Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2016

Influence of particle size, cycling rate and temperature on the lithiation process of anatase TiO_2

H. Liu[a] and C.P. Grey[a]

[a]Department of Chemistry, Lensfield Road, University of Cambridge, CB2 1EW, UK

Particle size distribution

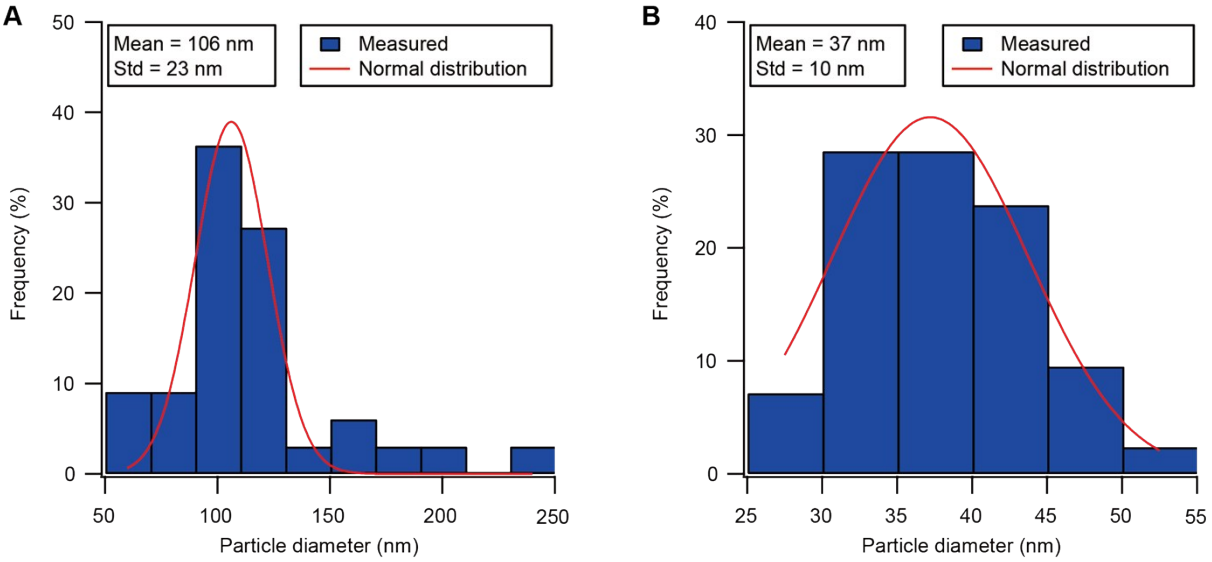

Figure S1. Particle diameter distribution of the 100 nm (A) and the 25 nm (B) sample measured for 33 and 42 particles, respectively, in Figure 2. The particles are measured as ellipses, and the diameter of an equivalent circle of the same circumference is used as an indicator of the particle size. The vertical axis represents the fraction of particles of an equivalent diameter within the range. The measured frequencies are shown as blue bars. The red curve shows the best fit normal distribution to the measured frequency. The mean and standard deviation (std) of the fitted normal distribution are shown in the top left corner of each graph.

It is noted that the mean diameter (37 nm) of the 25 nm sample obtained from the SEM image differs from the one (~25 nm) obtained from the XRD peak broadening analysis. The size obtained from the Scherrer equation (peak broadening analysis) is weight by volume, i.e. the volume averaged size. For spherical particles, the volume average size, L_v, is related to the spherical diameter, L_d, through:

$$L_d = 4/3 \cdot L_v \quad \text{S1}$$

For volume averaged sizes of 25 nm and 90 nm, the corresponding diameters are 33 nm and 120 nm, respectively, which are in good agreement with the mean diameter obtained in Figure S1.

