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1 **Ethylene carbonate adsorption on the major surfaces of lithium manganese oxide $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$**
2 **spinel ($0.000 < x < 0.375$): a DFT+*U*-D3 study**

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12 **Abstract**

13 Understanding the surface reactivity of the commercial cathode material LiMn_2O_4 towards the
14 electrolyte is important to improve the cycling performance of secondary lithium-ion batteries and to
15 prevent manganese dissolution. In this work, we have employed spin-polarized density functional
16 theory calculations with on-site Coulomb interactions and long-range dispersion corrections
17 [DFT+*U*-D3-(BJ)] to investigate the adsorption of the electrolyte component ethylene carbonate
18 (EC) onto the (001), (011) and (111) surfaces of the fully lithiated and partially delithiated $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$
19 spinel ($0.000 < x < 0.375$). The surface interactions were investigated by evaluating the adsorption
20 energies of the EC molecule and the surface free energies. Furthermore, we analyzed the impact of
21 the EC adsorption on the Wulff crystal morphologies, the molecular vibrational frequencies and the
22 adsorbate/surface charge transfers. The adsorption energies indicate that the EC molecule strongly
23 adsorbs on the (111) facet, which is attributed to a bidentate binding configuration. We found that the
24 EC adsorption enhances the stability of the (111) facet, as shown by the Wulff crystal morphologies.
25 Although a negligible charge transfer was calculated between the spinel surfaces and the EC
26 molecule, a large charge rearrangement takes place within the surfactant upon adsorption. The
27 wavenumbers of the C=O stretching mode for the interacting EC molecule are red-shifted with respect
28 to the isolated adsorbate, suggesting that this bond becomes weaker. The surface free energies show
29 that both the fully lithiated and partially delithiated forms of the LiMn_2O_4 surfaces are stabilized by
30 the EC molecule.

31
32 **Keywords:** *Density functional theory, spinels, Li-ion batteries, surface chemistry*

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33 1. Introduction

34 Over the last few decades, renewable energy storage has become of significant interest in the
35 development of electric vehicles, which could facilitate a lesser reliance on fossil fuels and thus lower
36 impact on global warming. Although many studies have aimed at discovering or developing
37 sustainable, earth-abundant and/or low-cost alternative materials [1, 2, 3], there is still no viable
38 replacement for the current lithium-based batteries. However, the development of more efficient and
39 stable cathode materials would offer a major step forwards in the performance of lithium-ion batteries.
40 Various cathode materials have been studied, including LiCoO_2 [4, 5], $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ [6], LiMn_2O_4 [7,
41 8], $\text{Li}_4\text{Mn}_5\text{O}_{12}$ [9], LiFePO_4 [10] and NMCs [11] in order to improve the electrochemical performance
42 of lithium-ion batteries.

43 Among these materials, lithium manganese oxide (LiMn_2O_4) spinel has attracted the most attention
44 as a potential cathode material because of its three-dimensional crystal structure that allows a
45 reversible diffusion of Li^+ ions [12, 13]. Moreover, LiMn_2O_4 is considered a safer substitute for the
46 currently commercialized LiCoO_2 owing to its low environmental impact, the abundance of
47 manganese and its high energy density [14]. However, the use of LiMn_2O_4 spinel as a cathode material
48 is limited by the irreversible fading of the capacity, which is attributed to the dissolution of
49 manganese, electrolyte oxidation at high voltages, and the Jahn-Teller distortion of the octahedral
50 Mn^{3+} atoms [15, 16].

51 A number of methods have attempted to mitigate the manganese dissolution, including (i) cation
52 doping [17, 18]; (ii) the replacement of commercially used LiPF_6 as the electrolyte ionic conductor
53 to limit the production of the scavenging hydrofluoric acid produced by its degradation [19, 20, 21];
54 and (iii) surface coating to create an artificial barrier that limits the direct electrode-electrolyte contact
55 [22, 23, 24, 25]. However, there is currently no substitute ionic conductor for the electrolyte which
56 has better conductivity, thermal stability and affordability than LiPF_6 , whereas the alternative route
57 of introducing dopant ions might change the spinel crystal structure, thereby affecting the Li^+
58 transport in the battery [26]. An effective electrolyte solvent will not only be a good solvent for the
59 ionic conductor but will also improve the lifetime of LiMn_2O_4 -based lithium-ion batteries. Guyomard
60 et al. [27] demonstrated that alkyl carbonates, such as propylene carbonate (PC) [28], vinylene
61 carbonate (VC) [29, 30], allyl ethyl carbonate (AEC) [31] and ethylene carbonate (EC), are some of
62 the most stable solvents for the lithium-ion battery electrolytes. Numerous subsequent studies [32,
63 33, 34] have shown that the ethylene carbonate (EC) is the most stable electrolyte solvent and shows
64 improved electrochemical performance. Compared to other commercially used electrolyte solvents,

65 EC has the largest dielectric constant ($\epsilon \approx 90.5$) [35, 36] and melting point owing to its high molecular
66 symmetry. However, the reactivity of EC at the spinel surface and its effect on the crystal
67 morphologies is not yet completely understood.

