Potential Function Development

A. $LiFePO_4$ Quantum Chemistry

Solid-state density function theory (DFT) calculations were performed on bulk, crystalline $LiFePO_4$ for the purpose of estimating partial atomic charges to be used in subsequent molecular dynamics (MD) simulations. Spin unrestricted hybrid DFT calculations were performed using the CRYSTAL software suite[i] which is based on the periodic, linear combination of atomic orbitals (LCAO) formalism where the Bloch orbitals of the crystals are expanded using atom centered Gaussian orbitals with *s*, *p* or *d* symmetry. The Li , O , P and Fe atoms were represented by 6-11G, 6-31d1G, 85-21d1G and 86-411d41G basis set respectively. Becke's three parameter hybrid functional (B3LYP)[ii] was used for the treatment of electron exchange and correlation in the calculations. Solid state calculations using this functional have been shown to yield band structure[iii] and structural properties[iv] excellent agreement with experiment for various materials.

All DFT calculations of $LiFePO_4$ were performed on the crystallographic unit cell. Crystallographically $LiFePO_4$ is a orthorhombic structure (Pnma , space group 62) and contains six symmetry independent atoms (Li, Fe, P and three O atoms). The initial $LiFePO_4$ unit cell was built from x-ray diffraction data[v] which gave the positions of the atoms in the unit cell as: Li (0,0,0), Fe (0.28222, 0.25, 0.97472), P (0.09486, 0.25, 0.4182), O1 (0.09678, 0.25, 0.74279), O2 (0.45710, 0.25, 0.20602) and O3 (0.16558, 0.04646, 0.28478), placing them in Wyckoff positions 4a (Li), 4c (Fe), 4c (P), 4c (O1), 4c (O2) and 8d (O3) respectively and thereby creating a 28 atom unit cell structure. The cell parameters of the unit cell were 10.332 Å , 6.010 Å and 4.692 Å.[v] Once the unit cell was created the atoms and cell parameters were relaxed. The reciprocal space integration was performed by sampling the Brillouin zone using an Monkhorst-Pack scheme with a shrinking factor of eight. The Mulliken charges obtained from the solid-state DFT calculations on the $LiFePO_4$ bulk are given in Table 1.

B. Atomistic Force Field Development

Force field parameters (bonded interactions, dispersion/repulsion parameters, partial atomic charges and dipole polarizabilities) for the electrolytes (solvent and salt) were taken from the previously developed and extensively validated quantum chemistry based polarizable potential Apple&P™.[vi] These force field parameters and their implementation (functional forms) can be obtained directly from Wasatch Molecular, Incorporated.[vi] Details of the derivation and validation of the force field for the OLE (EC:DMC doped with $LiPF_6$) have been recently reported.**Error! Bookmark not defined.** Molecular mechanics calculations utilizing the developed force field were found to accurately predicted binding energies and geometries of EC_nDMC_m/Li^+ ($n+m \leq 4$) complexes in the gas-phase, while MD simulations of EC and DMC solvents and EC:DMC/$LiPF_6$ electrolytes yielded electrolyte conductivity as well as liquid solvent density, viscosity and dielectric constant in excellent agreement with experiments. Most of parameters for the ILE were taken from recent work on EMIM:bis(trifluoromethanesulfonyl)imide (TFSI).[vii-ix] MD simulations with the developed force field accurately predict density, self-diffusion coefficients and heat of vaporization for molten EMIM:TFSI and lattice parameters for the crystalline phase of EMIM:TFSI. Details of the LiFSI force field development and validation demonstrating excellent prediction of ion transport in EMIM:FSI doped with LiFSI will be published separately.[x]

In this work we have derived parameters for $LiFePO_4$ and its interactions with the electrolyte as described below.

