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Theoretical Studies of Organic Solvent Decomposition on Lithium Manganese Oxide and Lithium Peroxide Surfaces

Advanced Batteries and Energy Conversion

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Motivation (LMO)

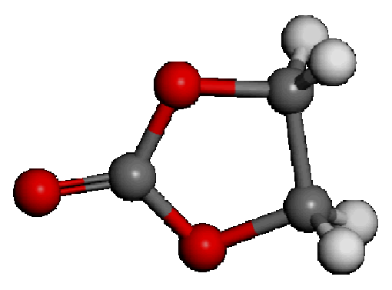
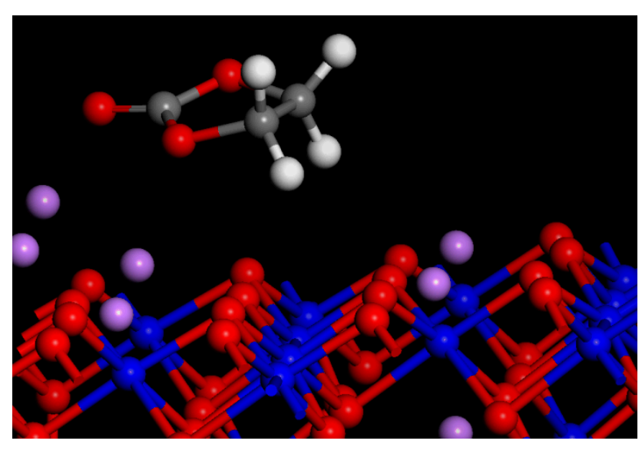
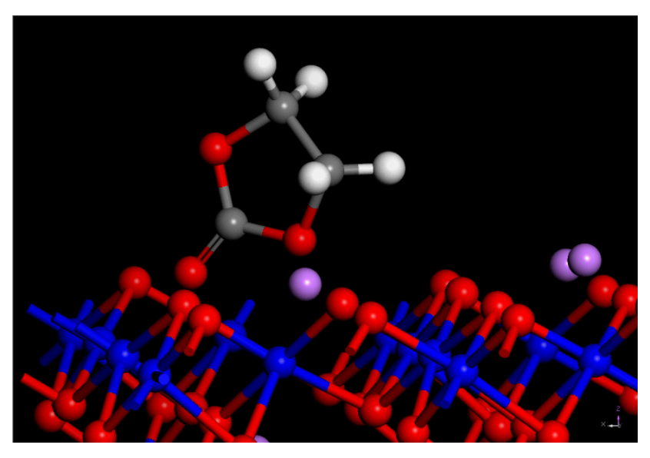
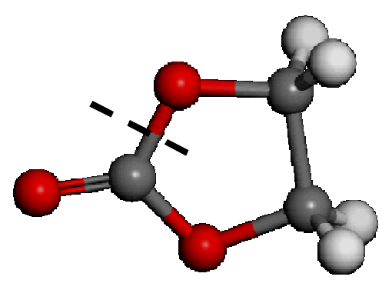
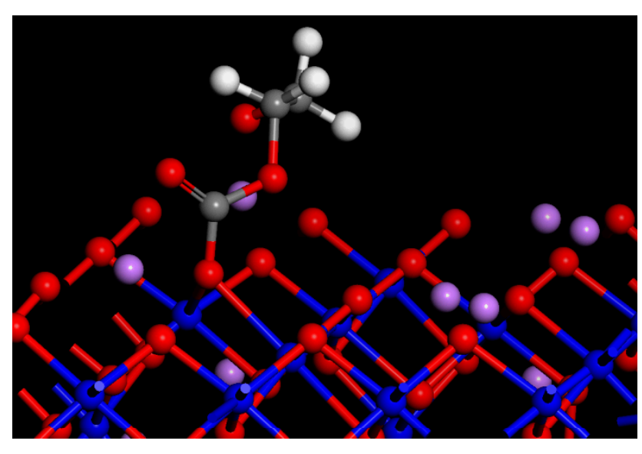
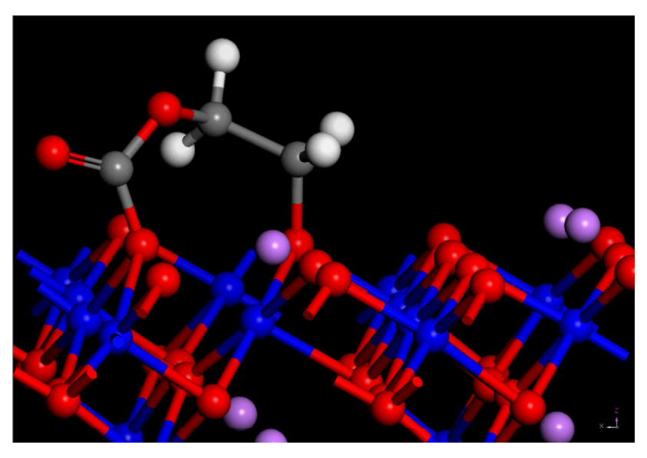
- $LiMn_2O_4$ (LMO) spinel is a promising cathode material[1] due to advantages like low cost due to high abundance of manganese (Mn), better safety and low toxicity to environment.
- The LMO cathode can be used in rechargeable Li-ion battery applications such as in making high power battery as required by hybrid electric vehicles, portable power tools etc.
- Mn dissolution and eventually electrolyte degradation is a major problem in the application of LMO as cathode.

