Supplementary Information

The surface models used in this study were constructed from the bulk Li$_4$Ti$_5$O$_{12}$ structure proposed by Lu et al.[1] These authors considered a simple hexagonal Li$_8$Ti$_{10}$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$_4$Ti$_5$O$_{12}$.[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 $2 \times 2 \times 1$ 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. Tanaka et al. and Weber et al. 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, and this same approach was subsequently used by Tanaka et al. Weber et al. generated four random 16d Li/Ti distributions, and selected the lowest energy of these for their subsequent calculations. We have included the structures reported by Ouyang et al. and Weber et al. in our set of calculations.

Figure S1: Relative energies for 168 atom Li$_4$Ti$_5$O$_{12}$ supercells with various Li/Ti 16d distributions. The lowest energy structure considered is that proposed by Lu et al., which is used as the energy zero here. We also consider 20 random Li/Ti 16d configurations in equivalent hexagonal $2 \times 2 \times 1$ supercells, and the cubic supercells described by Weber et al. and by Ouyang et al.

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


(7) Laino, T. personal communication.