Supporting Information

Surface and Interface Issues in Spinel $LiNi_{0.5}Mn_{1.5}O_4$: Insights into a Potential Cathode Material for High Energy Density Lithium-Ion Batteries

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Table S1 The electrochemical performance of $LiNi_{0.5}Mn_{1.5}O_4$ with different oriented growth surfaces.

Orientation	Shape	Initial capacity [mAh g^{-1}]	Measuring parameters	Synthesis method	Ref.
(112)	plate	~121	3.0-5.0 V, C/5	molten-salt	[1]
(111)	octahedral	~136	3.0-5.0 V, C/5	molten-salt	[1]
(111)	octahedral	133	2.7-4.8 V, C/6	CSTR[a)]	[2]
(111) (100)	truncated octahedral	124	2.7-4.8 V, C/6	co-precipitation	[2]
(111) (11-2)	cubic	241	3.5-5.0 V, C/2	hydrothermal	[3]
(111)	spherical	248	3.5-5.0 V, C/2	CSTR	[3]
(111)	octahedral	249	3.5-5.0 V, C/2	CSTR	[3]
(111) (110) (100)	truncated octahedral	229	3.5-5.0 V, C/2	co-precipitation	[3]
(001) (110) (113) (103)	polyhedral	141	3.5-5.0 V, 1C	polymer auxiliary method	[4]
(001)	flake	133.5	3.5-4.9 V, 1C	in situ template	[5]
(111)	octahedral	69	3.5-4.9 V, 1C charge/50C discharge	polymer auxiliary method	[6]
(001) (110) (113) (103)	chamfered polyhedral	103	3.5-4.9 V, 1C charge/50C discharge	polymer auxiliary method	[6]

[a)] CSTR is the abbreviation of continuously stirred tank reactor.

Table S2. Electrochemical performance of $LiNi_{0.5}Mn_{1.5}O_4$ under various modification strategies to suppress the side reactions on the interfaces of $LiNi_{0.5}Mn_{1.5}O_4$/electrolyte and $LiNi_{0.5}Mn_{1.5}O_4$/anode.

Changing morphology								
Morphology	Anode materials	Electrolyte formula	Initial capacity [mAh g-1]	Capacity retention	Working potential [V]	Cycles	Current density	Temp.
50 nm nanoparticles[7]	Li	1M $LiPF_6$/EC/DMC (1:1, v/v)	~136	95.7%	3.5-4.95	100	1C	RT
>500 nm nanoparticles[8]	Li	1M $LiPF_6$/EC/DMC (1:2, w/w)	123	81%	3.5-5.0	40	1C	RT
800 nm sphere[9]	Li	1M $LiPF_6$/EC/EMC (3:7)	122	92%	3.5-4.9	500	2C	RT
diameters of 100-400 nm and lengths of more than 10 μm, nanoporous[10]	Li	1M $LiPF_6$/EC/DMC (1:1, v/v)	124	91%	3.5-4.95	500	5C	RT
1-3 μm polyhedral[11]	Li	1.2M $LiPF_6$/EC/DEC (3:7, w/w)	133.5	86%	3.5-4.9	500	1C	RT
1-3 μm polyhedral[11]	Li	1.2M $LiPF_6$/EC/DEC (3:7, w/w)	132	63.3%	3.5-4.9	100	1C	55 °C
Coating								
Coating layer	Anode materials	Electrolyte formula	Initial capacity [mAh g-1]	Capacity retention	Working potential [V]	Cycles	Current density	Temp.
5 wt% PPy[12]	Li	1M $LiPF_6$/EC/DEC (3:7, v/v)	124	91%	3.5-4.9	300	1C	RT
5 wt% PPy[12]	Li	1M $LiPF_6$/EC/DEC (3:7, v/v)	115.6	91%	3.5-4.9	100	1C	55 °C
5 nm $Li_{0.1}B_{0.967}PO_4$[13]			137	91.3%	3.5-4.95	400	1C	RT
concentration-gradient shell, from $LiMg_{0.056}Ni_{0.444}Mn_{1.5}O_4$ to $LiMg_{0.5}Mn_{1.5}O_4$ (outmost)[14]	Li	1M $LiPF_6$/EC/DMC (1:1, v/v)	127	98.9%	3.0-4.9	200	1C	RT

