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Supplementary information for Surface Properties of α-MnO_2: Relevance to Catalytic and Supercapacitor Behaviour

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Surface Energies of α-MnO_2 from Interatomic Potentials

This study employs well-established interatomic potentials methods, which are reviewed in detail elsewhere.[1,2] The model due to Parker and co-workers[3,4] for rutile β-MnO_2, that has been utilised successfully in several studies,[5,6] is augmented by the inclusion of a core-shell model for the oxygen. The interactions between ions are represented in terms of a long-range Coulmbic term with the addition of an analytic term representing short-range interactions such as chemical bonding. In the model employed these short-range effects are modeled by a Buckingham potential with the form:

$$V_{ij}(r_{ij}) = A\exp(-r_{ij}/\rho) - C/r_{ij}^6 \tag{1}$$

where r is the interatomic separation and A, ρ, and C are ion-ion potential parameters. In the model used by Parker *et al.* for rutile MnO_2 the charges on the Mn and O ions are represented

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*To whom correspondence should be addressed by a rigid ion model, with partial charges. The potential parameters are presented in Table S1. To apply interatomic potentials to the lower symmetry α-MnO$_2$ structure we have split the charge of $O^{1.1-}$ into a shell of charge $-1.8e$ and a core of charge $0.7e$, with a spring constant of $K = 34.3$ eV·Å^{-2}. With this change the calculated lattice parameters are within 1.5% of those observed experimentally. In this work we use this accurate interatomic potential model to calculate the surface energies using METADISE[7] up to high indexes. The calculated surface energies are shown in Table S2. The resulting equilibrium crystal morphology from a Wulff construction is shown in Figure S1.

Table S1: Parameters describing the interatomic potentials model.

interaction	A (Å)	ρ (Å)	C (eV/Å^{-6}	species	q(e)
$Mn^{2.2+}$– $Mn^{2.2+}$	23530.50	0.156	16.00	$Mn^{2.2+}$	2.20
$Mn^{2.2+}$– $O^{1.1-}$	15538.20	0.195	22.00		
$O^{1.1-}$– $O^{1.1-}$	11782.76	0.234	30.22	$O^{1.1-}$	-1.10

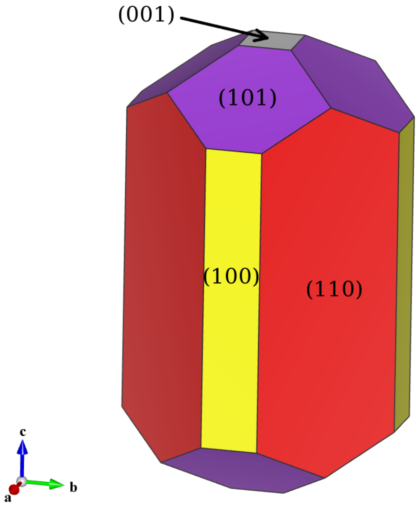

Figure S1: Predicted morphology of α-MnO$_2$ from interatomic potentials.

Methodology in the PBE+U Framework

When using PBE+U the selection of an appropriate U value for the system is important. This may be achieved for a given material within the framework of Density Functional Theory (DFT) by a self-consistent calculation.[8] In the present work an additional complication is introduced due to the desire to study oxygen vacancy formation at surfaces, which results in a change of oxidation state of the transition metal from Mn^{4+} to Mn^{3+}. Therefore, a value of U must be chosen to represent the system in both states. To achieve this we have followed the practice in previous DFT+U works involving changes in oxidation state, for instance for Li-ion intercalation,[9] by calculating the value of U in both oxidation states and then utilizing the average between the two. It is important to note that the self-consistent calculation of U is employed to calculate the spherical part of the PBE+U interaction, which in the framework of the fully-localized limit is appropriately expressed as $(U-J)$,[10] which we do from here on. In this work we choose a value of $(U-J) = 5.2$ eV, which is the average of the self-consistently calculated values for Mn^{4+} ($(U-J) = 5.6$ eV) and Mn^{3+} ($(U-J) = 4.8$ eV). The Mn^{3+} calculation was performed using α-$LiMnO_2$, which retains the same structural features as α-MnO_2 with a differing oxidation state for Mn. Since the Slater integrals F^2 and F^4 (that determine exchange and the anisotropy of the Coulomb ineraction) are typically weakly screened in solids[11,12] we employ an atomic-limit value of $J = 1.0$ eV, which is appropriate to Mn^{4+} and Mn^{3+}.

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Table S2: Predicted surface energies for α-MnO_2 from our interatomic potential model. The subscripts after the miller indices of a single surface indicate different surface terminations. Note that only the three lowest energy terminations are shown for each surface.

Miller Index	E_{surf} (Jm^{-2})	Termination
(001)	1.89	MnO
$(100)_a$	1.15	O
$(100)_b$	1.15	MnO
$(100)_c$	1.23	O
$(101)_a$	1.70	O
$(101)_b$	1.94	Mn
$(101)_c$	1.99	MnO
$(110)_a$	0.99	O
$(110)_b$	1.31	O
$(110)_c$	1.45	O
$(111)_a$	2.03	MnO
$(111)_b$	2.04	O
$(111)_c$	2.09	MnO
$(210)_a$	2.07	MnO
$(210)_b$	2.58	MnO
$(210)_c$	2.61	O
$(201)_a$	2.02	MnO
$(201)_b$	2.10	MnO
$(201)_c$	2.13	O
$(102)_a$	1.91	O
$(102)_b$	2.06	MnO
$(102)_c$	2.09	MnO
$(211)_a$	1.77	O
$(211)_b$	2.45	Mn
$(112)_a$	1.88	Mn
$(112)_b$	1.98	Mn
$(112)_c$	2.06	Mn
$(122)_a$	1.97	O
$(122)_b$	2.02	MnO
$(122)_c$	2.05	MnO
$(221)_a$	1.89	MnO
$(221)_b$	2.10	O
$(221)_c$	2.24	O
$(211)_a$	1.77	O
$(211)_b$	2.24	Mn