Supplementary Information

First-principles Formulation of Spinel-like Structured $Li_{(4-3x)}Y_xCl_4$ as Promising Solid-State Electrolytes to Enable Superb Lithium Ion Conductivity and Matching Oxidation Potentials to High-voltage Cathodes

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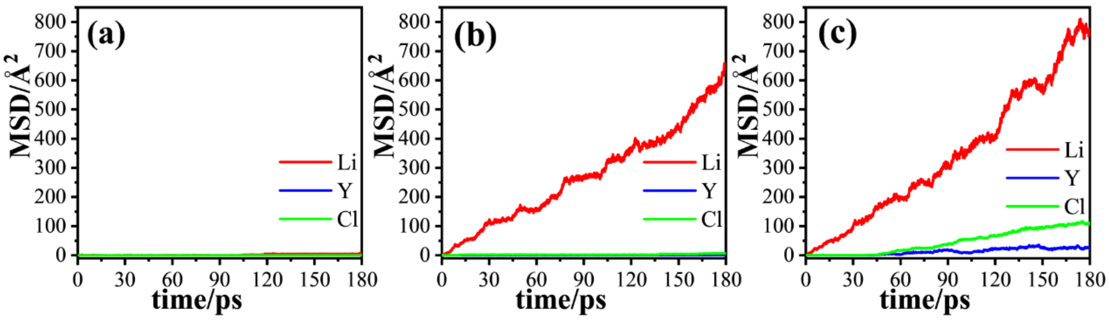

Fig. S1 Mean square displacements (MSD) of Li, Y and Cl atoms in $Li_{2.5}Y_{0.5}Cl_4$ at (a) 500K, (b) 900K and (c) 1000K.

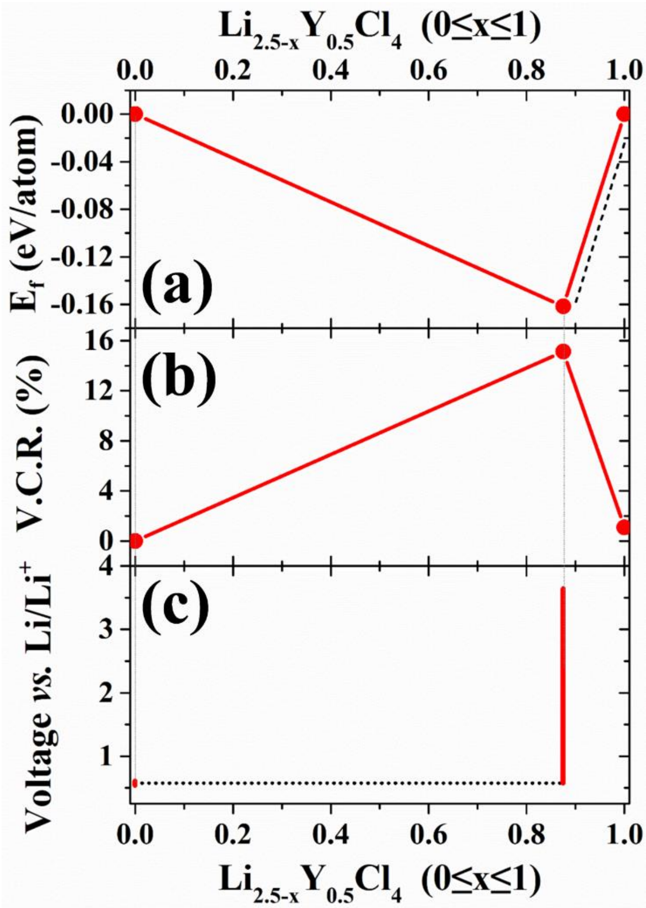

Fig. S2 (a) Convex hull, (b) the volumetric change rate (V.C.R.), and (c) the corresponding electrochemical potential for $Li_{2.5-x}Y_{0.5}Cl_4$ (0≤x≤1). The dash line in (a) indicates the region of unstable compositions.

