Design Principle of Disordered Rocksalt Type Overlithiated Anode for High Energy Density Batteries

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Table S1. The average voltage, capacity, and energy density of 23 redox centers of overlithiated disordered rock-salt (DRX) $Li_{3+x}M_2O_5$ ($0 \leq x \leq 2$) (M= Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Ge, Zr, Nb, Mo, Rh, Ru, Sn, Sb, Te, Hf, Ta, W, Re, Ir, and Ce) and reported $Li_{4+x}Ti_5O_{12}$ ($0 \leq x \leq 3$).

DRX $Li_{3+x}M_2O_5$ ($0 \leq x \leq 2$)	**Average voltage (V)**	**Capacity (mAh/g)**	**Energy density (Wh/kg)**
$Li_{3+x}Ti_2O_5$	0.0	0.0	0.0
$Li_{3+x}V_2O_5$	0.48	264.44	930.22
$Li_{3+x}Cr_2O_5$	1.14	261.72	749.05
$Li_{3+x}Mn_2O_5$	1.39	254.41	663.02
$Li_{3+x}Fe_2O_5$	1.94	252.24	519.74
$Li_{3+x}Co_2O_5$	2.26	245.11	427.37
$Li_{3+x}Ni_2O_5$	2.41	245.65	391.68
$Li_{3+x}Cu_2O_5$	2.87	235.19	265.49
$Li_{3+x}Ge_2O_5$	1.58	217.801	527.79
$Li_{3+x}Zr_2O_5$	0.0	0.0	0.0
$Li_{3+x}Nb_2O_5$	0.19	187.01	711.60
$Li_{3+x}Mo_2O_5$	1.27	91.57	249.30
$Li_{3+x}Rh_2O_5$	1.32	174.81	469.17
$Li_{3+x}Ru_2O_5$	0.98	176.93	535.21
$Li_{3+x}Sn_2O_5$	1.43	158.48	407.12
$Li_{3+x}Sb_2O_5$	1.71	155.67	356.31
$Li_{3+x}Te_2O_5$	1.85	150.56	323.15
$Li_{3+x}Hf_2O_5$	0.0	0.0	0.0
$Li_{3+x}Ta_2O_5$	0.0	0.0	0.0
$Li_{3+x}W_2O_5$	0.28	85.81	318.97
$Li_{3+x}Re_2O_5$	1.22	113.27	315.18
$Li_{3+x}Ir_2O_5$	1.70	110.46	254.62
$Li_{3+x}Ce_2O_5$	0.21	43.96	166.39
$Li_{4+x}Ti_5O_{12}$ ($0 \leq x \leq 3$)	1.55	175.14	429.09

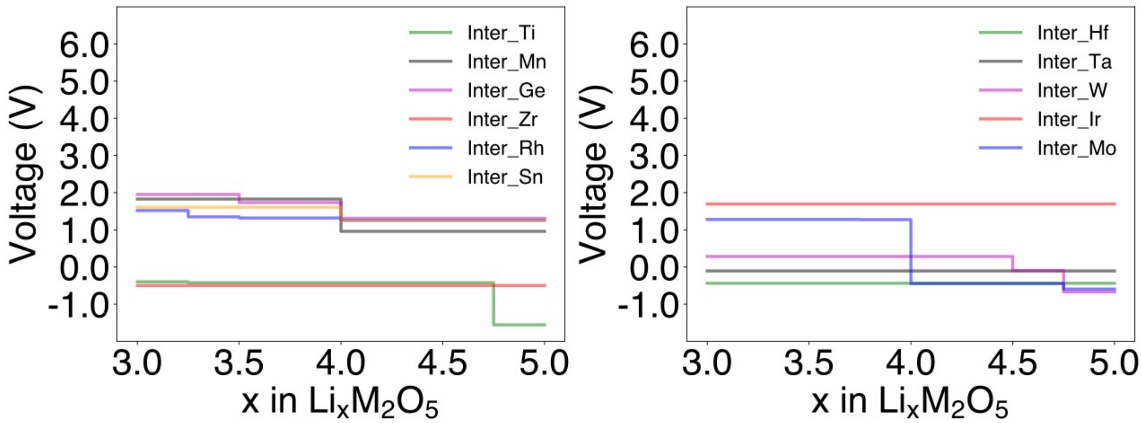

Fig. S1: the intercalation voltage of DRX $Li_{3+x}M_2O_5$ ($0 \leq x \leq 2$) (M = Ti, Mn, Ge, Zr, Rh, Sn, Hf, Ta, W, Ir, and Mo).

