**(Sub)surface Promoted Disproportionation and Absolute Band Alignment in High-Power LiMn**2**O**4 **Cathodes**

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**Abstract**

We present an isotropic (Ueff) and anisotropic (U-J) Hubbard and van der Waals (vdW) corrected Density Functional Theory study of bulk and low-index surfaces of lithium manganese oxide LiMn2O4 (LMO), a promising cathode material for high-power Li-ion batteries. Use of anisotropic (U-J) corrections in the simulation of bulk LMO leads to improved agreement with available experimental data, whereas vdW corrections do not affect the results. Carefully converged relaxation of slab geometries indicates that, when vdW-corrections are included, the spinel reconstructed Literminated (111) surface is always energetically favored for both Ueff and (U-J) methods, regardless of the LMO phase. In contrast, neglect of vdW corrections leads to the (001) surface in orthorhombic phase being favored when applying (U-J) corrections. Independently of the simulation protocol and crystalline phase, (111) truncation, reconstructed or not, promotes LMO disproportionation and appearance of Mn+2 cations, without the need of any chemical or electrochemical surface treatment. Absolute band-alignment of the considered surfaces reveals increased reductive propensity for the (111) terminations. Finally, our computational findings are discussed with respect to available data on the observed surface dependence of Mn disproportionation and electrochemical passivation of LMO substrates.

Keywords: Lithium-ion batteries, Lithium Manganese Oxide, Disproportionation, Hubbard corrected Density Functional Theory, Electronic Structure

**1. README for the data catalogue**

This archive contains open-data for "(Sub)surface Promoted Disproportionation and Absolute Band Alignment in High-Power LiMn2O4 Cathodes" by Scivetti, Ivan; Teobaldi, Gilberto. To be published in the Journal of Physics Chemistry C.

The open data is organized as follows

==== Figure\*.agr
xmgrace files and raw data of the figures in the paper

==== Figure-S\*.agr
xmgrace files and raw data of the figures in the supporting information

Description of the Methods used to generate the data follows in Section 2.

**2. Methods**

All the calculations in this work were spin-polarized and performed using the DFT+U approach50-54 together with periodic boundary conditions (PBCs) and the projector augmented wave method, 58 as implemented in the VASP code.59-61 Following previous work,41 the electronic exchange-correlation was treated according to the GGA-PW91 approximation62 and the interpolation formula of Vosko et. al.63 We considered two different DFT+U alternatives: i) the “fully anisotropic” approach where both Coulomb and exchange terms (U and J, respectively) are matrices that account for the spatial anisotropy of the d-orbitals, and ii) the effective U approach (Ueff), where U is spherically averaged and J is set to zero.52 In principle, the fully anisotropic scheme (U-J from now on) is a more accurate approximation for the description of the d-orbitals and has been successfully applied to β-MnO2 to correct the limitations of the Ueff approach.56 However, the improvement in accuracy is governed by the accuracy of the *U* and *J* parameters. Following previous work,44,45,64 we set Ueff=5.0 eV and, under the assumption that the Slater integrals *F*2 and *F*4 are weakly screened in crystals, we chose J=1.2 eV, which corresponds to the computed value for Mn+4 in the atomic-limit.65 Accordingly, in order to compare both DFT+U methods, the value of U for the (U-J) case was set to 6.2 eV.

For easier comparison with previous results,42,45 we used cubic and tetragonal supercells containing eight formula units of LMO for bulk simulations. For the simulation of surfaces we used the slabs approximation and tested the smallest thickness required to converge surface energies (see below). A vacuum separation of 10 Å was used to avoid spurious interactions between opposite surfaces of the PBC-replicated slabs.

