

Citation for published version:

Li, W, Fukunishi, M, Morgan, B, Borkiewicz, O, Chapman, K, Pralong, V, Maignan, A, Lebedev, O, Ma, J, Groult, H, Komaba, S & Dambournet, D 2017, 'A Reversible Phase Transition for Sodium Insertion in Anatase TiO<sub>2</sub>', Chemistry of Materials, vol. 29, no. 4, pp. 1836-1844. https://doi.org/10.1021/acs.chemmater.7b00098

DOI: 10.1021/acs.chemmater.7b00098

Publication date: 2017

Document Version Early version, also known as pre-print

Link to publication

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To access the final edited and published work see https://doi.org/10.1021/acs.chemmater.7b00098

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# A Reversible Phase Transition for Sodium Insertion in Anatase TiO<sub>2</sub>

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Figure S1. Powder x-ray diffraction pattern of anatase TiO<sub>2</sub>.



**Figure S2.** Cycling behavior of anatase  $TiO_2$  upon Na insertion/de-insertion. The capacity obtained after 50 cycles is 165 mAh/g, corresponding to ca. 0.5 Na<sup>+</sup> per TiO<sub>2</sub>.



**Figure S3. (a)** High-energy X-ray diffraction pattern of the pristine and fully discharged  $TiO_2$  electrodes. **(b)** The X-ray diffraction pattern of the fully discharged electrode was indexed with an O3-type NaTiO<sub>2</sub> rhombohedral structure (space group: R-3m).



**Figure S4.** PDF refinement of the TiO<sub>2</sub> electrode discharged to 0.3V, *i.e.* 0.3 Na<sup>+</sup> per TiO<sub>2</sub>.



**Figure S5.** High-energy X-ray diffraction pattern of the fully charged electrode. The peak at 2-theta  $\approx 25^{\circ}$  can be assigned to the (101) of the anatase type structure, indicating the recovery of anatase framework upon charging.



**Figure S6.** PDF refinement of the electrode charged to 2 V using O3-type NaTiO<sub>2</sub> (space group: R-3m) and TiO<sub>2</sub> (space group: I4<sub>1</sub>/amd) models. The results show that the desodiated electrode is composed by 20 % O3-type Na<sub>x</sub>TiO<sub>2</sub> and 80 % TiO<sub>2</sub>, which agrees with the capacity delivered during the 1<sup>st</sup> charge. Note that the high value of the Rw is due to strong disorder occurring in Na<sub>x</sub>TiO<sub>2</sub> phase.