



Chemical Communications

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Supporting Information

Understanding memory effects in Li-ion batteries: evidence of kinetic origin in TiO₂ upon hydrogen annealing

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Experimental Section

Chemicals and thermal treatments

Two types of commercial anatase TiO₂ with a specific surface area of 300 m² g⁻¹ and 95 m² g⁻¹ were used as-received from Sachtleben Chemie (Duisburg, Germany). Annealing was carried out in a horizontal furnace equipped with a quartz tube reactor. Typically, the TiO₂ powder sample (1 g) was heated in a quartz boat at a temperature gradient of 10 °C min⁻¹ till reaching 300 °C under flowing helium (99.999 %, 100 sccm). After reaching the desired temperature, the gas flow was switched to pure hydrogen (99.999 %, 100 sccm) and maintained for 4 or 24 h before cooling down to room temperature.

Structural characterization

XRD studies were performed using a PANalytical MPD diffractometer (the Netherlands), with CuK_α radiation. Static nitrogen physisorption measurements were carried out at 77 K using an Autosorb-1 MP Quantachrome system (USA). Samples were degassed at 200 °C for 2 h before measurements. UV/Vis spectra were recorded in the diffuse reflectance mode using a PerkinElmer Lambda 650 UV/Vis spectrometer (USA), with a Praying-Mantis mirror construction.

Electrochemical characterization

Electrochemical experiments were carried out using three-electrode Swagelok-type cells assembled in an argon-filled glove box. The working electrodes were prepared using the doctor-blade technique. They consisted of the active material (TiO₂), a conductive additive (C65 carbon black, Timcal, Bodio, Switzerland), and a binder (polyvinylidene difluoride, Solef S5130, Solvay, Belgium) in a weight ratio of

75:15:10 pasted on a 12 mm copper disc. The mass loading of the resulting electrode was 1.5-2.0 mg cm⁻². Glass fiber (WhatmanGF/D, Sigma-Aldrich, Germany) filters soaked in LP40 electrolyte (1 M LiPF₆ in ethylene carbonate : diethyl carbonate (1:1), Merck, Germany) were used as separators. Lithium foil (Sigma-Aldrich, Germany) was used as counter and reference electrode. Galvanostatic cycling of the assembled cells was carried out using a Bio-Logic VMP-3 (Bio-Logic SAS, Claix, France) in the potential range of 1.0-3.0 V. All potentials are reported versus the Li/Li⁺ potential in 1 M LiPF₆.

Results and discussion

Structural characterization

XRD patterns of TiO₂_pristine and TiO₂_24h (Figure S1a) revealed only the reflections derived from the anatase phase confirming that no anatase/rutile transformation occurred during the annealing.

UV/Vis spectroscopy has previously been used to confirm the presence of oxygen vacancies.¹⁻³ The reduction of TiO₂ leads to an increase in absorption between 400-2500 nm due to free electrons (a continuum at wavelengths >825 nm), local Ti³⁺ centers (a band at 620 nm), and oxygen vacancies (bands at 1060, 441, and 486 nm).⁴ The UV-Vis spectra of TiO₂_pristine and TiO₂_24h (Figure S1b) shows an increase in the absorbance in the visible range after annealing which confirms the expected introduction of oxygen vacancies.