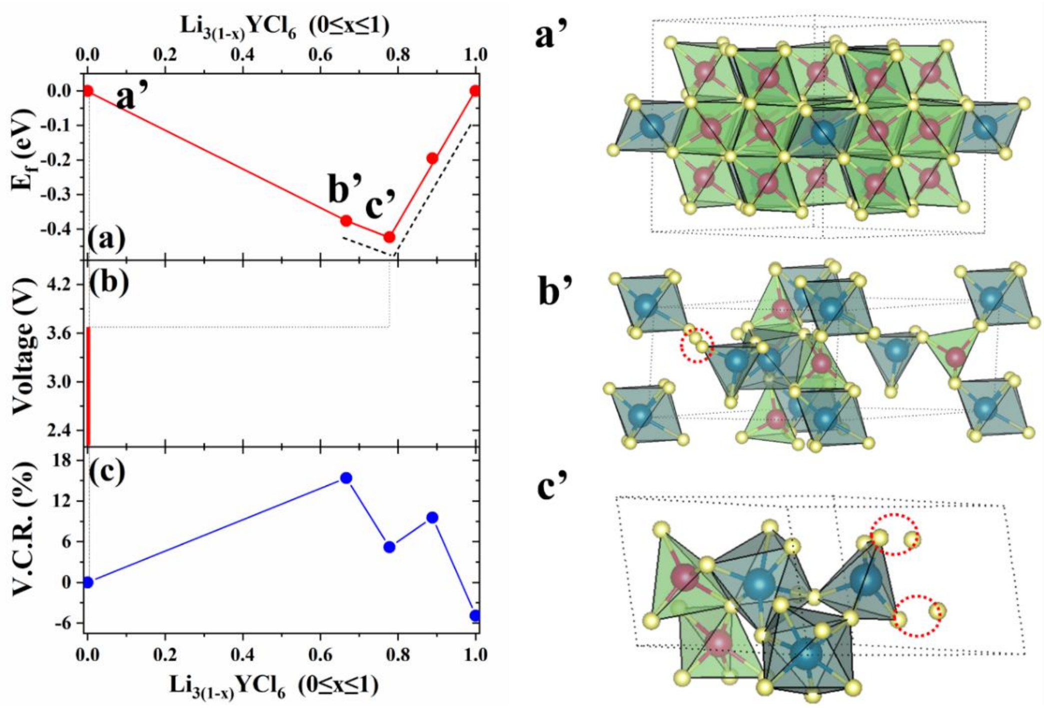

Fig. S3 (a) Convex hull, (b) the corresponding electrochemical potential, and (c) the volumetric change rate (V.C.R.) for $Li_{3(1-x)}YCl_6$ (0≤x≤1). The structure for (a') Li_3YCl_6, (b') $Li_{5/3}YCl_6$, and (c') $LiYCl_6$. The dash line in (a) indicates the region of unstable compositions.

