Molecular dynamics simulation and ab initio studies of electrolytes and electrolyte/electrode interfaces

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Project ID: ES058

Overview

Timeline

Start	1/01/11
Complete	12/31/13

- 50% complete

Budget

- Total project funding
  - DOE $524 K
  - Contractor $ 0 K
- Funding received
  - $262 K FY11
  - $262 K FY12

Barriers

- Barriers addressed
  - operating temperature range
  - power density
  - energy density

Partners

- Collaborations
  - Arizona State University (Angell)
  - Penn State University (van Duin)
  - North Caroline State (Henderson)
  - Army Research Lab (Jow)
  - Argonne National Laboratory (Curtiss)
  - University of Rhode Island (Lucht)

Objectives

- **Use molecular simulations to gain understanding into the chemical composition of the electrode/electrolyte interface as a function of electrode potential**
- **Understand double layer structure, capacitance and transport at the anode and cathode interface as a function of potential and temperature**
- **Use ab initio calculations to gain insight into electrolyte oxidation (cathode) and reduction (anode) mechanisms**
- **Use molecular simulations to predict the chemical composition and structure of SEI layers at the anode and cathode**
- **Use molecular simulations to understand the role of additives in the formation of SEI layer**
- **Gain molecular level understanding of Li^+ cation transport mechanisms in SEI layers**
- **Gain molecular level understanding of Li^+ cation transport mechanisms in electrolytes comprised of new salts and solvents in collaboration with experimental BATT projects**
- **Provide guidance for design of electrolytes with improved lithium transport, reduced interfacial resistance and/or improved electrochemical stability**

Impact

Provide guidance for design of electrolytes with

- **improved lithium transport**
- **reduced interfacial resistance**
- **improved electrochemical stability**
- **ability to form stable SEI with good transport properties at high density anodes**
- **ability to form stable SEI with good transport properties at high energy cathodes**

Milestones

- **Prediction of low energy surface structures and electrolyte reactivity for high voltage cathodes. (Jan. 2012, delayed).**

- **Prediction and understanding of properties of novel high voltage electrolytes and additives including oxidative stability and degradation products on the cathode. (Mar. 2012, on target)**

- **MD simulations of electric double layer structure, capacitance and transport as a function of electrode potential and temperature for high voltage cathode. (Jun. 2011, on target)**

- **Prediction and investigation of structure and formation of the SEI at high voltage cathodes (Sep. 2012, on target)**

Approach

No single modeling technique is capable to address all molecular level phenomena relevant to processes determining performance of Li-ion batteries (electrolyte decomposition at electrodes, SEI formation, ionic transport in bulk electrolyte and through SEI/electrolyte and SEI/electrode interfaces).

An integrated multiple methodology modeling approach combining *ab-initio DFT calculations* on molecular clusters and electrode surfaces, *reactive molecular dynamics simulations* allowing modeling of SEI formation, and *classical molecular dynamics simulations* using high-fidelity force fields to sample thermodynamic and transport properties of electrolytes in bulk and interfaces is employed.

Approach

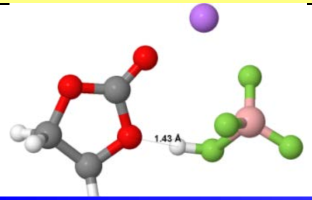
Molecular level modeling of structure, transport and mechanical properties:

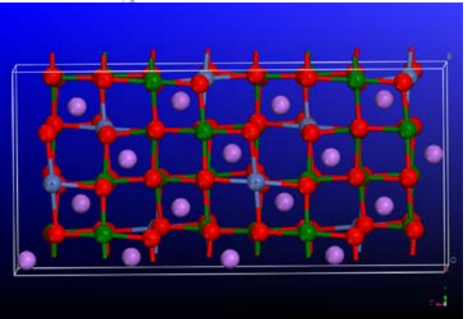
- **bulk electrolytes**
- **model SEI compounds**
- **electrode/electrolyte interfaces**
- **Li^+ intercalation**

Property prediction, mechanisms and design

Quantum chemistry calculations:

Electrolyte/ion binding energies, oxidative potential, decomposition pathways, electrode surface properties, etc.

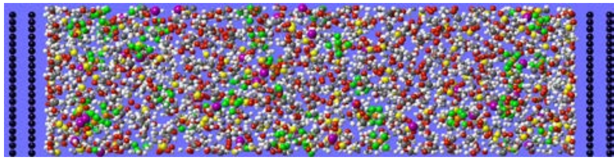


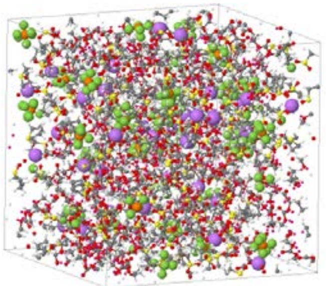


Reactive and non-reactive force fields parameterization

Molecular dynamics simulations:

Properties of bulk electrolytes (structure, thermodynamics, transport), interfacial properties of electrolyte at electroactive interfaces, mechanisms of SEI formation





Comparison with experiment (validation):

Electrolyte viscosity, conductivity, structure, oxidative stability, reaction products.

Technical Accomplishments and Progress

Ab initio study of oxidative stability and decomposition reaction pathways of electrolyte components

Molecular dynamics simulations of bulk electrolytes and electrolytes on electroactive interfaces (Comparison of EC-based and Sulfolane-based electrolytes)

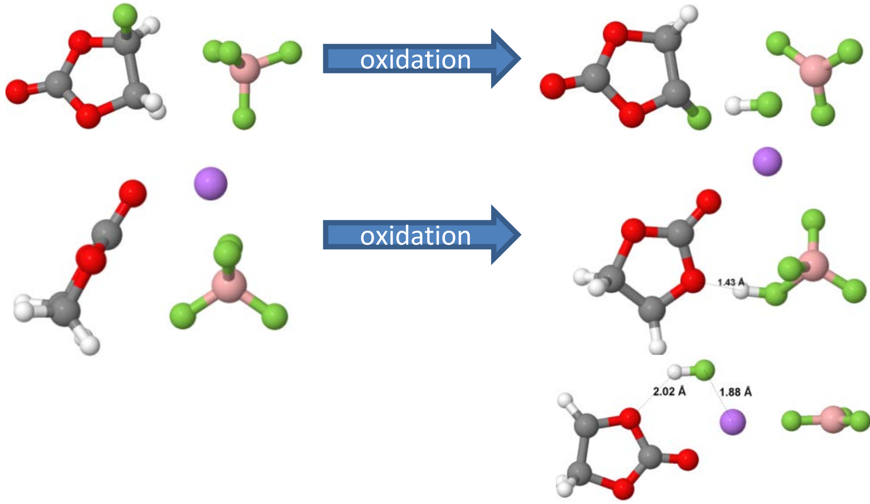
Molecular dynamics simulations of Li transport through model SEI

Ab initio study of surface properties of lithiated $LiNi_{0.5}Mn_{1.5}O_4$ and delithiated $Ni_{0.5}Mn_{1.5}O_4$ spinels

Oxidative stability and decomposition of electrolytes

Oxidation Potential of the Solvent/Anion Complexes

complex	H or F transfer	ε=1	ε=4.2	ε=20.5	ε=78.4
DMC/BF_4^-	Yes	4.14	5.79	6.21	6.29
EC/BF_4^-	Yes	4.55	5.95	6.28	6.34
EC/$LiBF_4$ (v1)	Yes	8.74		6.64	
EC/$LiBF_4$ (v2)	Yes	8.46		6.82	
PC/BF_4-	Yes	4.57		6.25	
FEC/BF_4^-	Yes	4.93	6.31	6.62	6.68
TMS/BF_4^-	Yes	5.23	6.33	6.49	6.52
EMS/BF_4^-	Yes	5.31	6.41	6.62	6.66
VC/BF_4^-	No	4.17	5.16	5.46	5.49
EC/ClO_4^-	YES	5.01		6.65	
EC/$DFOB^-$	No			6.10	
EC/$DFOB^-$	No			6.18	
EC/$DCTA^-$	No	4.66		5.83	
EC/ClO_4^-	YES	5.01		6.65	

