

# Porosity and stoichiometry as efficient means to optimize Li storage in anatase

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Anatase  $\text{TiO}_2$  is a stable, cheap, non-toxic and environmentally benign candidate for use as an anode active material for lithium ion batteries (LIB). Due to the comparably high lithium insertion potential of around 1.8 V vs.  $\text{Li}/\text{Li}^+$ , typical battery electrolytes can be used in their thermodynamic stability window. Anatase offers high capacity and high cycling stability, and due to the oxidic framework, the anode cannot contribute to combustion reactions upon LIB failure, leading to improved cell safety. Despite all advantages, anatase electrodes suffers from poor chemical diffusivity of lithium; both electron and lithium ion transport are extremely slow and therefore lithium storage kinetics and rate performance are quite limited in this material. Here, several techniques come into play, that allow one to optimize ionic transport and electronic transport towards and inside the particles. Note that the storage of  $\text{Li}$  ( $= \text{Li}^+ + \text{e}^-$ ) in an electrode implies conductivity of lithium ions and electrons.

A simple way of improving lithium ion transport in battery materials (“ionic wiring”) is the introduction of open porosity. Fast  $\text{Li}^+$  transport is available in the liquid electrolyte. If the electrolyte penetrates the pores, it brings  $\text{Li}^+$  ions to the interior of electrode particles, and therefore reduces the length for the slow solid state diffusion transport. Liquid transport systems with hierarchical pores of different diameters have proven to be extremely efficient distribution systems. (This is a similar principle as in many biological systems, where liquids in transport channels [e.g. blood in blood vessels, or sap in trees] are employed for fast ion transport.)

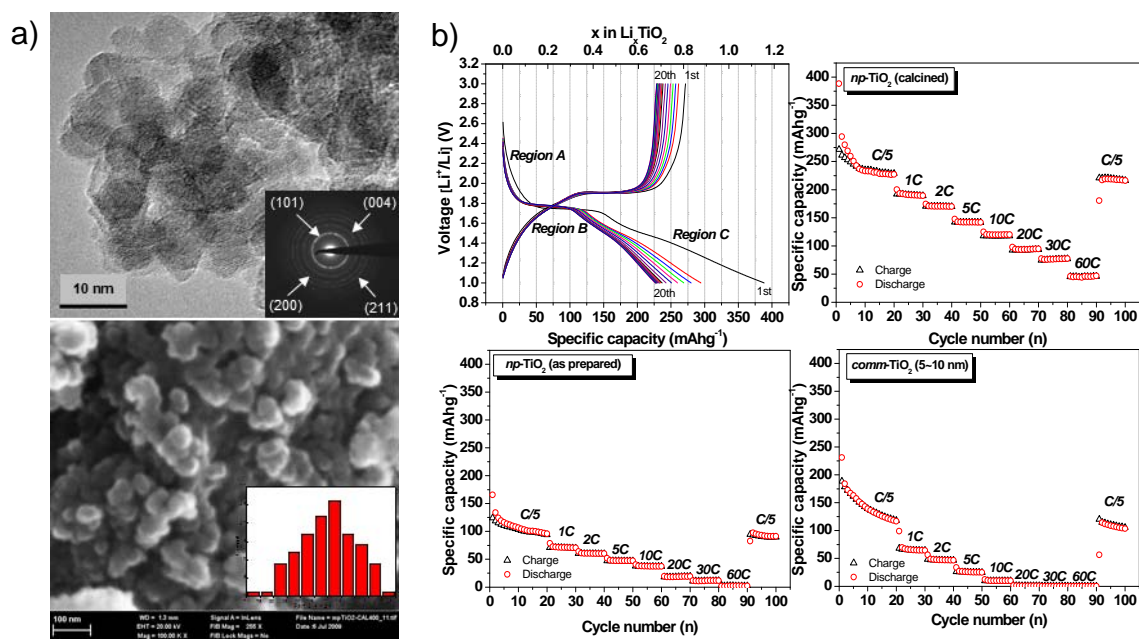


Figure 1: (a) TEM and FESEM images of the calcined microporous  $\text{TiO}_2$  anode material. The SAED pattern in the TEM micrograph clearly confirms pure anatase phase. Primary particle size is below 10 nm. The HRTEM micrograph shows the agglomerates formed from the particles, with an average size of  $\sim 100$  nm. (b) battery performance data: charge-discharge curves and rate capability of the calcined anatase material, and for comparison rate capabilities of the non-calcined anatase and of commercial 10 nm anatase particles. Reprinted with permission from [1]. Copyright 2011 WILEY-VCH Verlag GmbH & Co. KGaA.

Figure 1a shows an anatase electrode material that has been optimized with respect to ionic wiring [1]. The material is made of extremely small particles with diameters of only around 8 nm. Since nanopowders of such small particles typically cannot be packed very efficiently (volumetric energy density is a key performance parameter for nowadays batteries), it is important for battery application that the particles form larger agglomerates, as shown here. Still, there is enough void space in the fairly dense agglomerates so that the liquid electrolyte can ionically contact each primary particle.