Objectives (LMO)

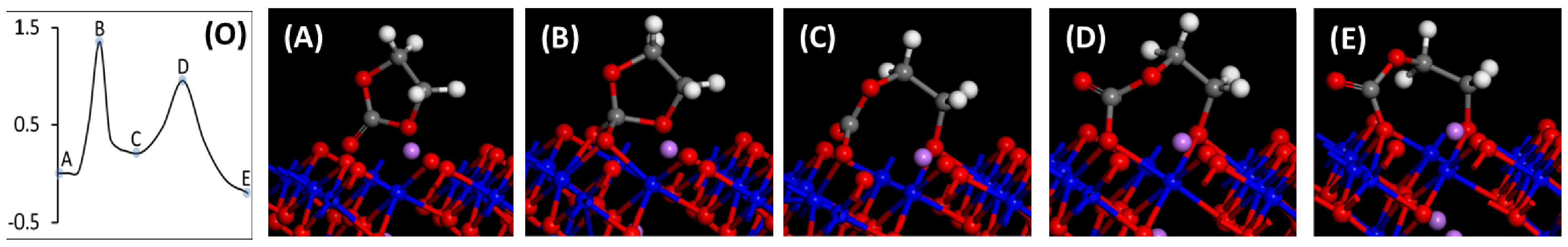
- Developing atomic level understanding of degradation mechanisms at LMO cathodes. This can potentially facilitate engineering of electrode surfaces to minimize electrolyte oxidation and hence permit the use of traditional electrolyte in high-voltage batteries.
- Ultimately consider the effects of oxygen vacancies, Ni substitution, and other defects on Mn dissolution and electrolyte decomposition from spinel cathode oxide surfaces. New electrolytes will also be considered.

Accomplishments (LMO)

- A new surface reconstruction for LMO (111) surface is proposed. This has lower surface energy than (100) surface, consistent with experimental findings[2].
- The exposed Mn makes this surface more reactive than one previously reported[3].
- The adsorption energy ($E_{ads} = E_{configuration} - E_{surface} - E_{molecule}$) for newly proposed and previously[3] reported surface:

	Previous [3] LMO (111)		New LMO (111)	
Intact EC 		-1.36 eV		-1.12 eV
Broken EC [O-CO] 		-0.55 eV		-1.61 eV

- EC reacts exothermally with the newly proposed reconstruction with respect to the intact configuration. These predicted decomposed EC intermediates are similar to those observed on LMO (100)[4] surface.
- We studied the decomposition mechanism for EC from Intact to Broken configuration which comprises two steps:



- In first step, the molecule bonds to the surface with higher reaction barrier followed by decomposition. In second step, the molecule reorients and relaxes.
- Predicted barriers suggests reactions much slower than battery cycling timescales. Other explanations for cathode “SEI” formation (e.g., H^+ transfer) is being studied.
- Insight gained on LMO(111) will be applied to study SEI on high-voltage, Ni-doped spinel surfaces and facilitate future collaborations with industry (e.g., Ford Motor Co.)

