Structure of the Li$_4$Ti$_5$O$_12$ anode during charge-discharge cycling

Wei Kong Pang,$^{1,2}$ Vanessa K. Peterson,$^{1,a}$ Neeraj Sharma,$^3$ Je-Jang Shiu,$^4$ and She-huang Wu$^4$

$^1$Australian Nuclear Science and Technology Organization, Locked Bag 2001, Kirrawee DC, NSW 2232, Australia
$^2$Faculty of Engineering, School of Mechanical, Materials, and Mechatronic Engineering, Institute for Superconducting and Electronic Materials, University of Wollongong, NSW 2522, Australia
$^3$School of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia
$^4$Department of Materials Engineering, Tatung University, No.40, Sec. 3, Zhongshan N. Rd., Taipei City 104, Taiwan

(Received 8 September 2014; accepted 30 September 2014)

The structural evolution of the “zero-strain” Li$_4$Ti$_5$O$_12$ anode within a functioning Li-ion battery during charge–discharge cycling was studied using in situ neutron powder-diffraction, allowing correlation of the anode structure to the measured charge–discharge profile. While the overall lattice response controls the “zero-strain” property, the oxygen atom is the only variable in the atomic structure and responds to the oxidation state of the titanium, resulting in distortion of the TiO$_6$ octahedron and contributing to the anode’s stability upon lithiation/delithiation. Interestingly, the trend of the octahedral distortion on charge–discharge does not reflect that of the lattice parameter, with the latter thought to be influenced by the interplay of lithium location and quantity. Here we report the details of the TiO$_6$ octahedral distortion in terms of the O–Ti–O bond angle that ranges from 83.7(3)$^\circ$ to 85.4(5)$^\circ$. © 2014 International Centre for Diffraction Data.

[doi:10.1017/S0885715614001067]

Key words: Li-ion battery, Li$_4$Ti$_5$O$_12$, neutron diffraction, phase evolution

I. INTRODUCTION

Li-ion batteries (LIBs) have higher-energy density, portable design, and longer lifetime than comparable battery technologies (Tarascon and Armand, 2001). Spinel Li$_4$Ti$_5$O$_12$, a so-called zero-strain insertion material, has been commercialized as an anode material because of its exceptionally high rate performance, excellent cycling stability, and Li-insertion electrochemistry with formal potential of 1.55–1.56 V versus Li$^+$/Li (Ozhuku et al., 1995; Cho et al., 2001; Ronci et al., 2002). Generally speaking, Li-(de)intercalation in Li$_{4z}$Ti$_5$O$_{12}$ ($z = 0–3$) proceeds through a two-phase reaction, as given in Eq. (1), resulting in flat plateaus in the charge and discharge curves.

$$\text{(Li)}^{8x}(\text{Li}_{1/3}\text{Ti}_{5/3})^{16d}\text{O}_{4}^{2e} + x\text{Li}^+ + x\text{e}^- \xrightarrow{\sim 1.55 \text{ V}} (1-x)(\text{Li})^{8x}(\text{Li}_{1/3}\text{Ti}_{5/3})^{16d}\text{O}_{4}^{2e} + x(\text{Li}_2)^{16c}(\text{Li}_{1/3}\text{Ti}_{5/3})^{16d}\text{O}_{4}^{2e}$$

$$\text{(Li)}^{8x}(\text{Li}_{1/3}\text{Ti}_{5/3})^{16d}\text{O}_{4}^{2e} + x\text{Li}^+ + x\text{e}^- \xrightarrow{\sim 1.55 \text{ V}} (1-x)(\text{Li})^{8x}(\text{Li}_{1/3}\text{Ti}_{5/3})^{16d}\text{O}_{4}^{2e} + x(\text{Li}_2)^{16c}(\text{Li}_{1/3}\text{Ti}_{5/3})^{16d}\text{O}_{4}^{2e}$$

(1)

Li-(de)intercalation of Li$_4$Ti$_5$O$_{12}$ is also reported to occur via the following solid-solution reaction [Eq. (2)]:

$$\text{(Li)}^{8x}(\text{Li}_{1/3}\text{Ti}_{5/3})^{16d}\text{O}_{4}^{2e} + x\text{Li}^+ + x\text{e}^- \xrightarrow{\sim 1.55 \text{ V}} (\text{Li}_{1-x})^{8a}(\text{Li}_{1/3}\text{Ti}_{5/3})^{16d}\text{O}_{4}^{2e}$$

(2)

where $z, y \leq 1$.

The phase transition between Li$_4$Ti$_5$O$_{12}$ and Li$_{4z}$Ti$_5$O$_{12}$ (Li$_{4z}$Ti$_5$O$_{12}$ in the two-phase mechanism), as outlined in Eqs. (1)–(2), involves a $<0.1\%$ change in the lattice volume. The Li accommodated by the anode results in changes to the Ti oxidation state, affecting the structure of the TiO$_6$ octahedral framework (Figure 1).