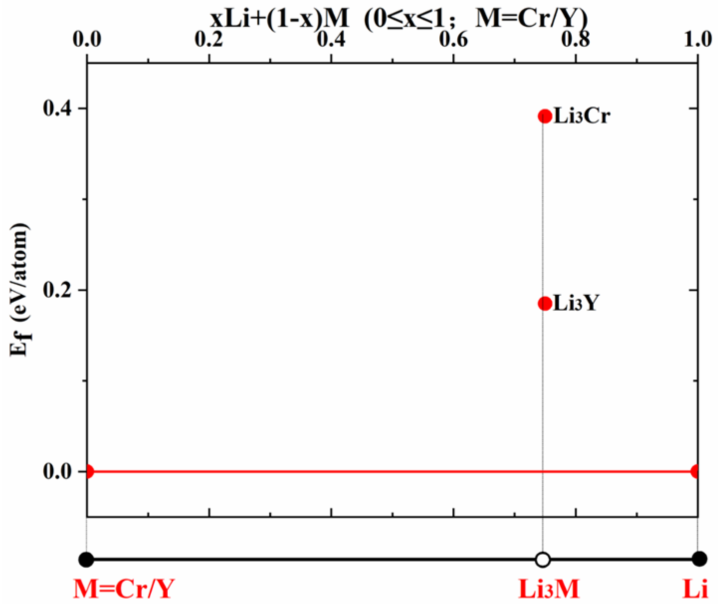

Fig. S4 Equilibrium phase diagram and formation energy for Li-Y alloys with reference to the corresponding stable constituent phases.

Table S1. The low-energy states and formation energies with respect to that of stable constituent ones, over the de-lithium process of $Li_{(2-x)}YCl_4$ ($0 \le x \le 1$).

Compounds	Equilibrium Phases	E_f (eV/atom)
Li_2YCl_4	$2LiCl+(1/3)YCl_3+(1/3)Y_2Cl_3$	0.0717
$Li_{23/12}YCl_4$	$23/12LiCl+(14/36)YCl_3+(11/36)Y_2Cl_3$	0.0643
$Li_{1.875}YCl_4$	$1.875LiCl+(5/12)YCl_3+(7/24)Y_2Cl_3$	0.0612
$Li_{1.75}YCl_4$	$1.75LiCl+(0.5)YCl_3+(0.25)Y_2Cl_3$	0.0493
$Li_{5/3}YCl_4$	$5/3LiCl+(5/9)YCl_3+(2/9)Y_2Cl_3$	0.0438
$Li_{13/8}YCl_4$	$13/8LiCl+(7/12)YCl_3+(5/24)Y_2Cl_3$	0.0440
$Li_{1.5}YCl_4$	$1.5LiCl+(2/3)YCl_3+(1/6)Y_2Cl_3$	0.0394
$Li_{1.375}YCl_4$	$1.375LiCl+(3/4)YCl_3+(1/8)Y_2Cl_3$	0.0423
$Li_{1.25}YCl_4$	$1.25LiCl+(5/6)YCl_3+(1/12)Y_2Cl_3$	0.0446
$Li_{7/6}YCl_4$	$7/6LiCl+(8/9)YCl_3+(1/18)Y_2Cl_3$	0.0478
$Li_{9/8}YCl_4$	$9/8LiCl+(11/12)YCl_3+(1/24)Y_2Cl_3$	0.0489
$Li_{13/12}YCl_4$	$13/12LiCl+(17/18)YCl_3+(1/36)Y_2Cl_3$	0.0497
$LiYCl_4$	$LiCl+YCl_3$	0.050

Table S2. The low-energy states and formation energies with reference to that of the stable constituents, over the lithiation process $Li_{2+x}Y_{1-x}Cl_4$ ($0 \le x \le 1$). Highlighted are spinel-like phases significantly stabilized. Over lithiation beyond the YCl_3-0.5LiCl constituent line leads to lowered stability.

Compounds	Equilibrium Phases	E_f (eV/atom)
Li_2YCl_4	$2LiCl+(1/3)YCl_3+(1/3)Y_2Cl_3$	0.0717
$Li_{25/12}Y_{11/12}Cl_4$	$25/12LiCl+(13/36)YCl_3+(5/18)Y_2Cl_3$	0.0625
$Li_{2.125}Y_{0.875}Cl_4$	$2.125LiCl+(9/24)YCl_3+(3/12)Y_2Cl_3$	0.0522
$Li_{26/12}Y_{10/12}Cl_4$	$26/12LiCl+(7/18)YCl_3+(2/9)Y_2Cl_3$	0.0557
$Li_{2.25}Y_{0.75}Cl_4$	$2.25LiCl+(5/12)YCl_3+(1/6)Y_2Cl_3$	0.0310
$Li_{2.375}Y_{0.625}Cl_4$	$2.375LiCl+(11/24)YCl_3+(1/12)Y_2Cl_3$	0.0176
$Li_{2.5}Y_{0.5}Cl_4$	**$2.5LiCl+(0.5)YCl_3$**	**0.00135**
$Li_{21/8}Y_{3/8}Cl_4$	$21/8LiCl+(3/8)YCl_3+(1/8)Cl_2$	0.0392
$Li_{2.75}Y_{0.25}Cl_4$	$2.75LiCl+(0.25)YCl_3+(0.25)Cl_2$	0.0750
$Li_{2.875}Y_{0.125}Cl_4$	$2.875LiCl+(0.125)YCl_3+(0.375)Cl_2$	0.0962
Li_3Cl_4	$3LiCl+(0.5)Cl_2$	0.1438

