Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


Supporting information

# Ethylene carbonate adsorption on the major surfaces of lithium manganese oxide $Li_{1-x}Mn_2O_4$ spinel ($0.000 < x < 0.375$): a DFT+*U*-D3 study

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1. ***The effect of surface delithiation on the lattice parameter and volume.***

   Based on the crystal lattice changes that might occur as a result of surface delithiation when modelling the delthiated phases, we carried out benchmark calculations to check the changes that might occur to the volume due to this defect. The benchmark calculations were carried out through the following steps:

   a) Taking both the representative lithiated and delithiated slab model
   b) Unfreeze the bottom two layers and add ISIF=3 to the INCAR
   c) Compare the resulting surface areas.

   The Table I below summarizes the lattice parameters and the surface area for the (001) surface at different Li concentration with respect to the bulk lattice parameters and surface area.

Table I. The effect of surface delithiation on the lattice parameter and volume. The calculation was performed by allowing all the atoms to move and setting the ISIF = 3 in the INCAR.

| | | Lattice parameters | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Composition | *a* | *b* | *c* | Surface area | %par | %area | |
| Bulk | | 8,35 | 8,35 | 22,35 | 69,72 | | | |
| (001) surface | $Li_7Mn_{16}O_{32}$ | 8,35 | 8,35 | 22,35 | 69,72 | 0 | 0 | |
| | | 8,35 | 8,35 | 22,35 | 69,72 | | | ISIF=3 |
| | $Li_6Mn_{16}O_{32}$ | 8,35 | 8,35 | 22,35 | 69,72 | 2.4 | 4.9 | |
| | | 8,15 | 8,15 | 12,27 | 66,40 | | | ISIF=3 |

We found that the slabs had minor changes with difference of ~0.02 Å, which is equivalent to 3% and an area difference of ~0.05 $Å^3$, which is equivalent to 5%. Indeed, only minor changes in the lattice parameter of the cathode material are expected since a major change in the structure of the cathode would mean loss of possible recharge ability leading to deterioration.

2. ***The effect of delithiation on the surface free energies and particle morphologies.***

   For validation, we calculated the surface free energies of the $LiMn_2O_4$ spinel surfaces with the same stoichiometry, and also constructed their morphologies for each Li concentration. Very similar morphologies were observed, which showed a decrease of the (001) plane, while the (111) surface became more prominent for low Li content decrease. The (011) surface does not appear in the Wulff morphology after delithiation

or adsorption of the EC molecule, because of its higher surface free energy with respect to the (001) and (111) planes (see Figure 1 below).

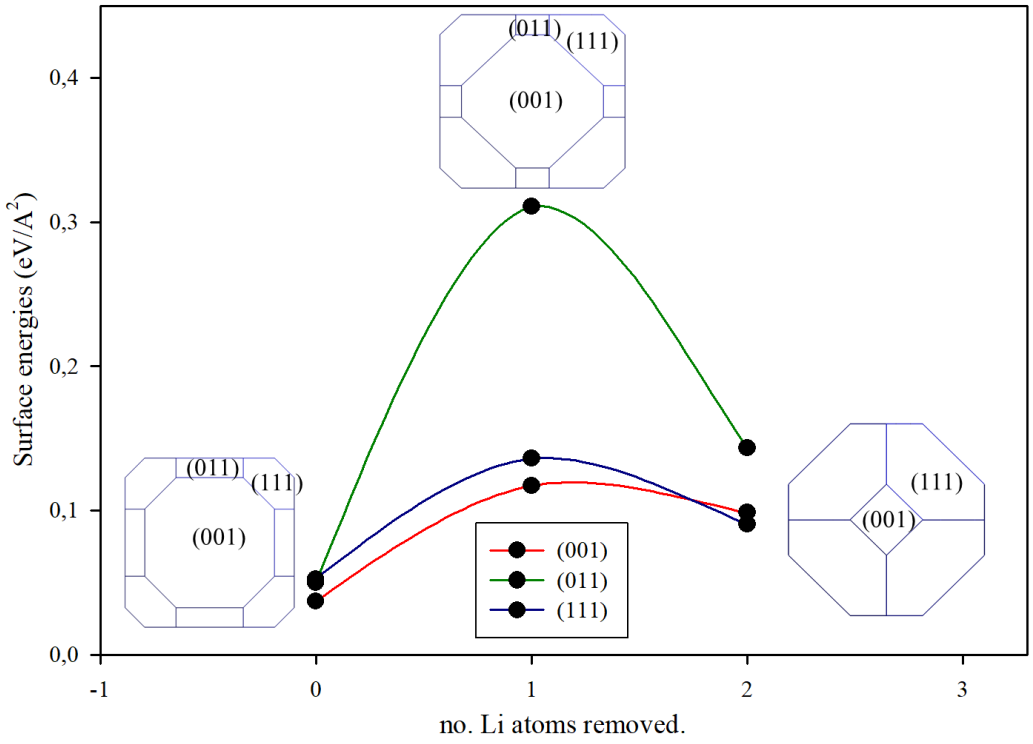


Figure 1. The effect of delithiation onto the $LiMn_2O_4$ spinel surfaces at different Li content. The plot indicate the surface free energies calculated for the three slabs containing the same number of lithium vacancies at different Li concentrations. The particle morphologies indicate the effect of surface delithiation on the nano particles. Note that for $x = 0$, the surface free energy is equivalent to the surface energy ($\sigma = \gamma$).