concentration-gradient shell, from $LiMg_{0.056}Ni_{0.444}Mn_{1.5}O_4$ to $LiMg_{0.5}Mn_{1.5}O_4$ (outmost)[14]	Li	1M $LiPF_6$/EC/DMC (1:1, v/v)	128	99%	3.0-4.9	100	1C	55 °C
2wt% Al_2O_3[15]	Li	1M $LiPF_6$/EC/DEC (1:1)	130	99.7%	3.5-5.0	50	20 mA g^{-1}	RT
2wt% Al_2O_3[15]	Li	1M $LiPF_6$/EC/DEC (1:1)	119	98%	3.5-5.0	50	20 mA g^{-1}	55 °C
2wt% Bi_2O_3[15]	Li	1M $LiPF_6$/EC/DEC (1:1)	132	99.0%	3.5-5.0	50	20 mA g^{-1}	RT
2wt% Bi_2O_3[15]	Li	1M $LiPF_6$/EC/DEC (1:1)	120	93.9%	3.5-5.0	50	20 mA g^{-1}	55 °C
10 nm PI[16]	Li	1M $LiPF_6$/EC/DMC (1:1, v/v)	131	93.2%	3.5-5.0	100	1C	RT
10 nm PI[16]	Li	1M $LiPF_6$/EC/DMC (1:1, v/v)	128	93.7%	3.5-4.9	50	1C	55 °C
6wt% $La_{0.7}Sr_{0.3}MnO_3$[17]	Li	1M $LiPF_6$/EC/DMC (1:1, v/v)	115	91%	3.0-4.9	100	2C	RT
6wt% $La_{0.7}Sr_{0.3}MnO_3$[17]	Li	1M $LiPF_6$/EC/DMC (1:1, v/v)	120	90%	3.0-4.9	100	2C	60 °C
1 nm LiPON[18]	Li	1.2M $LiPF_6$/EC/DMC (1:2, v/v)	136	97.5%	3.5-4.9	50	1C	RT
5 nm Al_2O_3[19]	natural graphite with 5 nm Al_2O_3 coating	1M $LiPF_6$/EC/DEC (1:1, v/v)	107	84%	3.0-4.8	100	10 mA g^{-1}	RT
5 nm Al_2O_3[19]	natural graphite	1M $LiPF_6$/EC/DEC (1:1, v/v)	75	56%	3.0-4.8	100	10 mA g^{-1}	RT
5-6 nm Li_3PO_4[20]	Li	1M $LiPF_6$/EC/DEC (1:1, w/w)	122	80%	3.0-5.0	650	C/2	RT
less than 2 nm Al_2O_3[21]	Li	1M $LiPF_6$/EC/DEC (45:55, v/v)	127	98.4%	3.5-5.0	20	C/10	RT
less than 2 nm Al_2O_3[21]	graphite	1M $LiPF_6$/EC/DEC (45:55, v/v)	110		3.5-4.9		C/20	RT
1.5wt% ZnO[22]	Li	1M $LiPF_6$/EC/DMC (1:1)	103	100%	3.0-5.0	100	C/3	RT
<10 nm $Li_4P_2O_7$[23]	Li	1M $LiPF_6$/EC/DEC	123.8	74.3%	3.0-5.0	893	C/2	RT