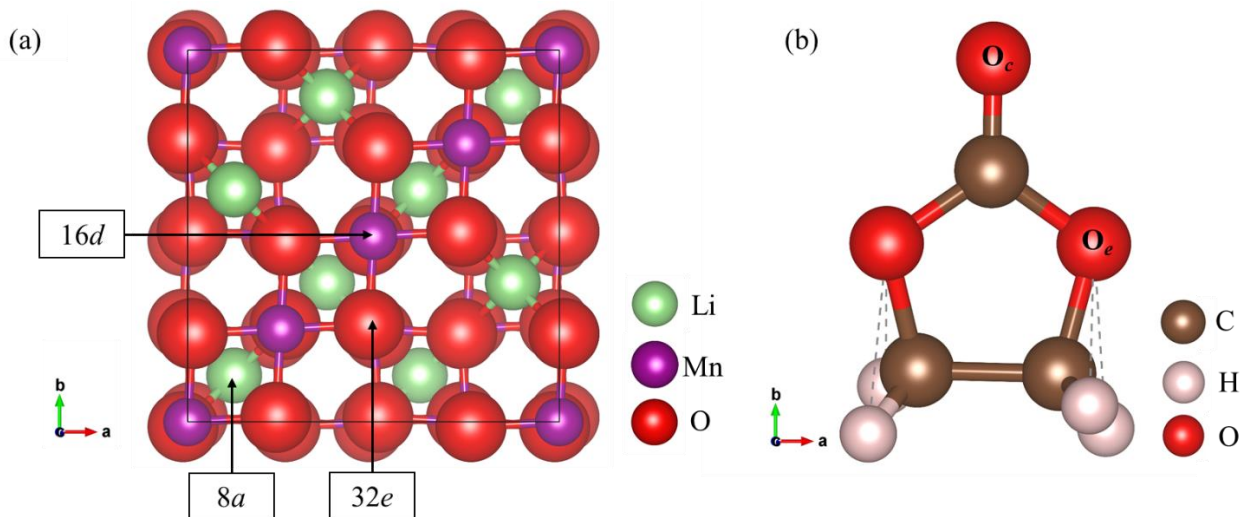
68 In this work, we report on calculations based on the density functional theory to study the interaction
69 between EC and the non-polar surfaces of the fully lithiated and partially delithiated spinel
70 $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ material ($0.000 < x < 0.375$). We discuss the binding energies of EC on the (001), (011)
71 and (111) surfaces, the nanoparticle morphologies for $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ before and after adsorption, the
72 inter- and intra-phase charge transfers, and the molecular vibrational frequencies.

73 **2. Computational methods**

74 2.1 Calculation details

75 The surface spinel calculations were performed using spin-polarized density functional theory (DFT)
76 techniques as implemented in the Vienna Ab initio Simulation Package (VASP) [37]. All calculations
77 were carried out within the generalized gradient approximation (GGA) using the Perdew, Burke, and
78 Ernzerhof (PBE) exchange-correlation functional [38]. The kinetic energy cut-off was fixed at 560
79 eV for the expansion of the Kohn-Sham (KS) valence states. A Γ -centred Monkhorst-Pack grid of
80 $5 \times 5 \times 1$ k-points was used for the integration in the reciprocal space of all surfaces. The core electrons
81 and their interaction with the valence electrons were described using the projector augmented-wave
82 (PAW) method [39] in the implementation of Kresse and Joubert [40]. The core electrons are
83 comprised of the levels up to the $3s$ for manganese and $1s$ for carbon and oxygen, while all the
84 electrons are treated as valence electrons for lithium and hydrogen. The semi-empirical method of
85 Grimme with the Becke-Johnson damping [D3-(BJ)] [41, 42] was also included in our calculations
86 to model the long-range dispersion interactions, which are required to describe the surfaces properly
87 [43, 44, 45, 46, 47, 48]. Gaussian smearing with a width of 0.05 eV was set to improve the
88 convergence of the Brillouin zone integrations during geometry optimizations [42]. The tetrahedron
89 method with Blöchl corrections was used to obtain accurate electronic and magnetic properties as
90 well as total energies [49]. The Hubbard correction [50] in the formulation of Dudarev et al. [51] was
91 applied to improve the description of the localized $3d$ Mn electrons. We have used the effective
92 parameter $U_{\text{eff}} = 4.0$ eV, which we developed in our study of the bulk properties of the fully lithiated
93 LiMn_2O_4 [52] and which is within the range of values reported in the literature [53, 54, 55, 56].

94 The spinel LiMn_2O_4 has a face-centered cubic crystal structure with a space group $Fd\bar{3}m$ (No. 227)
 95 [57] and a lattice constant of $a = 8.24 \text{ \AA}$ [58, 59]. In our calculations, we have ignored the changes in
 96 the crystal lattice, resulting from the introduction of Li vacancies, when modelling the delithiated
 97 phases. Indeed, only minor changes in the lattice parameter of the cathode material are expected since
 98 a major change in the structure of the cathode would mean loss of possible recharge ability leading
 99 to deterioration of the battery efficiency. Similar methodologies have been employed in previous
 100 studies [60, 61, 55]. Furthermore, we have run benchmarking calculations to establish the difference
 101 in lattice parameters and surface areas of the fully lithiated and partially delithiated surface. We found
 102 that the slabs showed minor changes with a difference of only $\sim 0.02 \text{ \AA}$, which is equivalent to 5%
 103 (see electronic supporting information). The structure consists of a cubic close-packed array of
 104 oxygen atoms occupying the $32e$ sites, where lithium and manganese atoms occupy one-eighth of the
 105 tetrahedral ($8a$) sites and one-half of the octahedral ($16d$) sites, respectively, [62] (see Figure 1a).



106

107 Figure 1: Schematic diagram of (a) conventional unit cell of LiMn_2O_4 spinel and (b) ethylene
 108 carbonate (EC) molecule, showing the ethereal (O_e) and carbonyl (O_c) oxygens.

