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# Nanostructuring of $\beta$ -MnO<sub>2</sub>: The important role of surface to bulk ion migration

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## Abstract

Manganese oxide materials are attracting considerable interest for clean energy storage applications such as rechargeable Li-ion and Li-air batteries, and electrochemical capacitors. The electrochemical behavior of nanostructured mesoporous  $\beta$ -MnO<sub>2</sub> is in sharp contrast to the bulk crystalline system, which can intercalate little or no lithium; this is not fully understood on the atomic scale. Here, electrochemical properties of  $\beta$ -MnO<sub>2</sub> are investigated using density functional theory with Hubbard U corrections (DFT+U). We find good agreement between the measured experimental voltage, 3.0 V, and our calculated value of 3.2 V. We consider the pathways for lithium migration and find a small barrier of 0.17 eV for bulk  $\beta$ -MnO<sub>2</sub> which is likely to contribute to its good performance as a lithium intercalation cathode in the mesoporous form. However, by explicit calculation of surface to bulk ion migration we find a higher barrier of > 0.6 eV for lithium insertion at the (101) surface, that dominates the equilibrium morphology. This is likely to limit the practical use of bulk samples, and demonstrates

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the quantitative importance of surface to bulk ion migration in Li-ion cathodes and supercapacitors. Based on the calculation of the electrostatic potential near the surface we propose an efficient method to screen systems for the importance of surface migration effects. Such insight is valuable for the future optimization of manganese oxide nanomaterials for energy storage devices.

**Keywords:** lithium battery; surface; supercapacitor; DFT; cathode; manganese oxides

## Introduction

Energy storage for hybrid electric vehicles and renewable energy sources is a pressing technological challenge for which Li-ion batteries and supercapacitors are key candidate systems. Due to rising future needs there has been an intensive research effort to search for an alternative to the layered  $\text{LiCoO}_2$  system conventionally used in rechargeable Li-ion batteries.<sup>1-4</sup> Co-based materials pose problems due to high cost and environmental hazards upon disposal. Therefore, manganese based oxides have been a promising class of materials for electrochemical energy storage.<sup>5-10</sup>

$\beta\text{-MnO}_2$  has been extensively investigated as a cathode for rechargeable Li-ion cells, but early work showed that bulk samples did not permit significant Li-ion intercalation.<sup>7,10,11</sup> Initial work on  $\beta\text{-MnO}_2$  supercapacitors<sup>12</sup> also indicated lower capacitance than for other polymorphs such as hollandite  $\text{MnO}_2$ . Yet recent investigations have reinvigorated interest in the material. Mesoporous<sup>10,13,14</sup> and needle-like nanostructured<sup>15,16</sup>  $\beta\text{-MnO}_2$  have been shown to allow good intercalation of Li-ions. Both pore size and wall thickness of the mesoporous structures have been demonstrated to affect the rate capability.<sup>9</sup> The mesoporous  $\beta\text{-MnO}_2$  cell has a capacity<sup>10</sup> of 284 mAh/g and good cycling stability. Recent studies of kinetics using ac impedance measurements<sup>17</sup> have demonstrated increased Li-ion diffusion in nanosized materials. Additionally,  $\beta\text{-MnO}_2$  has shown promise as a catalyst for the oxygen reduction reaction that is the basis of the Li-air battery system<sup>18,19</sup> and as a supercapacitor electrode material.<sup>12,20</sup> The formation of nanostructured small particles has been shown to dramatically increase the capacitance<sup>20</sup> of  $\beta\text{-MnO}_2$  to 294 F g<sup>-1</sup>,

compared to  $\sim 9 \text{ F g}^{-1}$  for bulk crystals.<sup>12</sup>

However, the fundamental basis for the contrasting intercalation properties of nanostructured mesoporous  $\beta\text{-MnO}_2$  and bulk crystalline  $\beta\text{-MnO}_2$  is not fully understood. To understand the factors influencing their electrochemical and nanoionic behavior it is clear that greater knowledge of the diffusion pathways and activation energies that govern Li-ion mobility within the bulk and at the surface is needed on the atomic scale. Motivated by renewed interest in  $\beta\text{-MnO}_2$ , we perform an *ab initio* study of its intercalation behavior extending our recent computational work on lithium battery materials.<sup>21,22</sup> Of key interest is how mesoporous structuring enables intercalation into  $\beta\text{-MnO}_2$ . Indeed, the rapidly growing interest in nanostructuring of many electrode materials<sup>23,24</sup> calls for investigation of the influence of surfaces and interfaces. It is known that, in many cases, nanomaterials have enabled higher intercalation/deintercalation rates (and hence higher power) by reducing the diffusion path length to facilitate fast Li-ion transport, and by increasing the surface area to promote Li-ion exchange across the electrode/electrolyte boundary.