		(1:1, w/w)						
<0.5 nm TiO_2[24]	Li	1M $LiPF_6$/EC/DMC (1:1, v/v)	105		3.5-4.85		C/7.5	RT
<0.5 nm Al_2O_3[24]	Li	1M $LiPF_6$/EC/DMC (1:1, v/v)	111		3.5-4.85		C/7.5	RT
Doping								
Doped LNMO	Anode materials	Electrolyte formula	Initial capacity [mAh g-1]	Capacity retention	Working potential [V]	Cycles	Current density	Temp.
$LiMn_{1.5}Ni_{0.42}Cr_{0.08}O_4$[25]	Li	1M $LiPF_6$/EC/DEC (1:2)	135	96%	3.5-5.0	100	C/6	RT
$LiMn_{1.5}Ni_{0.42}Cr_{0.08}O_4$[25]	Li	1M $LiPF_6$/EC/DEC (1:2)	133	95%	3.5-5.0	50	C/6	55 °C
$LiMn_{1.5}Ni_{0.42}Fe_{0.08}O_4$[25]	Li	1M $LiPF_6$/EC/DEC (1:2)	125	96%	3.5-5.0	100	C/6	RT
$LiMn_{1.5}Ni_{0.42}Fe_{0.08}O_4$[25]	Li	1M $LiPF_6$/EC/DEC (1:2)	127	97%	3.5-5.0	50	C/6	55 °C
$LiMn_{1.5}Ni_{0.42}Ga_{0.08}O_4$[25]	Li	1M $LiPF_6$/EC/DEC (1:2)	133	95%	3.5-5.0	100	C/6	RT
$LiMn_{1.5}Ni_{0.42}Ga_{0.08}O_4$[25]	Li	1M $LiPF_6$/EC/DEC (1:2)	133	100%	3.5-5.0	50	C/6	55 °C
$LiNi_{0.5}Mn_{1.5}O_{3.95}F_{0.05}$[26]	Li	1M $LiPF_6$/EC/DEC (1:1, v/v)	130		3.5-5.0		27 mA g^{-1}	30 °C
$LiNi_{0.5}Mn_{1.5}O_{3.9}F_{0.1}$[26]	Li	1M $LiPF_6$/EC/DEC (1:1, v/v)	127		3.5-5.0		27 mA g^{-1}	30 °C
$LiNi_{0.5}Mn_{1.2}Ti_{0.3}O_4$[27]	Li	1M $LiPF_6$/EC/EMC (1:1, v/v)	120	87%	3.5-4.9	200	C/5	30 °C
$LiNi_{0.5}Mn_{1.2}Ti_{0.3}O_4$[27]	graphite	1M $LiPF_6$/EC/EMC (1:1, v/v)	109	75%	3.4-4.8	200	C/5	30 °C
$LiMn_{1.5}Ni_{0.42}Fe_{0.08}O_4$[28]	Li	1M $LiPF_6$/EC/DEC (1:1)	136	100%	3.5-5.0	100	C/6	RT
$LiMn_{1.42}Ni_{0.42}Fe_{0.16}O_4$[28]	Li	1M $LiPF_6$/EC/DEC (1:1)	131	99%	3.5-5.0	100	C/6	RT
$LiMn_{1.5}Ni_{0.34}Fe_{0.16}O_4$[28]	Li	1M $LiPF_6$/EC/DEC (1:1)	127	100%	3.5-5.0	100	C/6	RT
$LiCr_{0.2}Ni_{0.4}Mn_{1.4}O_4$[29]	Li	1M $LiPF_6$/EC/DMC (1:1, v/v)	128	99%	3.4-5.2	40	charge C/2 and	RT

							discharge 1C	
$LiCr_{0.2}Ni_{0.4}Mn_{1.4}O_4$[29]	Li	1M $LiPF_6$/EC/DMC (1:1, v/v)	140	97%	3.4-5.2	40	charge C/2 and discharge 1C	55 °C
Electrolyte								
Electrolyte formula	Anode materials	Cathode materials	Initial capacity [mAh g-1]	Capacity retention	Working potential [V]	Cycles	Current density	Temp.
1 M $LiPF_6$/ trimethyl phosphate (TMP)[30]	$Li_4Ti_5O_{12}$	$LiNi_{0.5}Mn_{1.5}O_4$	136	96%	3.0-3.75	50	C/10	RT
1.2 M $LiPF_6$/fluorinated cyclic carbonate (F-AEC)/EMC/fluorinated ether (F-EPE) (2:6:2, w/w)[31]	$Li_4Ti_5O_{12}$	$LiNi_{0.5}Mn_{1.5}O_4$	114	98%	2.0-3.45	80	C/2	55 °C
1.2 M $LiPF_6$/F-AEC/fluorinated linear carbonate (F-EMC)/F-EPE (2:6:2, w/w)[31]	$Li_4Ti_5O_{12}$	$LiNi_{0.5}Mn_{1.5}O_4$	118	100%	2.0-3.45	80	C/2	55 °C
1.2 M $LiPF_6$/EC/F-EMC/F-EPE (2:6:2, w/w)[31]	$Li_4Ti_5O_{12}$	$LiNi_{0.5}Mn_{1.5}O_4$	116	93%	2.0-3.45	80	C/2	55 °C
1 M $LiPF_6$/tetramethylsilane (TMS)/EMC (1:1, v/v)[32]	$Li_4Ti_5O_{12}$	$LiNi_{0.5}Mn_{1.5}O_4$	80	96%	2.0-3.45	1000	2C	RT
1 M $LiPF_6$/PEC/F-EMC/F-EPE (3:5:2, v/v)[33]	graphite	$LiNi_{0.5}Mn_{1.5}O_4$	130	84.6%	3.5-4.9	100	C/3	RT
1 M $LiPF_6$/PEC/F-EMC/F-EPE (3:5:2, v/v)[33]	graphite	$LiNi_{0.5}Mn_{1.5}O_4$	122	68%	3.5-4.9	100	C/3	55 °C
Additives								
Additives	Anode materials	Electrolyte formula	Initial capacity [mAh g-1]	Capacity retention	Working potential [V]	Cycles	Current density	Temp.
1wt% lithium bis(oxalato) borate (LiBOB)[34]	Li	1 M $LiPF_6$/EC/EMC (3:7, v/v)	140	97.6%	3.5-4.9	3	C/10	RT
4wt% Li_2CO_3[35]	Li	1 M $LiPF_6$/EC/PC/DEC (1:1:3, w/w)	250	70%	2.0-5.0	55	C/2	RT