Rietveld refinement

Figure S2 A and B show typical fitting patterns obtained from Rietveld refinement for the 100 nm particles at 0.33 overall cycled Li per f.u. and 25 nm particles at 0.24 overall cycled Li per f.u., respectively, during 2 C discharge at room temperature (RT). Reflections overlapped with the Li metal ones are not included in the refinement. The dips at ~28° are due to the presence of less efficient pixels of the detector and are also excluded from the refinement. The two big humps at ~11° and ~20°, 2θ, arise from the glassy carbon window and the liquid electrolyte in the cell[1] and are treated as background. The extremely small R_{wp} factors (<1%), which indicate the quality of fit, are due to the relatively high background intensities with respect to the intensities of the Bragg reflections. Figure S3 shows the R_{wp} factors in all Rietveld refinements carried out in this study. It can be seen that R_{wp} stays almost constant for all refinements carried out for each cycling condition, except for the cycling at room temperature for 25 nm particles, where R_{wp} increases with the overall Li composition but still remains in the same range with R_{wp} obtained for cycling at 80°C for 25 nm particles.

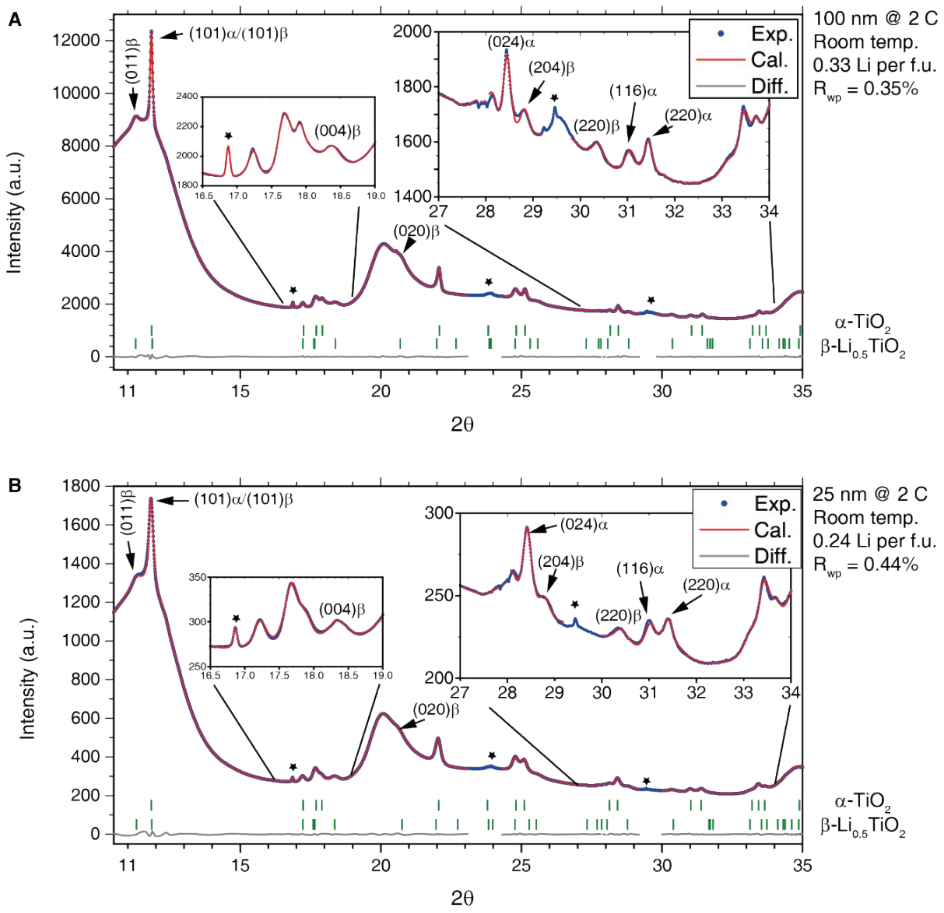

Figure S2. Typical fitting results obtained from Rietveld refinement for *in situ* XRD patterns collected for (A) 100 nm and (B) 25 nm particles. The green ticks mark the Bragg reflection positions of the corresponding phases. The asterisks indicate the Bragg reflections due to Li metal. The insets show the magnified 16.5° – 19° and 27° – 28° 2θ regions. The regions not accounted for by the calculated curves are excluded from the refinement. The blue dots represent the measured intensity, red curves are the calculated intensities from the refined models and grey curves are the differences between the measured and calculated intensities.