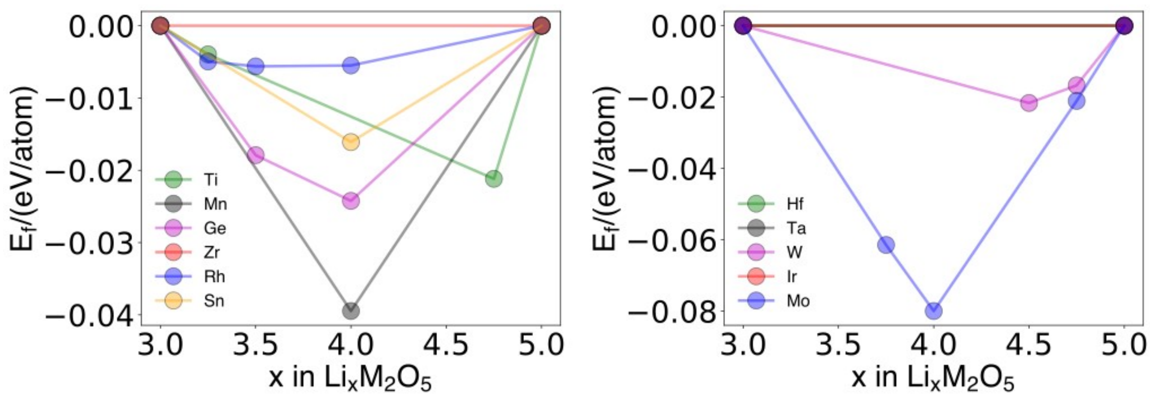

Fig. S2: the intercalation convex hull of DRX $Li_{3+x}M_2O_5$ ($0 \leq x \leq 2$) (M = Ti, Mn, Ge, Zr, Rh, Sn, Hf, Ta, W, Ir, and Mo).