1wt% tris(trimethylsilyl)borate (TMSB)[36]	Li	1 M $LiPF_6$/EC/DMC (1:2, w/w)	101	104%	3.5-4.9	200	1C	RT
4wt% succinic anhydride (SA)[37]	Li	1 M $LiPF_6$/EC/DMC (1:1, v/v)	135	100%	3.5-4.95	50	C/2	RT
1wt% 3,5-bis(trifluoromethyl)-pyrazole (BTFMP)[38]	Li	1.5 M $LiPF_6$/EC/DEC (1:1, v/v)	121	50%	3.5-4.9	100	C/2	55 °C
1wt% triallyl cyanurate (TAC)[38]	Li	1.5 M $LiPF_6$/EC/DEC (1:1, v/v)	112	44%	3.5-4.9	100	C/2	55 °C
1wt% fluorinated ethylene carbonate (FEC)[38]	Li	1.5 M $LiPF_6$/EC/DEC (1:1, v/v)	127	56.7%	3.5-4.9	100	C/2	55 °C
0.4wt% LiF[38]	Li	1.5 M $LiPF_6$/EC/DEC (1:1, v/v)	113	35%	3.5-4.9	100	C/2	55 °C
1wt% LiBOB[39]	Li	1.1 M $LiPF_6$/EC/DEC (1:2, v/v)	135	90%	3.0-4.9	15	C/5	RT
0.25wt% LiBOB[38]	Li	1.1 M $LiPF_6$/EC/DEC (1:2, v/v)	141	92%	3.0-4.9	15	C/5	RT
0.5wt% tris (pentafluorophenyl) phosphine (TPFPP)[40]	Li	1 M $LiPF_6$/EC/DMC/DEC (1:1:1, v/v)	125.8	85%	3.0-4.9	55	C/5	RT
2wt% SA + 3wt% 1,3-propane sultone (PS)[41]	graphite	1 M $LiPF_6$/EC/EMC (1:2, v/v)		65%	3-4.8	200	C/2	RT
1wt% lithium difluoro(oxolato)borate (LiDFOB)[42]	graphite	1.2 M $LiPF_6$/EC/EMC (3:7, w/w)	71	109.8%	3.5-4.9	25	C/3	RT
1wt% FEC[42]	graphite	1.2 M $LiPF_6$/EC/EMC (3:7, w/w)	86	116.2%	3.5-4.9	25	C/3	RT
1wt% tris-hexafluoro-isopropyl phosphate (HFiP)[42]	graphite	1.2 M $LiPF_6$/EC/EMC (3:7, w/w)	106	100%	3.5-4.9	25	C/3	RT
Ionic liquid								
Ionic liquid	Anode	Cathode materials	Initial	Capacity	Working	Cycles	Current	Temp.

