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

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

Abstract

$Li_4Ti_5O_{12}$ is a "zero-strain" lithium-ion anode material that shows excellent stability over repeated lithium insertion–extraction cycles. Although lithium (de)intercalation in the bulk material has been well characterised, our understanding of surface atomic-scale–structure and the relationship with electrochemical behaviour is incomplete. To address this, we have modelled the $Li_4Ti_5O_{12}$ (111) , $Li_7Ti_5O_{12}$ (111) and α-Li_2TiO_3 (100), (110), and (111) α-Li_2TiO_3 surfaces using Hubbard-corrected density-functional theory (GGA+U), screening more than 600 stoichiometric $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$ (111) surfaces. For $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$ we find Li-terminated surfaces are more stable than mixed Li/Ti-terminated surfaces, which typically reconstruct. For α-Li_2TiO_3, the (100) surface energy is significantly lower than for the (110) and (111)

surfaces, and is competitive with the pristine $Li_7Ti_5O_{12}$ (111) surface. Using these stoichiometric surfaces as reference, we also model variation in Li surface coverage as a function of lithium chemical potential. For $Li_4Ti_5O_{12}$, the stoichiometric surface is most stable across the full chemical potential range of thermodymamic stability, whereas for $Li_7Ti_5O_{12}$, Li deficient surfaces are stablised at low Li chemical potentials. The highest occupied electronic state for $Li_7Ti_5O_{12}$ (111) is 2.56 eV below the vacuum energy. This is 0.3 eV smaller than the work function for metallic lithium, indicating an extreme thermodynamic drive for reduction. In contrast, the highest occupied state for the α-Li_2TiO_3 (100) surface is 4.71 eV below the vacuum level, indicating a substantially lower reduction drive. This result demonstrates how stoichiometry can strongly affect the thermodynamic drive for reduction at metal-oxide–electrode surfaces. In this context, we conclude by discussing the design of highly-reducible metal-oxide electrode coatings, with the potential for controlled solid-electrolyte–interphase formation via equilibrium chemistry, by electrode wetting in the absence of any applied bias.

Methods

Calculations were performed using the DFT code VASP,[1,2] with valence electrons described within a plane-wave basis and an energy cutoff of 500 eV. Valence–core interactions were treated with the projector augmented wave (PAW) method,[3,4] with cores of [Mg] for Ti, [He] for O, and [He] for Li. Calculations were performed using the PBE generalised gradient approximation (GGA) functional,[5] supplemented with a Dudarev $+U$ correction applied to the Ti d states (GGA+U). The previous study of Lu *et al.* presented EELS data for $Li_7Ti_5O_{12}$ that showed distinct "Ti^{3+}" and "Ti^{4+}" oxidation states,[6] alongside DFT calculations using both standard GGA (PBE), and GGA+U (PBE+U) functionals. These GGA calculations qualitatively failed to describe the distinct Ti oxidation states observed in the EELS spectra. This is due to the self-interaction error inherent to standard GGA (and LDA) functionals,[7–9] and similar behaviour is well known for many transition metal oxides with mixed formal

oxidation states.[10–12] By applying a $+U$ correction of $U = 4.5\,\mathrm{eV}$ to the Ti d states, Lu *et al.* predicted charge disproportionation into distinct "Ti^{3+}" and "Ti^{4+}" oxidation states, recovering qualitative agreement with the experimental EELS data. We use this same value of $U_{\mathrm{Ti}^d} = 4.5\,\mathrm{eV}$, noting this is close to the value of $U_{\mathrm{Ti}^d} = 4.2\,\mathrm{eV}$ used previously to study partially reduced TiO_2.[13,13,14]