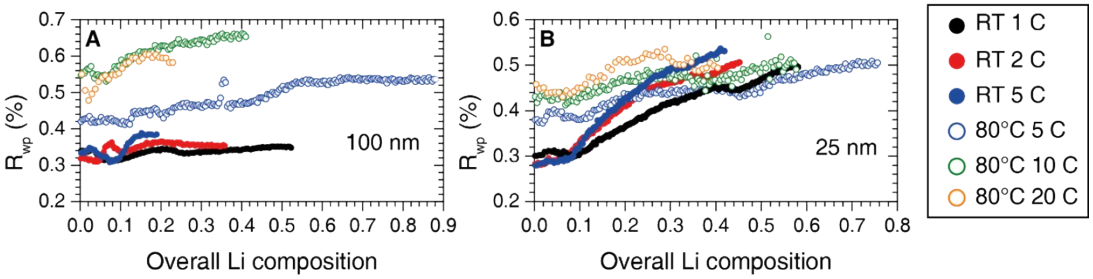

Figure S3. The R_{wp} factors in the Rietveld refinements for (A) 100 nm and (B) 25 nm particles. RT is short for room temperature.

Lattice parameter as a function of Li composition

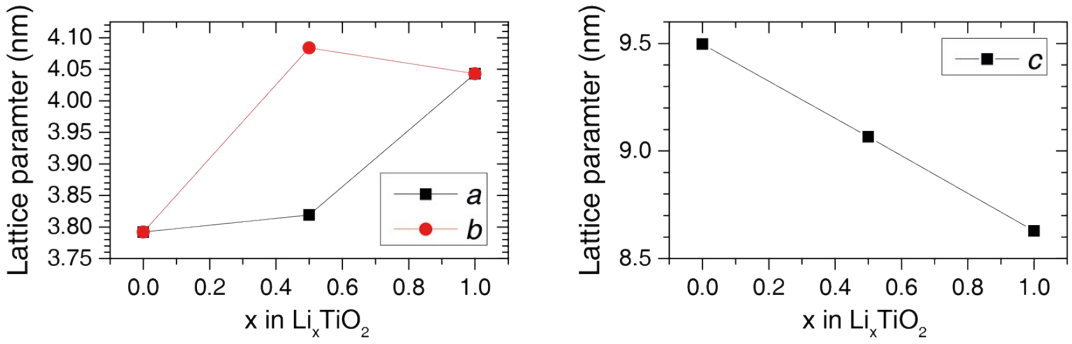

Figure S4. The lattice parameters of TiO_2, $Li_{0.5}TiO_2$ and $LiTiO_2$ as reported in reference [2]. Only the *c* lattice parameter varies linearly with *x* across the entire Li composition range.