Table S3. The low-energy states and formation energies with respect to that of equilibrium phases during the de-lithium process of $Li_{2.5-x}Y_{0.5}Cl_4$ (0≤x≤1).

Compounds	Equilibrium Phases	E_f (eV/atom)
$Li_{2.5}Y_{0.5}Cl_4$	**$2.5LiCl+(0.5)YCl_3$**	**0.00135**
$Li_{1.625}Y_{0.5}Cl_4$	$1.625LiCl+(0.5)YCl_3+(0.4375)Cl_2$	0.0548
$Li_{1.5}Y_{0.5}Cl_4$	$1.5LiCl+(0.5)YCl_3+(0.5)Cl_2$	0.1465

Table S4. The states and associated formation energies with respect to each corresponding equilibrium phases during the de-lithium process of $Li_{2.25-x}Y_{0.75}Cl_4$ (0≤x≤1).

Compounds	Equilibrium Phases	E_f (eV/atom)
$Li_{2.25}Y_{0.75}Cl_4$	**$2.25LiCl+(5/12)YCl_3+(1/6)Y_2Cl_3$**	**0.0310**
$Li_2Y_{0.75}Cl_4$	$2LiCl+(7/12)YCl_3+(1/12)Y_2Cl_3$	0.0266
$Li_{31/16}Y_{0.75}Cl_4$	$31/16LiCl+(5/8)YCl_3+(1/16)Y_2Cl_3$	0.0242
$Li_{15/8}Y_{0.75}Cl_4$	$15/8LiCl+(2/3)YCl_3+(1/24)Y_2Cl_3$	0.0212
$Li_{1.75}Y_{0.75}Cl_4$	**$1.75LiCl+(3/4)YCl_3$**	**0.0134**
$Li_{13/8}Y_{0.75}Cl_4$	$13/8LiCl+(3/4)YCl_3+(1/16)Cl_2$	0.0310
$Li_{1.5}Y_{0.75}Cl_4$	$1.5LiCl+(3/4)YCl_3+(1/8)Cl_2$	0.0426
$Li_{11/8}Y_{0.75}Cl_4$	$11/8LiCl+(3/4)YCl_3+(3/16)Cl_2$	0.0689
$Li_{10/8}Y_{0.75}Cl_4$	$10/8LiCl+(3/4)YCl_3+(1/4)Cl_2$	0.1022

Table S5. The low-energy states and formation energies with respect to that of equilibrium phases during the de-lithium process of $Li_{2.375-x}Y_{0.625}Cl_4$ (0≤x≤1).