109 2.2 Surface models

110 All the surface terminations were generated by cutting the geometry-optimized bulk structure [52],
 111 using the Tasker [63] dipole method, as implemented in METADISE (Minimum Energy Techniques
 112 Applied to Dislocations, Interfaces and Surface Energies) code [64], to create non-dipolar surfaces.
 113 The surfaces were represented by keeping fixed the atoms in the bottom-most layers at their relaxed
 114 bulk positions to simulate the bulk phase of LiMn_2O_4 and relaxing the rest the atoms during geometry
 115 optimization, resulting in a single relaxed slab. The surface areas, total number of layers and the

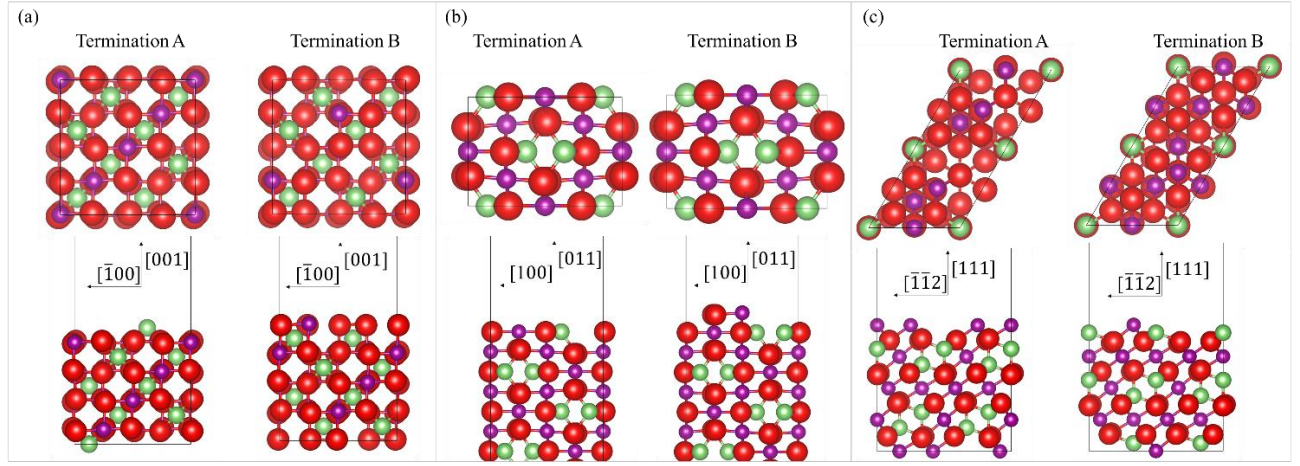
116 number of lithium atoms in the simulation cells considered for the fully lithiated and partially
 117 delithiated low-Miller index surfaces are shown in Table 1. The number of Li atoms with dangling
 118 bonds removed from the exposed layers of the fully lithiated LiMn_2O_4 are denoted by x . In every slab,
 119 a vacuum region of 15 \AA was added perpendicularly to the surface to avoid interactions between the
 120 periodic images. We performed convergence tests with respect to the total number of layers, the
 121 number of relaxed atomic layers, and the vacuum thickness until the energy was constant within 1
 122 meV of accuracy. We also applied dipole corrections perpendicular to the surface plane during our
 123 calculations, to enhance the convergence of the electronic energy. Geometry optimizations were
 124 conducted using the conjugate-gradient technique and were considered converged when the
 125 Hellmann-Feynman forces were below 0.01 eV/\AA .

126 Table 1. Surface area (A_{surface}) and number of layers (N_{layers}) for each cell composition of the fully
 127 lithiated and partially delithiated surfaces of $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$.

Surface	A_{surface} (\AA^2)	N_{layers}	Cell composition		x	
			Lithiated	Delithiated	Lithiated	Delithiated
(001)	69.72	9	$\text{Li}_8\text{Mn}_{16}\text{O}_{32}$	$\text{Li}_5\text{Mn}_{16}\text{O}_{32}$	0	0.375
(011)	49.30	9	$\text{Li}_8\text{Mn}_{16}\text{O}_{32}$	$\text{Li}_5\text{Mn}_{16}\text{O}_{32}$	0	0.375
(111)	60.38	13	$\text{Li}_8\text{Mn}_{16}\text{O}_{32}$	$\text{Li}_6\text{Mn}_{16}\text{O}_{32}$	0	0.250

128

129 For each surface orientation, we have modeled the two possible terminations using stoichiometric,
 130 non-polar and symmetric slabs along the z -direction, as shown in Figure 2. When constructing the
 131 surface terminations, we considered the stacking sequence for low Miller index facets [65, 66, 67,
 132 68]. The (001) surface terminations were cleaved from atomic planes perpendicular to the [001]
 133 direction and consist of an alternation of Li and Mn/O planes. The top species in the (001) surface
 134 were 0.5 ML of Li atoms on the bulk-like Mn–O layer for termination *A* and two Mn for every four
 135 O atoms for termination *B*. The (111) facets were created from atomic planes consisting of six
 136 possible bulk-like surface terminations (O_1 , Mn_1 , O_2 , Li_1 , Mn_2 and Li_2) which are dipolar. However,
 137 upon reconstruction, only two non-dipolar terminations were possible for the (111), i.e. a Li- and a
 138 Li/Mn/O-termination. The (011) surface can be cleaved along the Li/Mn/O and Mn/O planes. The
 139 slabs were terminated by half of the Li/Mn/O and Mn/O bulk layers, respectively.



140

141 Figure 2: Top and side view of the simulated slabs for the fully lithiated LiMn_2O_4 spinel.
 142 Crystallographic directions for the top view of (001) surface terminations is $[100]$ for the abscissae
 143 towards the right, for the (011) surface terminations it is $[0\bar{1}1]$ for the abscissae towards the right, and
 144 for the (111) surface terminations it is $[0\bar{1}1]$ for the longest axis towards the top.