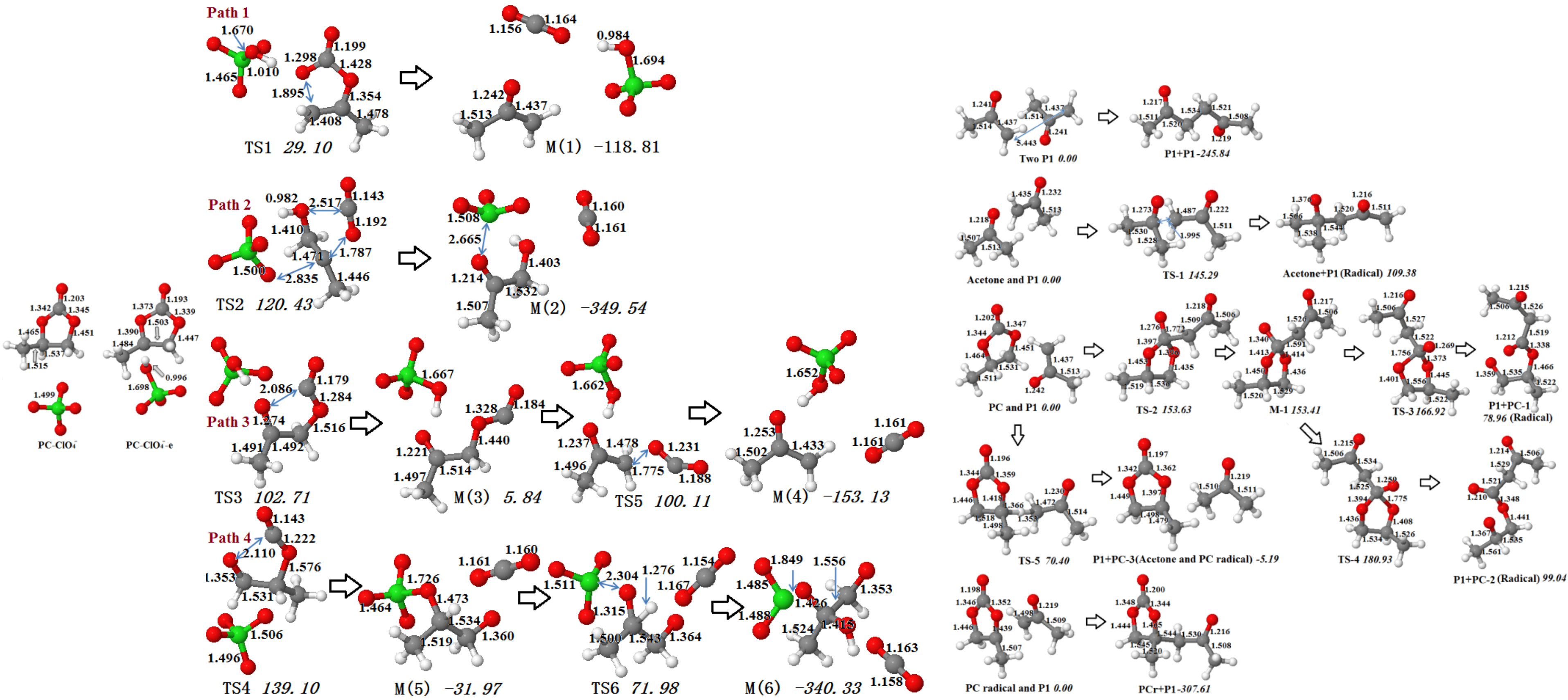


	ε=1	ε=4.2	ε=20.5	ε=78.4
BF_4^-	6.06	8.00	8.48	8.57
PF_6^-	6.70	8.49	8.93	9.01
$B(CN)_4^-$	6.45	7.71	7.99	8.04
FSI^-	4.77	6.26	6.60	6.66
ClO_4^-	4.10	6.04	6.49	6.57
$DCTA^-$	4.05	5.44	5.75	5.80
DFOB-	4.05		5.95	

- ***Oxidation potential of the solvent/anion is reduced due to spontaneous H or F abstraction for complexes with high oxidative stability anions such as PF_6^-, BF_4^-, $B(CN)_4^-$.***
- ***In the investigated solvent-anion complexes with low oxidative stability anions such as $DCTA^-$, $DFOB^-$ no spontaneous H- or F- abstraction was observed and anion oxidized.***

Extending work by Borodin, O.; Jow, T. R., *ECS Transactions* **2011**, *33* (28), 77-84.

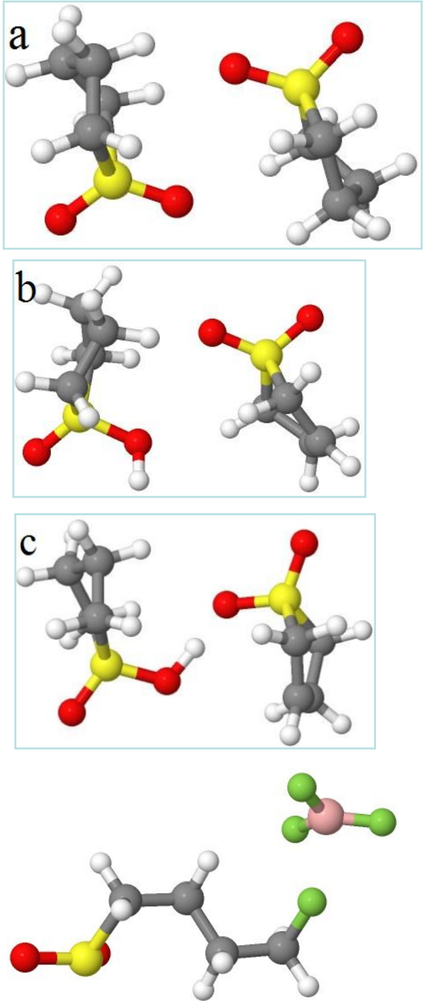
Oxidation of the PC/ClO_4^- Complex



- ***Oxidation decomposition reactions for PC/ClO_4^- at ε=1 and 20.4 (shown above) were compared with the PC/PF_6^- decomposition.***
- ***Acetone radical and CO_2 were the most probable reaction products at room temperature, similar to PC/PF_6^- oxidation reactions.***
- ***Acetone radical (P1) termination and propagation reactions were studied. P1+P1 termination reaction was the most exothermic among studied reactions.***

Xing, L.; Borodin, O.; Smith, G. D.; Li, W., Density Functional Theory Study of the Role of Anions on the Oxidative Decomposition Reaction of Propylene Carbonate. *J. Phys. Chem. A* **2011**, *115*, 13896-13905. (in cooperation with ABR program)

Oxidation of Sulfolane (TMS) Complexes



Oxidized complexes
(optimized geometries)

Oxidation Potential in eV

	ε=1	ε=20.5	ε=78.4
TMS (isolated)	8.70	6.74	
TMS_2 (a) (metastable)		6.71	7.07
TMS_2 (b) (H-abstraction)		6.00	5.92
TMS_2 (c) (H-abstraction)		5.61	5.54
TMS/BF_4^- (open TMS)	3.82	5.68	
TMS/BF_4^- (TMS closed)	5.23	6.49	6.52

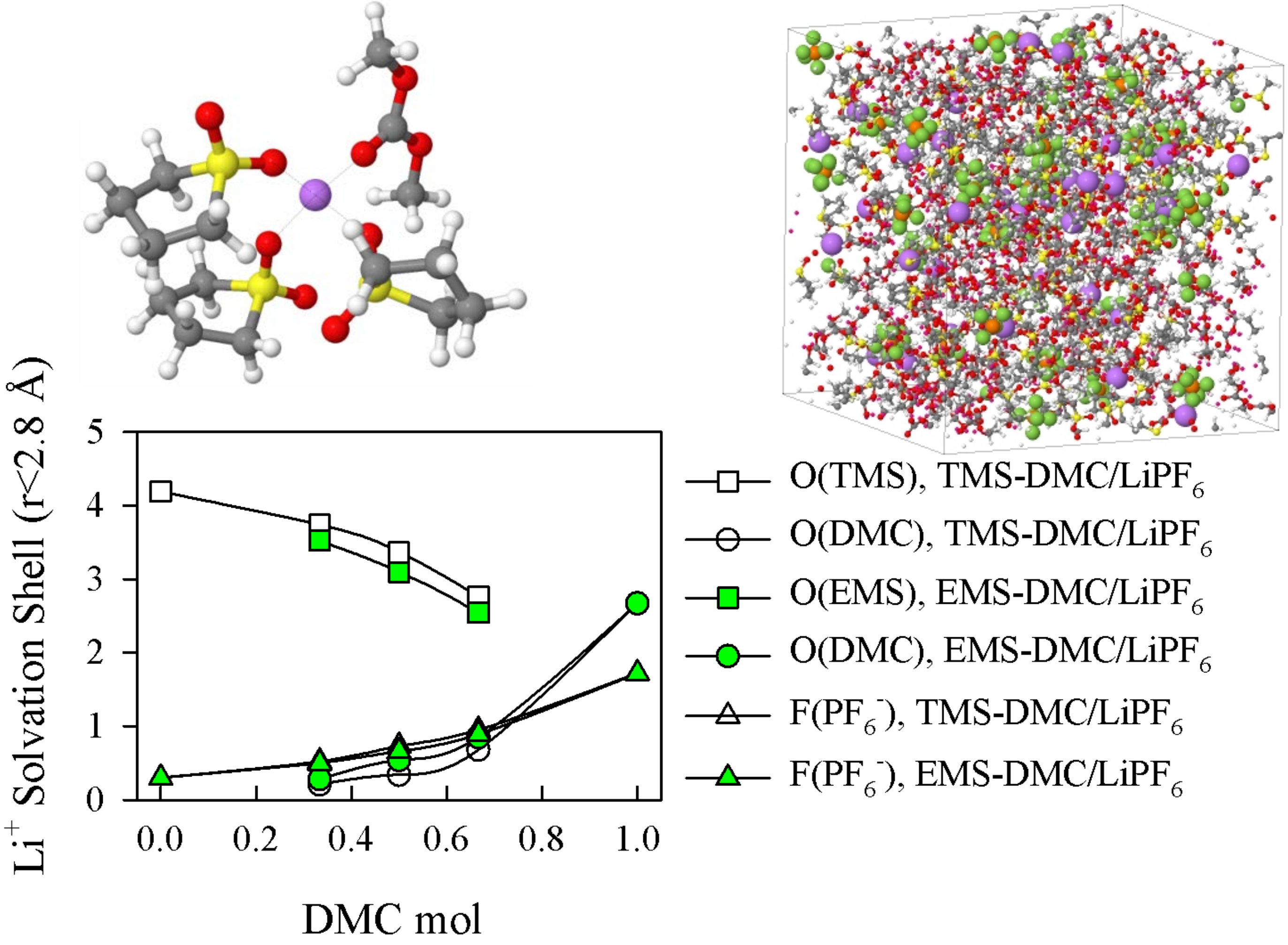
- ***Previous studies of the influence of anion on the TMS oxidation potential (O. Borodin and T. R. Jow, ECS Transactions 33, 77-84 (2011)) were extended to incorporate the explicit solvent interactions during oxidation. Spontaneous H-abstraction from TMS by another TMS was found to occur upon oxidation that reduced TMS oxidation potential compared to the intrinsic TMS oxidation potential in implicit solvent.***

- ***Oxidation potential of TMS_2 dimer was found to be similar to that for TMS/BF_4^- complex indicating that both oxidation decomposition pathways are expected to be active.***

- ***Predicted oxidation potential is in good agreement with the value of 5.8 V for 1M $LiPF_6$ on Pt reported in Russ J. Electrochem. 44, 575 (2008).***

