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Particle shapes and surface structures of olivine $NaFePO_4$ in comparison to $LiFePO_4$

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Table S1: Interatomic potential parameters for $LiFePO_4$ and $NaFePO_4$

a) Two-body Buckingham and shell potential parameters

Interaction	A (eV)	ρ (Å)	C (eV.Å^6)	Y (e)	K (eV.Å^{-2})
Li^+ - O^{2-}	632.1010	0.2906	0.0	1.0	99999.0
Na^+ - O^{2-}	629.757635	0.317034	0.0	1.0	99999.0
Fe^{2+} - O^{2-}	1105.2409	0.3106	0.0	2.997	19.26
P^{5+} - O^{2-}	897.2648	0.3577	0.0	5.0	99999.0
O^{2-} - O^{2-}	22764.3	0.149	44.53	-2.96	65.0

b) Three-body harmonic potential

Bond	k (eVrad^{-2})	θ_0 (°)
O^{2-} - P^{5+} - O^{2-}	632.1010	0.2906

Table S2: Calculated properties of surfaces of $NaFePO_4$

	Tasker	d-spacing	Surface energy $E_{surface}$/J m^{-2}	
Surface	surface type	d_{hkl}/Å	Unrelaxed	Relaxed
(010)	III	3.09	1.31	0.52
(110)	II	2.65	3.06	0.54
(221)	II	2.33	2.29	0.58
(120)	III	1.48	2.95	0.59
(021)	II	1.31	2.14	0.62
(201)	III	3.56	1.25	0.63
(211)	III	3.08	2.36	0.63
(011)	III	3.85	2.54	0.64
(210)	III	3.96	2.33	0.68
(111)	III	3.60	2.64	0.68
(100)	III	5.16	1.73	0.68
(101)	III	4.44	1.41	0.74
(121)	II	2.54	2.21	0.70
(212)	III	2.09	2.27	0.75
(012)	II	1.14	4.24	0.77
(112)	III	2.23	2.46	0.79
(122)	II	1.89	3.43	0.81
(102)	III	2.39	2.90	0.82
(001)	III	2.46	2.29	0.90

Table S3: Comparison of energies of low index surfaces of $NaFePO_4$ and $LiFePO_4$

Na surface	Tasker surface type	Relaxed $E_{surface}$/Jm^{-2}	Li surface	Tasker surface type	Relaxed $E_{surface}$/Jm^{-2}
(010)	III	0.52	(201)	III	0.71
(110)	II	0.54	(011)	III	0.75
(221)	II	0.58	(010)	III	0.75
(120)	III	0.59	(211)	III	0.80
(021)	II	0.62	(122)	III	0.80
(201)	III	0.63	(021)	II	0.82
(211)	III	0.63	(221)	II	0.84
(011)	III	0.64	(212)	III	0.86
(210)	III	0.68	(120)	III	0.86
(111)	III	0.68	(100)	III	0.87
(100)	III	0.68	(101)	III	0.88
(101)	III	0.74	(111)	III	0.89
(121)	II	0.70	(210)	III	0.90
(212)	III	0.75	(110)	II	0.92
(012)	II	0.77	(112)	III	0.94
(112)	III	0.79	(012)	III	0.94
(122)	II	0.81	(121)	II	0.94
(102)	III	0.82	(102)	III	0.96
(001)	III	0.90	(001)	III	1.11

Table S4: Literature survey of $LiFePO_4$ morphologies, dimensions and synthesis conditions.