We organise our results as follows. First, results on the prediction of the Li-ion intercalation voltage and the associated structural changes are compared to experiment. We then consider transition state calculations of the Li-ion migration properties in bulk migration of  $\beta\text{-MnO}_2$ . Finally, we explicitly treat the migration from the surface to bulk in  $\beta\text{-MnO}_2$ .

Figure 1 shows the crystal structure of  $\beta\text{-MnO}_2$  where the approximate  $\text{MnO}_6$  octahedra are indicated by polyhedra.  $\beta\text{-MnO}_2$  occurs in the rutile structure<sup>25</sup> with only corner sharing octahedra in-plane that create  $1 \times 1$  tunnels clearly visible along the c-axis in Figure 1(a). These tunnels are expected to play a key role in the ion migration considered in this work. Migration paths A and B in Figure 1(a) involve movement between these tunnels, while path C in Figure 1(b) is characterised by movement along these tunnels. We will return to consider the energetics of these migration paths in detail.

Lithium insertion into mixed  $\beta\text{-MnO}_2$  and ramsdellite  $\text{MnO}_2$  has previously been studied by Maphanga *et al.* using interatomic forcefield methods.<sup>26</sup> In that work, finite temperature molecular dynamics calculations indicated the presence of increased twinning and a tendency to form

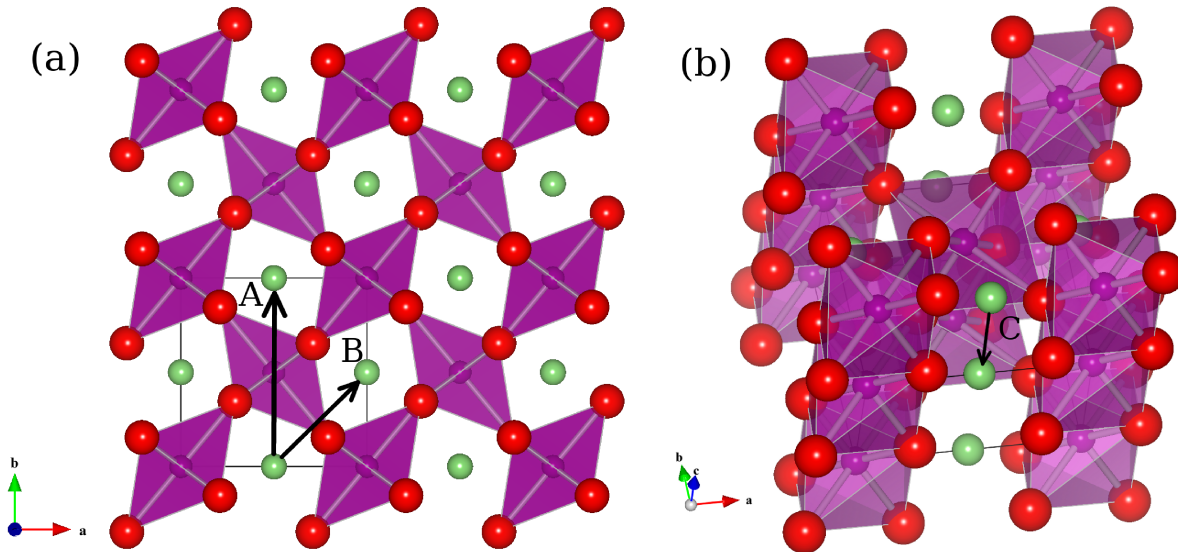


Figure 1: Crystal structure of  $\beta$ -MnO<sub>2</sub> showing the connecting MnO<sub>6</sub> octahedra and the intercalated Li-ions viewed (a) along the *c*-axis and (b) obliquely. Red spheres are oxygen, purple manganese and green lithium. The thin black lines indicate the conventional unit cell. Migration paths indicated by bold arrows are associated with the calculated migration barriers in Table 2.

ramsdellite units upon the intercalation of lithium. Sayle *et al.*<sup>27</sup> have also investigated  $\beta$ -MnO<sub>2</sub> using interatomic potentials and have considered the microstructure, nanoparticle formation and mechanical properties in detail using large-scale molecular dynamics methods.