Given that the underlying mechanism of the phase transitions upon lithiation remains controversial and, importantly, may control the performance of the Li$_4$Ti$_5$O$_{12}$ anodes, we have studied the Li$_{4z}$Ti$_5$O$_{12}$ structure in detail during battery cycling. Neutron powder-diffraction (NPD) data were collected during the non-equilibrium charge and discharge of a LiFePO$_4$//Li$_4$Ti$_5$O$_{12}$ battery within the 1.0–3.0 V window (versus Li$_4$Ti$_5$O$_{12}$). While the details of the Li diffusion within the Li$_{4z}$Ti$_5$O$_{12}$ structure is thought to control the lattice response and is discussed in detail elsewhere in work focusing on particle-size differences (Pang et al., 2014a), here we focus on the structural details and distortion of the TiO$_6$ octahedron. In this work, we extract and discuss the Ti–O bond length and O–Ti–O angle that dictate the size of the TiO$_6$ unit and assist in maintaining the stability of the anode during lithiation and delithiation.

---

$^a$Author to whom correspondence should be addressed. Electronic mail: vanessa.peterson@ansto.gov.au
II. EXPERIMENTAL

A. Preparation

LiFePO₄ cathode powder was provided by Tatung Fine Chemicals Co., Taiwan. Li₄Ti₅O₁₂ anode powder was prepared via a sol–gel method using Li acetate (98%, Acros) and titanium butoxide (98.0%, Acros). The stoichiometrically mixed powders were dissolved in an adequate amount of ethanol (99.5%, Shimakyu) and the solution aged for 3 h to form a white-colored gel. The resulting gel was heated at 80 °C to yield an organic precursor with a fine, white powder-product obtained by heat-treating in air at 800 °C for 4 h.

A purpose designed LiFePO₄||Li₄Ti₅O₁₂ pouch-type battery (Figure 2) was used in the collection of in situ NPD data. The LiFePO₄ cathode was prepared by casting a slurry of the active materials (80 wt%), acetylene black (10 wt%), and polyvinylidene difluoride (PVDF) binder (10 wt%) onto an Al foil. The Li₄Ti₅O₁₂ anode was prepared using the same procedure, but with Li₄Ti₅O₁₂ powder as the active material. The loading ratio between the anode and cathode was designed to be ~4:6 by weight. The electrodes were cut into 1 × 4 cm strips. Immobilon-P PVDF membrane (Millipore) was used as a separator because of its lower hydrogen content relative to the conventionally used the Celgard membrane, where the strong incoherent neutron-scattering of hydrogen is detrimental to the NPD signal. The LiFePO₄||Li₄Ti₅O₁₂ battery was prepared by stacking 30 anode/septor/cathode assemblies with a parallel connection. The stack was placed in an Ar-filled glove box for 24 h and then wrapped in a polypropylene-coated Al foil to form a pouch. Prior to the in situ NPD experiment, deuterated electrolyte-solution (1 M lithium hexafluorophosphate (99.99%, Sigma-Aldrich) in a 1:1 volume ratio of deuterated dimethyl carbonate (99.5%, Novachem) to deuterated ethylene carbonate (98%, Novachem) was injected into the pouch, which was heat-sealed under Ar. After 1 day of wetting, the battery was used in the in situ NPD experiment. During the in situ NPD experiment the pouch-type battery was cycled galvanostatically using a potentiostat/galvanostat (Autolab PG302N) at currents of 11 mA (theoretically equivalent to 0.1 °C) for 1 cycle between 1.0 and 3.0 V (versus Li₄Ti₅O₁₂).

B. Data collection and analysis

High-resolution NPD data of the as-prepared Li₄Ti₅O₁₂ sample were collected using ECHIDNA, the high-resolution neutron powder-diffraotmeter at the Open Pool Australian Light-water (OPAL) research reactor at the Australian Nuclear Science and Technology Organisation (ANSTO; Liss et al., 2006). The neutron beam wavelength was 1.6214 Å, determined using the La11B6 NIST standard reference material 660b. NPD data were obtained in the 2θ angular range 4°–164° with a step size of 0.125°. Rietica ver. 1.77 (Hunter, 1998) was used to perform Rietveld analysis of the high-resolution NPD data. The refinable parameters included the background coefficients, zero-shift, peak shape parameters, lattice parameters, O positional parameter, and isotropic atomic displacement parameters. Micrographs of the as-prepared Li₄Ti₅O₁₂ were collected using field-emission scanning electron microscopy (SEM) with a SU8000.
Figure 3. (Color online) Waterfall plot (left) of a collection of NPD patterns shown for a restricted 2θ range taken during battery charge and discharge. Labels are phase reflections for LiFePO$_4$ (LFP), FePO$_4$ (FP), Li$_4$Ti$_5$O$_{12}$ (LTO), and Al. A typical Rietveld-refinement profile before cycling (right) is also shown. The figures-of-merit for the refinements were in the range $\chi^2 = 3.9 - 8.95$, $R_{wp} = 14.3 - 17.1$, and $R_B = 1.0 - 3.9\%$.