Bonded parameters. Parameterization of bonded interactions for $LiFePO_4$ was carried out through MD simulations of a 3D periodic bulk $LiFePO_4$ supercell (3 X 5 X 6 of the 28 atom unit cells described above) comprised of 2520 atoms. The initial atomic positions and unit cell dimensions were taken from crystallographic data for $LiFePO_4$ (see above), yielding dimensions of 30.996 Å X 30.05 Å X 28.152 Å for the supercell. In our MD simulations we have chosen to maintain the structure of $LiFePO_4$ through the use of stiff bond and bend potentials. There are three unique P-O bond lengths and four unique Fe-O bond lengths in $LiFePO_4$, described in our model with stiff (force constant = 5000 kcal/mol/ Å^2) harmonic functions. In addition, there are four unique O-P-O bond angles and nine unique O-Fe-O bond angles described with stiff (force constant = 5000 kcal/mol/radian^2) bending functions. The equilibrium bond lengths and angles for each of these unique functions were adjusted so as to give the best agreement between force field prediction from MD simulations at 363 K (see below) and solid state DFT values for the unique bond lengths and bond angles as summarized in Table 2. For this purpose 3D periodic $LiFePO_4$ supercell (Figure 2a of main text) were run in the NPT ensemble with $P_{xx} = P_{yy} = P_{zz} = 1$ atm and T = 363 K. Initial coordinates were taken from the crystallographic unit cell. Ewald parameters $\alpha = 0.29$ and $k_{limit-x} = k_{limit-y} = k_{limit-z} = 8$ were utilized. The bond and bend equilibrium angles (see Table 2) were adjusted so that average bond lengths and valence bend angles were in good agreement with DFT predictions (see Table 2) and the supercell dimensions were in good agreement with experiment. The average supercell dimensions yielding $P_{xx} = P_{yy} = P_{zz} = 1$ atm for a three nanosecond trajectory were 31.15 Å X 30.04 Å X 28.2 Å at 363 K.

We note that our treatment of $LiFePO_4$ utilizing stiff bonds and bends not allow for significant surface restructuring when the crystal is cut to form surfaces (see below). Furthermore, the rigid $LiFePO_4$ geometry does not provide an accurate representation of lattice distortion associated with motion of Li^+ within the $FePO_4$ galleries and hence the energy barrier for transport of Li^+ through $LiFePO_4$ will not be accurately reproduced. The implications of this on our studies of the free energy penalty associated with Li^+ desolvation and initial intercalation are considered below.

Partial atomic charges and dipole polarizabilities. Coulombic interactions between $LiFePO_4$ and the electrolyte are represented by partial atomic charges and atomic dipole polarizabilities.

Partial atomic charges for $LiFePO_4$ were determined from Mulliken charges obtained from solid state DFT calculations on the bulk crystal as described above. The charges for $LiFePO_4$ were adjusted slightly in order to yield a +1e (unity) charge for Li^+. The charges for the surface Fe and O atoms whose coordination was reduced upon formation of the surfaces (see below) were reduced by 1/6 compared to the bulk charges in order to account for reduced Fe-O coordination. The resulting charges are given in Table 1.

The dipole polarizability for Li^+ is essentially zero and was adopted from the Apple&P™ force field.[vi] We conducted a quantum chemistry study of $(Li_6PO_4)^{3+}$ at the MP2/aug-cc-pvdz level using Gaussian03[xi] and assigned atomic polarizabilities for P and O to reproduce the total polarizability of the complex. The values used in our simulation were reduced from these values to account for condensed phase effects that tend to reduce polarizabilities from those determined from gas-phase quantum chemistry calculations.[xii] For Fe^{2+} quantum chemistry calculations at the MP2/6-311++G(3df) level yielded an atomic polarizability of 0.49 Å^3. A reduced value of 0.3 Å^3 was used in our simulations. Dipole polarizabilities for the atoms of $LiFePO_4$ are given in Table 3.

Repulsion and dispersion parameters . Because the structure of $LiFePO_4$ is maintained by rigid bond and bend potentials in our simulations, nonbonded interactions between Fe, O and P in $LiFePO_4$ are relatively unimportant in determining the structure of $LiFePO_4$. However, the Fe, O and P nonbonded self interactions are important in determining nonbonded repulsion and dispersion interactions with the electrolytes, as we have employed mixing rules for establishing nonbonded interactions between $LiFePO_4$ and the electrolytes. Furthermore, the Li-O and Li-Fe nonbonded interactions (in addition to Coulomb interactions) determine whether Li^+ is correctly located within the $FePO_4$ galleries. The dispersion/repulsion parameters for the atoms comprising $LiFePO_4$ were adapted from the Apple&P™ force field. Modification of the parameters from Apple&P™ values were undertaken to maintain Li^+ in the correct position within the $FePO_4$ channels, since using unmodified parameters resulted in displacement of the lithium toward the oxygen atoms. Dispersion/repulsion parameters for Fe, P and O atoms of $LiFePO_4$ and their cross interactions with the OLE and ILE atoms, used in exp-6 functions of the form