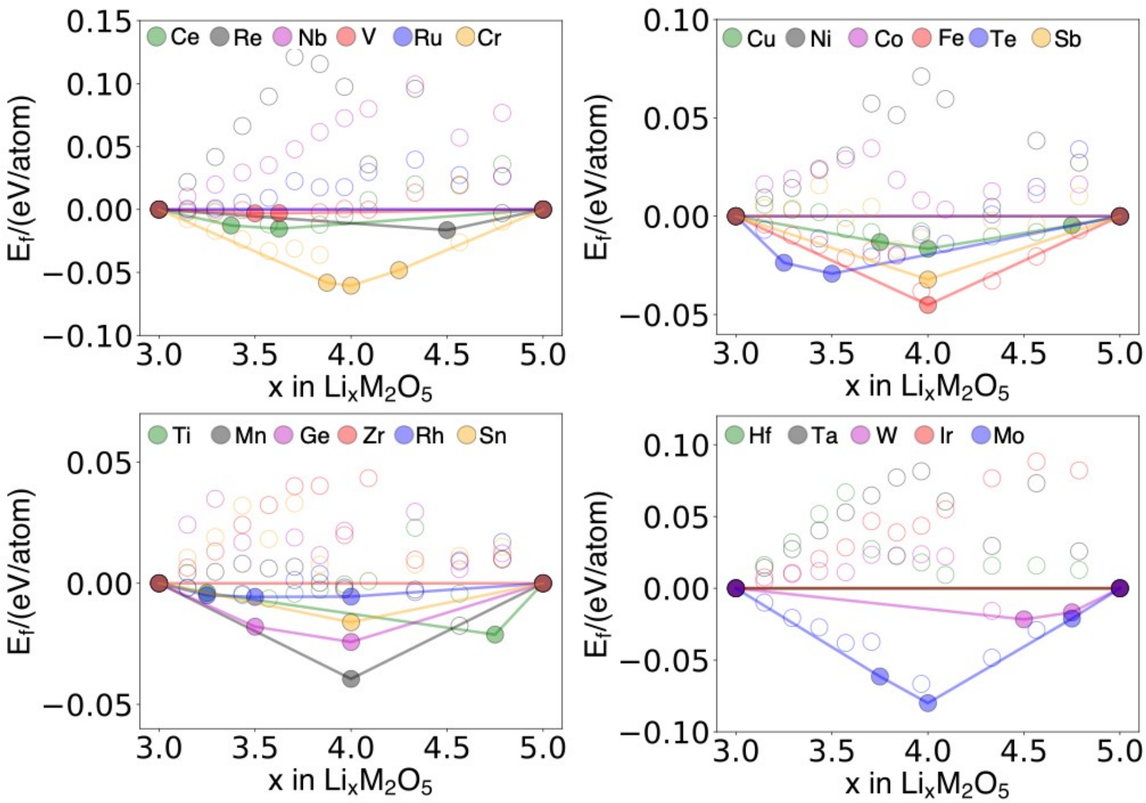

Fig. S3: the intercalation convex hull of all searched DRX $Li_{3+x}M_2O_5$ ($0 \leq x \leq 2$) (M= Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Ge, Zr, Nb, Mo, Rh, Ru, Sn, Sb, Te, Hf, Ta, W, Re, Ir, and Ce) with stable and unstable phases (solid circle and open circle represents stable and unstable phases respectively).