	materials		capacity [mAh g-1]	retention	potential [V]		density	
0.5 M LiTFSI[a)]/BMPTFSI[b)][43]	Li	$LiNi_{0.5}Mn_{1.5}O_4$	104	100%	4.0-5.0	42	C/16	30 °C
0.5 M LiTFSI/MPPpTFSI[c)][43]	Li	$LiNi_{0.5}Mn_{1.5}O_4$	143	93.7%	4.0-5.0	50	C/16	30 °C
1 M $LiBF_4$/$EMIBF_4$[d)][44]	Mo_6S_8	$LiNi_{0.5}Mn_{1.5}O_4$	100	95%	1.5-3.2	38	C/6	30 °C
1 LiTFSI/PMPyr-TFSI[e)][45]	Li	$LiNi_{0.5}Mn_{1.5}O_4$	118	95%	3.5-4.9	10	29.6 mA g^{-1}	55 °C

[a)] LiTFSI is the abbreviation of $LiN(SO_2CF_3)_2$; [b)] BMPTFSI is the abbreviation of 1-methyl-1-butylpyrrolidiniumbis(trifluoromethylsufonyl)imide; [c)] MPPpTFSI is the abbreviation of 1-methyl-1-propylpiperidinium bis(trifluoromethylsufonyl)imide; [d)] $EMIBF_4$ is the abbreviation of 1-methyl-3-methylimidazolium tetrafluoroborate; [e)] PMPyr-TFSI is the abbreviation of propylmethylpyrrolidinium bis(trifluoromethylsulfonly)imide.

References

(1) Hai, B.; Shukla, A. K.; Duncan, H.; Chen, G. The Effect of Particle Surface Facets on the Kinetic Properties of $LiMn_{1.5}Ni_{0.5}O_4$ Cathode Materials. *J. Mater. Chem. A* **2013**, *1*, 759-769.

(2) Chemelewski, K. R.; Shin, D. W.; Li, W.; Manthiram, A. Octahedral and Truncated High-Voltage Spinel Cathodes: The Role of Morphology and Surface Planes in Electrochemical Properties. *J. Mater. Chem. A* **2013**, *1*, 3347-3354.

(3) Chemelewski, K. R.; Lee, E.-S.; Li, W.; Manthiram, A. Factors Influencing the Electrochemical Properties of High-Voltage Spinel Cathodes: Relative Impact of Morphology and Cation Ordering. *Chem. Mater.* **2013**, *25*, 2890-2897.

(4) Chen, Z.; Zhao, R.; Li, A.; Hu, H.; Liang, G.; Lan, W.; Cao, Z.; Chen, H. Polyhedral Ordered $LiNi_{0.5}Mn_{1.5}O_4$ Spinel with Excellent Electrochemical Properties in Extreme Conditions. *J. Power Sources* **2015**, *274*, 265-273.

(5) Chen, Z.; Qiu, S.; Cao, Y.; Ai, X.; Xie, K.; Hong, X.; Yang, H. Surface-Oriented and Nanoflake-Stacked $LiNi_{0.5}Mn_{1.5}O_4$ Spinel for High-Rate and Long-Cycle-Life Lithium Ion Batteries. *J. Mater. Chem.* **2012**, *22*, 17768-17772.

(6) Chen, Z.; Zhao, R.; Du, P.; Hu, H.; Wang, T.; Zhu, L.; Chen, H. Polyhedral $LiNi_{0.5}Mn_{1.5}O_4$ with Excellent Electrochemical Properties for Lithium-Ion Batteries. *J. Mater. Chem. A* **2014**, *2*, 12835-12848.

(7) Yang, J.; Han, X.; Zhang, X.; Cheng, F.; Chen, J. Spinel $LiNi_{0.5}Mn_{1.5}O_4$ Cathode for Rechargeable Lithium Ion Batteries: Nano vs Micro, Ordered Phase (P4332) vs Disordered Phase (Fd-3m). *Nano Res*. **2013**, *6*, 679-687.

(8) Cabana, J.; Zheng, H.; Shukla, A. K.; Kim, C.; Battaglia, V. S.; Kunduraci, M. Comparison of the Performance of $LiNi_{1/2}Mn_{3/2}O_4$ with Different Microstructures. *J. Electrochem. Soc.* **2011**, *158*, A997-A1004.