145 2.3. Surface and adsorption energies

146 The surface energies were calculated for the relaxed and unrelaxed slabs. The unrelaxed surface
 147 energies (γ_u) were evaluated from static calculations as

$$148 \quad \gamma_u = \frac{E_{u,\text{slab}} - E_{\text{bulk}}}{2A} \quad (1)$$

149 where $E_{u,\text{slab}}$ is the total energy of the unrelaxed slab, E_{bulk} is the total energy of the bulk with the
 150 same number of formula units as the slab and A is the surface area of the slab. The relaxed surface
 151 energies (γ_r) were also calculated for the spinel material following geometry optimization of the slab,
 152 where the bottom half of the layers were kept fixed at their relaxed bulk positions, while the top layers
 153 were allowed to relax. Since the slabs were comprised of both relaxed and unrelaxed sides, the relaxed
 154 surface energies were calculated as:

$$155 \quad \gamma_u + \gamma_r = \frac{E_{r,\text{slab}} - E_{\text{bulk}}}{A} \quad (2)$$

156 where E_r is the total energy of the half-relaxed surface. The degree of relaxation (R) was also
 157 calculated for all the surfaces as:

$$158 \quad R = \frac{\gamma_u - \gamma_r}{\gamma_u} \times 100 \quad (3)$$

159 To characterize the interaction of EC on both the fully lithiated and partially delithiated (001), (011)
 160 and (111) spinel facets, we have calculated the adsorption energy (E_{ads}) for different adsorption sites
 161 at different orientations of the molecule. The adsorption energy was calculated according to the
 162 equation:

$$163 \quad E_{\text{ads}} = E_{\text{EC+slab}} - (E_{\text{EC}} + E_{\text{slab}}) \quad (4)$$

164 where $E_{\text{EC+slab}}$ is the total energy of the slab with the EC molecule adsorbed, E_{EC} is the total energy
 165 of the isolated EC molecule and E_{slab} is the total energy of the pristine slab. The energy minimization
 166 for an isolated EC molecule was performed sampling only the Γ point of the Brillouin zone using a
 167 cell of $10 \text{ \AA} \times 11 \text{ \AA} \times 12 \text{ \AA}$ to avoid spurious interactions. A positive value of E_{ads} indicates an
 168 endothermic and unfavourable adsorption process, whereas a negative value indicates an exothermic
 169 and favourable adsorption process.

170 We further calculated the surface free energies (σ) for the modified slabs, *i.e.* when it is partially
 171 delithiated or interacting with the EC molecule via the equation:

$$172 \quad \sigma = \gamma_r + \frac{E_M - E_r + (8 - N_{\text{Li}})E_{\text{Li}} - E_{\text{EC}}}{A} \quad (5)$$

173 where E_M is the energy of the modified slab, $8 - N_{\text{Li}}$ is the number of lithium atoms removed from the
 174 slab, E_{Li} is the energy of one atom in the bulk of the body-centred cubic (*bcc*) lithium, E_r is the energy
 175 of the pristine slab and E_{EC} is the energy of the isolated ethylene carbonate molecule. Where there is
 176 no surface modification, the surface energies and the surface free energies have the same value, but
 177 a correction expression is added to account for surface modifications, such as adsorptions, doping,
 178 delithiation and lithiation.

179 2.4. Vibrational frequencies

180 Vibrational frequencies for the isolated and adsorbed EC molecule were calculated using the central
 181 finite differences approach. The method comprises calculations of vibrational frequencies from the
 182 second derivatives of the potential energy with respect to the atomic positions. These were allowed
 183 to move by small displacements in the three Cartesian planes to ensure they fall within the harmonic
 184 part of the potential well. The fundamental vibrational modes were classified into symmetric (v_{sym})
 185 and asymmetric stretching (v_{asy}), as well as bending (δ) modes.

186 2. Results and discussions

187 3.1. Surface energies

188 The stabilities of the surface terminations obtained from the fully optimized spinel bulk structure [52]
189 were analyzed by calculating the surface energies for the unrelaxed and relaxed slabs, see Table 2.
190 Before and after relaxation, we observed the same trend of increasing surface energies and decreasing
191 stability, which is (001) < (011) < (111). We also observed that termination *A* of the (001) surface,
192 i.e. the Li-terminated LiMn_2O_4 surface, is the most stable plane with $\gamma_r = 0.04 \text{ eV}/\text{\AA}^2$. This lowest
193 energy termination is in agreement with the reported literature [56, 55], and also compares well with
194 the lowest energy of the Mg-terminated MgAl_2O_4 surface [69]. Among all the surface terminations,
195 the (111) termination *B* showed the largest geometry relaxation. For the sake of simplicity and to
196 identify the salient behaviour of the surfaces interacting with the ethylene carbonate, we have as an
197 approximation neglected in this study potentially modifying factors such as an external field caused
198 by the double layer generated on the surface, voltage or electric current.

199 Table 2. Calculated surface energies for the unrelaxed (γ_u) and relaxed (γ_r) slabs of the low-Miller
200 index surfaces of the fully lithiated LiMn_2O_4 .

