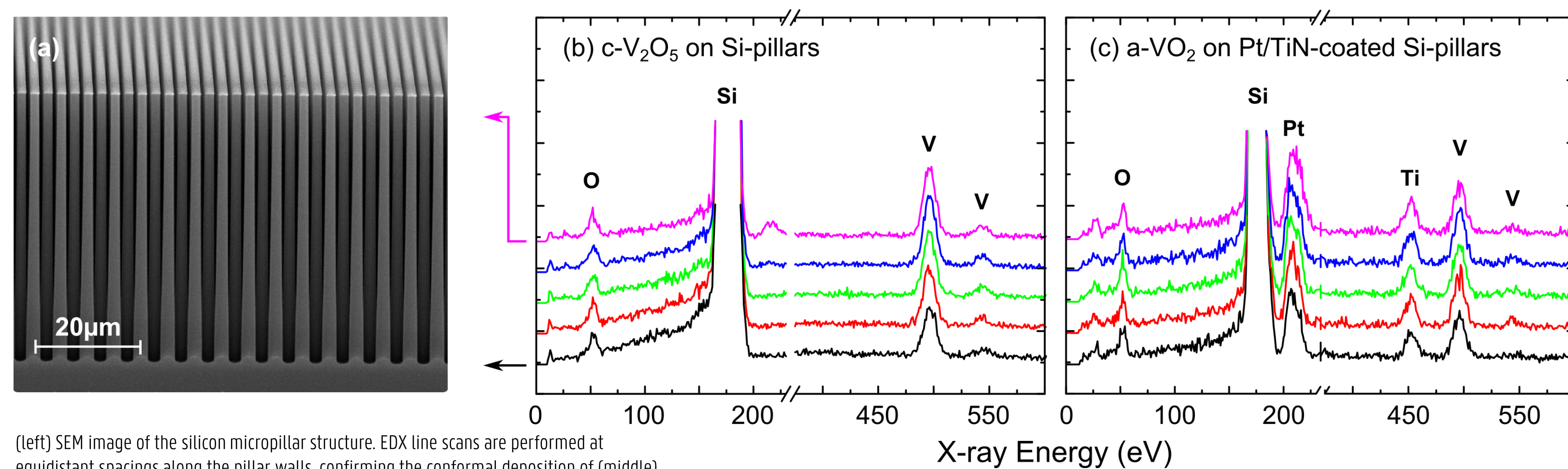


(Above) Capacity of the (top) VO_2 and (bottom) V_2O_5 thin films at different (dis)charge rates. A C-rate of 1 corresponds to charging in 1 hour, 100 corresponds to 36 seconds. (right) cyclability measurements at 2C.

Typically, research is devoted to obtaining a specific crystal state for electrode materials. Amorphous materials are often overlooked, and typically very hard to obtain. ALD is almost uniquely an ideal technique to investigate this, as it allows for the deposition of high-purity amorphous thin films.

From the figure on the right, it is clear that the amorphous vanadium oxides have considerably higher capacities and are much faster (higher power) than their crystalline counterparts, making them very interesting as cathode materials.

The deposition of 3D thin-film lithium-ion electrodes on challenging substrates



(left) SEM image of the silicon micropillar structure. EDX line scans are performed at equidistant spacings along the pillar walls, confirming the conformal deposition of (middle) $c-V_2O_5$ on silicon pillars and (right) $a-VO_2$ on pillars coated with current collectors.