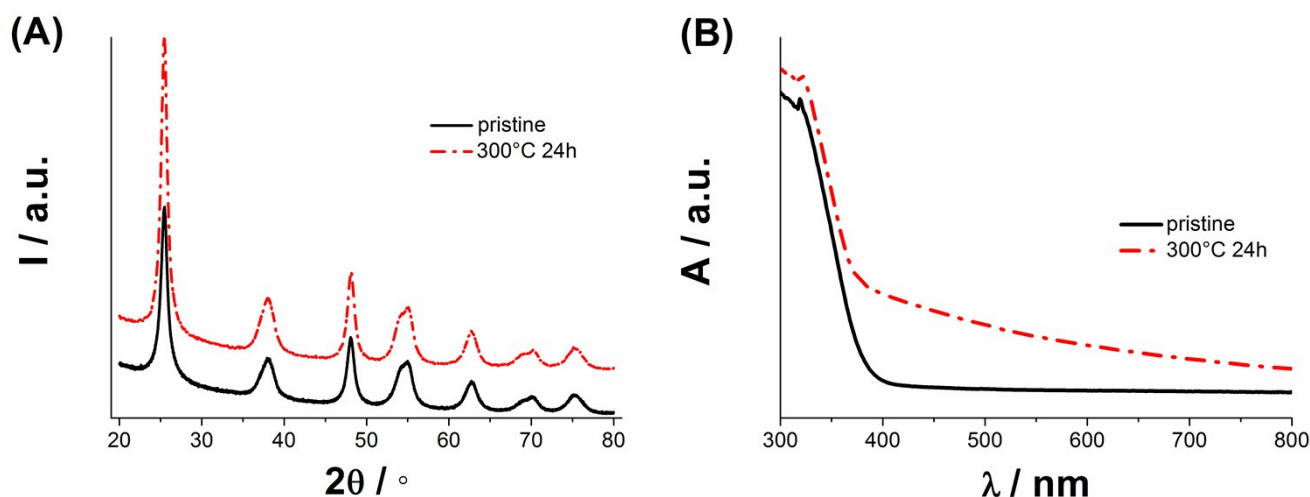


Figure S1. (A) XRD patterns and (B) UV-Vis spectra of TiO₂_pristine and TiO₂_24h

Specific surface area and its effect on specific charge.

The specific surface area (or particle size) is known to influence the specific charge in anatase TiO₂.^{5,6} As the specific surface area decreases, the length of the Li-ion diffusion from the liquid/solid interface to the core of the particle increases and, consequently, the specific charge at high C-rates decreases. According

to the changes in surface area, the specific charge from TiO₂_pristine to TiO₂_4h should slightly decrease and should remain constant from TiO₂_4h to TiO₂_24h. However, this is not the experimental trend (Figure 2). On the other hand, this experimental trend is consistent with expected one for H₂ annealing (oxygen vacancies).⁷ The specific charge increases from TiO₂_pristine to TiO₂_4h due to the increased electric conductivity and decrease for prolonged annealing time (TiO₂_24h) since the decrease in Li-ion mobility outweighs the increase in electric conductivity.⁷ Therefore, the trend observed in the specific charge primary derives from the introduction of oxygen vacancies in TiO₂ upon H₂ annealing, as shown in previous reports.^{1-3,7}

Galvanostatic potential profiles.

Figure S2 shows the potential profiles of all samples from which the magnitude of memory effect and overshoot were estimated.