Previous DFT based studies on  $\beta$ -MnO<sub>2</sub> have considered hydrogen insertion,<sup>28</sup> the phase stability of competing polymorphs,<sup>29</sup> Ruetschi defects in nanosheets,<sup>30</sup> and magnetic properties.<sup>31,32</sup> Given the promising experimental results for intercalation of Li-ions into mesoporous  $\beta$ -MnO<sub>2</sub> there is a need to extend these studies to understand the Li-ion intercalation processes. In particular to determine why nanostructured and mesoporous crystals may improve the properties so greatly.

Koudriachova *et al.* have previously studied the intercalation properties of nanostructured rutile TiO<sub>2</sub> by *ab initio* methods. This work highlighted anisotropic diffusion and the ability of local structural distortions to create Li-ion traps that inhibit diffusion.<sup>33</sup> They also argued that short diffusion lengths and increased structural flexibility near the surface of nanostructures reduces these effects.<sup>34</sup>

## Methods

We have calculated the electronic structure using the Generalized Gradient Approximation<sup>35</sup> (GGA) with Hubbard U corrections GGA+U. The VASP<sup>36</sup> code was employed using PAW potentials. The cutoff for the planewave basis set was 520 eV. A minimum of  $6 \times 6 \times 6$  k-points was used for each calculation. Where stated in the results the all electron full-potential code Wien2k<sup>37</sup> was also employed. Here  $RK_{max}$  was set to 7.0 and the radii of the muffin tins was  $2.01 a_0$  for manganese,  $1.51 a_0$  for oxygen and  $1.51 a_0$  for lithium.

The value of the  $U$  parameter for our GGA+U calculations was determined *ab initio* using Wien2k.<sup>38,39</sup> For  $\beta$ -MnO<sub>2</sub> we obtain  $U_{\text{Eff}} = 5.5$  eV and after lithium intercalation we obtain  $U_{\text{Eff}} = 4.7$  eV for Li- $\beta$ -MnO<sub>2</sub>. To obtain intercalation voltages we require a single value of  $U$  for both the delithiated and lithiated materials. We therefore follow the practice in previous studies<sup>40</sup> and use the average from the two calculations,  $U_{\text{Eff}} = (U - J) = 5.1$  eV, for the spherical part of the interaction for the remainder of this study. All calculations were performed in a ferromagnetic spin polarized configuration with the fully localized limit double counting correction.<sup>41</sup> Since the exchange interaction is poorly screened in solids<sup>38,42</sup> we employ an atomic limit value  $J = 1.0$  eV for  $\beta$ -MnO<sub>2</sub>, an approach extensively justified in previous work.<sup>43</sup>

## Results and Discussion

### Structures and Voltages

Pristine  $\beta$ -MnO<sub>2</sub> occurs in the tetragonal space group  $P4/mnm$  (# 136) with lattice parameters<sup>44</sup>  $a = b = 4.398$  Å and  $c = 2.873$  Å. Intercalation of Li-ions in mesoporous  $\beta$ -MnO<sub>2</sub> occurs by a two-phase reaction on first discharge<sup>9</sup> to form  $\beta$ -LiMnO<sub>2</sub> with a voltage of approximately 3.0 V.<sup>10</sup> X-ray diffraction results<sup>45</sup> indicate that the intercalation reduces the tetragonal symmetry to orthorhombic space group  $Pnnm$  (# 58). The lattice parameters are  $a = 5.1419(7)$  Å,  $b = 5.003(2)$  Å and  $c = 2.8131(8)$  Å representing a contraction of the c-axis with an accompanying expansion

in-plane. This is attributed to the Jahn-Teller distortion when Li-ion intercalation causes  $\text{Mn}^{4+}$  to become  $\text{Mn}^{3+}$ .