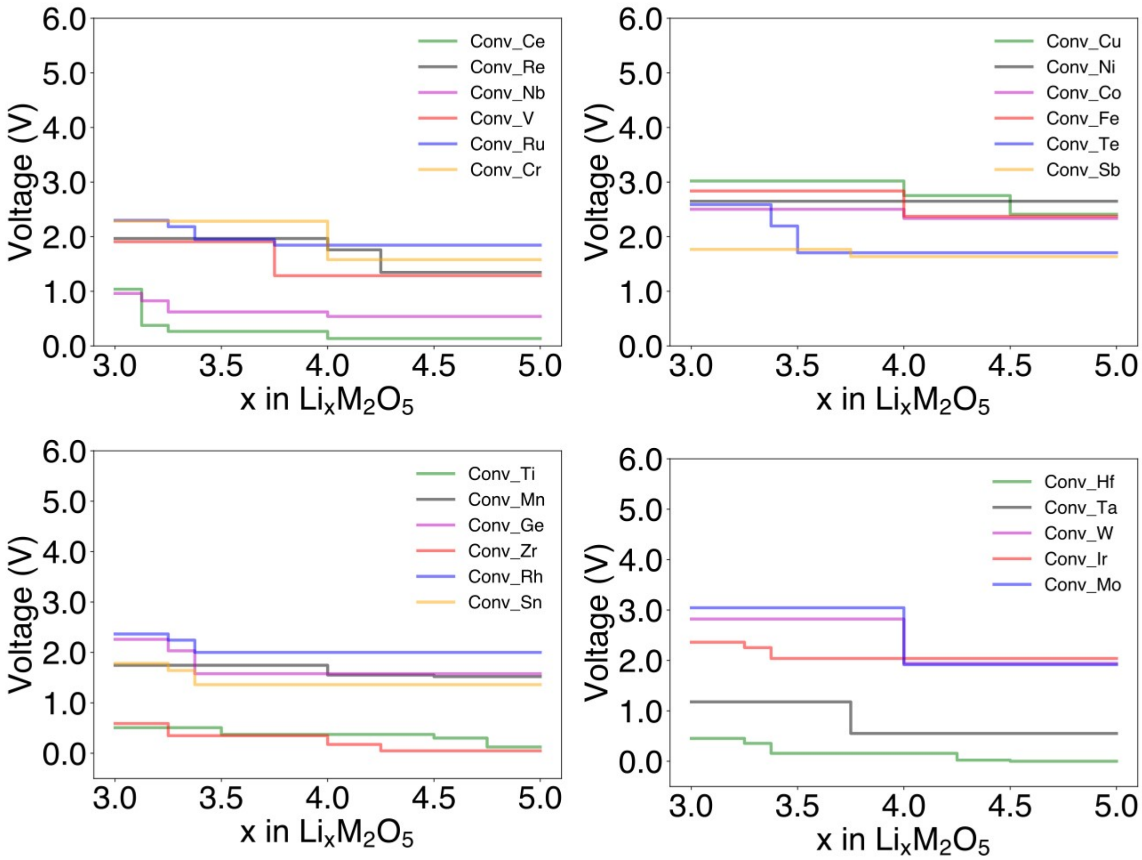

Fig. S4: the conversion voltage curve of all searched DRX $Li_{3+x}M_2O_5$ ($0 \leq x \leq 2$) (M= Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Ge, Zr, Nb, Mo, Rh, Ru, Sn, Sb, Te, Hf, Ta, W, Re, Ir, and Ce).

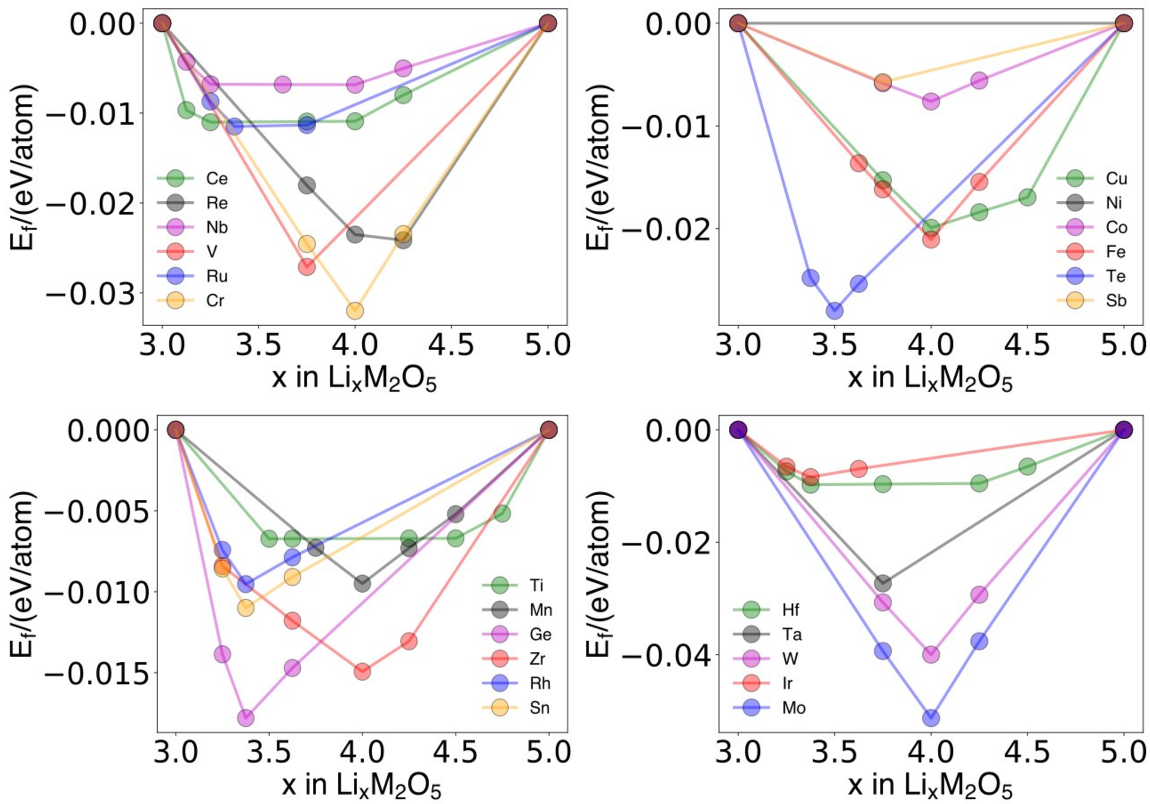

Fig. S5: the conversion convex hull of all searched DRX $Li_{3+x}M_2O_5$ ($0 \leq x \leq 2$) (M= Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Ge, Zr, Nb, Mo, Rh, Ru, Sn, Sb, Te, Hf, Ta, W, Re, Ir, and Ce).

