Thrust C: modeling Li_xMnO_2 bulk and interfaces (in progress)

SAND2011-8090C

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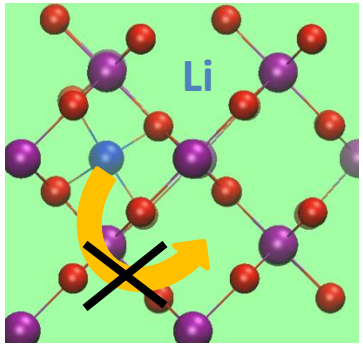
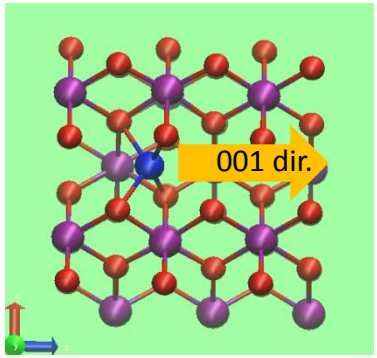
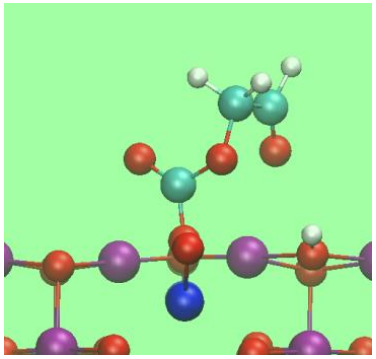
Collaborators: Kevin Zavadil, Janice Robey-Reutt, Yu Qi

directional Li diffusion in β-MnO_2





electrolyte decomposition on electrode surfaces



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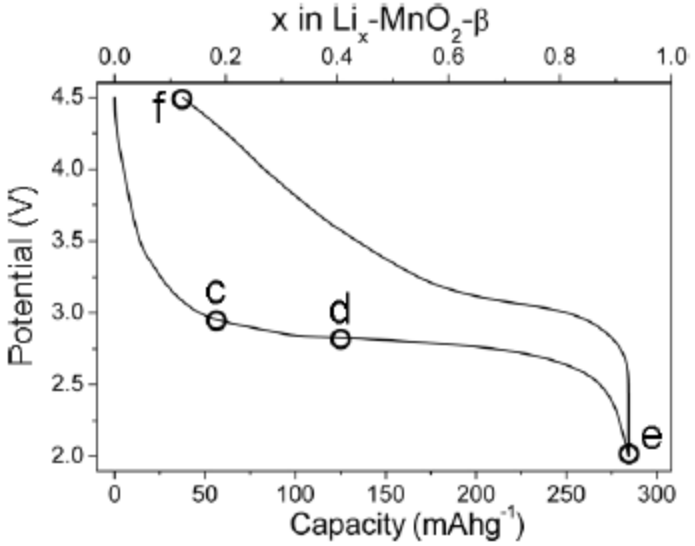
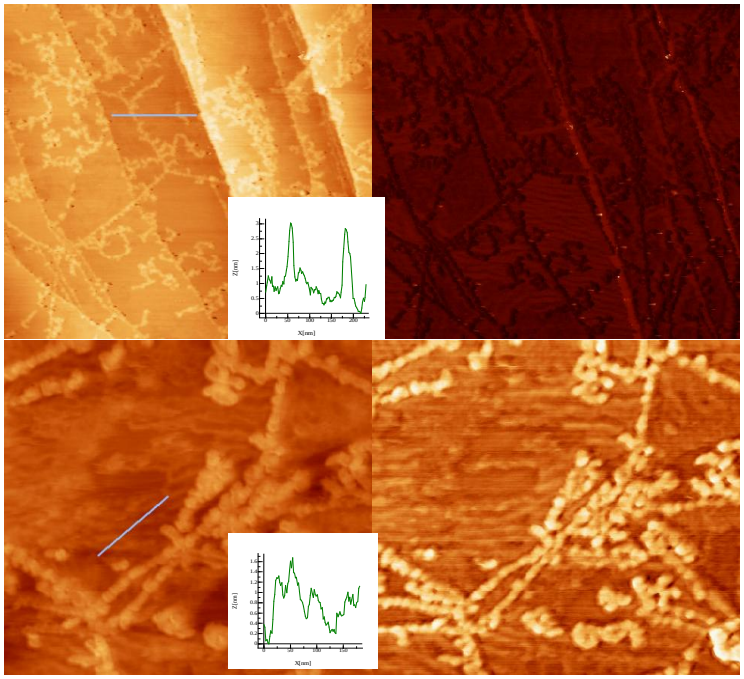
1. Li diffusion in β-MnO_2: expt. & theory