In Table 1 we show the GGA+U predicted lattice parameters for  $\beta\text{-MnO}_2$  and its lithiated structure via a two-phase reaction. If we first consider  $\beta\text{-MnO}_2$ , the lattice parameters predicted by GGA+U agree with those from experiment to within 3%, but the usual tendency for GGA+U to overestimate the unit cell volume is evident. For the lithiated  $\beta\text{-LiMnO}_2$  structure, the Jahn-Teller distortion experimentally results in a c-axis reduced by 2% while the a-axis has expanded by 17% and the b-axis by 14%. The GGA+U results shown in Table 1 also predict this contracted structure. All of the GGA+U lattice parameters lie within 3% of those from experiment. It should be noted that the experimental data for  $\beta\text{-LiMnO}_2$  is derived from mesoporous samples and this may affect the structure.

Table 1: Calculated and experimental<sup>10,45</sup> lattice parameters for  $\beta\text{-MnO}_2$  and its lithiated form. Cell voltages are also included for  $\beta\text{-LiMnO}_2$ .

$\beta\text{-MnO}_2$	$a$ Å	$b$ Å	$c$ Å	V (V)
GGA+U	4.442	4.442	2.933	-
Experiment	4.398	4.398	2.873	-
$\beta\text{-LiMnO}_2$				
GGA+U	5.204	5.148	2.853	3.2
Experiment	5.141	5.003	2.813	3.0

Experimentally the intercalation voltage of mesoporous  $\beta\text{-MnO}_2$  is 3.0 V<sup>10</sup> for the two phase process. From our GGA+U total energy calculations for bulk  $\beta\text{-MnO}_2$  we obtain a value of 3.2 V. The small difference between our GGA+U result and experiment is typical of the accuracy obtained with this method over a large class of intercalation compounds.<sup>46</sup> Furthermore, structural contributions to the total energy due to the mesoporous structure are not accounted for in our calculations. Nevertheless, despite the fact that bulk  $\beta\text{-MnO}_2$  permits little intercalation experimentally, the accuracy of our calculated voltage indicates good reproduction of the key contributions to the thermodynamics of intercalation in mesoporous  $\beta\text{-MnO}_2$ . The result also makes clear that the inability to intercalate into bulk  $\beta\text{-MnO}_2$  is not because the process is thermodynamically unfavorable, but is due to kinetic barriers.

## Bulk Migration

Lithium migration properties are important to the rate at which a battery may charge/discharge and hence deliver power. Materials may intercalate with suitable thermodynamics for the voltage, but poor migration rate properties can render them of no practical use, such as  $\text{MoO}_3$ .<sup>47,48</sup> Understanding the difficulty of inserting even minor amounts of lithium into bulk  $\beta\text{-MnO}_2$  is a key problem.

In Fig. 1 we show the three probable paths for migration of Li-ions in the dilute limit of bulk  $\beta\text{-MnO}_2$ . Path A corresponds to migration in the a,b-plane (along [010] and symmetry equivalent [100]). Path B is migration simultaneously along the c-axis and in the a,b-plane (along [111] and symmetry equivalent paths). Path C is migration along the  $1\times 1$  c-axis tunnel (directed along [001]). Using the nudged elastic band method the migration barriers were calculated in the dilute limit of a  $4\times 4\times 6$  supercell corresponding to one lithium in a unit cell of 192 formula units. Table 2 lists the migration barriers. It is clear that migration along the c-axis (path C) is the most favorable path with a barrier of 0.17 eV. Paths A and B both involve migration between  $1\times 1$  tunnels and possess very high migration barriers  $> 2$  eV. This is due to the fact that migration between the c-axis tunnels requires large distortion of the  $\text{MnO}_6$  octahedra which incurs a large energy cost. Our migration barriers therefore imply that lithium diffusion in bulk  $\beta\text{-MnO}_2$  is primarily one-dimensional(1D). Large anisotropy in Li-ion diffusion has also been observed experimentally<sup>49</sup> and from *ab initio* calculations<sup>50</sup> in rutile  $\text{TiO}_2$ . Furthermore, previous work on olivine materials<sup>51,52</sup> has emphasized the capacity for 1D diffusion to make Li-ion transport susceptible to blocking defects. The tendency for polymorphism, microtwinning and grain boundary formation in  $\text{MnO}_2$  has also been highlighted<sup>27</sup> for its influence on the intercalation properties of bulk  $\beta\text{-MnO}_2$ .