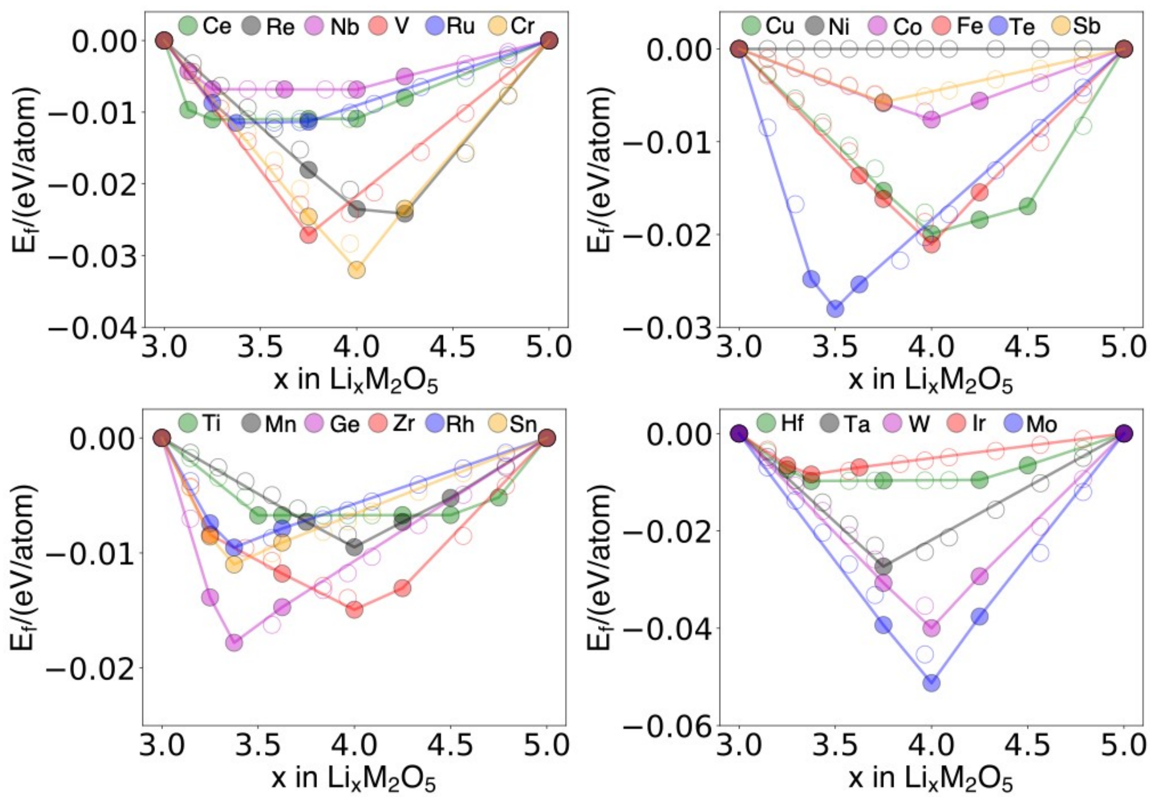

Fig. S6: the conversion convex hull of all searched DRX $Li_{3+x}M_2O_5$ ($0 \leq x \leq 2$) (M= Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Ge, Zr, Nb, Mo, Rh, Ru, Sn, Sb, Te, Hf, Ta, W, Re, Ir, and Ce) with stable and unstable phases (solid circle and open circle represents stable and unstable phases respectively).

Table S2. The competing phase of the ground state of conversion convex hull.