Molecular dynamics simulations of bulk electrolytes

Li^+ Solvation in TMS-DMC/$LiPF_6$ and EMS-DMC/$LiPF_6$ Electrolytes

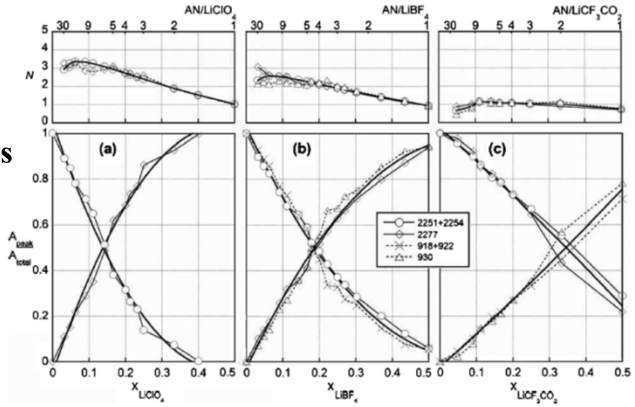


- ***Both in TMS(sulfolane):DMC/$LiPF_6$ and ethylmethyl sulfone(EMS):DMC/$LiPF_6$ electrolytes with solvent:Li=10, sulfolane shows a strong preference for the lithium coordination unlike previous results for EC:DMC/$LiPF_6$ electrolytes. Strong preference for TMS and EMS to dominate Li^+ solvation is expected to influence the competitive reduction process and SEI formation.***

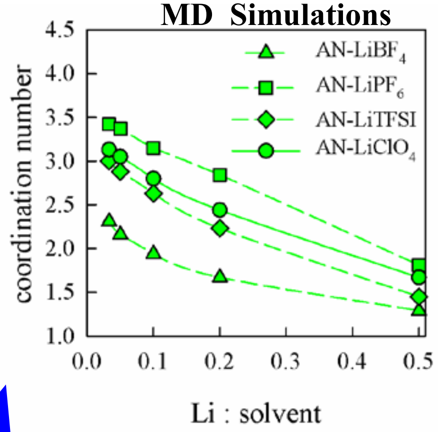
Validation of Simulations

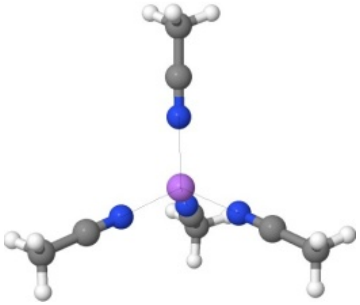
Level of Theory	M05-2X	MP2	ΔE (in kcal/mol)	
Basis Set	aug-cc-pvTz	aug-cc-pvTz	G4MP2	Force Field
Complex				
(AN)Li$^+$BF$_4^-$	-167.7	-162.6	-162.4	-164.8
(AN)$_4$Li$^+$	-123.1	-119.2	-117.5	-112.7
(AN)$_3$Li$^+$BF$_4^-$	-195.0	-189.0	-188.2	-188.9
(AN)$_2$Li$^+$(BF$_4^-$)$_2$		-203.0	-202.6	-203.8
(AN)$_2$(Li$^+$)$_2$(BF$_4^-$)$_2$	-368.0	-356.8		-362.8

Solvation shell structure from Raman experiments (Henderson group)



MD Simulations





Molecular Dynamics (MD) simulations

Acetonitrile, carbonates solvents doped LiBF$_4$, LiPF$_6$, LiTFSI, LiDFOB, LiClO$_4$

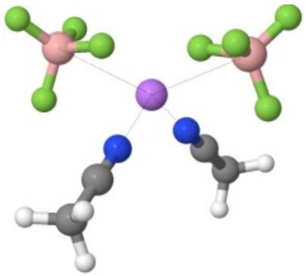
DFT and QC calculations:

Scaling and shift of Raman intensities upon Li$^+$ binding to aid assignments

<u>Experiments NCSU Prof. Henderson</u>

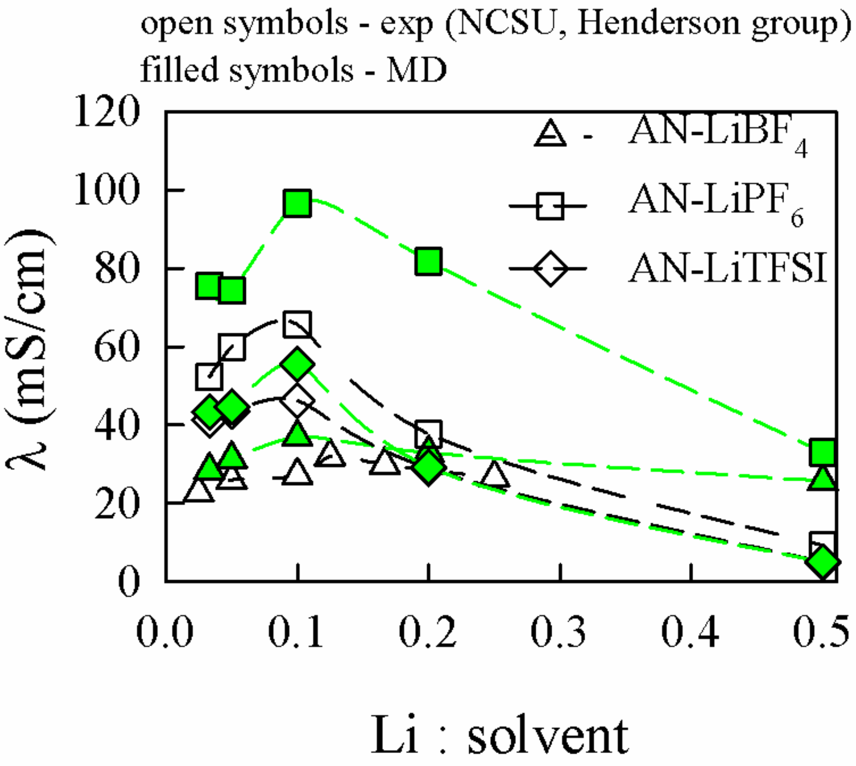
Raman: Li$^+$-coordination, ion clustering

Conductivity, Viscosity, Density



	Frequencies (cm^{-1})				Raman Intensity Ratio		
	Complex		Complex Shift vs. AN		Complex/AN		
Complex	C–C	C≡N	C–C	C≡N	C–C	C≡N	(C–C)/(C≡N)
			B3LYP/aug-cc-pvDz				
(AN)$_4$Li$^+$	941	2365	14	25	0.91	1.23	0.74
(AN)$_3$Li$^+$BF$_4^-$	942	2368	15	28	0.82	1.19	0.69
(AN)$_2$Li$^+$(BF$_4^-$)$_2$	943	2369	16	29	0.85	1.12	0.76
(AN)$_3$Li$^+$ClO$_4^-$	943	2368	16	28	0.92	1.23	0.75
(AN)$_2$Li$^+$(ClO$_4^-$)$_2$	943	2369	15	29	0.85	1.19	0.72
(AN)Li$^+$ClO$_4^-$	943	2366	16	26	0.67	1.07	0.63

Validation of Simulations



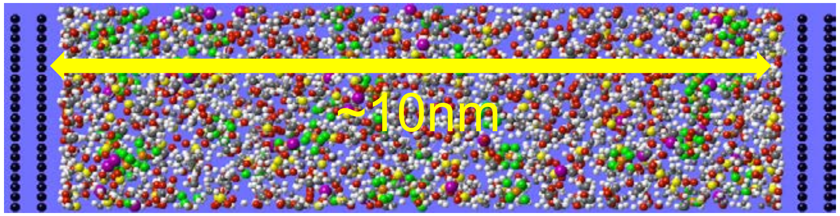
- ***An extensive validation of MD simulation predictions was performed in collaboration with Dr. Henderson group (NCSU). Distribution of solvent separated ion pairs and ion aggregates from MD simulations was compared with Raman spectroscopy analysis.***
- ***Electrolyte density, viscosity and conductivity predicted from MD simulations were also compared with experiments.***
- ***Validation of force field and simulations focused on the following systems: LiDFOB, LiClO$_4$, LiPF$_6$, LiBF$_4$ in acetonitrile. This work is currently extended to carbonate solvents.***

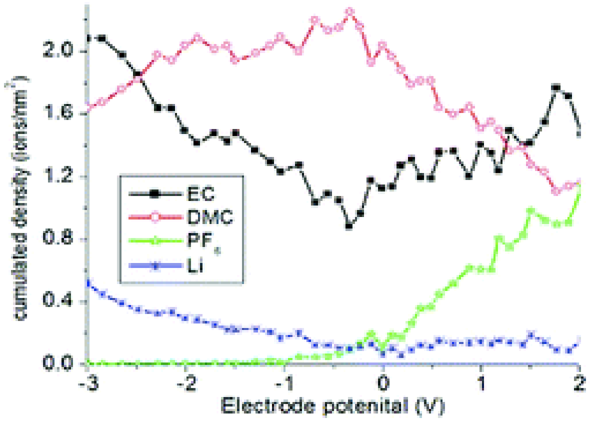
Seo, D. M.; Borodin, O.; Han, S.-D.; Ly, Q.; Boyle, P. D.; Henderson, W. A., Electrolyte Solvation and Ionic Association. I. Acetonitrile-Lithium Salt Mixtures: Intermediate and Highly Associated Salts. *J. Electrochem. Soc 2012, 159 (5), A553-A565.*

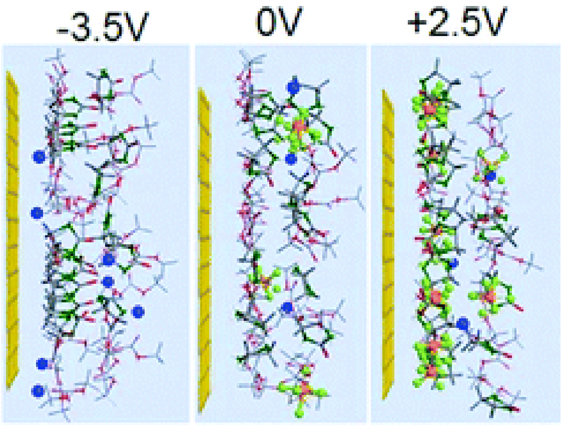
Seo,D. M.; Borodin,O.; Han, S.-D.; Ly, Q.; Boyle, P. D.; Henderson, W. A. Electrolyte Solvation and Ionic Association (II): Acetonitrile-Lithium Salt Mixtures – Highly Dissociated Salts, *J. Electrochem. Soc (submitted)*