The low migration barrier of 0.17 eV for path C indicates why the rate performance of the mesoporous form of  $\beta\text{-MnO}_2$  is so good. Jiao *et al.*<sup>10</sup> found that the discharge capacity fell by only 19 % when the discharge rate is increased from 15 to 300 mA/g. Also, since the facile c-axis migration in bulk  $\beta\text{-MnO}_2$  is principally along c-axis it is likely that lithium may only enter the



Table 2: Energy barriers and Li-Li distances for the lithium migration paths in bulk  $\beta$ -MnO<sub>2</sub> shown in Fig. 1.

Path	Description	$\Delta E$ (eV)	Dist. (Å)
A	Along [010]	7.33	4.44
B	Along [111]	2.22	3.48
C	Along [001]	0.17	2.94

material via surfaces with a component perpendicular to this direction. The mesoporous and nanocrystals that allow cycling are likely to give greater exposure of these surfaces, a topic we will return to.

## Surface Migration

The importance of surfaces and interfaces to both ionic and electronic conductivity in nanoionic materials has been highlighted.<sup>53</sup> The influence of Li-ion migration at surfaces on electrode kinetics may be explored using theoretical means. However, while surface energies and morphologies of cathode materials have previously been studied,<sup>54–56</sup> explicit work on Li-ion migration barriers at surfaces is lacking. In Figure 2 we show an adaptation of the equilibrium crystal morphology determined by using interatomic potential methods.<sup>57</sup> The simulated morphology is consistent with the macroscopic shape of  $\beta$ -MnO<sub>2</sub> determined by scanning electron microscopy (SEM).<sup>18,58,59</sup> Figure 2(a) shows an oblique view, while 2(b) shows a view along c-axis and demonstrates that access to the route of facile c-axis migration is only available at the (101) and symmetry equivalent surfaces. The prominence of the (101) surface is consistent with previous *ab initio* work on rutile MnO<sub>2</sub><sup>60</sup> and TiO<sub>2</sub>.<sup>61</sup> Consequently, it is likely that this is the surface through which most lithium must migrate into bulk crystals.

Using a slab of 288 atoms (cleaved with symmetric (101) surfaces terminated by an oxygen layer and having a vacuum of 12 Å) the Li-ion migration from the surface to the bulk-like slab center has been studied using VASP. One lithium atom was inserted into this slab and the total energy with full structural relaxation evaluated at 42 depths of insertion between the surface and centre of the slab. Constrained minimisation was used to hold the depth of the Li-ion fixed while

all other degrees of freedom are relaxed. The results are shown in Fig. 3. The key finding is that the initial barrier to Li-ion insertion at the surface is  $> 0.6$  eV, which is much greater than the bulk migration energy of 0.17 eV. The small plateau in the Li-ion site energy at a depth of  $\sim 1.3$  Å has an energy well that is too shallow to be a stable lattice site. This barrier of  $> 0.6$  eV occurs predominantly over the first 5 Å after the Li-ion passes the outermost surface oxygen layer. Furthermore, between 10 and 15 Å in depth it can be seen that the migration is becoming bulk-like with a barrier close to 0.17 eV.

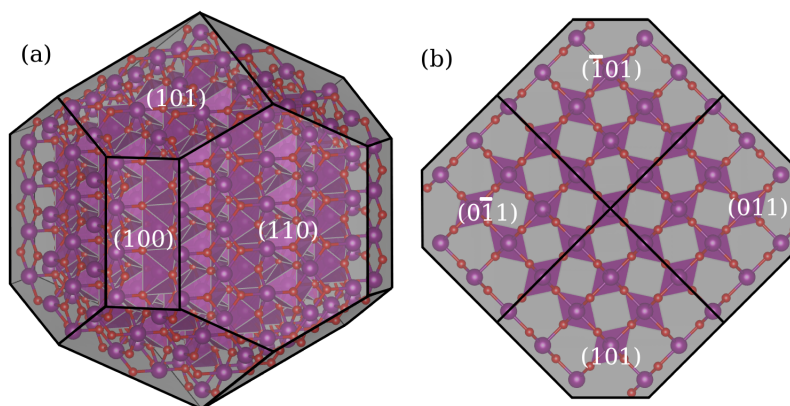


Figure 2: The predicted equilibrium morphology<sup>57</sup> of  $\beta$ -MnO<sub>2</sub> (a) from an oblique view and (b) along c-axis. Adapted from the results of reference.<sup>57</sup>