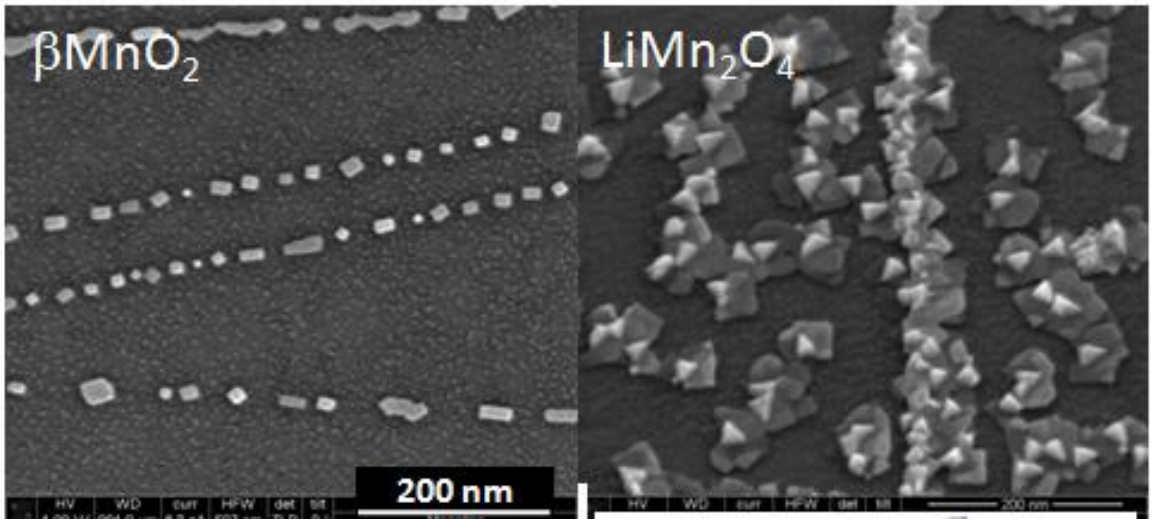
- bulk β-Mn_2O_4 little capacity but nanoscale shows good capacity

Jiao & Bruce, Adv. Mater. 19:657 (2007)





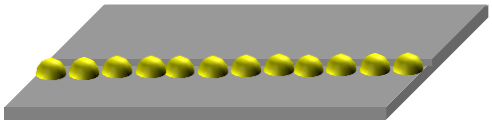
Phase images

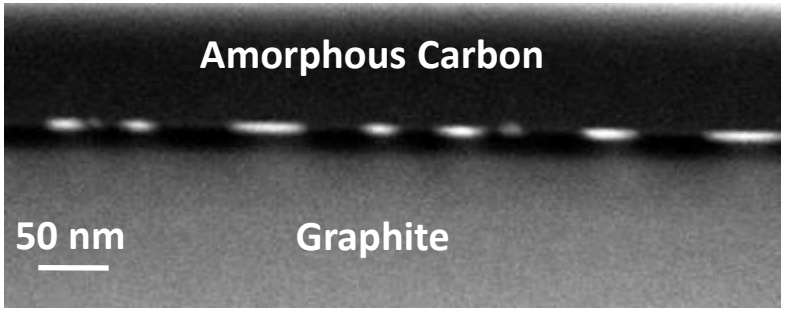


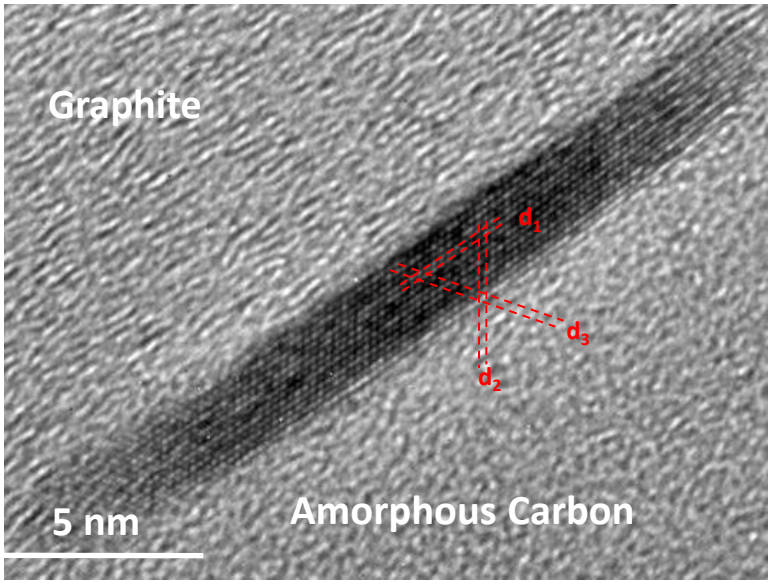
Robey-Reutt group (UMD): $LiMn_2O_4$ ready formation – under excess Li

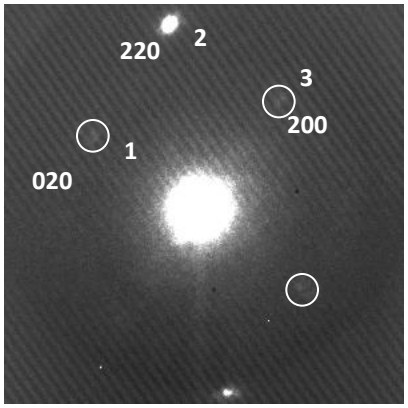
Zavadil group, TEM image

TEM Indexing of β MnO_2 particles at SNL







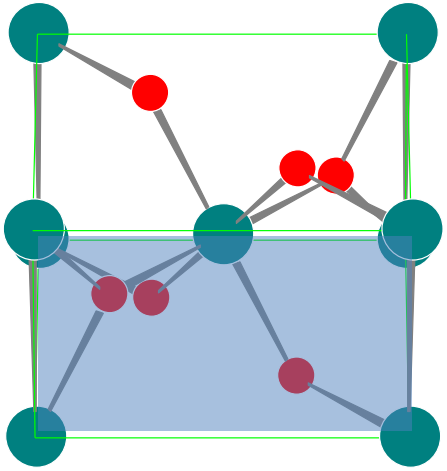


d_1= 0.220nm
d_2=0.156nm
d_3=0.218nm

Tetragonal structure of βMnO_2

a = 0.440 nm

b = 0.287 nm



Particles oriented by substrate

MnO2 100 plane is parallel to graphite basal plane

Tutorial: DFT computational approach for β-MnO_2

LDA

PHYSICAL REVIEW VOLUME 140, NUMBER 4A 15 NOVEMBER 1965

Self-Consistent Equations Including Exchange and Correlation Effects*

W. KOHN AND L. J. SHAM

$$E=\int v(\mathbf{r})n(\mathbf{r})\,d\mathbf{r}+\frac{1}{2}\int\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}'+G[n] \qquad G[n]\equiv T_s[n]+E_{xc}[n]$$

