

In-situ Synchrotron XRD investigation on hydrogenation process of rutile nanorods for lithium ion batteries

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Rutile TiO₂ powder was hydrogenated under 40 bar H₂ pressure at 450°C in this work. The hydrogenated rutile TiO₂ (H-TiO₂) exhibits superior performance compared with pristine rutile TiO₂ as anode materials for lithium ion batteries (LIBs). However, the mechanism behind this improvement is still unclear. Because synchrotron X-ray Diffraction (XRD) can provide a powerful tool for *in-situ* monitoring the crystalline phase, unit cell and volume in the course of hydrogenation of rutile, together with other materials characterization tools, it was used for *in-situ* investigation of the hydrogenation process of the rutile TiO₂ to explore the mechanism.

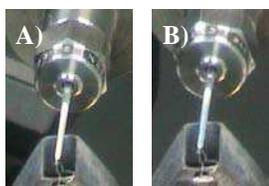


Fig. 1 In-situ synchrotron XRD sample setup where the colour change of the rutile sample could be *in-situ* observed. A: the pristine white rutile TiO₂; B: the Blue TiO₂

As shown in Figure 1, high-resolution synchrotron powder XRD (HRXRD) data was collected on rutile TiO₂ powder samples on a powder diffraction beamline (10BM-1) at the Australian Synchrotron using a Mythen II Microstrip detector. For phase identification and structure determination, samples were loaded into pre-dried 0.7 mm quartz capillary tubes and sealed into an in-house designed flow cell for XRD measurements. Hydrogenation behaviors of the samples were studied by *in-situ* heating the sample within quartz tube under high purity H₂ gas (99.99%) at around 40 bar with a Cyberstar hot air blower. The samples were heated from 30 °C to various temperatures at a heating rate of 50 °C min⁻¹. The advantages of this *in-situ* synchrotron investigation system includes

1. Good time resolution: The crystalline phase changes could be determined in a narrow time window ca. 3-5 minutes due to the use of strong intensity beam light of the synchrotron. This is in strong contrast with the conventional XRD, where 30 minutes are commonly needed.

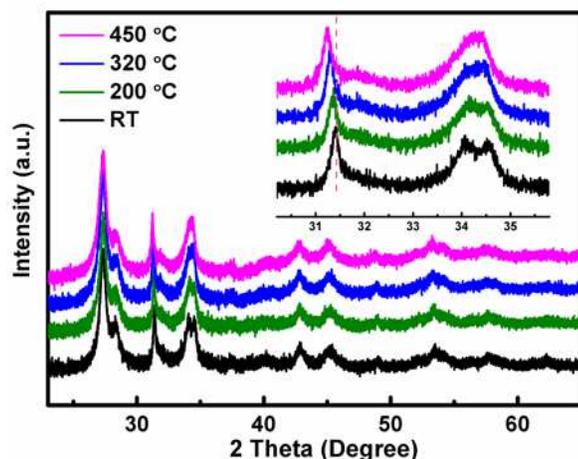


Fig. 2 In-situ synchrotron XRD pattern of the pristine and hydrogenated TiO₂ treated at different temperatures (the inset is the zoomed view of 2θ range of 30°-36°).

2. Good temperature resolution: Due to the use of quartz capillary (0.7 mm ID and 0.5mm thickness, very small amount of sample (only 1-2mg) and more

importantly the powerful heater, the sample can be heated up rapidly, at a ramp of 50 degree per minute. This provides an excellent temperature resolution for investigation of the hydrogenation kinetics.

3. The change of appearance e.g. the colour changes of the samples could be observed *in-situ* due to the use of transparent quartz capillary and heating set up.

With this experimental setup, we could visually observe the white colour of the rutile TiO₂ powder turned into blue colour in 5 min at sufficient temperature. In strong contrast, such change was not observed for anatase nanoparticles under identical experimental conditions.

All the samples were in good crystalline state of rutile and showed good crystallinity as shown in Fig. 2. Rietveld refinement for all samples was conducted using starting structure model from ICDD database (2012) by TOPAS4.2 (Bruke, Germany). The peak profile was defined with fundamental parameters approach, the nanocrystalline size was derived from whole pattern modelling method. The refined unit cell lattice parameters and crystalline size results are were calculated based on a two-phase. The changes along *a* and *b* directions were very trivial, but significant expansion along the *c* direction was observed. The *c* values increased in the order of the increase of the temperature which implies that the hydrogenation could result in expansion of cell units and the *c* values would increase with the depth of hydrogenation reaction.

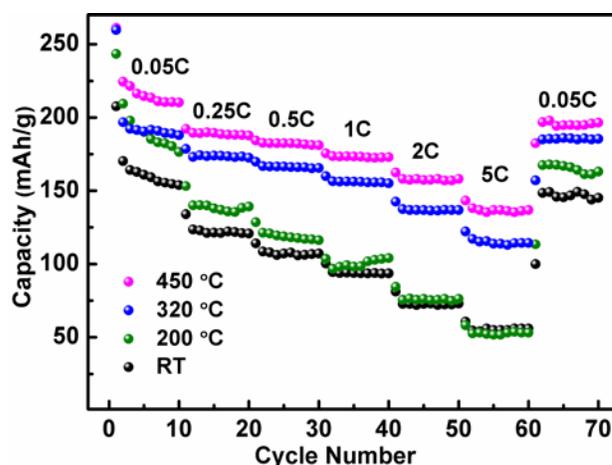


Fig. 3 Rate capacity comparison of the pristine and hydrogenated TiO₂ treated at different temperature (1C=336 mAh/g).

Hydrogenation process could enhance the LIB performance of anatase TiO₂ via the improvement of conductivity¹⁻³. We found that extend of the hydrogenation, i.e., crystalline properties (unit cell and volume) of the rutile nanorods, was enhanced by increase of the hydrogenation conditions (pressure, temperature, time). As shown in Fig. 3, the hydrogenated rutile demonstrated significantly higher specific capacity and rate capacity than the pristine rutile. Furthermore, the rate capacity increased with the increase of treatment temperature and pressure. The significant performance of the blue TiO₂ LIBs over the white TiO₂ LIBs can be attributed to two reasons, the boosted electronic conductivity (i.e., reduced impedance) and augmented TiO₂ lithium ion diffusion in the insertion/extraction process.

The findings of this work provide guidance for the engineering of the properties of the metal oxide materials for LIBs via the hydrogenation processing.

Reference:

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