(9) Qian, Y.; Deng, Y.; Shi, Z.; Zhou, Y.; Zhuang, Q.; Chen, G. Sub-Micrometer-Sized $LiMn_{1.5}Ni_{0.5}O_4$ Spheres as High Rate Cathode Materials for Long-Life Lithium Ion Batteries. *Electrochem. Commun.* **2013**, *27*, 92-95.

(10) Zhang, X.; Cheng, F.; Yang J.; Chen, J. $LiNi_{0.5}Mn_{1.5}O_4$ Porous Nanorods as High-Rate and Long-Life Cathodes for Li-Ion Batteries. *Nano Lett.* **2013**, *13*, 2822-2825.

(11) Chen, Z.; Qiu, S.; Cao, Y.; Ai, X.; Xie, K.; Hong, X.; Yang, H. Surface-Oriented and Nanoflake-Stacked $LiNi_{0.5}Mn_{1.5}O_4$ Spinel for High-Rate and Long-Cycle-Life Lithium Ion Batteries. *J. Mater. Chem.* **2012**, *22*, 17768-17772.

(12) Gao, X.-W.; Deng, Y.-F.; Wexler, D.; Chen, G.-H.; Chou, S.-L.; Liu, H.-K.; Shi, Z.-C.; Wang, J.-Z. Improving the Electrochemical Performance of the $LiNi_{0.5}Mn_{1.5}O_4$ Spinel by Polypyrrole Coating as a Cathode Material for the Lithium-Ion Battery. *J. Mater. Chem. A* **2015**, *3*, 404-411.

(13) Yang, X.; Yang, T.; Liang, S.; Wu, X.; Zhang, H. Modification of $LiNi_{0.5}Mn_{1.5}O_4$ High Potential Cathode from the Inner Lattice to the Outer Surface with Cr^{3+}-Doping and Li^+-Conductor Coating. *J. Mater. Chem. A* **2014**, *2*, 10359-10464.

(14) Wen, W.; Wang, X.; Chen, S.; Shu, H.; Yang, X. Design and Preparation of Spherical High Voltage $LiNi_{0.5}Mn_{1.5}O_4$ with a Novel Concentration-Gradient Shell for Lithium Ion Batteries. *J. Power Sources* **2015**, *281*, 85-93.

(15) Liu, J.; Manthiram, A. Kinetics Study of the 5 V Spinel Cathode $LiMn_{1.5}Ni_{0.5}O_4$ Before and After Surface Modifications. *J. Electrochem. Soc.* **2009**, *156*, A833-A838.

(16) Cho, J.-H.; Park, J.-H.; Lee, M.-H.; Song, H.-K.; Lee, S.-Y. A polymer Electrolyte-Skinned Active Material Strategy toward High-Voltage Lithium Ion Batteries: A Polyimide-Coated $LiNi_{0.5}Mn_{1.5}O_4$ Spinel Cathode Material Case. *Energy Environ. Sci.* **2012**, *5*, 7124-7131.

(17) Zhao, G.; Lin, Y.; Zhou, T.; Lin, Y.; Huang, Y.; Huang, Z. Enhanced Rate and High-Temperature Performance of $La_{0.7}Sr_{0.3}MnO_3$-Coated $LiNi_{0.5}Mn_{1.5}O_4$ Cathode Materials for Lithium Ion Battery. *J. Power Sources* **2012**, *215*, 63-68.

(18) Li, J.; Baggetto, L.; Martha, S. K.; Veith, G. M.; Nanda, J.; Liang, C.; Dudney, N. J. An Artificial Solid Electrolyte Interphase Enables the Use of a $LiNi_{0.5}Mn_{1.5}O_4$ 5 V Cathode with Conventional Electrolytes. *Adv. Energy Mater.* **2013**, *3*, 1275-1278.

(19) Xiao, X.; Ahn, D.; Liu, Z.; Kim, J.-H.; Lu, P. Atomic Layer Coating to Mitigate Capacity Fading Associated with Manganese Dissolution in Lithium Ion Batteries. *Electrochem. Commun.* **2013**, *32*, 31-34.

(20) Chong, J.; Xun, S.; Zhang, J.; Song, X.; Xie, H.; Battaglia, V.; Wang, R. Li_3PO_4-Coated $LiNi_{0.5}Mn_{1.5}O_4$: a Stable High-Voltage Cathode Material for Lithium-Ion Batteries. *Chem. Eur. J.* **2014**, *20*, 7479-7485.