DFT is exact
but E_{xc} unknown

$$E_{xc}[n]=\int n(\mathbf{r})\epsilon_{xc}(n(\mathbf{r}))\,d\mathbf{r}$$

"Local density approximation" (LDA); "PBE" is related
electron density n(r) almost constant

- surprisingly good accuracy for solid state physics (e.g., Si, Al crystals)
- give reproducible trends for main group elements
- terrible for 3d, 4d, 4f, 5f localized electrons (transition metal oxides, lanthanides, actinides)

DFT+U, hybrid functionals

- DFT+U: cheap, tune U parameter to expt., usuall works – but not for β-MnO_2!
- hybrid functional: add fractional $\frac{1}{2}\int\int\frac{n_1(\mathbf{r},\mathbf{r}')n_1(\mathbf{r}',\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}'$ $n_1(r,r') = \psi(r)\,\psi(r')$
- very expensive for crystals, chemists use for molecules, becoming mainstream in physics

β-MnO_2: only hybrid DFT predicts finite band gap

TABLE IV. Results of DFT, DFT+U, and hybrid DFT calculations for the electronic gap (eV). The label HM refers to a half-metallic ground state, for which the gap corresponding to the insulating spin channel is given. For Mn_3O_4 and α-Mn_2O_3, we list both the minority and majority PBE0 and HSE gaps.

	PBEU6	PBEU4	PBEU3	PBE	PBE0	HSE	Expt.
MnO	2.1	1.8	1.6	0.9	3.8	2.9	3.6–4.2[a,b]
Mn_3O_4	0.5	0.4	0.3	0.0	2.4	1.7	
	HM	HM	HM		3.2	2.3	
α-Mn_2O_3	4.1	3.5	3.1	0.0	1.1	0.1	
	HM	HM	HM		5.8	4.0	
β-MnO_2	0.0	0.0	0.0	0.0	1.5	0.6	

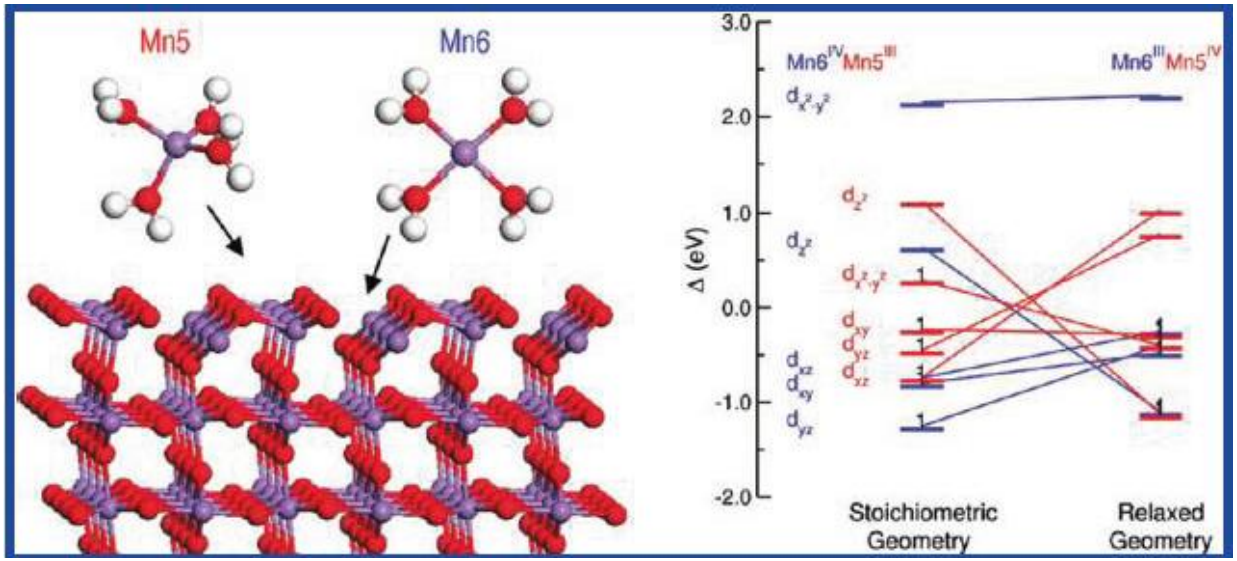
Franchini et al., PRB 75:195128 (2007)

- further improving DFT for d, f-electrons, excited states, deserve another Nobel prize

These DFT issus are often, regrettably, ignored by geochemists and friends (no DFT+U, no hybrids)