Peak fitting

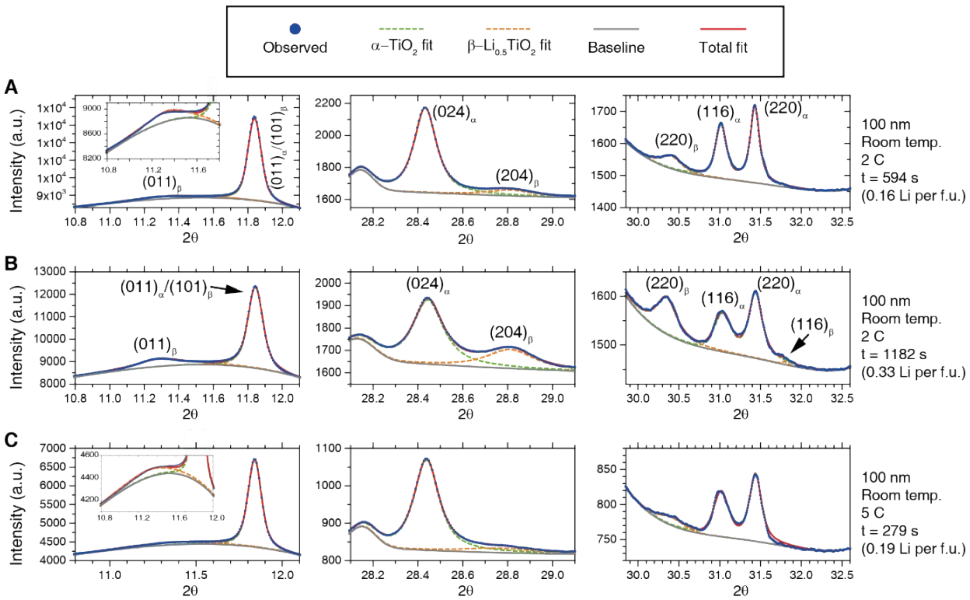

Figure S5. Typical peak fitting patterns for 100 nm particles during room temperature charge at cycles rates of (A-B) 2 C and (C) 5 C. Blue dots are the experimental data, and red curves represent the overall fit.

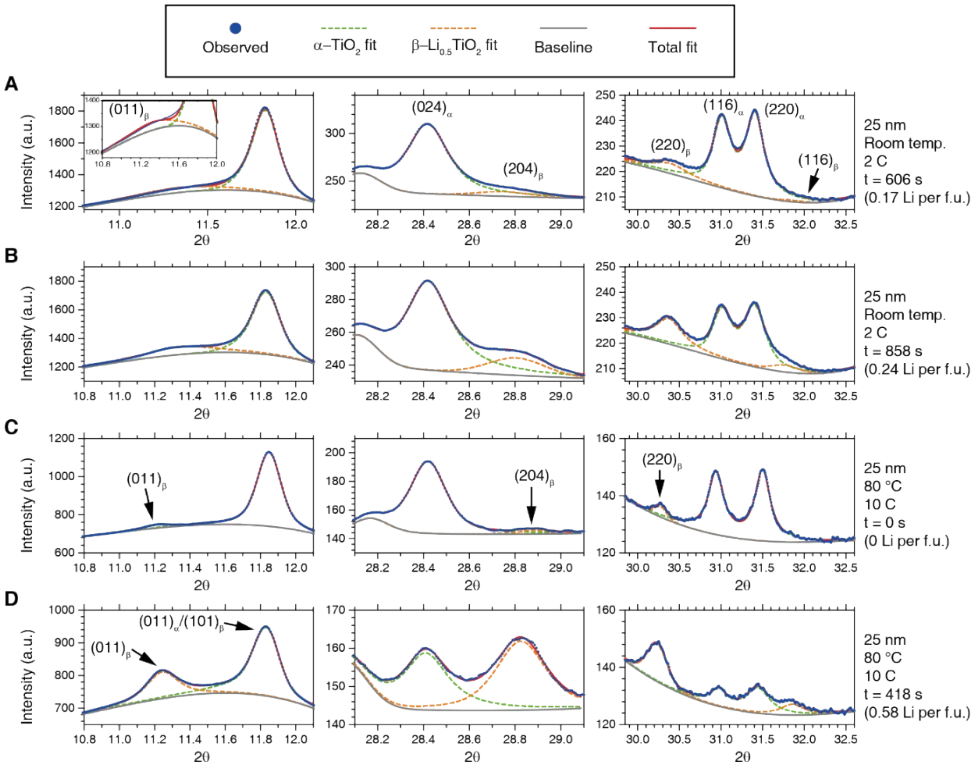

Figure S6. Representative peak fitting patterns for 25 nm particles during charge at cycle rates of (A-B) 2 C at room temperature and (C-D) 5 C at 80°C.

References

1 O. J. Borkiewicz, B. Shyam, K. M. Wiaderek, C. Kurtz, P. J. Chupas and K. W. Chapman, *J. Appl. Crystallogr.*, 2012, **45**, 1261–1269.

2 M. Wagemaker, W. J. H. Borghols and F. M. Mulder, *J. Am. Chem. Soc.*, 2007, **129**, 4323–4327.