Electrolytes at electroactive interfaces

Recently EC:DMC(3:7)/LiPF6 has been investigated (*J. Phys. Chem. C*, **2012**, 116, 1114)

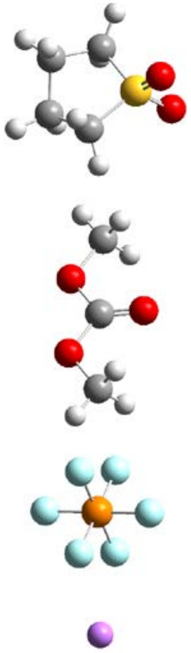






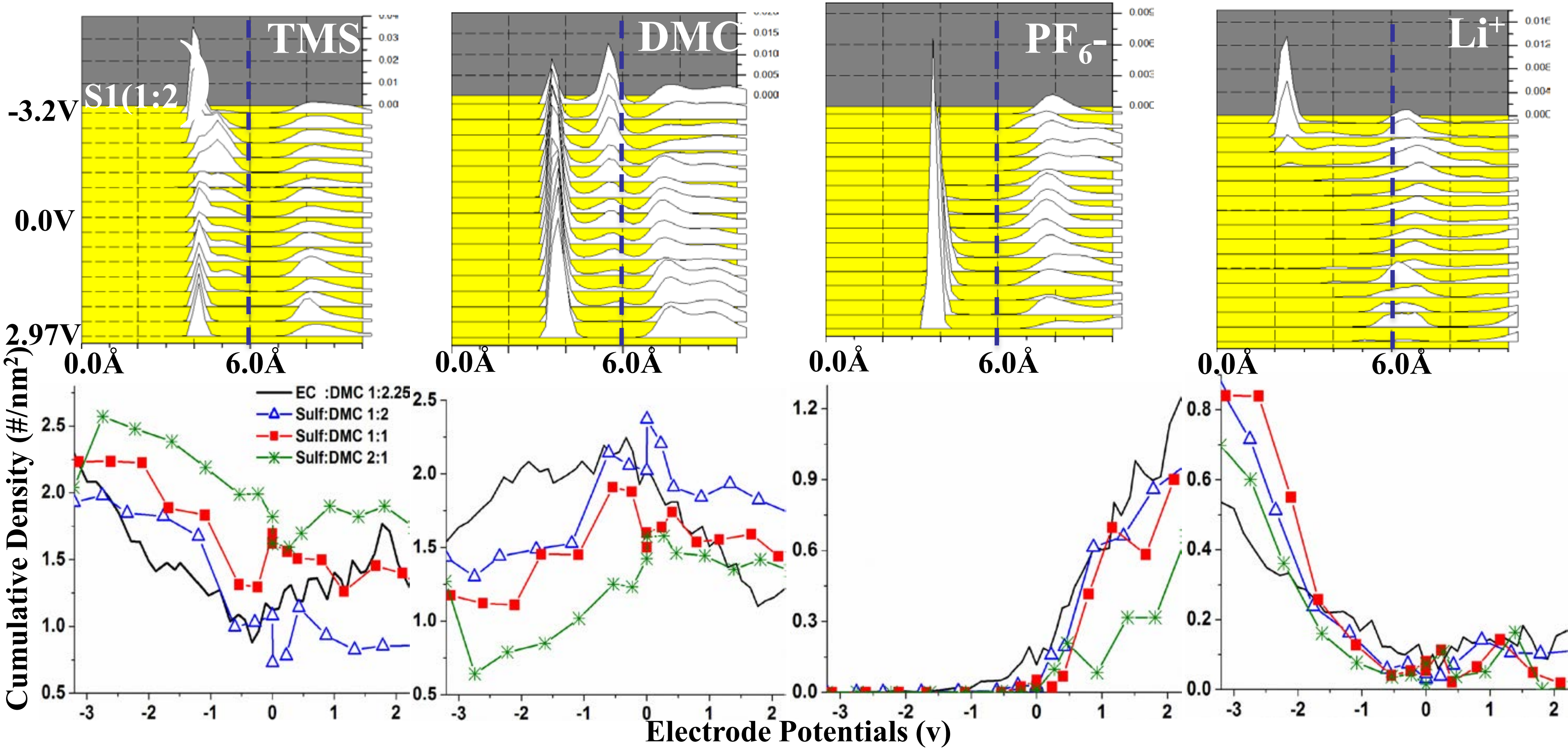
EC preferentially partitions to the the charged surfaces (both positive and negative)

Extended this study to sulfolane(TMS):DMC/LiPF6



System	# Sulfolane (TMS)	# DMC	# $LiPF_6$
S1 (1:2)	120	240	36
S2 (1:1)	180	180	36
S3 (2:1)	240	120	36
Simulation time	50ns		
Temperature	333K		
Force Field	Polarizable APPLE&P Force Field.		

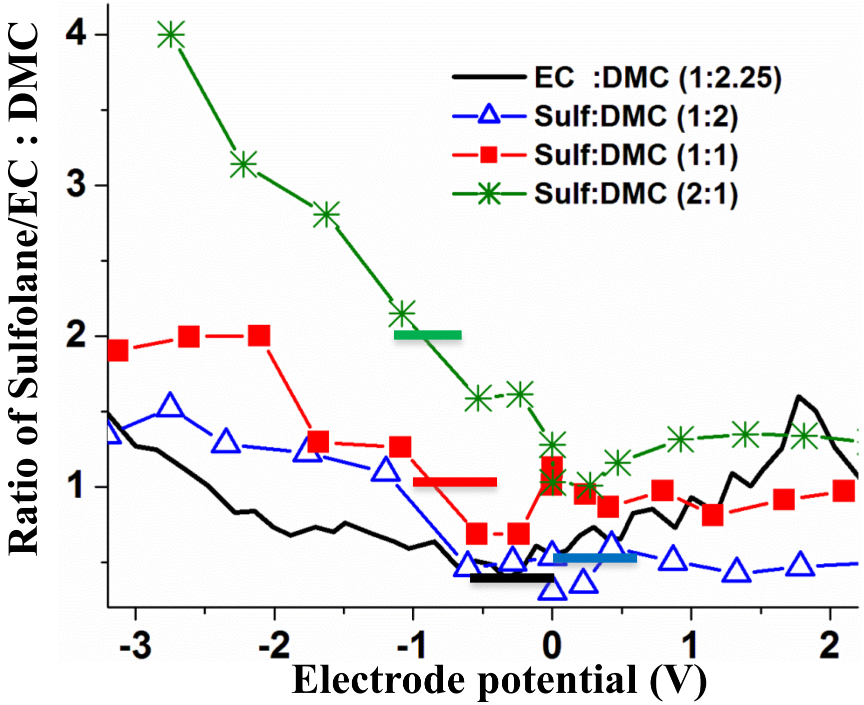
Densities of Electrolyte Species at Interfaces



For EC:DMC, the density of EC increase with the increase potential on both electrodes. For TMS:DMC, the density of TMS increase with the increase negative potential, but stays almost constant with the increase of positive electrode potential.

EC:DMC has higher PF_6^- density near the positive electrode and lower Li^+ density on the negative electrode surface compared to TMS:DMC systems.

Electrolyte Composition at Interfaces



In EC:DMC electrolyte, the EC/DMC ratio near both electrodes is noticeably higher than in the bulk.

In TMS:DMC systems, the TMS/DMC ratio near negative electrode is also higher than in the bulk. However, it is lower or similar to that in the bulk near the positive electrode.

The higher fraction of EC or TMS near negative electrodes is explained by a higher dipole moment and stronger binding energy of these solvents with Li^+ compared to DMC.

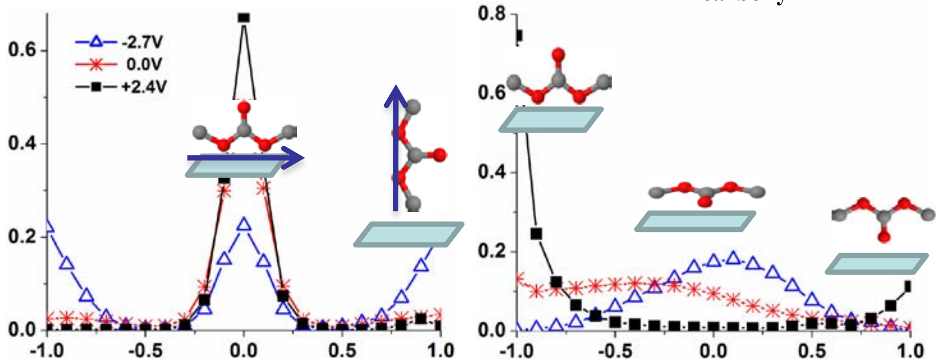
On the positive electrode, the lower fraction of TMS compared to EC is likely due to stronger binding energy between TMS and Li^+ which restricts the TMS molecules to approach the positively charged surface.

Both systems show that electrolyte environment near the surface can be very different from bulk compositions.