Hence, only the last 4 nm to the middle of the primary particle have to be bridged by slow solid state chemical diffusion of lithium.

After ionically wiring the particles, it is now important to look at the electronic transport towards and inside the electrode. A frequently used way for improving electronic transport (“electronic wiring”) between current collector and active material in a battery consists of superimposing a conductive network of a secondary phase, such as carbon. This method is almost universally employed in today’s batteries, but has two principal drawbacks: First, volume demand for this secondary phase can be quite high (up to 30% by volume) since the carbon network has to fully percolate. Adding the volume demand of the porosity required for ionic wiring leads to space requirements of up to 50% that cannot be used for the active material and therefore increase overall battery volume by up to a factor of two. Second, unlike liquid electrolyte in pores, the carbon network usually does not penetrate the active materials’ particles and thus cannot increase electronic transport inside a single particle.

Taking this into account, it is desirable to actually increase electronic conductivity within the electrode material itself. This would not only lead to improved chemical diffusivity of lithium, but could also – for high enough conductivity – make a conductive second phase dispensable. In many electrode materials, donor doping can lead to the desired effect, but very often is limited by the very low concentration thresholds of the solid solution region. Also, preparation of homogeneously doped nanoparticle samples can be quite difficult.

We have employed a much simpler approach for introducing additional electronic charge carriers into  $\text{TiO}_2$ , that to our surprise was not applied before [2]. By heat-treating commercial 20 nm anatase  $\text{TiO}_2$  nanoparticles at 450 °C in hydrogen/argon atmosphere, oxygen is removed from the crystallites; the left-behind oxygen vacancies are charge compensated by additional electrons. After cooling the sample down to room temperature, the oxygen vacancies remain inside the sample, since re-oxidation kinetics now are completely frozen. The heat-reduction treatment therefore leads to samples with permanently increased electronic conductivity after cooling down.