As discussed elsewhere,44-46 the low-index surfaces of LMO are polar and possess a net dipole moment. Due to the use of PBCs, such a dipole introduces undesirable artificial electrostatic interactions between the infinite replicas of the simulation cell, causing the energy of the system to diverge with the thickness of the slab. This severe drawback can be remedied by using either surface defects or reconstructions to cancel out the dipole moment.66,67 For simplicity and sake of comparison with previous results, 44-46 we applied the method of Tasker68 and only considered stoichiometric slabs, cancelling the slab dipole moment by transferring atoms between the two opposite surfaces. This procedure and its application to LMO slabs has been thoroughly described previously.44-46

We used a plane-wave energy cutoff of 550 eV. For the Brillouin zone sampling of bulk calculations, we set 3x3x3 k-points within the Monkhorst-Pack scheme,69 whereas for slabs calculations we sampled the 2D Brillouin zone with 3x3 and 2x4 k-point grids for the (001) and the (111) surfaces, respectively. These parameters were checked to lead to values of total energy and magnetic moments converged within 5 meV and 0.02 µB, respectively.

Given the far from immediate link between atom-partitioned (projected) charges and oxidation states for transition metal elements in oxides,70,71 and following previous work,46 Mn+4, Mn+3 and Mn+2 sites where identified on the basis of the computed atomic magnetic moments, whose magnitudes depend on the adopted DFT+U method, as well as the crystalline phase and overall magnetic ordering. The range of computed magnetic moments of Mn+4 and Mn+3 in bulk are 3.03─3.40 µB and 3.88­─4.00 µB, respectively. For surfaces, in contrast, we obtain 2.98─3.50 µB, 3.77─4.03 µB and 4.55─4.60 µB for Mn+4, Mn+3 and Mn+2, respectively. The computed surface-enhancement of Mn atomic moment is in line with previous results in Ref. 46. We recall that computed magnetic moments for the Mn atoms [as well as DFT+Ueff (U-J) total energy] depend on both the value of Ueff (U-J) and the choice of the DFT+Ueff (U-J) projectors.72

Finally, for consistency with future simulations of LMO interfaces with the electrolyte, we also investigated the effects of including and neglecting dispersion interactions. To this purpose, we used the van der Waals corrected (DFT-vdW) formalism and parameterization proposed by S. Grimme57 that account for vdW interactions via element-specific semi-empirical pair potentials and a global scale factor (S6), that in turn depends on the adopted approximation to the exchange-correlation potential. Here, we used the recommended S6 value of 0.7 for the PW91 exchange-correlation functional.57

**References**

(41) Ouyang C. Y.; Shi, S. Q.; Lei, M. S. Jahn-Teller Distortion and Electronic Structure of LiMn2O4. *J. Alloys Compd.* **2009**, *474*, 370–374.

(42) Hoang, K. Understanding the Electronic and Ionic Conduction and Lithium Over-Stoichiometry in LiMn2O4 Spinel. *J. Mater. Chem. A* **2014**, *2*, 18271–18280.

(44) Nakayama M.; Hiroyuki T.; Nakamura T.; Tokuda S.; Jalem R.; Kasuga, T. ; Combined

Computational and Experimental Study of Li Exchange Reaction at the Surface of Spinel LiMn2O4 as a Rechargeable Li-Ion Battery Cathode. *J. Phys. Chem. C* **2014**, *118*, 27245–27251.

(45) Karim, A.; Fosse, S.; Persson, K. A. Surface Structure and Equilibrium Particle Shape of the LiMn2O4 Spinel from First-Principles Calculations. *Phys. Rev. B* **2013**, *87*, 075322.

(46) Benedek, R.; Thackeray, M. M. Simulation of the Surface Structure of Lithium Manganese

Oxide Spinel. *Phys. Rev. B* **2011**, *83*, 195439.

(50) Anisimov, V. I.; Zaanen, J.; Andersen, O. K. Band Theory and Mott Insulators: Hubbard U instead of Stoner I. *Phys. Rev. B* **1991**, *44*, 943–954.