Solvent Orientation at Charged Surfaces

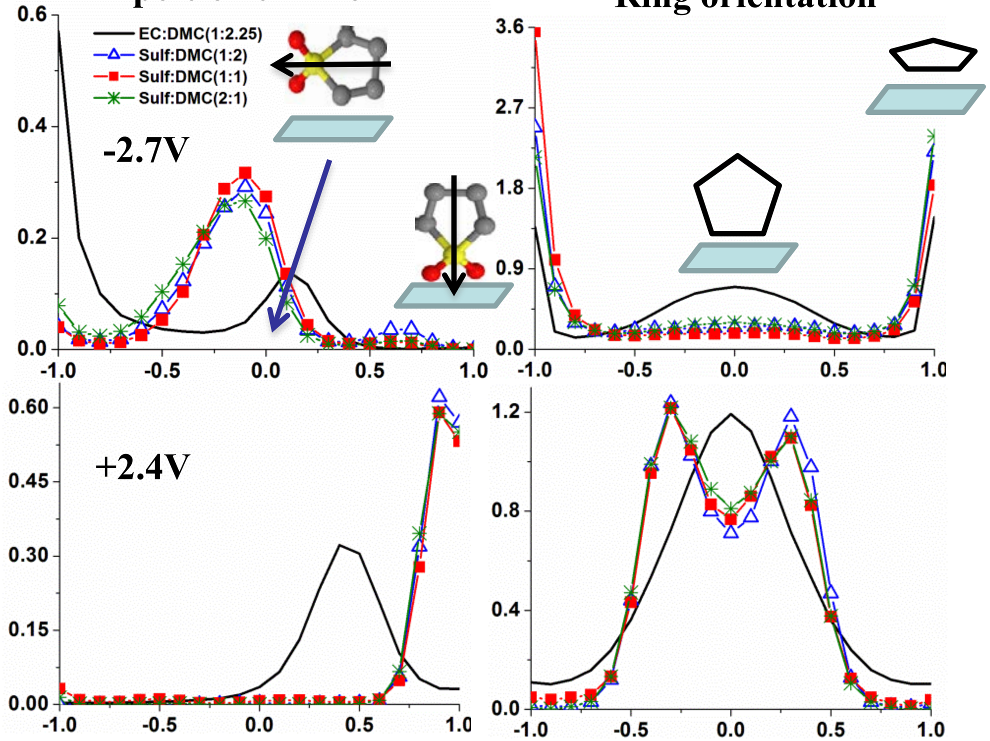
DMC orientation

O_{ether}-O_{ether} vector   C-$O_{carbonyl}$ vector



EC and TMS orientation

Dipole orientation   Ring orientation



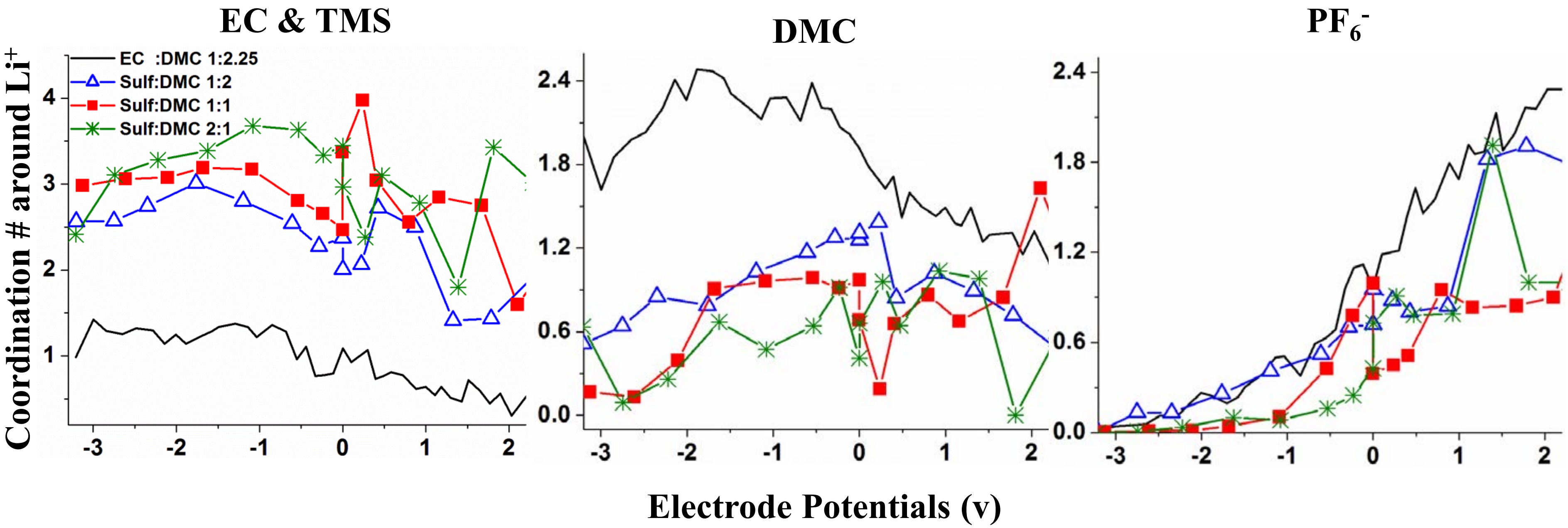
cos(θ)   cos(θ)

Orientation of electrolyte molecules in the interfacial layer strongly depend on electrode potential.

Orientation of DMC is qualitatively different depending whether its co-solvent EC or DMC.

Orientation of TMS and EC are also very different.

Li^+ Coordination at Interfaces



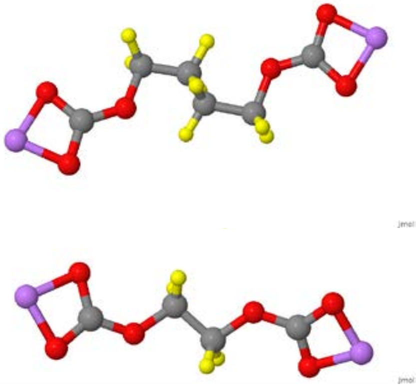
In EC/DMC based electrolytes Li^+ is primarily coordinated with DMC while in all TMS/DMC electrolytes it is primarily coordinated by TMS molecules.

Also in EC/DMC electrolyte at positive electrodes Li^+ is more correlated with anion than in TMS/DMC electrolytes.

Li transport through model SEI

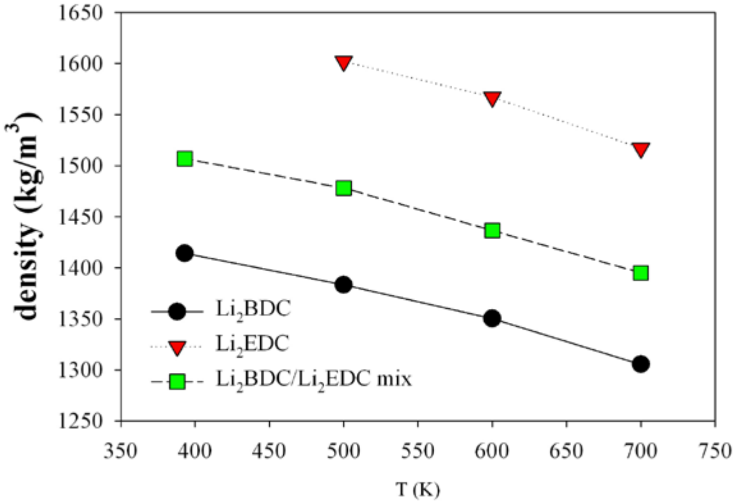
Bulk SEI

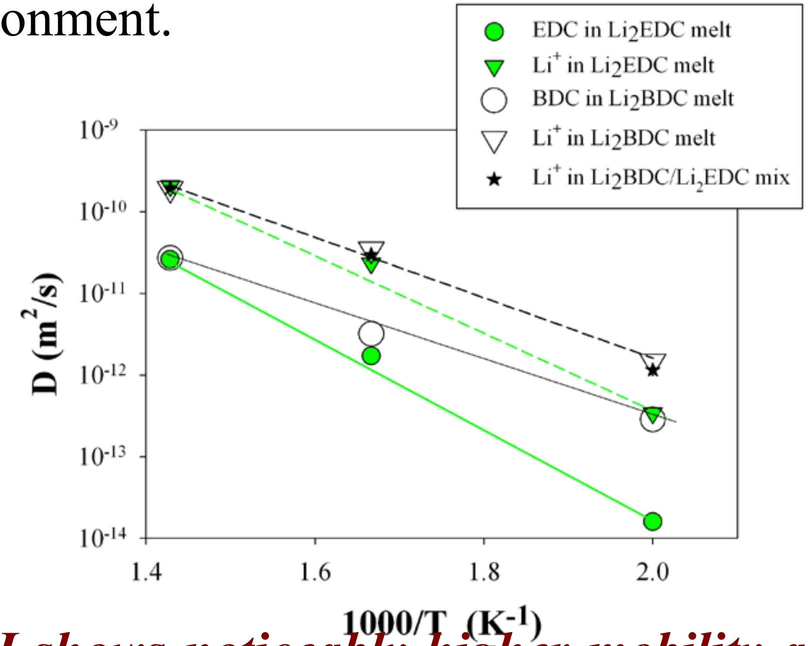
Goals: To understand mechanisms of Li^+ transport through model SEI formed at anode.



Systems: Amorphous and crystal dilithium ethylene dicarbonate (Li_2EDC) and dilithium butylene dicarbonate (Li_2BDC)

Our previous ReaxFF MD simulations showed that the formation of various alkyl carbonates from singly-reduced ethylene carbonate radicals can be kinetically favored depending on local ionic environment.