Figure 4. (Color online) (a) Charge–discharge profile, (b) refined anode lattice-parameter, (c) refined oxygen positional-parameter, (d) $\alpha$ bond-angle, and (e) Ti–O bond length, during battery charge and discharge. The titanium oxidation-state in (f) is estimated using the approximate BVS method.
continuously covers 120° in 2θ and has a relatively intense neutron beam, allowing the rapid collection of data. A neutron beam wavelength of 2.9592(2) Å was used, determined using the La$^{11}$B$_6$ NIST standard reference material 660b. The diffractograms were obtained with an exposure time of 5 min in the angular range 16.1–136.9° in 2θ during the charge-discharge cycling of the batteries. Sequential Rietveld refinements were carried out using the NPD data using Fullprof with visualization in WinplotR (Rodríguez-Carvajal, 1993; Roisnel and Rodriguez-Carvajal, 2000). The refinements were performed using data in the range 60–120° in 2θ.

III. RESULTS AND DISCUSSION

A. Crystallography and microstructure of the Li$_4$Ti$_5$O$_12$ anode

Using high-resolution NPD data, the crystallographic details of the anode was established. As reported by Pang et al. (2014a), the anode adopts Fd$ar{3}$m space-group symmetry, with a minor amount [1.9(3) wt%] of monoclinic Li$_2$TiO$_3$. The crystallographic details are summarized in Pang et al. (2014a). The as-prepared anode particles are cube-like with an average particle-size of ~200 nm.

B. In situ NPD

In situ NPD data of the battery are shown in Figure 3. In the absence of peak splitting in the NPD pattern for the cathode, we modeled the anode lattice evolution as single-phase Li$_{1+x}$Ti$_5$O$_{12}$ (solid-solution reaction) after Wagemaker et al. (2006), the details of which are presented in Pang et al. (2014a). The two-phase reaction between LiFePO$_4$ and FePO$_4$ in cathode is also observed in Figure 3.

To effectively refine the O positional parameter, it was necessary to fix the Li occupancy at 8a and 16c sites in the sequential Rietveld refinement, as per previous work (Pang et al., 2014a, 2014b). Figure 4 summarizes the lattice and crystallographic changes occurring during battery cycling, including the variation of lattice parameter, O positional parameter, O–Ti–O bond angle ($\alpha$), Ti–O bond length, and the estimated Ti oxidation state. During charge, the anode lithiates and the lattice undergoes rapid expansion, followed by a gradual contraction. The non-linearity in the lattice response is attributed to the interplay of the amount and site of Li insertion (Sharma et al., 2013; Pang et al., 2014a), with the population of Li at the two crystallographic sites (i.e., 8a and 16c) having a different effect on the lattice. Interestingly, these lattice changes are not reflected in the trend of TiO$_6$ octahedral distortion, with no measurable distortion occurring during the initial lattice-expansion. We find that the gradual lattice-contraction, associated with population of Li at the 16c site in the anode (Pang et al., 2014a), is strongly correlated to the trend of the TiO$_6$ distortion. The repositioning of the O atom in response to lithiation at the 16c site is important in maintaining the stability of the anode, and reflects the trend in the estimated oxidation-state of the Ti. As shown in Figure 4, during battery charge the O atom moves further away from the Ti atom, at (0.5, 0.5, 0.5), resulting in an increase in the length of the O–Ti–O bond that occurs alongside a decrease in the average Ti valence as estimated by the bond-valence summation (BVS) method (Brown and Altermatt, 1985). We note that the BVS method will yield an approximate Ti valence as the Ti shares the 16d site with Li. The ideal Ti$^{+4}$–O$^{2-}$ bond-length of 1.815 Å and an empirical constant of 0.37 Å (Brown et al., 1985) are used in this estimation. The bond angle or $\alpha$ also varies with the oxygen positional-parameter, characterizing the distortion of the TiO$_6$ octahedron (Figure 5). The TiO$_6$ octahedron deformation and distortion result in a stable structure during the lithiation and delithiation processes. Alongside the Li repositioning, it is the oxygen positional-parameter changes during battery charge and discharge that completes the picture of the Li$_4$Ti$_5$O$_{12}$ structural response and anode function.

IV. CONCLUSION

We have successfully monitored the crystallographic change in the Li$_{4+z}$Ti$_5$O$_{12}$ anode within in a battery during charge and discharge. We report the details of the change to the TiO$_6$ structural unit occurring during Li diffusion that contributes to the structural stability of this “zero strain” anode. We find that while the initial expansion of the lattice upon lithiation is not reflected in the trend of TiO$_6$ octahedral distortion, the gradual lattice-contraction experienced during further lithiation is strongly correlated to the trend of the TiO$_6$ distortion, and associated with the repopulation of Li at the 16c site in the anode.

ACKNOWLEDGEMENTS

The authors acknowledge the travel support funded by National Synchrotron Radiation Research Center (2013-3-100-1). The research was supported by the Australian Nuclear Science and Technology Organization’s (ANSTO) Energy Materials project. The authors are also grateful to Professor Lin, Jeng-Yu of Tatung University for providing Li$_4$Ti$_5$O$_{12}$.
sample, Tatung Fine Chemicals Co., Taiwan for providing LiFePO₄ sample, and the staff members at the Bragg Institute, ANSTO for their operations support.