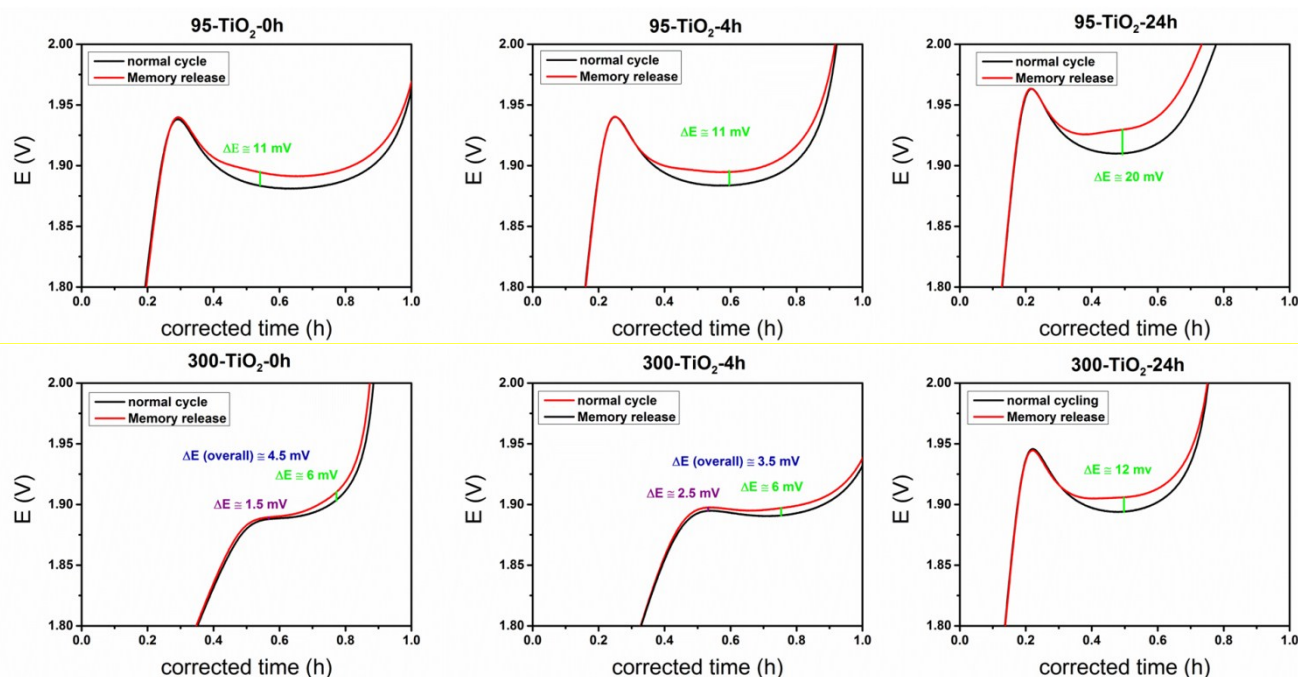


Figure S2. Galvanostatic potential profiles of all evaluated samples.

Magnitude of the overshoot.

The overshoot peak observed in the anodic galvanostatic potential profiles before the phase transformation plateau (Figure 2b in the main text) has been previously correlated with the memory effect.^{8,9} Figure S3 shows the magnitude of the overshoot for the samples. For the sample with smaller particle size (TiO₂_300), a significant increase in the overshoot was observed when the sample was annealed for 24 h which seems to indicate a relationship between Li-ion mobility, overshoot and memory effect: slower mobility leads to an increase in both overshoot and memory effect. However, the

magnitude of the overshoot for the sample with larger particle size (TiO₂_100) remained practically constant at 55 mV. Therefore, this relationship appears to be highly non-linear and it saturates at ca. 55 mV.

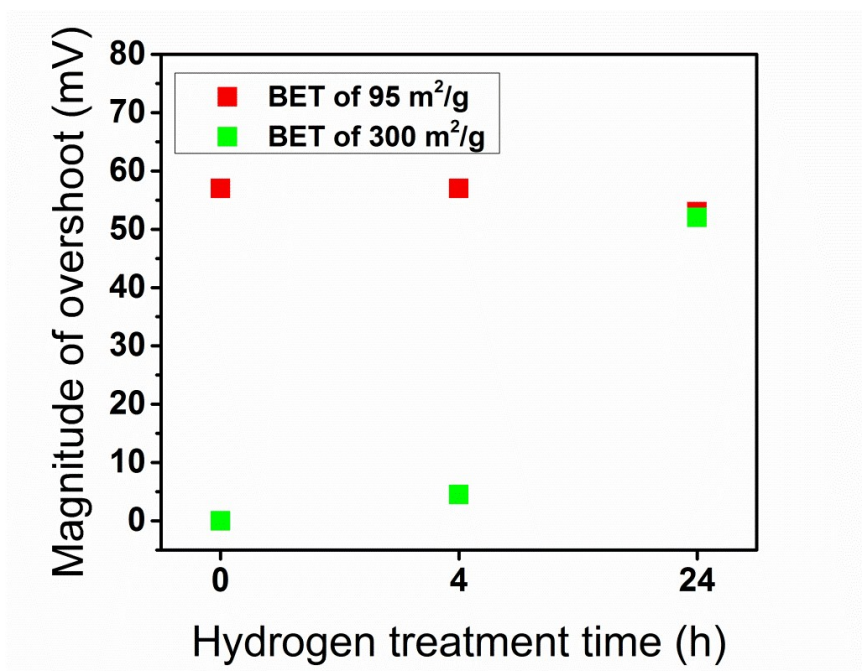


Figure S3. Dependence of the magnitude of the memory effect (MME) on the duration of H₂ annealing time (pristine, 4 h and 24 h) for two commercial TiO₂ samples with 300 m² g⁻¹ in green and with 95 m² g⁻¹ in red.

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