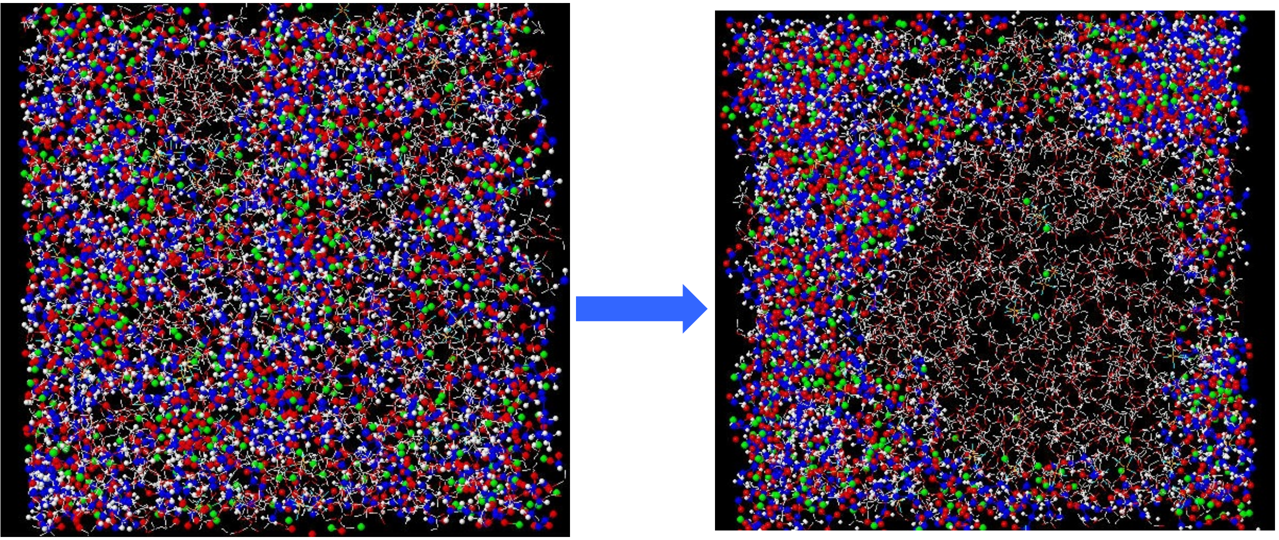




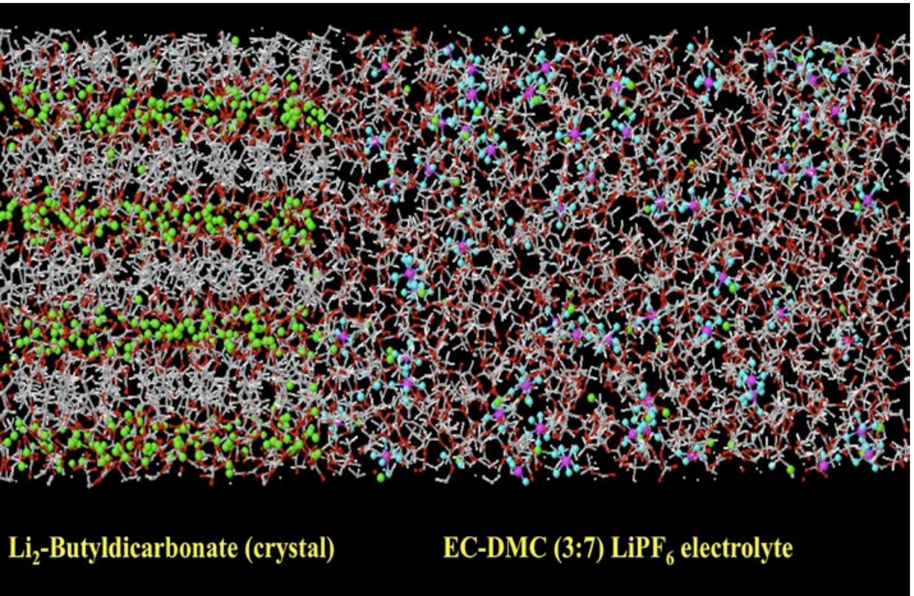
In amorphous phase Li_2BDC-based SEI shows noticeably higher mobility and lower activation energy for Li than in Li2EDC-based SEI.

SEI/Electrolyte interface

Electrolyte: EC/DMC(3:7)Li/PF_6



Li_2BDC initially dispersed in electrolytes relatively quickly separates in the bulk.

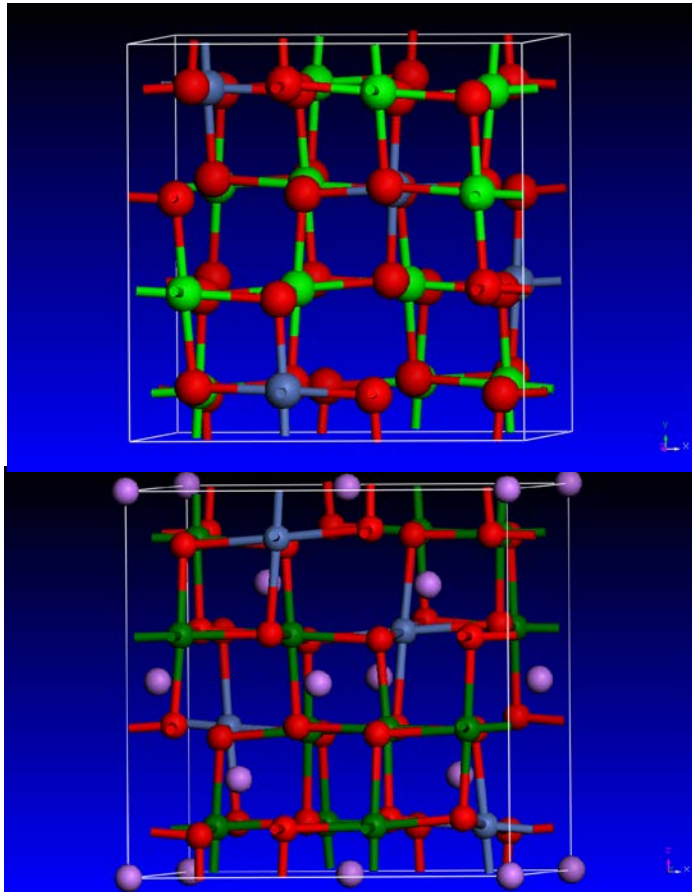


Simulations of interface between Li_2BDC and electrolyte show that the barrier for transition Li^+ from electrolyte to SEI is about 2-3 kcal/mol. Several events exchange of Li^+ between SEI and electrolyte were observed on a 30ns time scale in MD simulation.

Ab initio study of surface properties of lithiated $LiNi_{0.5}Mn_{1.5}O_4$ and delithiated $Ni_{0.5}Mn_{1.5}O_4$ spinels

Goals:

- **Study surface properties of these poorly understood materials.**
- **Find lowest energy surfaces and investigate decomposition pathways of electrolyte at electrode surfaces.**
- **Use these calculations for parameterization of force field for reactive and non-reactive molecular dynamics simulations.**



Bulk Calculations

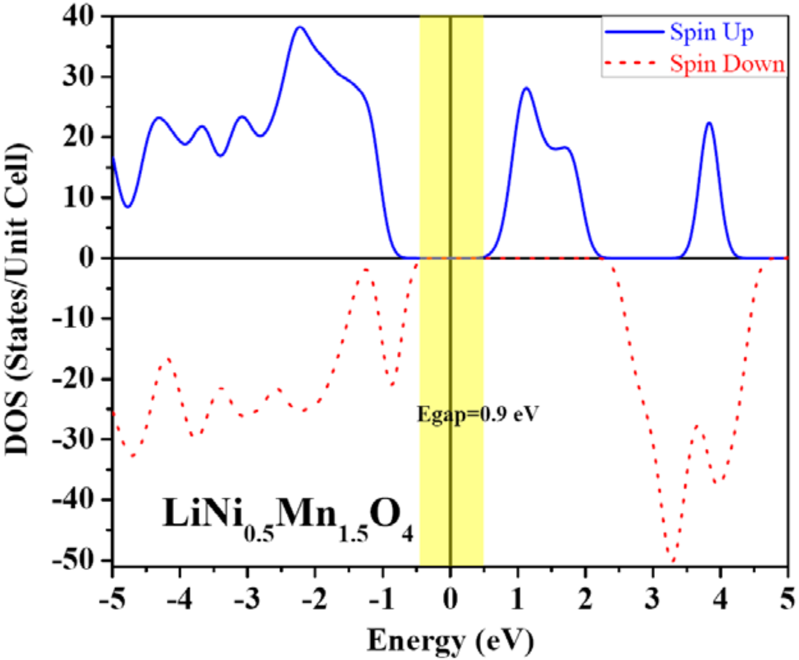
- ➢To validate the methods and values of parameters U&J
- ➢Cubic unit cells with Space group $P4_332$
- ➢56(48) atoms per unit cell in $LiNi_{0.5}Mn_{1.5}O_4$ ($Ni_{0.5}Mn_{1.5}O_4$)

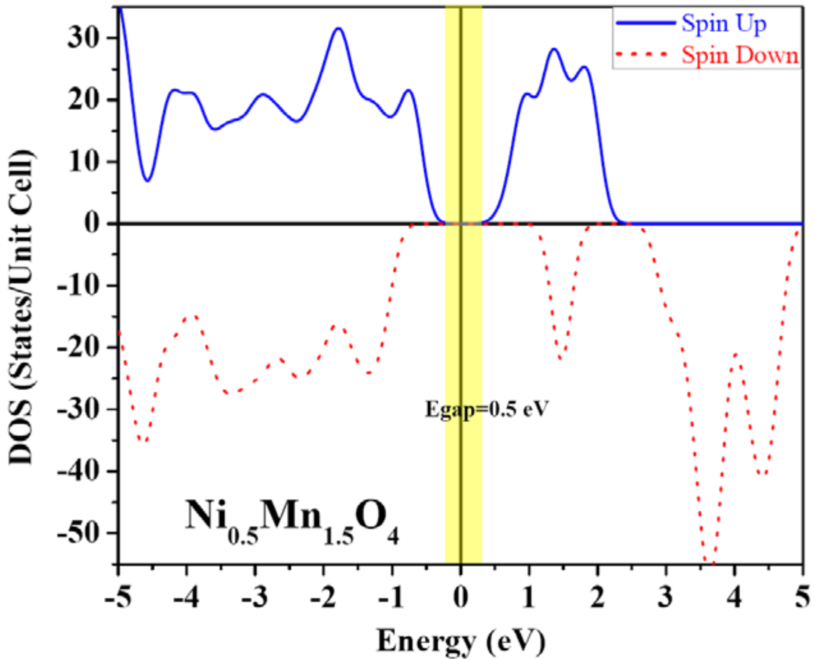
Bulk Calculations (Structural and Magnetic Properties)

Method	$LiNi_{0.5}Mn_{1.5}O_4$ (Å)	$Ni_{0.5}Mn_{1.5}O_4$ (Å)
GGA	8.25	8.11
GGA+U (U_{Ni}=5.96 eV, U_{Mn}=5 eV)	8.32 (8.31*, 8.17#)	8.21(8.19*, 8.01#)
	Ferrimagnetic $\mu_{Mn}=3.20\mu_B \vert \mu_{Ni}=-1.68\mu_B$	Ferromagnetic $\mu_{Mn}=3.29\mu_B \vert \mu_{Ni}=0.25\mu_B$