In addition to the migration barrier calculated from total energies, Fig. 3 also depicts the electrostatic potential experienced by a positive charge with the formal charge  $+1e$  of a Li-ion along the path of the migration. This has been calculated by the sum of the ionic and Hartree potentials in a delithiated slab. The ionic potential is due to the nuclear charge and core electrons. The Hartree potential is the electrostatic potential due to the valence electrons in the system, the distribution of which is calculated explicitly by the density functional theory method we employ. From Fig. 3 it is clear that there is a strong correspondence between the locations of the peaks in the electrostatic potential and the peaks in the plot of the Li-ion site energy. However, the associated electron is able to screen the potential from the Li-ion. Furthermore, effects of chemical bonding will influence the site energy and these factors together make the correspondence, while useful and computationally efficient, qualitative. From the correspondence outlined above, the Li-ion site energies near the

surface in Fig. 3 appear to be predominantly affected by the large oscillations in the electrostatic potential. As the ion passes further towards the bulk the oscillations in electrostatic potential become smaller and will still influence the site energy. However, bonding and structural relaxation effects may then have a proportionately greater role in determining the site energy as we approach the bulk-like region.

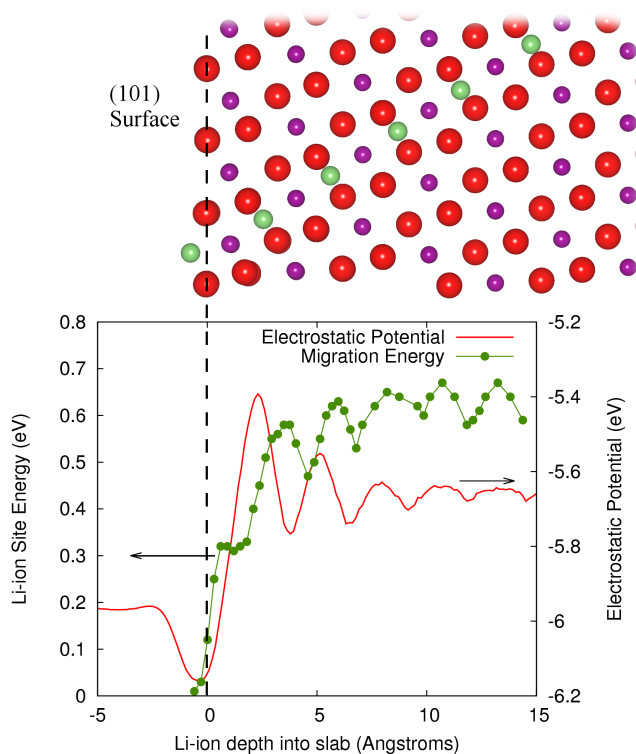


Figure 3: The surface to bulk Li-ion migration barrier at the (101) surface of  $\beta$ - $\text{MnO}_2$  is shown along with the corresponding electrostatic potential in the lower panel. Upper panel schematically shows the migration path from this surface. Red spheres are oxygen, purple manganese and green lithium. The green dotted line is a guide to the eye. The vertical dashed line at zero depth is aligned with the outermost oxygen layer.

As well as the surface potential, structural strain as the lithium ion enters the surface may be a contributing factor. To quantify the strain we have calculated the ionic displacements of the near neighbors to the lithium ions at depths of 0, 2, 4.5 and 9.5 Å. The results are shown in Table 3. The displacements for all depths beyond the surface are non-zero, but it is clear that the displacements in the bulk-like region near 9.5 Å, averaging 0.128 Å, are similar to those near the surface at 2 and 4.5 Å with averages of 0.150 and 0.126 Å respectively. Therefore, we argue that the main barrier

between the surface and bulk is due to the surface electrostatic potential rather than structural strain.