$Li_{3+x}V_2O_5$	**$Li_{5.0}V_2O_5$: Li_2O, Li_3VO_4, V** **$Li_{3.75}V_2O_5$: Li_3VO_4, V** **$Li_3V_2O_5$: $Li_3V_2O_5$**
$Li_{3+x}Cr_2O_5$	$Li_{5.0}Cr_2O_5$: $LiCrO_2$, Li_2O, Cr $Li_{4.25}Cr_2O_5$: $LiCrO_2$, Li_2O, Cr $Li_{4.0}Cr_2O_5$: $LiCrO_2$, Li_2O $Li_{3.75}Cr_2O_5$: Li_3CrO_4, $LiCrO_2$, Li_2O $Li_{3.0}Cr_2O_5$: $Li_3Cr_2O_5$
$Li_{3+x}Mn_2O_5$	$Li_{5.0}Mn_2O_5$: $LiMnO_2$, Li_6MnO_4, MnO $Li_{4.5}Mn_2O_5$: $LiMnO_2$, Li_6MnO_4 $Li_{4.25}Mn_2O_5$: $LiMnO_2$, Li_6MnO_4, Li_2O $Li_{4.0}Mn_2O_5$: $LiMnO_2$, Li_2O $Li_{3.75}Mn_2O_5$: $LiMnO_2$, Li_2MnO_3, Li_2O $Li_{3.0}Mn_2O_5$: $Li_3Mn_2O_5$

$Li_{3+x}Nb_2O_5$	$Li_{5.0}Nb_2O_5$: Li_2O, $LiNbO_2$, Nb $Li_{4.25}Nb_2O_5$: Li_2O, $LiNbO_2$, Nb $Li_{4.0}Nb_2O_5$: Li_2O, $LiNbO_2$ $Li_{3.625}Nb_2O_5$: $Li_8Nb_2O_9$, Li_2O, $LiNbO_2$ $Li_{3.25}Nb_2O_5$: $Li_8Nb_2O_9$, Li_2O, $LiNbO_2$ $Li_{3.125}Nb_2O_5$: $Li_8Nb_2O_9$, $LiNbO_2$, Li_3NbO_4 $Li_{3.0}Nb_2O_5$: $Li_3Nb_2O_5$
$Li_{3+x}Ru_2O_5$	$Li_{5.0}Ru_2O_5$: Li_3RuO_4, Li_2O, Ru $Li_{3.75}Ru_2O_5$: Li_3RuO_4, Ru $Li_{3.375}Ru_2O_5$: Li_2RuO_3, Li_3RuO_4, Ru $Li_{3.25}Ru_2O_5$: Li_2RuO_3, RuO_2, Ru $Li_{3.0}Ru_2O_5$: $Li_3Ru_2O_5$
$Li_{3+x}Rh_2O_5$	$Li_{5.0}Rh_2O_5$: Li_2RhO_3, Li_2O, Rh $Li_{3.625}Rh_2O_5$: Li_2RhO_3, Li_2O, Rh $Li_{3.375}Rh_2O_5$: Li_2RhO_3, Li_2O, Rh $Li_{3.25}Rh_2O_5$: Li_2RhO_3, $LiRhO_2$, Rh $Li_3Rh_2O_5$: $Li_3Rh_2O_5$
$Li_{3+x}Te_2O_5$	$Li_{5.0}Te_2O_5$: Li_2TeO_3, Li_6TeO_6, $LiTe_3$ $Li_{3.625}Te_2O_5$: Li_2TeO_3, Li_6TeO_6, $LiTe_3$ $Li_{3.5}Te_2O_5$: Li_2TeO_3, Li_6TeO_6, $LiTe_3$ $Li_{3.375}Te_2O_5$: Li_2TeO_3, $Li_2Te_2O_5$, $LiTe_3$ $Li_{3.0}Te_2O_5$: $Li_{3.0}Te_2O_5$
$Li_{3+x}Sb_2O_5$	$Li_{5.0}Sb_2O_5$: Li_5SbO_5, Sb $Li_{3.75}Sb_2O_5$: Li_3SbO_4, Sb $Li_{3.0}Sb_2O_5$: $Li_3Sb_2O_5$
$Li_{3+x}Sn_2O_5$	$Li_{5.0}Sn_2O_5$: Li_2SnO_3, Li_8SnO_6, Sn $Li_{3.625}Sn_2O_5$: Li_2SnO_3, Li_8SnO_6, Sn $Li_{3.375}Sn_2O_5$: Li_2SnO_3, Li_8SnO_6, Sn $Li_{3.25}Sn_2O_5$: Li_2SnO_3, SnO, Sn $Li_{3.0}Sn_2O_5$: $Li_3Sn_2O_5$
$Li_{3+x}Ge_2O_5$	$Li_{5.0}Ge_2O_5$: Li_4GeO_4, Ge $Li_{3.625}Ge_2O_5$: Li_2GeO_3, Li_4GeO_4, Ge $Li_{3.375}Ge_2O_5$: Li_2GeO_3, Li_4GeO_4, Ge $Li_{3.25}Ge_2O_5$: Li_2GeO_3, $Li_4Ge_5O_{12}$, Ge $Li_{3.0}Ge_2O_5$: $Li_3Ge_2O_5$
$Li_{3+x}Fe_2O_5$	$Li_{5.0}Fe_2O_5$: Li_5FeO_4, $LiFeO_2$, Fe $Li_{4.25}Fe_2O_5$: Li_5FeO_4, $LiFeO_2$, Fe $Li_{4.0}Fe_2O_5$: Li_5FeO_4, $LiFeO_2$ $Li_{3.75}Fe_2O_5$: Li_5FeO_4, $LiFeO_2$, LiO_8 $Li_{3.625}Fe_2O_5$: Li_5FeO_4, $LiFeO_2$, LiO_8 $Li_{3.0}Fe_2O_5$: $Li_3Fe_2O_5$