To obtain equilibrium structures and reference energies for bulk $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$, full geometry optimisations were performed for hexagonal cells with compositions $Li_8Ti_{10}O_{24}$ and $Li_{14}Ti_{10}O_{24}$ respectively, oriented with the close-packed (111) layers perpendicular to the c axis. k-point sampling used a $3\times3\times2$ Monkhorst-Pack mesh. Bulk α-Li_2TiO_3 was modelled using $3\sqrt{2}\times3\sqrt{2}\times3$ supercells of $Li_{24}Ti_{12}O_{36}$, with a $2 \times 3 \times 2$ Monkhorst-Pack mesh. All calculations were spin-polarised. Structures were deemed converged when all atomic forces were smaller than $0.01\,\mathrm{eV\,Å^{-1}}$. For each structure zero-pressure volumes were obtained by performing a series of constant-volume cell relaxations and fitting the resultant energy–volume data to the Murnaghan equation of state. The optimised bulk structures were used as starting points for the surface models. For all surface models, to minimise spurious slab–slab interactions a vacuum gap of at least 15 Å was placed between slab periodic images along the c direction normal to the surface plane. The reference energy for metallic lithium, used to calculate surface energies as a function of the lithium chemical potential, was calculated using a body-centered cubic 2-atom unit cell with a $16 \times 16 \times 16$ Monkhorst-Pack k-point mesh.

Acknowledgements

Support from the EU FP7 program SIRBATT (contract No. 608502) is gratefully acknowledged. B. J. M. acknowledges support from the Royal Society (UF130329), and from EPSRC grant EP/N004302/1. J. C. is supported by the MiNECO through a Ramón y Cajal Fellowship and acknowledges support by the Marie Curie Career Integration Grant FP7-PEOPLE-

2011-CiG: Project NanoWGS and the Royal Society through the Newton Alumnus scheme. G. T. is supported by EPSRC-UK (EP/I004483/1).

References

(1) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54*, 11169–11186.

(2) Kresse, G.; Furthmuller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors using a Plane-Wave Basis Set. *Comp. Mater. Sci.* **1996**, *6*, 15–50.

(3) Blöchl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, *50*, 17953–17979.

(4) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, *59*, 1758–1775.

(5) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(6) 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.

(7) Pacchioni, G.; Frigoli, F.; Ricci, D.; Weil, J. A. Theoretical Description of Hole Localization in a Quartz Al Center: The importance of Exact Electron Exchange. *Phys. Rev. B* **2000**, *63*, 054102.

(8) Zhou, F.; Cococcioni, M.; Marianetti, C. A.; Morgan, D.; Ceder, G. First-Principles Prediction of Redox Potentials in Transition-Metal Compounds with LDA+U. *Phys. Rev. B* **2004**, *70*, 235121.

(9) Mori-Sánchez, P.; Cohen, A. J.; Yang, W. Localization and Delocalization Errors in Density Functional Theory and Implications for Band-Gap Correction. *Phys. Rev. Lett.* **2008**, *100*, 146401.

(10) Allen, J. P.; Scanlon, D. O.; Watson, G. W. Electronic Structure of Mixed-Valence Silver Oxide AgO from Hybrid Density-Functional Theory. *Phys. Rev. Lett.* **2010**, *81*, 161103.

(11) Chen, J.; Wu, X.; Selloni, A. Electronic structure and bonding properties of cobalt oxide in the spinel structure. *Phys. Rev. B* **2011**, *83*, 245204.

(12) Padilha, A. C. M.; Osorio-Guillén, J. M.; Rocha, A. R.; Dalpian, G. M. Ti_nO_{2n-1} Magnéli Phases Studied using Density Functional Theory. *Phys. Rev. B* **2014**, *90*, 035213.

(13) Morgan, B. J.; Watson, G. W. Intrinsic n-Type Defect Formation in TiO_2: A Comparison of Rutile and Anatase from GGA+U Calculations. *J. Phys. Chem. C* **2010**, *114*, 2321–2328.

(14) Morgan, B. J.; Watson, G. W. Polaronic Trapping of Electrons and Holes in Anatase TiO_2. *Phys. Rev. B* **2009**, *80*, 233102.