In situ SEM Study of Lithium Intercalation in individual V$_2$O$_5$ Nanowires

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Supporting information

**Figure S1.** In situ morphological changes - bending: a) Initial shape of a V$_2$O$_5$ whisker; b) Whisker submerged into electrolyte; c) Whisker pulled out of electrolyte after 2 charge-discharge cycles; d) after 3 cycles; e) final whisker distortion after 5 cycles; f) zoomed-in image of the formed kink in e).

**Figure S2.** Multi-nanowire Pd/V$_2$O$_5$ electrodes voltammograms measured with: a) RE – Li, CE - Pt; b) RE – Pt, CE - Li; c) RE – Pt, CE – Pt.
To elucidate the particularities of intercalation process in V$_2$O$_5$ nanowires *en masse* and test the possibility of using electrodes other than metallic lithium, which is hard to use in *in situ* SEM, we have recorded voltammograms in 3-electrode systems. The working electrode was a Pd wire with a forest of vanadia nanostructures grown on it, completely submerged in electrolyte (same as used for *in situ* SEM measurements). When lithium metal was used as either counter or reference electrode, well-shaped intercalation peaks appeared in voltammograms for the ε and δ phases (Fig. S2 a & b). However, in the absence of Li sources other than the electrolyte itself, *i.e.* when both counter and reference electrodes were Pt wires, no intercalation took place and only a small capacitive current was detected (ca. 2 orders of magnitude lower than in other instances – see Fig. S2 c). Thus, in *in situ* SEM experiments the counter electrode must be a source of Li ions, for which reason LiCoO$_2$ was used (it is also more stable in air than Li metal). Another important feature of switching between different electrode designs is the potential scale, which experiences linear shifts, when one type of reference electrode is replaced with another one. A similar shift of potential scale is seen in the voltammograms of the main paper. Position of the peaks, then, can be used to relate potential as measured vs. LiCoO$_2$/Au in a 2-electrode system to potential measured vs. Li metal in a 3-electrode system.

**Notes and references**

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