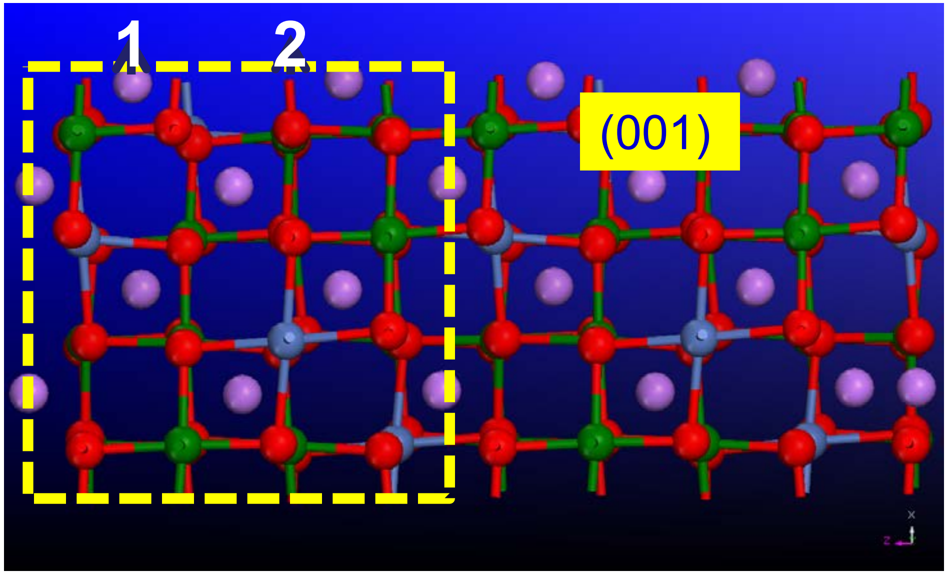
* H. Xia *et al*., J. Electrochem. Soc., 154, A737 (2007). Calculated values.

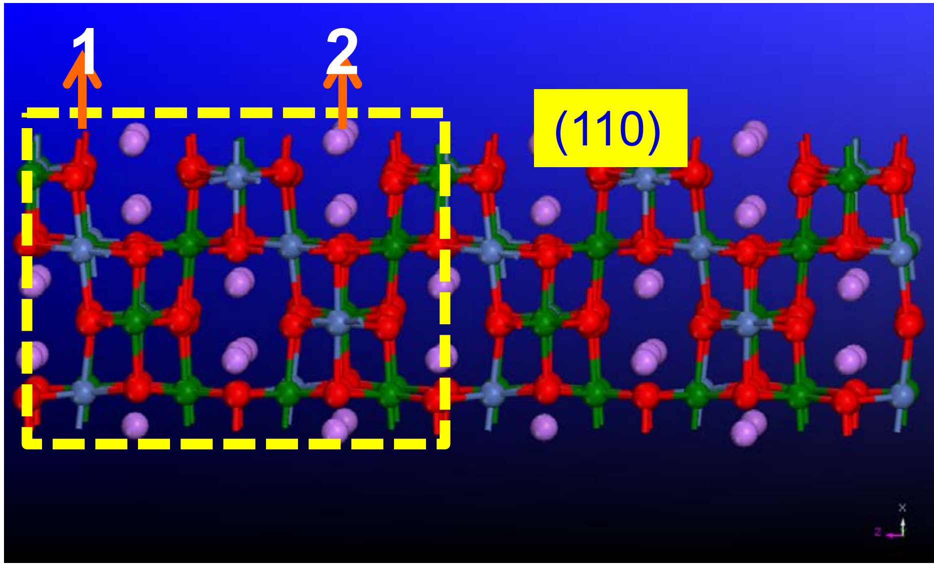
\# K. Ariyoshi *et al*., J. Electrochem. Soc., 151, A296 (2004). Experimental values.

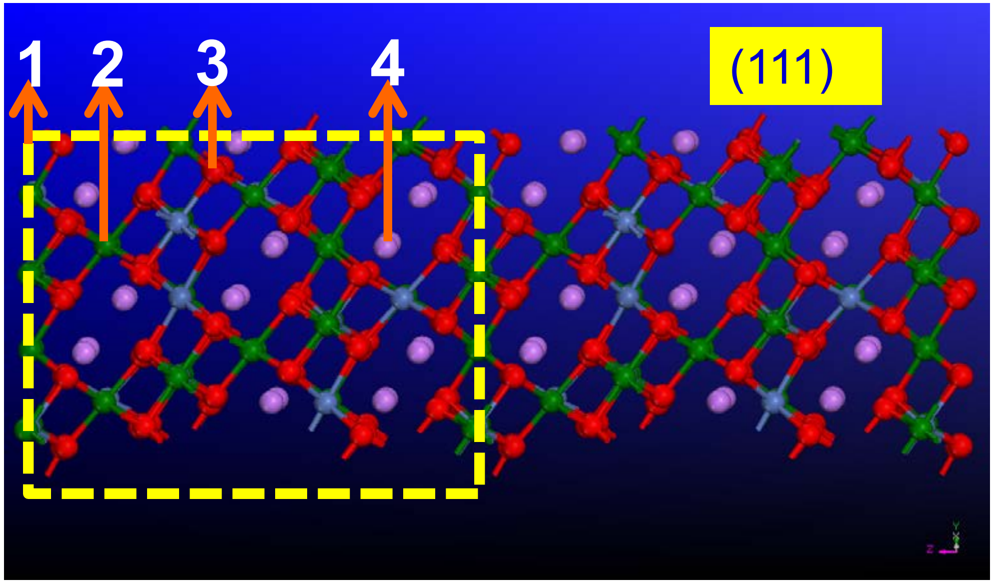




Surface Properties (Stoichiometric Compositions)

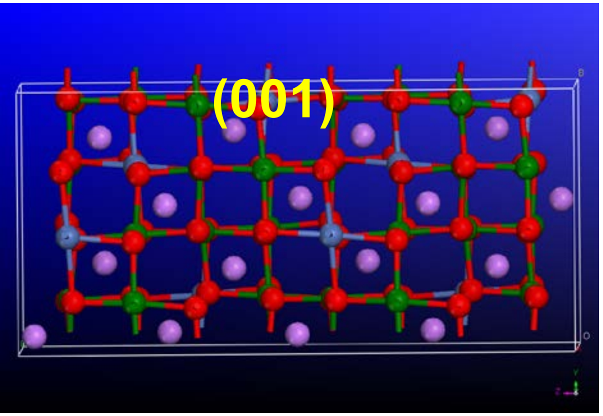


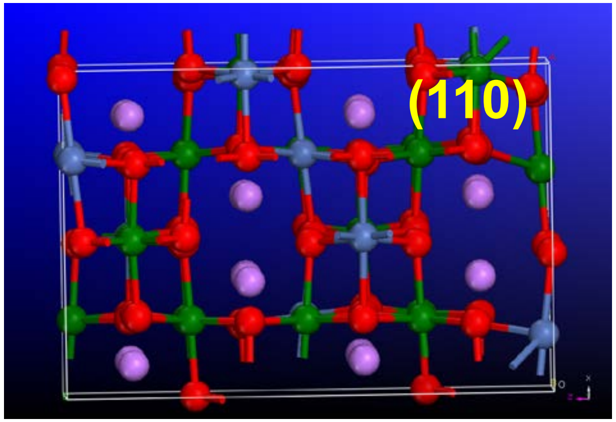


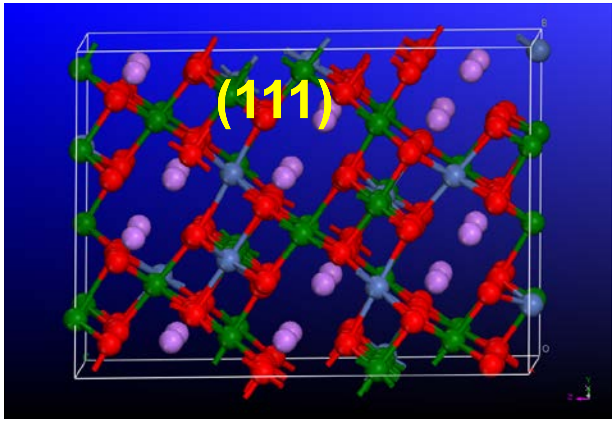


For each plane all possible cuts have been investigated

Surface Properties (Stoichiometric Compositions)







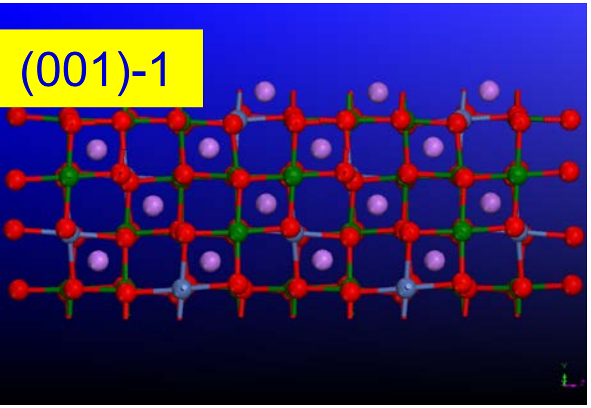
Surface Energies (Stoichiometric,meV/Å^2)

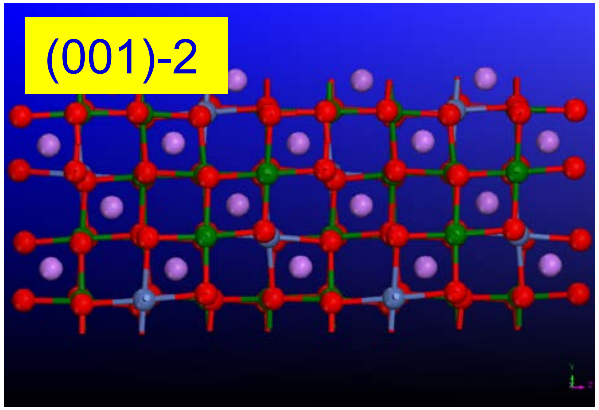
$LiNi_{0.5}Mn_{1.5}O_4$								
Surface	(001)		(110)		(111)			
Configurations	1	2	1	2	1	2	3	4
	64.89	114.73	94.10	90.74	188.42	86.48	129.31*	109.31*