First-Principles Calculations of Clean, Oxidized, and Reduced β-MnO_2 Surfaces

Gloria A. E. Oxford* and Anne M. Chaka

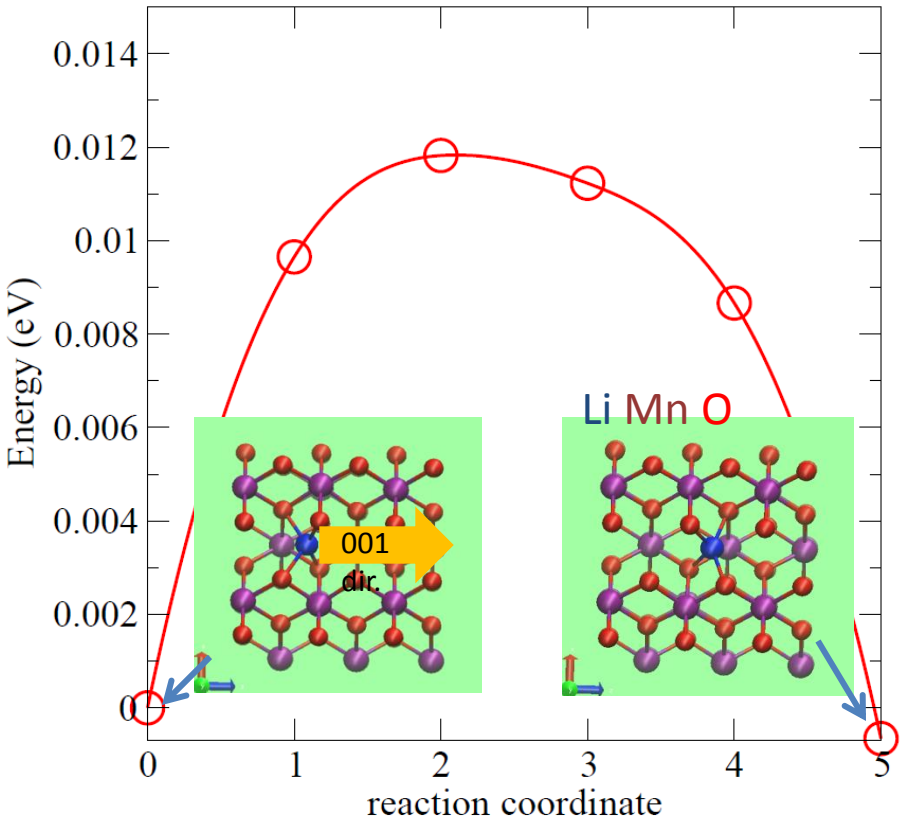


Predictions: Li^+ transport along (110), (001) in β-MnO_2

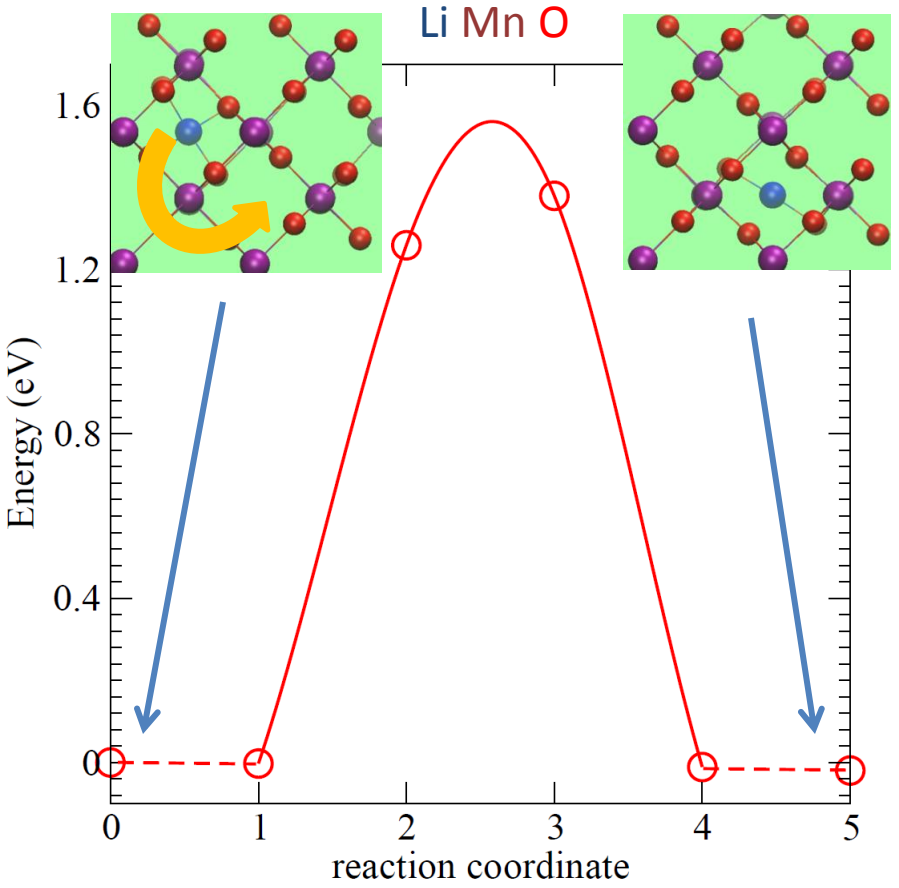
- bulk β-Mn_2O_4 little capacity but nanoscale shows good capacity Jiao & Bruce, Adv. Mater. 19:657 (2007)
- Potentially useful for solid state electrolyte surface layer?

