Variation in Surface Energy and Reduction Drive of a Metal Oxide Lithium-Ion Anode with Stoichiometry: A DFT Study of Lithium Titanate Spinel Surfaces — Supporting Information

Benjamin J. Morgan,*,† Javier Carrasco,*,‡ and Gilberto Teobaldi*,¶

†*Department of Chemistry, The University of Bath, Claverton Down, Bath, BA2 7AY*

‡*CIC Energigune, Albert Einstein 48, 01510 Miñano, Álava, Spain*

¶*Stephenson Institute for Renewable Energy, Department of Chemistry, The University of Liverpool, Liverpool, L69 3BX*

E-mail: b.j.morgan@bath.ac.uk; jcarrasco@cicenergigune.com; g.teobaldi@liverpool.ac.uk

Supplementary Information

The surface models used in this study were constructed from the bulk $Li_4Ti_5O_{12}$ structure proposed by Lu *et al.*[1] These authors considered a simple hexagonal $Li_8Ti_{10}O_{24}$ cell and optimised the Li/Ti configuration across the 16d sites. In the lowest energy structure for this 42 atom cell the 16d lithium ions maximise their mutual separation, to give the 16d cation distribution in **??**. Using these small calculation cells enforces Li/Ti ordering in the close-packed (111) planes. Experimental X-ray diffraction data obtained by Kataoka *et al.* however, when refined using the $Fd\bar{3}m$ space group, do not indicate any Li/Ti ordering over the 16d sites, and these cations are often considered fully disordered in $Li_4Ti_5O_{12}$.[2] It is therefore necessary to examine the stability of the ordered structure proposed by Lu

et al. in a larger supercell versus cation-disordered alternatives. To this end, we performed calculations on $2\times2\times1$ hexagonal supercells (168 atoms) for the structure identified by Lu *et al.* and for 20 cells with random 16d Li/Ti configurations. Large [001]-aligned supercells have previously been modelled by Ouyang *et al.*,[3] Tanaka *et al.*,[4,5] and Weber *et al.*[6] Ouyang *et al.* considered the lowest energy configurations of cubic $Li_{10}Ti_{14}O_{32}$ and $Li_{11}Ti_{13}O_{32}$ cells, which were then combined to give a composite $Li_{32}Ti_{40}O_{96}$ supercell,[3] and this same approach was subsequently used by Tanaka *et al.*[4] Weber *et al.* generated four random 16d Li/Ti distributions, and selected the lowest energy of these for their subsequent calculations.[6] We have included the structures reported by Ouyang *et al.* and Weber *et al.*[7] in our set of calculations.

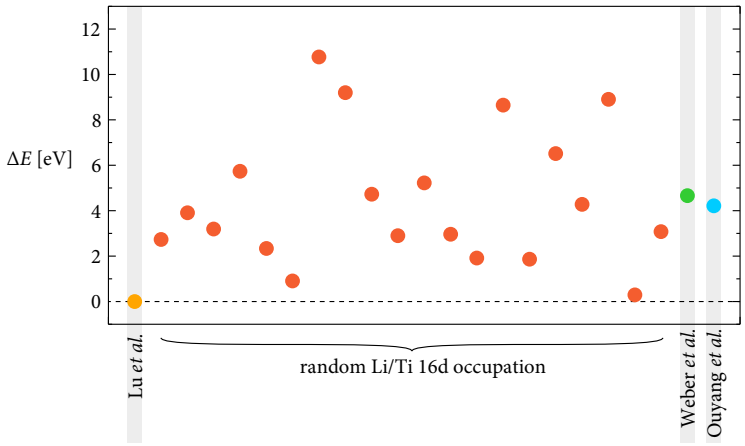

Figure S1: Relative energies for 168 atom $Li_4Ti_5O_{12}$ supercells with various Li/Ti 16d distributions. The lowest energy structure considered is that proposed by Lu *et al.*,[8] which is used as the energy zero here. We also consider 20 random Li/Ti 16d configurations in equivalent hexagonal $2\times2\times1$ supercells, and the cubic supercells described by Weber *et al.*[6] and by Ouyang *et al.*[3]

For the supercell configurations considered, the ordered hexagonal cell proposed by Lu *et al.* is most stable. In real systems configurational and thermal entropy are expected to introduce some site disorder, and the hexagonal cell of Lu *et al.* used in our calculations therefore represents an idealised structure. Providing the degree of cation disorder is small, however, we can still expect significant differences in the stability and electrostatic properties

of (111) surfaces with different terminating planes, with the variations described by our calculations showing the magnitude of these differences in the low temperature limit of low cation disorder.

References

(1) Lu, X. et al. Lithium Storage in $Li_4Ti_5O_{12}$ Spinel: The Full Static Picture from Electron Microscopy. *Adv. Mater.* **2012**, *24*, 3233–3238.

(2) Kitta, M.; Matsuda, T.; Maeda, Y.; Akita, T.; Tanaka, S.; Kido, Y.; Kohyama, M. Atomistic structure of a spinel $Li_4Ti_5O_{12}(111)$ surface elucidated by scanning tunneling microscopy and medium energy ion scattering spectrometry. *Surf. Sci.* **2014**, *619*, 5–9.

(3) Ouyang, C. Y.; Zhong, Z. Y.; Lei, M. S. Ab Initio Studies of Structural and Electronic Properties of $Li_4Ti_5O_{12}$ Spinel. *Electrochem Comm.* **2007**, *9*, 1107–1112.

(4) Tanaka, S.; Kitta, M.; Tamura, T.; Akita, T.; Maeda, Y.; Kohyama, M. First-Principles Calculations of O-*K* ELNES/XANES of Lithium Titanate. *J. Phys. D* **2012**, *45*, 494004–5.

(5) Tanaka, S.; Kitta, M.; Tamura, T.; Maeda, Y.; Akita, T.; Kohyama, M. Atomic and electronic structures of $Li_4Ti_5O_{12}/Li_7Ti_5O_{12}$ (001) interfaces by first-principles calculations. *J. Mater. Sci.* **2014**, *49*, 4032–4037.

(6) Weber, V.; Laino, T.; Curioni, A.; Eckl, T.; Engel, C.; Kasemchainan, J.; Salingue, N. Computational Study of Lithium Titanate as a Possible Cathode Material for Solid-State Lithium–Sulfur Batteries. *J. Phys. Chem. C* **2015**, *119*, 9681–9691.

(7) Laino, T. personal communication.

(8) Lu, X.; Gu, L.; Hu, Y.-S.; Chiu, H.-C.; Li, H.; Demopoulos, G. P.; Chen, L. New Insight

into the Atomic-Scale Bulk and Surface Structure Evolution of $Li_4Ti_5O_{12}$ Anode. *J. Am. Chem. Soc.* **2015**, *137*, 1581–1586.