[Supporting Information]

*Operando* Identification of Chemical and Structural Origin of Li-Ion Battery Aging at Near-Ambient Temperature

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Experimental Section

Figures S1 to S22
**EXPERIMENTAL SECTION**

**Materials.** Titanium (IV) n-butoxide (TBOT) was purchased from Strem Chemicals, Inc. (Newburyport, MA 01950-4098, USA). Tetraethyl orthosilicate (TEOS), resorcinol, formaldehyde solution (37 wt% in H$_2$O) and polyvinylpyrrolidone (PVP) (MW = 55,000) were purchased from Sigma Aldrich (St. Louis, MO, USA). Acetonitrile (98 %), anhydrous ethanol (99.9%), sodium hydroxide (NaOH) and aqueous ammonia solution (28 – 30 wt%) were purchased from Samchun Chemical (Seoul, Korea). All reagents were used as received without further purification.

**Synthesis of 12 NT.** Synthesis of 12 NT were based on layer-by-layer sol-gel coating method modified from previous reports (See ref. 27 and 35 in main text for details). Briefly, SiO$_2$ NP was synthesized using Stöber method. TEOS (99%, 0.86 ml) was added in a mixture solution of EtOH (23 ml), H$_2$O (4.3 ml) and aqueous ammonia (28-30 wt%, 0.6ml). After vigorously stirring for 6 h, reaction product (SiO$_2$ NP) was washed with water and ethanol. For TiO$_2$ overlayer coating, the prepared SiO$_2$ NP was dispersed in 40 ml of anhydrous ethanol. Then aqueous ammonia (28 – 30 wt%, 0.4 ml) and acetonitrile (98%, 14 ml) were added on the SiO$_2$ NP solution. The resulting solution was sonicated for 10 min to obtain well-dispersed SiO$_2$ NP prior to TiO$_2$ overlayer coating. Meanwhile, TBOT (0.8 ml) was added in the mixture of anhydrous ethanol (99.9%, 6 ml) and acetonitrile (98%, 2 ml) (solution 2). Solution 2 was added to SiO$_2$ NP solution and vigorously stirred for 3 h for TiO$_2$ overlayer coating. Resulting SiO$_2$@TiO$_2$ NP solution was washed with ethanol and water. For resorcinol-formaldehyde overlayer coating, the above SiO$_2$@TiO$_2$ NP was dispersed in H$_2$O (56 ml). Aqueous CTAB solution (2 mL, 0.01 M) was added on the above solution. After vigorous stirring for 1 h, resorcinol (0.08 g), formaldehyde (37 wt%, 0.112 ml) and diluted aqueous ammonia solution (2.8-3.0 wt%, 0.4 ml) were added. After 24 h of reaction, the resulting SiO$_2$@TiO$_2$@RF NP
was washed with ethanol and water. The products were dried in convection oven at 80°C overnight. For crystallization of amorphous TiO$_2$ and calcination of RF layer, SiO$_2$@TiO$_2$@RF NP was heated at 750 °C (static air, 150 °C h$^{-1}$ and 2 h). Note that initial brown powder becomes white after calcination due to RF overlayer calcination. For SiO$_2$ etching, calcined SiO$_2$@TiO$_2$@RF NP was dispersed in NaOH solution (0.5 M) and heated to 90 °C under continuous stirring. After stirring for 6 h, the product was washed with H$_2$O and ethanol, and dried overnight in a convection oven at 80 °C. The resulting 12 NT was used for various electrochemical measurements and characterizations without further modification.

**Electrochemical measurement.** The slurry of working electrodes is prepared by mixing active materials (12 NT), Super P and poly(vinylidene fluoride) (PVDF) in N-Methyl-2-pyrrolidone (NMP) (Sigma-Aldrich) with a weight ratio of 8:1:1. The evenly blended slurry is casted on the Cu current collector by doctor blade method and dried in vacuum at 120 °C for 8 h. The electrochemical cells (CR2032 type coin cell) were assembled in the Ar-filled glove box. Lithium metal was used as reference electrodes. Poly (ethylene) was used as separator and 1M LiPF$_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 v/v) as electrolyte. Electrochemical tests were performed using WBCS3000 (WonAtech, Korea) in a voltage range of 1.0-2.5 V at four different temperatures (RT, 45 °C, 60 °C, and 90 °C).

**Characterization.** Transmission electron microscopy (TEM) was performed on a JEOL EM-2010 microscope at 200 kV operation. The field emission scanning electron microscopy (FESEM) was performed on a JEOL JSM-7800F-Prime microscope. Cs-corrected scanning transmission microscopy (Cs-STEM) imaging was performed using a spherical aberration-corrected JEM ARM-200F microscope (Cold FEG Type, JEOL), installed at the National Center for Inter-University Research Facilities (NCIRF) at Seoul National University. X-ray diffraction analysis was conducted on a Rigaku D/MAX-2500H system employing Cu Kα.
radiation. Collected data were analyzed by pattern fitting using HighScore Plus software.