Li^+ motion fast along (001) channels of rutile structure, consistent with rutile TiO_2*

*Sebastian et al, JPCC. 113:20998 (2009)



... much higher barrier perpendicular to (001)

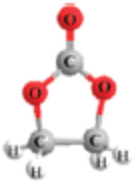


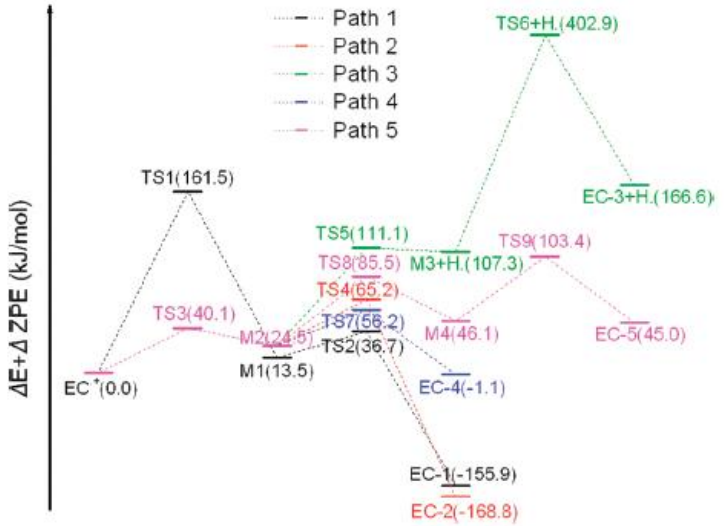
preliminary DFT/PBE0 results; not completely converged

2. Organic solvent decomposition on spinel $Li_xMn_2O_4$

- "SEI on cathode," "oxidative decomposition of electrolyte," controversial
- DFT+U, T=0 barriers, AIMD; hybrid DFT to check results

- ex-situ TEM: SEI on (110) & (111), Mn dissolves from (110) Hirayama et al, JACS 132:15268 (2010)
- in-situ mass-spec.: acetone, CO_2 "oxidative decomposition product" from propylene carbonate Ufheil et al., Electrochem. Commun. 7:1380 (2005)
- in-situ FTIR: acetone, CO_2 evolution Joho et al., Electrochim Acta 45:3589 (2000)
- Ex-situ XPS, TEM: LiF, polyether on surface Eriksson et al, JECS 149:A69 (2002)





structure	ΔE	$\Delta E + \Delta ZPE$	ΔH	ΔG	ω
$EC^{\bullet+}$	0.0	0.0	0.0	0.0	
TS1	166.0	161.5	163.7	158.7	464 *i*
M1	31.1	13.5	17.7	6.8	
TS2	40.8	36.7	40.8	29.4	553 *i*
EC-1	−134.6	−155.9	−147.8	−171.8	
TS3	41.8	40.1	40.2	39.8	426 *i*
M2	35.1	24.5	27.0	20.9	
TS4	73.5	65.2	70.1	54.6	688 *i*
EC-2	−145.8	−168.8	−160.6	−186.4	
TS5	140.2	111.1	113.0	110.2	415 *i*
$M3+H^{\bullet}$	140.8	107.3	113.8	81.8	
$TS6+H^{\bullet}$	457.2	402.9	414.0	370.6	437 *i*
$EC-3+H^{\bullet}$	219.9	166.6	182.9	120.4	
TS7	40.9	56.2	41.4	42.8	124 *i*
EC-4	19.0	−1.1	6.4	−18.7	
TS8	103.7	85.5	88.5	82.8	235 *i*
M4	67.1	46.1	53.4	37.0	
TS9	128.2	103.4	110.1	94.4	569 *i*
EC-5	78.4	45.0	58.4	20.0	

- DFT calculation (no electrode): high (>1.7 eV) overall barrier Xing et al., JCPB 113: 16596 (2009)

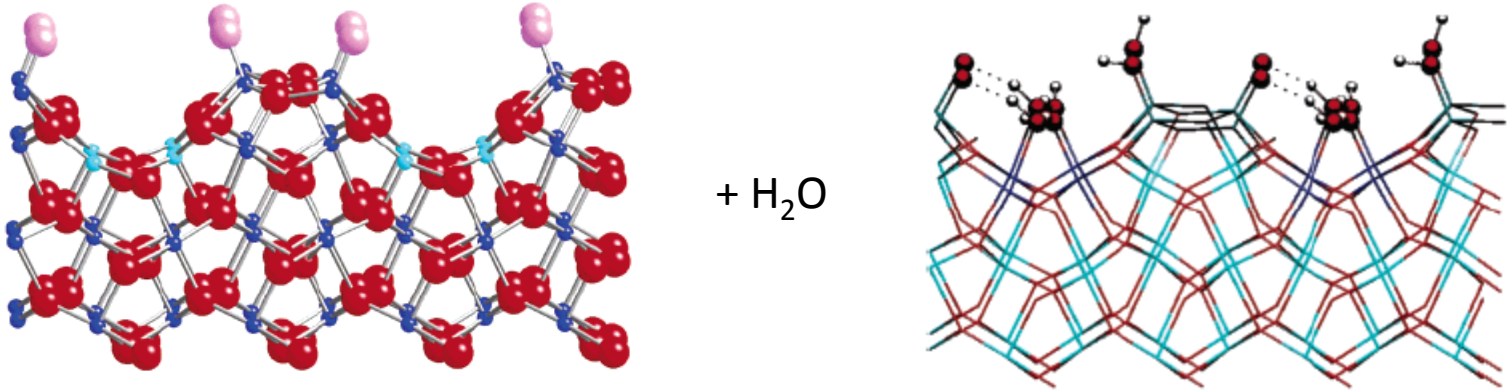
Focus on analogy with water-on-transition metal oxides