Compounds	Equilibrium Phases	E_f (eV/atom)
$Li_{2.375}Y_{0.625}Cl_4$	$2.375LiCl+(11/24)YCl_3+(1/12)Y_2Cl_3$	0.0176
$Li_{2.25}Y_{0.625}Cl_4$	$2.25LiCl+(13/24)YCl_3+(1/24)Y_2Cl_3$	0.0145
$Li_{2.125}Y_{0.625}Cl_4$	**$2.125LiCl+(0.625)YCl_3$**	**0.0162**
$Li_2Y_{0.625}Cl_4$	$2LiCl+(0.625)YCl_3+(0.0625)Cl_2$	0.0305
$Li_{1.875}Y_{0.625}Cl_4$	$1.875LiCl+(0.625)YCl_3+(0.125)Cl_2$	0.0427
$Li_{1.75}Y_{0.625}Cl_4$	$1.75LiCl+(0.625)YCl_3+(0.1875)Cl_2$	0.0600
$Li_{1.625}Y_{0.625}Cl_4$	$1.625LiCl+(0.625)YCl_3+(0.25)Cl_2$	0.0770
$Li_{1.5}Y_{0.625}Cl_4$	$1.5LiCl+(0.625)YCl_3+(0.3125)Cl_2$	0.0949
$Li_{1.375}Y_{0.625}Cl_4$	$1.375LiCl+(0.625)YCl_3+(0.375)Cl_2$	0.1130

Table S6. The low-energy states and formation energies with respect to that of equilibrium phases during the de-lithium process $Li_{3(1-x)}YCl_6$ (0≤x≤1).

Compounds	Equilibrium Phases	E_f (eV/atom)
Li_3YCl_6	**$3LiCl+YCl_3$**	**0.0171**
$Li_{5/3}YCl_6$	$(5/3)LiCl+YCl_3+(2/3)Cl_2$	0.0648
$LiYCl_6$	$LiCl+YCl_3+Cl_2$	0.0691

Table S7. Structural characteristics of nearly stable phases: stoichiometries, lattice parameters and space groups

Compounds (stoichiometries)	lattice parameters a	b	c	α	β	γ	space groups
$Li_{1.75}Y_{0.75}Cl_4$	15.11760	7.66070	10.63360	90°	90°	90°	P1
$Li_{2.125}Y_{0.625}Cl_4$	15.11760	7.66070	10.63360	90°	90°	90°	P1
$Li_{2.5}Y_{0.5}Cl_4$	15.11760	7.66070	10.63360	90°	90°	90°	P1

Table S8 The ionic conductivities of Li_3YCl_6 and various alloys at 900K to 300K from AIMD simulations.

Temperature (K)	σ (Li_3YCl_6) (mS/cm)	σ ($Li_{1.75}Y_{0.75}Cl_4$) (mS/cm)	σ ($Li_{2.125}Y_{0.625}Cl_4$) (mS/cm)	σ ($Li_{2.5}Y_{0.5}Cl_4$) (mS/cm)
900	973.34	1604.91	1134.06	1446.81
850	850.28	1342.44	997.00	127.49
800	727.65	1094.07	859.33	110.17
750	607.38	864.05	723.13	929.75
700	491.72	656.63	590.87	762.24
600	284.70	324.57	350.13	455.45
300	4.22	1.59	6.11	8.42

Table S9. The reaction energies (E_R) of identified SSEs to react with the Li anode.

Reactants	Products	E_R (eV/atom)
Li_3YCl_6+3Li	$6LiCl+Y$	-0.139
$Li_3YCl_6+(3/2)Li$	$4.5LiCl+0.5Y_2Cl_3$	-0.0903
$Li_{2.5}Y_{0.5}Cl_4+1.5Li$	$4LiCl+0.5Y$	-0.097
$Li_{2.5}Y_{0.5}Cl_4+0.75Li$	$3.25LiCl+0.25Y_2Cl_3$	-0.0572
$Li_{2.375}Y_{0.625}Cl_4+1.625Li$	$4LiCl+(0.625)Y$	-0.1157
$Li_{2.375}Y_{0.625}Cl_4+0.6875Li$	$3.0625LiCl+(0.3125)Y_2Cl_3$	-0.0678
$Li_{2.25}Y_{0.75}Cl_4+1.75Li$	$4LiCl+0.75Y$	-0.1377
$Li_{2.25}Y_{0.75}Cl_4+0.625Li$	$2.875LiCl+0.375Y_2Cl_3$	-0.083