$$E_{dispersion/repulsion}(r_{ij}) = A_{ij}\exp\left(-B_{ij}r_{ij}\right) - c_{ij}/r_{ij}^{6} \qquad (5)$$

where r_{ij} is the separation between atoms i and j, are summarized in Table 3. We note that the Li^+ potential for Li^+ in $LiFePO_4$ is identical to that used to describe Li^+ in the electrolyte, i.e., the Apple&P™ Li^+ potential is utilized and can be obtained from Wasatch Molecular Incorporated.[vi]

References

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Table 1. DFT (Mulliken) and Force Field Partial Atomic Charges for $LiFePO_4$

atom	Charge (electrons)	
	DFT bulk	Force Field
P	+2.2	+2.2
Fe	+1.65	+1.65
Fe (surface)	--	+1.375
O	-1.18	-1.2125
O (surface)	--	-0.9375
Li	+0.76	+1
Li (surface)	--	+1

Table 2. Comparison of $LiFePO_4$ Geometry from DFT and Molecular Dynamics Simulations

bond or bend	DFT Å or degrees	MD Å or degrees	Equilibrium value for harmonic potential function Å or degrees
P-O	1.52	1.52	1.53
P-O	1.54	1.54	1.53
P-O	1.56	1.56	1.57
Fe-O	2.20	2.20	2.23
Fe-O	2.11	2.11	2.11
Fe-O	2.25	2.25	2.22
Fe-O	2.06	2.06	2.06
O-P-O	113.0	112.9	113.4
O-P-O	113.3	113.3	112.8
O-P-O	106.4	106.5	105.9
O-P-O	103.6	103.5	105.4
O-Fe-O	178.6	178.4	180.0
O-Fe-O	90.8	90.8	92.3
O-Fe-O	81.6	81.5	80.1
O-Fe-O	89.9	90.0	90.4
O-Fe-O	97.3	97.2	95.6
O-Fe-O	87.1	87.1	87.8
O-Fe-O	152.7	152.6	153.1
O-Fe-O	119.4	119.4	119.3
O-Fe-O	65.8	65.9	64.1

Table 3. Nonbonded Parameters for $LiFePO_4$

atom or pair		A kcal/mol	B $Å^{-1}$	C kcal/mol $Å^6$	α $Å^3$
		$LiFePO_4$ atoms and pairs			
P		48826	2.91	1140	0.30
O		15923	2.53	239	1.15
Fe		721134	6.50	23	0.30
O	Fe	107157	4.52	74	
O	P	27883	2.72	522	
Fe	P	187644	4.70	162	
electrolyte atom	$LiFePO_4$ atom				
C	O	39381	3.03	352	
C	Fe	265067	5.06	109	
C	P	68972	3.26	769	
C (methyl)	O	41523	3.03	366	
C (methyl)	Fe	279439	5.07	113	
C (methyl)	P	72712	3.27	799	
O	O	15923	3.03	239	
O	Fe	107157	5.07	74	
O	P	27883	3.28	522	

H	O	8028	3.25	73
H	Fe	62126	5.43	22
H	P	16165	3.64	160
P	O	22484	2.62	843
P	Fe	187644	4.70	262
P	P	48826	2.91	1842
F	O	10450	2.93	189
F	Fe	71644	4.96	59
F	P	18642	3.16	414
Li	O	84068	4.00	15
Li	Fe	110721	6.25	5
Li	P	18750	2.35	56
N (EMIM)	O	20152	3.28	170
N (EMIM)	Fe	167900	5.53	53
N (EMIM)	P	43688	3.74	372
N (FSI)	O	23978	2.87	446
N (FSI)	Fe	167900	4.91	138
N (FSI)	P	43688	3.11	974
S	O	21707	2.49	869
S	Fe	202532	4.62	270
S	P	52700	2.82	1897