Table 3: Displacements of near neighbors to the Li-ion at intercalation depths of -0.7, 2, 4.5 and 9.5 in Å from the (101) surface. Depths measured relative to the outermost oxygen layer, consistent with the scale in Fig. 3. The co-planar oxygen atoms are in the same plane as the Li-ion, the plane being drawn perpendicular to the direction of migration. Note that the surface adsorbed lithium at -0.7 Å is three-fold coordinate therefore some near neighbours are not applicable (NA).

	Li-ion Depth			
	-0.7 Å	2 Å	4.5 Å	9.5 Å
O1-coplanar	NA	0.143	0.145	0.159
O2-coplanar	0.000	0.144	0.140	0.158
O3	0.000	0.121	0.106	0.109
O4	NA	0.166	0.105	0.116
O5	0.000	0.052	0.105	0.078
O6	NA	0.175	0.096	0.121
Mn1-coplanar	NA	0.261	0.168	0.141
Mn2-coplanar	NA	0.138	0.144	0.142
Average	0.000	0.150	0.126	0.128

To assess the surface to bulk migration barrier at alternative surfaces the (001) surface has been considered. The (001) surface was chosen as it is calculated<sup>57</sup> to have the lowest energy, after (101), amongst surfaces giving access to the tunnel for c-axis migration. The other surfaces of lower energy, (110) and (100), do not give access to the c-axis tunnel due to the high migration barriers A and B presented in Table 2. It is useful to discuss some general properties of the two surfaces we treat, namely the (101) and the (001). According to the classification of Tasker,<sup>62</sup> ‘as-cut’ surfaces can be one of three structural types, which are normally referred to as Types I, II and III. Type I surfaces are formed from layers containing a charge-neutral combination of cations and anions, and thus have no net dipole perpendicular to the surface plane. For Type II surfaces, a finite group of atomic layers parallel to the surface form a charge-neutral, repeated unit with no net dipole normal to the surface normal. For Type III surfaces, by contrast, irrespective of where the crystal is cut, a dipole moment always exists perpendicular to the surface plane; in this case, convergent surface energies can only be obtained if the surface layer is reconstructed in some way to remove the dipole moment. This usually involves removing a suitable number of ions from one side of the crystal to the other in order to make the crystal slab symmetric about its midpoint.

In this scheme the (101) surface of  $\beta$ -MnO<sub>2</sub> falls into the Type II category, with a repeat unit of three layers oxygen-manganese-oxygen lying parallel to the surface. The (001) surface, however, is Type I with charge neutral MnO<sub>2</sub> layers parallel to the surface.

Figure 4 shows the migration barrier profile calculated using constrained minimization for the (001) surface. The largest single barrier, near a depth of 6 Å, is less than 0.3 eV. It is clear that the barrier to migration at this surface is much smaller than at the (101) surface. The electrostatic potential associated with the Type I (001) surface, possesses only small variations compared to that due to the Type II (101) surface. Consequently the metal-oxygen layers dominate and we see a peak in the migration barrier profile as the lithium passes each one. Based upon this correspondence we suggest that the form of the electrostatic potential in the near surface regions may be used to efficiently screen systems for the importance of surface migration effects. It is argued that nanostructuring is capable of exposing alternative surfaces, such as the (001), and that this is a means via which intercalation processes may be enhanced in both Li-ion batteries and supercapacitors.

A further consideration is that in real battery and supercapacitor systems these surfaces will be surrounded by electrolyte solutions. The charged ions in solution may become adsorbed to surface sites, particularly at the partial charges of the oxygen terminated surfaces.<sup>63</sup> This adsorption is likely to alter the form of the surface potential and will be the subject of future investigation. The precise nature of the effects will depend upon the pH and other characteristics of the electrolyte solution. However, we suggest that due to the finite size of adsorbed ions the addition of a Stern-type charge layer will largely affect the electrostatic potential in the region outside the surface, while the primary contribution to the migration barriers in Fig. 3 and Fig. 4 occurs in the initial sub-surface layers.