Shape	Synthesis conditions	Particle size (single particle)	Identified surface planes, notes	Ref.
Nanoplate	Hydrothermal at 120 ºC for 5 h; pH 7.56	3 μm long		[1]
	Hydrothermal at 220 ºC for 3 h; pH ~7	4 μm × 2 μm × 200nm	010, long in *c*	[2]
	Hydrothermal at 170 ºC for 12 h; pH 5.15	1-2 μm long	010	[3]
	Hydrothermal at 190 ºC for 5 h	~2 μm long	010	[4]
	Hydrothermal at 170 ºC for 12 h; pH 6.5	~3 μm long	010	[5]
	Hydrothermal at 190 ºC for 12 h; pH 5	~2 μm long	010	[6]
	Hydrothermal at 150-220 ºC for 5 h; ascorbic acid	1-3 μm × 100 nm		[7]
	Hydrothermal at 200 ºC for 6 h; pH 10 with hydrazine	0.5 μm thick		[7]
	Hydrothermal at 150-175 ºC; with PEG	1-3 μm × 200-300 nm		[7]
	Hydrothermal at 180 ºC for 3 h; with PEG	~5 μm long		[7]
	Hydrothermal at 180 ºC for 3 h, pH 8.5	~4 μm × ~400 nm	010	[8]
	Solvothermal in 3:5 ethanol/water at 180 ºC for 3 h, pH 8.5	~1 μm × ~200 nm	010	[8]
	Solvothermal in 3:5 ethanol/water at 180 ºC for 3 h w/C, pH 8.5	~1 μm × ~200 nm	010	[8]
	Solvothermal in 2:3 PEG400/water at 140 ºC for 24 h	800 nm × 100 nm	010	[9]
	Solvothermal in 2:3 PEG400/water at 180 ºC for 9 h	3 μm × 300 nm	010	[9]
	Hydrothermal at 120 ºC for 3 h	2 μm × 200 nm	010, long in *c*	[10]
	Solvothermal at 170 ºC for 2 h in DEG	~250 nm	100	[11]
	Solvothermal at 170 ºC for 8 h in DEG	~600 nm (broadly distributed)		[11]
	Solvothermal at 170 ºC for 16 h in DEG	~450 nm		[11]
	Solvothermal at 170 ºC for 36 h in DEG	~450 nm		[11]
	Solvothermal at 230 ºC for 6 h in DEG	100 × 100 × 20nm	010	[12]
Orthorhombic or rhombic	Hydrothermal at 335 ºC for 16 h with TTEG	20 × 40nm	010	[13]
	Hydrothermal at 180 ºC for 3-5 h, pH ~7 with citric acid and ammonia	5 μm		[14]
	Solvothermal in DEG at 230 ºC for 16 h	200-250 nm × 180 nm × 100 nm		[15]
Rod or needle	Hydrothermal at 220C for 1 h	30 μm long		[16]
	Hydrothermal at 170 ºC for 12 h; pH 3.5	(~2 μm × 600 nm)	Large in *bc* plane, long in *c*	[5]
	Microwave solvothermal in TEG at 300 ºC w/ 5 min hold	100 nm × 25 nm × ? nm	Long in 001, wide in 100	[17]
	Microwave hydrothermal at 235 ºC w/ 15 min hold	300 × 225 × ? nm	Long axis perpendicular to *b*	[17]
	Microwave solvothermal in TEG at 300 ºC w/ 5 min hold	(~ 100 × 30 × ? nm)	Long in 001, wide in 100	[18]
	Aqueous under reflux for 24 h at ambient pressure	40 nm × 35 nm × 13 nm (60 nm × 15 nm × ?)	010 × 001 × 100	[19]
	Solvothermal in ionic liquids at 250 ºC for 24h	10-100μm × 1μm	Long in *b*	[20]
		Primary particles 1μm × <100nm	Primary particles long in 101	
	Reflux in TEG at 320 ºC for 3-20h	15 × 50 nm - 25 × 100 nm	Long in *c*	[21]
	Hydrothermal at 180 ºC for 3 h pH ~7	~300 nm long		[10]
	Reflux in TEG for 4 h	38 nm × 46 nm × 56 nm (68 nm × 26 nm)	100, 010, 001; long in *c*	[22]
		40 nm × 20 nm × 58 nm (195 nm × 37 nm)	100, 010, 001; long in *c*	
	Reflux in tEG for 4 h	24 nm × 25 nm × 40 nm (90 × 40nm)	100, 010, 001; long in *c*	[22]
		36 nm × 15 nm × 62 nm (600 × 39 nm)	100, 010, 001; long in *c*	
	Hydrothermal at 260 ºC for 48 h	80-120 μm long	Long in *b*	[23]
	Hydrothermal at 260 ºC for 10 days	300-350 μm long	Long in *b*	[23]
	Hydrothermal at 260 ºC for 48 h with EMI-TFSI IL	170 × 50 μm	Long in *b*	[23]
Tabular	Hydrothermal at 180 ºC for 5 days, pH ~7 with citric acid and ammonia	4 μm × 6 μm	010, 100, 101, 011	[14]
	Hydrothermal at 260 ºC for 30 days with EMI-TFSI ionic liquid	700 μm × 250μm × 150 μm		[23]

