Ethylene Carbonate decomposition on $LiMn_2O_4$ (111) surface

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$LiMn_2O_4$ (LMO) spinel is a promising cathode material for rechargeable Li-ion battery applications [1] due to factors like high abundance of manganese (Mn), low cost, and the environmentally friendly nature of the material. The (111) facet of LMO has been experimentally found to be most stable [2]. Recently, theoretical work by Karim et al. [3] showed that by choosing proper reconstruction, it is possible to obtain the (111) surface as the most stable facet of LMO. We have studied the decomposition of ethylene Carbonate (EC), a main component of Li-ion battery electrolytes, on Karim et al.'s [3] prescribed (111) LMO surface. The static calculations show that the EC adsorbs molecularly on this surface and the EC decomposition reactions on this LMO (111) surfaces are endothermic.

Karim et al.'s [3] prescribed (111) LMO surface has no exposed Mn. However, it is well known that Mn dissolves in the electrolyte. In this context, we propose a new reconstruction (Fig. 1) where 5-coordinated Mn is exposed on the (111) surface. This surface is slightly higher in energy than Karim et al.'s surface [3] but it is still more stable than the (100) facet. Interestingly, we find that EC reacts exothermally with the newly proposed reconstruction. Moreover, some EC decomposition intermediates predicted for our LMO (111) surface are similar to those on (100) [4]. We will be discussing the reaction barriers for the EC decomposition on the newly proposed LMO (111) surface. The implications of these reactions on Mn(II) dissolution will be explored.

References

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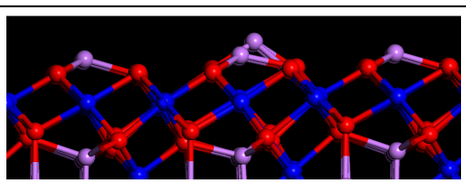

Fig 1. Proposed $LiMn_2O_4$ (111) reconstructed surface. Li, Mn and O atoms are shown as purple, blue and red spheres.