Motivation (Li-O_2)

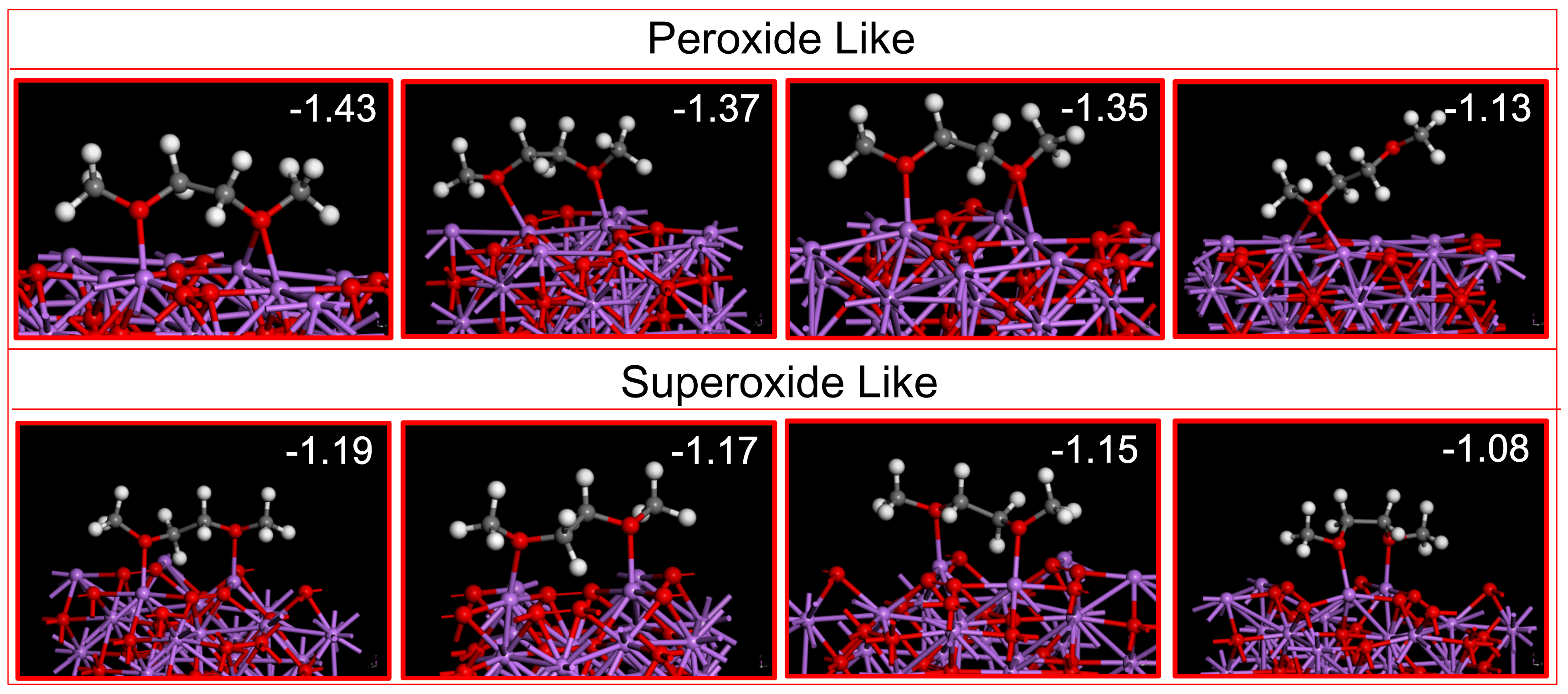
- Li-O_2 battery is a promising alternative to Li-ion battery with the possibility of providing low cost and around five times higher specific energy[5].
- Electrolyte stability is a major challenge faced in the application of Li-O_2 batteries[6].

Objectives (Li-O_2)

- Modeling electrolyte/electrode interface to understand electrolyte degradation at atomistic scale which can further aid in screening electrolytes suitable for Li-O_2 batteries.

Accomplishments (Li-O_2)

- Major discharge product of Li-O_2 battery is Li_2O_2.
- We use classical Monte Carlo technique followed by DFT optimization to obtain the starting configurations for DME adsorption on peroxide and superoxide like Li_2O_2 surfaces[7].
- The top four most stable configurations for the two surfaces along with corresponding adsorption energy:



- DME adsorbs strongly when both of its oxygens binds with the surface Li.

Future Work

- The high energy barrier obtained in LMO study suggests that we should consider other reaction sites on the surface. The effect of salt on decomposition processes will also be studied.
- In Li-O_2, we will be exploring decomposition routes such as proton abstraction.

References

1. K. Kang et al., Science, 311 (5763), 977–980 (2006).
2. M.-R. Huang et al., Appl. Surf. Sci. 177, 103 (2001).
3. A. Karim et al., Phys. Rev. B 87, 075322 (2013).
4. K. Leung, J. Phys. Chem. C 116, 9852 (2012).
5. B. D. McCloskey et al., J. Phys. Chem. Lett. 3, 997-1001 (2012).
6. V. S. Bryantsev et al., J. Electrochem. Soc., 160 (1) A160-A171 (2013).
7. M. Radin et al., J. Mater. Sci., 47, 7564-7570 (2012).

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