(51) Anisimov, V. I. ; Solovyev, I. V.; Korotin, M. A.; Czyzyk, M. T. ; Sawatzky, G. A. Density-Functional Theory and NiO Photoemission Spectra. *Phys. Rev. B* **1993**, *48*, 16929–16934.

(52) Dudarev, S. L.; Botton, G. A.; Savrasov, S. Y. ; Humphreys, C. J.; Sutton, A. P. Electron-Energy-Loss Spectra and the Structural Stability of Nickel Oxide: An LSDA+U Study. *Phys. Rev. B* **1998**, *57*, 1505–1509.

(53) Cococcioni, M. ; de Gironcoli, S. Linear Response Approach to the Calculation of the Effective Interaction Parameters in the LDA+U Method. *Phys. Rev. B* **2005**, *71*, 035105.

(54) B. Himmetoglu, B. ; Floris, A.; de Gironcoli, S.; Cococcioni, M. Hubbard-Corrected DFT Energy Functionals: The LDA+U Description of Correlated Systems. *Int. J.Quantum Chem.* **2014**, *114*, 14–49.

(55) O’Regan, D. D. ; M. Hine, N. D.; Payne, M. C.; Mostofi, A. A. Linear-Scaling DFT+U with Full Local Orbital Optimization. *Phys. Rev. B* **2012**, *85*, 085107.

(56) Tompsett, D. A.; Middlemiss, D. S.; Islam, M. S. Importance of Anisotropic Coulomb Interactions and Exchange to the Band Gap and Antiferromagnetism of β-MnO2 from DFT+U. *Phys. Rev. B* **2012**, *86*, 205126.

(57) Grimme, S. Semiempirical GGA-type Density Functional Constructed with a Long-Range Dispersion Correction. *J. Comp. Chem.* **2006**, *27*, 1787–1799.

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

(59) Kresse, G.; Furthmuller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals

and Semiconductors Using a Plane-Wave Basis Set. *Comput. Mater. Sci.* **1996**, *6*, 15–50.

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

(61) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmentedwave

Method. *Phys. Rev. B* **1999**, *59*, 1758–1775.

(62) Wang, Y. ; Perdew, J. P. Correlation Hole of the Spin-Polarized Electron Gas, with

Exact Small-wave-vector and High-Density Scaling. *Phys. Rev. B* **1991**, *44*, 13298–13307.

(63) Vosko, S. H. ; Wilk, L.; Nusair M. Accurate Spin-Dependent Electron Liquid Correlation

Energies for Local Spin Density Calculations: a Critical Analysis. *Can. J. Phys.* **1980**, *58*, 1200–1211.

(64) 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.

(65) Madsen, G. ; Novak, P. Charge Order in Magnetite. An LDA+U Study. *Europhys. Lett.* **2005**, *69*, 777–783.

(66) Noguera, C. Polar Oxide Surfaces. *J. Phys. Condens. Matter* **2000**, *12*, R367–R410.

(67) Wolf, D. Reconstruction of NaCl Surfaces from a Dipolar Solution to the Madelung Problem. *Phys. Rev. Lett.* **1992**, *68*, 3315–3318.

(68) Tasker, P. W. The Stability of Ionic Crystal Surfaces. *J. Phys. C* **1979**, *12*, 4977–4984.

(69) Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-Zone Integrations. *Phys. Rev. B* **1976**, *13*, 5188–5192.

(70) Raebiger, H., Lany, S.; Zunger, A. Charge Self-Regulation Upon Changing the Oxidation State of Transition Metals in Insulators. *Nature* **2008**, *453*, 763–766.

(71) Jansen, M.; Wedig, U. A Piece of the Picture - Misunderstanding of Chemical Concepts.

*Angew. Chem. Int. Ed.* **2008**, *47*, 10026–10029.

(72) O’Regan, D. D.; Hine, N. D. M.; Payne, M. C.; Mostofi, A. A. Projector Self-Consistent DFT+U Using Nonorthogonal Generalized Wannier Functions. *Phys. Rev. B* **2010**,

82, 081102(R).