- EC – the "new water" of electrical energy storage
- critical for graphitic carbon anode to work
- H_2O adsorption on oxide much studied
- tend to dissociates into OH^- and H^+

J|A|C|S
ARTICLES
Published on Web 06/17/2005

Adsorption of Water on Reconstructed Rutile TiO_2(011)-(2×1): Ti═O Double Bonds and Surface Reactivity

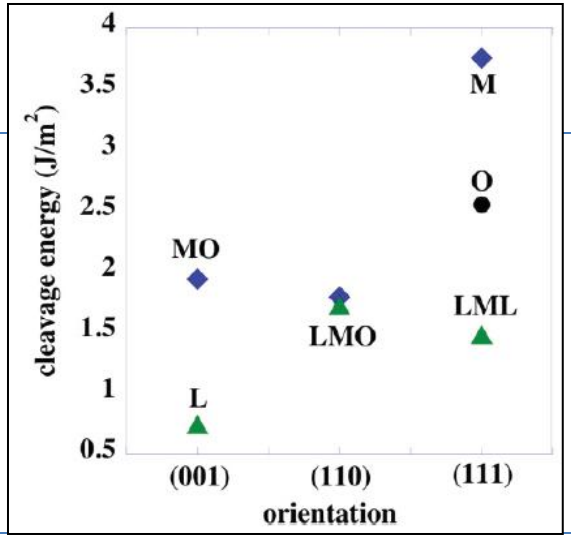
A. Sellnoi group (Princeton)



[Aschauer & Sellnoi, PRL 106:116102 (2011)]

Spinel $Li_xMn_2O_4$ (100) surface

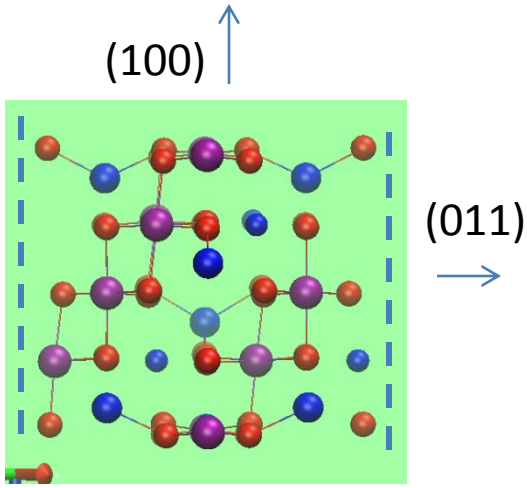
- don't worry too much about battery SEI experiments
- focus on basis science, clean oxide surface, potentially verified by UHV expts.



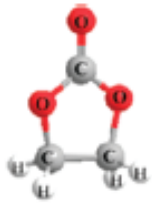
- fully discharged (x=1), (100) surface most stable
- reproduces DFT+U surface energy in literature

Benedek & Thackeray PRB 83:195439 (2011)

- Partial charging (e.g. x=0.6) more pertinent to SEI studies
- Use a $Li_6Mn_{20}O_{40}$ slab, optimal Li vacancies determined by computing energies of all 105 possible configurations



Unlike water, EC thermodynamically unstable



$CO_2 + CH_3CHO$ $\Delta E \sim$ -0.3 eV

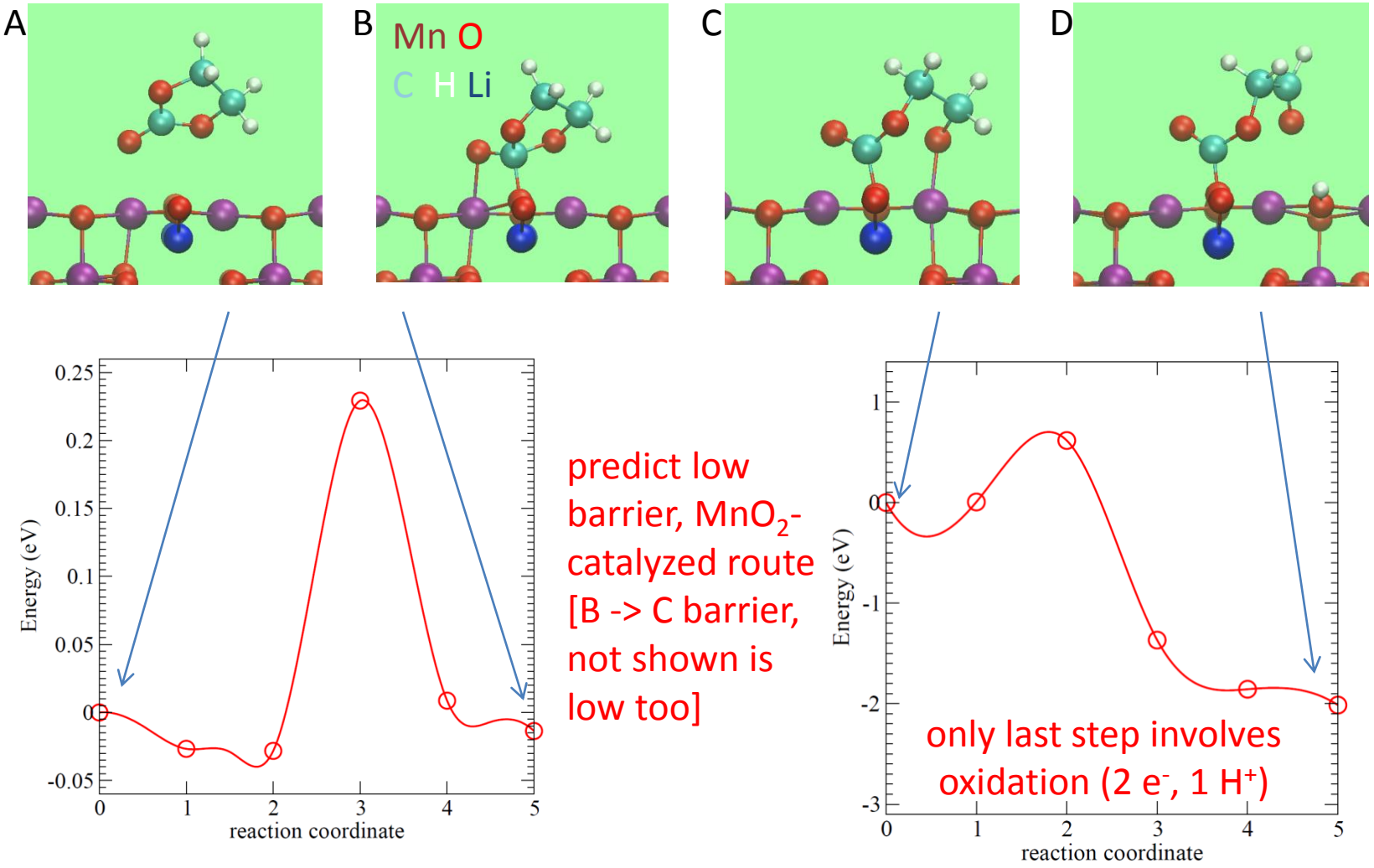
- disproportionation, not oxidation despite release of CO_2
- underscores that batteries are only kinetically stable