Surfaces	Termination	γ_u (eV/ \AA^2)	γ_r (eV/ \AA^2)	Relaxation (%)
(001)	<i>A</i>	0.07	0.04	43.7
	<i>B</i>	0.15	0.11	28.7
(011)	<i>A</i>	0.10	0.05	50.0
	<i>B</i>	0.10	0.07	37.2
(111)	<i>A</i>	0.08	0.05	38.0
	<i>B</i>	0.21	0.09	57.9

201

202 3.2. Ethylene carbonate adsorption

203 Here, we discuss the spinel surface interactions towards the ethylene carbonate electrolyte
204 component. First, we explored the preferred adsorption geometries for different orientations of the
205 EC molecule and various binding sites on the $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ (001), (011) and (111) surfaces. The
206 adsorption sites investigated included the atop, bottom, bridge, and hollow positions, as shown in
207 Figure 3. The initial interaction configurations of the EC molecule included coordination to the
208 surface via the carbonyl and ethereal oxygen, both in flat and perpendicular orientations. Before

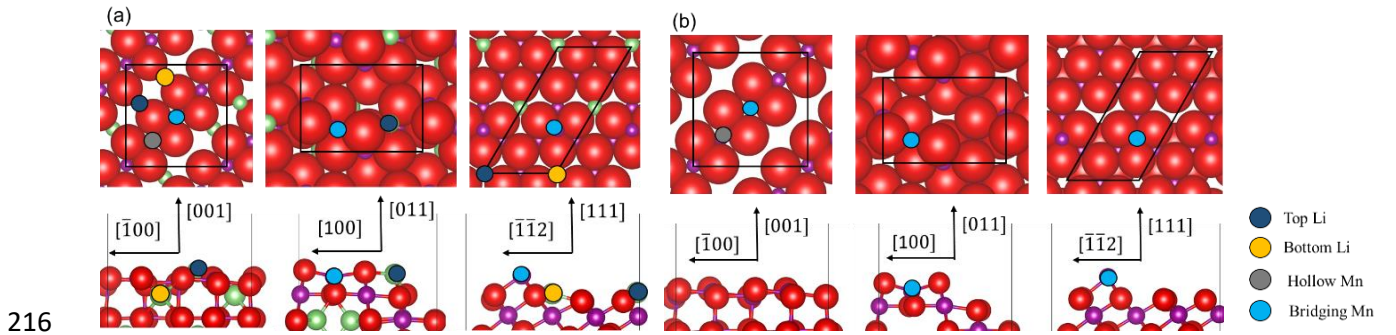
209 adsorption, we measured the structural parameters of the relaxed EC molecule and compared them
 210 with the available literature data to ensure the accuracy of our results. Table 3 summarises the
 211 equilibrium bond distances and angles, and which are in good agreement with the available literature.

212

213 Table 3. The equilibrium bond distances and angles in the EC molecule calculated and compared to
 214 literature.

Parameters	This work	Experimental [70]	B3PW91 [71]	Monte Carlo [72]
$d(\text{C}=\text{O})/\text{\AA}$	1.20	1.20	1.15	1.20
$d(\text{C}-\text{O})/\text{\AA}$	1.37	1.39	1.33	1.36
$d(\text{C}-\text{C})/\text{\AA}$	1.50	1.54	1.52	1.43
$d(\text{C}-\text{H})/\text{\AA}$	1.10	1.09	-	1.09
$\angle(\text{O}-\text{C}-\text{O})/^\circ$	110.5	125.2	124.1	110.6
$\angle(\text{C}-\text{O}-\text{C})/^\circ$	108.9	109.5	109.0	110.5