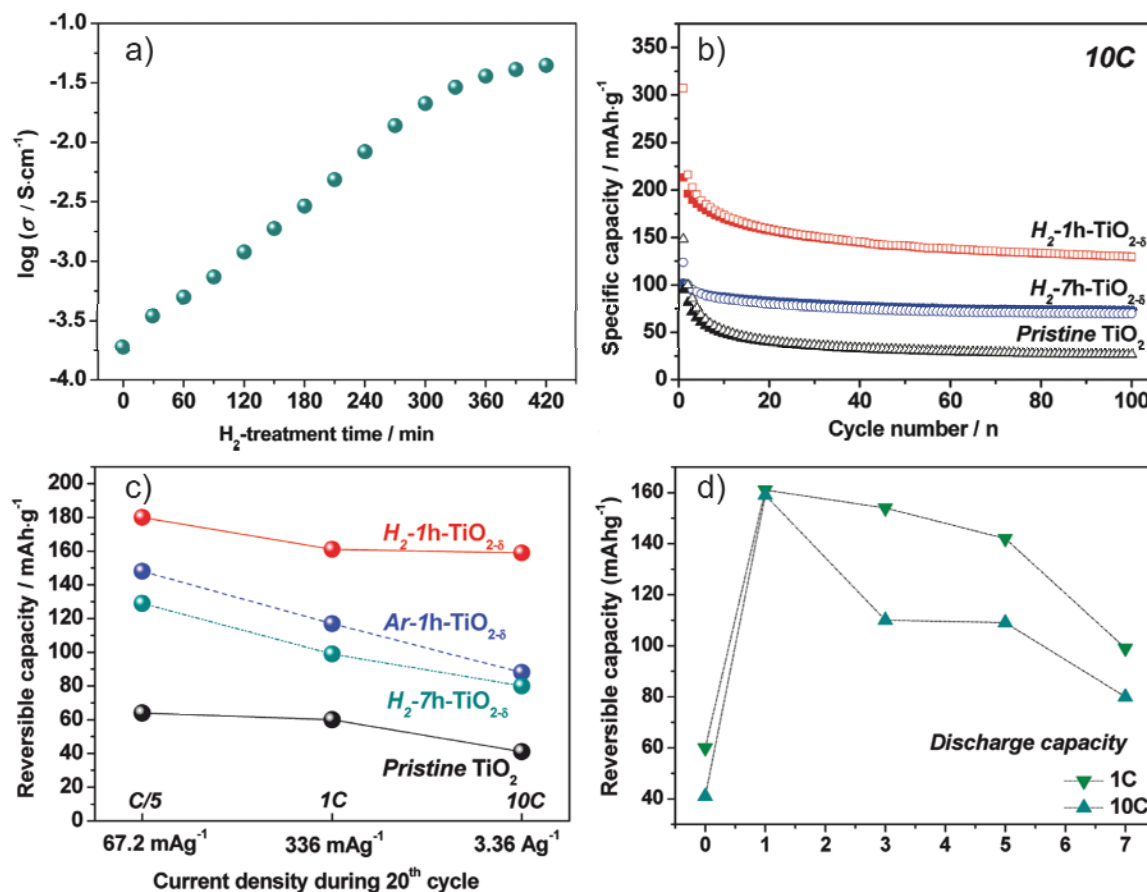


Figure 2: (a) electronic conductivity variation during treatment of anatase particles in 5%H<sub>2</sub>/Ar atmosphere at 450 °C. Up to three orders of magnitude increase in electronic conductivity are possible, until equilibrium is reached after ~7 hours. (b) Charge/discharge capacities for untreated, 1h and 7h reduction-treated material at 10C (=3.36 A g<sup>-1</sup>) current. (c) Reversible capacities at the 20th discharge cycle for pristine, 1h and 7h treated anatase material at currents of C/5, 1C and 10C. (d) Achievable discharge capacities at the 20th cycle for discharge currents of 1C and 10C at different reduction treatment times (A discharge/charge rate of *n*C denotes an insertion/extraction of 1 Li in 1/*n* h. In case of Li storage in TiO<sub>2</sub>, 1C is equivalent to 0.336 A h g<sup>-1</sup>). Reprinted with permission from [2]. Copyright 2012 American Chemical Society.

The storage capacity of the treated anatase material surpasses that of the pristine 20nm anatase nanoparticles by almost a factor of three. More importantly, it is now possible to charge and discharge electrodes based on the treated material at much higher currents; there is e.g. only a negligible drop in capacity when the current is increased by 1 order of magnitude (going from 1C to 10C in Fig. 2c) for the 1 h treated material.

A fact that may be surprising at a first glance is shown in Figure 2b. Despite much higher electronic conductivity (Fig. 2a), the battery performance of the 7h treated anatase particles is worse than that of 1h treated material. The reason for this non-monotonic behavior can be found in the defect equilibria of the Li<sub>x</sub>TiO<sub>2-δ</sub> system and is due to the necessity of both ion and electron transport [2,3]. Due to strong interaction between e<sup>-</sup> and Li<sup>+</sup> charge carriers, most of these carriers exist in a neutral associate, leading to an opposite variation of the concentrations of the free e<sup>-</sup> and Li<sup>+</sup>. Increased electron concentration from the treatment process therefore leads to decreased Li<sup>+</sup> carrier concentration. Under the assumption, that the initial mobility of Li<sup>+</sup> is higher than that of e<sup>-</sup>, it can be shown that the overall chemical diffusivity of Li in fact exhibits a maximum as a function of reduction treatment time (see also Fig. 2d and Fig. 3), with a predicted optimum reduction time between 1-2 hours at 450 °C. (The maximum is however also explainable for an opposite mobility behavior. See [2] for details.)

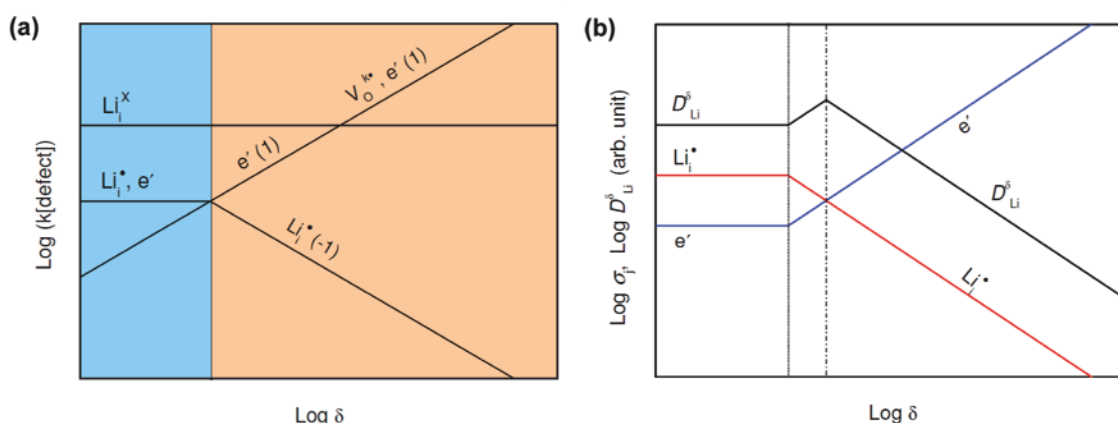


Figure 3: Dependence of (a) defect concentrations, (b) conductivities, and chemical diffusion coefficient of Li in Li<sub>x</sub>TiO<sub>2-δ</sub>, on oxygen nonstoichiometry  $\delta$ . Reprinted with permission from [2]. Copyright 2012 American Chemical Society.

In short: The combination of micro-porosity and non-stoichiometry in TiO<sub>2</sub> leads to an improvement of electronic conductivity (inside TiO<sub>2</sub>) and ionic conductivity (in the network). This results in a remarkable performance enhancement which is limited by the concomitant decrease of ionic conductivity within the TiO<sub>2</sub> particles.

## References:

- [1] Shin, J.-Y., D. Samuelis, and J. Maier. *Advanced Functional Materials* **21**, 3464-3472 (2011).
- [2] Shin, J.-Y., J.H. Joo, D. Samuelis, and J. Maier. *Chemistry of Materials* **24**, 543-551 (2012).
- [3] Shin, J.-Y., D. Samuelis, and J. Maier. *Solid State Ionics* **225**, 590-593 (2012).