Next, consider interface between EC and $LiMn_2O_4$

- will apply DFT+U functional, which works for spinel
- DFT/PBE0 based studies under way to check results

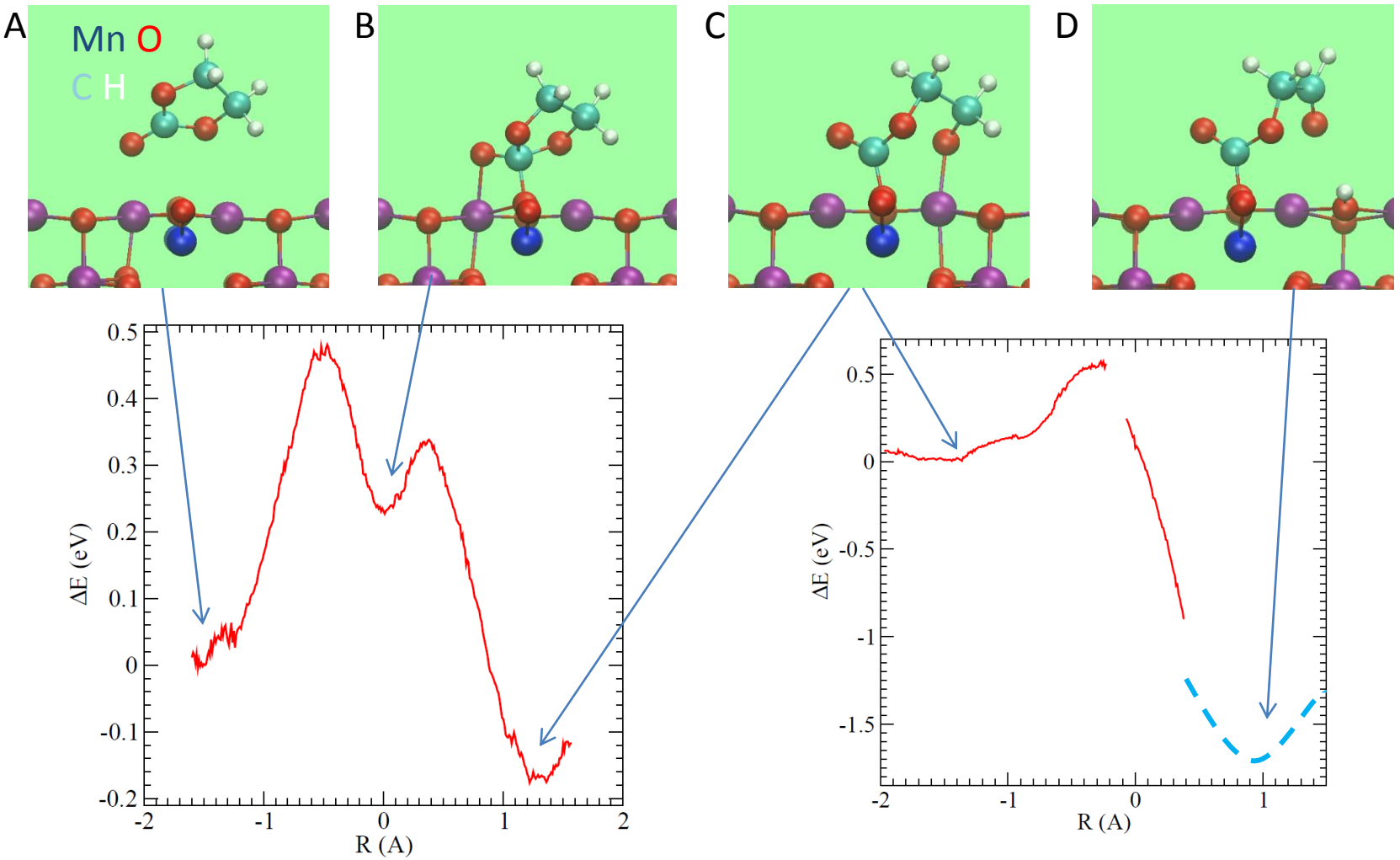
EC/$Li_{0.6}Mn_2O_4$ (100) interface: isolated EC decomposes at T=0 K