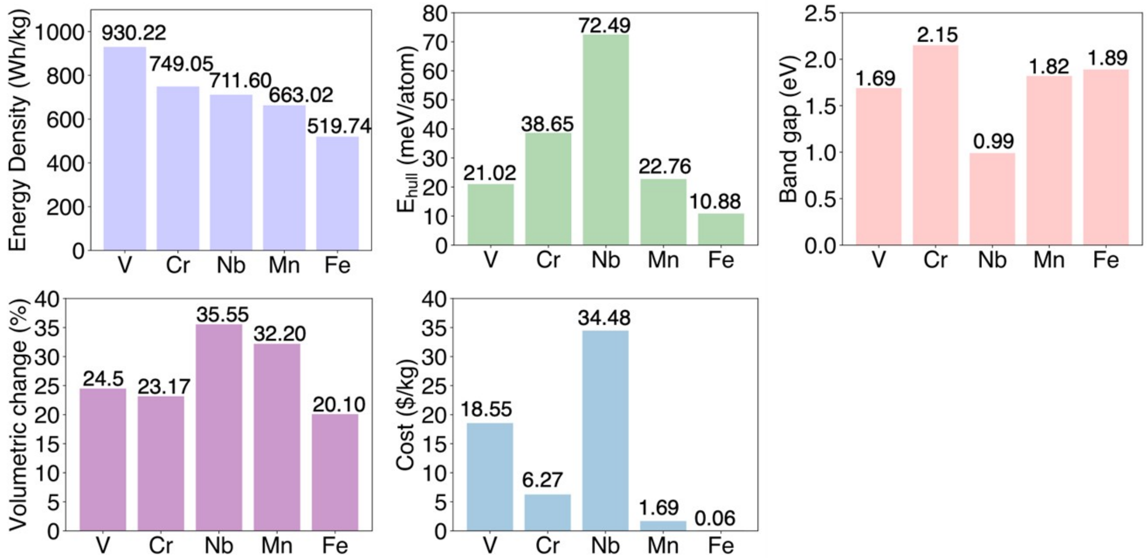

Fig. S7: The energy density, E_{hull} of $Li_3M_2O_5$, average band gap, maximum volumetric change, and cost of promising DRX $Li_{3+x}M_2O_5$ ($0 \leq x \leq 2$) (M = V, Cr, Nb, Mn, and Fe).

Table S3. E_{hull} of $Li_{1.2}Mn_{0.4}Ti_{0.4}O_2$ at different synthesis conditions.

Material	**E_{hull}(1273K) (meV/atom)**	**E_{hull}(1873K) (meV/atom)**	**E_{hull}(SQS) (meV/atom)**	**E_{hull}(SQS)-E_{hull}(ESGS) (meV/atom)**
$Li_{1.2}Mn_{0.4}Ti_{0.4}O_2$	54.3	69.0	139.3	>85