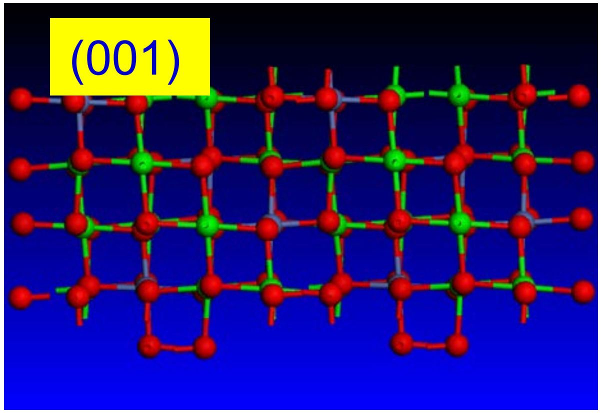
$Ni_{0.5}Mn_{1.5}O_4$				
Surface	(001)	(110)	(111)	
Configurations	1	1	1	2
	62.67	74.47	82.90	74.87

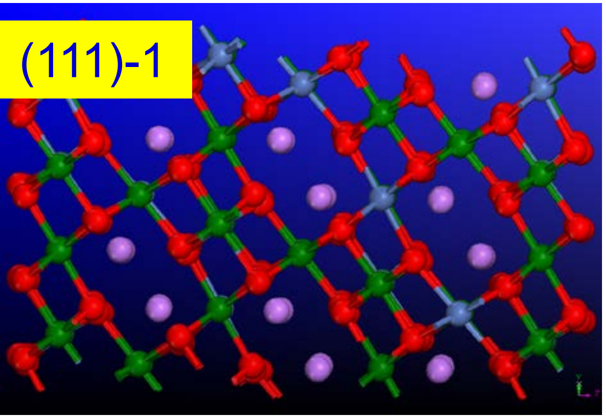
(001) surface is more stable than (111) and (110) surfaces, which is in contradiction with experimental observations

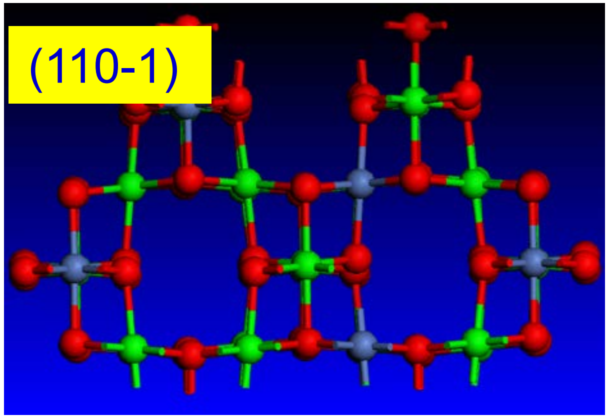
Surface Properties (Non-Stoichiometric Compositions)

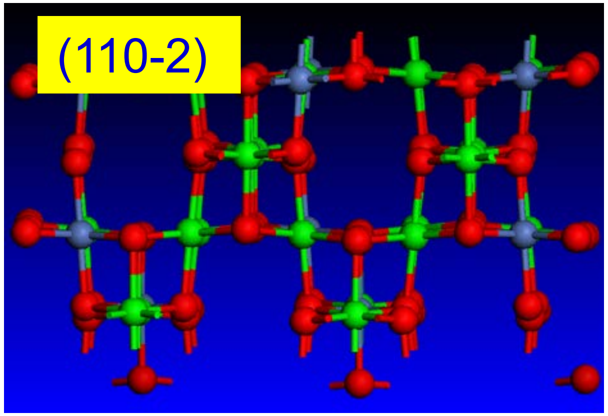

(001)-1

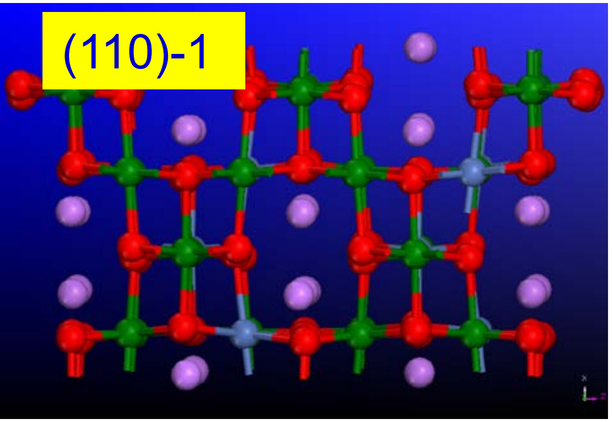

(001)-2

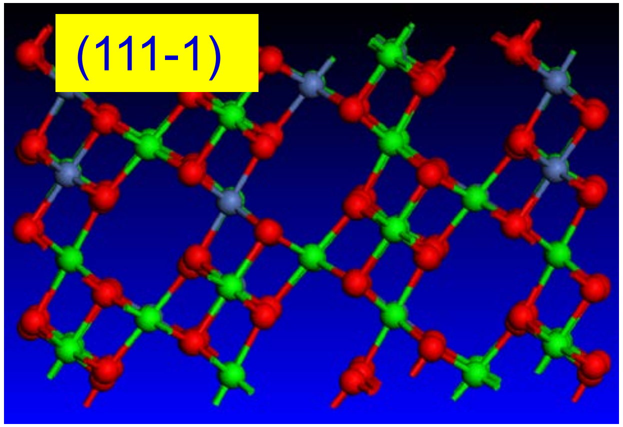

(001)

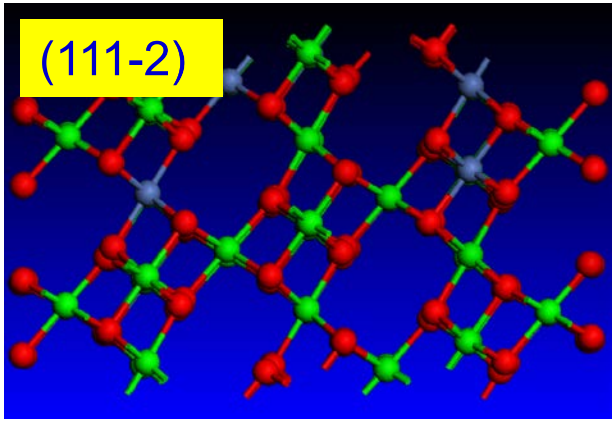

(111)-1


(110-1)


(110-2)


(110)-1


(111-1)


(111-2)

Surface Properties (Non-Stoichiometric Compositions)

Surface Energies (Non-stoichiometric,meV/Å^2)

$LiNi_{0.5}Mn_{1.5}O_4$

Surface	(001)		(110)		(111)			
Configurations	1	2	1	2	1	2	3	4
	107.89	114.96	138.58	143.98	151.56	104.74	98.35	237.44

$Ni_{0.5}Mn_{1.5}O_4$

Surface	(001)	(110)		(111)	
Configurations	1	1	2	1	2
	97.39	98.91	56.88	83.39	59.04

Some non-stochiometric surface cuts (including the (111)) show lower surface energies then surface energy of stoichiometric (001). These are the surfaces terminated with oxygen atoms.

Surface Properties of Spinels

- ***The structural, magnetic, electronic, and electrochemical properties of bulk $LiNi_{0.5}Mn_{1.5}O_4$ and $Ni_{0.5}Mn_{1.5}O_4$ are well reproduced, validating the employed methods for surface calculations***

- ***Among different configurations of each surface, the one with less ion coordination loss is more stable***

- ***For surfaces with stoichiometric compositions, (001) surfaces are calculated to be the most stable surface for both $LiNi_{0.5}Mn_{1.5}O_4$ and $Ni_{0.5}Mn_{1.5}O_4$, in agreement with Benedek and Thackeray study on $LiMnO_4$***

- ***When non-stoichiometric surfaces considered, we found that (111) surface are more stable than (001) and (110) surfaces for $LiNi_{0.5}Mn_{1.5}O_4$, and (110) surface is the most stable surface for $Ni_{0.5}Mn_{1.5}O_4$***

Collaboration and Coordination with Other Institutions

- Argonne National Laboratory
  - Collaboration, Federal laboratory, within VT
  - Ab initio/MD simulations of electrolyte reduction/oxidation reactions
- Arizona State University
  - Collaboration, University, within VT
  - Properties of high voltage electrolytes
- North Caroline State University
  - Collaboration, University, both within and outside VT
  - Structural and transport properties of electrolytes, force filed validation
- Army Research Laboratory
  - Collaboration, Federal Laboratory, inside VT (ABRT program)
  - Transport through SEI
- University of Rhode Island
  - Collaboration, University, inside VT
  - Analysis of oxidation reactions at cathode surface
- Pennsylvania State University
  - subcontract, University, outside VT
  - Parameterization of ReaxFF for cathode reactions, code development

Proposed Future Work

- **Understand electrolyte oxidative decomposition reactions and passivation layer formation at non-active electrodes and high voltage NMC cathode surfaces** (van Duin, Penn State; Lucht, URI)

- **Investigate the role of sacrificial additives on cathode SEI formation** (Lucht, URI)

- **Investigate electrode/electrolyte interfacial composition of mixed high-voltage electrolytes as a function of electrode potential**

- **Investigate properties of Li transport through SEI and electrolyte/SEI interfaces at anode and cathode as a function of electrolyte and SEI composition** (Lucht, URI; Jow, ARL)

Summary

- **Ab initio studies reveal that electrolyte oxidative and reductive decomposition (related to cathode and anode SEI formation) depend strongly on the local chemical composition.**

- **Molecular dynamics simulations reveal that the local chemical environment at electrode surface can significantly deviate from bulk composition, strongly depends on electrode potential and chemical composition of electrolyte.**

- **Understanding and determining the structure for the lowest energy of high-voltage cathode surfaces is crucial for further understanding of electrolyte oxidative stability and decomposition pathways.**