- pathway and product channels controversial [Eriksson et al., JECS 149:A69 (2002); Yang et al., JPS 72:66 (1998)]
- high (~2eV) oxidative barrier predicted previously [Xing et al., J. Phys. Chem. B 113:16596 (2009)]



$EC/Li_{0.6}Mn_2O_4$ (100) interface: liquid EC decomposes at T=450 K

- Non-oxidative step: barrier slightly higher than T=0 (no liquid) due to entropy
- Oxidative step barrier slightly reduced reduced in liquid EC (ε=90)
- Overall barrier < 0.6 eV, reaction time scale < 1 second: viable pathway



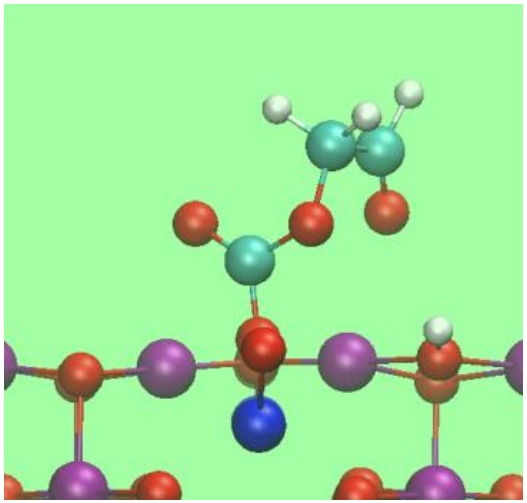
AIMD simulations not completely converged

Conclusions

- New EC decomposition pathways on (100) $LiMn_2O_4$ surface, barrier much lower than previously predicted
- Remains to be seen whether EC decomposition products form SEI or desorb
- MnO_2 is unstable when heavily hydroxylated

Future work: what is the final oxidative product?

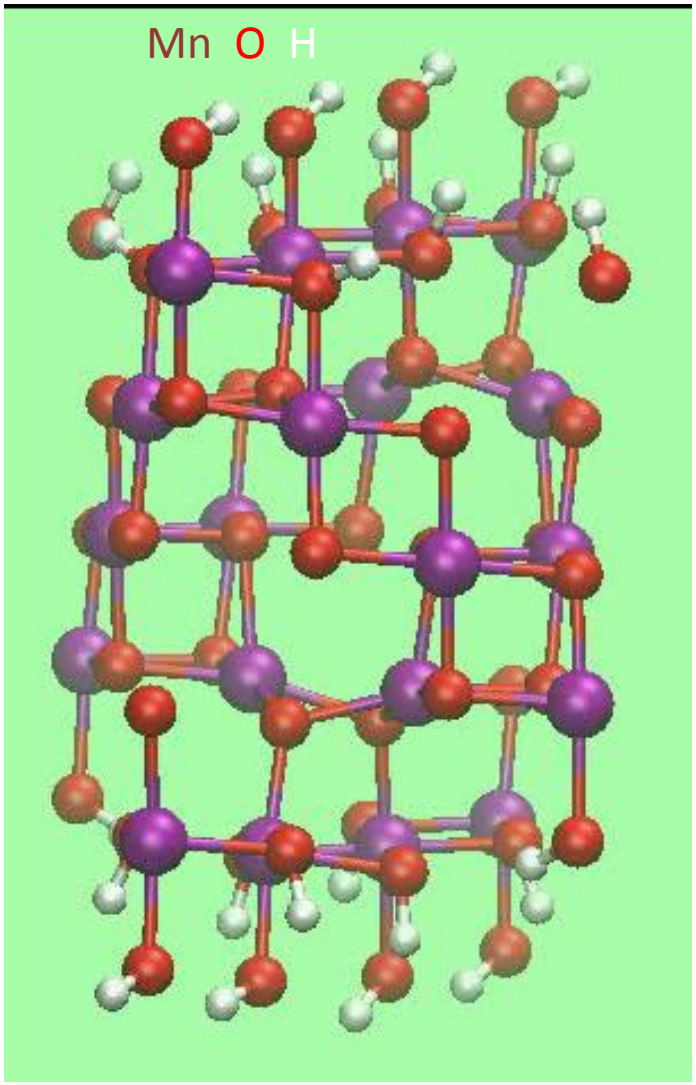
D



?

- polymeric?
- desorb from surface?
- loss of Mn & O from surface

Appendix: H_2O, H^+ degrade spinel MnO_2 (100)



- H_2O dissociates to H^+, OH^- on $Li_xM_2O_4$ surface, x< 1
- protons, hydroxyls on MnO_2 (100) known to leads to Mn, O loss [Xia et al, JECS 144:2593 (1997)]
- AIMD shows surface H^+ migrates to interior sites
- H^+ & OH^- recombine to form H_2O
- surface OH groups probably unstable at battery discharge conditions