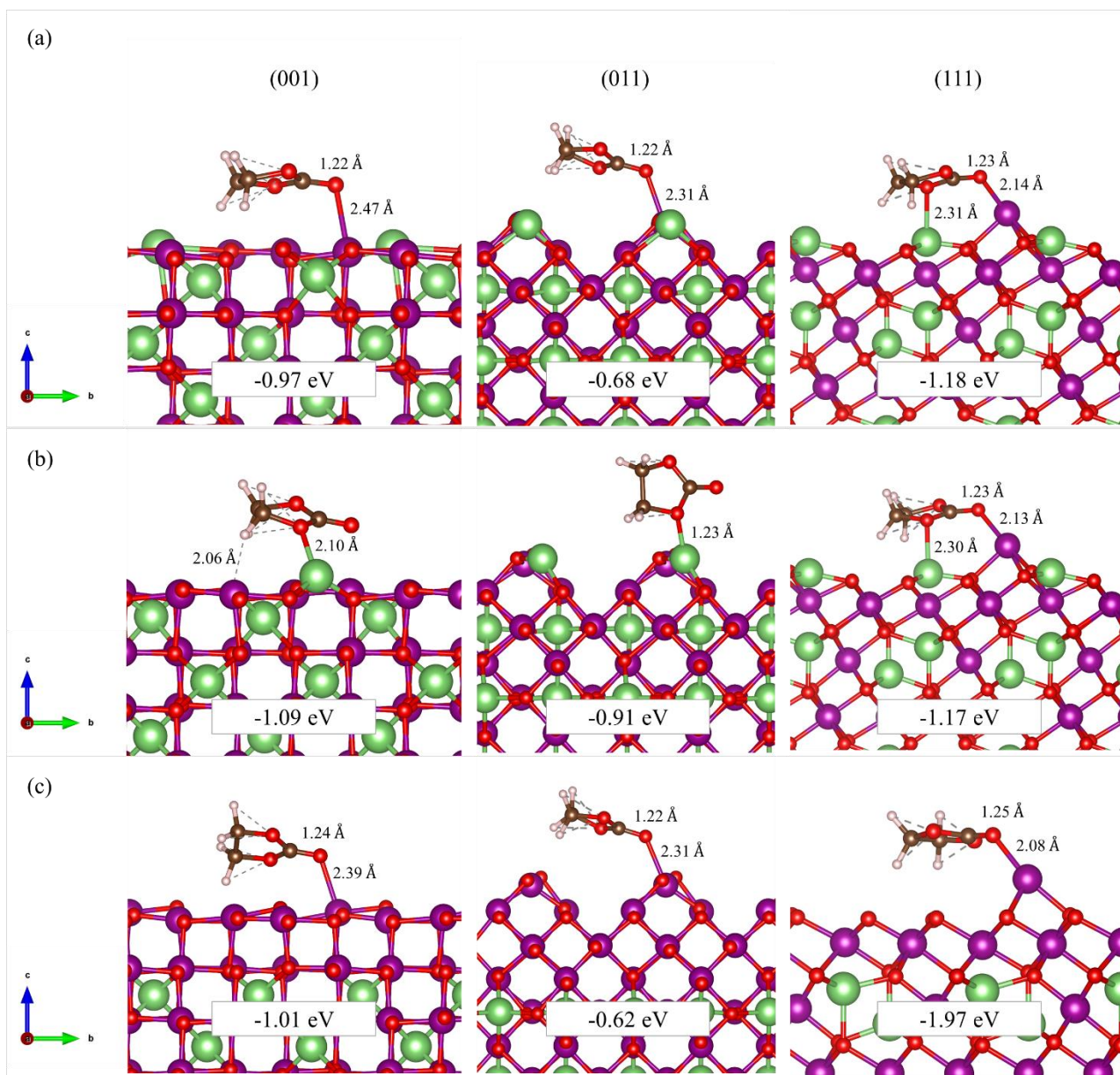
215



217 Figure 3. Top and side view of the modelled slabs for (a) the fully lithiated LiMn_2O_4 and (b) the
 218 partially delithiated $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$. Crystallographic directions for the top view of (001) surface
 219 terminations is $[100]$ for the abscissae towards the right, for the (011) surface terminations it is $[0\bar{1}1]$
 220 for the abscissae towards the right, and for the (111) surface terminations it is $[0\bar{1}1]$ for the longest
 221 axis towards the top.

222 In all our simulations, the EC molecule was placed initially at 2.5 \AA from the surface to favour the
 223 attractive forces over the repulsive ones between the molecule and the surface. However, during
 224 geometry optimization, the adsorbate and the surface were free to move and allowed to change their
 225 adsorption geometry. Figure 4 displays the most stable interactions between the EC molecule and the
 226 $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ surfaces, together with the relevant binding energies. First, we explored the EC

227 adsorption onto the fully lithiated spinel surface through the Mn atom, where our calculations indicate
228 that the EC molecule prefers to bind to the surface through the carbonyl oxygen at a distance of 2.47
229 Å, when placed parallel to the surface. This mode is in excellent agreement with previous work [73],
230 where the EC molecule was found to bind strongly to the fully lithiated spinel (001) surface through
231 the Mn atom. In our work, we also explored the EC adsorption on the (001), (011) and (111) where
232 we found that the process releases the largest adsorption energy at the (111) facets due to bidentate
233 binding modes to the Li and Mn atoms. Next, we studied the EC adsorption onto the fully lithiated
234 surfaces through the Li atom, where it strongly binds with the surfaces through the ethereal oxygen
235 (O_e). However, upon geometry optimization, the molecule interacted with the exposed Mn and Li
236 atoms in (111) surface with a very exothermic adsorption energy. The EC molecule preferred to
237 interact with the (001) Li atom through the ethereal oxygen at a distance of 2.31 Å and by forming
238 one hydrogen-bond of 2.16 Å with one surface oxygen. Moreover, the EC molecule was found to
239 bind perpendicularly to the (011) surface at 2.00 Å via the ethereal oxygen. We also studied the EC
240 adsorption onto the partially delithiated surfaces, where the only available adsorption sites are the
241 exposed manganese atoms. Similar to the (001) lithiated surfaces, the EC molecule preferred to bind
242 with the delithiated surfaces through the carbonyl oxygen where the strongest binding energy was
243 calculated on the (111) facet.



244

245 Figure 4. Most stable adsorption configurations for the EC molecule on the $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ surfaces.
 246 Adsorption sites in the fully lithiated spinel are (a) Mn atom, (b) Li atom; and in the partially
 247 delithiated surface it is (c) Mn atom. Crystallographic directions for the top view of (001) surface
 248 terminations is $[100]$ for the abscissae towards the right, for the (011) surface terminations it is $[0\bar{1}1]$
 249 for the abscissae towards the right, and for the (111) surface terminations it is $[0\bar{1}1]$ for the longest
 250 axis towards the top.

251

252 3.3.Surface free energies

253 Table 4 summarises the surface free energies of the fully lithiated surfaces interacting with the EC
 254 molecule, as well as the partially delithiated surfaces, both pristine and interacting with the adsorbate.
 255 The calculated surface free energies are higher as compared to the surface energies of the fully-
 256 lithiated facets. This increase in energy of the partly delithiated surfaces as compared to the fully
 257 lithiated surfaces indicates that upon delithiation, the surfaces become less stable, thus a destabilising
 258 effect. However, the addition of the EC molecule can affect the stabilities of both the fully lithiated
 259 and partially delithiated systems. For example, when the EC molecule is adsorbed onto the (001)
 260 surface by coordinating one of the manganese atoms, an increase of $0.08 \text{ eV}/\text{\AA}^2$ in the surface free
 261 energy is observed, indicating that the adsorbate has a destabilizing effect. On the other hand, we
 262 have also observed a decrease in the surface free energies for the other modified surfaces with respect
 263 to the pristine planes, but proportionally smaller than in the (011) facet [44].

264 Table 4: Surface free energy (σ) for the fully lithiated and partially delithiated $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ surfaces
 265 interacting with the EC molecule.