(21) Park, J. S.; Meng, X.; Elam, J. W.; Hao, S.; Wolverton, C.; Kim, C.; Cabana, J. Ultrathin Lithium-Ion Conducting Coatings for Increased Interfacial Stability in High Voltage Lithium-Ion Batteries. *Chem. Mater.* **2014**, *26*, 3128-3134.

(22) Brutti, S.; Gentili, V.; Reale, P.; Carbone, L.; Panero, S. Mitigation of the Irreversible Capacity and Electrolyte Decomposition in a $LiNi_{0.5}Mn_{1.5}O_4$/nano-TiO_2 Li-Ion Battery. *J. Power Sources* **2011**, *196*, 9792-9799.

(23) Chong, J.; Xun, S.; Song, X.; Liu, G.; Battaglia, V. S. Surface Stabilized $LiNi_{0.5}Mn_{1.5}O_4$ Cathode Materials with High-Rate Capability and Long Cycle Life for Lithium Ion Batteries. *Nano Energy* **2013**, *2*, 283-293.

(24) Cho, H. M.; Chen, M. V.; MacRae, A. C.; Meng, Y. S. Effect of Surface Modification on Nano-Structured $LiNi_{0.5}Mn_{1.5}O_4$ Spinel Materials. *ACS Appl. Mater. Interfaces* **2015**, *7*, 16231-16239.

(25) Shin, D. W.; Bridges, C. A.; Huq, A.; Paranthaman, M. P.; Manthiram, A. Role of Cation Ordering and Surface Segregation in High-Voltage Spinel $LiMn_{1.5}Ni_{0.5-x}M_xO_4$(M = Cr, Fe, and Ga) Cathodes for Lithium-Ion Batteries. *Chem. Mater.* **2012**, *24*, 3720-3731.

(26) Oh, S.-W.; Park, S.-H.; Kim, J.-H.; Bae, Y. C.; Sun, Y.-K. Improvement of Electrochemical Properties of $LiNi_{0.5}Mn_{1.5}O_4$ Spinel Material by Fluorine Substitution. *J. Power Sources* **2006**, *157*, 464-470.

(27) Kim, J.-H.; Pieczonka, N. P. W.; Lu, P.; Liu, Z.; Qiao, R.; Yang, W.; Tessema, M. M.; Sun, Y.-K.; Powell, B. R. In Situ Formation of a Cathode-Electrolyte Interface with Enhanced Stability by Titanium Substitution for High Voltage Spinel Lithium-Ion Batteries. *Adv. Mater. Interfaces* **2015**, *2*, 1500109.

(28) Liu, J.; Manthiram, A. Understanding the Improved Electrochemical Performances of Fe-Substituted 5 V Spinel. *J. Phys. Chem. C* **2009**, *113*, 15073-15079.

(29) Aklalouch, M.; Amarilla, J. M.; Rojas, R. M.; Saadoune, I.; Rojo, J. M. Chromium Doping as a New Approach to Improve the Cycling Performance at High Temperature of 5V $LiNi_{0.5}Mn_{1.5}O_4$-Based Positive Electrode. *J. Power Sources* **2008**, *185*, 501-511.

(30) Matsumoto, K.; Martinez, M.; Gutel, T.; Mailley, S.; De vito, E.; Patoux, S.; Inoue, K.; Utsugi, K. Stability of Trimethyl Phosphate Non-Flammable Based Electrolyte on the High Voltage Cathode ($LiNi_{0.5}Mn_{1.5}O_4$). *J. Power Sources* **2015**, *273*, 1084-1088.

(31) Zhang, Z.; Hu, L.; Wu, H.; Weng, W.; Koh, M.; Redfern, P. C.; Curtiss, L. A.; Amine, K. Fluorinated Electrolytes for 5 V Lithium-Ion Battery Chemistry. *Energy Environ. Sci.* **2013**, *6*, 1806-1810.

(32) Abouimrane, A.; Belharouak, I.; Amine, K. Sulfone-Based Electrolytes for High-Voltage Li-Ion Batteries. *Electrochem. Commun.* **2009**, *11*, 1073-1076.