References:

1 S. F. Yang, P. Y. Zavalij and M. S. Whittingham, *Electrochem. Commun.*, 2001, **3**, 505-508.
2 G. Y. Chen, X. Y. Song and T. J. Richardson, *Electrochem. Solid-State Lett.*, 2006, **9**, A295-A298.
3 K. Kanamura, S. H. Koizumi and K. R. Dokko, *J. Mater. Sci.*, 2008, **43**, 2138-2142.
4 B. Ellis, W. H. Kan, W. R. M. Makahnouk and L. F. Nazar, *J. Mater. Chem.*, 2007, **17**, 3248-3254.
5 K. Dokko, S. Koizumi, H. Nakano and K. Kanamura, *J. Mater. Chem.*, 2007, **17**, 4803-4810.
6 H. Nakano, K. Dokko, S. Koizumi, H. Tannai and K. Kanamura, *J. Electrochem. Soc.*, 2008, **155**, A909-A914.
7 J. J. Chen, M. J. Vacchio, S. J. Wang, N. Chernova, P. Y. Zavalij and M. S. Whittingham, *Solid State Ionics*, 2008, **178**, 1676-1693.
8 X. Qin, X. H. Wang, H. M. Xiang, J. Xie, J. J. Li and Y. C. Zhou, *J. Phys. Chem. C*, 2010, **114**, 16806-16812.
9 S. L. Yang, X. F. Zhou, J. G. Zhang and Z. P. Liu, *J. Mater. Chem.*, 2010, **20**, 8086-8091.
10 X. Qin, J. M. Wang, J. Xie, F. Z. Li, L. Wen and X. H. Wang, *Phys. Chem. Chem. Phys.*, 2012, **14**, 2669-2677.
11 J. Lim, J. Gim, S. W. Kang, S. Baek, H. Jeong and J. Kim, *J. Electrochem. Soc.*, 2012, **159**, A479-A484.
12 D. Kim, J. Lim, V. Mathew, B. Koo, Y. Paik, D. Ahn, S. M. Paek and J. Kim, *J. Mater. Chem.*, 2012, **22**, 2624-2631.
13 D. H. Kim and J. Kim, *Electrochem. Solid-State Lett.*, 2006, **9**, A439-A442.
14 Z. G. Lu, H. L. Chen, R. Robert, B. Y. X. Zhu, J. Q. Deng, L. J. Wu, C. Y. Chung and C. P. Grey, *Chem. Mater.*, 2011, **23**, 2848-2859.
15 J. Lim, J. Gim, J. Kang, J. Song, H. Park, S. Baek and J. Kim, *J. Electrochem. Soc.*, 2012, **159**, A459-A463.
16 S. Franger, F. Le Cras, C. Bourbon and H. Rouault, *J. Power Sources*, 2003, **119**, 252-257.
17 A. V. Murugan, T. Muraliganth and A. Manthiram, *J. Phys. Chem. C*, 2008, **112**, 14665-14671.
18 A. V. Murugan, T. Muraliganth, P. J. Ferreira and A. Manthiram, *Inorg. Chem.*, 2009, **48**, 946-952.
19 P. Gibot, M. Casas-Cabanas, L. Laffont, S. Levasseur, P. Carlach, S. Hamelet, J. M. Tarascon and C. Masquelier, *Nat. Mater.*, 2008, **7**, 741-747.
20 N. Recham, L. Dupont, M. Courty, K. Djellab, D. Larcher, M. Armand and J. M. Tarascon, *Chem. Mater.*, 2009, **21**, 1096-1107.
21 S. P. Badi, M. Wagemaker, B. L. Ellis, D. P. Singh, W. J. H. Borghols, W. H. Kan, D. H. Ryan, F. M. Mulder and L. F. Nazar, *J. Mater. Chem.*, 2011, **21**, 10085-10093.
22 T. Azib, S. Ammar, S. Nowak, S. Lau-Truing, H. Groult, K. Zaghib, A. Mauger and C. M. Julien, *J. Power Sources*, 2012, **217**, 220-228.
23 N. Recham, J. Oro-Sole, K. Djellab, M. R. Palacin, C. Masquelier and J. M. Tarascon, *Solid State Ionics*, 2012, **220**, 47-52.