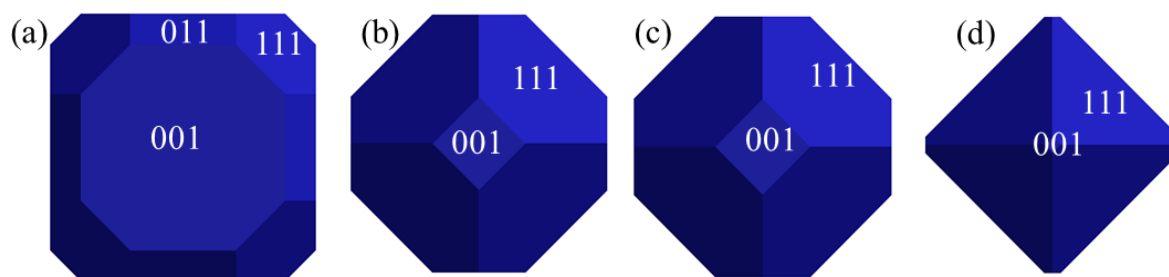
Surface	x	Adsorption site	σ ($\text{eV}/\text{\AA}^2$)
(001)	0	Mn	0.12
	0	Li	0.02
	0.375	–	0.13
	0.375	Mn	0.02
(011)	0	Mn	0.13
	0	Li	0.04
	0.375	–	0.13
	0.375	Mn	0.04
(111)	0	Mn	0.07
	0	Li	0.02
	0.250	–	0.11
	0.250	Mn	0.02

266

267 3.4. Morphology

268 Here we discuss the Wulff crystal morphologies for the fully lithiated and partially delithiated
 269 $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$, which were obtained using the termination with the lowest surface free energy for each
 270 pristine and modified surface [74, 75]. As shown in Figure 5, the (001) plane dominates the
 271 morphologies for the fully lithiated material and the (111) is the major surface for the partially
 272 delithiated spinel. The (011) surface does not appear in the Wulff morphology after delithiation or

273 adsorption of the EC molecule, because of its higher surface free energy with respect to the (001) and
274 (111) planes. We have also carried out test calculations to determine the effect of different Li content
275 and found similar Wulff crystal morphologies to the ones represented in figure 5 using slabs
276 containing the same stoichiometry (see electronic supporting information). Our morphology for the
277 delithiated material interacting with the electrolyte is in excellent agreement with the work of Kim et
278 al. [76], who found that the octahedron-shaped $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ particles are dominated by the (111)
279 surface.



280
281 Figure 5. Surface morphologies for $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$, (a) before and (b) after adsorption of EC on the fully
282 lithiated spinel, (c) before and (d) after adsorption of EC on the partially delithiated material.

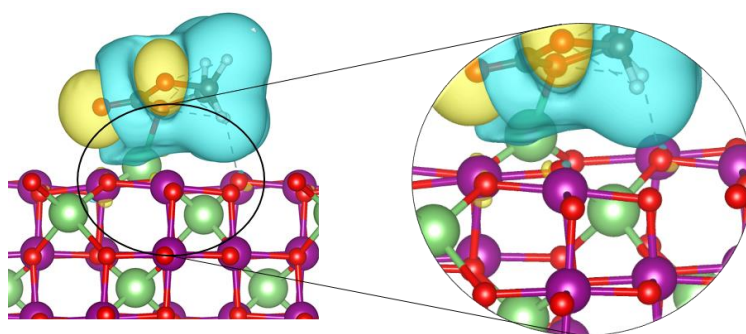
283

284 3.5. Charge transfer and work function

285 We have carried out a Bader charge analysis to quantify the electron transfer upon adsorption of the
286 electrolyte to the surfaces of the cathode (Table 5). For all the adsorbed systems, we generally observe
287 a negligible charge transfer which suggests that this process only plays a minor role in the adsorption
288 mechanism. The largest charge transfer of $\Delta q = -0.05 e^-$ was observed at the Li site of the (001)
289 surface. We further explored the electronic structure by plotting the charge density difference for the
290 adsorption configuration with the largest inter-phase charge transfer, see Figure 6. Despite the surface
291 donating a minor charge to the electrolyte molecule, the electron flow is dominated by an internal
292 charge rearrangement within the EC molecule. We have also compared the charge transfer between
293 the carbonyl oxygen (O_c) and the directly bonded atoms following adsorption, by subtracting from
294 the charge density of the total adsorbate-surface system the sum of the charge density of the isolated
295 adsorbate and clean surface in the same geometry. We observe partial oxidation of carbon and
296 reduction of oxygen, owing to intramolecular electron rearrangement caused by the electron transfer
297 from the $\text{C}=\text{O}$ π -bond to an oxygen-surface σ -bond. In all cases, there is transfer of ~ 1 electron from
298 the carbon to the oxygen, which could lead to heterolytic cleavage of the $\text{C}=\text{O}$ π -bond under working
299 conditions. We have also compared the charge difference between the O_e in the isolated and adsorbed

300 molecule, when it is interacting with the surface via this atom. We generally observe a minor charge
301 accumulation on the O_e , which suggests that the ethereal bond is unlikely to break upon adsorption of
302 the EC molecule to the surface.

303 We next calculated the work function (Φ) for the modified surfaces, which measures the energy
304 required to bring a surface electron to the vacuum [46]. Generally, we observe a decrease in the work
305 function as we adsorbed the molecule, although in the delithiated surfaces the work function remains
306 fairly constant. The lowest value of the work function is observed when the EC molecule is adsorbed
307 on the pristine surfaces through the lithium (Li-O).



308
309 Figure 6. Charge density flow ($\Delta\rho$) for the EC molecule adsorbed on the LiMn_2O_4 (001) surface. The
310 charge density difference schemes were constructed by subtracting the sum of the electron charge
311 densities of the clean surface and isolated adsorbate, with identical structures as in the adsorbed form,
312 from the electron density of the total adsorbate-surface system. The electron density gain and
313 depletion are represented by yellow and blue respectively. The isosurfaces display a value of 0.003 e
314 \AA^{-3} ; the purple spheres indicate the manganese atoms, red spheres indicate the oxygen atoms and the
315 green spheres represent the Li atoms.