It is stressed that we have investigated key low-energy surfaces that allow access to the favored c-axis tunnel for Li-ion diffusion. Clearly other surfaces may be exposed by nanostructuring, but due to the very large computational demands of these calculations their treatment warrants future studies. Nevertheless, this work demonstrates quantitatively that the migration barrier at surfaces can be the limiting process for ion intercalation. Furthermore, given that supercapacitors rely

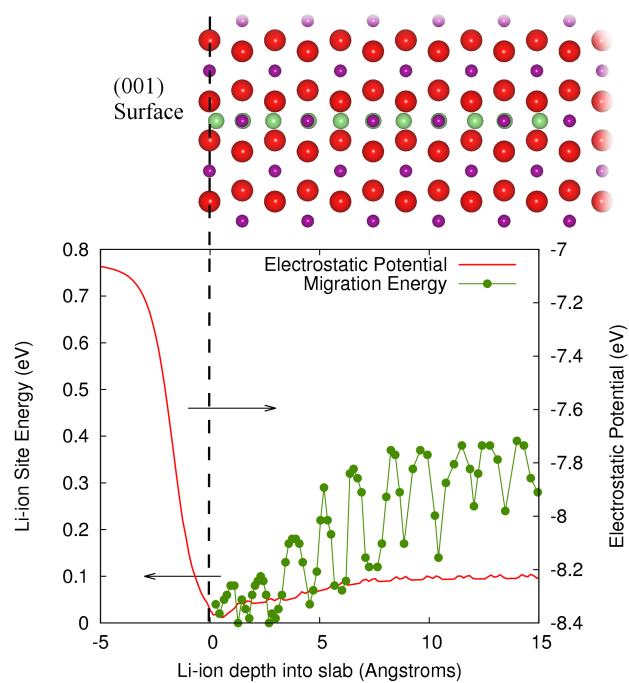


Figure 4: The surface to bulk Li-ion migration barrier at the (001) surface of  $\beta$ -MnO<sub>2</sub> is shown along with the corresponding electrostatic potential in the lower panel. Upper panel schematically shows the migration path from this surface. Red spheres are oxygen, purple manganese and green lithium. The green dotted line is a guide to the eye. The vertical dashed line at zero depth is aligned with the outermost oxygen layer.

upon ion intercalation for much of their capacitance, it is likely that the same influences are active in  $\beta$ -MnO<sub>2</sub> supercapacitors. Furthermore, it is likely that the impact of surfaces upon the Li-ion migration characteristics is significant in other cathode and anode materials and this will be subject of future work.

## Conclusions

This investigation has provided new atomic-scale insights into the intercalation properties of  $\beta$ -MnO<sub>2</sub>, especially the importance of considering surface effects. The key results include:

- 1) GGA+U shows good reproduction of experimental crystal structures, including Jahn-Teller distortions, and lithium intercalation voltages.
- 2) The migration of Li-ions in bulk  $\beta$ -MnO<sub>2</sub> is primarily one-dimensional along the c-axis tunnels in the rutile structure indicating anisotropic diffusion.
- 3) The Li-ion migration barrier from the (101) surface to bulk is  $> 0.6$  eV and dominates over the bulk migration barrier of 0.17 eV. This surface migration barrier is likely to influence the difficulty in intercalating lithium into bulk samples of  $\beta$ -MnO<sub>2</sub>, and suggests why intercalation is switched on by moving to nanostructured crystals. Indeed, such intrinsic differences in the Li-ion mobility in the bulk and at the surfaces may be key factors in the intercalation behavior of nanostructured versus bulk crystalline systems for many materials.
- 4) Based on the calculation of the electrostatic potential near the surface, and its correlation with the Li-ion migration at that surface, we suggest an efficient means to screen systems for the importance of surface migration effects.
- 5) This work is a quantitative demonstration of a rate limiting surface to bulk ion migration barrier which is significant for the kinetics of intercalation/deintercalation and hence for charge/discharge rates.
- 6) These results suggest that synthesis techniques such as nano-sizing that are capable of exposing alternative surfaces may enhance intercalation processes in both battery and supercapacitor

systems.

Given the importance of understanding the ion intercalation process, the results presented in this paper provide valuable insight for the future optimization of nanostructured manganese oxides for energy storage devices.

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