(33) Hu, L.; Zhang, Z.; Amine, K. Fluorinated Electrolytes for Li-Ion Battery: An FEC-Based Electrolyte for High Voltage $LiNi_{0.5}Mn_{1.5}O_4$/Graphite Couple. *Electrochem. Commun*. **2013**, *35*, 76-79.

(34) Xu, M.; Tsiouvaras, N.; Garsuch, A.; Gasteiger, H. A.; Lucht, B. L. Generation of Cathode Passivation Films via Oxidation of Lithium Bis(oxalato) Borate on High Voltage Spinel ($LiNi_{0.5}Mn_{1.5}O_4$). *J. Phys. Chem. C* **2014**, *118*, 7363-7368.

(35) Wu, B.; Ren, Y.; Mu, D.; Liu, X.; Wu, F. Electrochemical Performance of 5 V $LiNi_{0.5}Mn_{1.5}O_4$ Cathode Modified with Lithium Carbonate Addition in Electrolyte. *J. Power Sources* **2014**, *272*, 183-189.

(36) Liao, X.; Huang, Q.; Mai, S.; Wang, X.; Xu, M.; Xing, L.; Liao, Y.; Li, W. Self-Discharge Suppression of 4.9 V $LiNi_{0.5}Mn_{1.5}O_4$ Cathode by Using Tris(trimethylsilyl)borate as an Electrolyte Additive. *J. Power Sources* **2014**, *272*, 501-507.

(37) Tarnopolskiy, V.; Kalhoff, J.; Nádherná, M.; Bresser, D.; Picard, L.; Fabre, F.; Rey, M.; Passerini, S. Beneficial Influence of Succinic Anhydride as Electrolyte Additive on the Self-Discharge of 5 V $LiNi_{0.4}Mn_{1.6}O_4$ Cathodes. *J. Power Sources* **2013**, *236*, 39-46.

(38) Kim, K.; Kim, Y.; Oh, E.-S.; Shin, H.-C. The Role of Fluoride in Protecting $LiNi_{0.5}Mn_{1.5}O_4$ Electrodes Against High Temperature Degradation. *Electrochim. Acta* **2013**, *114*, 387-393.

(39) Dalavi, S.; Xu, M.; Knight, B.; Lucht, B. L. Effect of Added LiBOB on High Voltage ($LiNi_{0.5}Mn_{1.5}O_4$) Spinel Cathodes. *Electrochem. Solid-State Lett.* **2011**, *15*, A28-A31.

(40) Xu, M.; Liu, Y.; Li, B.; Li, W.; Li, X.; Hu, S. Tris (pentafluorophenyl) Phosphine: An Electrolyte Additive for High Voltage Li-Ion Batteries. *Electrochem. Commun.* **2012**, *18*, 123-126.

(41) Lee, H.; Choi, S.; Choi, S.; Kim, H.-J.; Choi, Y.; Yoon, S.; Cho, J.-J. SEI Layer-Forming Additives for $LiNi_{0.5}Mn_{1.5}O_4$/Graphite 5 V Li-Ion Batteries. *Electrochem. Commun.* **2007**, *9*, 801-806.

(42) Delp, S. A.; Allen, J. L.; Richard Jow, T. Investigation of Electrolyte Additives with $LiNi_{0.5}Mn_{1.5}O_4$/Graphite Cells at High Temperature. *ECS Transactions* **2014**, *58*, 111-118.

(43) Borgel, V.; Markevich, E.; Aurbach, D.; Semrau, G.; Schmidt, M. On the Application of Ionic Liquids for Rechargeable Li Batteries: High Voltage Systems. *J. Power Sources* **2009**, *189*, 331-336.

(44) Markevich, E.; Baranchugov, V.; Aurbach, D. On the Possibility of Using Ionic Liquids as Electrolyte Solutions for Rechargeable 5V Li Ion Batteries. *Electrochem. Commun.* **2006**, *8*, 1331-1334.

(45) Mun, J.; Yim, T.; Park, K.; Ryu, J. H.; Kim, Y. G.; Oh, S. M. Surface Film Formation on $LiNi_{0.5}Mn_{1.5}O_4$ Electrode in an Ionic Liquid Solvent at Elevated Temperature. *J. Electrochem. Soc.* **2011**, *158*, A453-A457.