316 Table 5: Charge transfer between the surface and EC molecule (Δq_{EC}) as well as the charge
317 accumulation/depletion on the carbonyl and ethereal oxygen ($\Delta q_{OC/Oe}$), and work function for the
318 surfaces before (Φ_p) and after (Φ_a) adsorption. The vibrational wavenumbers are also included to
319 describe the symmetric stretching (ν_{sym}), asymmetric stretching (ν_{asy}) and bending (δ) modes.

Surface	Adsorption site	x	Δq_{EC} (e^-)	$\Delta q_{OC/Oe}$ (e^-)	Φ_p (eV)	Φ_a (eV)	CH ₂ vibrations		C=O	
							ν_{sym} (cm^{-1})	ν_{asy} (cm^{-1})	δ (cm^{-1})	ν (cm^{-1})
Isolated EC				0.00			2952	2990	1341	1829
EC (liquid films) [77]							2928	2955	1397	1803
(001)	Mn	0	-0.02	0.81 (O_c)	4.53	3.45	2994	2917	1489	1733
	Li	0	-0.05	0.07 (O_e)	4.53	3.16	2968	3043	1456	1770
	Mn	0.375	0.02	0.83 (O_c)	3.34	3.56	3028	3079	1465	1747
(011)	Mn	0	0.00	0.80 (O_c)	4.74	4.45	3021	3048	1477	1740
	Li	0	-0.01	0.03 (O_e)	4.74	4.26	3024	3089	1479	1787
	Mn	0.375	0.02	0.81 (O_c)	3.82	3.82	2998	3084	1479	1736
(111)	Li, Mn	0	0.00	0.78 (O_c)	3.66	3.55	2978	3007	1476	1705
	Li, Mn	0	0.02	0.08 (O_e)	3.66	3.57	3012	3065	1473	1720
	Mn	0.250	0.04	0.78 (O_c)	3.62	3.62	3001	3034	1443	1659

320

321 3.6. Vibrational frequencies

322 In order to characterize further the EC surface adsorption, we have computed the wavenumbers of
323 the fundamental vibrational modes for the lowest-energy adsorption geometries on the (001), (011)
324 and (111) spinel surfaces (Table 5). The quality of the vibrational modes calculated for the isolated
325 EC molecule was assessed by comparing them with the experimental values. Our simulated
326 vibrational modes for the isolated EC molecule compare closely with the experimental data, with the
327 largest difference being 56 cm^{-1} . For example, the asymmetric and symmetric $\nu(\text{C-H})$ stretching
328 modes for the free EC molecule were computed at 2952 and 2990 cm^{-1} , which compares well with
329 the experimental values of 2928 and 2955 cm^{-1} , respectively. These hydrogen stretching modes are
330 blue-shifted as a result of steric effects, since the hydrogen atoms are less mobile. We also analysed
331 the C=O stretching modes for the adsorbed EC molecule, which were in the range of $1700 - 1900$
332 cm^{-1} as reported by Fortunato et al [78]. Although we observed a minimal charge transfer between
333 the molecule and the surface, this does not prevent the stretching of the C=O bond. Our simulations

334 indicate that the vibrational modes are red-shifted with respect to the isolated EC molecule,
335 suggesting that the internal bonds in the adsorbate weaken upon adsorption onto the spinel surfaces.
336 This phenomenon was also observed in the charge transfers, where the carbonyl oxygen gains electron
337 density from the carbon atom, which further weakens the C=O bond.

338 **Conclusions**

339 DFT simulations have been performed to study the adsorption of the ethylene carbonate molecule on
340 the fully lithiated and partially delithiated $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ spinel surfaces. The lithium-terminated (001)
341 surface was found to be the most stable facet, which agrees with the reported literature. We further
342 investigated the partially delithiated surfaces, where we observed a larger surface free energy with
343 respect to the fully lithiated surface, indicating the destabilizing effect of delithiation.

344 We observed the strongest adsorption of the EC on the (111) surface, which was attributed to the EC
345 molecule interacting with both the manganese and lithium atoms in the surface. The surface free
346 energy was found to decrease following interaction with the adsorbate, which thus stabilizes the
347 material. The Wulff morphologies show that EC adsorption enhances the expression of the (111)
348 facet. Negligible charge transfer was observed between the adsorbate and surfaces, and the charge
349 density flow shows a strong electronic rearrangement within the EC molecule. The electron density
350 on the carbonyl oxygen is increased, due to partial carbon oxidation and oxygen reduction, i.e. an
351 intramolecular electron rearrangement from the C=O π -bond to an oxygen-surface σ -bond. The
352 vibrational frequencies also showed a red-shift in the C=O stretching mode of the adsorbed EC with
353 respect to the isolated molecule, which suggests the weakening of the C=O bond. Our simulations
354 show that the EC solvent binds to the spinel surfaces, releasing moderate adsorption energies. We
355 speculate that this binding protects the surface against Mn dissolution, while still allowing the EC
356 molecule to detach easily when the LiPF_6 ionic conductor approaches the surface to react with its Li
357 atoms. Moreover, the lack of charge transfer between the surfaces and the EC molecule indicates that
358 the solvent acts as a protective layer which shows no reactivity towards the spinel, but remains stable
359 while adsorbed. Furthermore, the particle morphologies indicate that upon surface delithiation, the
360 (111) facet becomes the most stable surface, which has also been reported as the surface that is most
361 resistant to manganese dissolution. In future work, we aim to explore explicit solvation of the spinel
362 surfaces during the charge/discharge processes, in addition to obtaining a clear understanding of the
363 kinetics and thermodynamics of the EC decomposition on the surfaces

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380 **Conflicts of interest**

381 There are no conflicts to declare.

382 **Reference**

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