**Characterization of operando heating XRD experiments.** To apply transmission operando heating XRD analysis, a customized coin cell with a hole in the center and Cu mesh electrode was used to reduce interference of Cu substrate. Operando XRD patterns were collected using Smartlab (Rigaku, Japan) with Cu Kα radiation (1.5406 Å). Each cell was discharged and charged at a current density of 25 mA g⁻¹ in same voltage range at RT and 60 °C. An XRD pattern was obtained at intervals of about 28 min. The obtained spectra were processed using PDXL software.
Figure S1. Representative TEM images of SiO$_2$@TiO$_2$@RF.
Figure S2. Representative TEM images of SiO$_2$@TiO$_2$@RF after calcination (750 °C, static air). RF polymers are removed after high temperature calcination. Amorphous TiO$_2$ layer crystallize into outer-shell comprising numerous 12 nm-sized anatase TiO$_2$ nanocrystals.
Figure S3. Low magnification TEM image of synthesized 12 NT after etching SiO$_2$ core.
Figure S4. High magnification TEM image (A, B) and selected area diffraction pattern (C) of synthesized 12 NT.
Figure S5. Representative FESEM image of 12 NT.
Figure S6. XRD pattern of as-prepared 12 NT.
Figure S7. (A) Voltage profile (current density of 100 mA g\(^{-1}\)) and (B) cyclic voltammetry (scan rate of 0.1 mV s\(^{-1}\)) of 12 NT at 45 °C.
Figure S8. (A) Voltage profile (current density of 100 mA g⁻¹) and (B) cyclic voltammetry (scan rate of 0.1 mV s⁻¹) of 12 NT at 90 °C.
Figure S9. Custom-made *operando* heating XRD measurement setup.
Figure S10. Crystal structure of anatase TiO\(_2\) during phase transition: (A) anatase TiO\(_2\), (B) Li\(_{0.55}\)TiO\(_2\) and (C) Li\(_1\)TiO\(_2\).

In anatase TiO\(_2\) and Li\(_1\)TiO\(_2\), Li ions are stored in the octahedral site. The octahedral site in anatase TiO\(_2\) is considerably distorted due to the Ti\(^{4+}\) ions, varying the edge length from 3.08 to 3.77 angstrom (O-O interatomic distance). The valence change of Ti\(^{4+}\) to Ti\(^{3+}\) upon lithium intercalation makes this octahedral site symmetric. The edge length of symmetric octahedron in Li\(_1\)TiO\(_2\) is much smaller (2.96 angstrom) than that of anatase TiO\(_2\), significantly increasing the Li migration barrier of Li\(_1\)TiO\(_2\). Consequently, predicted lithium diffusion coefficient of anatase TiO\(_2\) and Li\(_1\)TiO\(_2\) is in the order of 10\(^{-11}\) and 10\(^{-26}\) cm\(^2\) s\(^{-1}\), respectively.\(^{44}\)
Figure S11. $d$ values of the (101) planes (TiO$_2$ and Li$_x$TiO$_2$) and the (011) plane (Li$_{0.55}$TiO$_2$) extracted from Figure 2B and C (in situ XRD results).
Figure S12. A) Voltage profiles of anatase TiO$_2$ at a current density of 100 mA g$^{-1}$ in the 2$^{nd}$, 20$^{th}$, 40$^{th}$ cycles at RT. B) Capacity and ratio of region 1 and 2 in anatase TiO$_2$ in the 2$^{nd}$, 20$^{th}$, 40$^{th}$ cycles at RT.
Figure S13. A) Voltage profiles of anatase TiO$_2$ at a current density of 100 mA g$^{-1}$ in the 2$^{\text{nd}}$, 20$^{\text{th}}$, 40$^{\text{th}}$ cycles at 45 °C. B) Capacity and ratio of region 1 and 2 in anatase TiO$_2$ in the 2$^{\text{nd}}$, 20$^{\text{th}}$, 40$^{\text{th}}$ cycles at 45 °C.
Figure S14. A) Voltage profiles of anatase TiO$_2$ at a current density of 100 mA g$^{-1}$ in the 2$^{nd}$, 20$^{th}$, 40$^{th}$ cycles at 90 °C. B) Capacity and ratio of region 1 and 2 in anatase TiO$_2$ in the 2$^{nd}$, 20$^{th}$, 40$^{th}$ cycles at 90 °C.
Figure S15. Low magnification TEM and STEM images of 12 NT after the 20th lithium intercalation cycle at 60 °C. Nanostructures are well preserved.
Figure S16. High magnification BF-STEM images of 12 NT after the 20th lithium intercalation cycle at 60 °C. In A), a, b and c compose initial anatase TiO$_2$ crystal. White dotted line guides abrupt crystal interface. c part is missing upon continuous cycling. For comparison, identical image is shown on B) without figure legends.
Figure S17. Cs-corrected BF-STEM images of 12 NT after the 20\textsuperscript{th} lithium intercalation cycle at RT.
Figure S18. XRD patterns of 12 NT before 1st, 10th and 20th lithium intercalation cycle at 60 °C.
Figure S19. XRD patterns of 12 NT before the test and after the 1\textsuperscript{st}, 10\textsuperscript{th} and 20\textsuperscript{th} lithium intercalation cycle at 60 °C.
Figure S20. XRD patterns of 12 NT before the test and after the 1st, 10th and 20th lithium intercalation cycle at RT.
Figure S21. Voltage profiles of 12 NT after (A) 1st, (B) 2nd, (C) 10th and (D) 20th lithium intercalation cycle at 60 °C. The irreversible Li loss accounts 30%, 13%, 8%, and 7% on the 1st, 2nd, 10th, and 20th cycle, respectively.
Figure S22. (A) Voltage profile comparison before and after the battery degradation (90 °C, 100 mA g⁻¹), and (B) voltage profiles of the degraded electrode at different rates (90 °C, 100 mA g⁻¹, 50 mA g⁻¹, 25 mA g⁻¹, and 10 mA g⁻¹). During the battery degradation, significant shortage of voltage plateau at 1.75 V is observed (A). The capacity in the lower voltage slope (region 2) was partially recovered under lower cycling rates, while capacity at 1.75 V plateau remained unchanged (B).