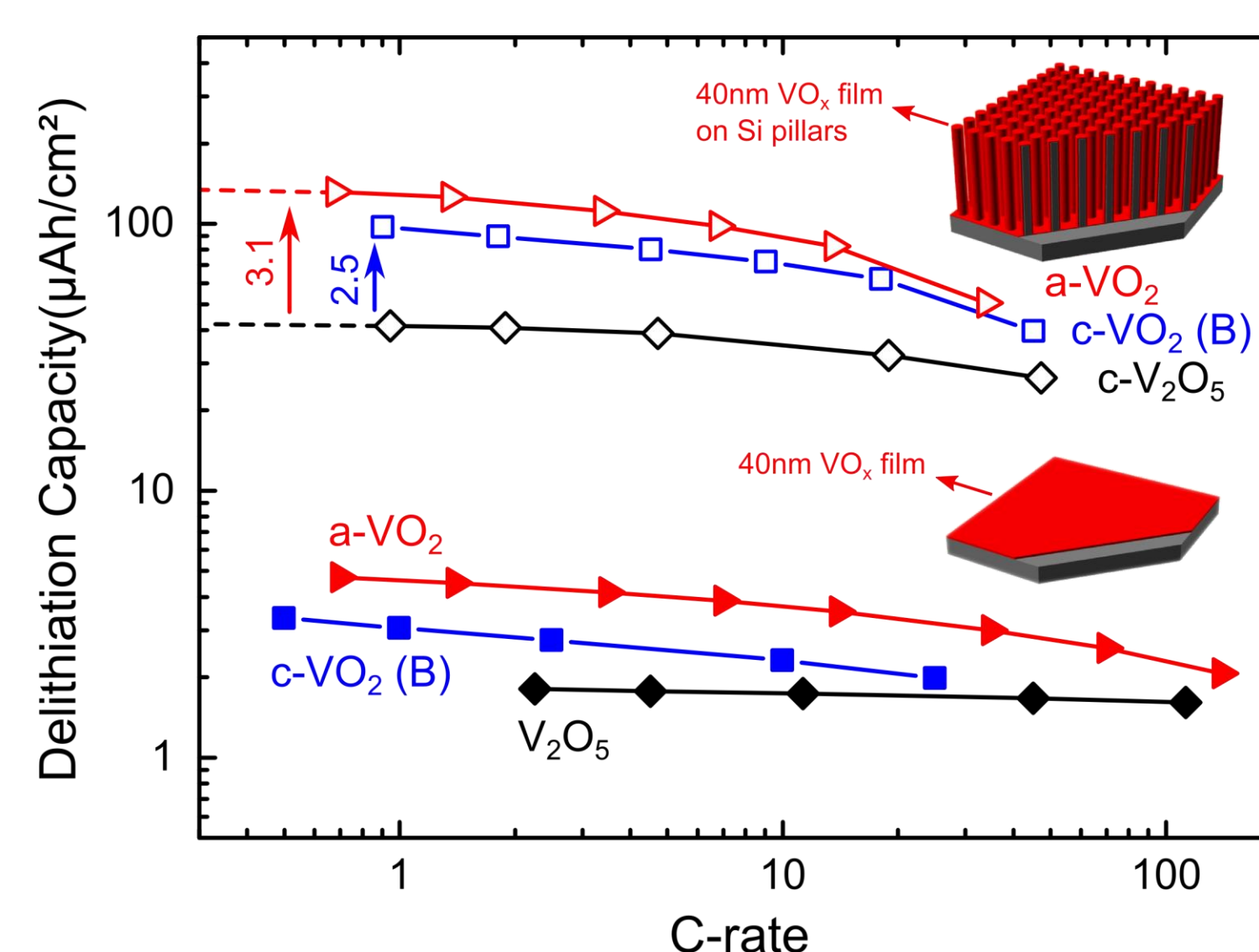
40 nm thin films of ALD vanadium oxides are deposited on $2 \times 50 \mu m$ silicon micropillars, spaced $2 \mu m$ apart. These are first coated with ALD TiN and ALD Pt to act as a current collector. This 3D-structured template yields a potential surface enhancement of $\sim 20 \times$ the footprint

EDX/SEM line scans along varying depths inside the pillars demonstrate the uniformity of the vanadium-containing films inside the pillar structures. No variation in vanadium signals is observed scanning down the pillar lengths, indicating a conformal deposition.

Ideally, the concept of 3D thin-film electrodes yields an enhancement in capacity equal to the surface enhancement of the 3D-structured template, while maintaining the fast charging and discharging inherent to the thin-film nature.

Indeed, from the graph on the right we can draw 3 conclusions:

- The capacity is indeed enhanced approx. 20 times, which is the surface enhancement factor of the silicon micropillar structure
- The fast thin-film kinetics are almost equal on the pillars compared to the planar films
- Amorphous VO_2 yields a capacity more than 3 times higher compared to V_2O_5 , and crystalline VO_2 2.5 times higher. This allows the use of thinner films, yielding even faster kinetics, or of films with the same thickness but with higher capacities, yielding high capacity and high power thin-film electrodes.



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References

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